Chain-growth Click Copolymerization for the Synthesis of Branched Copolymers with Tunable Branching Densities

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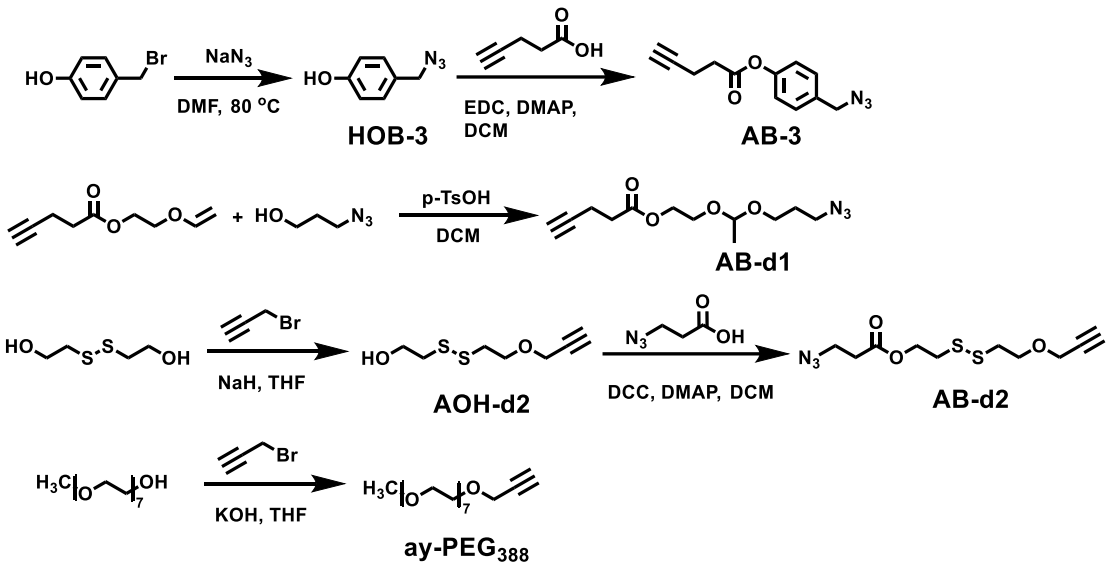
Materials. 3-Bromoprop-1-yne (TCI, 80% in Toluene, stabilized with MgO), 3-chloro-1-propanol (Alfa Aesar, 98%), sodium azide (EMD Millipore, 99%), p-toluenesulfonic acid monohydrate (Alfa Aesar, 97%), triethylamine (TEA, Sigma-Aldrich, 99.5%), sodium hydride (NaH, Aldrich, 60% dispersion in mineral oil), 4-pentynoic acid (Chem-Impex, 98%), 3-(3-dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride (EDC·HCl, Chem-Impex, 98%), 4-(dimethylamino) pyridine (DMAP, Sigma-Aldrich, ≥ 99%), *N,N′*-dicyclohexylcarbodiimide (DCC, Alfa Aesar, 99%), Polyethylene glycol monomethylether, 350 (Sigma-Aldrich), bis(2-hydroxyethyl) disulfide (Alfa Aesar, tech. 90%), hexafluoroisopropanol (HFIP, Chem-Impex, 99.91%), Nile Red (NR, Chem-Impex), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Chem-Impex, 100.2%), ascorbic acid (Alfa Aesar, ≥ 99%), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, BDH, ACS grade), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Sigma-Aldrich, 99%), dimethylformamide (DMF, Sigma-Aldrich, ≥ 99.8%), diethyl ether (EMD Millipore, ≥ 99%), deuterated chloroform ($CDCl_3$,

Cambridge Isotope Laboratories, Inc. 99.8%) were used as received. Dichloromethane (DCM, Sigma-Aldrich, > 99.5%) used for synthesis was distilled over CaH_2 prior to use. 3-Azidopropyl pent-4-ynoate (AB-1),[1] 2-(2-azidoethoxy)ethyl pent-4-ynoate (AB-2),[1] 3-azido-2-(azidomethyl)-2-((isobutyryloxy)methyl)propyl pent-4-ynoate (AB_2)[2] and 2-(vinyloxy)ethyl pent-4-ynoate[3] were synthesized according to published procedures. All azide compounds were synthesized, purified, and stored according to the standard safety rules with caution.[4]

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 °C with THF flow rate = 1.0 ml·min^{-1} and a Water 2414 RI detector. The apparent molecular weights were calculated based on linear poly(methyl methacrylate) (PMMA) standards. The DMF size exclusion chromatography (SEC) was equipped with a Waters 515 HPLC pump, Polymer Standards Services (PSS) columns (GRAM, 10^4, 10^3, and 10^2 Å) at 55 °C with DMF flow rate = 1.0 ml·min^{-1} and a Wyatt differential refractive index (RI) detector (Wyatt Technology, Optilab T-rEX). All apparent molecular weight was analyzed using PSS WinGPC 7.5 software. The detectors employed to measure the absolute molecular weights of polymers in DMF 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. The dn/dc values were determined by an offline approach at five concentrations, ranging 0.2 – 3 mg/mL, the solvent was injected as the base line and followed by each sample from the low concentration to high, after which, the differential refractive index was plotted vs. concentration and the dn/dc was

determined from the fitting curve. Absolute molecular weights were determined using ASTRA software from Wyatt Technology with the dn/dc = 0.0725 ml/g for **P1**, 0.0861 ml/g for **P2**, 0.0739 ml/g for **P7**, and 0.0955 ml/g for **P8**. The dn/dc for copolymers prepared by AB_2 and AB-1 was calculated based on the polymer composition in the monomer feed. Proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR were acquired on a Bruker 500 MHz spectrometer at 25 °C using $CDCl_3$ as solvent. 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). Thermogravimetric analyzer/differential scanning calorimeter (TGA/DSC-1, Mettler Toledo) was performed at temperatures ranging from 30 ºC to 600 ºC. The temperature was raised in a stepwise manner at a rate of 20 ºC/min, and these experiments were performed under a flow of N_2. Differential scanning calorimetry (DSC) analyses were performed under nitrogen purge (50 ml/min) on a DSC Q2000 (TA Instruments) at a heating rate of 10 ºC/min and cooling rate of 10 ºC/min. The thermograms were reported based on the second heating cycle in the temperature range of -80~120 ºC. Glass transition temperature (T_g) was determined based on the automatic mode of TA Universal Analysis software. Fourier-Transformed InfraRed (FTIR) was conducted using a Bruker Tenor 27 spectroscopy. UV-VIS spectra were obtained on a Thermo-Fisher GENESYS 140 spectroscopy.

