Side-chain Co(I) polymers featuring substituted CpCoCp units

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Supporting Information

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I. Experimental and Characterization

Materials: Manipulations were performed in a N_2 filled MBraun Labmaster 130 glovebox in 4 dr. vials affixed with Teflon lined screw caps, or using standard Schlenk techniques. Dichloromethane, THF, toluene, Et_2O, *n*-pentane, and *n*-hexane were obtained from Caledon Laboratories and dried using MBraun Solvent Purification System that utilizes dual molecular sieve columns. The dried solvents were stored in Straus flasks under a N_2 atmosphere or over 4 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy ($CDCl_3$, C_6D_6) were purchased from Cambridge Isotope Laboratories and dried by stirring overnight over CaH_2, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves.

Dicyclopentadiene, dimethyl carbonate, diphenyl acetylene, γ-Butyrolactone, 2-butyne and ^{n}BuLi (1.6*M* solution in hexanes) were purchased from Aldrich. Dicylopentadiene was distilled *via* a 30 cm column to obtain cyclopentadiene which was subsequently converted to the lithium cyclopentadienide[1] and stored in the glovebox. Lithium carbomethoxycyclopentadienide was prepared using the literature procedure for the synthesis of the sodium salt.[2] Triethylamine and N, N, N′, N′, N″-pentamethyldiethylene triamine (Pmdeta) were purchased from Aldrich and distilled from KOH prior to use. Methacryloyl chloride (Alfa Aesar), acryloyl chloride (Alfa Aesar) and hydroxyethyl acrylate (Alfa Aesar) were distilled before use and stored at -30 °C under nitrogen in dark. Lithium aluminium hydride ($LiAlH_4$), ethyl 2-bromoisobutyrate (EB^{i}B), azobisisobutyronitrile (AIBN) and CuBr were purchased from Alfa Aesar.

Lithium (1-carboxy-propan-3-ol)cyclopentadiene, was prepared following the procedure for sodium salt.[3] The Co(I) precursors $ClCo(PPh_3)_3$[4] and $Cb^*Co(CO)_2I$[5] were prepared following literature procedures. Neutral alumina (60 – 325 mesh, Brockman Activity 1) was obtained from Fischer Scientific and silica gel (230 – 400 mesh) was obtained from Silicycle.

Characterization: NMR spectra were recorded using a Varian INOVA 400 MHz (^{13}C = 100.52 MHz) or Varian INOVA 600 MHz spectrometer (^{13}C = 150.92 MHz). Proton and $^{13}C\{^1H\}$ NMR spectra were referenced relative to Me_4Si using the NMR solvent (^1H: $CHCl_3$, δ = 7.26 ppm; C_6HD_5, δ = 7.16 ppm) $^{13}C\{^1H\}$: $CDCl_3$, δ = 77.2 ppm; C_6HD_5, δ = 128.4 ppm). Fourier Transform Infrared Spectrometry (FT-IR) was conducted on samples as a KBr disk using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm^{-1}. Decomposition/melting points were recorded in flame sealed capillary tubes using a Gallenkamp Variable Heater. Suitable single crystals for X-ray diffraction studies were individually selected under Paratone-N oil and mounted on nylon loops and immediately placed in a cold stream of N_2 (150 K). Data was collected on a Bruker Nonius Kappa CCD X-ray diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The solution and subsequent refinement of the data were performed using the SHELXTL suite of programs. Elemental analyses were performed by Université de Montréal, Montreal, Quebec, Canada. Mass spectra were recorded using an electron ionization Finnigan MAT 8200 mass spectrometer.

