Supporting Information for

PHEA-g-PDMAEA Well-Defined Graft Copolymer: SET-LRP Synthesis, Self-Catalyzed Hydrolysis, and Quaternization

Fangxu Sun, Chun Feng,* Haoyu Liu, Xiaoyu Huang*

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

Experimental Section

Materials

2-(Dimethylamino)ethyl acrylate (DMAEA, Aldrich, 98%) was passed through a basic alumina column and distilled under reduced pressure from CaH₂ prior to use. Copper(I) chloride (CuCl, Aldrich, 99%) was purified by stirring overnight over CH₃CO₂H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying *in vacuo* at 40°C overnight. Dimethyl formamide (DMF, Aldrich, 99.8%) was dried over KOH and distilled from CaH₂ under N₂ prior to use. Tetrahydrofuran (THF, Aldrich, 99%) was dried over CaH₂ and distilled from sodium and benzophenone under N₂ prior to use. 1,4-Dioxane (Aldrich, 99%) and iodomethane (CH₃I, Aldrich, 99%) were used as received. 2-Hydroxyethyl 2-((2-chloropropanoyloxy)methyl)acrylate (HECPMA),¹ cumyl dithiobenzoate (CDB),² and tris(2-(di-methylamino)ethyl)amine (Me₆TREN)³ were synthesized according to previous literatures.

Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a 4 cm⁻¹ resolution. All ¹H (500 MHz) and ¹³C (125 MHz) NMR analyses were performed on a Bruker Avance 500 spectrometer in DMSO- d_6 , CDCl₃, and D₂O. Elemental analysis was carried out on a Carlo-Erba1106 system. 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 LiBr-added DMF ([LiBr] = 15 mM) as eluent (flow rate: 1.0 mL/min). The system was calibrated with linear poly(methyl methacrylate) standards. Absolute molecular weight of the macroinitiator was determined by GPC equipped with a multiangle light scattering detector (GPC/MALS), DMF was used as the eluent with a flow rate of 1.0 mL/min, detectors: Wyatt Optilab rEX refractive index detector and Wyatt DAWN HELEOS 18-angle light scattering detector with a 50 mW solid-state laser operating at 658 nm. UV/vis spectra were measured by a Hitachi U-2910 spectrophotometer with a rate of 100 nm/min. TEM images were obtained by a JEOL JEM-2100 instrument operated at 80 kV.

RAFT Homopolymerization of HECPMA

AIBN (9.3 mg, 0.057 mmol) and CDB (46.3 mg, 0.17 mmol) were first added into

a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N₂. Next, HECPMA **1** (1.00 g, 4.25 mmol) and 0.22 mL of anhydrous DMF 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 80°C. The polymerization was terminated by immersing the flask into liquid N₂ after 8 h. THF was added to dilute the solution and the solution was precipitated into cold diethyl ether. The crude product was purified by repeated dissolution and precipitation followed by drying *in vacuo* overnight to give 0.832 g of pink powder.

To remove the dithiobenzoate end moiety, AIBN (0.46 g, 2.8 mmol) and 0.7 g of pink powder (0.085 mmol of dithiobenzoate group determined from $M_{n,GPC/MALS}$ = 8,223 g/mol) were first added to a 100 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N₂. Next, 30 mL of anhydrous THF was added via a gastight syringe. The flask was immersed into an oil bath set at 60°C and the reaction was quenched by liquid N₂ after 48 h. The solution turned colorless and was precipitated into cold diethyl ether after concentration. After repeated purification via dissolution and precipitation, 0.50 g of white powder, poly(2-hydroxyethyl 2-((2-chloropropanoyloxy)methyl)acrylate) (PHECPMA) **2**, was obtained by drying *in vacuo* overnight. GPC: $M_{n,GPC}$ = 5,600 g/mol, M_w/M_n = 1.10. GPC/MALS: $M_{n,GPC/MALS}$ = 8,223 g/mol, M_w/M_n = 1.08. FT-IR: v (cm⁻¹): 3435 (v_{O-H}), 2953, 2876, 1735 ($v_{C=O}$), 1450, 1382, 1339, 1252, 1176, 1076, 1008, 972, 910, 846, 749, 702. ¹H NMR (DMSO-*d*₆): δ (ppm): 1.18 (12H, terminal

C(CH₃)₂), 1.66 (3H, CHClCH₃), 1.98 (2H, CH₂CCO₂), 3.56 (2H, CO₂CH₂CH₂OH), 3.82 (2H, CO₂CH₂CH₂OH), 4.07 (2H, CO₂CCH₂O), 4.63 (1H, CHClCH₃), 4.88 (1H, CH₂OH), 7.11-7.30 (5H, terminal C₆H₅). ¹³C NMR (DMSO-d₆): δ (ppm): 21.8 (CHClCH₃), 44.3 (CH₂CCO₂), 47.8 (CHClCH₃), 53.3 (CO₂CH₂CH₂OH), 58.5 (CO₂CCH₂O), 64.6 (CH₂CCO₂), 67.4 (CO₂CH₂CH₂OH), 126.0, 128.1 (C₆H₅), 169.2 (CH₂CCO₂), 172.3 (CO₂CHCl).