Synthesis of monomers.



Scheme S1. Synthesis procedures of AB-3, AB-d1, AB-d2 and ay-PEG_{388}.

4-(Azidomethyl)phenol (HOB-3). 4-(Bromomethyl)phenol (5.00 g, 26.7 mmol) and sodium azide (2.85 g, 43.8 mmol) were charged in 25 ml DMF. The reaction was allowed to stir at 80 °C for overnight before adding 50 ml of water. The aqueous layer was extracted with diethyl ether (50 ml x 3) and the organic layer was collected and washed successively with 5% $NaHCO_3$ (50 ml x 2) and dried over $MgSO_4$. Most of the solvent was removed under reduced pressure and the product was obtained in ether (70 wt%, 3.68 g, 98.0 % yield). ^{1}H NMR (ppm, in $CDCl_3$) δ 7.37 (dt, J = 20.0, 7.1 Hz, 5H), 4.36 (s, 2H).

4-(Azidomethyl)phenyl pent-4-ynoate (AB-3). 4-(Azidomethyl)phenol (1.0 g, 1.2 eq) and 4-pentynoic acid (0.55 g, 1.0 eq) were dissolved in 30 ml dry DCM, DMAP (0.27 g, 0.4 eq.) was added and the solution was stirred for 0.5 h before adding EDC·HCl (2.36 g, 2.2 eq). The mixture was stirred at room temperature for overnight

and washed with water (30 ml x 3). The DCM layer was dried over anhydrous $MgSO_4$, and the DCM was evaporated. The crude product was purified by column chromatography, using hexanes/ethyl acetate (8:1, v/v) as eluent to afford the final product (1.06 g, 82.5 % yield). ^{1}H NMR (ppm, in $CDCl_3$) δ 7.33 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 4.34 (s, 2H), 2.82 (s, 2H), 2.63 (s, 2H), 2.05 (t, J = 2.7 Hz, 1H).

2-(1-(3-Azidopropoxy)ethoxy)ethyl pent-4-ynoate (AB-d1). 2-(Vinyloxy)ethyl pent-4-ynoate (1.50 g, 8.9 mmol) and 3-azidopropan-1-ol (0.90 g, 8.9 mmol) were dissolved in 20 ml of DCM. A catalytic amount of p-toluenesulfonic acid monohydrate (93.31 mg, 0.5 mmol) was added to start the reaction. The reaction was allowed to stir for 1 h and then neutralized with a few drops of TEA. The solvent was removed under reduced pressure, and the product was purified by silica gel chromatography (hexanes/ethyl acetate, 10:1 v/v) as clear oil (1.15 g, 4.3 mmol, 47.9 % yield). ^{1}H NMR (ppm, in $CDCl_3$) δ 4.74 (q, J = 5.3 Hz, 1H), 4.25 (t, J = 4.9 Hz, 2H), 3.75 (dt, J = 11.2, 4.4 Hz, 1H), 3.73 – 3.58 (m, 2H), 3.49 (dt, J = 9.6, 6.0 Hz, 1H), 3.40 (t, J = 6.6 Hz, 2H), 2.59 (ddd, J = 7.6, 6.4, 1.6 Hz, 2H), 2.50 (ddt, J = 8.5, 4.6, 1.6 Hz, 2H), 1.97 (t, J = 2.6 Hz, 1H), 1.84 (p, J = 6.3 Hz, 2H), 1.31 (d, J = 5.4 Hz, 3H). ^{13}C NMR (ppm, in $CDCl_3$) δ 171.88, 99.90, 82.55, 69.19, 64.09, 62.55, 62.02, 48.58, 33.35, 29.28, 19.57, 14.43.

2-((2-(Prop-2-yn-1-yloxy)ethyl)disulfanyl)ethan-1-ol (AOH-d2). Bis(2-hydroxyethyl) disulfide (9.25 g, 60.0 mmol) and propargyl bromide (3.57 g, 30.0 mmol) were dissolved in THF (200 ml). Then, NaH powder (1.08 g, 45.0 mmol, 60% dispersion in mineral oil) was added into the reaction mixture in three successive batches under nitrogen atmosphere within 1 h at 0 °C. The mixture was further stirred

for overnight at room temperature, and then a few drops of water were added to quench the reaction. The mixture was filtered, and the solvent was removed by evaporation. The crude product was purified by column chromatography, using hexanes/ethyl acetate (4:1, v/v) as eluent to afford a pale-yellow clear oil (2.37 g, 12.3 mmol, 41.2 % yield). ^{1}H NMR (ppm, in $CDCl_3$) δ 4.20 (d, J = 2.4 Hz, 2H), 3.91 (t, J = 5.8 Hz, 2H), 3.81 (t, J = 6.3 Hz, 2H), 2.91 (dt, J = 17.2, 6.1 Hz, 4H), 2.47 (t, J = 2.4 Hz, 1H), 2.09 (s, 1H). 13C NMR (ppm, in $CDCl_3$) δ 79.41, 75.01, 68.23, 60.35, 58.34, 41.50, 38.45.

