

Supporting information for
PDMAEMA-*b*-PPOA-*b*-PDMAEMA Double-Bond-Containing
Amphiphilic Triblock Copolymer: Synthesis, Characterization,
and pH-Responsive Self-Assembly

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Experimental section

Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 97%) was passed through a basic alumina column and distilled *in vacuo* from CaH₂ 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 CH₃COOH at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying *in vacuo* at 40°C for one day. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. Dimethyl formamide (DMF, Aldrich,

99.8%) was dried over KOH and distilled from CaH₂ under N₂ prior to use. Triethylamine (Aldrich, 99.5%) was dried over KOH for several days followed by distilling from CaH₂ under Ar prior to use. Tetrahydrofuran (THF, Aldrich, 99%) and toluene (Aldrich, 99.5%) were dried over CaH₂ for a week and distilled from sodium and benzophenone under Ar prior to use. 2-Bromopropionyl chloride (Aldrich, 97%), hydroquinone (Aldrich, 99%), 4,4'-azobis(4-cyanopentanoic acid) (Acros, 97%), and thionyl chloride (Aldrich 99%) were used as received. Phenoxyallene (POA)¹ and tris(2-(di-methylamino)ethyl)amine (Me₆TREN)² were synthesized according to previous reports.

Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FTIR spectrophotometer with a resolution of 4 cm⁻¹. All ¹H (500 MHz) and ¹³C (125 MHz) NMR analyses were performed on a Bruker Avance 500 spectrometer in CDCl₃, TMS (¹H NMR) and CDCl₃ (¹³C NMR) were used as internal standards. Elemental analysis was carried out on a Carlo-Erba 1106 system. Bromine content was determined by the titration with Hg(NO₃)₂. 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

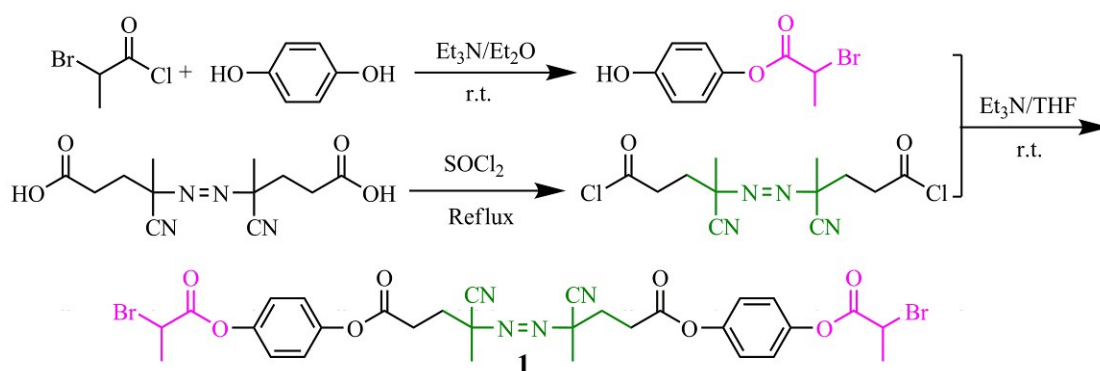
was calibrated with linear polystyrene standards. Absolute molecular weight of the macroinitiator was determined by GPC equipped with a multiangle light scattering detector (GPC/MALS), THF was used as the eluent with a flow rate of 1.0 mL/min, detectors: Wyatt Optilab rEX refractive index detector and Wyatt DAWN HELEOS 18-angle light scattering detector with a 50 mW solid-state laser operating at 658 nm. Steady-state fluorescent spectra were recorded on a Hitachi F-4500 spectrofluorometer at room temperature with the band widths of 10 nm for excitation and 2.5 nm for emission, where $\lambda_{\text{ex}} = 339$ nm. Transmission electron microscope (TEM) images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

Synthesis of azo-ATRP bifunctional initiator

Bifunctional initiator **1** was synthesized in three steps using 4,4'-azobis(4-cyanopentanoic acid), 2-bromopropionyl chloride, and hydroquinone as starting materials (Scheme S1).^{3,4} Hydroquinone (2.30 g, 20.91 mmol), diethyl ether (150 mL) and triethylamine (4 mL) were firstly added to a 250 mL three-neck flask followed by adding 2-bromopropionyl chloride (2 mL, 19.83 mmol) dropwise. After the reaction was complete monitored by thin layer chromatography (TLC), the mixture was filtered and the filtrate was concentrated. The purified 4-hydroxyphenyl 2-bromopropanoate (3.43 g, 70.5%) was obtained by silica column chromatography.

The mixture of 4,4'-azobis(4-cyanopentanoic acid) (4.2 g, 15 mmol) and thionyl chloride (30 mL) was refluxed at 75°C for 1 h. After the unreacted thionyl chloride was removed by pumping, the residue (yellow solid) was dissolved in 50 mL of THF

and this solution was then added dropwise to the mixture of 4-hydroxyphenyl 2-bromopropanoate (7.92 g) and triethylamine (4.2 mL) in 100 mL of THF. After the reaction was complete monitored by TLC, the mixture was filtered and the filtrate was concentrated followed by silica column chromatography and recrystallization from methanol to provide the desired azo-ATRP bifunctional initiator **1** (white solid) with a yield of 31.5% (3.47 g). Anal. Calcd. for $C_{30}H_{30}Br_2N_4O_8$: Calcd: C, 49.06%; H, 4.12%; N, 7.63%; Br, 21.76%. Found: C, 49.40%; H, 4.02%; N, 7.36%; Br, 21.49%. FT-IR: ν (cm^{-1}): 3116, 3075, 2995, 2925, 2237 ($C\equiv N$), 1756 ($C=O$), 1502, 1445, 1339, 1182, 1135, 930, 897, 840, 523 ($C-Br$). 1H NMR ($CDCl_3$): δ (ppm): 1.75 (6H, $CH_3C(CN)CH_2CH_2CO_2$), 1.95 (6H, CH_3CHBr), 2.61 (8H, $CH_3C(CN)CH_2CH_2CO_2$), 4.59 (2H, CH_3CHBr), 7.13 (8H, C_6H_4). ^{13}C NMR: δ (ppm): 21.4, 24.0, 29.1, 33.0, 39.4, 117.4, 122.2, 148.0, 168.5, 169.7.



