Supporting Information

Design A Highly Reactive Trifunctional Core Molecule to Obtain Hyperbranched Polymers with Over A Million Molecular Weight in One-Pot Click Polymerization

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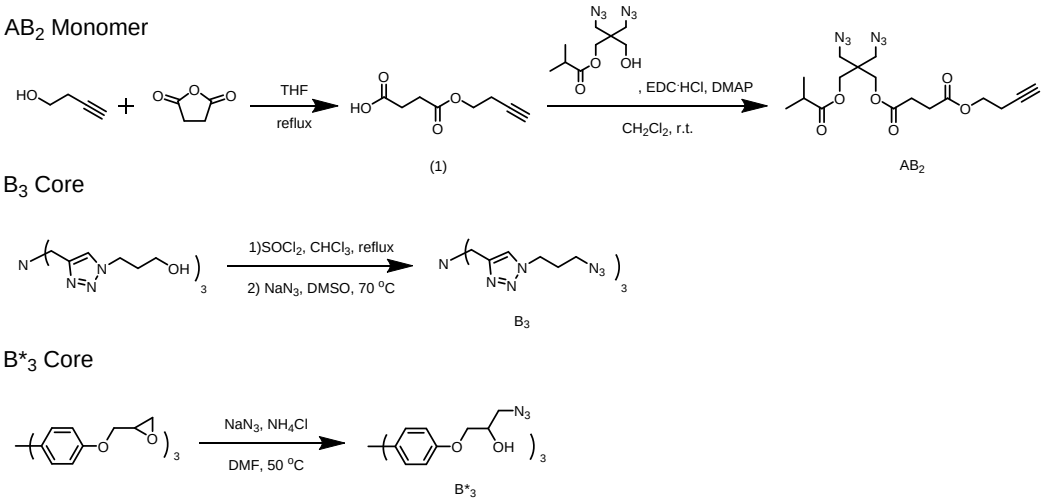
Materials. 3-Butyn-1-ol (Sigma-Aldrich, 97%), succinic anhydride (Sigma-Aldrich, ≥ 99%), 3-(3-dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride (EDC·HCl, Chem-Impex), 4-(dimethylamino) pyridine (DMAP, Sigma-Aldrich, ≥99%), thionyl chloride (TCI), chloroform (BDH, ≥99.8%), tris(4-glycidyloxy phenyl) methane (Sigma-Aldrich, 99%), sodium azide (VWR), ammonium chloride (Sigma-Aldrich, ACS grade), triethylamine (Sigma-Aldrich, ≥ 99%), isobutyryl chloride (Acros, 99%), acetyl chloride (Acros, 99%), ascorbic acid (Alfa Aesar, 99+%), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, BDH, ACS grade), triethylene glycol monoethyl ether (Sigma-Aldrich, 99%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Sigma-Aldrich, 99%), dimethylformamide (DMF, Sigma-Aldrich, ≥99.8%), and methanol (Sigma-Aldrich,

≥99.8%) were used as received. Tetrahydrofuran (THF, Sigma-Aldrich, ≥99.0%) was distilled over sodium/benzophenone and dichloromethane (DCM, Sigma-Aldrich, >99.5%) was distilled over CaH_2 prior to use.2,2-Bis(azidomethyl)propane-1,3-diol,[1,2] 3-azido-2-(azidomethyl)-2-(hydroxymethyl)propyl isobutyrate,[3] tris(3-hydroxypropyltriazolylmethyl)amine (THPTA)[4] were synthesized according to previous literature. Regarding to the explosive nature, all azide compounds were synthesized, purified and stored according to the standard safety rules with caution.[5]

Characterization. The THF size exclusion chromatography (SEC) was equipped with Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å SDV columns) at 35 ^oC with THF flow rate = 1.0 mL min^{-1}, a differential refractive index (RI) detector (Wyatt Technology, Optilab T-rEX) using PSS WinGPC 7.5 software. The apparent molecular weights were calculated based on linear poly(methyl methacrylate) (PMMA) standards. The detectors employed to measure the absolute molecular weights of hyperbranched polymers in THF SEC were the RI detector and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN HELEOS II) with the light wavelength at 658 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology with the pre-measured dn/dc value 0.0847 for all hyperbranched polymers. ^1H nuclear magnetic resonance (NMR), ^{13}C NMR, and rotating-frame Overhauser effect spectroscopy (ROESY) was acquired on a Bruker 500 MHz spectrometer at 25 °C. High resolution mass spectrometry (HRMS) measurements were performed on a Bruker MicroTOF-II

spectrometer (electrospray ionization source (ESI) with time-of-flight mass analyzer). The hydrodynamic size (D_h) of the samples were determined using dynamic light scattering (DLS) equipped with Zetasizer Nano-ZS (He-Ne laser wavelength at 633 nm, Malvern Instruments, Malvern, UK).

Synthesis of AB_2 monomer, B_3 and B^*_3 cores



Scheme S1. Synthetic procedures of AB_2 monomer, B_3 and B^*_3 cores

Synthesis of compound 1. 3-Butyn-1-ol (35.0 g, 499.6 mmol), succinic anhydride (25.0 g, 249.8 mmol) were dissolved in 50 mL dry THF in a 100 mL flask. The reaction mixture was allowed to reflux for 24 hours. The solvent was removed under reduced pressure and the residue was then dissolved in 100 mL of CH_2Cl_2 and washed with brine (3×100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. The crude product was recrystallized in toluene, giving compound 1 as white solid (36.4 g, 86% yield). ^{1}H NMR (in $CDCl_3$, δ, ppm): 1.99-2.01 (1H, *H*C≡CCH$_2$), 2.51-2.55 (2H, HC≡CC*H*$_2$CH$_2$OCO), 2.63-2.71 (4H, OCOC*H*$_2$C*H*$_2$COOH)**,** 4.19-4.23 (2H, HC≡CCH$_2$C*H*$_2$OCO), 9.61 (1H,

OCOCH$_2$CH$_2$COO*H*). ^{13}C NMR (in CDCl$_3$, δ, ppm): 19.11 (HC≡C*C*H$_2$CH$_2$OCO), 28.94-29.10 (OCO*C*H$_2$*C*H$_2$COOH), 62.67 (HC≡CCH$_2$*C*H$_2$OCO), 70.19 (H*C*≡CCH$_2$), 80.08 (HC≡*C*CH$_2$), 172.08 (O*C*OCH$_2$CH$_2$COOH), 178.52 (OCOCH$_2$CH$_2$*C*OOH). HRMS (ESI) calculated for $C_8H_{10}O_4$ $[M+Na]^+$ 193.0471; found 193.0462.

