

Supporting information for

**(PAA-*g*-PS)-*co*-PPEGMEMA Asymmetric  
Polymer Brush: Synthesis, Self-assembly,  
and Encapsulating Capacity for Both  
Hydrophobic and Hydrophilic Agents**

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**Experimental Section**

**Materials**

Poly(ethylene glycol) methyl ether methacrylate (PEGMEMA,  $M_n = 500$  g/mol, Aldrich, 99%) was passed through a basic alumina column to remove the stabilizer prior to use. Styrene (St, Aldrich, 99%) was washed with 5% aqueous NaOH solution and water, dried over  $MgSO_4$ , and distilled twice from  $CaH_2$  under reduced pressure

prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol twice. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH<sub>3</sub>COOH at room temperature, followed by washing with ethanol, diethyl ether, and acetone prior to drying at 40°C in vacuo for one day. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. *tert*-Butyl 2-((2-bromo-propanoyloxy)methyl)acrylate (*t*BBPMA),<sup>1</sup> cumyl dithiobenzoate (CDB),<sup>2</sup> and PEG<sub>113</sub>-*b*-PS<sub>100</sub> diblock copolymer<sup>3</sup> were synthesized according to previous literatures. Dichloromethane (Aldrich, 99.5%) was dried over KOH and distilled from CaH<sub>2</sub> under N<sub>2</sub> prior to use. Tetrahydrofuran (THF, Aldrich, 99%) and toluene (Aldrich, 99.8%) were dried over CaH<sub>2</sub> and distilled from Na and benzophenone under N<sub>2</sub> prior to use. Pyrene (Aldrich, 99%), Rhodamine 6G (R6G, Aldrich, 99%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), and trifluoroacetic acid (TFA, Aldrich, 99%) were used as received.

## Measurements

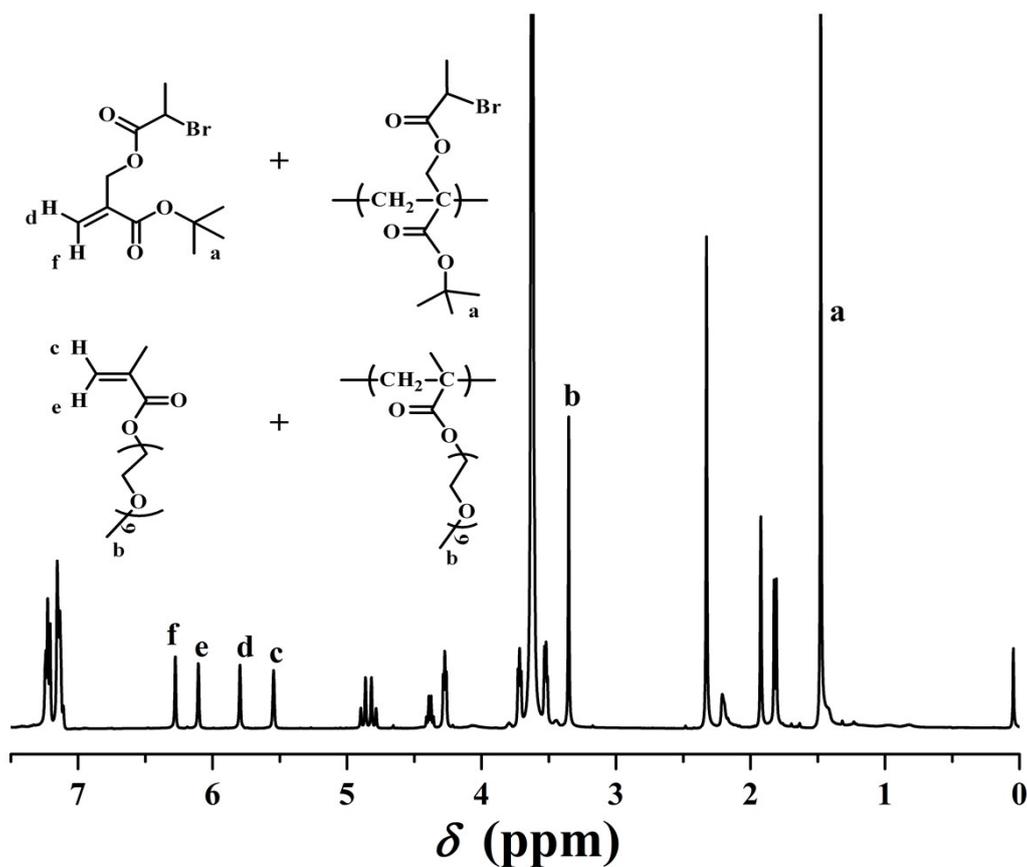
<sup>1</sup>H NMR analyses were performed on a Bruker Avance 500 spectrometer (500 MHz) in CDCl<sub>3</sub> and acetone-*d*<sub>6</sub>; tetramethylsilicone was used as internal standard. FT-IR spectra were recorded on a Nicolet AVATAR-360 spectrophotometer with a 4 cm<sup>-1</sup> resolution. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000) and

HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. UV/vis spectra were measured by a Hitachi U-2910 spectrophotometer with a rate of 200 nm/min. Steady-state fluorescence spectra were measured at 20°C on a Hitachi F-2700 spectrophotometer with the band width of 5 nm for excitation and emission, the emission intensity at 418 nm ( $\lambda_{\text{ex}} = 340$  nm) was recorded to determine the critical micelle concentration (*cmc*) and the emission intensity of R6G at 551 nm ( $\lambda_{\text{ex}} = 500$  nm) was recorded. Hydrodynamic diameter ( $D_h$ ) was measured by dynamic light scattering (DLS) with a Malvern Nano-ZS90 Zetasizer. TEM images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

### **Determination of Monomer Reactivity Ratio**

In a typical procedure ( $[t\text{BBPMA}]:[\text{PEGMEMA}] = 1:1$ ,  $[t\text{BBPMA}+\text{PEGMEMA}]:[\text{CDB}]:[\text{AIBN}] = 1200:3:1$ ), AIBN (0.41 mg, 0.0025 mmol) and CDB (2.043 mg, 0.0075 mmol) were first added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under  $\text{N}_2$ . Next,  $t\text{BBPMA}$  (0.44 g, 1.5 mmol), PEGMEMA (0.75 g, 1.5 mmol), and dry toluene (0.3 mL) were charged via a gastight syringe. The flask was degassed by three cycles of freezing- pumping-thawing followed by immersing the flask into an oil bath set at 70°C. The polymerization was terminated after 100 min by putting the flask into liquid  $\text{N}_2$ .

According to Eq 1 and 2 ( $S_a$  and  $S_b$  are the integration area of 9 protons of *tert*-butoxycarbonyl at 1.44 ppm (peak “a”) and 3 protons of methoxyl at 3.37 ppm (peak “b”) in Figure S1;  $S_c$  and  $S_e$  are the integration area of 2 protons of double bond of residual PEGMEMA monomer at 5.53 ppm (peak “c”) and 6.07 ppm (peak “e”) in Figure S1;  $S_d$  and  $S_f$  are the integration area of 2 protons of double bond of residual *t*BBPMA monomer at 5.81 ppm (peak “d”) and 6.29 ppm (peak “f”) in Figure S1), we can calculate the conversion of each monomer via  $^1\text{H}$  NMR spectrum (Figure S1). The conversions of *t*BBPMA and PEGMEMA monomer were 5.61% and 9.82%, respectively. Meanwhile, the total conversion of comonomers was estimated to be 7.72% ( $= (5.61\%+9.82\%)/2$ ), which was kept below 10%.



**Figure S1.**  $^1\text{H}$  NMR spectrum of *t*BBPMA/PEGMEMA copolymerization system in  $\text{CDCl}_3$ , [*t*BBPMA]:[PEGMEMA]:[CDB]:[AIBN] = 600:600:3:1.

