Polyfluorene with *p*-carborane in the backbone

Joseph J. Peterson, Yoan C. Simon, E. Bryan Coughlin* and Kenneth R. Carter*

Supplemental Information

Experimental Section

Materials. All reactants, reagents, and solvents were purchased from Aldrich Chemical Co and used as received unless specified otherwise. All reactions were performed under N_2 atmosphere unless otherwise noted. Anhydrous 1,2-Dimethoxyethane was stored over calcium hydride under N_2 atmosphere and freshly distilled before each use. p-carborane was supplied by KatChem. $Ni(COD)_2$ was purchased from Strem Chemicals and used as received. Copper chloride, potassium iodate, iodine, N-bromosuccinimide, 1-bromohexane, sodium hydroxide, anhydrous pyridine, and bipyridine were purchased from Acros Organics and used as received except for copper chloride, which was purified using methods described in literature.[1]

Thin layer chromatography (TLC) was performed on Analtech GF silica gel with gypsum binder on glass backing. In addition to using the fluorescent indicator under 254nm handheld lamp, TLC's of carborane containing compounds were developed by dipping the plates quickly into solution of $PdCl_2$ in dilute HCl_{aq} which upon heating produces Pd black where boron is present. Silica gel used for column chromatography was purchased from EMD (Silica gel 60).

Instrumentation. Gel permeation chromatography (GPC) measurements for the polymers were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 Pump with a K-2301 refractive index detector and a K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns at 40°C. Molecular weights are reported relative to polystyrene standards.

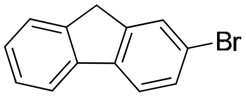
^{1}H NMR, and ^{13}C NMR were recorded at 400 MHz, and 100 MHz respectively on a Bruker NMR spectrometer at room temperature in deuterated chloroform. The individual NMR spectral assignments do not list the individual shifts of the carborane B-H resonances. Due to the quadrupolar nature of boron, the resonances for the 10 B-H are observed as broad multiplets (δ= ~4.1-1.4 ppm). The integration of these multiplets accounts for 10 H.

Mass spectral data were obtained at the University of Massachusetts Spectrometry Facility which is supported, in part, by the National Science Foundation.

Melting points were measured with a Thomas Hoover Uni-Melt capillary melting point apparatus. Differential scanning calorimetry was performed on a Thermal Analysis (TA) Q-2000 in aluminum pans using a heat-cool-heat cycle at 10°C/min. T_g was taken as the onset glass transition of the second heating cycle using TA Universal Analysis software.

Fluorescence measurements were taken on a Perkin-Elmer LS-50B using either quartz slides (25x25x1mm, Chemglass) or quartz cuvets with a 1cm path-length. UV-vis spectra were recorded on a Hitachi U-3010 spectrometer in 1cm path-length quartz cuvets. Infrared spectroscopy of polymer films were performed on a Nicolet 6700 FT-IR spectrometer equipped with a Harrick grazing angle ATR accessory (GATR)

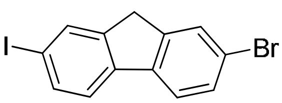
2-bromo-9H-fluorene (1).



1

Fluorene (30 g, 180 mmol, 1 equiv.) was placed into a 500 mL two neck round bottom flask and flushed with nitrogen. Propylene carbonate (250 mL) was added and the solution was heated to 60°C. *N*-bromosuccinimide (32.1 g, 180 mmol, 1 equiv.) was added quickly in one portion during a slight nitrogen overpressure. The oil bath was turned off and the reaction mixture was stirred as it cooled slowly to RT over the course of ~2hrs. The cooled reaction was precipitated into ~2L of water yielding an off- white solid, which was stirred as a slurry overnight. The solid was filtered, dissolved in 500mL toluene, and extracted with water (3x. 100mL). The organic phase was then dried over Na_2SO4, filter, and concentrated by rotary evaporator to give a white solid. The product was recrystallized from a minimum amount of refluxing ethanol/water (6/1) to yield off-white crystals (30.8g, 71%). m.p: 104-107 °C.