Size exclusion chromatography (SEC) was performed in tetrahydrofuran (THF) using a Waters 515 HPLC pump, Wyatt OptilabRex RI and miniDAWN-TREOS detectors and two ResiPore (300 x 7.5 mm) columns from Polymer Laboratories. Polymer molecular weights were calculated based on the multi-angle light scattering data using the Wyatt Astra software, with dn/dc values of the polymers determined from the RI detector using Astra. Column calibration was performed using polystyrene standards from Polymer Laboratories. The decomposition temperatures (T_d) were determined using a Q600 SDT TA Instrument. A 0.005-0.010 g sample was heated at a rate of 10 °C/min over a temperature range of 100-600 °C. Differential scanning calorimetry (DSC) was performed on a Q20 DSC TA Instrument at a heating rate of 10 °C/min from -100 to 250 °C for **1d** and Polymers **A**-**C** and -90 to 190 °C for **2c** and Polymer **D**. Glass transition temperatures (T_g) were obtained from the second heating cycle. All thermal analysis experiments were conducted in a N_2 atmosphere. UV-Vis spectra were recorded on a Cary instrument 300 UV-Vis spectrophotometer. All spectra were recorded in dry DCM using $10^{-4}M$ solutions. Voltammetric curves were obtained using an electrochemical workstation (CH-610A, CH Instruments, Austin TX). The electrochemical cell used consisted of a Pt disk embedded in a glass tube as the working electrode (0.03 cm^2), a Pt wire as the counter electrode, and Ag wire for the quasi-reference electrode. Solutions were prepared with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte and with 3.0 mL dry CH_2Cl_2 as the solvent. A 0.007-0.008 g of the compound was used. The solution was purged with argon for 2 min and the loaded cell was sealed with an air-tight Teflon cap. The electrochemical potential was calibrated at the end of each experiment by the addition of ferrocene as an internal standard taking the formal potential of Fc^+/Fc 0.400 V vs SHE.[6]

II. Monomer Synthesis:

Compound 1d: Hydroxyethylacrylate (HEA) (0.8 mL, 7.62 mmol) was added to a solution of **1c**[2] (2.00 g, 3.68 mmol; DCM, 20 mL) followed by the addition of Et$_3$N (3 mL, 21.52 mmol) at RT and the reaction mixture stirred for 15 h. The reaction was then quenched with water and the combined organic layers were collected, dried over MgSO$_4$ and concentrated to give orange oil. Further purification was carried out by column chromatography over neutral alumina and the compound eluted with 10% EtOAc/*n*-pentane. The solvent was removed *in vacuo* to obtain yellow solids. Yield 1.18 g, 50%. ^{1}H NMR: (CDCl$_3$; δ) 3.76 (t, ^3J = 4.6 Hz, 2H, C*H*$_2$), 4.14 (t, ^3J = 4.6 Hz, 2H, C*H*$_2$), 4.80 (*p*t, 2H, C$_5$*H*$_4$), 5.21 (*p*t, 2H, C$_5$*H*$_4$), 5.84 (d, ^3J = 10.4 Hz, 1H, =C*H*$_2$), 6.11 (dd, ^3J = 10.4 Hz, 17.3 Hz, 1H, C*H*=CH$_2$), 6.42 (d, ^3J = 17.3 Hz, 1H, =C*H*$_2$), 7.20-7.29 (m, 12H, C*H*(Ph), 7.43 (d, 8H, C*H*(Ph)). ^{13}C{^{1}H} NMR: (CDCl$_3$; δ) 62.1 (*C*H$_2$), 62.4 (*C*H$_2$), 76.7 (*Cb*), 85.0 (Cp_β), 86.4 (Cp_{ipso}), 86.6 (Cp_α), 127.0 (Ph and *C*H), 128.3 (Ph), 129.0 (Ph), 131.5 (=*C*H$_2$), 135.2 (Ph), 165.9 and 166.1 (CO). FT-IR (cm^{-1}) (ranked intensity): 565 (7), 588 (15), 703 (4), 746 (8), 783 (10), 809 (12), 1136 (3), 1198 (5), 1277 (6), 1298 (14), 1462 (13), 1499 (11), 1636 (26) (C=C), 1708 (1) (CO), 1728 (2) (CO). MP: 120 ºC. EI-MS (*m/z*): M$^+$ (622, 100%). HRMS (EI) for $C_{39}H_{31}CoO_4$ (found/calculated): (622.156/622.155). EA (found/calculated): C (75.21/75.24), H (5.13/5.02).

