Electronic Supporting Information (ESI) for

Self-Repairing Polymers: Poly(dioxaborolane)s Containing Trigonal Planar Boron

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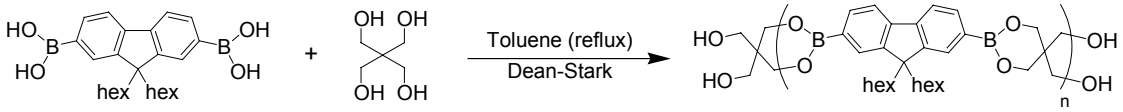


1

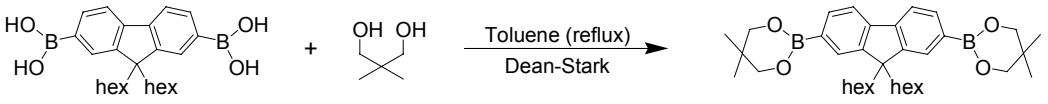
*(1) Synthesis of **1**:* To a mixture of 0.2212 g (0.5240 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid and 0.7150 g (5.252 mmol) of pentaerythritol in a flask fitted with a Dean-Stark trap, 60 ml of distilled toluene was added. Under an argon atmosphere, this resulting solution was refluxed for 1.25 hours to yield a cloudy solution which was then cooled to room temperature. A white solid was filtered off. The toluene was removed under reduced pressure to form a waxy solid film (0.2554 g, 85-95% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.90-7.58 (m, 6H, Ar H), 4.15 (s, 8H, O-CH_2-C), two terminal methylene groups as two shoulders at 4.06 and 3.99), 2.01 (br t, 4H, α-CH_2-), 1.19-0.93 (m, 12H, -CH_2-), 0.77 (t, 6H, -CH_3), 0.58 (br s, 4H, β-CH_2-); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.65, 144.05, 132.90, 130.43, 128.41, 119.56, 65.24, 55.16, 40.53, 36.92, 31.77, 29.97, 23.92, 22.86, 14.27; ^{11}B NMR in $CDCl_3$ (BF_3-OEt_2 = 0 ppm as external reference.): 20-23 ppm.

Table 1. Molecular weight determinations and distributions for a series of poly(dioxaborolane)s synthesized and/or processed under different conditions.

	diol equiv.[a]	reflux time[b]	vacuum processing time[c]	mol wt by ^{1}H NMR end-group analysis	M_w by GPC[e]	M_w/M_n
1	1	1.25 hr	0	28,300[c]	27,800	2.60
2	2	1.25 hr	0	11,400	13,500	3.81
3	10	1.25 hr	0	11,400	9,700	3.48
4	1	10 hr	0	46,100	45,000	5.38
5	10	10 hr	0	43,500	42,000	3.34
6	1	1.25 hr	7 days	76,900[d]	--[f]	--[f]
7	10	1.25 hr	3 days	15,000	15,900	3.79
8	10	1.25 hr	7 days	13,800	18,000	4.83

Notes: a) compared to 1 equiv. boronic acid, pentaerythritol is not fully soluble in toluene, therefore 10 equiv. is used to obtain a saturated solution. b) length of time sample was refluxed in toluene with azeotropic removal of water. c) length of time sample was stored under a vacuum of ~3 mm Hg beyond standard drying procedure. d) average molecular weight determined based on soluble portion, assuming all terminated with pentaerythritol. e) GPC measurements are referenced to polystyrene standards. f) data not available due to low solubility.

*(2) Synthesis of **2**:*



2

To a mixture of 0.3540 g (0.8385 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid and 0.1807 g (1.735 mmol) of neopentyl glycol in a flask fitted with a Dean-Stark trap, 80 ml of distilled toluene was added. Under an argon atmosphere, this resulting solution was refluxed for 30 hours to yield a clear solution which is then cooled to room temperature. Toluene was removed under reduced pressure to form a white crystalline solid which was Kugelrohred (120^{o}C, ~ 3 mm Hg) for 11 hours to remove the excess neopentyl glycol, yielding 0.4429 g of a white solid (95% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.82-7.66 (m, 6H, Ar H), 3.81 (s, 8H, O-CH_2-C), 2.04-