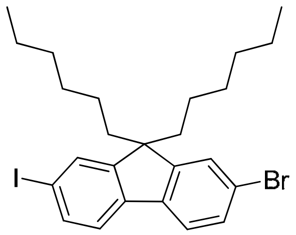
2-bromo-7-iodo-9H-fluorene (2):



2

2-bromo-9H-fluorene **1** (25 g, 102 mmol, 1 equiv.), iodine (10.85 g, 43 mmol, 0.42 equiv.), and potassium iodate (5.45 g, 25 mmol, 0.24 equiv.) were placed into a 1 L round-bottom flask. Water (20 mL), glacial acetic acid (425 mL) and concentrated sulfuric acid (10 mL) were added and the flask was heated in a 90° C oil bath under nitrogen. After 2 hours of stirring, the reaction was cooled to RT, at which point a light yellow precipitate formed. After filtration, the precipitate was washed with acetic acid and water and recrystallized from dichloromethane/methanol to yield white, wispy crystals (29.5 g, 78%) m.p.: 178-180 °C.[2]

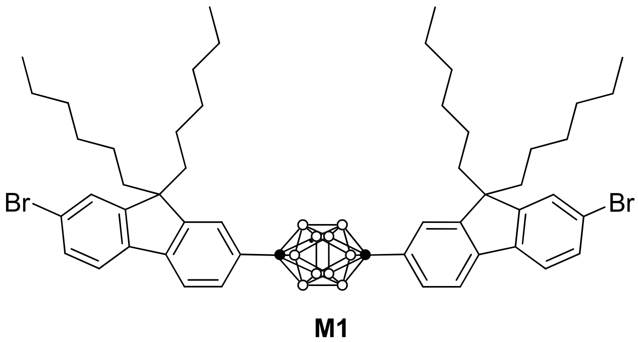
2-bromo-9,9-dihexyl-7-iodo-9H-fluorene (3):



3

In a 500 mL two-neck round-bottom flask fitted with a mechanical stirrer, 2-bromo-7-iodo-9H-fluorene **2** (25 g, 67.4 mmol, 1 equiv.) was added to 250 mL of dimethylsulfoxide under nitrogen atmosphere. 50% aq. NaOH (26 mL)was introduced drop-wise with giving a bright red solution, darkening quickly with time to a maroon. The solution was stirred vigorously as 1-bromohexane (23.8 mL, 168.5 mmol, 2.5 equiv.) was added and the solution turned purple. After 1 day of stirring at room temperature, the reaction was poured into 500 mL ethyl acetate, precipitating the salts. The solids were filtered off and the organic phase was washed (250mL portions) with 1x diluted NaOH, 1x brine, and 3x water with the red color fading to light yellow after the water washes. The organic phase was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to yield a viscous yellow oil. The oil was dissolved in a minimum amount of gently warmed isopropanol and allowed to cool slowly, yielding flaky amber crystals. (29.4g, 81%). . ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.67 (d, 1H, J = 7.5 Hz) , 7.66 (s, 1H), , 7.54 (d, 1H, J = 8.4 Hz) , 7.47 (d, 1H, J = 7.5 Hz) , 7.45 (s, 1H) , 7.43 (d, 1H, J = 8.4 Hz) , 1.92 (m, 4H,) , 1.10 (m, 12H,) , 0.80 (t, 6H, J = 7.0 Hz), 0.59 (m, 4H) ^{13}C NMR ($CDCl_3$): δ (ppm) = 152.7, 152.4, 139.7, 139.1, 136.0, 132.1, 130.1, 126.1, 121.6, 121.5, 121.2, 93.0, 55.6, 40.2, 31.5, 29.6, 23.6, 22.6, 14.0 ; HRMS (FAB+): m/z calcd 538.073, found 538.070; m.p.: 55-56 °C.

1,12-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-*closo*-dicarbodecaborane (M1):