Synthesis of AB$_2$ monomer. To a 250 mL round-bottom flask were added sequentially with compound 1 (8.6 g, 50.6 mmol), 3-azido-2-(azidomethyl)-2-(hydroxymethyl)propyl isobutyrate (11.8 g, 46.1 mmol), EDC·HCl (19.4 g, 101.2 mmol), dry methylene chloride (120 mL) and DMAP (2.1 g, 16.9 mmol). The reaction mixture was allowed to be stirred at room temperature overnight before washed with water (2×100 mL) and brine (100 mL), and dried over MgSO$_4$. The solvent was evaporated, and the remaining residual was purified by silica gel chromatography (hexanes/diethyl ether, 4:1 v/v) to give 15.4 g light yellow liquid of the targeted AB$_2$ monomer (82% yield). ^{1}H NMR (in CDCl$_3$, δ, ppm): 1.17-1.19 (6H, (C*H*$_3$)$_2$CHCOO), 2.00-2.02 (1H, *H*C≡CCH$_2$), 2.52-2.55 (2H, HC≡CC*H*$_2$CH$_2$OCO), 2.55-2.62 (1H, (CH$_3$)$_2$C*H*COO), 2.65-2.68 (4H, OCOC*H*$_2$C*H*$_2$COO), 3.43 (4H, (N$_3$C*H*$_2$)$_2$C), 4.02 (2H, CH$_2$CH$_2$COOC*H*$_2$C), 4.07 (2H, (CH$_3$)$_2$CHCOOC*H*$_2$C), 4.19-4.22 (2H, HC≡CCH$_2$C*H*$_2$OCO). ^{13}C NMR (in CDCl$_3$, δ, ppm): 19.13 ((*C*H$_3$)$_2$CHCOO), 29.07, 29.11 (OCO*C*H$_2$*C*H$_2$COO), 34.18 ((CH$_3$)$_2$*C*HCOO), 43.39 ((COOCH$_2$)*C*(CH$_2$OOC)(CH$_2$N$_3$)$_2$), 51.53 ((N$_3$*C*H$_2$)$_2$C), 62.64-62.70 (CHCOO*C*H$_2$C*C*H$_2$OOCCH$_2$), 63.08 (HC≡CCH$_2$*C*H$_2$OCO), 70.20 (H*C*≡CCH$_2$), 80.10 (HC≡*C*CH$_2$), 171.81, 172.05 (O*C*OCH$_2$CH$_2$*C*OO), 176.47 ((CH$_3$)$_2$CH*C*OO). HRMS (ESI) calculated for $C_{17}H_{24}N_6O_6$ $[M+Na]^+$ 431.1650; found

431.1622.

Synthesis of B_3 core.[6] THPTA (500.0 mg, 1.2 mmol) and chloroform (4 mL) were charged in a 25 mL flask. Thionyl chloride (542.9 mg, 4.6 mmol) was diluted with chloroform (2 mL) and then added dropwise to the suspension at room temperature. After refluxing for 12 hours, the mixture was cooled to room temperature and concentrated in vacuo. The resulting red-brownish viscous compound was then dissolved in DMSO (8 mL), to which NaN_3 (449.1 mg, 6.9 mmol) was added and stirred at 70 °C for 12 hours. The mixture was partitioned between ethyl acetate and saturated aqueous $NaHCO_3$, and the organic layer was washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The remaining residual was purified by silica gel chromatography (ethyl acetate/methanol, 3:1 v/v) to give 380.9 mg of brownish yellow solid (65% yield). ^{1}H NMR (in $CDCl_3$, δ, ppm): 2.09-2.16 (6H, $CH_2C\mathit{H}_2CH_2N_3$), 3.29-3.33 (6H, $CH_2CH_2C\mathit{H}_2N_3$), 3.69 (6H, $NC\mathit{H}_2C{=}CH$), 4.38-4.42 (6H, $NC\mathit{H}_2CH_2CH_2N_3$), 7.72 (3H, $CH_2C{=}C\mathit{H}N$). ^{13}C NMR (in $CDCl_3$, δ, ppm): 29.71 ($CH_2\mathit{C}H_2CH_2N_3$), 47.27, 47.42 ($N\mathit{C}H_2CH_2\mathit{C}H_2N_3$), 48.36 ($N\mathit{C}H_2C{=}CH$), 124.35 ($C{=}\mathit{C}HN$), 144.21($CH_2\mathit{C}{=}CHN$). HRMS (ESI) calculated for $C_{18}H_{27}N_{19}$ $[M+H]^+$ 510.2770; found 510.2776.

Synthesis of B^*_3 core. The B^*_3 molecule was synthesized according to previous literature with slight modification.[7] Tris(4-glycidyloxy phenyl) methane (2.3 g, 5 mmol), sodium azide (1.6 g, 25.0 mmol), ammonium chloride (1.3 g, 25.0 mmol) and dimethylformamide (10 ml) were charged in a 25 mL flask and magnetically stirred at 60 °C for 40 h. The reaction mixture was diluted with 50 mL ethyl acetate, washed

with water (2×50 mL) and brine (50 mL), and dried over $MgSO_4$. The solvent was evaporated, and the remaining residual was purified by silica gel chromatography (hexanes/ethyl acetate, 1:1 v/v) to give B^*_3 as a yellow solid (2.8 g, 94% yield). ^1H NMR (in $CDCl_3$, δ, ppm): 2.45-2.50 (3H, $(OCH_2)(CH_2N_3)CHO\mathit{H}$), 3.08-3.19, 3.47-3.56 (6H, $(OCH_2)(C\mathit{H}_2N_3)CHOH$), 3.85-4.18 (9H, $(OC\mathit{H}_2)(CH_2N_3)C\mathit{H}OH$), 5.41, 5.66, 5.98 ($C\mathit{H}(C_6H_4)_3$), 6.72-7.27 (12H, $CH(C_6\mathit{H}_4)_3$). ^{13}C NMR (in $CDCl_3$, δ, ppm): 43.92-54.54 ($(OCH_2)(\mathit{C}H_2N_3)CHOH$,$\mathit{C}H(C_6H_4)_3$), 68.95-69.54 ($(O\mathit{C}H_2)(CH_2N_3)\mathit{C}HOH$), 111.16-157.13 ($CH(\mathit{C}_6H_4)_3$). HRMS (ESI) calculated for $C_{28}H_{31}N_9O_6$ $[M+Na]^+$ 612.2290; found 612.2291.

CuAAC polymerization of AB_2 and B_3 in one pot. Typical procedures in the polymerization of AB_2 monomer using molar ratios of $[AB_2]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 900:1:10:50 are described. AB_2 monomer (800.0 mg, 2.0 mmol), B_3 core (1.1 mg, 2.2 μmol), $CuSO_4{\cdot}5H_2O$ (5.4 mg, 21.8 μmol) and 3.9 mL DMF ($[AB_2]_0$ = 0.5 mol L^{-1}) were charged in a 10 mL schlenk flask. This flask was capped with rubber septa and bubbled with nitrogen gas for 40 min, ascorbic acid (19.2 mg, 108.9 μmol) was then added into flask quickly and the flask was immersed in a thermostatic oil bath at 45 °C for initiating the polymerization. Samples were collected using deoxygenated syringes at each predetermined interval and were quenched by exposure to air and the addition of two equivalents of PMDETA. One portion was diluted by THF for SEC measurement. Another portion was diluted by $CDCl_3$ for the assessment of monomer conversion by ^1H NMR spectroscopy. The polymerization was stopped at 45 minutes and diluted

with 10 mL THF, and Cu catalyst was removed by adding two equivalents of PMDETA followed by passing a neutral alumina column[8], the catalyst-free hyperbranched polymers were then purified by precipitating into large amount of methanol three times. The final product was dried under vacuum to a constant mass. The procedures for polymerization of AB_2 monomer without core or with B^*_3 core were similar to those described above except removing B_3 core from the system or replacing B_3 core with 1 equiv. B^*_3 core.