*t*BBPMA:  $t = 0, (S_d + S_f)/S_a = 2/9$

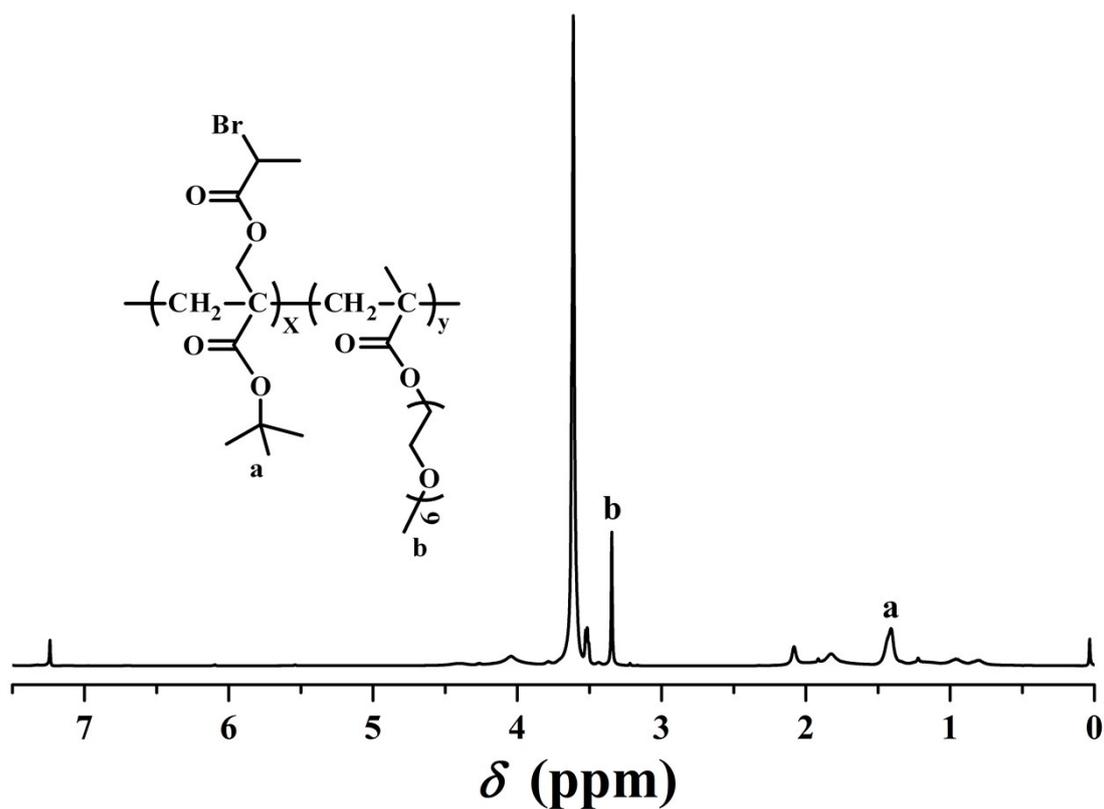
$$\text{Conv.}\% = [1 - 4.5(S_d + S_f)/S_a] \times 100\% \quad (1)$$

PEGMEMA:  $t = 0, (S_c + S_e)/S_b = 2/3$

$$\text{Conv.}\% = [1 - 1.5(S_c + S_e)/S_b] \times 100\% \quad (2)$$

The composition of the copolymer (*f*) was evaluated according to Eq 3 ( $S_a$  and  $S_b$  are the integration area of 9 protons of *tert*-butoxycarbonyl at 1.44 ppm (peak “a”) and 3 protons of methoxyl at 3.37 ppm (peak “b”) in Figure S2, respectively) via  $^1\text{H}$  NMR spectrum (Figure S2) and the result was 0.5633.

$$f = S_a/3S_b \quad (3)$$



**Figure S2.**  $^1\text{H}$  NMR spectrum of PtBBPMA-*co*-PPEGMEMA in  $\text{CDCl}_3$ , [*t*BBPMA]:

[PEGMEMA]:[CDB]:[AIBN] = 600:600:3:1.

Similarly, the conversions and compositions of other copolymerization systems with different feeding ratios were obtained with same method and the results are summarized in Table S1.