Compound 2a: A solution of LiC$_5$H$_4$CO(CH$_2$)$_3$OH[7] (2.42 g, 15.30 mmol; THF, 30 mL) was added to a solution of Cb*Co(CO)$_2$I (1.07 g, 3.06 mmol; THF, 30 mL) at RT. The reaction mixture was then refluxed for 2.5 h under N$_2$, after which, the solvent was removed by rotary evaporation. The residue was dissolved in DCM and washed with water. The organic layers were combined and dried over MgSO$_4$. The solvent was removed by rotary evaporation and the crude compound was subjected to column chromatography over neutral alumina. The compound was eluted with 30-50% EtOAc/DCM. The compound was redissolved in Et$_2$O and filtered through a kimwipe filter to remove any particles present. Yield 0.41 g, 50%. ^{1}H NMR: (CDCl$_3$; δ) 1.45 (s, 12H, (C*H*$_3$(Cb*)), 1.94 (m, 2H, C*H*$_2$), 2.69 (t, ^3J = 4.95 Hz, O*H*), 2.80 (t, ^3J = 3.76 Hz, C*H*$_2$CO), 3.71 (m, 2H, C*H*$_2$OH), 4.78 (*p*t, 2H, C$_5$*H*$_4$), 5.10 (*p*t, 2H, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR: (CDCl$_3$; δ) 10.3 (*C*H$_3$(Cb*)), 27.3 (*C*H$_2$*)*, 36.7 (*C*H$_2$*)*, 63.0 (*C*H$_2$CO), 77.5 (*Cb**), 80.8 (Cp_β), 85.4 (Cp_α), 92.5 (Cp_{ipso}), 200.3 (*C*O). FT-IR (cm^{-1}) (ranked intensity): 668 (11), 814 (8), 872 (14), 1027 (5), 1057 (4), 1260 (9), 1371 (3), 1419 (12), 1456 (1), 1559 (13), 1576 (15), 1653 (2) (CO), 2907 (6), 2936 (7), 3421 (10) (OH). EI-MS (*m/z*): M$^+$ (318, 100%). HRMS (EI) for $C_{17}H_{23}CoO_2$ (found/calculated): (318.104/318.103). EA (found/calculated): C (64.43/64.15), H (7.57/7.28).

Compound 2b: Methacryloyl chloride (0.24 mL, 2.36 mmol) was added to a solution of Et$_2$N (0.35 mL, 2.41 mmol) and **2a** (0.61 g, 0.11 mmol; DCM, 15 mL) at -15 °C and the reaction mixture stirred at RT for 5 h. The solution was then washed with water and brine to remove the ammonium salt formed, the organic layer dried over MgSO$_4$ and concentrated to give orange oil. The compound was further purified by column chromatography over neutral alumina and the compound eluted with 10% EtOAc/DCM. The compound was redissolved in *n*-pentane and filtered through a kimwipe filter to remove any particles, followed by the removal of pentane. Yield 0.46 g, 62%. ^{1}H NMR: (C_6D_6; δ) 1.33 (s, 12H, $C\mathit{H_3}(\mathrm{Cb}^*)$), 1.84 (s, 3H, $C\mathit{H_3}$), 2.03 (m, 2H, $C\mathit{H_2}$), 2.52 (t, ^3J = 7.3, $C\mathit{H_2}$CO), 4.17 (t, ^3J = 6.5, $C\mathit{H_2}$OCO), 4.54 (*p*t, 2H, $C_5\mathit{H_4}$), 5.05 (*p*t, 2H, $C_5\mathit{H_4}$), 5.22 (bs, 1H, =$C\mathit{H_2}$), 6.13 (bs, 1H, =$C\mathit{H_2}$). $^{13}C\{^1H\}$ NMR: ($CDCl_3$; δ) 10.3 ($\mathit{C}H_3(\mathrm{Cb}^*)$), 18.5 ($\mathit{C}H_3$), 23.7 ($\mathit{C}H_2$), 35.7 ($\mathit{C}H_2$CO), 64.5 ($\mathit{C}H_2$OCO), 77.3 (*Cb*), 80.7 (Cp_β), 85.1 (Cp_α), 92.6 (Cp_{ipso}), 125.5 (=$\mathit{C}H_2$), 136.6 (*C*(Me)=CH_2), 167.6 (O*C*O), 198.2 (*C*O). FT-IR (cm^{-1}) (ranked intensity): 668 (4), 1027 (14), 1165 (8), 1373 (9), 1437 (12), 1457 (3), 1507 (13), 1541 (10), 1559 (5), 1636 (7), 1653 (1) (CO), 1684 (11), 1700 (6), 1717 (2) (CO), 2907 (15). EI-MS (*m/z*): M^+ (386, 100%). HRMS (EI) for $C_{21}H_{27}CoO_3$ (found/calculated): (386.128/386.129). EA (found/calculated): C (65.35/65.28), H (7.11/7.04).

