Supporting Information for

Sequential Click Synthesis of Hyperbranched Polymers via A$_2$ + CB$_2$ Approach

Jin Han, Bo Zhao, Yanqin Gao, Aijin Tang, and Chao Gao*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science

and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

E-mail: chaogao@zju.edu.cn (C.G.)

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 Et$_3$N 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 ^{1}H NMR measurements were carried out on a Varian Mercury Plus 300 MHz NMR spectrometer at 20 $^{\mathrm{o}}$C. The ^{13}C NMR measurements were performed on a Bruker DMX 500MHz NMR spectrometer at 20 $^{\mathrm{o}}$C. The samples were dissolved with CDCl$_3$ 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 CH$_3$OH 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, Mix$_1$ and Mix$_2$

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 N_2 for 15 min to eliminate oxygen, and then was added dropwise with Et$_3$N (4.05 g, 40 mmol) under vigorous stirring. After the reaction system was kept at 30 ^{o}C for 5 h, volatiles such as ethyl acetate, Et$_3$N 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%. ^{1}H NMR (300 MHz, CDCl$_3$): 4.70 (d, 2H, CH≡CCH_2O), 2.84-2.58 (m, 4H, OCCH_2CH_2S), 2.51 (t, 2H, CH$_3$CH$_2$CH_2S), 2.50 (t, 1H, CH≡CCH$_2$O), 1.60 (m, 2H, CH$_3$CH_2CH$_2$S), 0.98 (t, 3H, CH_3CH$_2$CH$_2$S).

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 N_2 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%. ^{1}H NMR (300 MHz, CDCl$_3$): 4.4-4.2 (m, 2H, CH_2OOC), 3.0 (m, 1H, CH), 2.8-2.4 (12H, CH$_3$CH$_2$CH_2SCH_2CH_2COOCH$_2$CH(SCH_2CH$_2$CH$_3$)CH_2SCH_2 CH$_2$CH$_3$), 1.6 (m, 6H, CH$_3$CH_2CH$_2$S), 0.98 (m, 9H, CH_3CH$_2$CH$_2$S).

Two mixtures comprised of **Ter**, **Den** and **Lin** units, **Mix$_1$ and Mix$_2$** 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 N_2 and irradiated with UV light for 8 h. Toluene was evaporated and the residual was directly analyzed with ^{1}H NMR spectrum. ^{1}H NMR (300MHz, CDCl$_3$): 6.3 and 5.6 (m, OCH$_2$CH=CH moiety of **Lin**), 4.7 (d, CH_2OOC moiety of **Ter**), 4.58 (OCH_2CH=CH moiety of **Lin**), 4.4-4.2 (m, CH_2OOC moiety of **Den**), 3.0 (m, CH 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 Et$_3$N (1.01 g, 10 mmol) was dissolved in THF (4 mL). The solution was purged with N_2 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 ^{o}C and monitored with ^{1}H NMR spectroscopy. After 8 h, the proton signals of the CH$_2$=C moiety of methacrylate totally disappeared indicating the reaction completion. Rotary evaporation and vacuum evaporation of THF and Et$_3$N afforded the precursor (3.05 g) comprised of equal amounts of thiol and propargyl groups. ^{1}H NMR (300MHz, CDCl$_3$): 4.70 (d, 2H, CH≡CCH_2O), 3.73-

3.53 (m, 4H, HSCH$_2$C**H**$_2$OC**H**$_2$C**H**$_2$OC**H**$_2$CH$_2$S), 2.94-2.57 (m, 7H, HSC**H**$_2$CH$_2$OCH$_2$CH$_2$O CH$_2$C**H**$_2$SC**H**$_2$C**H**), 2.49 (t, 1H, C**H**≡C), 1.60 (m, 4H, **H**SCH$_2$), 1.27 (d, 3H, SCH$_2$CHC**H**$_3$COO).