**Table S1.** Determination of Monomer Reactivity Ratios

$[M_1]:[M_2]^a$	$F$	$f$	Conv. $_{[M_1]}^b$ (%)	Conv. $_{[M_2]}^b$ (%)	Conv. $_{[M_1+M_2]}^c$ (%)
2:8	0.2500	0.1600	5.77	9.27	8.57
3:7	0.4286	0.2567	4.48	7.98	6.93
4:6	0.6667	0.3800	5.30	8.44	7.18
5:5	1.0000	0.5633	5.61	9.82	7.72
6:4	1.5000	0.7733	3.82	7.59	5.33
7:3	2.3333	1.0267	5.74	9.64	6.91
8:2	4.0000	1.7033	4.94	9.78	5.91

<sup>a</sup>  $M_1$  and  $M_2$  represent *t*BBPMA and PEGMEMA, respectively. <sup>b</sup> Obtained from <sup>1</sup>H NMR. <sup>c</sup> Total conversion of *t*BBPMA and PEGMEMA comonomers obtained from <sup>1</sup>H NMR.

### RAFT Copolymerization of *t*BBPMA and PEGMEMA

In a typical procedure, AIBN (16.4 mg, 0.1 mmol) and CDB (81.6 mg, 0.3 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N<sub>2</sub>. Next, *t*BBPMA (0.88 g, 3 mmol), PEGMEMA (1.50 g, 3 mmol), and dry toluene (0.6 mL) were added via a

gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 70°C. The polymerization was terminated by immersing the flask into liquid N<sub>2</sub> after 16 h. The solution was precipitated into cold *n*-hexane. The crude product was purified by repeated dissolution and precipitation followed by drying *in vacuo* overnight to give 1.97 g of pink powder. Next, AIBN was used to remove the dithiobenzoate moiety of the copolymer at 65°C in THF according to previous report.<sup>4</sup> Finally, 1.74 g of white powder (73.1% yield), poly(*tert*-butyl 2-((2-bromopropanoyloxy)methyl)acrylate)-*co*-poly(poly(ethylene glycol) methyl ether methacrylate) (PtBBPMA-*co*-PPEGMEMA) **1b**, was obtained after drying *in vacuo* overnight. GPC:  $M_n = 8,300$  g/mol,  $M_w/M_n = 1.19$ . FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>): 2871, 1731, 1450, 1368, 1349, 1251, 1144, 1112, 951, 844, 750. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm): 0.82, 0.98, 1.16 (3H, CH<sub>2</sub>CCH<sub>3</sub>), 1.44 (9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.74, 1.85 (2H, CH<sub>2</sub>C and 3H, CH<sub>3</sub>CHBr), 3.37 (3H, OCH<sub>3</sub>), 3.54, 3.64 (4H, OCH<sub>2</sub>CH<sub>2</sub>), 4.06 (2H, CH<sub>2</sub>CCH<sub>2</sub>O<sub>2</sub>C and 2H, CH<sub>2</sub>CCO<sub>2</sub>CH<sub>2</sub>), 4.44 (1H, CH<sub>3</sub>CHBr). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm): 21.7 (CH<sub>2</sub>CCH<sub>3</sub>), 28.4 (C(CH<sub>3</sub>)<sub>3</sub>), 30.3 (CH<sub>3</sub>CHBr), 34.4 (CH<sub>2</sub>C), 45.2 (CH<sub>2</sub>C and CH<sub>3</sub>CHBr), 59.0 (OCH<sub>3</sub>), 71.1 (OCH<sub>2</sub>CH<sub>2</sub>), 72.0 (CH<sub>2</sub>CCH<sub>2</sub>O<sub>2</sub>C and CH<sub>2</sub>CCO<sub>2</sub>CH<sub>2</sub>), 83.4 (C(CH<sub>3</sub>)<sub>3</sub>), 169.9 (C=O).

### ATRP Graft Copolymerization of Styrene

In a typical procedure, CuBr (6 mg, 0.042 mmol) and PtBBPMA-*co*-PPEGMEMA **1b** ( $M_{n, \text{GPC}} = 8,300$  g/mol,  $M_w/M_n = 1.19$ , 40 mg, 0.042 mmol ATRP initiating group) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use)