Compound 2c: The same procedure was followed as for **2b** except that acrylolyl chloride was used instead of methacryloyl chloride. Acrylolyl chloride (0.11 mL, 1.36 mmol), Et_3N (0.19 mL, 1.36 mmol) and **2a** (0.34 g, 1.07 mmol; DCM, 15 mL) were used. Column chromatography was performed on neutral alumina and the compound eluted with 10% EtOAc/DCM. Yield 0.30 g, 76%. The compound was crystallized from a concentrated *n*-pentane solution at -30 °C for elemental analysis. X-ray quality crystals were obtained from a concentrated *n*-pentane solution at -30 °C.^{1}H NMR: ($CDCl_3$; δ) 1.42 (s, 12H, $C\mathit{H_3}(\mathrm{Cb}^*)$), 2.05 (m, 2H, $C\mathit{H_2}$), 2.71 (t, ^3J = 7.41, $C\mathit{H_2}$CO), 4.22 (t, ^3J = 6.40, $C\mathit{H_2}$OCO), 4.75 (*p*t, 2H, $C_5\mathit{H_4}$), 5.06 (*p*t, 2H, $C_5\mathit{H_4}$), 5.79 (d, ^3J = 10.4 Hz, 1H, =$C\mathit{H_2}$), 6.09 (dd, ^3J = 10.4 Hz, 17.3 Hz, 1H, $C\mathit{H}$=CH_2), 6.37 (d, ^3J = 17.3 Hz, 1H, =$C\mathit{H_2}$). $^{13}C\{^1H\}$ NMR: ($CDCl_3$; δ) 10.7 ($C\mathit{H_3}(\mathrm{Cb}^*)$), 23.5 ($\mathit{C}H_2$), 35.5 ($\mathit{C}H_2$CO), 64.3 ($\mathit{C}H_2$OCO), 77.3 ($Cb^*$), 80.6 ($Cp_\beta$), 85.1 ($Cp_\alpha$), 92.6 ($Cp_{ipso}$), 128.6 (*C*H=$CH_2$), 130.8 (=$\mathit{C}H_2$), 166.3 (*C*OO), 198.1 (*C*O). FT-IR (cm^{-1}) (ranked intensity): 811 (10), 987 (15), 1028 (9), 1057 (8), 1192 (4), 1273 (7), 1295 (11), 1371 (5), 1408 (6), 1455 (3), 1620 (16) (C=C), 1662 (2) (CO), 1725 (1) (CO), 2906 (12), 2937 (14), 2958 (13). EI-MS (*m/z*): M^+ (372, 100%). HRMS (EI) for $C_{20}H_{25}CoO_3$ (found/calculated): (272.112/372.114). EA (found/calculated): C (64.41/64.51), H (6.81/6.77).

III. Polymer Synthesis:

Polymerization of 1d: The reactions were performed in C_6D_6 in a J-Young tube and the progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Synthesis of Polymer A: Compound **1d** (0.254 g, 0.400 mmol; C_6D_6, 0.6 mL), CuBr (0.006 g, 0.042 mmol, 10.5 mol%), pmdeta (7.10 μL, 0.034 mmol, 8.5 mol%) and EB^iB (4.95 μL, 0.034 mmol, 8.5 mol%) (very sluggish reaction was observed when less initiator was used) were added to a J-Young tube in the glove box and heated at 80 °C in an oil bath for 4 d. No further change was observed in ^{1}H NMR on heating for more time and the proton NMR revealed a 70% conversion to the polymer. It should be noted that no reaction was observed with lower (2 mol%) catalyst loading. The reaction mixture was then filtered through a short pipette column of neutral alumina and the solvent removed *in vacuo*. The crude polymer was dissolved in DCM and precipitated into rapidly stirring *n*-pentane. The precipitation was repeated to obtain yellow solids, which were dried *in vacuo* for 24 h. Yield 0.15 g, 60%. M_n = 3,581 g/mol, PDI = 1.1.

