“AB_2 + AC_2” approach to hyperbranched polymers with a high degree of branching

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Experimental

Materials. 1,3,5-Tribromobenzene, n-butyllithium, 9-BBN, 4-bromoiodobenzene, pinacol, iodo chloride, and triisopropyl borate were purchased from Acros company and used without further purification. All solvents were purified or dried by standard methods. The catalyst precursor $Pd(PPh_3)_4$ and 4-[3-(3,5-dibromophenyl)propyl]-phenyltrimethylsilane was prepared by using the literature procedures. [12] ^{1}H and ^{13}C NMR spectra were recorded at 270 and 68 MHz in $CDCl_3$, respectively.

2-{4-[3-(3,5-Dibromophenyl)propyl]phenyl}-4,4,5,5-tetramethyl-[1,3,2]-dioxaborane (1) To a de-aired solution of **3** (8.36 g, 19.6 mmol) in CH_2Cl_2 (50 mL) was added dropwise BBr_3 (6.52 g, 26.0 mmol) at –78 oC over 10 min. The reaction was allowed to warm to room temperature and stirred for two days. Water was added, the organic layer separated, the water layer extracted with CH_2Cl_2 for 2 times, the combined organic phase dried over anhydrous Na_2SO_4, and evaporated to dryness. Chromatography on silica gel column eluting with CH_2Cl_2 increasing to CH_2Cl_2/ethyl acetate (5:1) gave the corresponding boronic acid (5.8 g, 74%) as a white solid. ^{1}H NMR δ 8.15 (AB system, 2H), 7.48 (s, 1H), 7.27 (AB system, 2H), 7.26 (s, 2H), 2.71 (t, 2H), 2.60 (t, 2H), 1.96 (p, 2H).

A mixture of boronic acid (5.80 g, 14.6 mmol) and pinacol (1.72 g, 14.6 mmol) in CH_2Cl_2 (200 mL) was refluxed for 6 h. Removal of solvents and chromatography on silica gel eluting with hexane/ethyl acetate (5:1) afforded **1** as a colourless solid (6.17 g, 88%). ^{1}H NMR δ 7.73 (AB system, 2H), 7.47 (s, 1H), 7.22 (s, 2H), 8.17 (AB system, 2H), 2.63 (t, 2H), 2.54 (t, 2H), 1.90 (p, 2H), 1.35 (s, 12H). ^{13}C NMR δ 146.15, 144.93, 134.96, 131.47, 130.30, 127.87, 122.74, 83.67, 35.37, 34.67, 32.25, 24.85.

1-Allyl-3,5-bis(trimethylsilyl)benzene (5) A mixture of **4** (18.60 g, 61.7 mmol), Mg powder (2.00 g, 83.3 mmol), I_2 (10 mg) in THF (200 mL) was refluxed for 6 h. This resulting Grignard reagent was cooled to 0 oC and $PdCl_2$ (30 mg) added. To this mixture was then added allyl bromide (12.1 g, 100 mmol). The reaction was allowed to warm to room temperature and kept stirring for 5 h. After that time, water and ether were added, the mixture was portioned into two phases and the organic phase separated. Tthe aqueous phase was extracted with ether and the combined organic phases were dried over Na_2SO_4. Removal of the solvent and vacuum distillation afforded **5** as a colourless oil (14.9 g, 92 %). ^{1}H NMR δ 7.50 (s, 1H), 7.30 (s, 2H), 6.05-5.90 (m, 1H), 5.05 (t, 2H), 3.38 (d, 2H), 0.25 (s, 18H). ^{13}C NMR δ 139.59, 137.59, 135.95, 134.13, 115.71, 40.48, -1.06.

9-{3-[3,5-Bis(trimethylsilyl)phenyl]propyl}-9-borabicyclo[3.3.1]nonane (6). To **5** (8.75 g, 33.32 mmol) was added a solution of 9-BBN in THF (0.5 M, 73.3 mL, 36.7 mmol) at room temperature under N_2 over 0.5 h. The reaction was kept stirring for 2 d and monitored with NMR until all ethylene groups were consumed. The formed borane adduct was used without further purification.

1-[3-(4-Bromophenyl)propyl]-3,5-bis(trimethylsilyl)benzene (7). To a solution of **7** in THF were added an aqueous NaOH solution (6 g in 80 mL water), toluene (100 mL), 4-bromoiodobenzene (11.3 g, 40 mmol), and $Pd(PPh_3)_4$ (1.14 g, 0.98 mmol). The mixture was carefully degassed, recharged with N_2, and stirred at room temperature for 3 d. Water and ether were added and the mixture was adjusted to pH = 2 with HCl. Then the organic layer was separated, the aqueous one extracted with ether, and the combined organic layers were dried over $MgSO_4$. After removal of solvents, the residue was chromatographically separated on silica gel column eluting with hexane to afford **7** as a colourless oil (12.0g, 86%).

