Supporting information for

Polyallene-Based Amphiphilic Triblock Copolymer via Successive Free Radical Polymerization and ATRP

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Experimental Section

Materials

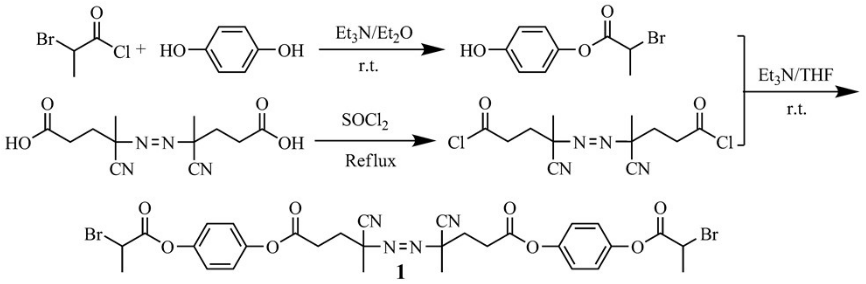
Oligo(ethylene glycol) methyl ether methacrylate (OEGMM, Aldrich, 99%, M_n= 300 g/mol) was passed through a basic alumina column prior to use. Styrene (St, Aldrich, 99%) was washed with 5% aqueous NaOH solution and water, dried over $MgSO_4$, and distilled twice from CaH_2 under reduced pressure prior to use. Methyl methacrylate (MMA, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$ and distilled twice *in vacuo* from CaH_2 prior to use. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3COOH at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying *in vacuo* at 40^{o}C for one day. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. Triethylamine (Aldrich, 99.5%) was dried over KOH for several days followed by distilling from CaH_2 under Ar prior to use. Tetrahydrofuran (THF, Aldrich, 99%) and toluene (Aldrich, 99.5%) were dried over CaH_2 for a week and distilled from sodium and benzophenone under Ar prior to use. 2-Bromopropionyl chloride (2-BPC, Aldrich, 97%), hydroquinone (Aldrich, 99%), thionyl chloride (Aldrich 99%), 4,4'-azobis(4-cyanopentanoic acid) (Acros, 97%), potassium carbonate (Aldrich 99%), and potassium persulfate (Aldrich 99%) were used as received. Phenoxyallene (POA)[1] and 4,4'-diheptal-2,2'-bipyridine (dHbpy)[2] were synthesized according to previous literatures.

Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FTIR spectrophotometer with a resolution of 4 cm^{-1}. All ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR analyses were performed on a Bruker Avance 500 spectrometer in $CDCl_3$, TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards. Elemental analysis was carried out on a Carlo-Erba1106 system. Bromine content was determined by the titration with $Hg(NO_3)_2$. 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. The phase transition temperature of the triblock copolymer was measured by UV/vis spectroscopy using a Hitachi U-2910 spectrophotometer over a temperature range between 22°C and 66°C, the temperature was controlled and measured using a DC-1006 variable temperature cryostat with an increasing rate of 2°C min^{-1}. Steady-state fluorescent spectra were recorded on a Hitachi F-2700 spectrofluorometer at 25°C with the band widths of 10 nm for excitation and 2.5 nm for emission, where λ_{ex} = 339 nm. Hydrodynamic diameter (D_h) is measured at 25°C by dynamic light scattering (DLS) with a Wyatt DynaPro laser photometer. 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 commercially available 2-BPC, hydroquinone, and 4,4'-azobis(4-cyanopentanoic acid) as starting materials (Scheme S1). Hydroquinone (2.30 g, 20.91 mmol), diethyl ether (150 mL) and triethylamine (4 mL) were added to a 250 mL three-neck flask followed by adding 2-BPC (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.



Scheme S1. Synthesis of Azo-ATRP Bifunctional Initiator **1**.