SET-LRP Graft Copolymerization of DMAEA

In a typical procedure, PHECPMA **2** (11.8 mg, $M_{n,GPC/MALS} = 8,223$ g/mol, M_w/M_n = 1.08, $N_{HECPMA} = 34.0$, 0.05 mmol (-OCOCH(CH₃)Cl group) and CuCl (5.0 mg, 0.05 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 N₂. Next, freshlydistilled DMF (1.52 mL) and DMAEA (1.52 mL, 10 mmol) were introduced via a gastight syringe. The solution was degassed by three cycles of freezing- pumpingthawing. Finally, Me₆TREN (13.6 µL, 0.05 mmol) was charged via a gastight syringe followed by stirring 5 min at room temperature, and the flask was then immersed into an oil bath set at 40°C. The polymerization was terminated by immersing the flask into liquid N₂ after 1 h. The reaction 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 *n*-hexane. After repeated purification by dissolving in THF and precipitating in cold *n*-hexane, 135 mg of faint yellow sticky solid, PHEA-g-PDMAEA **3a**, was obtained after drying *in vacuo* overnight. GPC: M_n = 47,100 g/mol, M_w/M_n = 1.17. FT-IR: v (cm⁻¹): 3433 (v_{0-H}), 2947, 2859, 2820, 2769, 1735 (v_{C=0}), 1455, 1399, 1266, 1166, 1101, 1044, 957, 839, 781. ¹H NMR (CDCl₃): δ (ppm): 1.26, 1.47, 1.66, 1.92 (2H, CH₂C of PHEA backbone and 3H, CH₂CH of PDMAEA side chains), 2.30 (6H, CO₂CH₂CH₂N(CH₃)₂), 2.58 (2H, CO₂CH₂CH₂N(CH₃)₂), 3.56 (2H, CO₂CH₂CH₂OH), 4.16 (2H, CO₂CH₂CH₂OH, 2H, CO₂CCH₂O, and 2H, CO₂CH₂CH₂N(CH₃)₂2H). Element analysis: N% = 8.97%.

Self-Catalyzed Hydrolysis of PHEA-g-PDMAEA

PHEA-*g*-PDMAEA **3** graft copolymer (8 mg) was dissolved in 0.8 mL of D_2O and 0.8 mL of basic D_2O buffer solution (pH = 10.1, Na₂CO₃ (19.1 mg)/NaHCO₃ (5.1 mg)/D₂O (3 mL)) at room temperature, respectively. ¹H NMR spectra of PHEA-*g*-PDMAEA **3** graft copolymer in different D_2O solutions were measured at different time intervals so as to determine the degree of hydrolysis.

Quaternization of PHEA-g-PDMAEA

PHEA-*g*-PDMAEA **3** graft copolymer (100 mg) was dissolved in 3 mL of 1,4dioxane at room temperature. Next, CH₃I (52 µL) was added via a gastight syringe. The solution was stirred at room temperature and yellow precipitation appeared after 20 min. The reaction was terminated by adding water followed by dialysis against saturated brine and deionized water. Finally, 102.3 mg of yellow solid was obtained by drying *in vacuo* overnight. ¹H NMR (D₂O): δ (ppm): 3.13 (9H, CO₂CH₂CH₂N⁺(CH₃)₃Cl⁻), 3.66 (2H, CO₂CH₂CH₂N⁺(CH₃)₃Cl⁻), 4.43 (2H, $CO_2CH_2CH_2OH$, 2H, CO_2CCH_2O , and 2H, $CO_2CH_2CH_2N^+(CH_3)_3CI^-$). The stability of quaternized product was examined by measuring ¹H NMR spectra in D₂O at different time intervals.

Micellar Morphology of Quaternized PHEA-g-PDMAEA

Quaternized PHEA-*g*-PDMAEA (2.9 mg) was dissolved in 2.9 mL of deionized water and the aqueous solution (1 mg/mL) was filtered through a 0.45 μ m membrane. The filtrate (0.4 mL) was added to 0.6 mL of deionized water and THF was added slowly (0.3 mL/h) to aqueous stock solution of quaternized PHEA-*g*-PDMAEA (0.4 mg/mL) until the desired THF content (25 wt% or 50 wt%) was reached. For TEM studies, 10 μ L of micellar solution was deposited on an electron microscopy copper grid coated with carbon film, and the water and THF were evaporated at room temperature.

References and Notes

- 1. Jiang, X. Y.; Lu, G. L.; Feng, C.; Huang, X. Y. Polym. Chem. 2014, 5, 4915-4925.
- Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* 2000, *49*, 993-1001.
- 3. Tillmanns, E. J.; Ritter, J. J. Org. Chem. 1957, 22, 839-840.



Figure S1. ¹H (A) and ¹³C (B) NMR spectra of PHECPMA 2 in DMSO-*d*₆.



Figure S2. FT-IR spectra of PHECPMA 2 (A) and PHEA-g-PDMAEA 3 (B).



Figure S3. GPC traces of PHECPMA 2 and PHEA-g-PDMAEA 3 in DMF.