General synthesis of Polymers B and C: Compound **1d** and AIBN were added to a J-Young tube in the glove box and heated at 60 °C in an oil bath for 2.5 d. No further change was observed in ^1H NMR on heating for more time and the proton NMR revealed a 90% conversion to the polymer. The reaction mixture was then quenched with MeOH resulting in precipitation of the polymer. The supernatant was removed (contained unreacted monomer), the precipitate dissolved in DCM (2 mL) and precipitated into rapidly stirring *n*-pentane (20 mL). The precipitation was repeated to obtain yellow solids, which were dried *in vacuo* for 24 h.

Polymer B: Compound **1d** (0.102 g, 0.16 mmol; C_6D_6, 0.6 mL) and AIBN (0.027 mg, 0.16 x 10^{-3} mmol, 0.1 mol%) were used. Yield 0.082 g, 70%. M_n = 30,500 g/mol, PDI = 2.1.

Polymer C: Compound **1d** (0.100 g, 0.16 mmol; C_6D_6, 0.6 mL) and AIBN (0.27 mg, 0.16 x 10^{-2} mmol, 1.0 mol%) were used. Yield 0.080 g, 70%. M_n = 26,100 g/mol, PDI = 1.9.

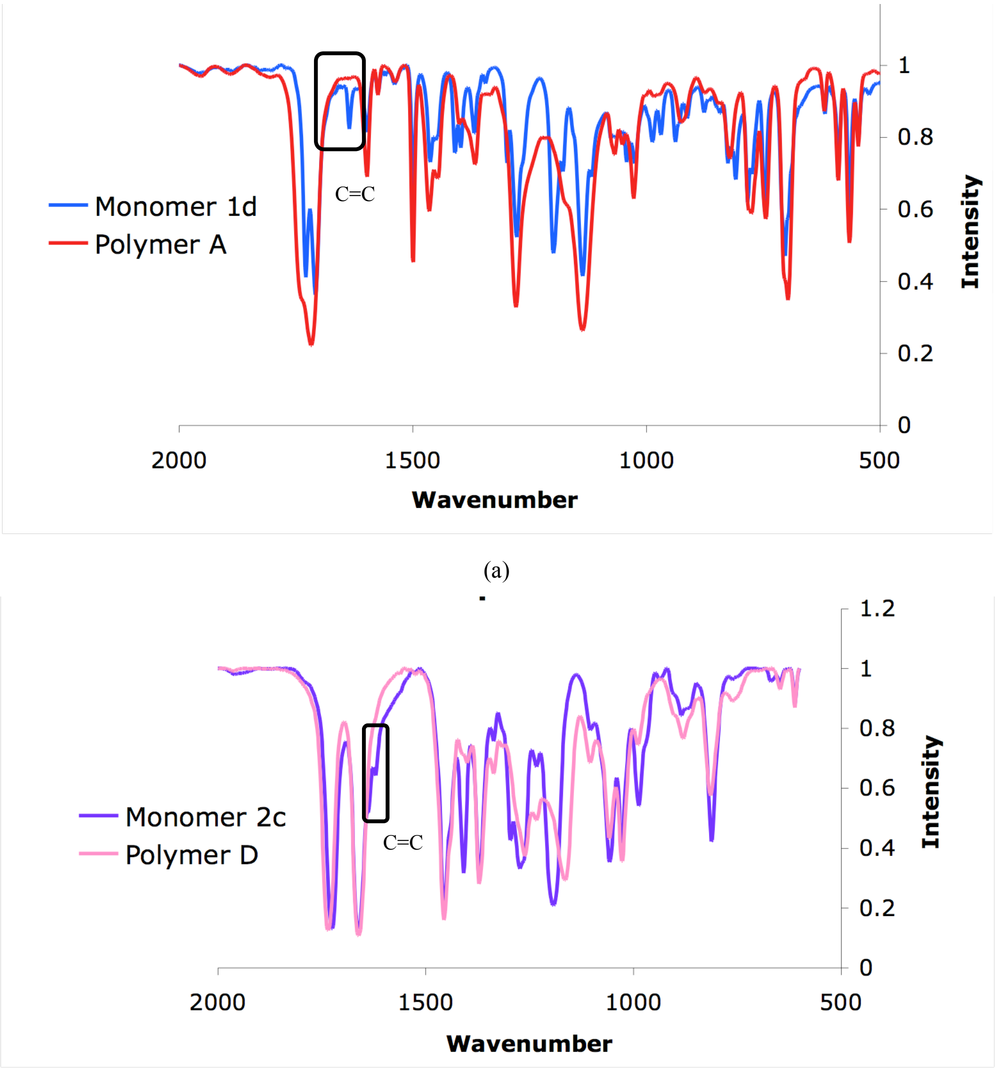
Polymers **A**, **B** and **C** have the same general structure only varying in the average number of monomer units incorporated in the polymer chain, and so, spectral characteristics are same for all of these polymers. ^1H NMR: ($CDCl_3$; δ) 3.59 (b, 2H, CH_2), 3.98 (b, 2H, CH_2), 4.71 (b, 2H, C_5H_4), 5.15 (b, 2H, C_5H_4), 7.19 (b, 12H, C*H*(Ph), 7.40 (m, 8H, C*H*(Ph)), other 3 protons are broadened out from 1.5 to 2.5 ppm. $^{13}C\{^1H\}$ NMR: ($CDCl_3$; δ) 42.0, 60.7, 61.5, 61.8, 62.2 (*C*H_2 and *C*H), 76.6 (*Cb*), 84.8 (Cp_{β}), 86.3 (Cp_{ipso}), 86.6 (Cp_{α}), 127.0 (Ph), 128.2 (Ph), 129.0 (Ph), 135.2 (Ph), 165.7 (CO). FT-IR (cm^{-1}) (ranked intensity): 546 (15), 565 (6), 589 (10), 696 (4), 744 (7), 821 (13), 1026 (9), 1067 (14), 1137 (2), 1279 (3), 1367 (12), 1464 (8), 1499 (5), 1579 (11), 1717 (1).