The mixture of 4,4’-azobis(4-cyanopentanoic acid) (4.2 g, 15 mmol) and thionyl chloride (30 mL) was refluxed at 75^{o}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≡N), 1756 (C=O), 1502, 1445, 1339, 1182, 1135, 930, 897, 840, 523 (C-Br). ^{1}H NMR: 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.

Free Radical Homopolymerization of Phenoxyallene

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 (17 mL, 144.2 mmol) and toluene (17 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 N_2 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, 9.2658 g of white powder, poly(phenoxyallene) (PPOA) **2** homopolymer, i.e. Br-PPOA-Br **2** macroinitiator, was obtained after drying *in vacuo* overnight. GPC: $M_{n,GPC}$ = 11,400 g/mol, M_w/M_n = 1.74. GPC/MALS: $M_{n,GPC/MALS}$ = 11,000 g/mol, M_w/M_n = 1.70. Element analysis: Br% = 1.43%. 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. ^{1}H NMR: δ (ppm): 1.61 (6H, CH_3CCN), 1.93 (6H, CH_3CHBr), 2.55 (2H×x, =C-CH_2), 4.57 (2H, CH_3CHBr), 5.00 (1H×y, CH_2=CCHO), 5.21 (2H×y, CH_2=CCHO), 6.85, 6.92, 7.01, 7.16 (1H×x, C=CHOC_6H_5 and 5H, C_6H_5). ^{13}C 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.

ATRP Block Copolymerization of OEGMM

Br-PPOA-Br **2** macroinitiator ($M_{n,GPC/MALS}$ = 11,000 g/mol, M_w/M_n = 1.70, Br% = 1.43%, 1.10 g, 0.2 mmol ATRP initiating group), CuBr (0.0288 g, 0.02 mmol), and dHbpy (0.0311 g, 0.2 mmol) 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. OEGMM (5.60 mL, 20 mmol) and THF (5.60 mL) 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 lasted 18 h and was quenched by putting the flask into liquid N_2. 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), POEGMM-*b*-PPOA-*b*-POEGMM **3** triblock copolymer (0.6892 g). GPC: M_n =13,600 g/mol, M_w/M_n =1.42. FT-IR: ν (cm^{-1}): 2955, 2924, 1730, 1674, 1644, 1595, 1491, 1456, 1228, 1168, 1133, 1030, 752, 691. ^1H NMR: δ (ppm): 0.87, 1.02, 1.26 (3H×2m, CH_2CCH_3), 1.61, 1.80 (2H×2m, CH_2CCH_3), 2.54 (2H×x, =C-CH_2), 3.38 (3H×2m, CH_2OCH_3), 3.55 (2H×2m, CH_2OCH_3), 3.65 (8H×2m, OCH_2CH_2), 4.08 (2H×2m, $COOCH_2CH_2$), 4.99 (1H×y, CH_2=CC*H*O), 5.19 (2H×y, CH_2=CCHO), 6.88, 6.92, 7.04 (1H×x, C=C*H*OC_6H_5 and 5H, C_6H_5).

Determination of Critical Micelle Concentration

PNA was used as fluorescence probe to measure the critical micelle concentration (*cmc*) of POEGMM-*b*-PPOA-*b*-POEGMM **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 POEGMM-*b*-PPOA-*b*-POEGMM **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^{o}C.

Micellar Morphology

Micellar solutions were prepared in two different ways: (1) direct addition method: THF solution of POEGMM-*b*-PPOA-*b*-POEGMM **3** triblock copolymer (2 mg/mL) was added dropwise to deionized water under vigorous stirring until the concentration of polymer reached 0.1 mg/mL. THF was evaporated by stirring moderately overnight at room temperature; (2) dialysis method: THF solution of POEGMM-*b*-PPOA-*b*-POEGMM **3** triblock copolymer (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 triblock 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.