The procedure for polymerization of AB_2 monomer with B_3 core using sequential monomer addition is as follows. The first batch of polymerization was conducted at molar ratios of $[AB_2]_0$:$[B_3]_0$:$[CuSO_4 \cdot 5H_2O]_0$:[ascorbic acid]$_0$ = 100:1:10:50 in DMF with $[AB_2]_0 = 0.5$ mol L^{-1}. After reaching a complete monomer conversion (> 99%), a 2nd batch of deoxygenated AB_2 monomer (200 equiv. to initial B_3) in DMF (0.5 mol L^{-1} of monomer) was added into the reaction system. Similarly, a 3rd batch of 600 equiv. and a 4th batch of 1800 equiv. of AB_2 monomers ($[AB_2]_0 = 0.5$ mol L^{-1} in DMF) were added sequentially when previous batch reached 99% conversion. Samples were taken using deoxygenated syringes right before adding each batch of monomers and diluted with THF for SEC measurement. The final hyperbranched polymers were purified by first adding two equivalents of PMDETA followed by passing a neutral alumina column, and then precipitating into large amount of methanol three times and then dried under vacuum to a constant mass.

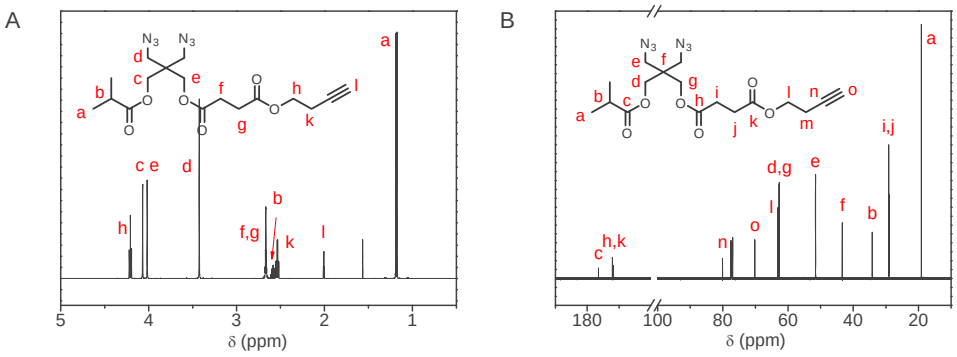


Figure S1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of AB_2 monomer in $CDCl_3$ at 25 ^{o}C.

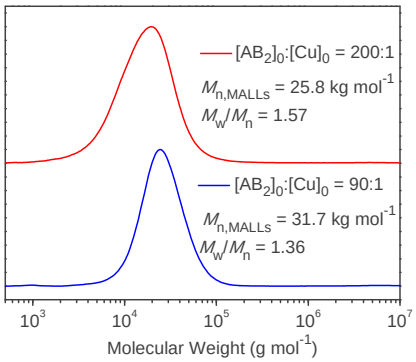


Figure S2. Comparison of the SEC traces of hyperbranched polymer synthesized by CuAAC polymerization of AB_2 monomer at feed ratios of $[AB_2]_0$: $[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 90:1:5 and 200:1:5, $[AB_2]_0$ = 0.5 mol L^{-1}.

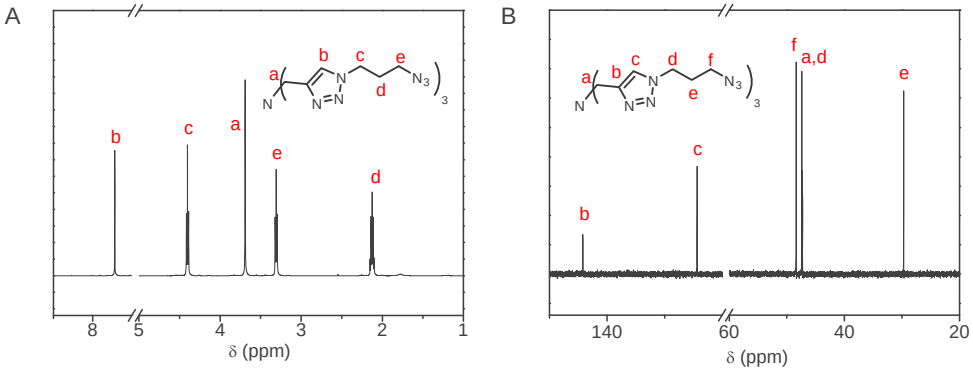


Figure S3. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of B_3 core in $CDCl_3$ at 25 ^{o}C.

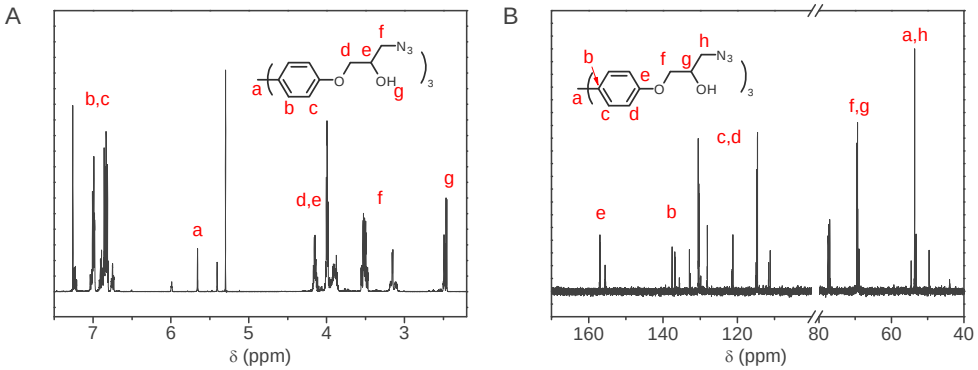
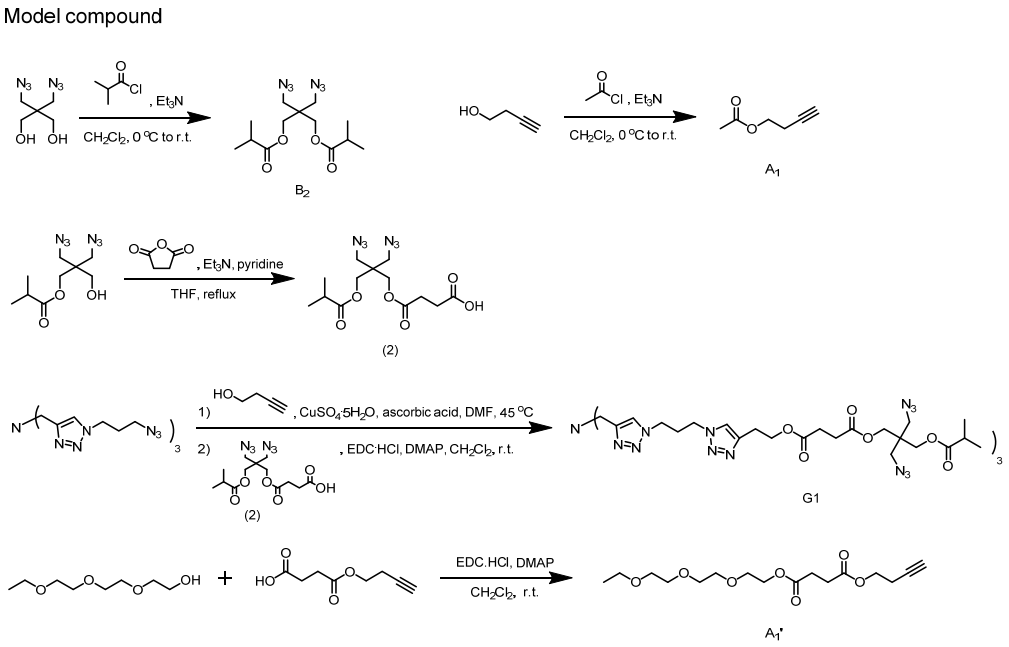


Figure S4. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of B*$_3$ core in $CDCl_3$ at 25 ^{o}C.