M1

p-Carborane (0.30g, 2.08 mmol, 1 eq.) was added to a 25 mL three-neck round-bottom flask fitted with condenser and a Merlic-type solid addition adapter "tip-tube" containing copper chloride (0.45g, 4.58 mmol, 2.2 eq.). A stir bar was added and the flask and condenser were carefully purged with N_2 so as not to disturb the powdered reactants for 10 minutes and then sealed with rubber septum. 1,2-dimethoxyethane (8.5 mL) was injected via syringe and the mixture was stirred. The reaction flask was cooled to 0° C for 30 minutes using an ice bath and n-butyllithium (2.6M in hexane, 1.64mL, 4.26 mmol, 2.05 eq.) was injected drop-wise via syringe. The reaction was stirred for 5 minutes, and pyridine (1.25mL) was injected drop-wise via syringe. The copper chloride was added in one portion by rotating the "tip-tube" towards the reaction flask and the reaction, slightly cloudy after the addition of the pyridine, immediately produced a brown ppt. The reaction was heated to reflux forming a dark purple, almost black solution. After 30 minutes, 2-bromo-9,9-dihexyl-7-iodo-9H-fluorene **3** (2.3g, 4.26 mmol, 2.05 equiv.) dissolved in 2 mL 1,2-dimethoxyethane was injected in one portion and the reaction was continued under reflux. After 96 hrs, the reaction was cooled to room temperature and ~100mL ether was added. The reaction was washed with water (3x 100mL, dilute HCl solution (1x 100mL), and again with water and the organic phase was dried over $MgSO_4$, filtered, and concentrated by rotary evaporator to a brown oil. The oil was loaded onto a silica column and eluted with methylene chloride/hexanes (1:1), giving a clear viscous oil after rotary evaporation. The product was recrystallized twice from ethanol/acetone (9:1) to give fine colorless crystals. (205mg, 10%) ***Note*:** Alkyllithiums, which are *extremely* reactive and pyrophoric, should be used under inert atmosphere and with extreme caution! ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.53-7.44 (m, 6H), 7.27-7.21 (m, 6H), 3.8-1.75 + 1.90 (bm + m, 18H), 1.10 (m, 24H), 0.82 (t, 12H, J = 7.3 Hz), 0.58 (bm, 8H), ^{13}C NMR ($CDCl_3$): δ (ppm) = 153.39, 150.25, 140.29, 139.00, 135.61, 130.08, 126.24, 121.82, 121.53, 121.30, 119.21, 119.16, 83.21, 55.47, 39.85, 31.31, 29.43, 23.54, 22.48, 14.02. MS (FAB+): m/z calcd 966.5163, found 966.5043; m.p. = 187-188°C.

Polymerization of M1

In a reaction tube equipped with a stir bar, the monomer (100 mg, 0.10 mmol,1 eq) was introduced along with bipyridine (40mg, 0.25 mmol, 2.5 eq). The tube was then pumped into an argon filled glove box and Ni(COD)$_2$ (71 mg, 0.25 mmol, 2.5eq) was added. The tube was sealed with a crimp-on aluminum cap with a PTFE coated septum seal and taken out of the glove box. Additional 1,5 COD (32 μL, 0.25 mmol), 2.5 eq) was added via syringe and the reagents were dissolved in 4 mL of an anhydrous toluene:DMF (4:1) mixture. The tube was quickly degassed and filled with nitrogen three times. The tube was placed in an oil bath heated to 80°C and stirred for 24 hrs. The still warm solution was then filtered using a syringe mounted with filter paper as well as a 0.45 μm PTFE syringe filter and precipitated into 100 mL of slightly acidified methanol (0.1M HCl). The *p*-carborane polymer **P1** was recovered as a white solid (72 mg, 85%). **P1:** ^{1}H

NMR ($CDCl_3$): δ (ppm) = 7.35 (m, 10H), 7.13 (m, 2H), 3.9-1.5 + 1.78 (bm + m, 18H), 0.97 (m, 24H), 0.85 (m, 12H), 0.30 (m, 8H).

1 Whitesides, G. M.; Sadowski, J. S.; Lilburn, J., *J.Am.Chem.Soc.,* 1974, *96,* pp. 2829-2835.

2 Kannan, R.; He, G. S.; Lin, T.; Prasad, P. N.; Vaia, R. A.; Tan, L., *Chemistry of Materials,* 2004, *16,* pp. 185-194.