Aqueous Polymerization of Styrene and Methyl Methacrylate Using POEGMM-*b*-PPOA-*b*-POEGMM as Stabilizer

To a 100 mL Schlenk flask containing 50 mL of deionized water, 3 mL of THF solution of POEGMM-*b*-PPOA-*b*-POEGMM **3** triblock copolymer (10 mg/mL) was first added under stirring. Next, monomer (St or MMA) (5 mL) and potassium carbonate (40 mg) were added, and the flask was sealed with a rubber septum followed by bubbling with Ar for 20 min at a preset temperature (70^{o}C for St or 75^{o}C for MMA). Another 5 mL of aqueous solution of potassium persulfate (40 mg) was first bubbled with Ar for 20 min and introduced into the flask via a gastight syringe. The reaction system was stirred at the preset temperature (70^{o}C for St or 75^{o}C for MMA) for another 8 h.

The reaction system was placed at room temperature overnight, and the suspension was not broken. After adding NaCl into the suspension systems until saturation, the suspension system was still stable. When pH value of the system was adjusted to 0 by HCl or 14.0 by NaOH, the suspension did not demulsify. The suspension was subjected to freeze at -20°C for 4 h and thaw at 35°C for 2 h. After five cycles of freezing and thawing, the polystyrene (PS) suspension was broken with the presence of precipitation after standing, while the poly(methyl methacrylate) (PMMA) suspension was still stable. PS suspension was stable after it was frozen at -20°C for 3 days followed by thawing, while PMMA suspension was still stable without precipitation after it was frozen at -20°C for a much longer period (16 days) followed by thawing.

After breaking PS suspension followed by centrifugation, PS polymer was dried *in vacuo* overnight to afford 1.503 g of final product (M_n = 42,700 g/mol, M_w/M_n = 2.47) with a yield of 33.2%. PMMA suspension was distillated under reduced pressure to remove water for providing the crude product, and the final product (4.541 g, 96.2% yield, M_n = 251,700 g/mol, M_w/M_n = 2.02) was obtained by drying *in vacuo* overnight.

References

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2. Leduc, M. R.; Hawker, C. I.; Dao, J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 11111-11118.

