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Supplementary Information

For

Thermally-labile segmented hyperbranched copolymers: Using reversible-covalent chemistry to investigate the mechanism of self-condensing vinyl copolymerization

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Materials

2-Bromo-2-methyl-propionic acid 2-(2,5-dioxo-2,5-dihydro-pyrrol-1-yl)-ethyl ester was synthesized in a manner derived from previous publications.^{1,2} Methyl methacrylate (MMA, 99%), methacryloyl chloride (97%), furfuryl alcohol (98%), diethyl ether (99.9%), methanol (99.8%), triethylamine (99.5%) and ethanolamine (99.5%) were purchased from VWR. 9-Anthracenemethanol (97%), benzene (98%), furan (>99%), poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 500$ g/mol, 99%), copper(I) bromide (99%), 2,2'-bipyridine (bpy, 99%), 2-bromoisobutyryl bromide (98%), 1-thioglycerol (98%), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 97%), 1,4-dioxane and maleic anhydride (99%) were purchased from Sigma-Aldrich and used as received. Toluene (99.8%, Sigma) was dried over molecular sieves. Tetrahydrofuran (THF, 99.8%, Sigma) was dried over calcium hydride and freshly distilled under reduced pressure. Monomers were passed through basic alumina columns to remove inhibitors and acidic impurities prior to polymerization. All other materials were used as received unless otherwise noted.

Experimental

Synthesis of 2-bromo-2-methyl-propionic acid 2-(1-hydroxymethyl-3, 5-dioxo-10-oxa-4-azatricyclo [5.2.1.02, 6] dec-8-en-4-yl)-ethyl ester. Maleimide initiator 2-bromo-2-methyl-propionic acid 2-(2,5-dioxo-2,5-dihydro-pyrrol-1-yl)-ethyl ester (10.0 g, 34.5 mmol) was suspended in dry benzene (50 mL). Furfuryl alcohol (7.50 mL, 86.3 mmol) was slowly added over 10 min. Following the addition, the reaction mixture was stirred at 75 °C. The reaction was monitored by ¹H NMR spectroscopy and quenched when the reaction was completed. The solvent was removed by rotary evaporator, and the crude product was purified by flash chromatography on silica gel with ethyl acetate/hexane (8:2) to yield the desired product as a colorless viscous oil (yield: 92%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.50 (m, 2H), 5.20 (s, 1H), 4.29 (m, 2H), 4.03 (s, 2H), 3.78 (m, 2H), 2.94 (dd, 2H), 1.87 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 175.6, 175.5, 171.4, 138.3, 137.0, 91.5, 80.8, 62.1, 60.6, 55.7, 50.1, 48.1, 37.8, 30.6. ESI-HRMS: Calcd. for [M+H]⁺: 388.0390. Found: 388.0396.

Synthesis of Diels-Alder inimer 2-bromo-2-methyl-propionic acid 2-(1-methacryloxymethyl-3, 5-dioxo-10-oxa-4-azatricyclo [5.2.1.02, 6] dec-8-en-4-yl)-ethyl ester. Diels-Alder initiator 2-bromo-2-methyl-propionic acid 2-(1-hydroxymethyl-3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl)-ethyl ester (3.35 g, 8.63 mmol) and triethylamine (1.44 mL, 10.4 mmol) were mixed with anhydrous THF (50 mL). Methacryloyl chloride (1.02 mL, 10.4 mmol) was added dropwise to the solution at 0 °C *via* addition funnel, and the reaction mixture was left to stir overnight. The solution was filtered, and the filtrate was concentrated by rotary evaporator and purified by flash chromatography on silica gel with ethyl acetate/hexane (6:4) to yield the desired product as a colorless viscous oil (yield: 42%) ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.56 (d, 1H), 6.44(d, 1H), 6.13(s, 1H), 5.60(s, 1H), 5.27 (s, 1H), 4.96(d, 1H), 4.57(d, 1H), 4.31 (m, 2H), 3.75 (m, 2H), 2.98 (dd, 2H), 1.95(s, 3H), 1.90 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 175.3, 173.9, 171.4, 166.7, 137.4, 137.2, 135.7, 126.3, 89.7, 81.0, 62.1, 61.4, 55.7, 50.0, 48.4, 37.8, 30.6, 18.3. ESI-HRMS: Calcd. for [M+H]⁺: 456.0652. Found: 456.0657.