2-((2-(Prop-2-yn-1-yloxy)ethyl)disulfanyl)ethyl 3-azidopropanoate (AB-d2). AOH-d2 (0.65 g, 3.4 mmol) and 3-azidopropanoic acid (0.39 g, 3.4 mmol) were dissolved in 20 ml dry DCM and was kept at 0 °C. DMAP (83.2 mg, 0.7 mmol) was added, and the mixture was stirred for 15 min before the solution of DCC (0.84 g, 4.1 mmol) in 10 ml DCM was added drop by drop. The mixture was stirred at room temperature for overnight and washed with water (20 ml x 3). The DCM layer was dried over anhydrous $MgSO_4$, and the DCM was evaporated. The crude product was purified by column chromatography, using hexanes/ethyl acetate (5:1, v/v) as eluent to afford a yellowish liquid (0.35 g, 1.2 mmol, 35.5 % yield). ^{1}H NMR (ppm, in $CDCl_3$) δ 4.40 (t, J = 6.6 Hz, 2H), 4.19 (d, J = 2.4 Hz, 2H), 3.79 (t, J = 6.4 Hz, 2H), 3.59 (t, J = 6.5 Hz, 2H), 2.94 (dt, J = 10.6, 6.5 Hz, 4H), 2.61 (t, J = 6.5 Hz, 2H), 2.46 (t, J = 2.4 Hz, 1H). ^{13}C NMR (ppm, in $CDCl_3$) δ 170.81, 79.45, 74.99, 68.14, 62.94, 58.35, 46.82, 38.70, 37.18, 34.02.

Ay-PEG$_{388}$. Polyethylene glycol monomethylether, 350 (18.48 g, 52.8 mmol) and potassium hydroxide (2.96 g, 52.8 mmol) were dissolved in dry THF (70 ml). Then,

propargyl bromide (6.28 g, 52.8 mmol) was added into the reaction mixture slowly at room temperature. The mixture was further stirred for overnight at room temperature before filtration, after which the solvent was removed by evaporation to afford a pale-yellow clear oil (17.98 g, 46.33 mmol, 87.7 % yield). ^{1}H NMR (ppm, in $CDCl_3$) δ 4.17 (d, J = 2.4 Hz, 2H), 3.73 – 3.49 (m, 30H), 3.34 (s, 3H), 2.45 (t, 1H).

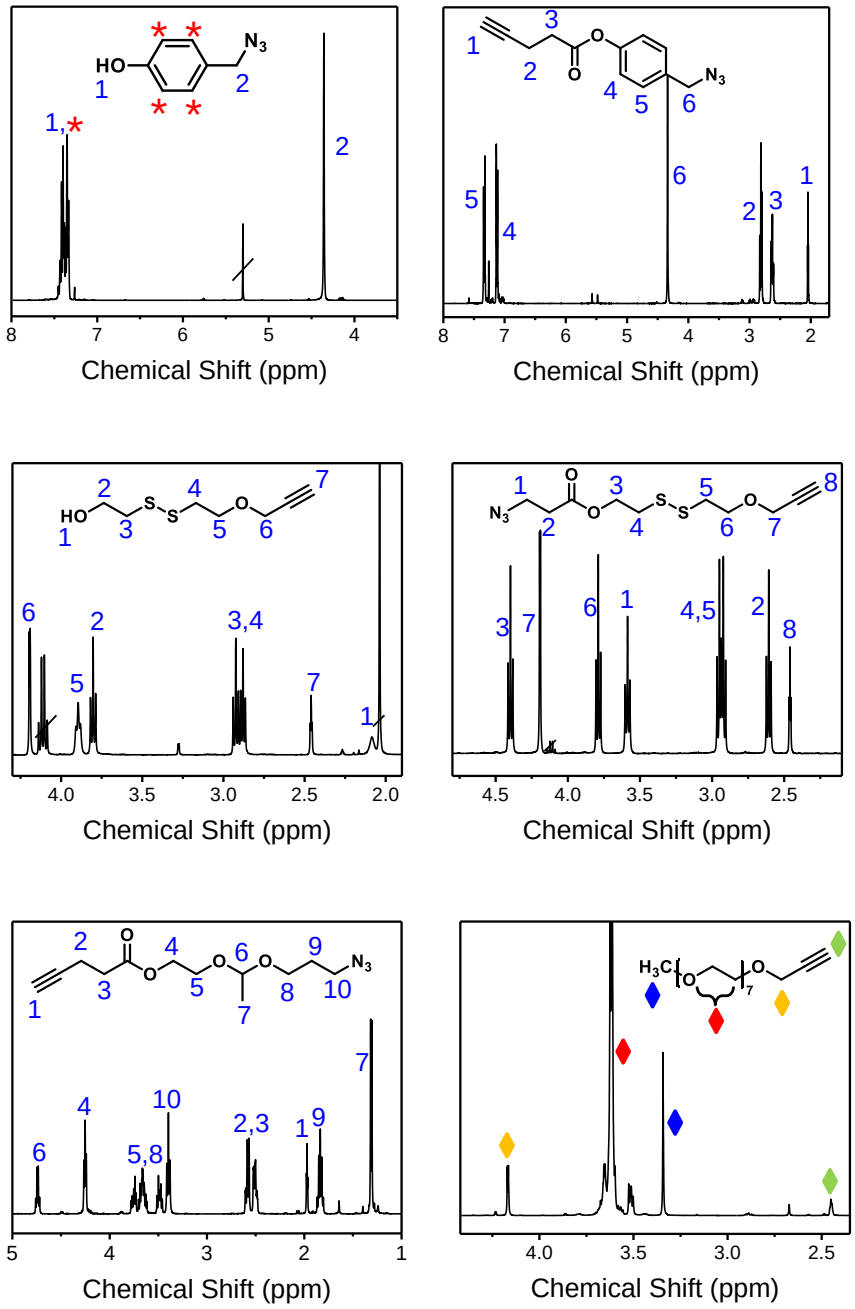


Figure S1. ^{1}H NMR spectra of AB precursors, monomers and ay-PEG$_{388}$ in $CDCl_3$ at 25 ^{o}C.