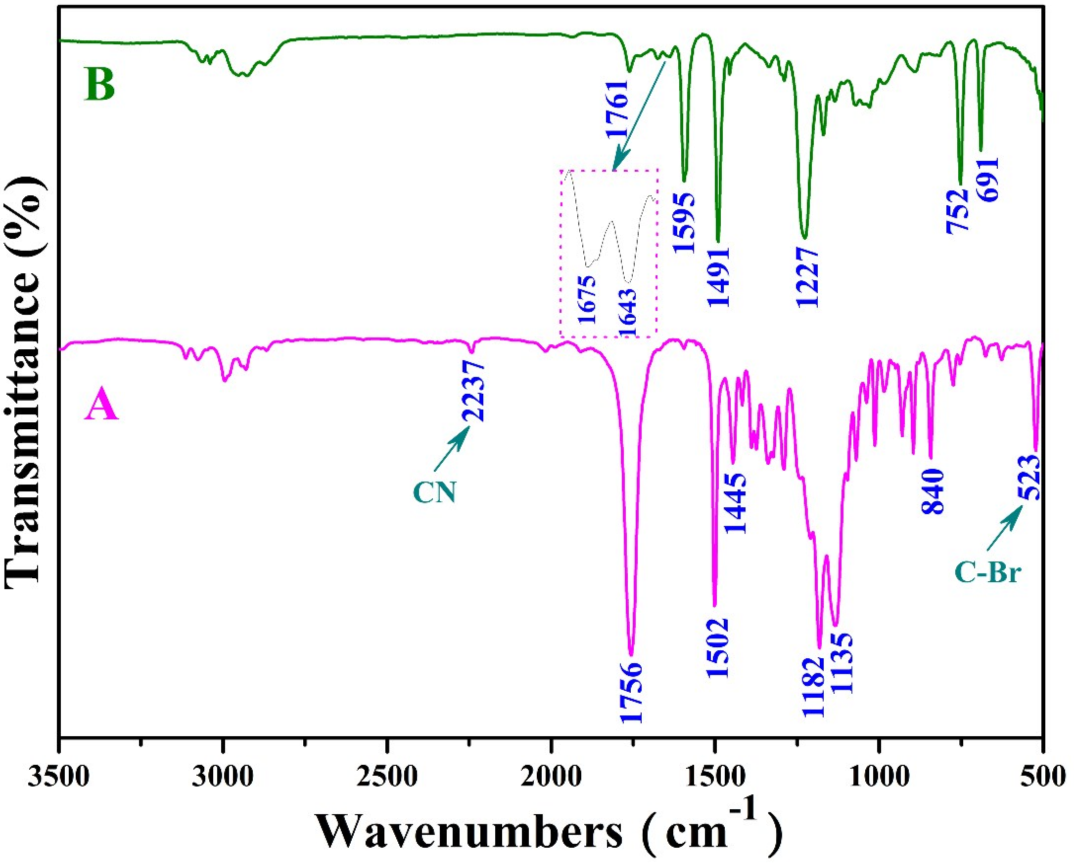

Figure S1. FT-IR spectra of bifunctional initiator **1** (A) and Br-PPOA-Br **2** (B).

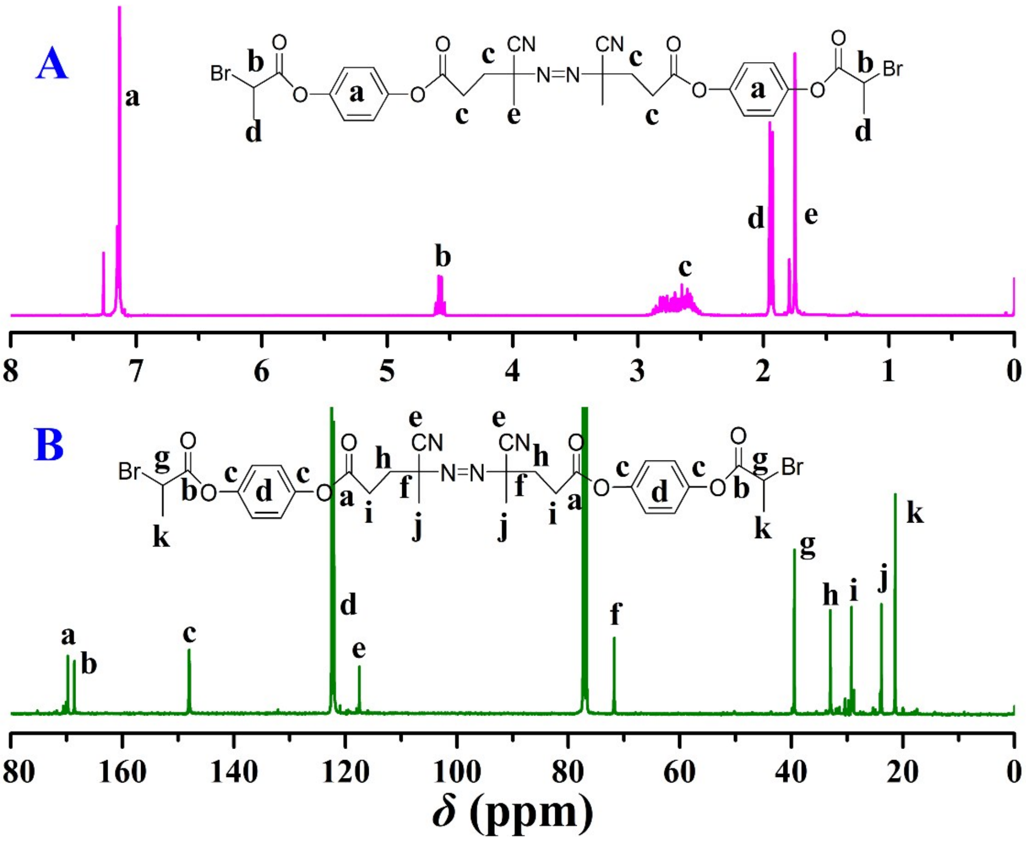

Figure S2. ^{1}H (A) and ^{13}C (B) NMR spectra of bifunctional initiator **1** in $CDCl_3$.