Synthesis of molecules B_2, A_1, G1, A_1'



Scheme S2. Synthetic procedures of model compounds B_2, A_1, G1, A_1'.

Synthesis of molecule B_2. 2,2-Bis(azidomethyl)propane-1,3-diol (2.0 g, 10.7 mmol), triethylamine (4.3 g, 43.0 mmol) and dried methylene chloride (50 mL) were charged in a dried 100 mL round bottomed flask. This flask was immersed in a

thermostatic ice bath at 0 °C. The solution was magnetically stirred for 10 min before dropwise addition of 2.1 equiv. of isobutyryl chloride (2.4 g, 22.6 mmol). The reaction was then allowed to proceed for additional 12 hours at room temperature before the methylene chloride solution was washed with brine (3×50 mL). The organic solution was dried overnight using anhydrous $MgSO_4$ before removing the solvent via rotary evaporation. The final product was purified via silica column chromatography with (hexanes/diethyl ether, 3:1 v/v) as the spreading solvent, yielding B_2 as a yellow liquid (3.5 g, 90% yield). ^{1}H NMR (in $CDCl_3$, δ, ppm): 1.13-1.15 (12H, $(CH_3)_2CHCOO$), 2.51-2.57 (3H, $(CH_3)_2CHCOO$), 3.38 (4H, $(N_3CH_2)_2C$), 3.98 (4H, $(COOCH_2)_2C$). ^{13}C NMR (in $CDCl_3$, δ, ppm): 19.10 ($(CH_3)_2CHCOO$), 34.16 ($(CH_3)_2CHCOO$), 43.40 ($(COOCH_2)_2C(CH_2N_3)_2$), 51.61 ($(N_3CH_2)_2C$), 62.67 ($(COOCH_2)_2C$), 176.45 ($(CH_3)_2CHCOO$). HRMS (ESI) calculated for $C_{13}H_{22}N_6O_4$ $[M+Na]^+$ 349.1595; found 349.1570.

Synthesis of molecule A_1. 3-Butyn-1-ol (3.0 g, 42.8 mmol), triethylamine (11.6 g, 114.2 mmol) and dried methylene chloride (100 mL) were charged in a 250 mL dried round bottomed flask. This flask was immersed in a thermostatic ice bath at 0 °C. The solution was magnetically stirred for 10 min before dropwise addition of 1.1 equiv. of isobutyryl chloride (3.7 g, 47.1 mmol). The reaction was then allowed to proceed for additional 12 hours at room temperature before the methylene chloride solution was washed with brine (3×100 mL). The organic solution was dried overnight using anhydrous $MgSO_4$ and condensed under reduced pressure. The final product was further purified via neutral alumina column chromatography to remove

residue quaternary ammonium salts, yielding colorless liquid (4.3 g, 91% yield). ^{1}H NMR (in $CDCl_3$, δ, ppm): 2.00 (1H, *H*C≡CCH$_2$), 2.08 (2H, HC≡CC*H*$_2$CH$_2$OCO), 2.51-2.55 (3H, C*H*$_3$COOCH$_2$), 4.16-4.19 (2H, HC≡CCH$_2$C*H*$_2$OCO). ^{13}C NMR (in $CDCl_3$, δ, ppm): 19.10 (*C*H$_3$COOCH$_2$), 20.97 (HC≡C*C*H$_2$CH$_2$OCO), 62.29 (HC≡CCH$_2$*C*H$_2$OCO), 70.07 (H*C*≡CCH$_2$), 80.22 (HC≡*C*CH$_2$), 170.91 (CH$_3$*C*OOCH$_2$). HRMS (ESI) calculated for $C_6H_8O_2$ $[M+Na]^+$ 135.0417; found 135.0410.

Synthesis of compound 2. 3-Azido-2-(azidomethyl)-2-(hydroxymethyl)propyl isobutyrate (1.1 g, 4.2 mmol), succinic anhydride (627.4 mg, 6.3 mmol) and DMAP (510.8 mg, 4.2 mmol) were dissolved in 60 mL dry THF in a 100 mL flask, 1.7 mL pyridine was then added. The reaction mixture was allowed to react at room temperature for 24h. The solvent was removed under reduced pressure and the residue was then dissolved in 50 mL of CH_2Cl_2 and washed with brine (3×50 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. The final product was purified via silica column chromatography with (hexanes/diethyl ether, 2:1 v/v) as the spreading solvent. Compound 2 was then obtained as colorless liquid (1.4 g, 95% yield). ^{1}H NMR (in $CDCl_3$, δ, ppm): 1.17-1.20 (6H, (C*H*$_3$)$_2$CHCOO), 2.54-2.63 (1H, (CH$_3$)$_2$C*H*COO), 2.64-2.73 (4H, OCOC*H*$_2$C*H*$_2$COO), 3.42 (4H, (N$_3$C*H*$_2$)$_2$C), 4.02 (2H, CH$_2$CH$_2$COOC*H*$_2$C), 4.07 (2H, (CH$_3$)$_2$CHCOOC*H*$_2$C), 9.58 (1H, CH$_2$CH$_2$COO*H*). ^{13}C NMR (in $CDCl_3$, δ, ppm): 19.11 ((*C*H$_3$)$_2$CHCOO), 28.95, 28.98 (OCO*C*H$_2$*C*H$_2$COOH), 34.20 ((CH$_3$)$_2$*C*HCOO), 43.36 ((COOCH$_2$)*C*(CH$_2$OOC)(CH$_2$N$_3$)$_2$), 51.51 ((N$_3$*C*H$_2$)$_2$C), 62.67, 63.17 (CHCOO*C*H$_2$C*C*H$_2$OOCCH$_2$), 171.67 (O*C*OCH$_2$CH$_2$COOH), 176.62