sealed with a rubber septum for degassing and kept under N<sub>2</sub>. Next, styrene (1.9 mL, 16.8 mmol) and PMDETA (9 μL, 0.042 mmol) were charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 80°C. The polymerization lasted 2 h and was terminated by immersing the flask into liquid N<sub>2</sub>. The mixture was diluted by THF and passed through an alumina column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold methanol. After repeated purification by dissolving in THF and precipitating in methanol, 79 mg of white powder (2.3% yield), (PtBA-*g*-PS)-*co*-PPEGMEMA **2d** asymmetric polymer brush was obtained as a white powder after drying *in vacuo* overnight. GPC:  $M_n = 35,000$  g/mol,  $M_w/M_n = 1.26$ . FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>): 3026, 2924, 1732, 1598, 1488, 1446, 1143, 757, 696. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  (ppm): 0.87, 0.97, 1.10 (3H, CH<sub>2</sub>CCH<sub>3</sub>), 1.28, 1.45, 1.59 (9H, C(CH<sub>3</sub>)<sub>3</sub>, 2H, CH<sub>2</sub>C, and 2H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>2</sub>), 1.93 (1H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>2</sub>), 3.27 (3H, OCH<sub>3</sub>), 3.47, 3.57 (4H, OCH<sub>2</sub>CH<sub>2</sub>), 4.08 (2H, CH<sub>2</sub>CCH<sub>2</sub>O<sub>2</sub>C and 2H, CH<sub>2</sub>CCO<sub>2</sub>CH<sub>2</sub>), 6.65, 7.08 (5H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm): 28.1 (C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (CH<sub>2</sub>C), 40.6 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>2</sub>), 45.4 (CH<sub>2</sub>C and C<sub>6</sub>H<sub>5</sub>CHCH<sub>2</sub>), 59.2 (OCH<sub>3</sub>), 70.8 (OCH<sub>2</sub>CH<sub>2</sub>), 72.1 (CH<sub>2</sub>CCH<sub>2</sub>O<sub>2</sub>C and CH<sub>2</sub>CCO<sub>2</sub>CH<sub>2</sub>), 125.8, 128.1, 145.4 (C<sub>6</sub>H<sub>5</sub>), 172.1 (C=O).

### Selective Acidic Hydrolysis of (PtBA-*g*-PS)-*co*-PPEGMEMA

(PtBA-*g*-PS)-*co*-PPEGMEMA **2d** asymmetric polymer brush ( $M_{n, \text{GPC}} = 35,000$  g/mol,  $M_w/M_n = 1.26$ , 48.0 mg, 0.015 mmol *tert*-butyloxycarbonyl) and CH<sub>2</sub>Cl<sub>2</sub> (20

mL) were added to a 100mL three-neck flask. The solution was stirred at 0°C for 30 min followed by adding TFA (23  $\mu$ L, 0.30 mmol) and the reaction mixture was warmed to 25°C. After stirring at room temperature for 48 h, the solution was concentrated and precipitated into cold *n*-hexane. After filtration, 30.0 mg of white powder (62.5% yield), (PAA-*g*-PS)-*co*-PPEGMEMA **3** asymmetric polymer brush, was obtained after drying *in vacuo* overnight. GPC:  $M_n = 34,100$  g/mol,  $M_w/M_n = 1.25$ . FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ): 3439 ( $\nu_{\text{OH}}$ ), 3026, 2923, 1731, 1598, 1488, 1446, 1143, 757, 696.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm): 0.88, 0.97, 1.12 (3H,  $\text{CH}_2\text{CCH}_3$ ), 1.29, 1.41, 1.60 (2H,  $\text{CH}_2\text{C}$  and 2H,  $\text{C}_6\text{H}_5\text{CHCH}_2$ ), 1.95 (1H,  $\text{C}_6\text{H}_5\text{CHCH}_2$ ), 3.29 (3H,  $\text{OCH}_3$ ), 3.48, 3.59 (4H,  $\text{OCH}_2\text{CH}_2$ ), 4.08 (2H,  $\text{CH}_2\text{CCH}_2\text{O}_2\text{C}$  and 2H,  $\text{CH}_2\text{CCO}_2\text{CH}_2$ ), 6.68, 7.16 (5H,  $\text{C}_6\text{H}_5\text{CHCH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm): 29.6 ( $\text{CH}_2\text{C}$ ), 40.4 ( $\text{C}_6\text{H}_5\text{CHCH}_2$ ), 45.7 ( $\text{CH}_2\text{C}$  and  $\text{C}_6\text{H}_5\text{CHCH}_2$ ), 59.3 ( $\text{OCH}_3$ ), 70.6 ( $\text{OCH}_2\text{CH}_2$ ), 72.0 ( $\text{CH}_2\text{CCH}_2\text{O}_2\text{C}$  and  $\text{CH}_2\text{CCO}_2\text{CH}_2$ ), 125.7, 128.0, 145.7 ( $\text{C}_6\text{H}_5$ ), 171.6 ( $\text{C}=\text{O}$ ).