2-{4-{3-[3,5-Bis(trimethylsilyl)phenyl]propyl}phenyl}-4,4,5,5-tetramethyl-[1,3,2]-dioxaborane (8). A solution of **7** (7.00 g, 16.68 mmol) in ether (300 mL) was cooled to –78 oC under N_2 and a solution of *n*-BuLi in hexane (1.6 M, 12.52 mL) added dropwise over 5 min. The reaction was kept stirring for 1 h at -78 oC, then allowed to warm to room temperature and stirred for further 0.5 h, before it cooled to -78 oC again, and triisopropyl borate (4.0 g, 21.0 mmol) added dropwise. The mixture was allowed to warm gradually to room temperature and stirred over night. Water was added and the organic layer separated. The aqueous layer was extracted with ether and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. Chromatography on silica gel eluting with CH_2Cl_2 increasing to CH_2Cl_2/ethyl acetate

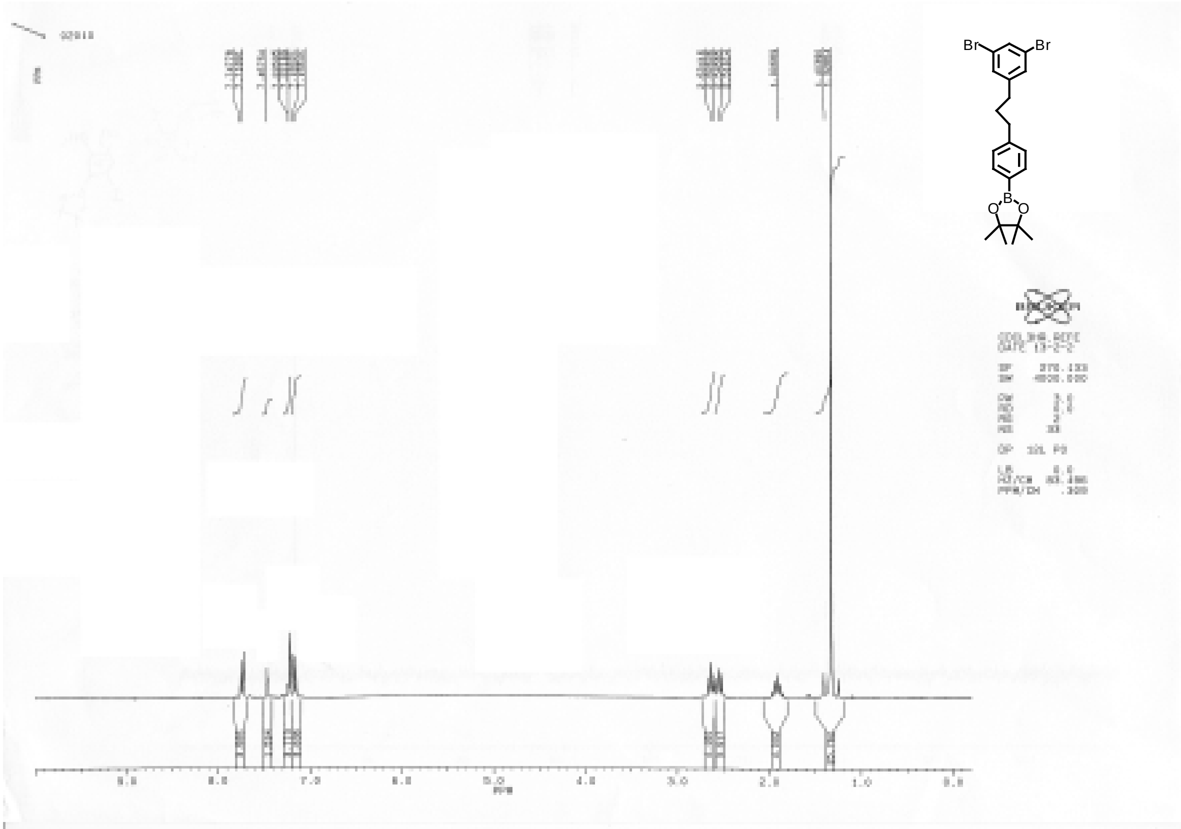
(2:1) afforded the corresponding boronic as a white solid (5.36 g, 83%). ^{1}H NMR δ 8.16 (AB system, 2H), 7.49 (s, 1H), 7.35 (two sets of signals incorporated together, 4H), 2.76 (t, 2H), 2.68 (t, 2H), 2.04 (p, 2H), 0.28 (s, 18H). ^{13}C NMR δ 147.32, 140.30, 139.43, 135.78, 135.70, 134.04, 128.22, 35.97, 35.71, 32.85, -1.03.

A mixture of this boronic acid (5.80 g, 14.58 mmol), pinacol (1.72 g, 14.6 mmol) in dry CH_2Cl_2 was refluxed for 2 h. Removal of solvent and flash chromatography of the residue on a short pad of silica gel eluting with hexane/ethyl acetate (5:1) afforded **8** as a white solid (6.17 g, 91%). ^{1}H NMR δ 7.74 (AB system, 2H), 7.48 (s, 1H), 7.32 (s, 2H), 7.21 (AB system, 2H), 2.69 (t, 2H), 2.64 (t, 2H), 1.97 (p, 2H), 1.34 (S, 12H), 0.26 (s, 18H). ^{13}C NMR δ 145.76, 140.35, 139.38, 135.64, 134.87, 134.04, 127.98, 83.63, 35.77, 35.62, 24.86, -1.04.

2-{4-[3-(3,5-Diiodophenyl)propyl]phenyl}-4,4,5,5-tetramethyl[1,3,2]dioxaborane (2). To a solution of **8** (1.58 g, 3.4 mmol) in CH_2Cl_2 was added dropwise a solution of ICl in CH_2Cl_2 (1.0 M, 13.0 mL) at 0 oC. The reaction was stirred for 1.5 h at 0 oC, and aqueous NaOH solution added. The organic layer separated and dried over $MgSO_4$. Removal of solvent and chromatography on a short pad of silica gel eluting with hexane/ethyl acetate (5:1) afforded **2** as a white solid (1.80 g, 92%). ^{1}H NMR δ 7.84 (s, 1H), 7.72 (AB system, 2H), 7.45 (s, 2H), 7.16 (AB system, 2H), 2.62 (t, 2H), 2.48 (t, 2H), 1.88 (p, 2H), 1.32 (s, 12H). ^{13}C NMR δ 146.46, 144.95, 142.49, 136.81, 134.96, 127.87, 94.76, 83.66, 35.38, 34.41, 32.28, 24.85.