Polymerizations

CuAAC homopolymerization of AB_2 or AB-1 monomers. The feed ratios were $[monomer]_0:[B_3]_0:[CuSO_4{\cdot}5H_2O]_0:[ascorbic\ acid]_0$ = 200:1:10:20, where monomer was AB_2 or AB-1. AB_2 (264.0 mg, 0.8 mmol) or AB-1 (142.2 mg, 0.8 mmol), B_3 core (2.0 mg, 3.9 μmol), $CuSO_4{\cdot}5H_2O$ (9.8 mg, 39.3 μmol) in DMF ($[AB_2]_0$ = 0.5 M or $[AB\text{-}1]_0$ = 0.5 M) were charged in a 10 ml Schlenk flask equipped with a magnetic stirring bar. The flask was degassed by three freeze-pump-thaw cycles. At the last cycle, the ascorbic acid (13.8 mg, 78.5 μmol) was quickly fed into the flask when the mixture was in frozen. The flask was vacuumed and backfilled with N_2 for 3 cycles before immersed in a thermostatic oil bath at 45 ℃ and the polymerization was initiated. Samples were withdrawn using deoxygenated syringes at each predetermined interval and were quenched by exposure to air and the addition of two equivalents of PMDETA. The polymerization was stopped at full conversion and diluted with 10 ml DCM for **P1** and 10 ml DMF for **P2**, and Cu catalyst was removed by adding two equivalents of PMDETA followed by passing a neutral alumina column, the polymer was then purified by precipitation in large amount of diethyl ether three times before the final product was dried under vacuum to a constant mass and stored in a freezer at -20 ^oC.

CuAAC copolymerization of AB_2 and AB monomers. Table 1 in the manuscript listed the copolymerization experiments with feed ratios of $[B_3]_0:[CuSO_4{\cdot}5H_2O]_0:[ascorbic\ acid]_0$ = 1:10:20 except entry **P10**. A typical synthesis of the copolymer with $[AB_2]_0:[AB\text{-}1]_0$ =100:100 (**P3**) was described below.

P3. AB_2 (99.0 mg, 0.3 mmol), AB-1 (53.3 mg, 0.3 mmol), B_3 core (1.5 mg, 2.9 μmol), $CuSO_4 \cdot 5H_2O$ (7.4 mg, 29.4 μmol) and 1.18 ml DMF ($[AB_2]_0+[AB\text{-}1]_0 = 0.5$ M) were charged in a 10 ml Schlenk flask equipped with a magnetic stirring bar. The flask was degassed by three freeze-pump-thaw cycles. At the last cycle, the ascorbic acid (10.4 mg, 58.9 μmol) was quickly fed into the flask when the mixture was in frozen. The flask was vacuumed and backfilled with N_2 for 3 cycles before immersed in a thermostatic oil bath at 45 ℃ and the polymerization was initiated. Samples were withdrawn using deoxygenated syringes at each predetermined interval and were quenched by exposure to air and the addition of two equivalents of PMDETA. The polymerization was stopped at full conversion and diluted with 10 ml DCM, and Cu catalyst was removed by adding two equivalents of PMDETA followed by passing a neutral alumina column, the branched polymer was then purified by precipitation in large amount of diethyl ether three times before the final product was dried under vacuum to a constant mass and stored in a freezer at -20 ^oC.

Procedures (including synthesis and purification) for **P7**, **P8, P9** and **P11-P15** were similar as those described in synthesis of **P3**. The synthesis of **P4**, **P5** and **P6** followed the procedure similar as the preparation of **P2**.

P10. AB_2 (66.0 mg, 0.2 mmol), AB-d2 (56.8 mg, 0.2 mmol), B_3 core (1.0 mg, 2.0 μmol), $CuSO_4 \cdot 5H_2O$ (2.5 mg, 9.8 μmol) and 0.79 ml DMF ($[AB_2]_0+[AB\text{-}d2]_0 = 0.5$ M) were charged in a 10 ml Schlenk flask equipped with a magnetic stirring bar. The flask was degassed by three freeze-pump-thaw cycles. At the last cycle, the sodium ascorbate (2.0 mg, 9.8 μmol) was quickly fed into the flask when the mixture was in frozen. The

flask was vacuumed and backfilled with N_2 for 3 cycles before immersed in a thermostatic oil bath at 45 ℃ and the polymerization was initiated. Samples were withdrawn using deoxygenated syringes at each predetermined interval and were quenched by exposure to air and the addition of two equivalents of PMDETA. The polymerization was stopped at full conversion and diluted with 10 ml DCM, and Cu catalyst was removed by adding two equivalents of PMDETA followed by passing a neutral alumina column, the branched polymer was then purified by precipitation in large amount of diethyl ether three times before the final product was dried under vacuum to a constant mass and stored in a freezer at -20 ºC.

P14-PEG and **P15-PEG**. After getting purified P14 and P15 (The feed ratios were $[AB_2]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 900:1:10:20 and $[AB_2]_0$:$[AB\text{-}1]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 450:450:1:10:20, respectively, and the procedure was described above), the **P14** or **P15** (1.0 mmol of -N_3), ay-PEG_{388} (1.0 mmol), $CuSO_4{\cdot}5H_2O$ (25.0 mg, 100.0 μmol) and 2.0 ml DMF were charged in a 10 ml Schlenk flask equipped with a magnetic stirring bar. The flask was degassed by three freeze-pump-thaw cycles. At the last cycle, the ascorbic acid (17.6 mg, 100 μmol) was quickly fed into the flask when the mixture was in frozen. The flask was vacuumed and backfilled with N_2 for 3 cycles before immersed in a thermostatic oil bath at 45 ℃ and the reaction was initiated. The mixture was allowed to stir for overnight to reach the complete reaction. The procedures for purification and storage of the obtained polymers (**P14-PEG** and **P15-PEG**) were similar to those described above. The complete

consumption of azide groups can be verified by the disappearance of the azido peak around 2100 cm^{-1} in FTIR spectra.

Chain extension reactions. The first batch of polymerization was conducted at molar ratios of $[AB_2]_0$:$[AB\text{-}1]_0$:$[B_3]_0$:$[CuSO_4 \cdot 5H_2O]_0$:[ascorbic acid]$_0$ = 100:100:1:10:20 in DMF with $[AB_2]_0+[AB\text{-}1]_0$ = 0.5 M. a 2nd and a 3rd batch of deoxygenated monomers mixture (50 equiv. of AB_2 and 50 equiv. of AB-1) in DMF (0.5 M of total monomers) were added in sequence into the system at > 99 % conversion of the prior batch of monomers. The final branched polymers were subjected to the same purification steps as above.