### Determination of Critical Micelle Concentration

PNA was used as fluorescence probe to measure the *cmc* of (PtBA-*g*-PS)-*co*-PPEGMEMA **2** and (PAA-*g*-PS)-*co*-PPEGMEMA **3** asymmetric polymer brushes in aqueous media. Acetone solution of PNA ([PNA] = 2 mM) was added to a large amount of water until the concentration of PNA reached 0.002 mM. The solutions for fluorescence measurement were obtained by adding different amounts of THF solutions of (PtBA-*g*-PS)-*co*-PPEGMEMA **2** or (PAA-*g*-PS)-*co*-PPEGMEMA **3** asymmetric polymer brush (1, 0.1, 0.01, 0.001, or 0.0001 mg/mL) to water containing

PNA ([PNA] = 0.002 mM).

### **Micellar Morphology**

THF solution of (*Pt*BA-*g*-PS)-*co*-PPEGMEMA **2** or (PAA-*g*-PS)-*co*-PPEGMEMA **3** asymmetric polymer brush (2 mg/mL) was added dropwise to deionized water under vigorous stirring until the concentration of polymer reached 0.05 mg/mL. THF was evaporated by stirring moderately overnight at room temperature. For TEM studies, 10  $\mu$ L of micelle solution was deposited on an electron microscopy copper grid coated with carbon film and the water was evaporated at room temperature. Similar procedure was used for PEG<sub>113</sub>-*b*-PS<sub>100</sub> diblock copolymer.

### **Encapsulation of Hydrophilic Rhodamine 6G in Micelles**

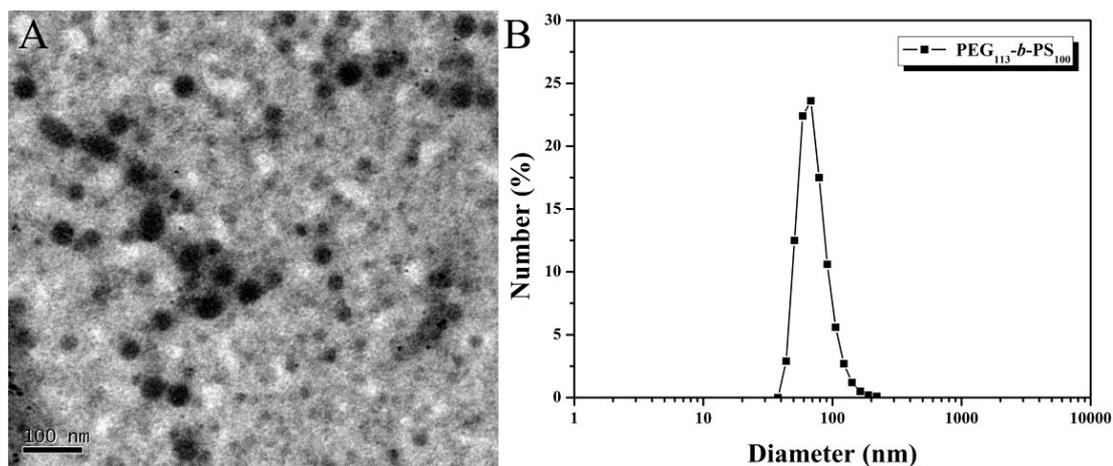
THF solution of (*Pt*BA-*g*-PS)-*co*-PPEGMEMA **2a** asymmetric polymer brush was added dropwise to deionized water under vigorous stirring until the concentration of polymer reached 0.08 mg/mL. Next, aqueous solution of Rhodamine 6G was added to the above solution until the concentration of R6G reached 0.02 mmol/L. THF was evaporated by stirring moderately overnight at room temperature. The resultant solution was dialyzed against water using dialysis membrane ( $MW_{\text{cut-off}} = 3.5$  kDa) until the dialysate did not show any detectable UV signal. The obtained solution was used for the measurements of UV absorption and fluorescence spectroscopy. Similar procedure was used for PEG<sub>113</sub>-*b*-PS<sub>100</sub> diblock copolymer.