Synthesis of thermally-reversible hyperbranched PMMA. A series of polymerizations at varying initial feed ratios ([MMA]₀:[Inimer]₀) and ([MMA]₀+ [Inimer]₀):[Catalyst] were performed at 45 °C as denoted in Table 1. The initial monomer concentration and inimer mass were kept constant at 5 M and 0.1 g, respectively. In a typical polymerization procedure, inimer (0.10 g, 0.22 mmol), MMA (0.35 mL, 3.29 mmol), toluene (0.21 mL), and 2,2'-bipyridine (26.3 mg, 0.17 mmol) were charged to a 10 mL Schlenk flask equipped with magnetic stir bar. The reaction mixture was degassed by three freeze-pump-thaw cycles, and then copper (I) bromide (12 mg, 0.08 mmol) was quickly added to the mixture followed by two additional freeze-pump-thaw cycles. Subsequently, the Schlenk tube was placed in a preheated oil bath at 45 °C for 4 h, after which time the monomer conversion had reached 99%. The polymer was isolated by exposing the polymerization solution to air, passing it through a short neutral aluminum column to remove residual copper, and then precipitating in cold methanol. The precipitate (**SHB P1**, **Table 1**) was dried under vacuum at room temperature for 24 h.

Extension of PEGMA from hyperbranched PMMA. SHB P2 (Table S1) was used as macroinitiator for the polymerization of PEGMA at 45 °C ([PEGMA]₀:[macroinitiator]₀ feed ratio of 60:1). In a typical procedure, **SHB P2** (100 mg, 0.03 mmol Br), PEGMA (0.83 mL, 1.80 mmol), toluene (0.1 mL), and 2, 2'-bipyridine (14 mg, 0.09 mmol) were charged to a 10 mL Schlenk flask equipped with magnetic stir bar. The reaction mixture was degassed by three freeze-pump-thaw cycles, and then copper (I) bromide (6.5 mg, 0.045 mmol) was quickly added to the mixture followed by two additional freeze-pump-thaw cycles. Subsequently, the Schlenk tube was placed in a preheated oil bath at 45 °C for 7 h, after which time the monomer conversion had reached 34%. The polymer was isolated by exposing the polymerization solution to air, passing it through a short neutral aluminum column to remove residual copper, and then precipitating in a large amount of cold diethyl ether. The precipitate was dried under vacuum at room temperature for 24 h.

Thermal degradation of Diels-Alder hyperbranched PMMA. In a typical procedure, **SHB P1** (100 mg) was dissolved in dry toluene (10 mL), and the reaction mixture was subjected to an oil bath at predetermined temperatures of either 90 or 120 °C. Samples were taken periodically, quenched in liquid nitrogen, and immediately analyzed by ¹H NMR spectroscopy and GPC at predetermined time points. The retro-Diels-Alder reaction conversion was determined by comparing the peak areas of the signals at 5.2-5.3 ppm (furfuryl bridgehead) and 6.7 ppm (maleimide vinyl protons).

Thermal reconstruction of hyperbranched PMMA. In a typical procedure, **L P1** (Table 4, 100 mg) was mixed with dry toluene (0.1 mL) in a 1 mL vial. The vial with viscous mixture was placed in a 50 °C oil bath. Samples were taken, quenched in liquid nitrogen and analyzed by ¹H NMR spectroscopy and GPC at predetermined time points.

Radical thiol-ene click reaction between hyperbranched PMMA and 1-thioglycerol. A Schlenk flask equipped with magnetic stirrer was charged with **SHB P2** (100 mg, 0.03 mmol DA linkage), 1-thioglycerol (318 mg, 2.94 mmol), DMPA (37 mg, 0.15 mmol) and 1,4-dioxane (2 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles, filled with nitrogen and irradiated by a UV lamp at 365 nm at room temperature. After 100 min, the polymer solution was precipitated three times into cold methanol. The final precipitate was dried under vacuum at room temperature for 24 h.

Instrumentation

Nuclear Magnetic Resonance (NMR), ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-d₆ using an Inova 500 MHz spectrometer.

Gel Permeation Chromatography (GPC). Molecular weight and polydispersity were determined by gel permeation chromatography in dimethylacetamide (DMAc) with 50 mM LiCl at 50 °C and a flow rate of 1.0 mL min⁻¹ (Agilent isocratic pump, degasser, and autosampler, columns: PLgel 5 μm guard + two ViscoGel I-series G3078 mixed bed columns: molecular weight range 0–20 × 10³ and 0–100 × 10⁴ g mol⁻¹). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm and a Wyatt miniDAWN Treos light scattering detector operating at 659 nm. Relative molecular weights were obtained through calibration with poly(methyl methacrylate) (PMMA) standards of molecular weights ranging from 9.88 × 10⁵ to 602 g/mol. Absolute molecular weights and polydispersities were calculated using the Wyatt ASTRA software.