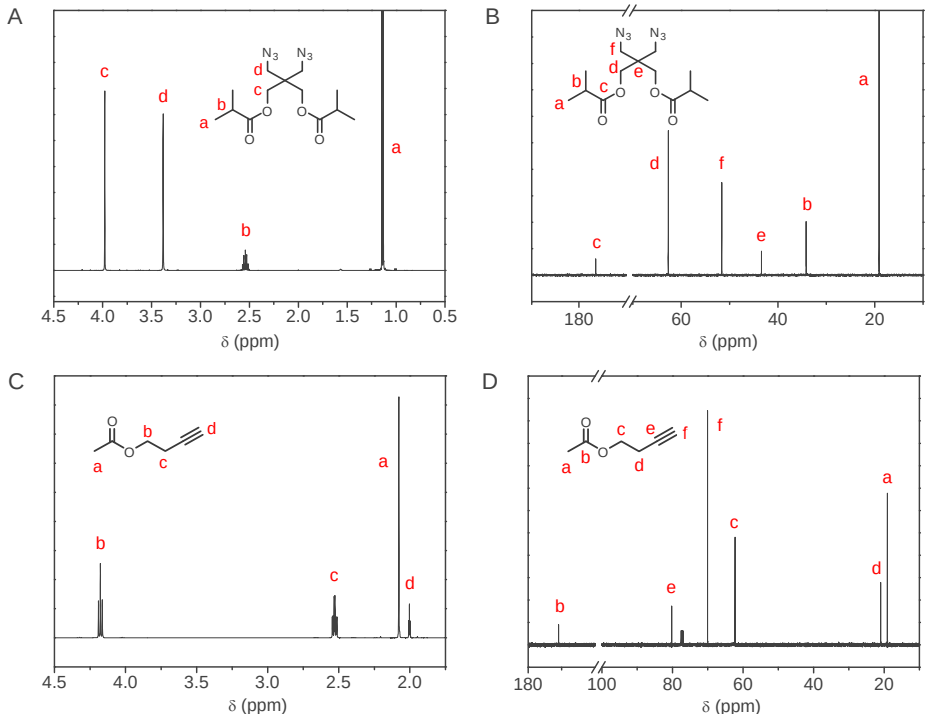
(OCOCH$_2$CH$_2$*C*OOH). HRMS (ESI) calculated for $C_{13}H_{20}N_6O_6$ $[M+Na]^+$ 379.1337; found 379.1310.

Synthesis of molecule G1. B_3 (200.0 mg, 392.7 μmol), butyryl alcohol (275.0 mg, 3.9 mmol), $CuSO_4 \cdot 5H_2O$ (9.8 mg, 39.3 μmol) and DMF (1 mL) were charged in a 10 mL schlenk flask. This flask was then capped and bubbled with nitrogen gas for 40 min, ascorbic acid (34.6 mg, 196.4 μmol) was added into flask quickly and the flask was immersed in a thermostatic oil bath at 45 °C. After 2 hours, the reaction was allowed cooling to room temperature, diluted with 10 mL H_2O and stirred with Cuprisorb resin to remove copper ions. The solution was filtered, solid washed and the combined solution concentrated under high vaccum to provide a brown solid. The residue was dispersed in acetonitrile, sonicated to break up the solid, filtered and washed with acetonitrile. After drying under vaccum, the resulting brownish yellow solid (270.2 mg, 96%) was transferred to a 25 mL round-bottom flask, and compound 2 (668.8 mg, 1.9 mmol), EDC·HCl (720.8 mg, 3.76 mmol), dry DMF (10 mL) and DMAP (76.6 mg, 626.7 μmol) were added sequentially. The reaction mixture was allowed to be stirred at room temperature overnight before diluted with 20 mL CH_2Cl_2, washed with water (2×30 mL) and brine (30 mL), and dried over $MgSO_4$. The solvent was evaporated, and the remaining residual was purified by silica gel chromatography (ethyl acetate/methanol, 1:1 v/v) to give 530.2 mg targeted G1 compound (yield 82%). ^{1}H NMR (in $CDCl_3$, δ, ppm): 1.17-1.19 (18H, (C*H*$_3$)$_2$CHCOO), 2.52-2.62 (9H, NCH$_2$C*H*$_2$CH$_2$N, (CH$_3$)$_2$C*H*COO), 2.63-2.65 (12H, OCOC*H*$_2$C*H*$_2$COO), 3.06-3.10 ppm (6H, CH=CC*H*$_2$CH$_2$OCO), 3.42 (12H, (N$_3$C*H*$_2$)$_2$C), 3.79 (6H, NC*H*$_2$C=CH),

4.01 (6H, $CH_2CH_2COOCH_2C$), 4.05 (6H, $(CH_3)_2CHCOOCH_2C$), 4.35-4.42 (18H, $NCH_2CH_2CH_2N$, $CH{=}CCH_2CH_2OCO$), 7.55 (3H, $N{-}CH{=}CCH_2CH_2OCO$), 7.84 (3H, $NCH_2C{=}CHN$). ^{13}C NMR (in $CDCl_3$, δ, ppm): 19.06 ($(CH_3)_2CHCOO$), 25.55 ($CH{=}CCH_2CH_2OCO$), 29.03, 29.07 ($OCOCH_2CH_2COO$), 30.73 ($NCH_2CH_2CH_2N$), 34.08 ($(CH_3)_2CHCOO$), 43.30 ($NCH_2C{=}CH$), 46.90-46.93 ($NCH_2CH_2CH_2N$), 47.67($(COOCH_2)C(CH_2OOC)(CH_2N_3)_2$), 51.47 ($(N_3CH_2)_2C$), 62.63, 63.02, 63.66 ($CH_2CH_2COOCH_2C$,$CH{=}CCH_2CH_2OCO$, $(CH_3)_2CHCOOCH_2C$), 122.64 ($N{-}CH{=}CCH_2CH_2OCO$), 124.51 ($NCH_2C{=}CHN$), 144.29, 144.53 ($N{-}CH{=}CCH_2CH_2OCO$, $NCH_2C{=}CHN$), 171.89, 172.16 ($OCOCH_2CH_2COO$), 176.41 ($(CH_3)_2CHCOOCH_2C$). HRMS (ESI) calculated for $C_{69}H_{99}N_{37}O_{18}$ $[M+H]^+$ 1734.8042; found 1734.8038.

Synthesis of molecule A_1'. To a 150 mL round-bottom flask were added sequentially with compound 1 (572.4 mg, 3.4 mmol), triethylene glycol monoethyl ether (500.0 mg, 2.8 mmol), EDC·HCl (1.3 g, 6.7 mmol), dry methylene chloride (10 mL) and DMAP (13.7 mg, 1.1 mmol). The reaction mixture was allowed to be stirred at room temperature overnight before washed with water (2×10 mL) and brine (10 mL), and dried over $MgSO_4$. The solvent was evaporated, and the remaining residual was purified by silica gel chromatography (hexanes/dichloromethane, 1:1 v/v) to give a colorless liquid (797.1 mg, 86% yield). ^1H NMR (in $CDCl_3$, δ, ppm): 1.19-1.23 (3H, CH_3CH_2O), 2.00 (1H, $HC{\equiv}CCH_2$), 2.51-2.55 (2H, $HC{\equiv}CCH_2CH_2OCO$), 2.65-2.68 (4H, $OCOCH_2CH_2COO$), 3.50-3.55 (2H, CH_3CH_2O), 3.57-3.72 (10H, $COOCH_2CH_2O(CH_2CH_2O)_2CH_2CH_3$), 4.18-4.22 (2H, $HC{\equiv}CCH_2CH_2OCO$),

4.24-4.27 (2H, COOCH_2CH$_2$OCH$_2$). ^{13}C NMR (in $CDCl_3$, δ, ppm) 15.31 (CH_3CH$_2$O), 19.06 (HC≡CCH$_2$), 29.14 (OCOCH$_2$$CH_2$COO), 62.48 (HC≡CCH$_2$$CH_2$OCO), 64.04, 66.76, 69.20, 69.96, 70.21, 70.74, 70.86, (COOCH$_2$$CH_2$O($CH_2$$CH_2$O)$_2$$CH_2CH_3$), 80.08 (HC≡$CCH_2$), 172.09, 172.32 (O$COCH_2CH_2$$C$OO). HRMS (ESI) calculated for $C_{16}H_{26}O_7$ $[M+Na]^+$ 353.1571; found 353.1548.



