Electronic Supplementary Material (ESI) for Polymer Chemistry.

A facile approach for preparing multicyclic polymer through combining ATRP and photo-induced coupling reaction

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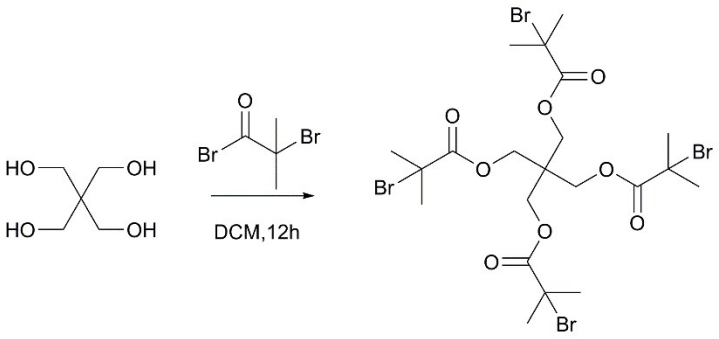
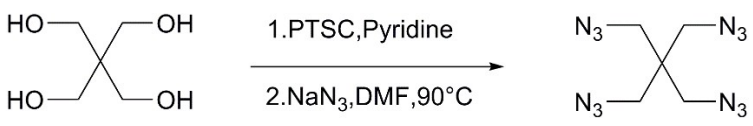
Synthesis of tetrafunctional initiator (*1*)



1

Pentaerythritol (1.0 g, 7.35 mmol) was added to a flask with 50 mL of dried THF and 5 mL of triethylamine (TEA), then 2-bromoisobutyryl bromide (4.35 mL, 35.25 mmol) was added dropwise to the flask at 0 ^{o}C within 30 min. The reaction was conducted for 12 h at room temperature. DCM (50 mL) was added to the flask and the reaction mixture was washed with water for three times, then the organic phase was dried with anhydrous Na_2SO_4. The crude product was obtained under reduced pressure and then it was purified by column chromatography using DCM as eluent to give the white solid (4.3 g, yield = 80%).

Synthesis of pentaerythritol tetraazide (2)

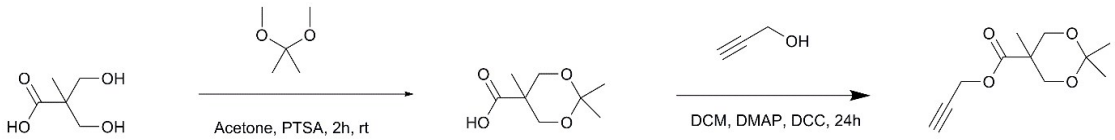


2

1). Pentaerythritol (3.0 g, 22.0 mmol) was slowly added to the flask containing the solution of p-toluenesulfonyl chloride (18.0 g, 94.0 mmol) in pyridine (30 mL) under ice bath within 0.5 h. Then the reaction mixture was stirred at room temperature overnight. Cold water (20 mL) was added and the mixture was stirred for another 2 h, then poured into cold water (200 mL). The obtained crude product was mixed with 100 mL of ethanol and then stirred for 4 h to give the white powder (13.2 g, yield = 80%) (pentaerythritol tetrakis (p-toluenesulfonyl)).

2). The white powder (8.0 g, 10.6 mmol) obtained from the previous step and sodium azide (6.5 g, 100 mmol) were added to the flask with 60 mL of DMF, then the mixture was stirred at 80 ^{o}C for 12 h. The solvent was removed under vacuum, then the residue was dissolved in 50 mL of diethyl ether, and the mixture was washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and concentrated, then dried under vacuum to give pentaerythritol tetraazide (**2**) as white solid (2.0 g, yield = 80%) (compound 2 is very unstable and explosive and it should be stored carefully).

