Supporting Information for

Synthesis of Multicyclic Polymer with Hyperbranched Structure by Click Polymerization of AB$_2$ Cyclic Macromonomer

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Materials

Styrene (St) was purchased from TCI (Shanghai, China) and purified by vacuum distillation and stored at -20 ^{o}C prior to use. CuBr was purchased from Shanghai Chemical Reagent Co. and stirred in acetic acid followed by washing with ethanol and dried at vacuum for 24 h. *N, N*-Dimethylformamide (DMF), dichloromethane, tetrahydrofuran (THF) of HPLC grade were purchased from Aladdin Reagent of China and used as received. Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 2,2-bis(hydroxymethyl)propionic acid, 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), triethylamine (TEA), 2-bromoisobutyryl bromide and 2,2'-bipyridine (bpy) were purchased from TCI (Shanghai, China) and used as received. All other reagents with analytical grade were purchased from Energy Chemical Reagent Co. and used without further purification.

Characterizations

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ and tetramethylsilane (TMS) was used as an internal reference.

The molecular weight and polydispersity of the polymers were obtained by triple-detection Gel permeation chromatography (TD-GPC) at 25 °C. The instrumentation consisted of a Waters 1515 isocratic HPLC pump with 5 μm Waters Styragel columns (guard, 0.5 HR, 1 HR, 3 HR, 4 HR and 5 HR, the molecular weight ranges of these columns are 0–1000, 100–5000, 500–30000, 5000–500000 and 50000–4000000 g/mol, respectively); a Waters 717 PLUS auto sampler; a Waters 2414 differential refractive index (DRI) detector operated at a detection wavelength of 880 nm; a multi-angle laser light scattering (MALLS) detector (Wyatt Mini Dawn TRISTAR light scattering, three detection angles are 45°, 90° and 135°, the wavelength and power are 690 nm and 220 W); a Wyatt Visco Star viscometer detector; and a Waters Breeze data manager. The eluent was HPLC-grade THF delivered at 1.0 mL min^{-1}. The refractive index increment (dn/dc) was determined using a Wyatt Optilab REX (λ = 640 nm) interferometric differential refractometer in a bath model at 25 °C. Monodisperse polystyrene standards were utilized for calibration.

The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were conducted on a Perspective Biosystem Voyager-DESTR MALDI-TOF

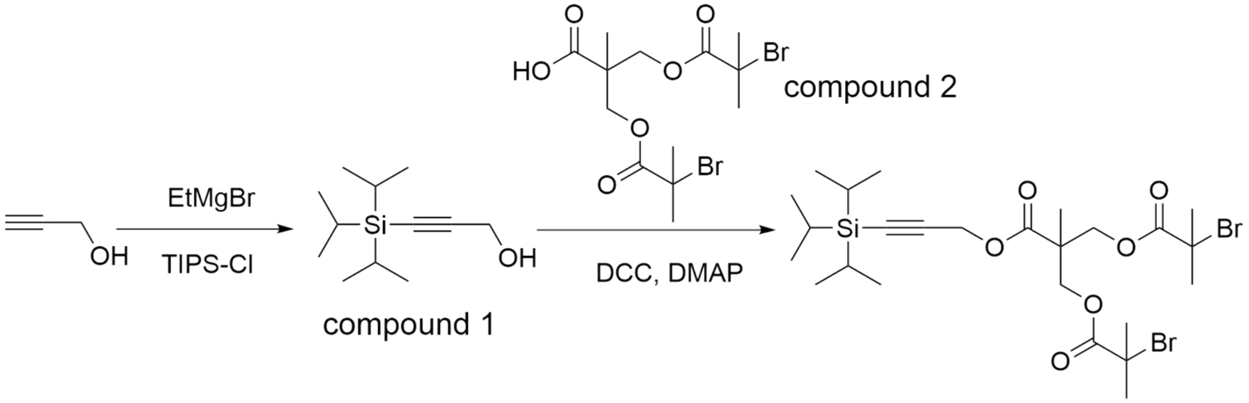
Mass spectrometer.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer.

UV/Vis measurements were performed on a Unico UV/Vis TU-1901 spectrophotometer.