Scheme S1. Synthesis of Azo-ATRP bifunctional initiator **1**.

Free radical homopolymerization of POA

Bifunctional initiator **1** (0.3694 g, 0.50 mmol) was first added to a 100 mL Schlenk flask (flame-dried *in vacuo* prior to use) sealed with a rubber septum for degassing and kept under Ar. Next, POA (16 mL, 135.7 mmol) and toluene (16 mL) were

introduced via a gastight syringe. The solution was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 75°C to start the polymerization. The polymerization was terminated by immersing the flask into liquid N₂ after 24 h. The reaction mixture was diluted by THF and precipitated into *n*-hexane. After repeated purification by dissolving in THF and precipitating in *n*-hexane, 8.4217 g of white powder, poly(phenoxyallene) (PPOA) **2** homopolymer, i.e. Br-PPOA-Br **2** macroinitiator, was obtained after drying *in vacuo* overnight. GPC: $M_{n, \text{GPC}} = 10,900$ g/mol, $M_w/M_n = 1.93$. GPC/MALS: $M_{n, \text{GPC/MALS}} = 10,400$ g/mol, $M_w/M_n = 1.91$. Element analysis: Br% = 1.52%. FT-IR: ν (cm⁻¹): 3070, 3039, 2952, 2926, 1761 (C=O), 1675, 1643 (C=C), 1595, 1491, 1456, 1337, 1290, 1227, 1171, 1135, 1030, 892, 752, 691. ¹H NMR (CDCl₃): δ (ppm): 1.61 (6H, CH₃CCN), 1.93 (6H, CH₃CHBr), 2.55 (2H×x, =C-CH₂), 4.57 (2H, CH₃CHBr), 5.00 (1H×y, CH₂=CCHO), 5.21 (2H×y, CH₂=CCHO), 6.85, 6.92, 7.01, 7.16 (1H×x, C=CHOC₆H₅ and 5H, C₆H₅). ¹³C NMR: δ (ppm): 19.4, 21.3, 25.5, 28.9, 30.4, 33.5, 35.9, 39.4, 72.6, 112.5, 115.7, 116.6, 120.8, 122.7, 141.8, 158.3, 169.0.

SET-LRP block copolymerization of DMAEMA

Br-PPOA-Br **2** macroinitiator ($M_{n, \text{GPC/MALS}} = 10,400$ g/mol, $M_w/M_n = 1.91$, Br% = 1.52%) and CuBr were first added to a 25 mL Schlenk flask (flame-dried *in vacuo* prior to use) sealed with a rubber septum for degassing and kept under Ar. DMAEMA monomer, DMF, and Me₆TREN were charged via a gastight syringe and the flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the

flask into an oil bath set at 50°C. The polymerization was quenched by putting the flask into liquid N₂ after certain time. 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 *n*-hexane. After repeated purification by dissolving in THF and precipitating in *n*-hexane, the crude product was dried *in vacuo* overnight to afford the final product (white powder), PDMAEMA-*b*-PPOA-*b*-PDMAEMA **3** triblock copolymer. FT-IR: ν (cm⁻¹): 2947, 2821, 2770, 1729, 1596, 1491, 1456, 1235, 1150, 1043, 965, 753, 692. ¹H NMR (CDCl₃): δ (ppm): 0.88, 1.04, 1.25 (3H×m, CH₂CCH₃), 1.81, 2.01 (2H×m, CH₂CCH₃), 2.28 (6H×m, CO₂CH₂CH₂N(CH₃)₂), 2.57 (2H×m, CO₂CH₂CH₂N(CH₃)₂ and 2H×x, =C-CH₂), 4.05 (2H×m, CO₂CH₂CH₂N(CH₃)₂), 5.02 (1H×y, CH₂=CCHO), 5.17 (2H×y, CH₂=CCHO), 6.85, 7.05 (1H×x, C=CHOC₆H₅ and 5H, C₆H₅).

Determination of critical micelle concentration

PNA was used as fluorescence probe to measure the *cmc* of PDMAEMA-*b*-PPOA-*b*-PDMAEMA **3** triblock copolymer 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 PDMAEMA-*b*-PPOA-*b*-PDMAEMA **3** copolymer (1, 0.1, 0.01, 0.001, or 0.0001 mg/mL) to water containing PNA ([PNA] = 0.002 mM). All fluorescence spectra were recorded at 25°C.

Micellar morphology

Micellar solutions were prepared via the dialysis approach. THF solution of PDMAEMA-*b*-PPOA-*b*-PDMAEMA **3** triblock copolymer (2 or 0.2 mg/mL) was first filtered through a membrane with a nominal pore size of 0.45 μm . Next, a certain amount of deionized water was added slowly (0.36 mL/h) to 1.00 g of THF solution of copolymer **3** by a microsyringe until the preset water content (50 wt%) was reached. Subsequently, the solution was dialyzed against deionized water with slow stirring for 3 days to remove THF completely, and deionized water was changed twice a day to obtain aqueous micellar solution. For TEM studies, 10 μL of micelle solution was deposited on an electron microscopy copper grid coated with carbon film and the water was evaporated at room temperature.

References

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