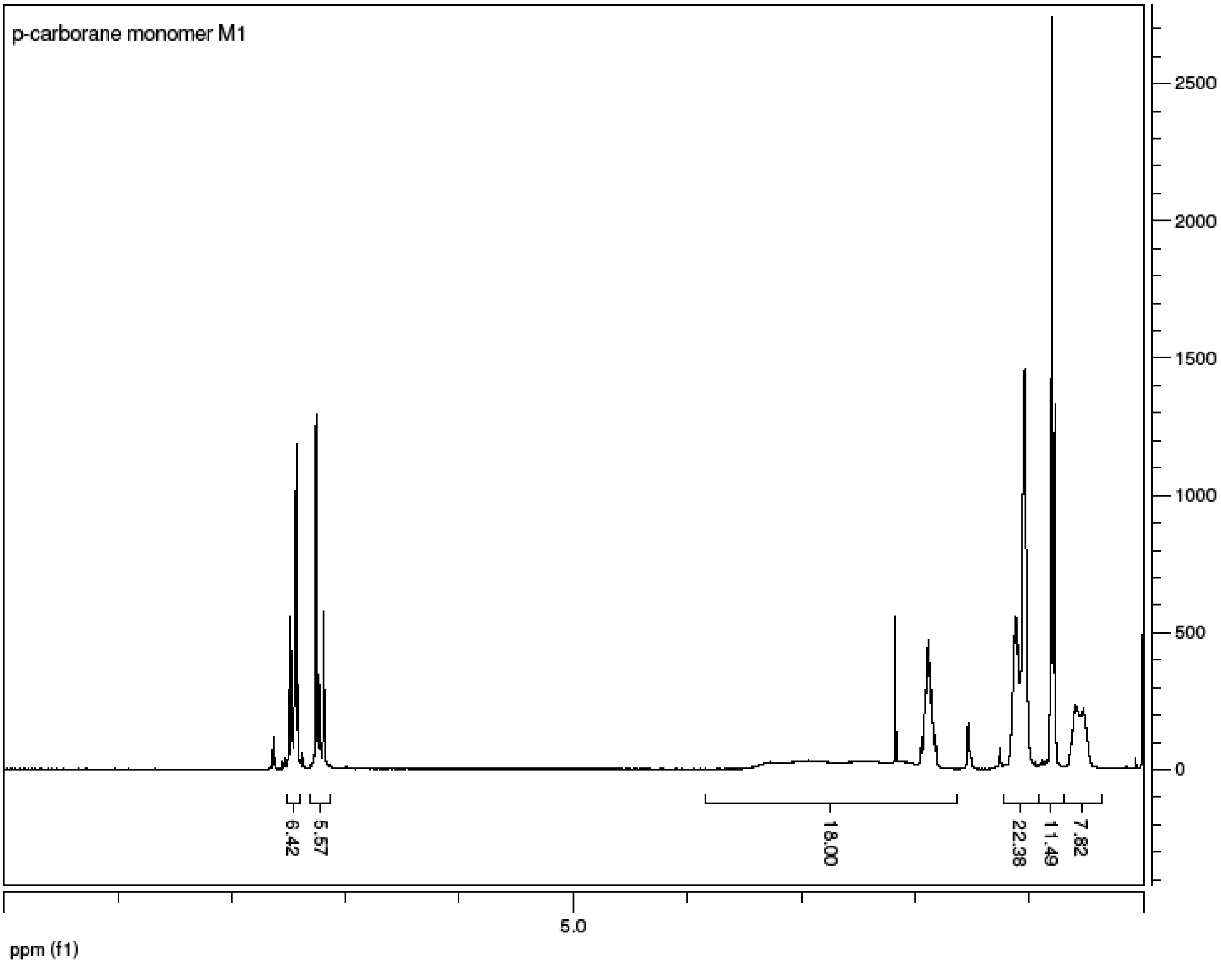


Figure S1: ^{1}HNMR of monomer M1 in $CDCl_3$

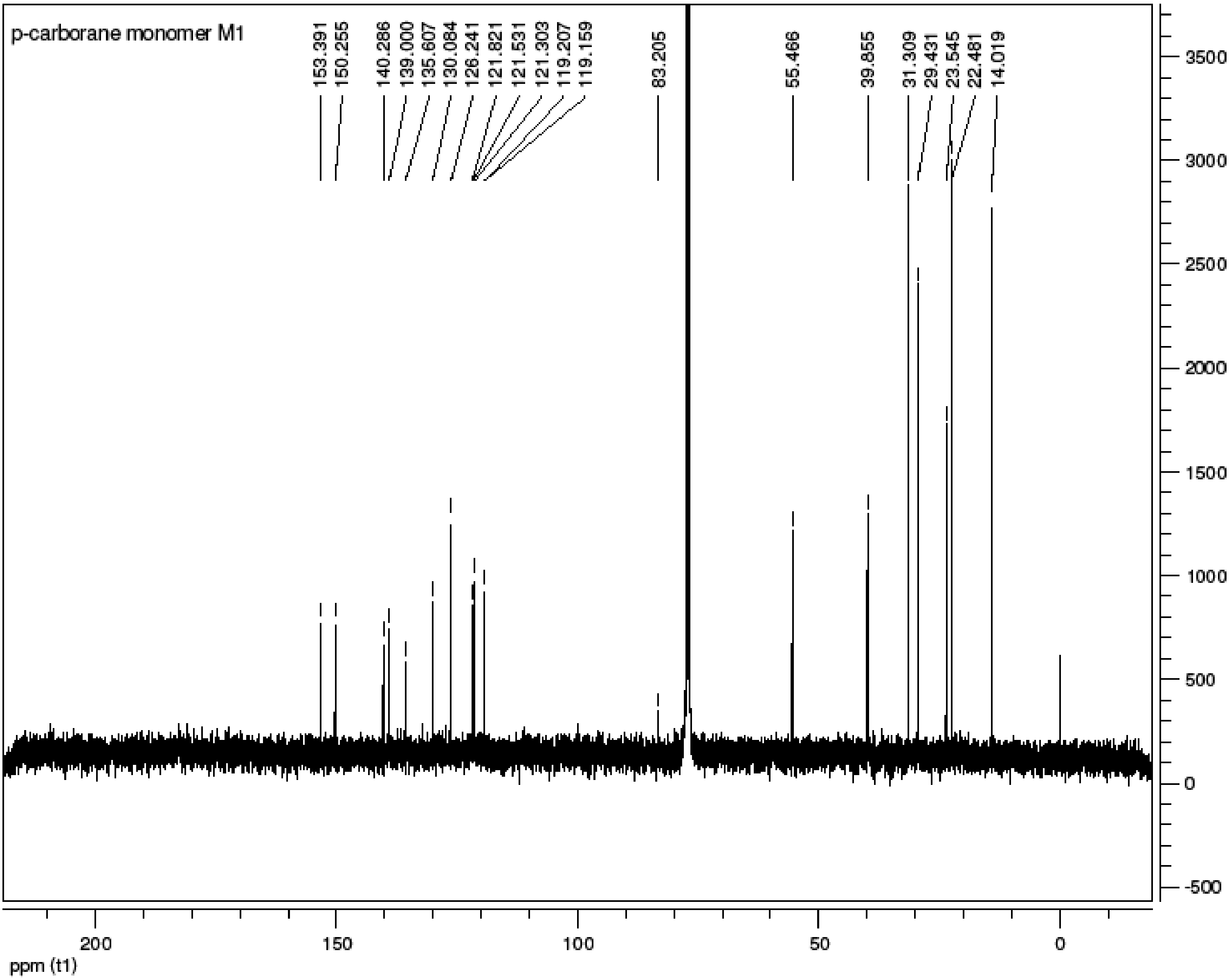


Figure S2: ^{13}C-NMR of monomer M1 in $CDCl_3$