Experimental section

1. Synthesis of compound 1



Scheme S1. Synthesis of the initiator

A solution of propargyl alcohol (2.85 g, 5.08 × 10^{-2} mol) in THF (50 mL) was added dropwise to a 3.0 M solution of ethylmagnesium bromide (50 mL, 15.23 ×10^{-2} mol) in 100 mL of THF at room temperature. The reaction mixture was refluxed for 24 h and cooled to room temperature. 1,1,1-Triisopropylsilyl chloride (TIPS-Cl) (6.53 g, 16.92 × 10^{-3} mol) in THF (25 mL) was added dropwise, and then the mixture was refluxed for 5 h. The reaction mixture was cooled to room temperature and poured into a 10% (m/m) HCl solution (20 mL). The aqueous layer was separated and extracted with diethyl ether for two times. The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 9:1, v/v) to afford the product as a colorless oil (yield = 40 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 4.30 (s, 2H), 1.73 (s, 1H), 1.07 (s, 21H).

2. Synthesis of compound 2

2,2-Bis(hydroxymethyl)propionic acid (10.0 g, 7.5×10^{-3} mol), TEA (25 mL, 1.8×10^{-2} mol) and 150 mL of THF were added into a 250 mL round-bottom flask with a magnetic bar, then the solution was cooled over an ice bath. 2-Bromoisobutyryl bromide (21 mL, 1.6×10^{-2} mol) dissolved in 20 mL of THF was added dropwise to the flask. The mixture was kept stirring at room temperature for 24 h. After the reaction was completed, the formed solid was removed by filtration, and the solvent was evaporated. Subsequently, the residual was dissolved in CH_2Cl_2, and 50 mL of water was added, the mixture was stirred at 50 ^{o}C for 2 h, then the organic layer was separated. The above procedure was repeated three times, and compound 2 was obtained as white solid after removing the solvent (yield: 90%).

3. Synthesis of the initiator

Compound 1 (3.0 g，0.014 mol), compound 2 (9.17 g，0.021 mol) and DMAP (0.85 g，0.007 mol) were dissolved in 50 mL of CH_2Cl_2, then the solution was cooled over an ice bath. DCC (4.24 g，0.021mol) dissolved in 20 mL of CH_2Cl_2 was added dropwise to the flask. The mixture was kept stirring at room temperature for 12 h. After the reaction was completed, the solvent was evaporated, subsequently, the residual was purified by silica gel column chromatography (petroleum ether/ CH_2Cl_2 = 1:1, v/v) to afford the product as a yellow oil (yield: 65%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 4.77 (s, 2H), 4.40~4.44 (m, 4H), 1.92 (s, 12H), 1.35 (s, 3H), 1.07 (s, 21H). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 178.02, 170.99, 81.83, 73.97, 66.00, 55.24, 50.91, 45.50, 30.62, 17.81, 17.69, 13.65.

MS (ESI) m/z calculated for $C_{25}H_{42}Br_2O_6SiNa$ [$M+Na^+$] 649.49, found 649.51.

4. Synthesis of TIPS-PS-Br$_2$

In a typical polymerization procedure, initiator (627 mg, 1 mmol), St (10.4 g, 0.1 mol), CuBr (286 mg, 2 mmol) and bpy (936 mg, 6 mmol) were added into a 15 mL glass tube with a magnetic bar. The tube was degassed by three freeze–pump–thaw cycles to remove oxygen and sealed under vacuum, then it was immersed in an oil bath at 110 ^oC for 45 min. After cooling to room temperature, the polymer solution was exposed to air and diluted with THF, followed by passing through a neutral alumina column to remove the copper salt. The solution was concentrated by a rotary evaporator, and was poured into excess of methanol, this dissolving–precipitation procedure was repeated for several times. TIPS-PS-Br_2 was obtained as white solid after filtration and dried under vacuum for 24 h at 50 ^oC (yield = 30%).