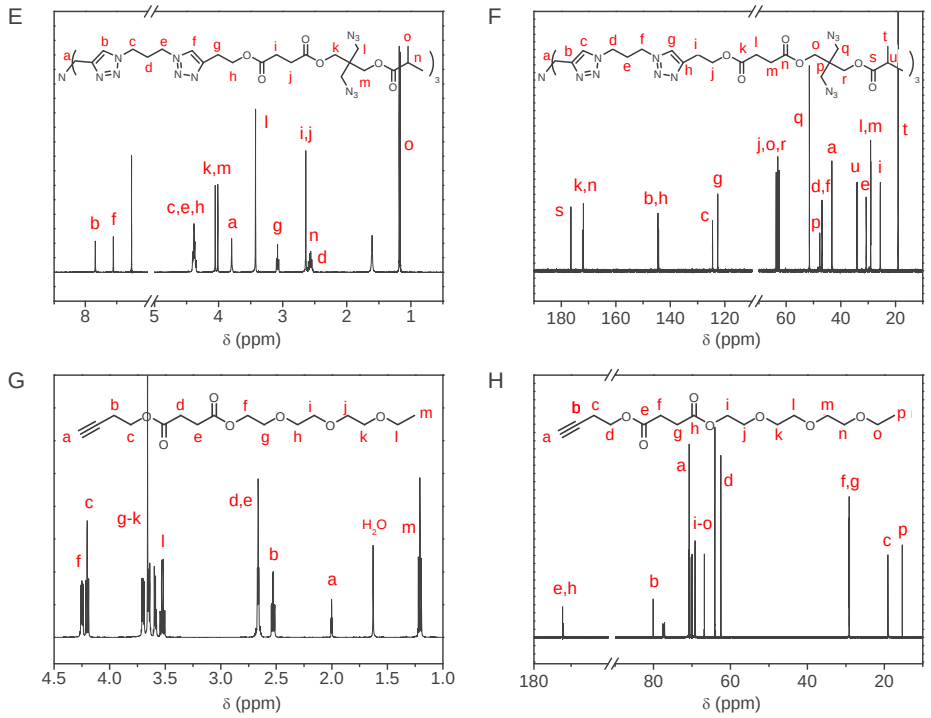


Figure S5. ^{1}H NMR spectra of model compounds (A) B_2, (C) A_1, (E) G1, (G) A_1' in $CDCl_3$ at 25 °C, and ^{13}C NMR spectra of model compounds (B) B_2, (D) A_1, (F) G1, (H) A_1' in $CDCl_3$ at 25 °C.

Model reaction 1. Compounds A_1 (66.0 mg, 589.1 μmol), B_2 (96.1 mg, 294.5 μmol), B_3 (100.0 mg, 196.4 μmol) and DMF (1.9 mL) were charged in a 10 mL schlenk flask (alkyne groups from A_1 equaled to azido groups from $B_2$and equaled to azido groups from B_3 core). The first sample was collected and diluted by $CDCl_3$ for ^{1}H NMR measurement before adding $CuSO_4 \cdot 5H_2O$ (49.1 mg, 196.4 μmol). This flask was then capped and bubbled with nitrogen gas for 40 min, ascorbic acid (172.8 mg, 981.8 μmol) was added into flask quickly and the flask was immersed in a thermostatic oil bath at 45 °C. The reaction mixture was allowed to be stirred for 1 hour to ensure fully consumption of alkynyl groups. The second sample was then

taken and diluted with $CDCl_3$, followed by adding 2 equiv. of PMDETA to Cu amount to reduce signal broadening. A precipitate with blue color was immediately observed representing a mixture of Cu, PMDETA, ascorbic acid and dehydroascorbic acid. Removal of the precipitate through filtration, extraction or neutral alumina chromatography offered better resolution in NMR spectra, however, was not applied since partial model compounds or products were also removed, introducing artifact.

The reaction was confirmed to be completed by disappearance of alkyne proton -C≡C*H* at 1.95 ppm as shown in ^{1}H NMR spectrum. To quantify the change in peak integrals, proton -CHC*H*$_3$ at 1.11 ppm was selected as internal standard. The key group of signals at 3.36 ppm and 3.31 ppm, were attributed to methylene protons adjacent to azido groups (-C*H*$_2$N$_3$) for B_2 and B_3, respectively (denoted as H_{b1} and H_{c1}). The remaining signals after click reaction clearly indicated a conversion of 13% and 89% for H_{b1} and H_{c1}. In other words, the azido groups on B_3 core were consumed 7 times faster than those on B_2. Importantly, the 51% total conversion for H_{b1} and H_{c1} was nearly equal to the theoretical value, indicating high reliability of the experiment. After coupling with alkyne, the signal of H_{b1} shifts to 4.40 ppm (H_{b3}) and 4.37 ppm (H_{b2}), which are from di-triazole product and mono-triazole product separately, similar as the concept of D and L units in corresponding hyperbranched polymers. Deconvolution of partially overlapped H_{b3} and H_{b2} shows roughly 2:1 ratio, in agreement with the ratio between D and L units in hyperbranched polymer when using equivalent catalyst to core species. Meanwhile, the signal of H_{c1} shifted to 4.33 ppm and overlapped with the peak of H_{c3} bearing similar chemical environment. Such

a high reactivity of azido groups on B_3 core is the key point to tune the molecular weight by simply adjusting the monomer to core ratio in polymerization.

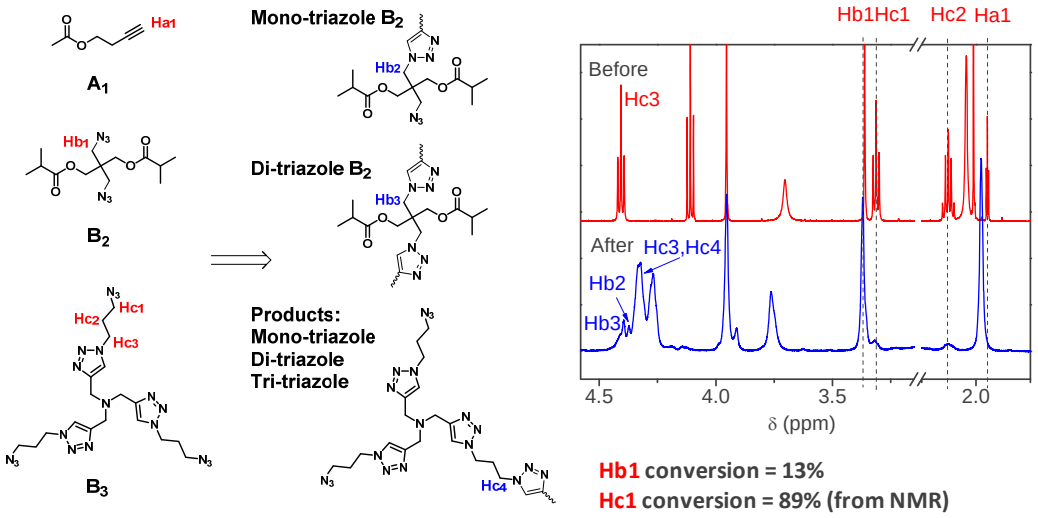


Figure S6. Model reaction 1 to illustrate higher reactivity of azido units on B_3 core with condition $[A_1]_0:[B_2]_0:[B_3]_0:[CuSO_4{\cdot}5H_2O]_0:[\text{ascorbic acid}]_0 = 3:1.5:1:1:5$ in DMF at 45 °C, $[B_3]_0 = 0.02$ mol L^{-1}. ^1H NMR spectra were taken in $CDCl_3$ before adding Cu and ascorbic acid, and after reaching 100% conversion of A_1 (2 equiv. of PMDETA to Cu amount was added to extract Cu from $B_3$and resulting derivatives, the mixture was without any purification).