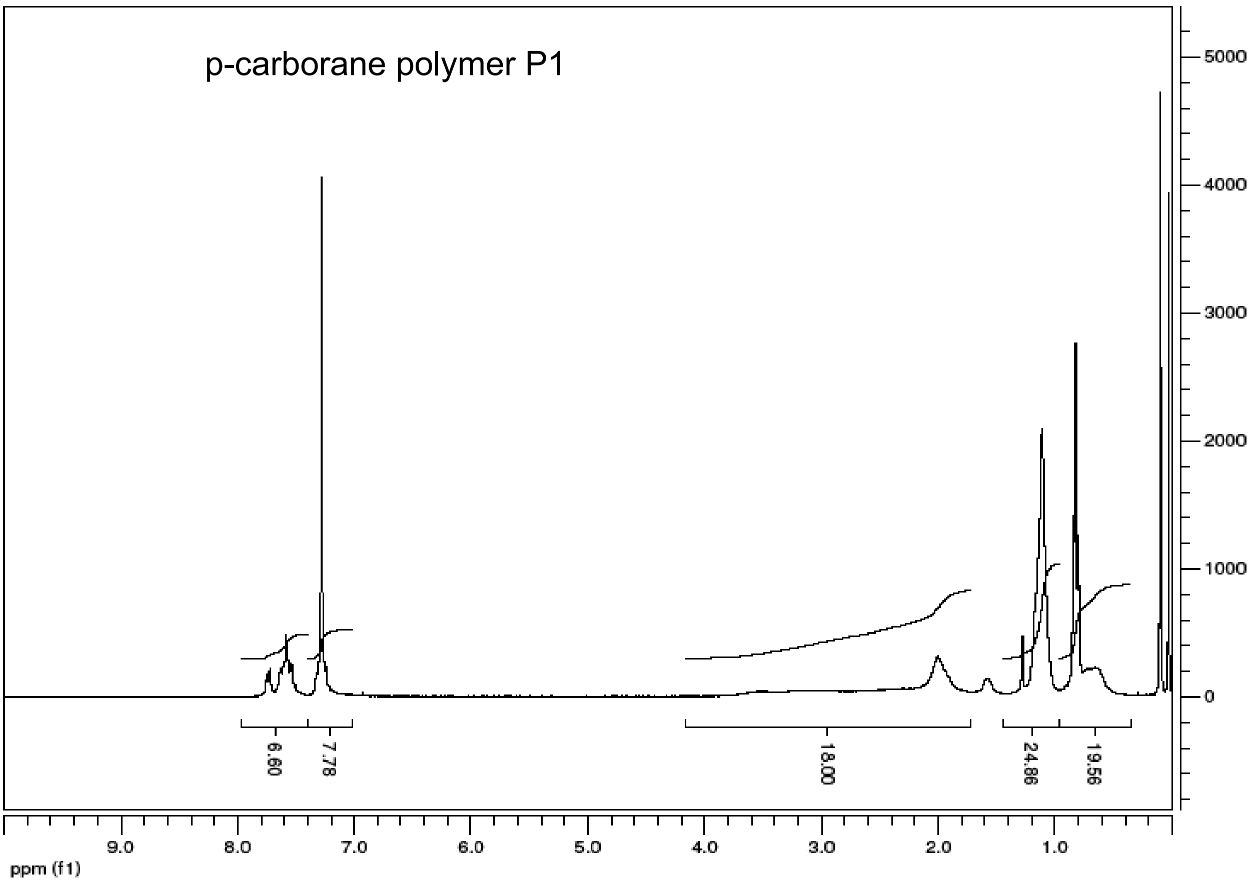


Figure S3: ^{1}HNMR of polymer P1 in $CDCl_3$

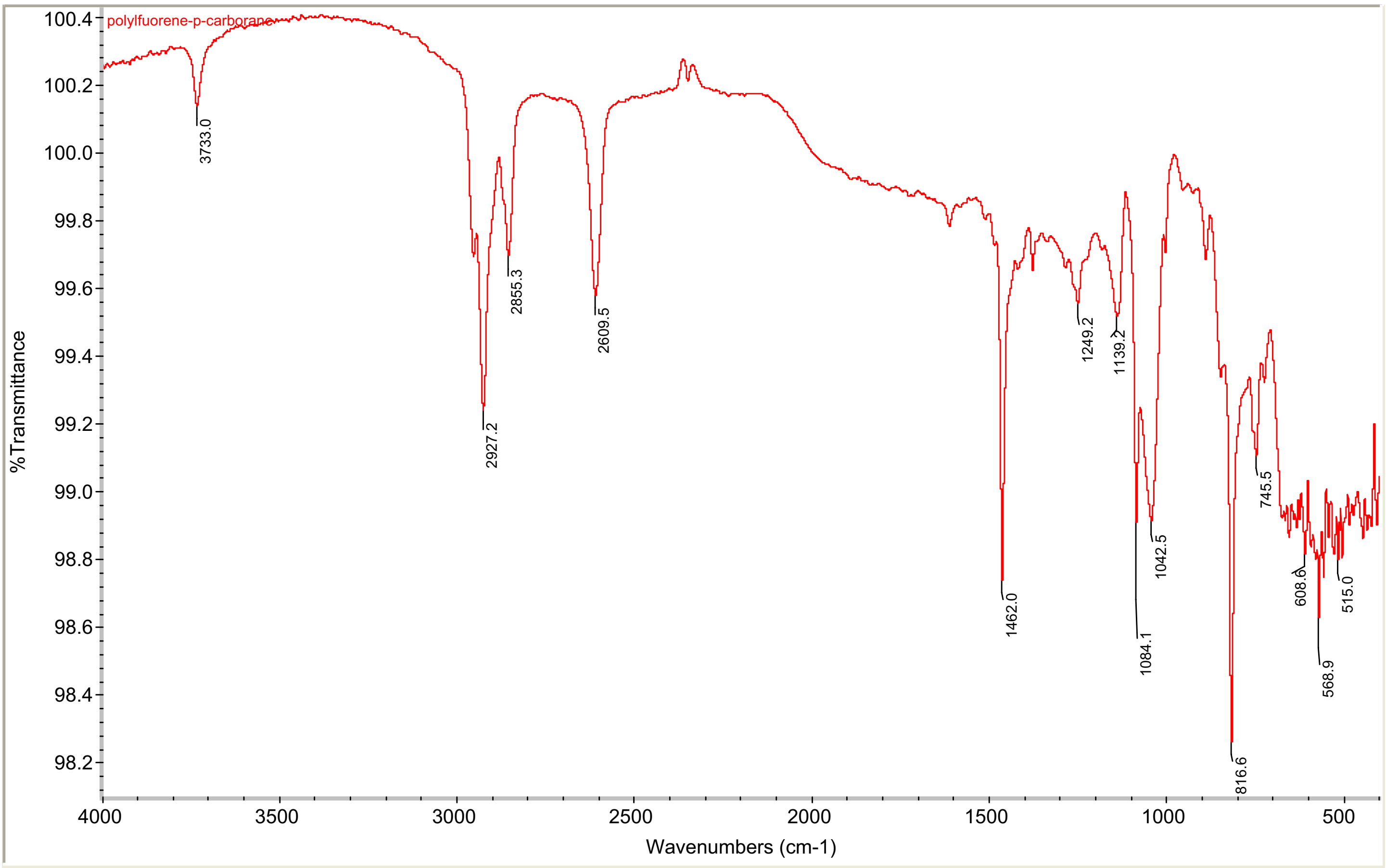