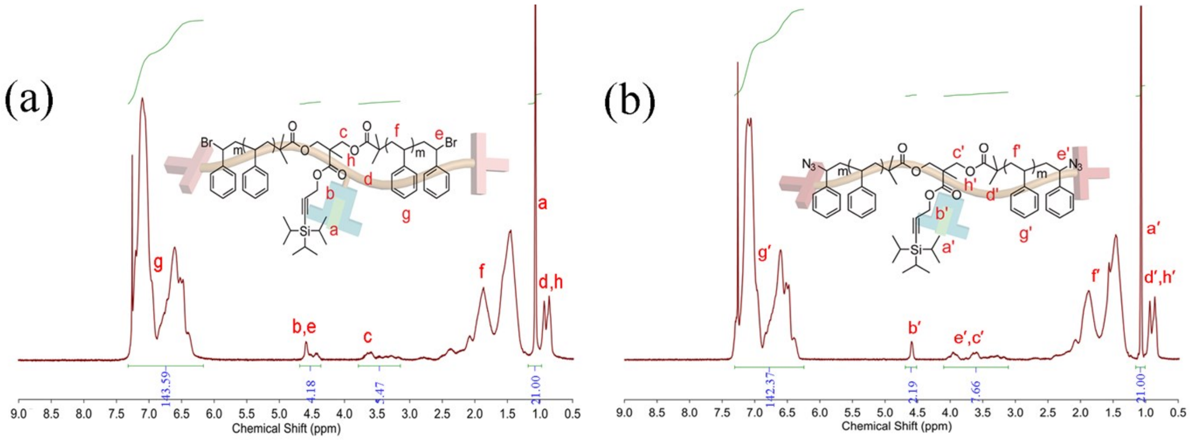


Figure S1. ^{1}H NMR spectra of (a) TIPS-PS-Br_2 and (b) TIPS-PS-$(N_3)_2$ recorded in $CDCl_3$.

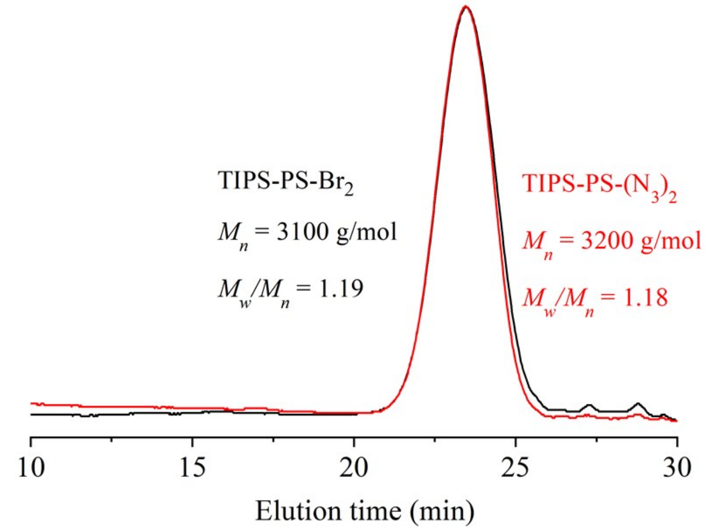


Figure S2. GPC curves of TIPS-PS-Br_2 (black line) and TIPS-PS-$(N_3)_2$ (red line) (refractive index (RI) detection; eluent, THF).

5. Synthesis of TIPS-PS-$(N_3)_2$

TIPS-PS-Br_2 (3.0 g, 0.68 mmol) and NaN_3 (2.2 g, 4.0 mmol) were dissolved in 50 mL of DMF and the mixture was kept stirring at room temperature overnight. After the azidation was completed, DMF was removed by vacuum distillation, and the residue was dissolved in THF followed by passing through a neutral alumina column to remove the excess NaN_3, then the polymer solution was concentrated and precipitated in methanol to obtain TIPS-PS-$(N_3)_2$ as white powder (yield = 95%).

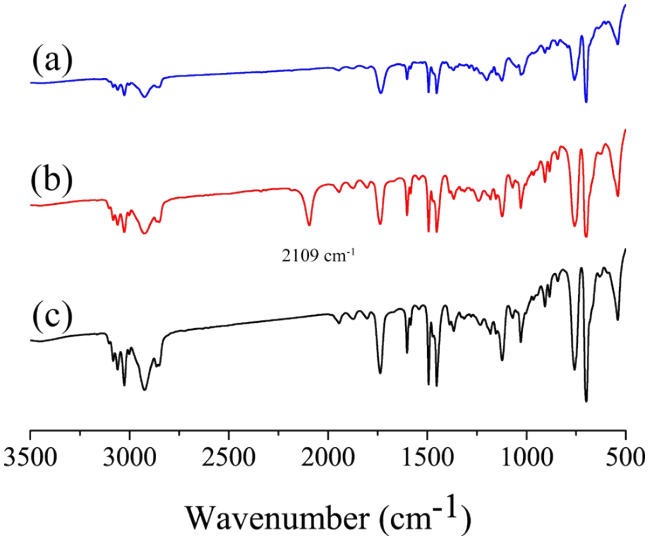


Figure S3. FT-IR spectra of (a) TIPS-PS-Br_2, (b) TIPS-PS-$(N_3)_2$ and (c) TIPS-PS-$(Ant)_2$

