Supporting Information for
Sequential Click Synthesis of Hyperbranched Polymers via A₂ + CB₂ Approach

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EXPERIMENT

Materials
1,6-Hexanedithiol and 3,6-dioxaoctane-1,8-dithiol were purchased from TCI. Propargyl acrylate, propargyl methacrylate, 2,2-dimethoxy-2-phenyl-acetophenone (DMPA), 2,2-azobisisobutyronitrile (AIBN) and toluene (HPLC grade) were purchased from Aldrich. THF, ethyl acetate, n-propylthiol and Et₃N were obtained from Sinopharm Chemical Reagent Co. Ltd. Propargyl acrylate and propargyl methacrylate were distilled under reduced pressure before use. All reagents were used as received.

Measurement and Techniques

Nuclear Magnetic Resonance Spectroscopy (NMR)
The ¹H NMR measurements were carried out on a Varian Mercury Plus 300 MHz NMR spectrometer at 20 °C. The ¹³C NMR measurements were performed on a Bruker DMX 500MHz NMR spectrometer at 20 °C. The samples were dissolved with CDCl₃ and the solutions were measured with tetramethylsilane (TMS) as an internal reference.

Gel Permeation Chromatography (GPC)
The molecular weights of polymers were measured on a PL PL-GPC220, using linear polystyrene as calibration, and THF as the eluent at a flow rate of 1 mL/min.

High Performance Liquid Chromatography (HPLC)
The HPLC measurement was carried out on a Shimadzu LCMS-2020 with a λ = 254 nm UV detector and CH₃OH as the eluent at a flow rate of 1 mL/min.

Mass Spectrometry (MS)
The MS analysis was carried out on a Thermo Finnigan Polaris Q quadrupole ion trap mass-spectrometer, employing electron impact ionisation. The sample in THF solution was passed through Gas Chromatography System before the MS analysis.
Synthesis of the Models, Ter, Den, Mix₁ and Mix₂

Compound Ter was prepared via thiol-ene addition between n-propylthiol and propargyl acrylate. Experimentally, n-propylthiol (1.83 g, 24 mmol) and propargyl acrylate (2.20 g, 20 mmol) was dissolved in ethyl acetate (8 mL) in a 50 mL flask. This solution was purged with N₂ for 15 min to eliminate oxygen, and then was added dropwise with Et₃N (4.05 g, 40 mmol) under vigorous stirring. After the reaction system was kept at 30 °C for 5 h, volatiles such as ethyl acetate, Et₃N and excess n-propylthiol were removed under reduced pressure, affording the compound Ter (3.58 g, 19.2 mmol) with a yield of 96.1%. ¹H NMR (300 MHz, CDCl₃): 4.70 (d, 2H, CH≡CC₂H₂O), 2.84-2.58 (m, 4H, OCC₂H₂C₂H₂S), 2.51 (t, 2H, CH₃CH₂C₂H₂S), 2.50 (t, 1H, C₃H≡CCH₂O), 1.60 (m, 2H, CH₃C₂H₂CH₂S), 0.98 (t, 3H, C₃H₃CH₂CH₂S).

Compound Den was formed by bisaddition of Ter with n-propylthiol via thiol-yne reaction. Experimentally, Ter (1.0 g, 5.4 mmol), n-propylthiol (1.07 g, 14.04 mmol), 2,2-dimethoxy-2-phenyl-acetophenone (51 mg, 0.2 mmol), and toluene (3 mL) were mixed in a 25 mL flask. After purged with N₂ for 15 min, the flask was irradiated under a UV lamp (λ = 365 nm) for 10 h. The resulting product Den (1.80 g, 5.3 mmol) was obtained via vacuo evaporation of all the volatiles with the yield of 98.7%. ¹H NMR (300 MHz, CDCl₃): 4.4-4.2 (m, 2H, C₃H₂OOC), 3.0 (m, 1H, C₃H), 2.8-2.4 (12H, CH₃CH₂C₂H₂SC₂H₂COOCH₂CH(SCH₂CH₂CH₃)CH₂SCH₂CH₂CH₃), 1.6 (m, 6H, CH₃CH₂CH₂S), 0.98 (m, 9H, CH₃CH₂CH₂S).