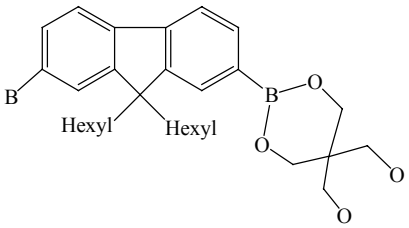
1.94 (m, 4H, α-CH_2-), 1.14-0.92 (m, 24H, β-CH_2- and -C-CH_3), 0.74 (t, 6H, -CH_3), 0.62-0.48 (m, 4H, -CH_2-); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.53, 143.80, 132.75, 131.40, 128.26, 119.35, 72.56, 55.13, 40.48, 32.12, 31.71, 29.94, 23.87, 22.82, 22.24, 14.23; ^{11}B NMR (160 MHz, $CDCl_3$, δ): 25 ppm. MS calcd for $C_{35}H_{52}B_2O_4$: 558.4064; found: *m/z* 558.4061.

(3) Gel Permeation Chromatography (GPC). The analyses were performed at room temperature with chloroform as eluent, at a flow rate of 1.0 mL/min, using two Polymer Laboratories technology columns PLgel 5μm MIXED-D connected in series (200-400,000 molecular weight). The detector used is a SPD-M10 A VP Shimadzu Diode Array Detector. Calibration was performed using polystyrene standards (Polymer Laboratories for molecular weights, MW, 299 400, 143 400, 66 350, 38 100, 19 880, 9920, 4920, 2360, 1260 and 580).

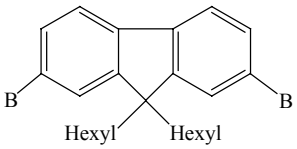
*(4) Terminal group analysis of polymer **1** by ^{1}H Nuclear Magnetic Resonance.* ^{1}H NMR experiments were carried out on a Varian Unity 500 MHz instrument at room temperature, with deuterated chloroform $CDCl_3$ as solvent. The internal standard was tetramethylsilane. In the proton NMR spectrum, the main-chain methylenes of this polymer appear at 4.15 ppm. The two terminal methylene groups appear as two shoulders at 4.06 ppm and 3.99 ppm (by 2D ghsqc, these three resonances couple to the ^{13}C resonances at 65 ppm indicating that they are the methylene protons). Deconvolution on these peaks was then carried out to get a more accurate integration. The number of repeat units of the polymers (n), is equal to the ratio of the integration of the methylene peak at 4.15 ppm to the integration of the shoulder peak at 3.99 ppm. The molecular weight of this polymer (MW) is obtained using the following equation:

$$MW = n(M_R) + 1(M_c) + 2(M_t) = n(486.26) + 354.14 + 268.26$$

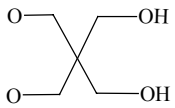
MW is the molecular weight of this polymer; M_R is the formula weight of the repeat unit; M_c is the formula weight of the central fluorene piece; and M_t is the formula weight of the terminal diol.



main-chain repeat unit



central fluorene-core piece



terminal diol

Figure SI1: The repeat unit, the center fluorene-core piece and the terminal diol used in this calcualtion.

Figure SI-1: 2-Dimensional HSQC NMR showing correlation between three proton resonances all relating to the same carbon resonance.