Figure S4: FT-IR of polymer P1 film. B-H signal at 2609 $^{-1}$cm

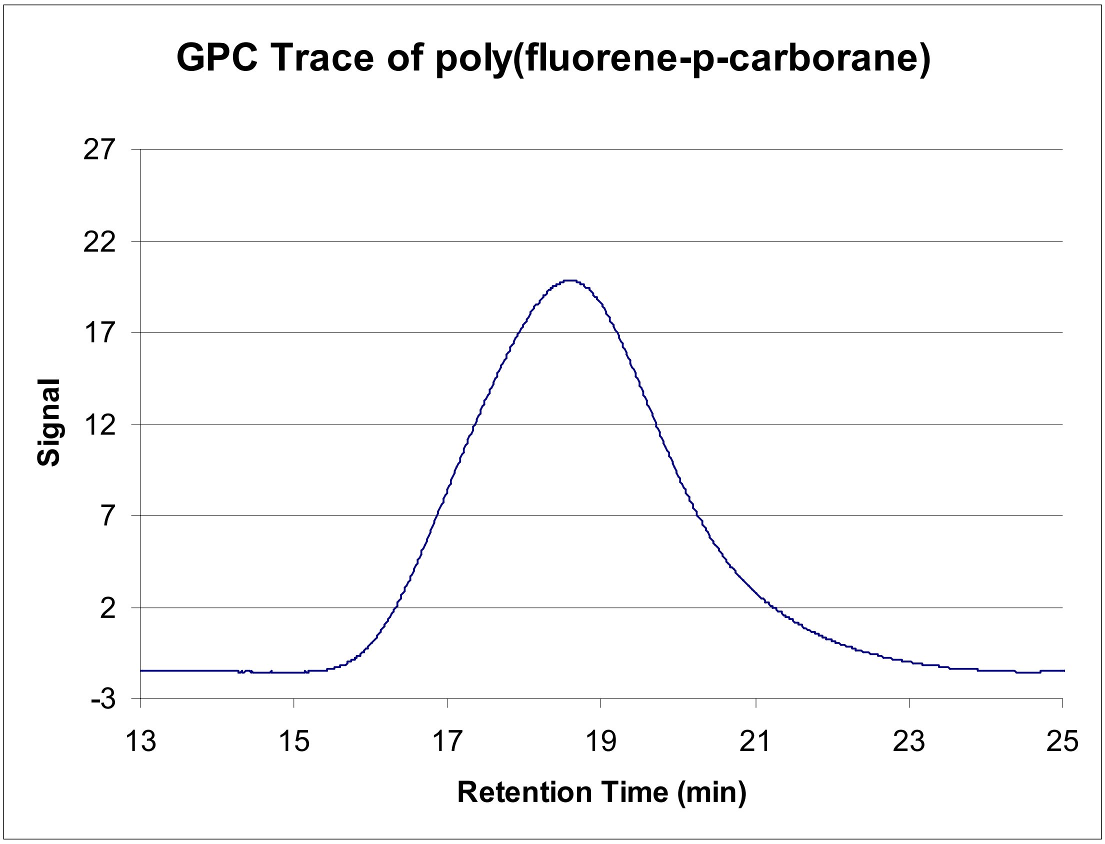


Figure S5: GPC trace of polymer P1 in THF vs PS. $M_n = 50x10^3$ g/mol, PDI 2.3.