Synthesis of compound 3



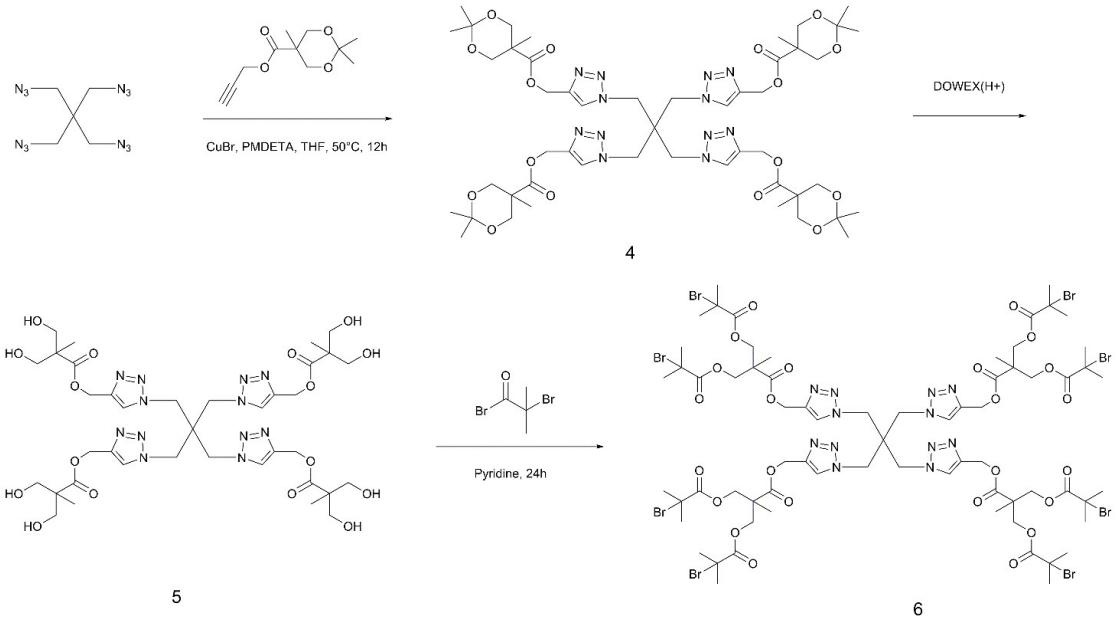
3

1). 2,2-Dimethylol propionic acid (30.0 g, 224.0 mmol) and PTSA (2.0 g, 11.6mmol) were added into the solution of 2,2-dimethoxypropane (41.4 mL, 337.0 mmol) in acetone (150 mL) and the mixture was stirred at room temperature for 2 h. $NH_3 \cdot H_2O$ / ethanol (v/v=1:1) mixture (3 mL) was added into flask, then the solvent was removed under vacuum. Subsequently, the residue was dissolved in 200 mL of DCM. The mixture was washed with water three times and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum to give the white solid (37.5 g, yield = 96%) (2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid).

2). 2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (15.0 g, 86.0 mmol), propargyl alcohol (7.5 mL, 128.0 mmol) and DMAP (5.1 g, 42.0 mmol) were added into the

flask with 150 mL of DCM. The solution of DCC (20.0 g, 97.1 mmol) in DCM (30 mL) was added dropwise to the flask under ice bath within 0.5 h, then the mixture was stirred for 24 h at room temperature. After reaction, the salt was removed by filtration and the filtrate was collected and washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography using ethyl acetate/hexane (1/25, v/v) as eluent to give the compound 3 as colorless oil (15.0 g, yield = 82%).