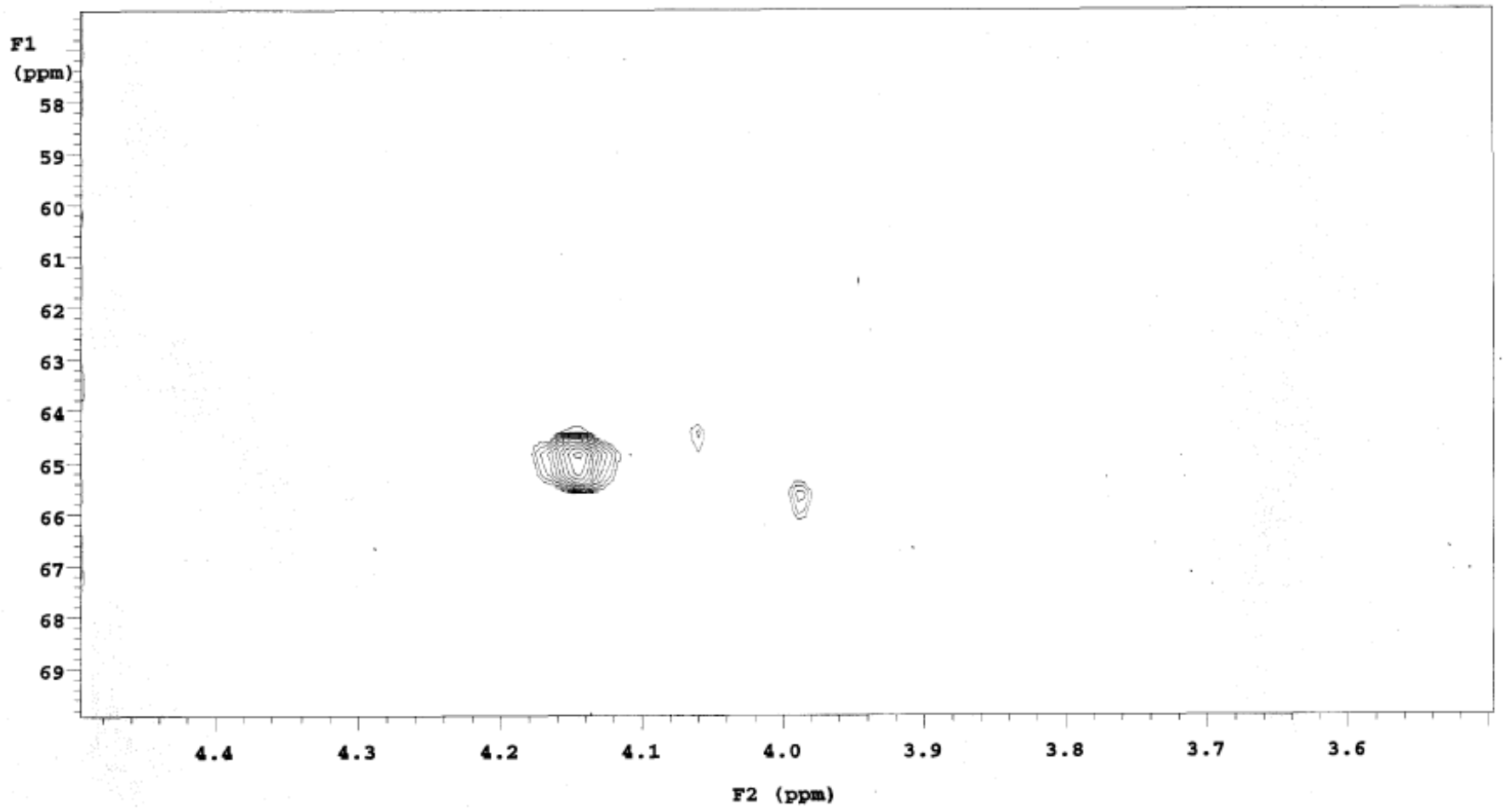


Figure SI-2: Deconvolution spectrum of the methylene region of the ^{1}H NMR of polymer **1**. In this particular spectrum the hydroxyl proton can also be seen as well as some unbound pentaerythritol.

LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	2073.77	83.13	8.21	0.000	1072.49
2	2043.02	2.16	9.22	0.000	31.30
3	2031.06	7.02	3.88	0.000	42.82 r
4	1995.92	7.13	3.83	0.000	42.89 y
5	1952.98	0.47	2.66	0.000	1.97
6	1914.67	1.52	9.76	0.000	23.36