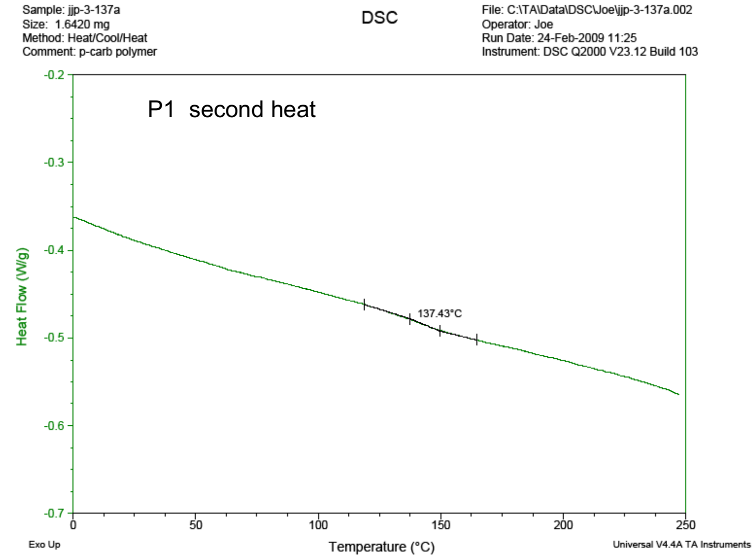


Figure S6: Differential scanning calorimetry curve for polymer P1 showing the T_g on the second heating cycle.