Synthesis of octafunctional initiator (6)

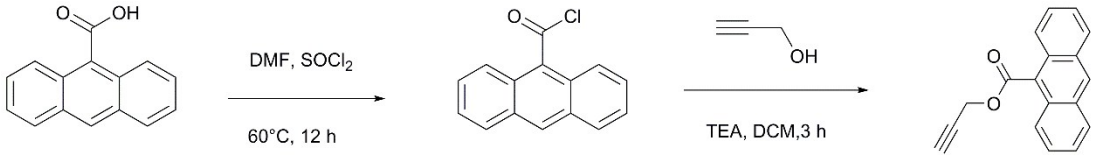


1) CuBr (1.33g, 9.32 mmol) and PMDETA (1.65 mL, 9.32 mmol) were added to a Schlenk flask containing the solution of compound 2 (0.55 g, 2.33 mmol) and 3 (1.98 g, 9.32 mmol) in THF (10 mL). The mixture was pumped with nitrogen for 10 min and then the reaction was conducted at 50 ^oC for 12 h. After reaction, the mixture was passed through alumina column to remove copper salts and further purified by column chromatography using DCM/ethyl acetate (3/1, v/v) as eluent to give the white solid (compound 4) (2.0 g, yield = 80%).

2) Compound 4 (1.3 g, 1.2 mmol) in 10 mL of methanol was added to flask with DOWEX resin (1.0 g) and the suspension was stirred at 50 ^oC for 3 h. Then suspension was filtered and the filtrate was concentrated under vacuum to give compound 5 as white solid (1.0 g, yield = 90%).

3) Compound 5 (0.5 g, 0.54 mmol) was added to the flask with 30 mL of pyridine, and the solution of 2-bromoisobutyryl bromide (1.03 g, 4.5 mmol) in pyridine (10 mL) was added dropwise under ice bath within 0.5 h. Then the mixture was stirred at room temperature for 3 days. After reaction, 50 mL of DCM was added into the flask, then the mixture was washed with HCl solution (1 mol/L) three times and the organic layer was dried with anhydrous Na_2SO_4. Compound 6 was obtained by removing the solvent under vacuum (0.7 g, yield = 61%).

Synthesis of prop-2-yn-1-yl anthracene-9-carboxylate



7

1) Anthracene-9-carboxylic acid (4.0 g, 18.0 mmol) was added to flask with 10 mL of $SOCl_2$, and a few drops of DMF were added to the reaction mixture as the catalyst. The reaction was carried out at 60 ^oC for 12 h. After removal of the solvent, anthracene-9-carbonyl chloride was obtained as yellow solid (4.1 g, yield = 95%).

2) Anthracene-9-carbonyl chloride (3.0 g, 12.0 mmol) was dissolved in 100 mL of DCM, and TEA (1.57 g, 15 mmol) was added to the flask. Then the solution of propargyl alcohol (0.58 g, 10 mmol) in DCM (10 mL) was added dropwise to the flask under ice bath within 0.5 h. The reaction was stirred for 3 h at room temperature. The mixture was washed with saturated aqueous solution of NaCl three times and dried with anhydrous Na_2SO_4. The crude product was concentrated and then purified by column chromatography using DCM/hexane (3/1, v/v) as eluent to give prop-2-yn-1-yl anthracene-9-carboxylate as yellow solid (2.8 g, yield = 90%).

Synthesis of Br-terminated 8-arm star polystyrene (8-arm PS-Br) by ATRP

CuBr (287 mg, 2.0 mmol), 2,2-bipyridyl (bpy) (937 mg, 6.0 mmol), 8-arm initiator (366 mg, 0.5 mmol) and styrene (10.4 g, 0.1 mol) were added to a tube. The reaction tube was carefully degassed by three freeze-pump-thaw cycles, sealed under vacuum, and placed in the oil bath at 110 ^oC. After the reaction mixture was stirred for 40 min, the polymerization was quenched by exposing to air. The reaction mixture

was diluted with 2 mL of THF and then passed through alumina column to remove the copper salts. The polymer was obtained by precipitation in methanol for three times and then dried under vacuum to afford 2.6 g product (M_n (GPC) = 11000, PDI = 1.10).