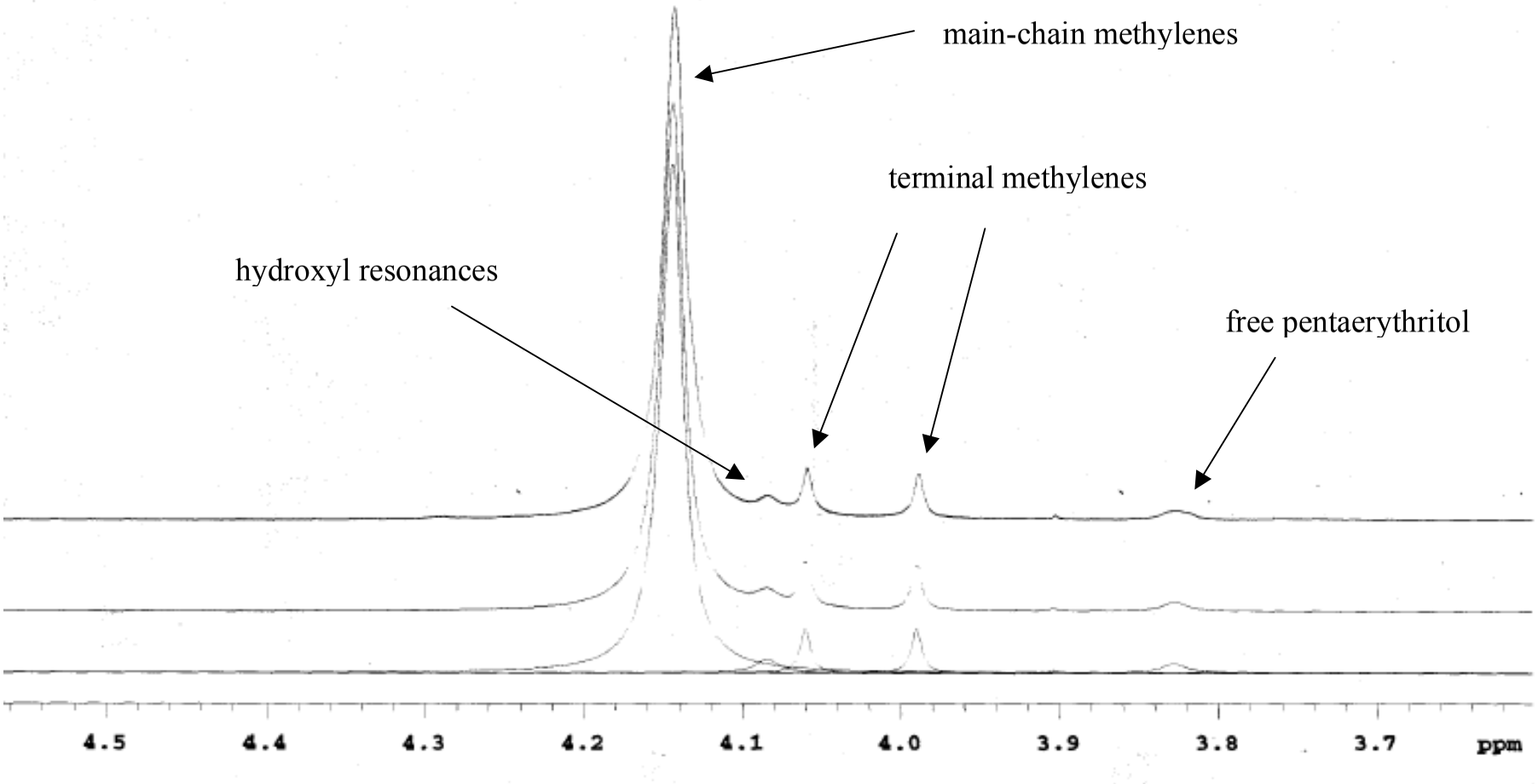
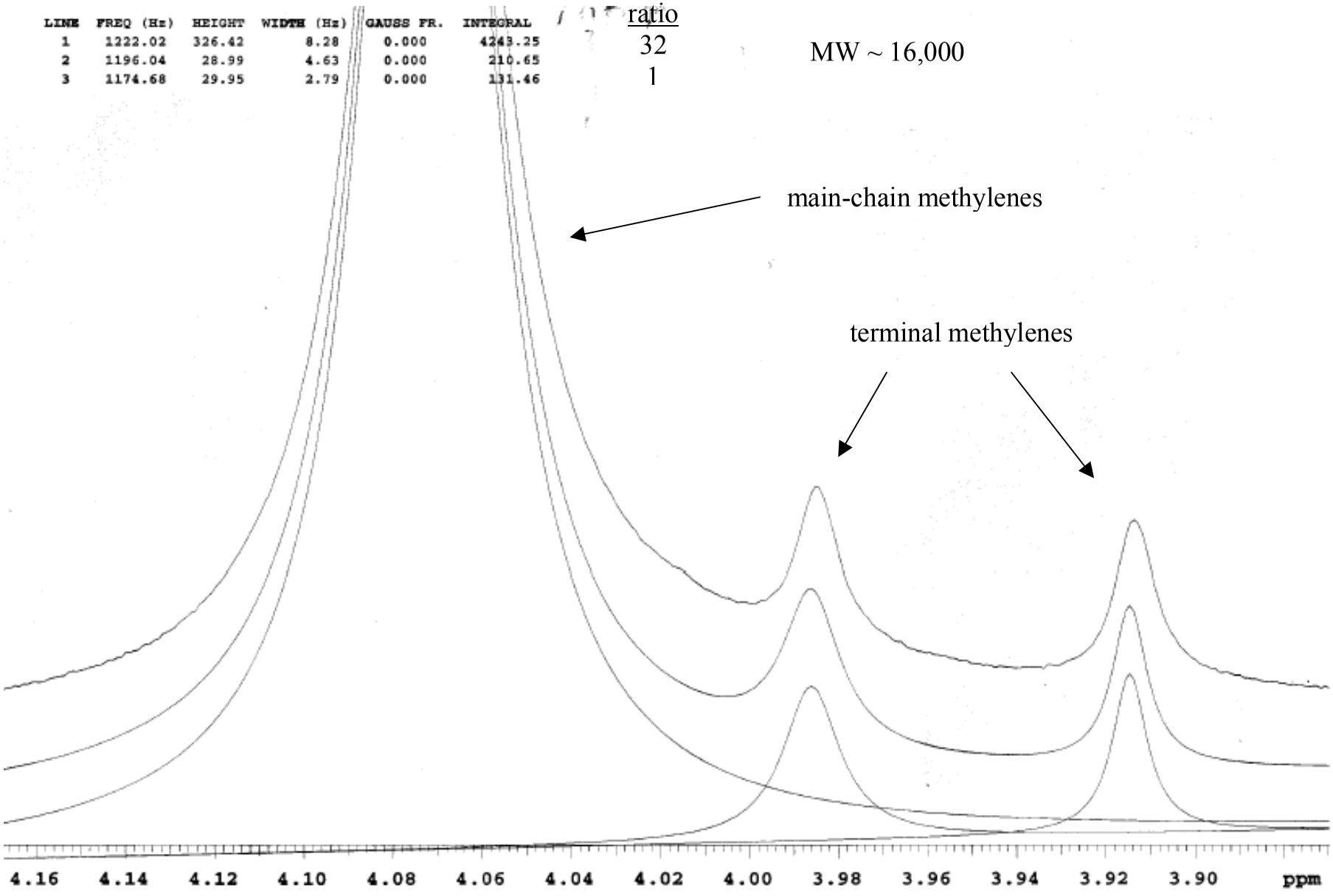
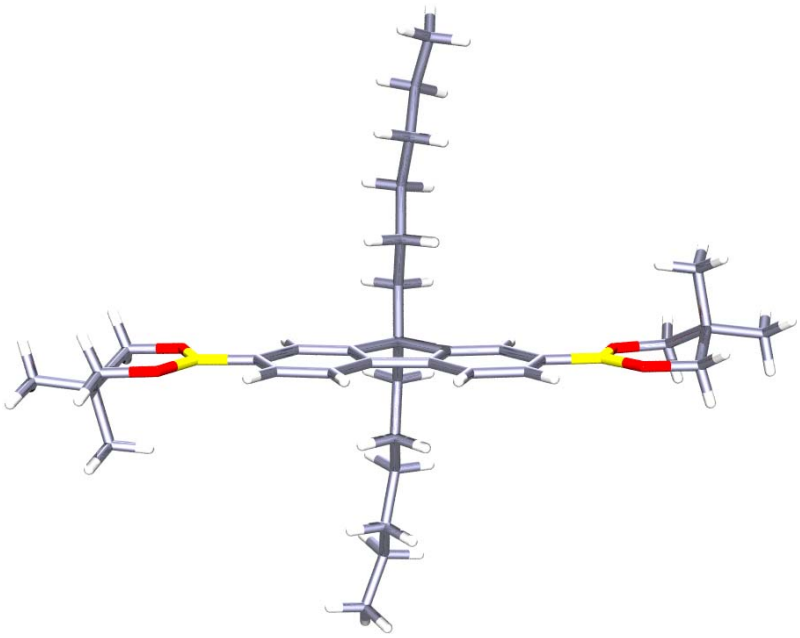


Figure SI-3: Typical deconvolution spectrum of the methylene region of the ^{1}H NMR of polymer **1**. Ratios are indicated at the top resulting in a polymer with a molecular weight around 16, 000.



*(5) X-Ray Structure of **2*** for single crystal x-ray analysis were obtained from a solution of **2** in CH_2Cl_2/hexane by slow evaporation. These crystals have a composition of $(\mathbf{2})_2$·(hexane).



Crystal data for **2**: $C_{35}H_{52}B_2O_4 \cdot 0.5C_6H_{14}$ (or $C_{38}H_{59}B_2O_4$), M = 601.47, triclinic, space group P-1, a = 11.7222(5), b = 13.0633(6), c = 24.9056(11) Å, α = 91.5780(10)°, β = 101.1870(10), γ = 97.8820(10)°, V= 3700.2(3) $Å^3$, T = 200(2) K, Z = 4, 9724 independent reflections measured, final $R1$ = 0.0536, and $wR2$ = 0.1470