Preparation of hyperbranched polymers (from 1). A mixture of **1** (751.4 mg, 1.57 mmol), $NaHCO_3$ (2.0 g), H_2O (20 mL), THF (30 mL), $Pd(PPh_3)_4$ (15.6 mg, 0.015 mmol) was carefully degassed, recharged with N_2, and refluxed for 3 d. CH_2Cl_2 was added, the organic layer separated, dried over $MgSO_4$, and evaporated to dryness. The residue was redissolved in the minimum volume of CH_2Cl_2 and precipitated into ether. The precipitate was collected, dissolved into benzene, and freeze-dried to afford the hyperbranched polymer as a white solid (295 mg, 69%). ^{1}H NMR δ 7.53-7.24 (broad, 7H), 2.67 (broad, 4H), 1.95 (broad, 2H). ^{13}C NMR δ 146.18, 144.76, 143.06, 141.56, 141.38, 141.05, 140.69, 138.96, 131.47, 130.29, 129.97, 128.82, 127.50, 127.20, 125.90, 123.47, 122.76, 35.63, 35.17, 34.99, 34.82, 34.71, 32.95, 32.67, 32.37.

Preparation of hyperbranched polymers with high DB (from 1+2). A mixture of **1** (341 mg, 0.71 mmol), **2** (389 mg, 0.68 mmol), $NaHCO_3$ (2.0 g), H_2O (20 mL), THF (30 mL), and $Pd(PPh_3)_4$ (15.8 mg, 0.016 mmol) was carefully degassed, and recharged with N_2. The mixture was stirred at 45 oC for 1 d and then heated to reflux for 2 d. CH_2Cl_2 was added, the organic layer separated, dried over $MgSO_4$, and evaporated to dryness. The residue was redissolved in the minimum volume of CH_2Cl_2 and precipitated into ether. The precipitate was collected, dissolved into benzene, and freeze-dried to afford the hyperbranched polymer as a white solid (306 mg, 81%). ^{1}H NMR δ 7.53-7.24 (broad, 7H), 2.67 (broad, 4H), 1.95 (broad, 2H). ^{13}C NMR δ 146.17, 143.09, 141.55, 141.35, 140.67, 139.03, 138.83, 131.44, 130.27, 129.38, 128.78, 127.22, 126.01, 123.44, 122.74, 35.62, 35.15, 34.81, 34.68, 32.93, 32.65, 32.34.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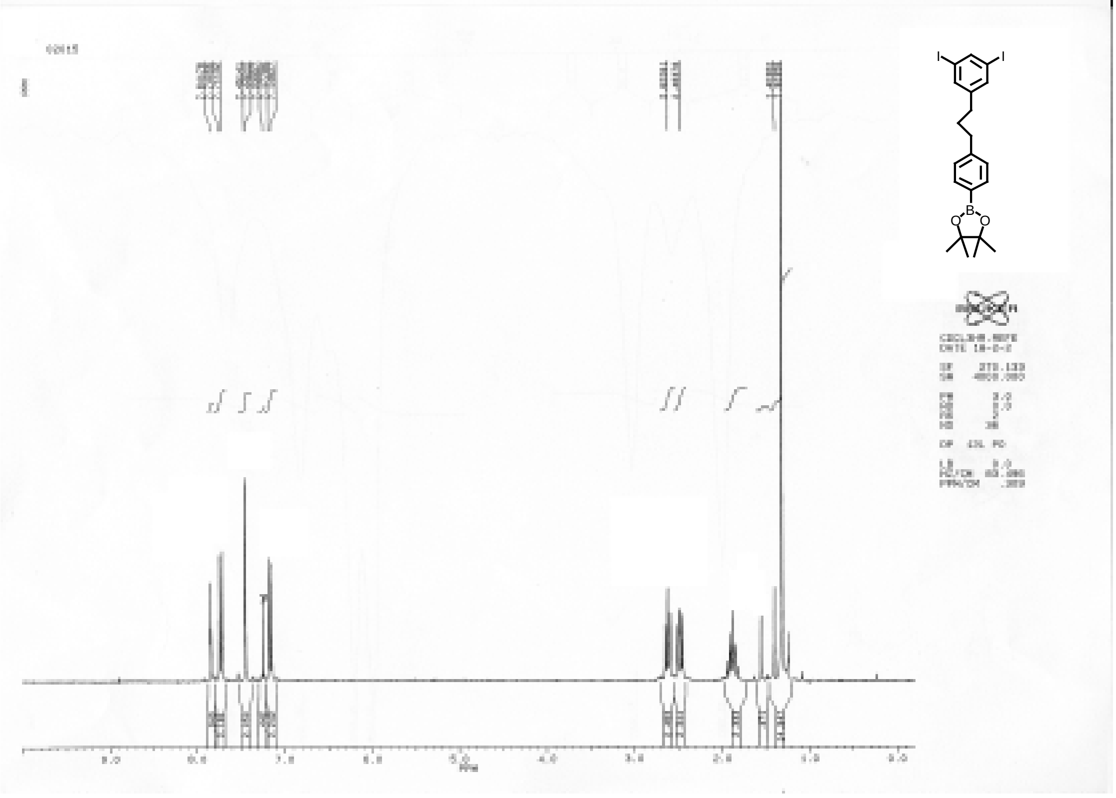
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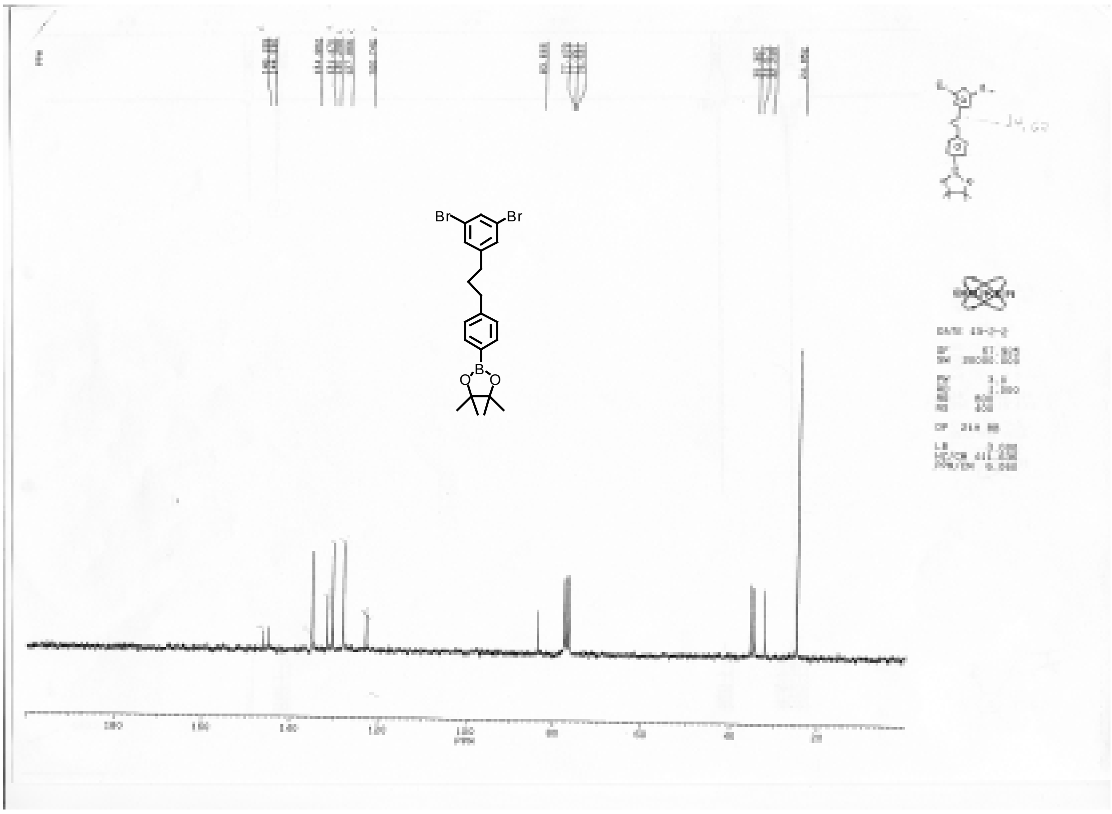