Synthesis of azido-terminated 8-arm star polystyrene (8-arm PS-N_3)

8-arm PS-Br (1.0 g, 0.15 mmol) and sodium azide (0.16 g, 2.46 mmol) were added to a flask with 15 mL of DMF, and the reaction was conducted at room temperature for 24 h. The reaction mixture was passed through alumina column to remove residual sodium azide, then the solvent was removed under reduced pressure. Subsequently, 20 mL of DCM was added to dissolve the residue and then the solution was washed with water for three times. The polymer was obtained by precipitation in methanol for three times and dried under vacuum (0.9 g, yield = 90%).

Synthesis of anthracene-terminated 8-arm star polystyrene (8-arm PS-ant)

CuBr (250 mg, 1.74 mmol), PMDETA (0.36 mL, 1.74 mmol) and 8-arm PS-N_3 (300 mg, 0.05 mmol) were added to a Schlenk flask with the prop-2-yn-1-yl anthracene-9-carboxylate (300 mg, 1.15 mmol) solution in 20 mL of DMF, then nitrogen was pumped into the solution for 10 min to degas. The reaction was conducted at 40 ^oC for 12 h. The solvent was removed under reduced pressure, 20 mL of THF was added to dissolve the residue and then passed through alumina column to remove copper salts. The solution was concentrated, then precipitated into an excess of methanol for three times. The resulting polymer was dried under vacuum and then kept in dark place (250 mg, yield = 80%).

Synthesis of tetracyclic polystyrene and conversion to 8-arm star counterpart

8-arm PS-ant (100 mg) was added to a flask with 500 mL of THF, then the dilute solution was irradiated at 365 nm for 5 h. The reaction mixture was concentrated by evaporating majority of THF and then precipitated in methanol to obtain tetracyclic polymer (80 mg, yield = 80%).

Tetracyclic polystyrene (10 mg) was added to a tube and sealed in vacuum, then the tube was placed in the oil bath at 150 ^oC for 5 h to obtain the resulting product.

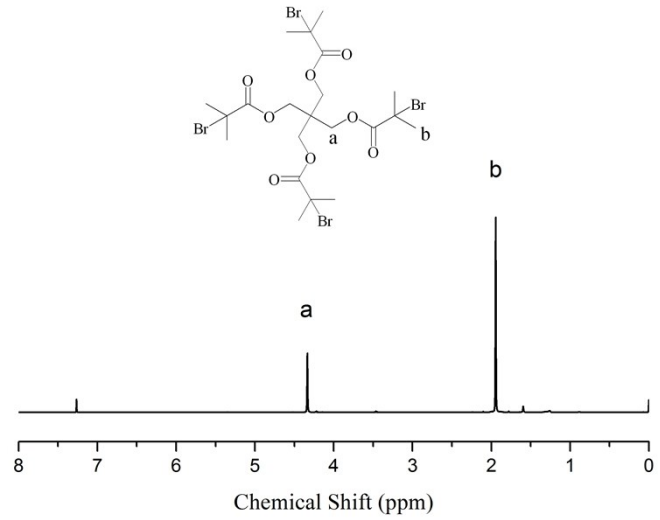


Figure S1. ^{1}H NMR spectrum of tetrafunctional initiator (pentaerythritol tetrakis(2-bromoisobutyrate)) in $CDCl_3$.