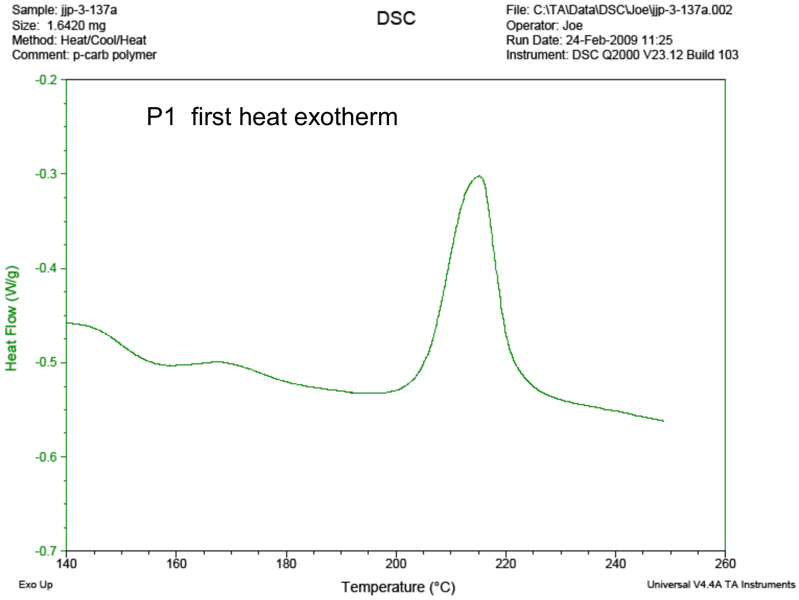


Figure S7: Differential scanning calorimetry curve showing the exotherm near 220°C during the first heating cycle.