### **Encapsulation of Hydrophobic Pyrene in Micelles**

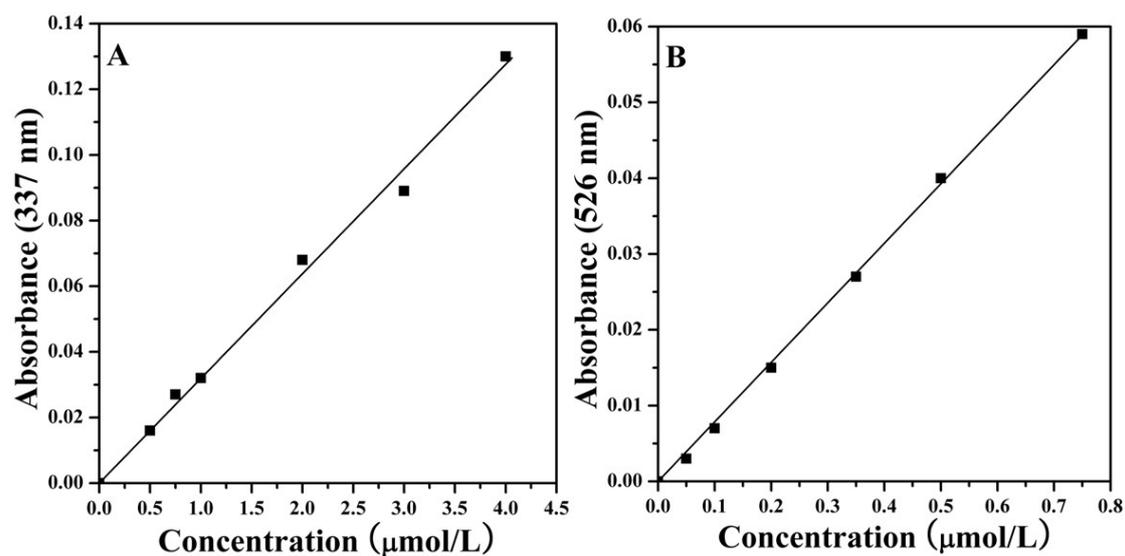
THF solution containing (PtBA-*g*-PS)-*co*-PPEGMEMA **2a** asymmetric polymer brush and pyrene was added dropwise to deionized water under vigorous stirring until the concentrations of polymer and pyrene reached 0.08 mg/mL and 0.01 mmol/L, respectively. THF was evaporated by stirring moderately overnight at room temperature. For the control experiment, only pyrene was added to deionized water. Both solutions were filtered through a 0.45  $\mu\text{m}$  syringe filter and the obtained solutions were employed for the measurement of UV absorption spectroscopy.

### **Coencapsulation of Rhodamine 6G and Pyrene in Micelles**

THF solution containing (PtBA-*g*-PS)-*co*-PPEGMEMA **2a** asymmetric polymer brush and pyrene was added dropwise to deionized water under vigorous stirring until the concentration of polymer and pyrene reached 0.08 mg/mL and 0.01 mmol/L, respectively. Rhodamine 6G aqueous solution was then added to the above solution until the concentration of R6G reached 0.02 mmol/L. THF was evaporated by stirring moderately overnight at room temperature. The resultant solution was dialyzed against water using dialysis membrane ( $MW_{\text{cut-off}} = 3.5 \text{ kDa}$ ) until the dialysate did not show any detectable UV signal. The obtained solution was used for the measurement of UV absorption spectroscopy.



**Figure S3.** (A) TEM image and (B) hydrodynamic diameter distribution of spherical micelles formed by PEG<sub>113</sub>-b- PS<sub>100</sub> diblock copolymer.



**Figure S4.** (A) UV-vis absorbance standard curve of pyrene at 337 nm,  $A = 0.031C$ .

(B) UV-vis absorbance standard curve of R6G at 526 nm,  $A = 0.081C$ .

## References and Notes

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