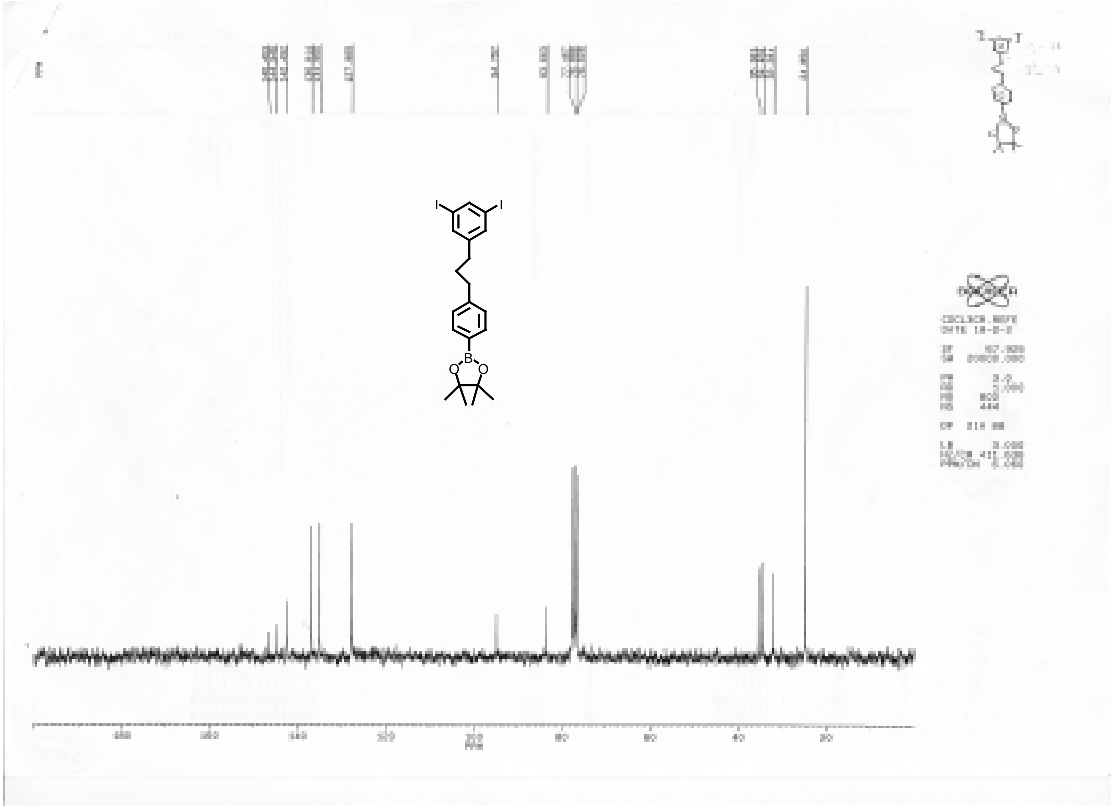

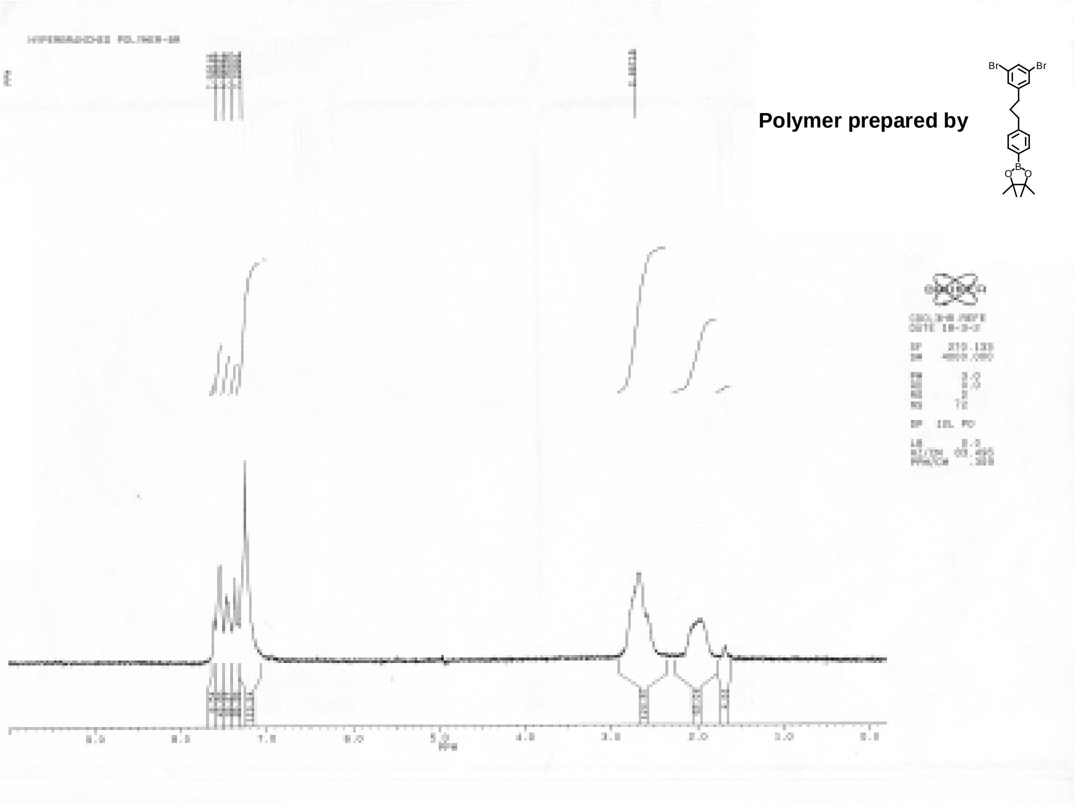