NR loading. Stock solutions of 1 mg/ml polymer (**P14-PEG** or **P15-PEG**) in HFIP and the stock solution of NR (0.1 mg/ml) in HFIP were prepared separately. 0.3 ml polymer solution was mixed with 0.3 ml (for **P14-PEG**) or 0.33 ml (for **P15-PEG**) NR solution and the mixture was sonicated for 20 min before removing the solvent by rotary evaporation. The residue pellets were reconstituted in 1 ml aqueous buffer (20 mM HEPES, pH 7.4) with 30 min sonication before centrifugation to remove any unloaded NR, and each experiment was reproduced in triplicate. The encapsulated NR was confirmed by the UV-VIS spectroscopy, and the amount was quantified according to the NR calibration curve.

$$Conv = 1 - f_{AB_2}^0 \left[\frac{(AB_2)_t}{(AB_2)_0}\right] - \left(1 - f_{AB_2}^0\right)\left[\frac{(AB_2)_t}{(AB_2)_0}\right]^{r_{AB}} \quad \text{(A)}$$

$$Conv = 1 - f_{AB_2}^0 \left[\frac{(AB)_t}{(AB)_0}\right]^{r_{AB_2}} - \left(1 - f_{AB_2}^0\right)\left[\frac{(AB)_t}{(AB)_0}\right] \quad \text{(B)}$$

Equation S1. BSL integrated fitting equations, where $f_{AB_2}^0$ is the initial molar feed fraction of AB_2 monomer. $(AB_2)_t$ and $(AB)_t$ are the instantaneous concentrations of AB_2 and AB at time t, respectively, and $(AB_2)_0$ and $(AB)_0$ are the initial concentrations of AB_2 and AB, respectively, r_{AB_2} and r_{AB} are the reactivity ratios of AB_2 and AB in the copolymerization.

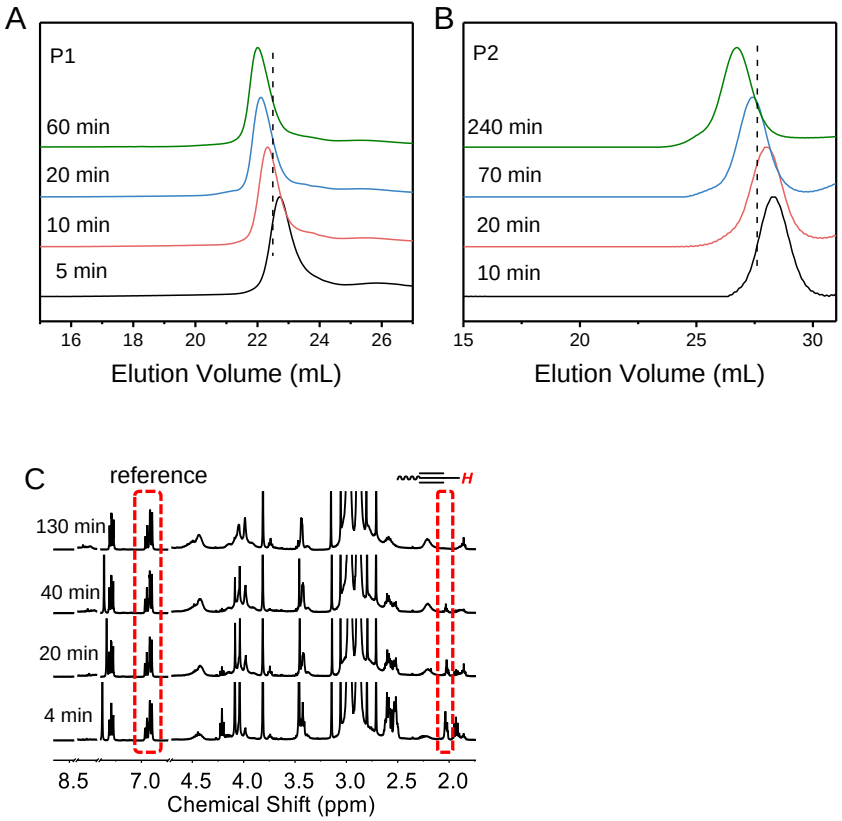


Figure S2. Stacked SEC traces as a function of time for A) **P1** and B) **P2**; C) stacked ^{1}H NMR spectra of **P3** at different time intervals.

Table S1. TGA measurements of **P1**, **P2** and **P3**.

Entry	Feed ratio[a] $[AB_2]_0$:$[AB\text{-}1]_0$:$[B_3]_0$	$T_{d,5\%}$ (°C)[b]	$T_{d,10\%}$ (°C)[c]	$T_{d,50\%}$ (°C)[d]
P1	200:0:1	248.7	262.2	380.1
P2	0:200:1	341.6	363.6	413.9
P3	100:100:1	255.5	272.4	398.7

a). Feed ratios of $[AB_2]_0$:$[AB\text{-}1]_0$:$[B_3]_0$ in DMF at 45 °C, and $[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 1:10:20 b). $T_{d,5\%}$: temperature at 5% weight loss. c). $T_{d,10\%}$: temperature at 10% weight loss. d). $T_{d,50\%}$: temperature at 50% weight loss.