Model reaction 2. Compounds A_1' (32.8 mg, 103.8 μmol), B_2 (16.9 mg, 51.9 μmol), G1 (30.0 mg, 17.3 μmol) and 0.9 mL DMF were sequentially charged in a 10 mL schlenk flask (alkyne groups from A_1' equaled to azido groups from B_2, equaled to azido groups from G1). The first and second sample were collected before and after adding A_1', and diluted by THF for SEC measurement. After adding $CuSO_4{\cdot}5H_2O$ (4.3

mg, 17.3 μmol), the flask was then capped and bubbled with nitrogen gas for 40 min, ascorbic acid (15.2 mg, 86.5 μmol) was added into flask quickly and the flask was immersed in a thermostatic oil bath at 45 °C. The reaction mixture was allowed to be stirred for 1 hour to ensure fully consumption of alkyne groups. The third sample was taken, from which one portion was diluted with THF without any further treatment while another portion was diluted by $CDCl_3$ and 2 equivalents of PMDETA to Cu amount for the assessment of alkyne conversion by ^1H NMR spectroscopy.

The reaction was confirmed to be completed by disappearance of alkyne signal in ^1H NMR spectroscopy. SEC peak integration was used to quantify the conversion of B_2 and G1 since the NMR peaks from -C*H*$_2N_3$ protons overlapped due to the similar chemical environment. For better distinguishing the peaks between different products, A_1' with specific molecular weight was designed, in which the possible species in the product mixture after reaction, B_2, B_2+A_1', B_2+2A_1', G1, G1+nA_1' with formula weights of 326, 656, 986, 1734, 2064~3514 separately, exhibited well-resolved peaks in SEC traces with RI detector. The reaction solvent DMF was used as an internal standard to calculate the conversion and yield of each species. In the first sample, the elution volume of B_2 was 29.7 mL while G1 was 27.4 mL with slight tailing due to the amine group. In the second sample, A_1' and B_2 fully overlaps and the doubled peak height confirmed very similar mass between A_1' and B_2. The total peak area of reaction mixture in the third sample nearly equals second sample since mass before and after click reaction are constant, indicating high reliability of the experiment. Three new peaks appeared at 25.7 mL, 27.7 mL and 28.5 mL

represented G1+nA_1', di-triazole product and mono-triazole, respectively. Importantly, only 22% B_2 was reacted and the G1 peak almost disappeared, indicating a higher reactivity of azido groups in B_3-containing G1 molecule.

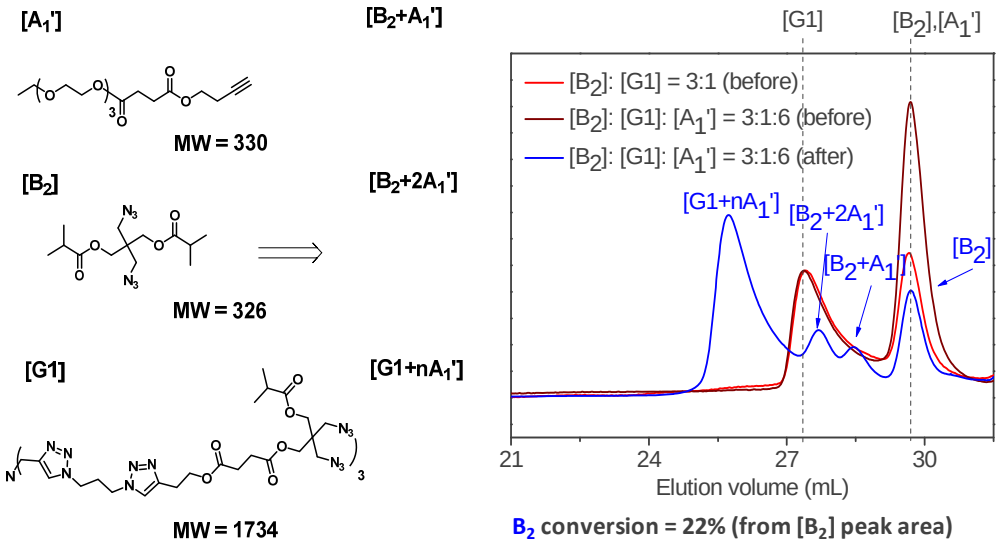


Figure S7. Model reaction 2 to illustrate the relayed higher reactivity of azido groups on core species with conditions $[A_1']_0$:$[B_2]_0$:$[G1]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$= 6:3:1:1:5 in DMF at 45 °C, $[G1]_0$ = 0.02 mol L^{-1}. SEC samples (diluted with THF) were taken before adding Cu and ascorbic acid, and after reaching 100% conversion of A_1' using DMF as an internal standard.

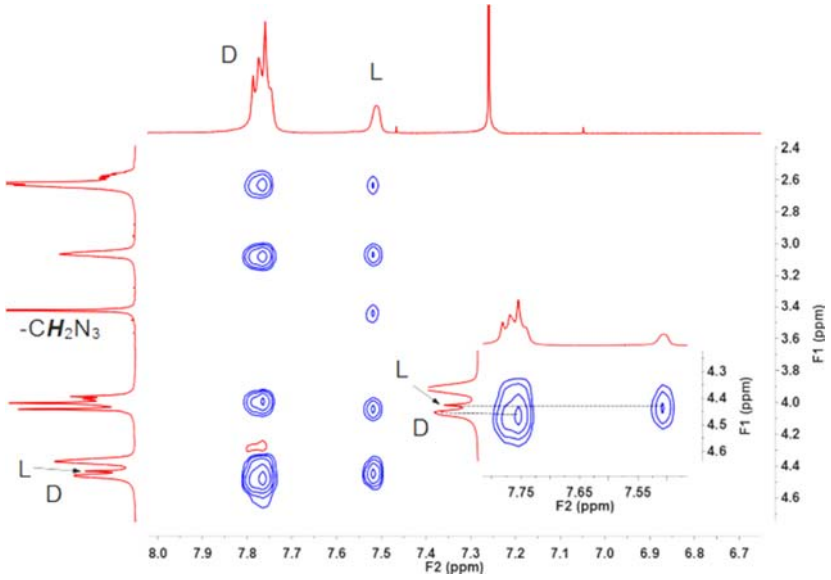


Figure S8. 2D ROESY NMR spectrum of a purified hyperbranched polymer (reaction condition: $[AB_2]_0$:$[CuSO_4 \cdot 5H_2O]_0$:[ascorbic acid]$_0$ = 900:1:10:50, $[AB_2]_0$ = 0.5 mol L^{-1}, conv. 99%) in $CDCl_3$ at 25 °C.