Polymerization of 2c:

Synthesis of Polymer D: Compound **2c** (0.20 g, 0.53 mmol; C_6D_6, 0.6 mL) and AIBN (7.80 mg, 4.75 x 10^{-2} mmol, 9.0 mol%) were used at 60 °C for 3 d. The progress of the reaction was monitored by ^1H NMR spectroscopy and 65% completion was observed at the end of 3 d. The reaction mixture was then quenched with MeOH (under N_2) and the solvent removed *in vacuo.* The residue was redissolved in DCM-Et_2O (0.5 mL: 2 mL) and precipitated into rapidly stirring *n*-pentane (20 mL). The precipitation was repeated to obtain yellow solids, which were dried *in vacuo* for 24 h. Yield 0.10 g, 50%. ^1H NMR: ($CDCl_3$; δ) 1.44 (b, 12H, CH_3(Cb*)), 1.98 (b, 2H, CH_2), 2.69 (CH_2), 4.09 (b, CH_2), 4.74 (*b*, 2H, C_5H_4), 5.10 (*b*, 2H, C_5H_4), other 3 protons are broadened out from 1.5 to 2.5 ppm. $^{13}C\{^1H\}$ NMR: ($CDCl_3$; δ) 10.4 (*C*H_3(Cb*)), 23.6 (*C*H_2), 35.5 (*C*H_2CO), 41.5, 42.0 (*C*H_2 and *C*H), 64.6 (*C*H_2OCO), 80.7 (Cp_{β}), 85.1 (Cp_{α}), 92.7 (Cp_{ipso}), 198.0 (*C*O), *Cb** not observed. FT-IR (cm^{-1}) (ranked intensity): 611 (12), 647 (14), 813 (10), 880 (11), 1027 (6), 1058 (8), 1164 (5), 1261 (7), 1371 (4), 1455 (3), 1661 (1), 1734 (2), 2906 (9), 3100 (13), 3443 (15). M_n = 10,610 g/mol, PDI = 1.3.