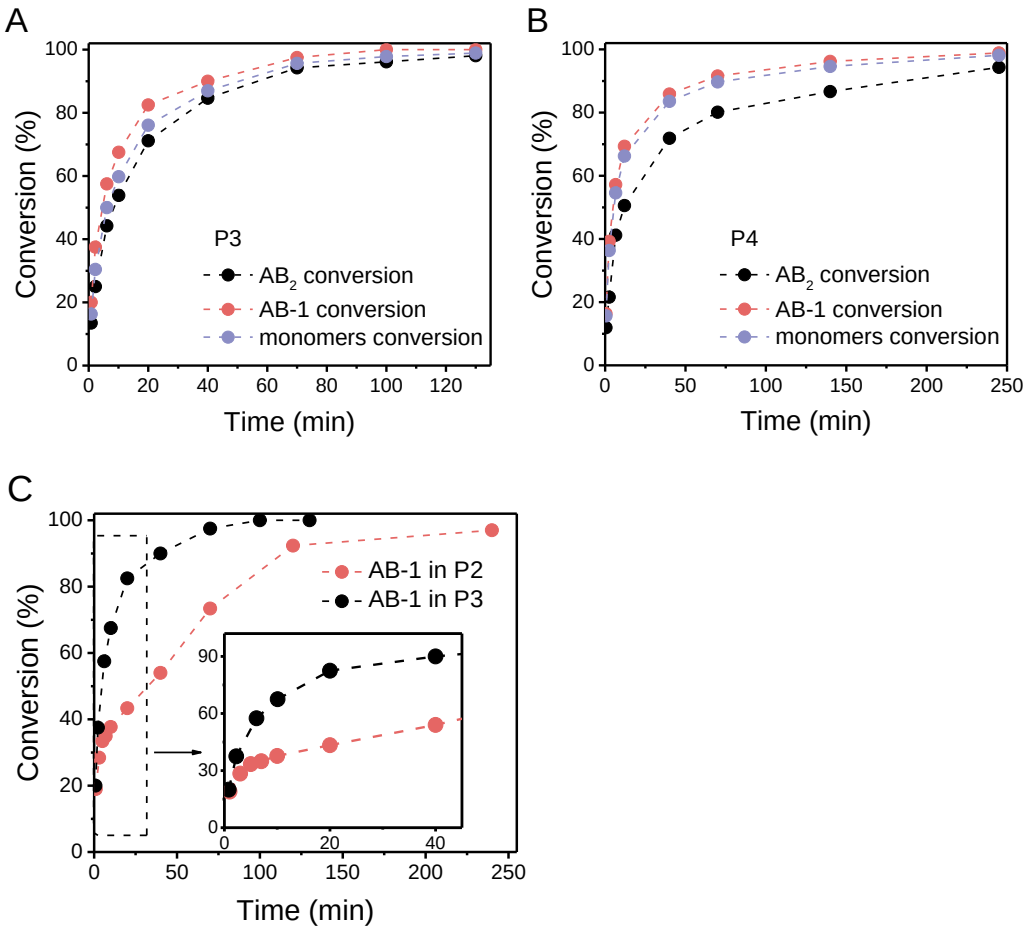


Figure S3. Kinetics of AB_2 and AB-1 during the syntheses of A) P3 and B) P4. C) Kinetics of AB-1 in the copolymerization and homopolymerization.

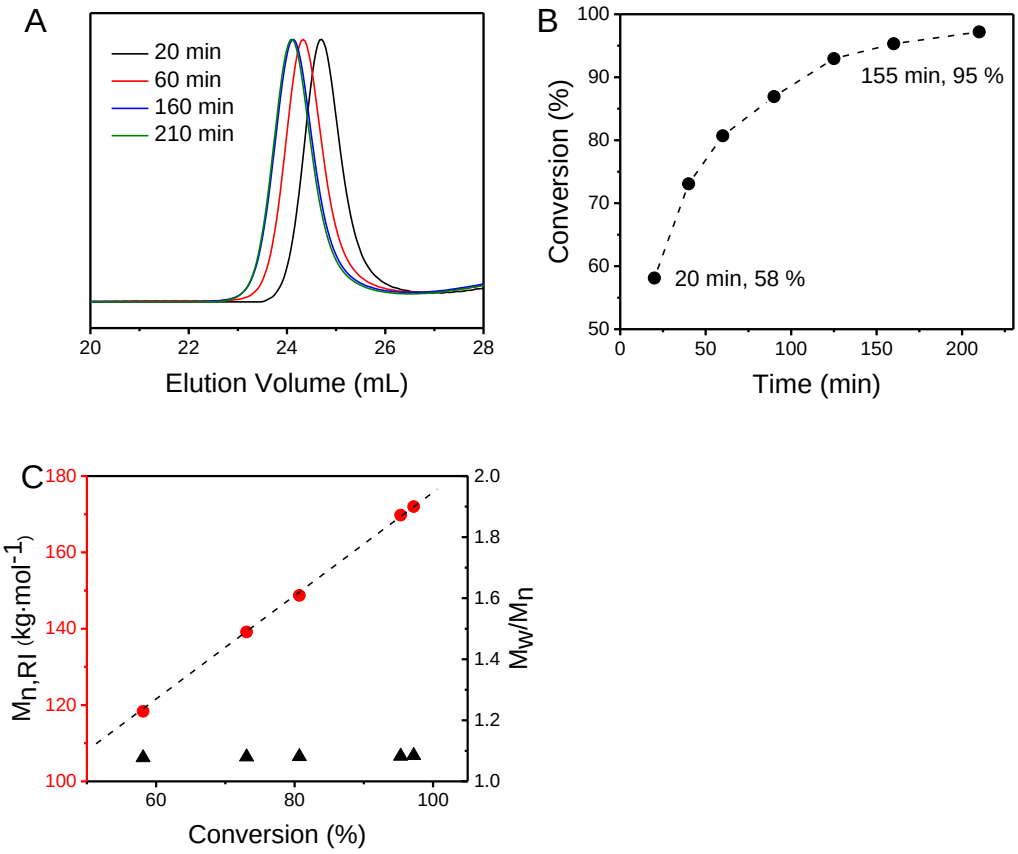


Figure S4. A) Stacked SEC traces as a function of time for **P13**; B) Kinetics and C) evolution of number-average molecular weights (Mn,RI) of branched polymers in the one-pot CuAAC copolymerization of monomers at feed ratios of $[AB_2]_0$:$[AB\text{-}1]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 1000:1000:1:10:20 in DMF at 45 °C, $[AB_2]_0$+$[AB\text{-}1]_0$ = 0.5 M.