6. Synthesis of TIPS-PS-$(Ant)_2$

TIPS-PS-$(N_3)_2$ (2.0 g, 0.45 mmol), alkynyl-OH-ant (500 mg, 9.0 mmol), CuBr (129 mg, 0.90 mmol) and PMDETA (156 mg, 0.90 mmol) were added into a 50 mL round-bottom flask with a magnetic bar, DMF (30 mL) was poured subsequently as solvent and bubbled with N_2 for 30 min, then the flask was sealed and kept stirring at 60 ^{o}C for 12 h. After the completion of reaction, DMF was removed by vacuum distillation, and the residue was dissolved in THF followed by passing through a neutral alumina column to remove the copper salt. The polymer solution was concentrated by a rotary evaporator and precipitated into methanol. The precipitate was dissolved in THF and precipitated into methanol, this process was repeated for another two times.

TIPS-PS-$(Ant)_2$ was obtained as yellow solid after filtration and dried under vacuum for 24 h at 50 ^{o}C (yield = 95%).

7. Synthesis of TIPS-cPS-$(OH)_2$ and its topological conversion

TIPS-cPS-$(OH)_2$ was synthesized by the cyclization of TIPS-PS-$(Ant)_2$. The typical experimental procedure is as follows. TIPS-PS-$(Ant)_2$ (100 mg, 0.02 mmol) was dissolved in 500 mL of THF, followed by irradiating with 365 nm UV light (0.2 W/cm^2) for 4 hours, then THF was evaporated to give TIPS-cPS-$(OH)_2$ as faint yellow solid (yield = 95%).

The topological conversion of TIPS-cPS-$(OH)_2$ was achieved via cleavage of anthracene dimer at 150 ℃. The detailed process is as follows: TIPS-cPS-$(OH)_2$ (5 mg, 1×10^{-3} mmol) was added into a 1 mL glass tube. The tube was degassed and sealed under vacuum, then it was immersed in an oil bath at 150 ^{o}C for 5 h. After cooling to room temperature, the resultant polymer was subjected to GPC and UV-Vis analysis.

8. Synthesis of TIPS-cPS-Br_2

TIPS-cPS-$(OH)_2$ (1.0 g, 0.20 mmol) and TEA (0.44 g, 4.4 mmol) were dissolved in dry CH_2Cl_2 (10 mL), 6-bromohexanoyl chloride (0.85 g, 0.40 mmol) was added dropwise to the flask at 0 ^{o}C. The reaction was conducted at room temperature for 24 h, after that, the solution was washed with brine for three times and dried with anhydrous sodium sulfate. Pure TIPS-cPS-Br_2 was obtained as a yellow solid by precipitating in methanol for three times (yield = 95%).

9. Synthesis of TIPS-cPS-$(N_3)_2$

TIPS-cPS-Br_2 (550 mg, 0.10 mmol) and NaN_3 (650 mg, 10 mmol) were dissolved in 5 mL of DMF, and kept stirring at 70 ^{o}C overnight. After the azidation process was completed, DMF was removed by vacuum distillation, and the residue was dissolved in THF followed by passing through a neutral alumina column to remove the excess NaN_3, then the polymer solution was concentrated and precipitated in methanol to obtain TIPS-cPS-$(N_3)_2$ as pale yellow powder (yield = 92%).

10. Synthesis of alkynyl-cPS-$(N_3)_2$

TIPS-cPS-$(N_3)_2$ (500 mg, 0.09 mmol) was dissolved in 5 mL of THF, 0.9 mL of TBAF solution in THF (1.0 M, 0.9 mmol) was added and the mixture was stirred for 24 h at 25 °C. The polymer solution was directly precipitated into methanol to obtain alkynyl-cPS-$(N_3)_2$ as pale-yellow powder (yield = 90%).