Two mixtures comprised of Ter, Den and Lin units, Mix₁ and Mix₂ were prepared to mimic the unit structure of HP by inadequate additions of 1.8 and 0.5 equivalent of n-propylthiol to Ter, respectively. Ter (1.0 g, 5.4 mmol), n-propylthiol (0.76 g, 9.72 mmol or 0.21 g, 2.7 mmol), 2,2-dimethoxy-2-phenyl-acetophenone (51 mg, 0.2 mmol), and toluene (3 mL) were charged to a 25 mL flask. The flask was then purged with N₂ and irradiated with UV light for 8 h. Toluene was evaporated and the residual was directly analyzed with ¹H NMR spectrum. ¹H NMR (300MHz, CDCl₃): 6.3 and 5.6 (m, OCH₂C=CH moiety of Lin), 4.7 (d, C₃H₂OOC moiety of Ter), 4.58 (OCH₂CH=CH moiety of Lin), 4.4-4.2 (m, C₃H₂OOC moiety of Den), 3.0 (m, C₃H moiety of Den).

Synthesis of HP from 3,6-Dioxaoctane-1,8-dithiol

The whole preparation procedure can be completed within 12 h.

In a 50 mL flask, 3,6-dioxaoctane-1,8-dithiol (1.82 g, 10 mmol) and Et₃N (1.01 g, 10 mmol) was dissolved in THF (4 mL). The solution was purged with N₂ for 10 min to eliminate oxygen and then added dropwise with a THF (2 mL) solution of propargyl methacrylate (1.24 g, 10 mmol) in 30 min with vigorous stirring. The reaction system was kept in a water bath at 35 °C and monitored with ¹H NMR spectroscopy. After 8 h, the proton signals of the CH=CH moiety of methacrylate totally disappeared indicating the reaction completion. Rotary evaporation and vacuum evaporation of THF and Et₃N afforded the precursor (3.05 g) comprised of equal amounts of thiol and propargyl groups. ¹H NMR (300MHz, CDCl₃): 4.70 (d, 2H, CH≡CCH₂O), 3.73-
3.53 (m, 4H, HSCH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$S), 2.94-2.57 (m, 7H, HSCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$CH$_2$S), 2.49 (t, 1H, CH≡C), 1.60 (m, 4H, HSCH$_2$), 1.27 (d, 3H, SCH$_2$CH)}}

The precursor was diluted with toluene to 0.5 M and added with AIBN (82.1 mg, 0.5 mmol) to make a stock solution. After purged with N$_2$ for 10 min, the flasks heated at 65 °C for 3h. Then, the flasks were exposed to air, and the polymer solutions were analyzed by $^1$H NMR (Figure S4). The polymers collected by precipitation into methanol were characterized by GPC and have a $M_n$ of 6300 and $M_w$ of 19300.
**Fig. S1** $^{13}$C NMR spectra of precursor prepared from 1,6-hexanedithiol and propargyl acrylate via thiol-ene click reaction. (The difference between the three components in the precursor cannot be detected by the $^{13}$C NMR spectroscopy, so we only show the signal assignment of AB$_2$ monomer for concision.)
Fig. S2 Mass spectrum of the three components, dithiols, AB$_2$ monomer and diynes, in the AB$_2$-type intermediate prepared from 1,6-hexanediol and propargyl acrylate via thiol-ene click reaction.
Fig. S3 $^{13}$C NMR spectra of precursor prepared from 1,6-hexanediithiol and propargyl acrylate via thiol-ene click reaction.
Fig. S4 $^1$H NMR spectra of precursor prepared from 3,6-dioxaoctane-1,8-dithiol via thiol-ene click reaction (b) and the corresponding hyperbranched polymer (a).