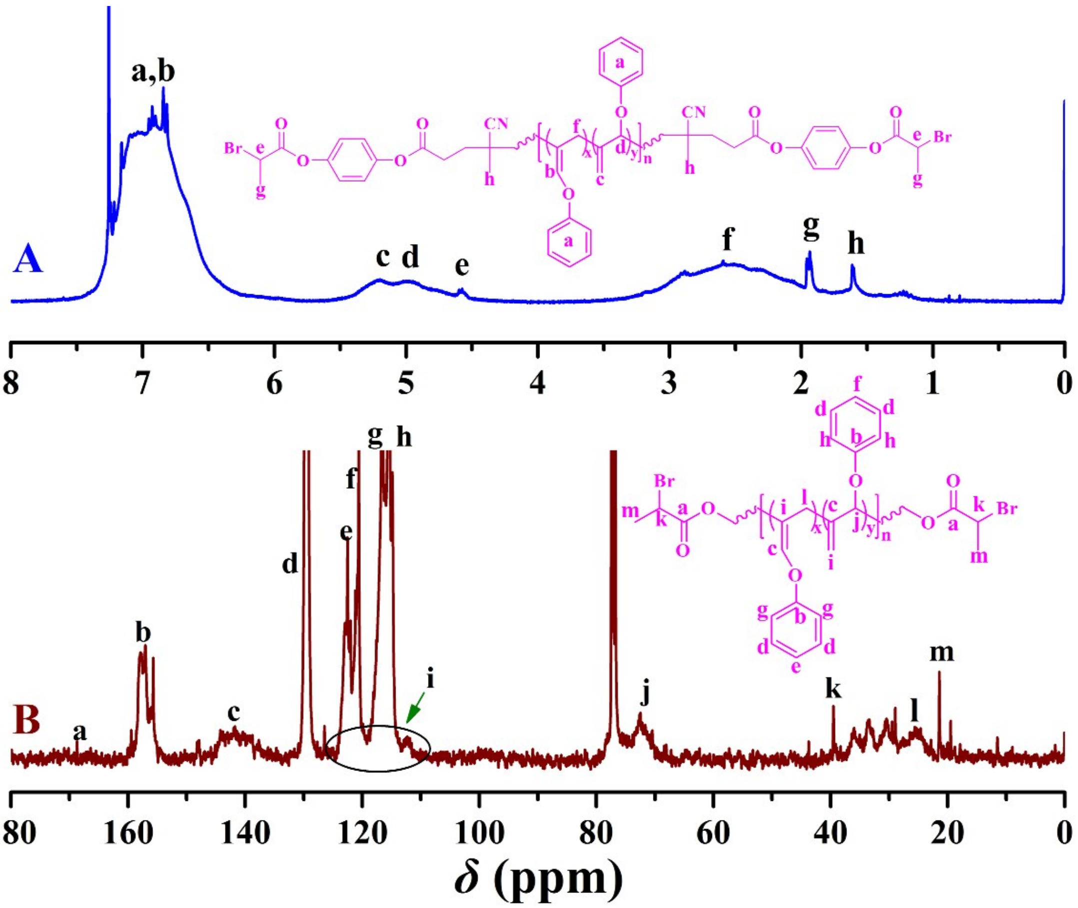

Figure S3. ^{1}H (A) and ^{13}C (B) NMR spectra of Br-PPOA-Br **2** in $CDCl_3$.