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 ^{o}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.
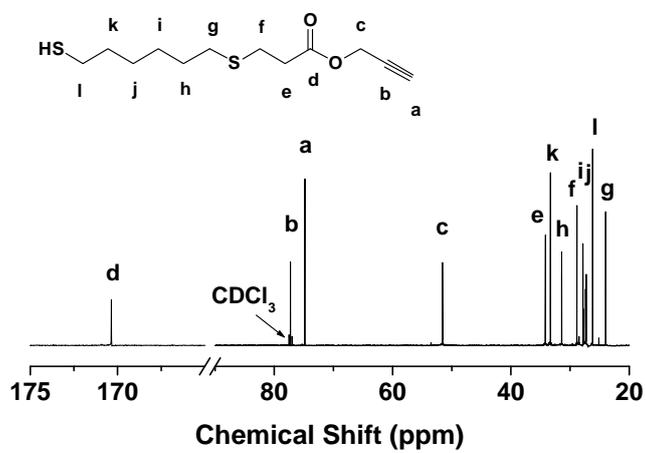
Fig. S1 ^{13}C NMR spectra of precursor prepared from 1,6-hexanedithiol and propargyl acrylate via thiol-ene click reaction. (The difference between the three components in the precursor cannot be detected by the ^{13}C NMR spectroscopy, so we only show the signal assignment of AB_2 monomer for concision.)
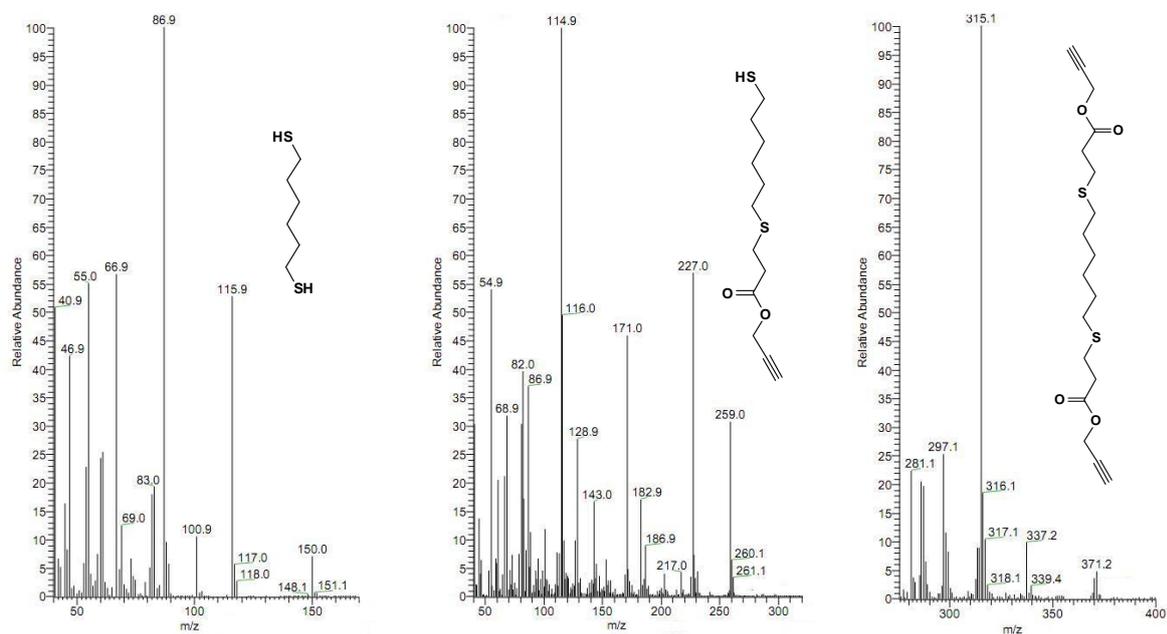