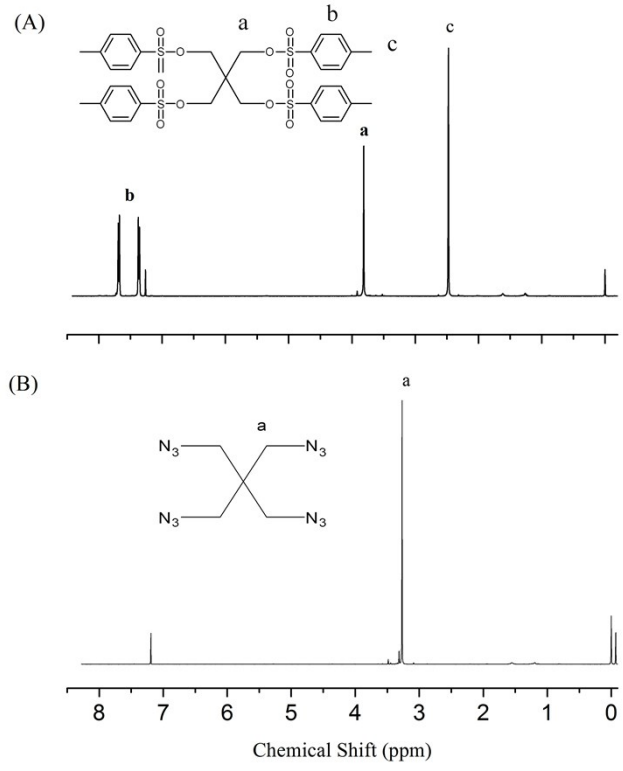


Figure S2. ^{1}H NMR spectra of pentaerythritol tetrakis (p-toluenesulfonyl) (A) and pentaerythritol tetraazide (B) in $CDCl_3$.

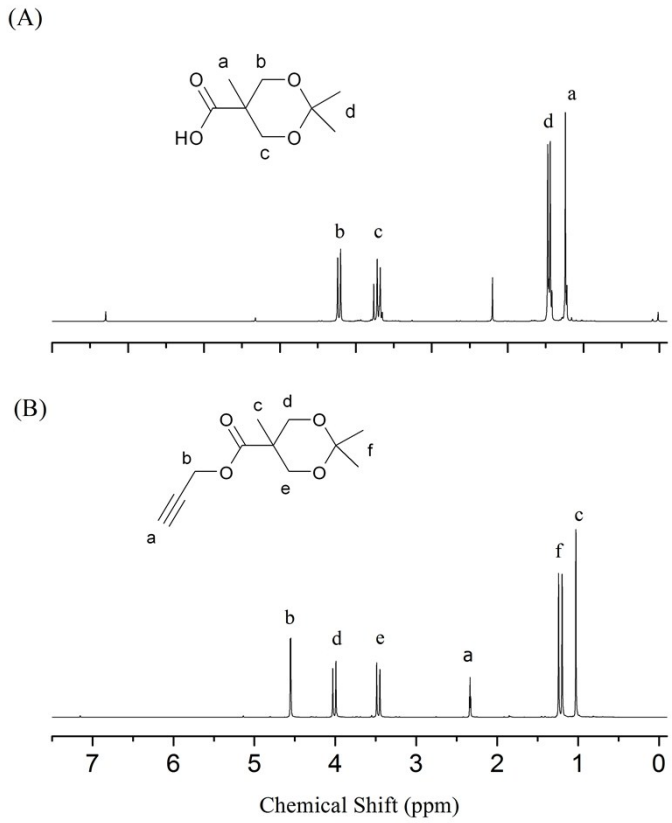


Figure S3. ^{1}H NMR spectra of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (A) and compound 3 (B) in $CDCl_3$.

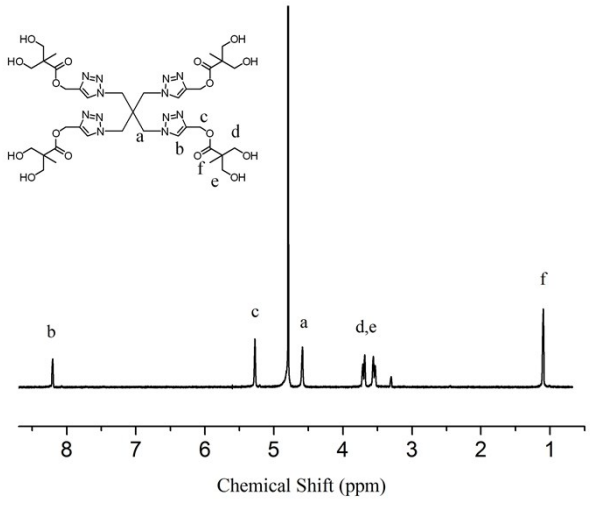


Figure S4. ^{1}H NMR spectrum of compound 5 in $CDCl_3$.