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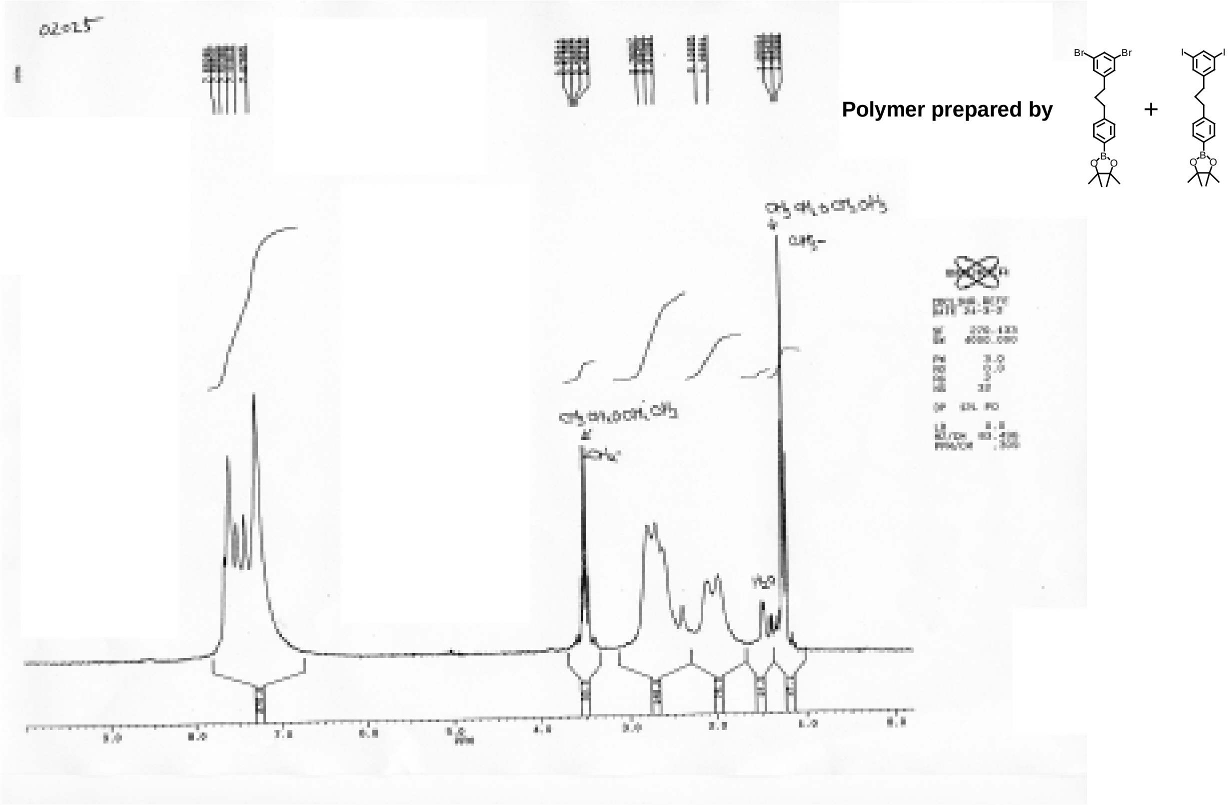