Transmission Electron Microscopy (TEM). Five microliters of the sample was applied onto a formvar coated 200-mesh Cu grid that was freshly glow discharged (Pelco easiGlow™, Ted Pella, Inc.). The grids were observed on a Hitachi H7000 microscope operating at 100 kV. The images were recorded with a slow-scan CCD camera (Veleta 2k × 2k).

Dynamic Light Scattering (DLS). Dynamic light scattering (DLS) analysis was conducted at room temperature on a Zetasizer Nano-ZS (Malvern) operating at a wavelength of 633 nm.

High-Resolution Mass Spectrometry (HRMS). HRMS was carried out using an Agilent 6220 TOF-MS mass spectrometer in the Direct Analysis in Real Time (DART) mode with the IonSense DART source unless otherwise specified.

1. NMR spectra of precursor of inimer

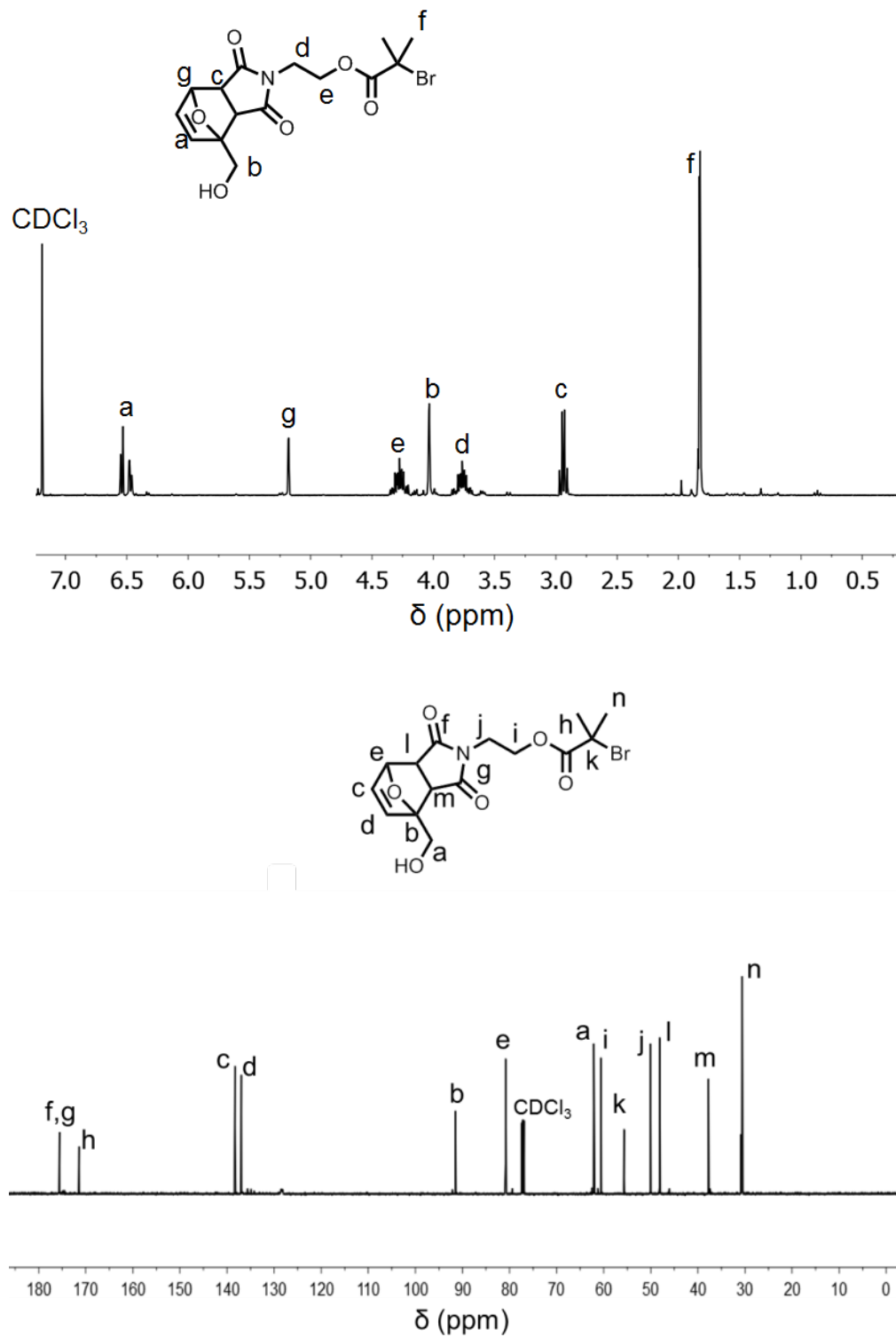


Figure S1. ¹H NMR and ¹³C NMR spectra of precursor to the Diels-Alder inimer

2. Synthesis and ^1H NMR spectra of “hyper-star”

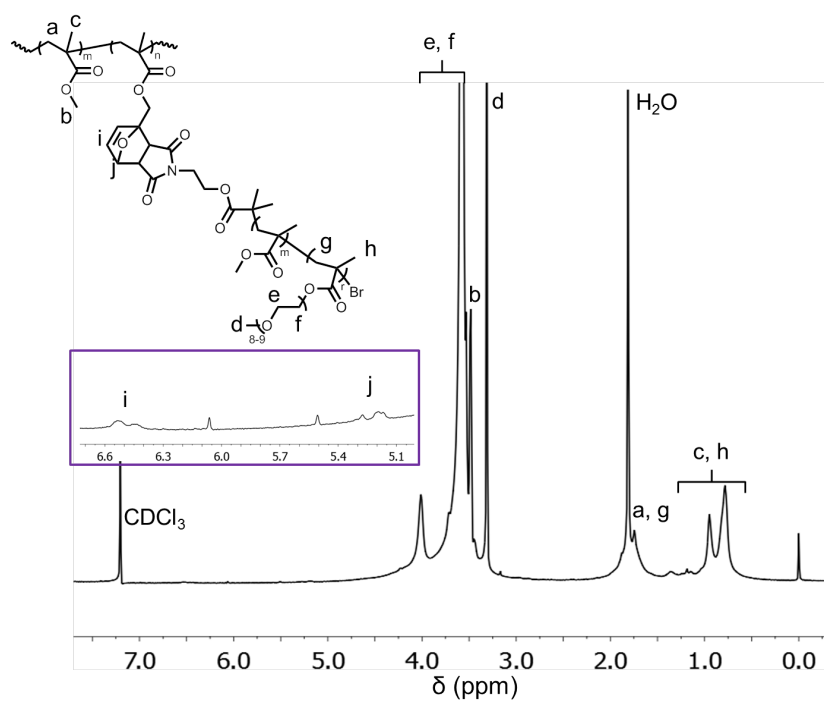
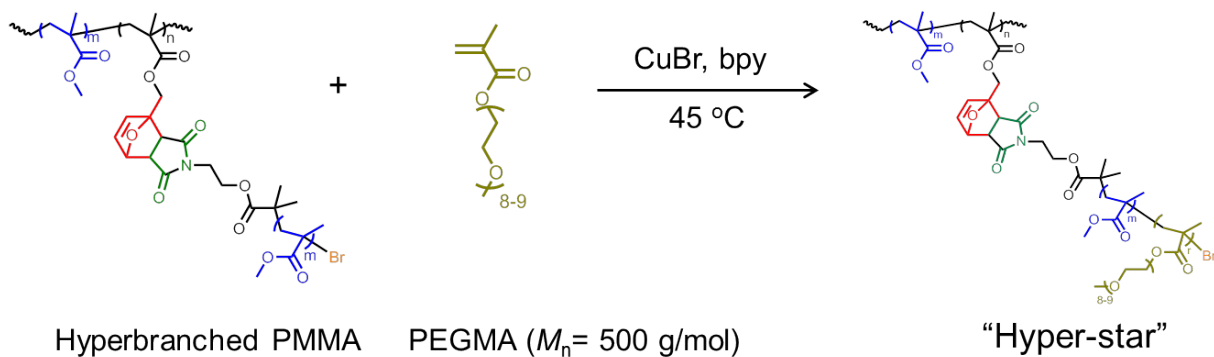


Figure S2. Synthesis and ^1H NMR spectrum of hyperbranched PMMA-*b*-PPEGMA (“hyper-star”)