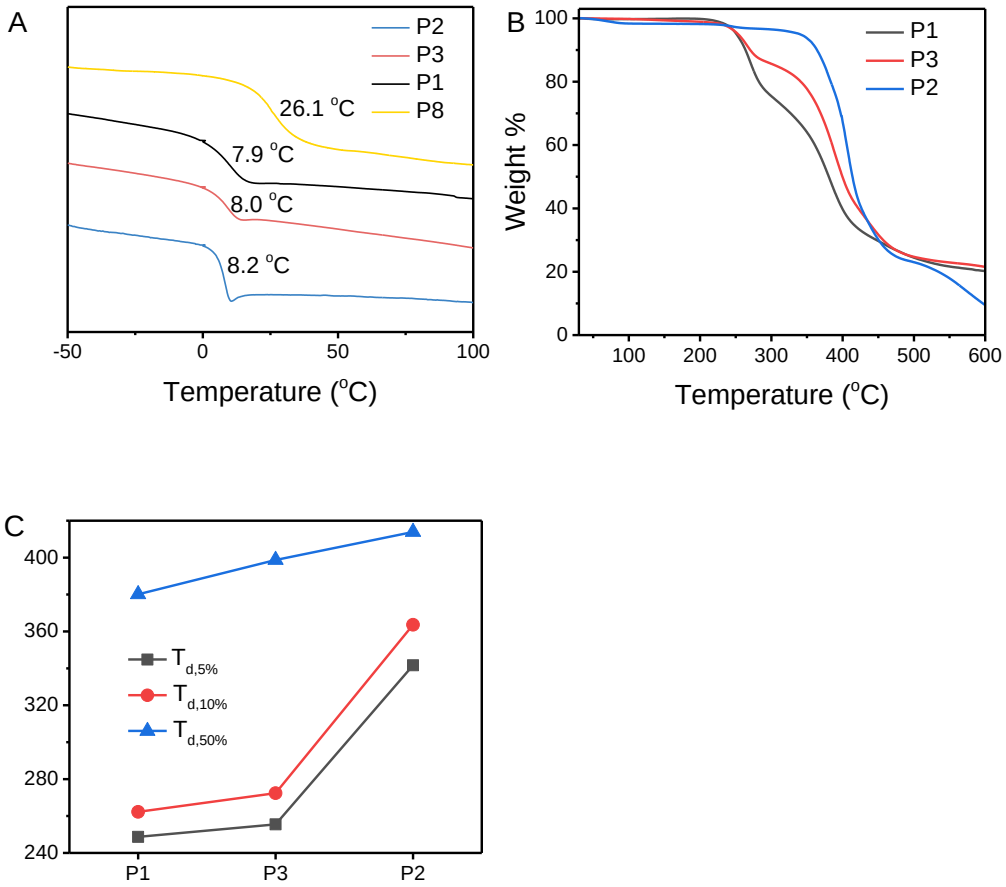


Figure S5. A) DSC curves of **P1, P2, P3** and **P8** B), C) TGA curves of **P1, P2** and **P3**.

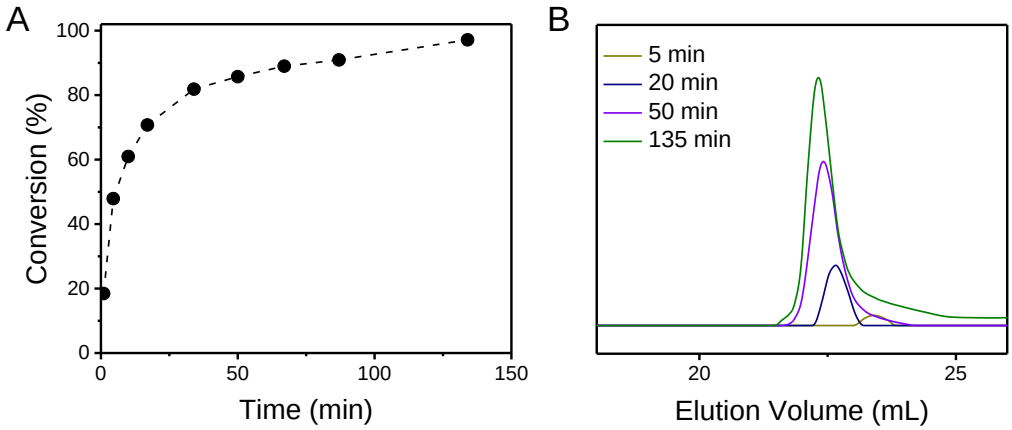


Figure S6. A) Kinetics and (B) Stacked SEC traces as a function of time for branched polymer in the one-pot CuAAC copolymerization at feed ratios of $[AB_2]_0$:$[AB\text{-}2]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 100:100:1:10:20 (**P7**) in DMF at 45 °C, $[AB_2]_0$+$[AB\text{-}2]_0$ = 0.5 M.