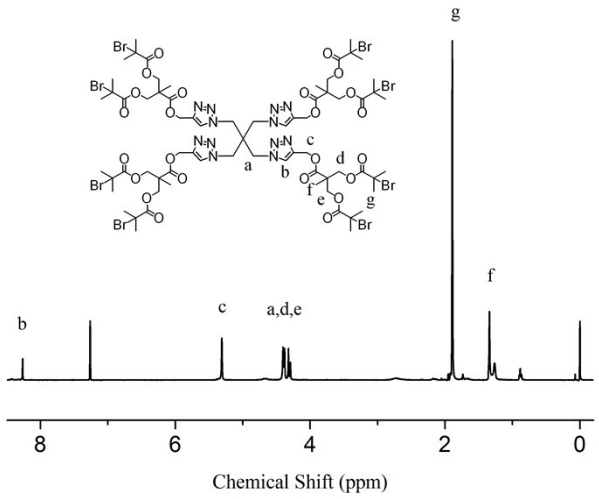


Figure S5. ^{1}H NMR spectrum of compound 6 in $CDCl_3$.

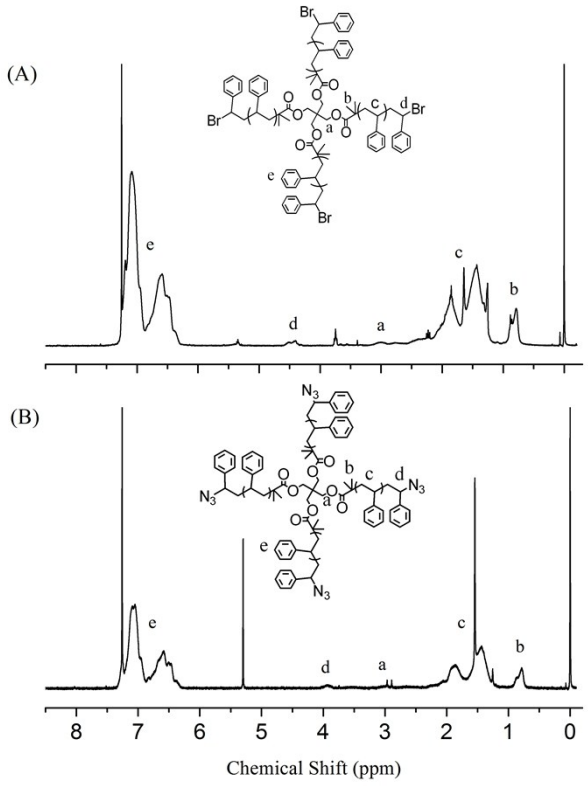


Figure S6. ^{1}H NMR spectra of 4-arm PS-Br (A) and 4-arm PS-N_3 (B) in $CDCl_3$.