3. Thermal cleavage of hyper-star

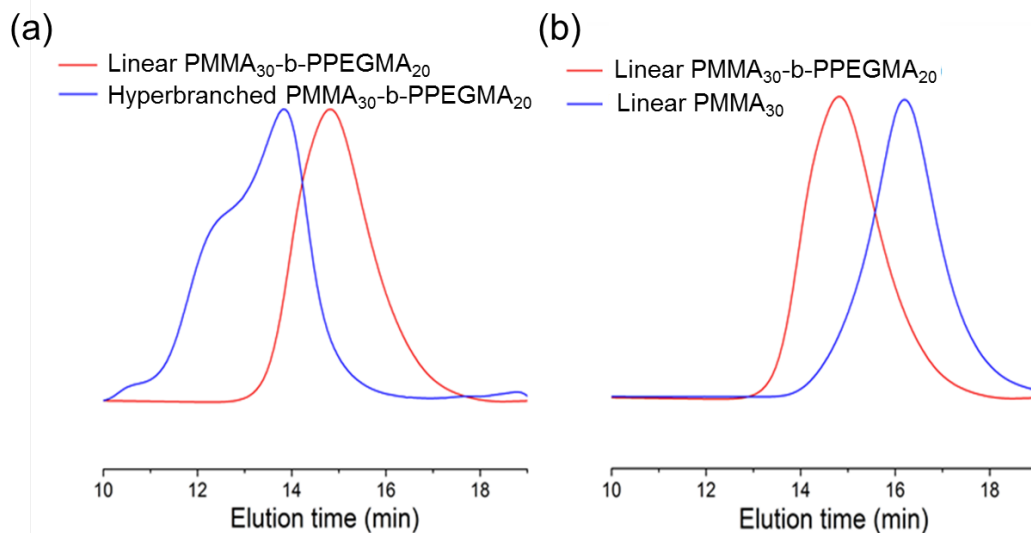


Figure S3. (a) GPC traces of hyperbranched PMMA - b - PPEGMA and thermally cleaved PMMA - b - PPEGMA ; (b) GPC traces of linear PMMA - b - PPEGMA and PMMA cleaved from segmented hyperbranched polymers.

4. Thermal cleavage of segmented hyperbranched polymer

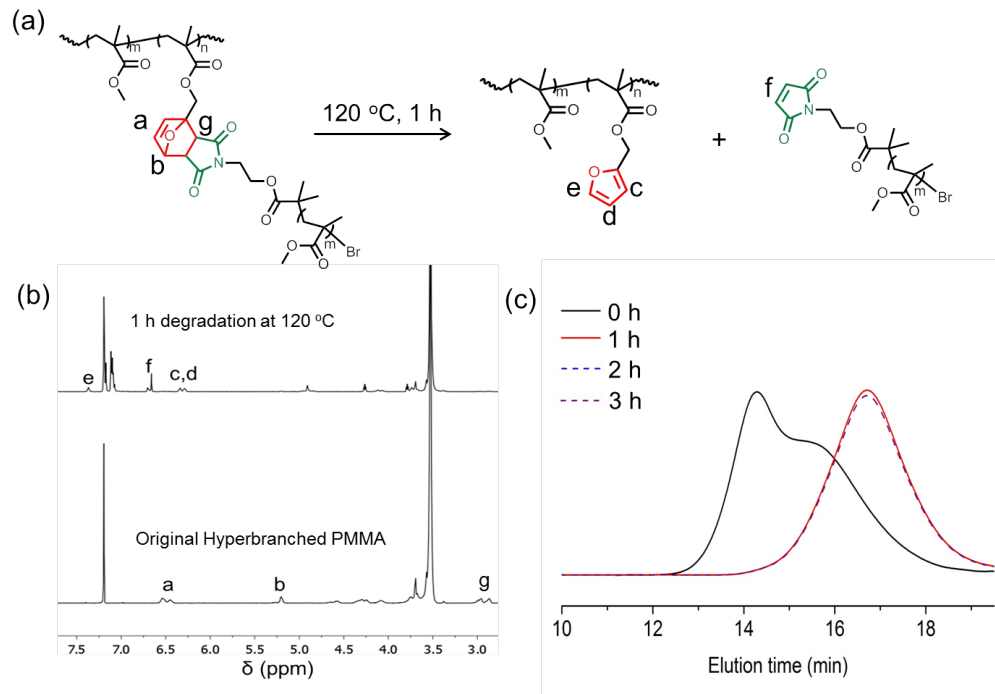


Figure S4. (a) Retro Diels-Alder reaction of **SHB P1**; (b) ^1H NMR spectrum before and after thermal treatment of **SHB P1**; (c) GPC traces before and after thermal treatment of **SHB P1**