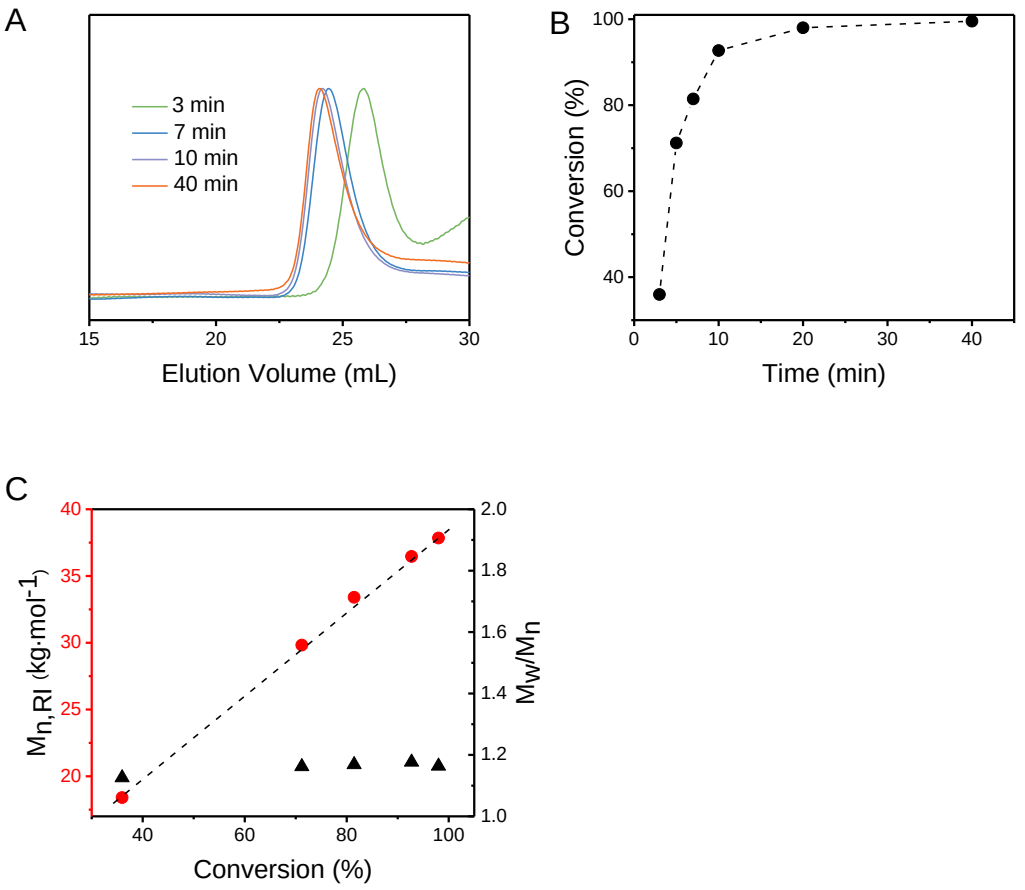


Figure S7. A) Stacked SEC traces as a function of time for **P8**; B) Kinetics and C) evolution of number-average molecular weights ($M_{n,RI}$) of branched polymers in the one-pot CuAAC copolymerization of monomers at feed ratios of $[AB_2]_0$:$[AB\text{-}3]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 100:100:1:10:20 in DMF at 45 °C, $[AB_2]_0$+$[AB\text{-}3]_0$ = 0.5 M.

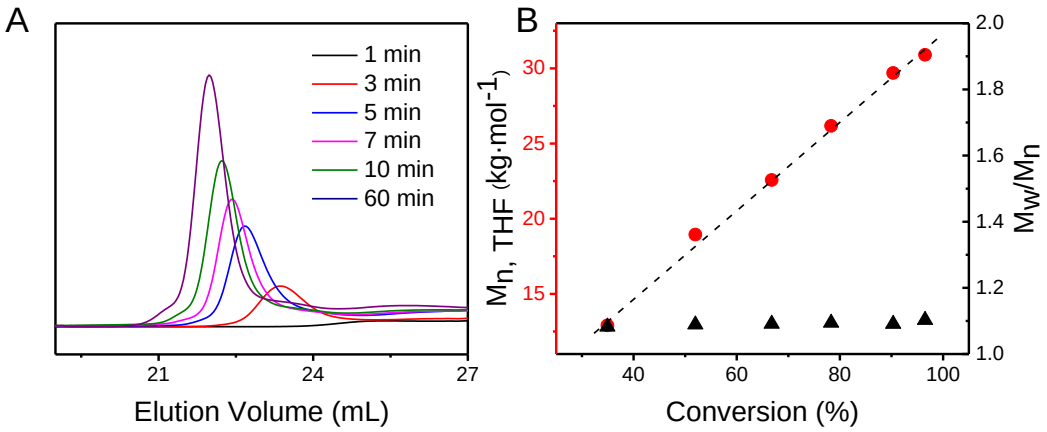


Figure S8. A) Stacked SEC traces as a function of time for **P9**; B) Evolution of number-average molecular weights ($M_{n,RI}$) of branched polymers in the one-pot CuAAC copolymerization of monomers at feed ratios of $[AB_2]_0$:$[AB\text{-}d1]_0$:$[B_3]_0$:$[CuSO_4{\cdot}5H_2O]_0$:[ascorbic acid]$_0$ = 100:100:1:10:20 in DMF at 45 °C, $[AB_2]_0$+$[AB\text{-}d1]_0$ = 0.5 M.

$$NR\ loading\ content = \frac{\mathrm{m(loaded\ NR)}}{\mathrm{m(loaded\ NR + polymer)}} \times\ 100\%$$

$$NR\ loading\ efficiency = \frac{\mathrm{m(loaded\ NR)}}{\mathrm{m(fed\ NR)}} \times\ 100\%$$

Equation S2. Calculation equations of NR loading content and NR loading efficiency.

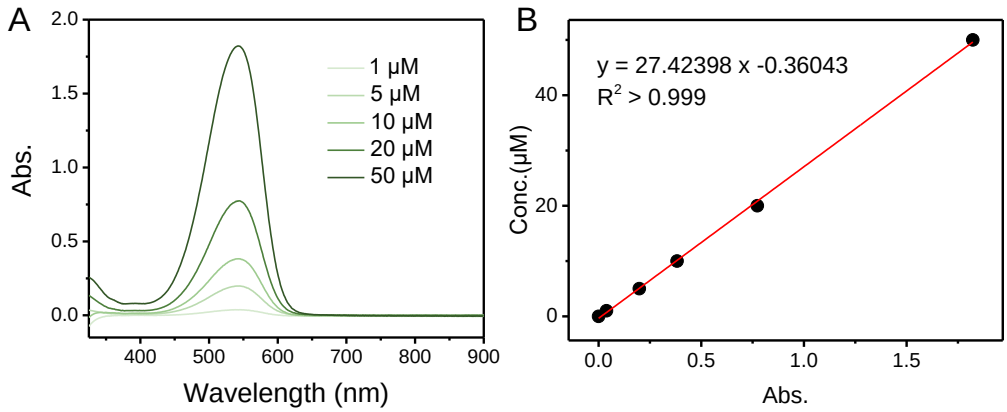


Figure S9. A) UV-VIS spectra of NR with different concentrations in DMF. B) Calibration curve of NR absorption in DMF.

References.

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