IV. Characterization of Side-Chain CpCoCb Polymers

In addition to IR and GPC, full characterization of the polymerizable monomers and polymers was carried out using TGA, DSC, UV-Vis and CV experiments.



(a)

(b)

Figure S1. IR Spectra (a) monomer (**1d**) and Polymer **A** (b) monomer (**2c**) and Polymer (**D**).

Thermal stability of the polymerizable monomers and their polymers was characterized by TGA (**Figure S2**). Phenyl substituted monomer and the corresponding polymers **A-C** exhibit stability up to 360 °C. The methyl substituted monomer **2c** exhibits lower thermal stability (T_d = 214 °C) as expected due to the lower stability of $CpCoC_4Me_4$ compounds in general. Methyl substituted polymer **D**, prepared from **2c**, exhibited 2 continuous stages of weight loss: 235-306 °C and 310-410 °C. The first event is likely due to the degradation of the cobalt unit followed by the degradation of the polymer backbone. This indicates high thermal stability of C_4Ph_4 species over C_4Me_4 group.

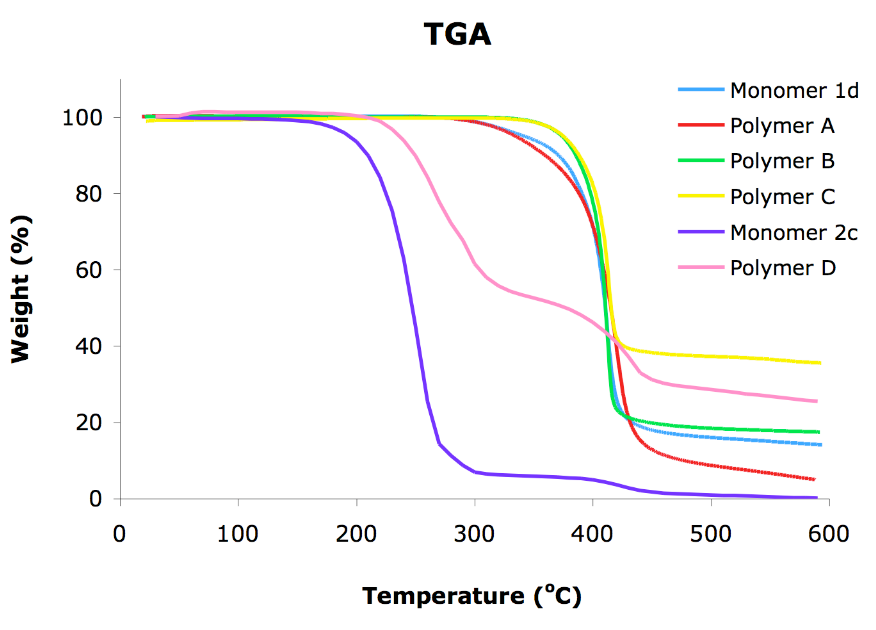


Figure S2. TGA curve displaying the decomposition temperatures (T_d) of the monomers and corresponding polymers. Monomer **1d** (T_d = 367 °C), Polymer **A** (T_d = 364 °C), Polymer **B** (T_d = 384 °C), Polymer **C** (T_d = 387 °C), Monomer **2c** (T_d = 214 °C), Polymer **D** (T_d = 235 °C).

Differential Scanning Calorimetry (DSC) of monomer **1d** showed a melting endotherm at 120 °C and an exotherm for polymerization at 128 °C. Only a glass transition (T_g = 68 °C) was observed in the second heat cycle showing thermal polymerization of the monomer (**Figure S3**, **S4**). However, for **2c**, no endotherm or exotherm was observed from -80 °C to 200 °C (before decomposition).