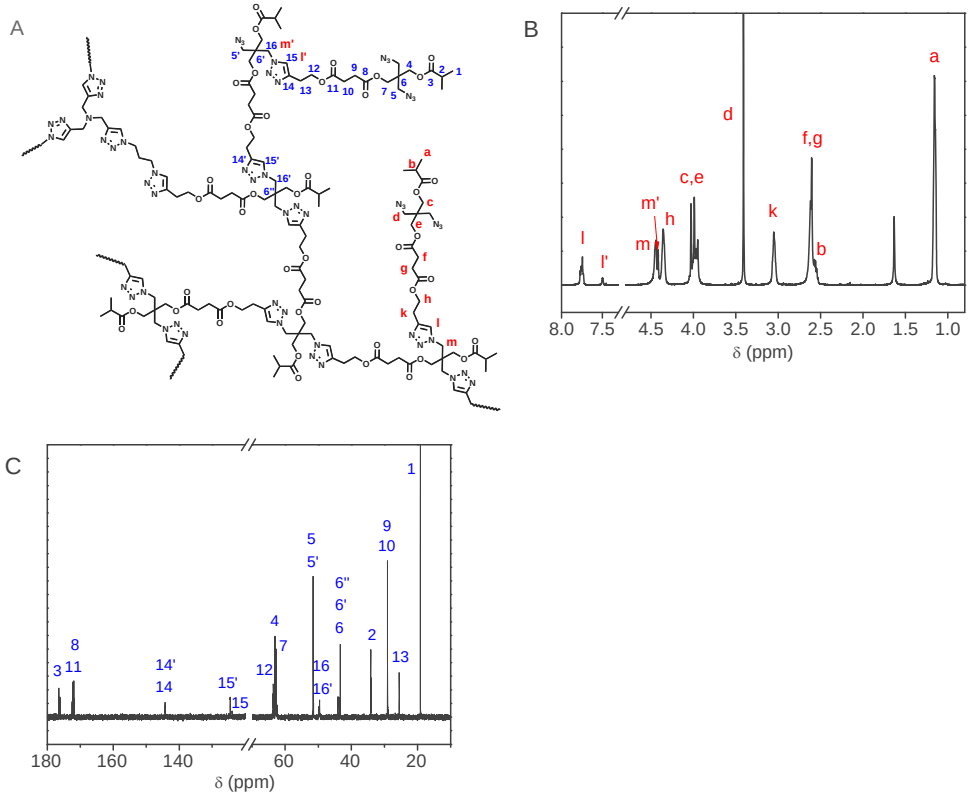


Figure S9. A) Representative structure, B) ^{1}H NMR spectrum and C) ^{13}C NMR spectrum of a purified hyperbranched polymer (reaction condition: $[AB_2]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 900:1:10:50, $[AB_2]_0$ = 0.5 mol L^{-1}, conv. 99%) in $CDCl_3$ at 25 °C.

The ligand-exchange experiment. B_3 and a purified hyperbranched homopolymer (denoted as HP, synthesized at feed ratio of $[AB_2]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 90:1:5) were individually prepared in DMF-d_7 solution: $[B_3]_0$ = 0.5 mol L^{-1} (A, Figure S10), [triazole]$_0$ in HP = 1.5 mol L^{-1} (C, Figure S10) and transferred to NMR tubes for ^{1}H NMR analysis. The triazole protons in B_3 core, D units and L units in HP were observed at 8.16 ppm, 8.08-8.13 ppm and 8.00-8.02 ppm, respectively. B_3-Cu^{I} complex (B, Figure S10) was then prepared by adding $CuSO_4{\cdot}5H_2O$ and ascorbic acid to B_3 in DMF-d_7 solution at the feed ratio of $[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 1:1:2, which generated immediate shift and broadening of the triazole proton signal to 8.52 ppm. Subsequently, addition of HP solution in the complex solution at 1:1 volume ratio introduced fast ligand exchange of Cu^{I} catalyst between the B_3 and the polytriazole units in HP, indicated by diagnostic NMR chemical shifts to 8.43 ppm, 8.13-8.25 ppm and 8.07-8.10 ppm for the triazole protons in B_3 core, D units and L units of HP, respectively.

In Figure S10-D, the fraction of Cu^{I} in each complex was estimated based on the equation:[9]

$$\delta = n_a\delta_a + n_b\delta_b$$

where δ= 8.43 ppm represents the population-averaged chemical shifts of B_3/B_3-Cu^I triazole protons, δ_a= 8.16 ppm and δ_b= 8.52 ppm represent the chemical shifts of triazole protons in free B_3 core (Figure S10-A) and B_3-Cu^I complex (Figure S10-B), and n represents the mole fraction of each complex. It was calculated that roughly 25% of copper was complexed with hyperbranched homopolymer in sample D.

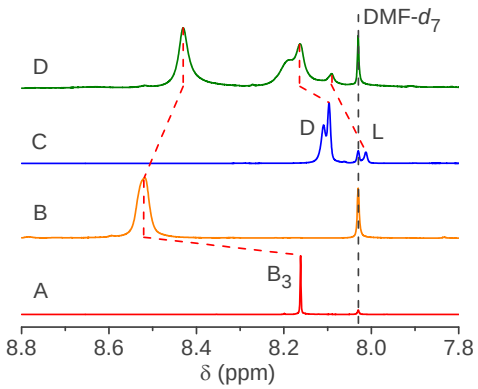


Figure S10. ^{1}H NMR spectra (DMF-d_7, 25 °C) of the triazole protons in (A): B_3 core, (B): B_3 core with the addition of Cu catalyst ($[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 1:1:2), (C): purified hyperbranched homopolymer (HP), (D): equilibrated mixture of (B) and (C).

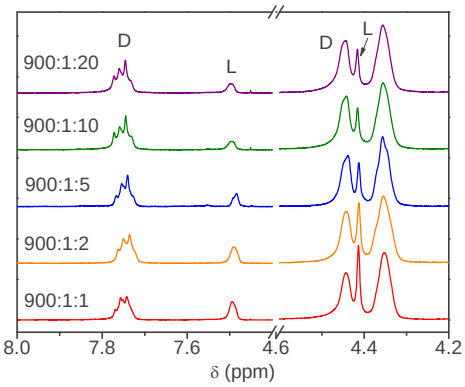


Figure S11. ^{1}H NMR peaks of triazole protons and methylene protons adjacent to triazole groups in hyperbranched polymers at various molar ratios of B_3 to Cu catalyst. Reaction condition: $[AB_2]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 900:1:x:5x in DMF at 45 °C, $[AB_2]_0$ = 0.5 mol L^{-1}.

Figure S12. Pictures of a typical hyperbranched polymer before and after extraction of Cu catalyst using 2 equiv. of PMDETA to Cu. The hyperbranched polymer in this picture was synthesized under conditions of $[AB_2]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 900:1:10:50.

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