11. Synthesis of hyper-cPS

PMDETA (52 mg, 0.30 mmol), CuBr (43 mg, 0.30 mmol), alkynyl-cPS-$(N_3)_2$ (200 mg, 0.04 mmol) and 1 mL of DMF were added into a 2 mL glass tube with a magnetic bar. The tube was degassed by three freeze–pump–thaw cycles to remove oxygen and sealed under vacuum, then it was immersed in an oil bath at 70 ^{o}C for 48 h. After cooling to room temperature, the polymer solution was exposed to air, diluted with CH_2Cl_2 and washed with ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) aqueous solution for three times, followed by drying with anhydrous sodium sulfate. The polymer solution was concentrated and precipitated in methanol for three times to give hyper-cPS as a yellow solid (yield = 85%).

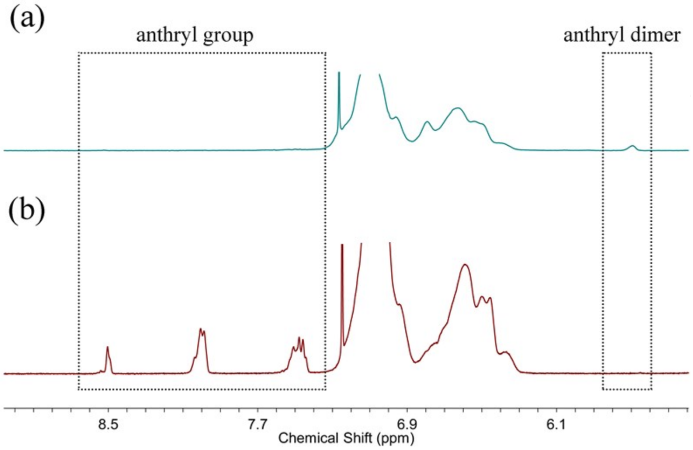


Figure S4. ^1H NMR spectra of hyper-cPS (a) and h-lPS (b) in $CDCl_3$.

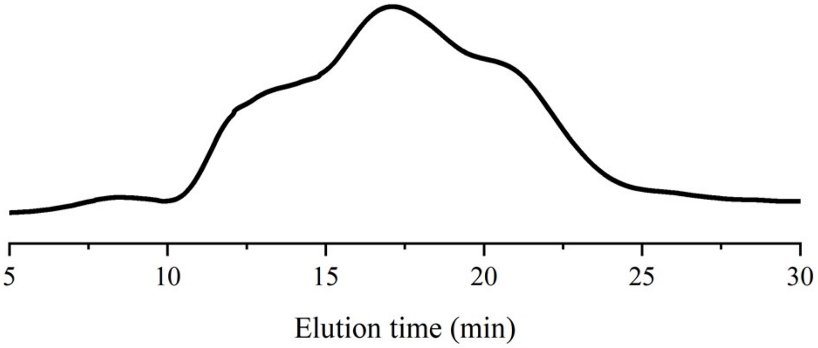


Figure S5. GPC curve of h-lPS (RI detection; eluent, THF).

12. Topological conversion of hyper-cPS

The hyper-cPS (15 mg) was dissolved in 500 μL of $CHCl_3$, followed by irradiating with 254 nm UV light (0.2 W/cm^2) for 5 hours, then $CHCl_3$ was evaporated to give h-lPS as faint yellow solid (yield = 95%).

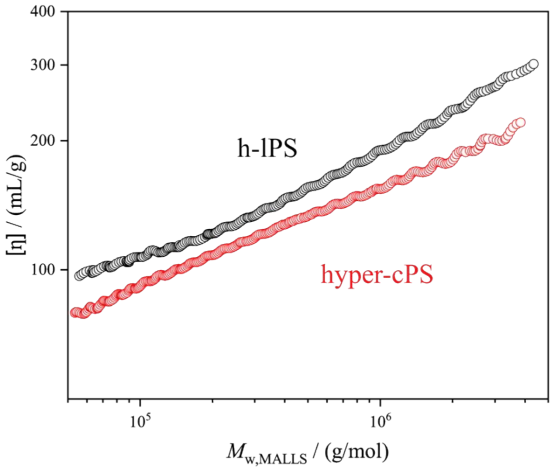


Figure S6. $M_{w,MALLS}$ dependence of intrinsic viscosity ([η]) for hyper-cPS (red) and h-lPS (black).