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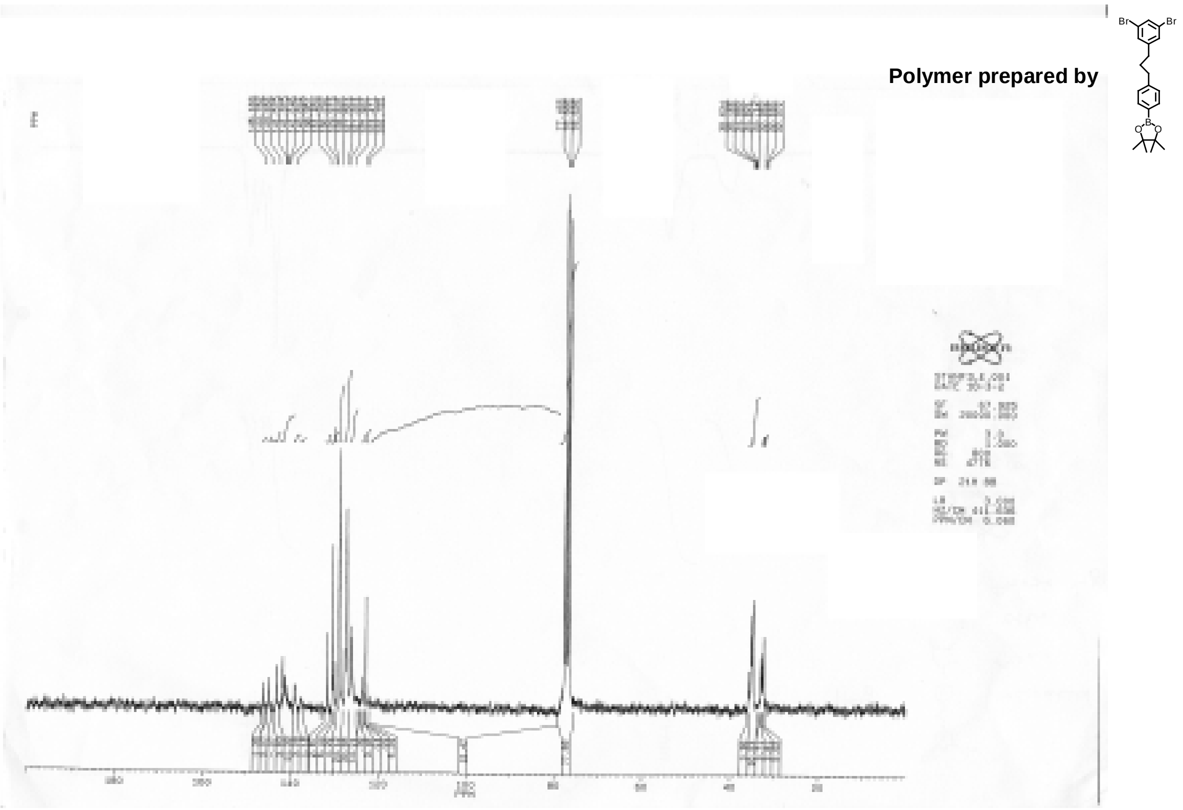
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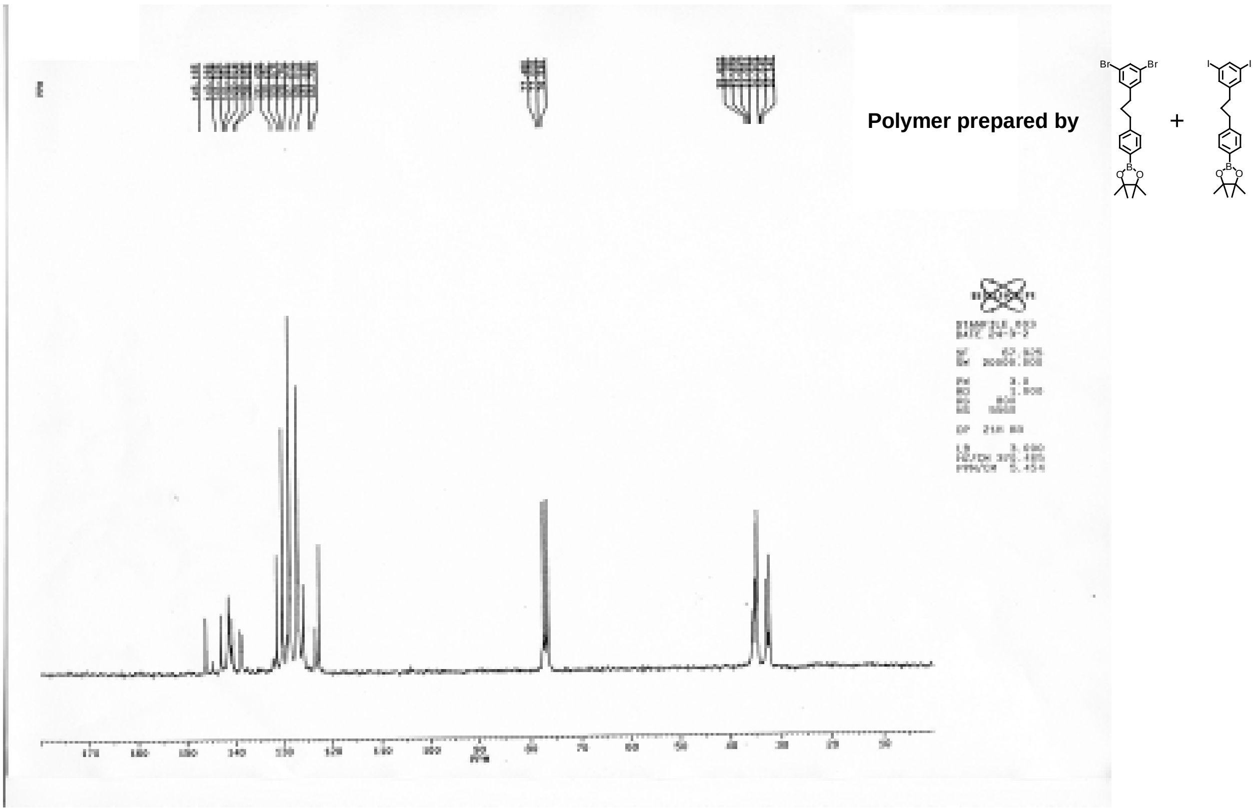
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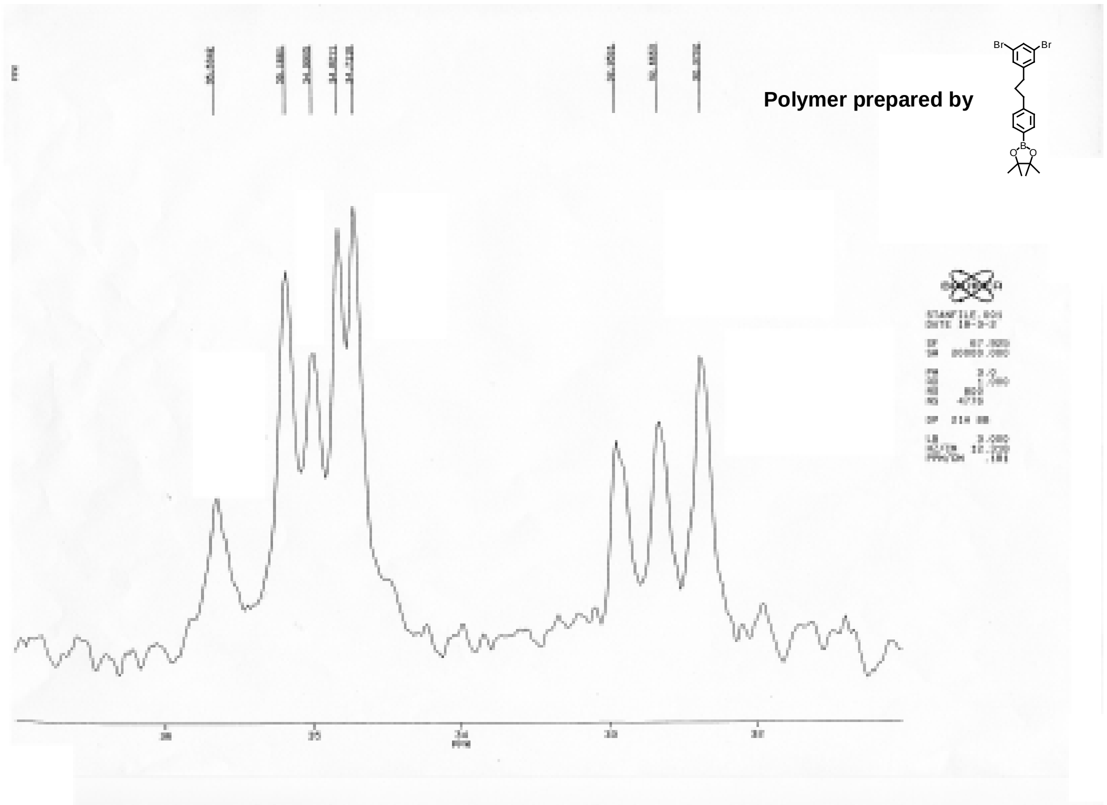