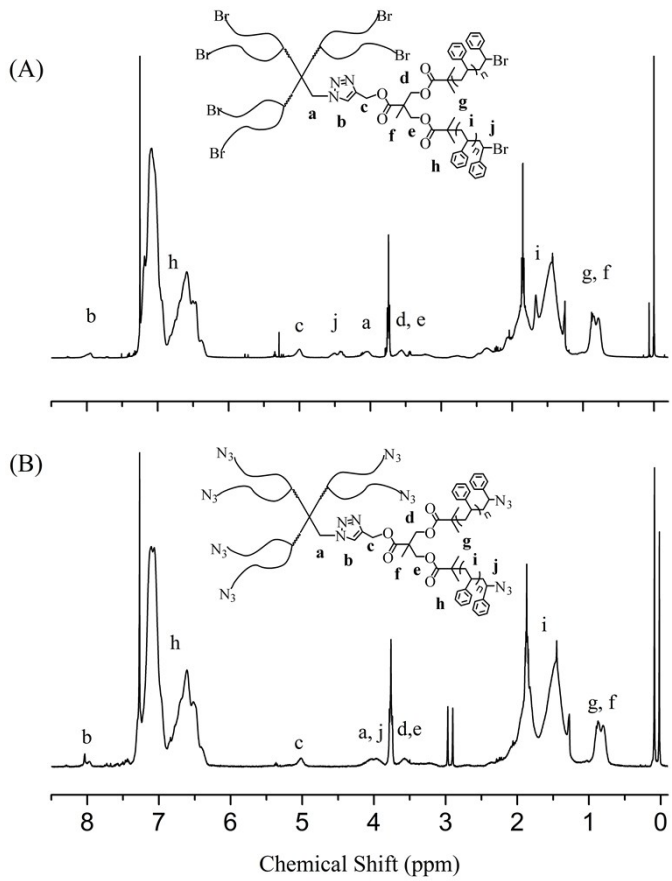


Figure S7. ^{1}H NMR spectra of 8-arm PS-Br (A) and 8-arm PS-N_3 (B) in $CDCl_3$.

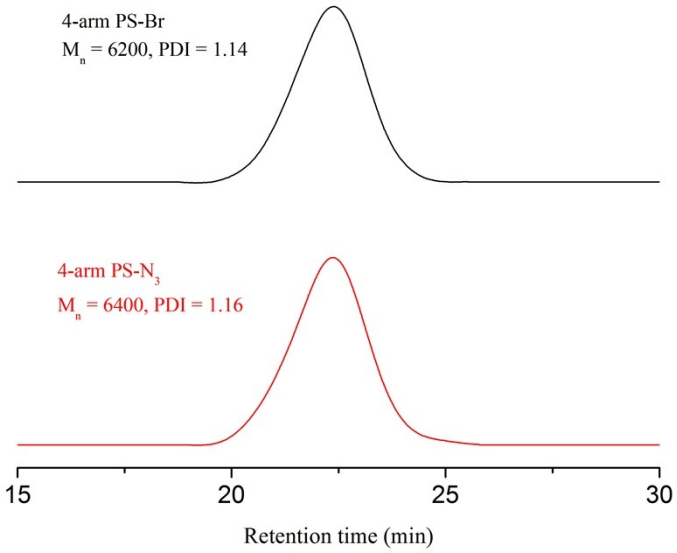


Figure S8. GPC traces of 4-arm PS-Br (black) and 4-arm PS-N_3 (red).

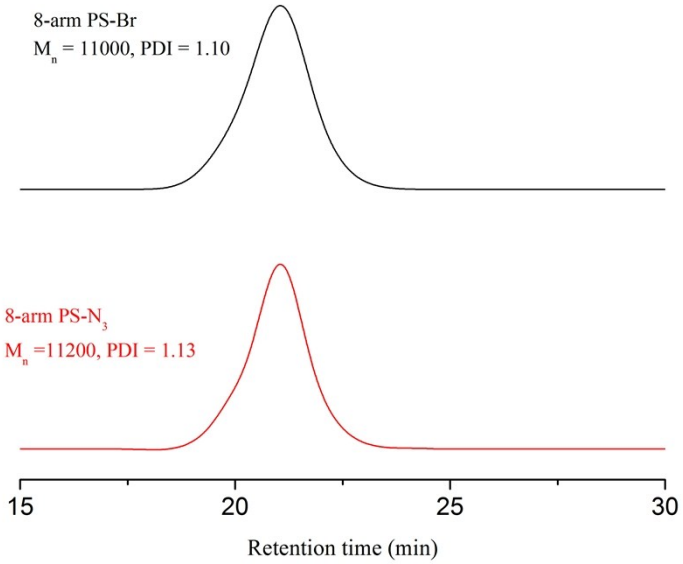


Figure S9. GPC traces of 8-arm PS-Br (black) and 8-arm PS-N_3 (red).