Table S1. Molecular weight characteristics of segmented hyperbranched polymers and their degradation products (120 °C for 1 h)

Entry	Before thermo-degradation		After thermo-degradation		
	GPC		GPC-MALLS	GPC	
	M_n (g/mol)	M_w/M_n	M_w (g/mol)	M_n (g/mol)	M_w/M_n
SHB P1	11 000	3.62	120 000	3 500	1.65
SHB P2	17 000	4.95	260 000	5 600	1.78
SHB P3	36 300	5.37	515 000	8 700	1.73
SHB P4	8 800	2.33	23 400	3 300	1.54
SHB P5	10 700	1.83	33 100	4 950	1.47

5. Model reaction of segmented hyperbranched polymer with 9-anthracenemethanol

- SHB P4
- L P4 obtained by cleaving SHB P4 in the presence of 9-anthracenemethanol
- L P4 after thermal treatment at 50 °C for 48 h

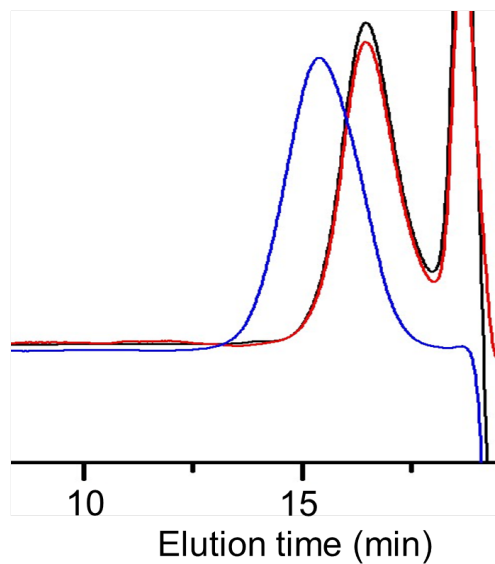


Figure S5. GPC traces of SHB P4, cleaved L P4 in the presence of 9-anthracenemethanol before and after thermal treatment at 50 °C for 48 h

6. Model reaction of segmented hyperbranched polymer with 1-thioglycerol

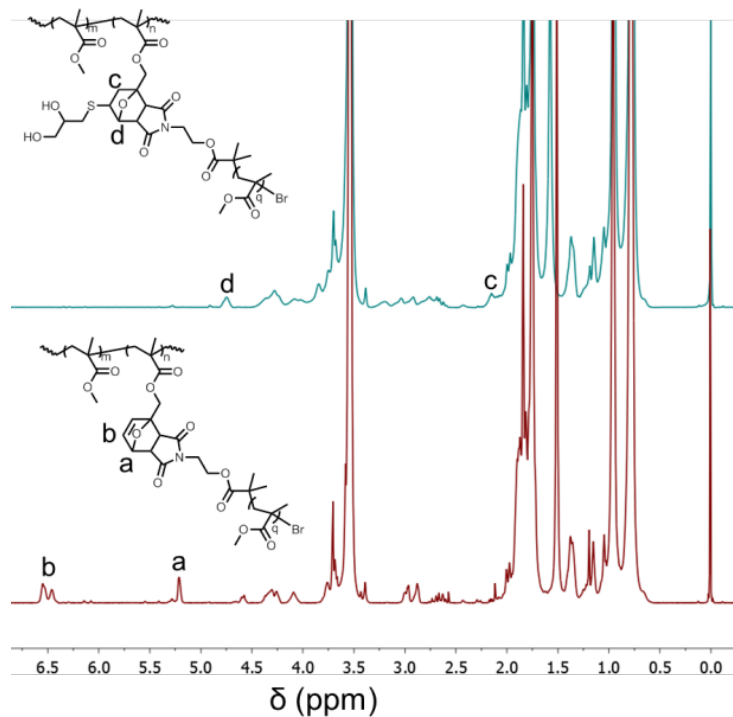


Figure S6. ¹H NMR spectrum of **SHB P2** before (bottom) and after (top) radical thiol-ene reaction with 1-thioglycerol.

References

1. J. A. Syrett, G. Mantovani, W. R. S. Barton, D. Price and D. M. Haddleton, *Polym. Chem.*, 2010, **1**, 102.
2. H. Mori, C. D. Seng, H. Lechner, M. Zhang and A. H. E. Müller, *Macromolecules*, 2002, **35**, 9270.