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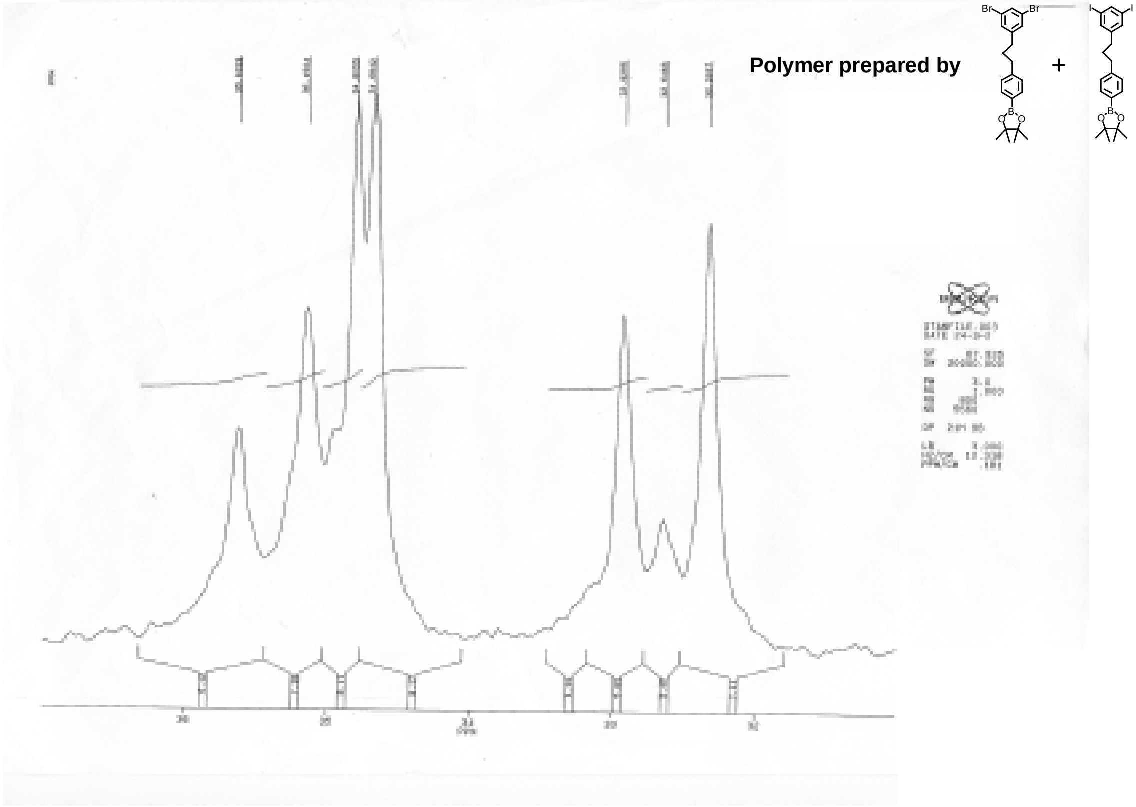
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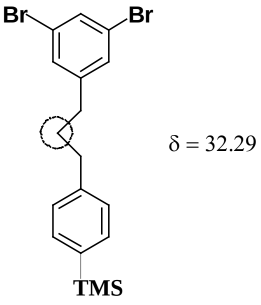
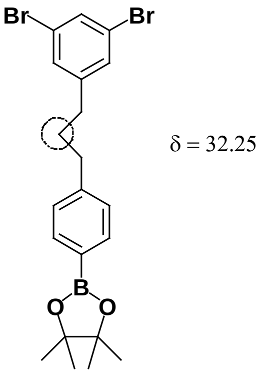
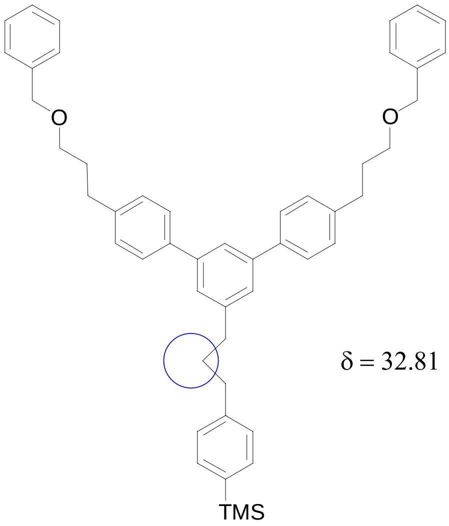
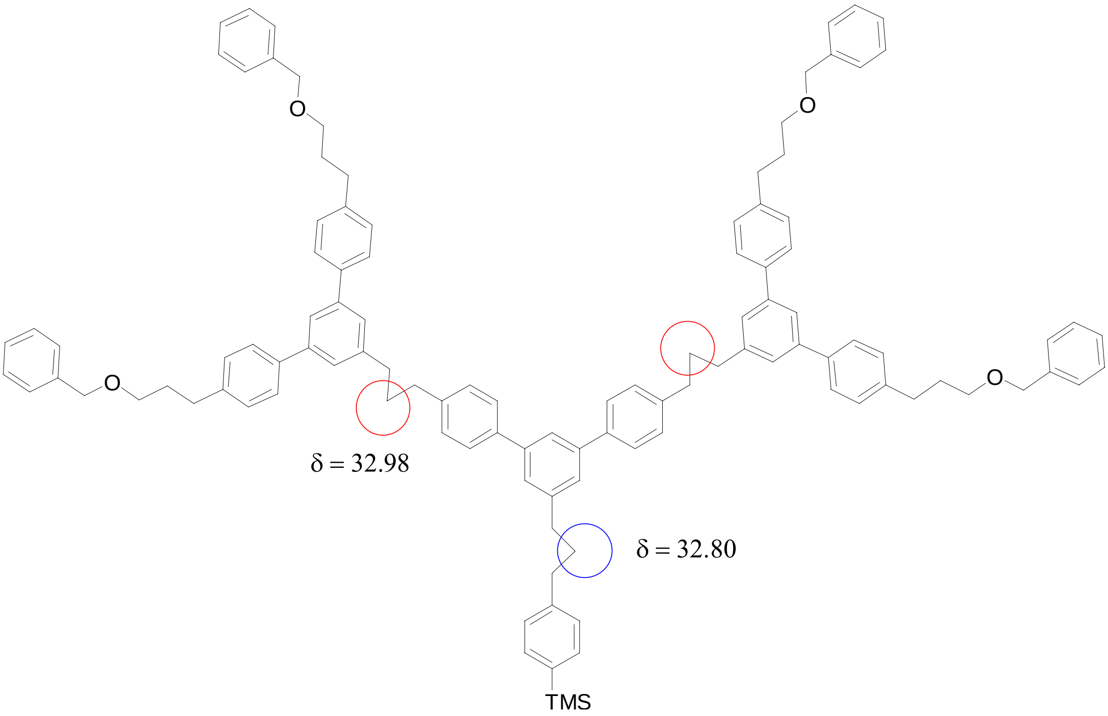
Model Compounds for determination of the chemical shifts (^{13}C NMR) of alkylene carbons are listed below (For the synthetic details and full characterization, see Z. S. Bo and A. D. Schlüter, *J. Org. Chem.* 2002, **67**, 53.):









GPC eluting curves of hyperbranched polymers prepared by **1** and **1**+**2**, respectively.