Fig. S2 Mass spectrum of the three components, dithiols, AB_2 monomer and di-ynes, in the AB_2-type intermediate prepared from 1,6-hexanedithiol and propargyl acrylate via thiol-ene click reaction.
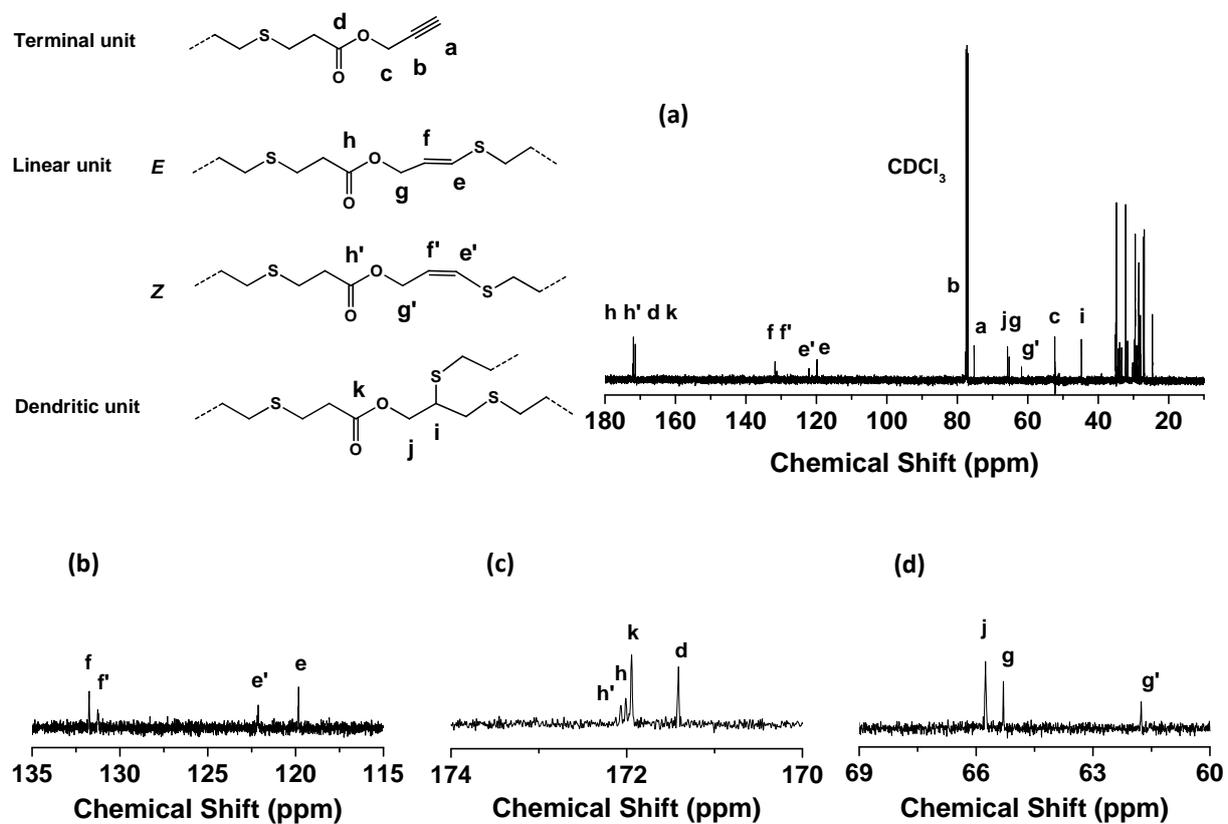
Fig. S3 ^{13}C NMR spectra of precursor prepared from 1,6-hexanedithiol and propargyl acrylate via thiol-ene click reaction.
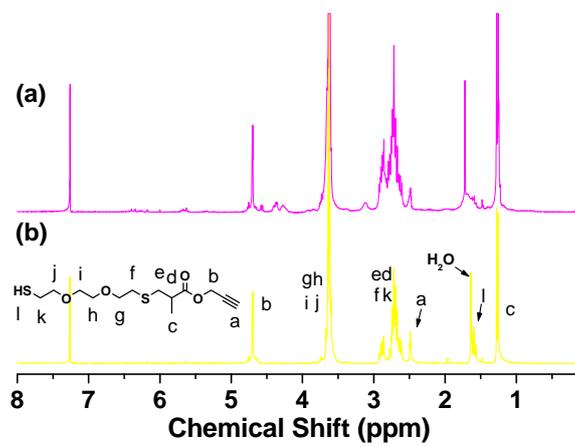
Fig. S4 ^{1}H NMR spectra of precursor prepared from 3,6-dioxaoctane-1,8-dithiol via thiol-ene click reaction (b) and the corresponding hyperbranched polymer (a).