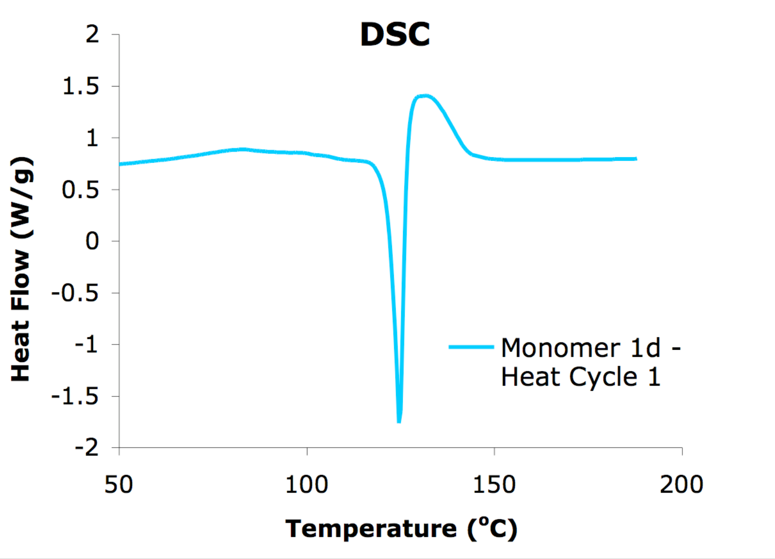


Figure S3. DSC curve of monomer **1d** showing a melting endotherm (T_m = 120 °C), followed by an exotherm for polymerization.

Glass Transition Temperature (T_g) of the polymers was determined by DSC (**Figure S3**). Polymers **A**, **B** and **C** exhibited T_g at 99 °C, 125 °C and 130 °C respectively, showing that the T_g is higher for higher molecular weight polymers. Methyl substituted polymer **D** had a much lower T_g at 43 °C.

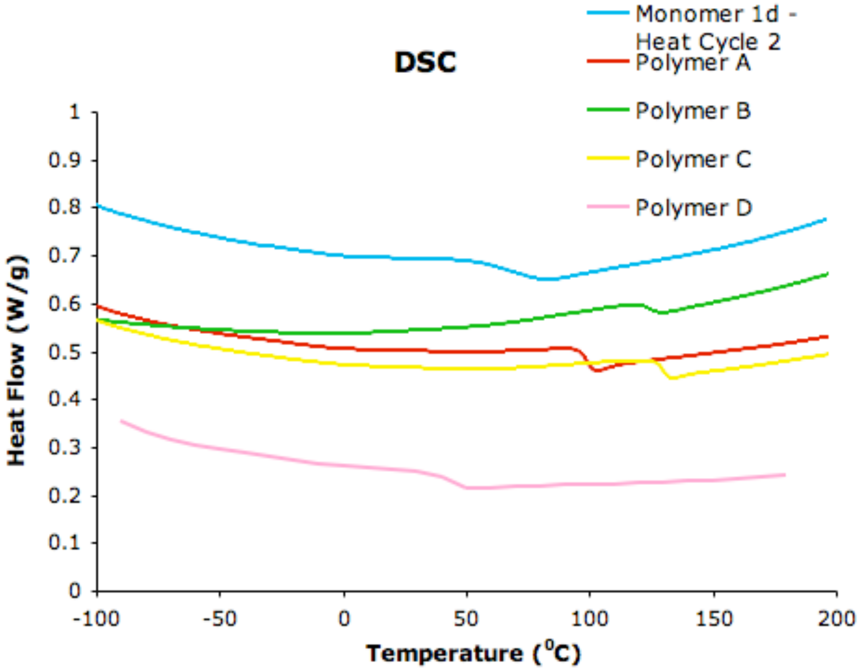


Figure S4. DSC curve displaying the glass transition temperatures (T_g) of the monomers and corresponding polymers. Monomer **1d** (T_g = 68 °C), Polymer **A** (T_g = 99 °C), Polymer **B** (T_g = 125 °C), Polymer **C** (T_g = 130 °C) and Polymer **D** (T_g = 43 °C).

UV-Vis spectra of the polymer and the corresponding monomer reveal a similar pattern (**Figure S5**) suggesting that the cobalt unit is intact on polymer formation. A slight blue shift of the characteristic π-π^* transition in these type of compounds[8] is observed in the methyl derivative, when compared with the phenyl derivative.

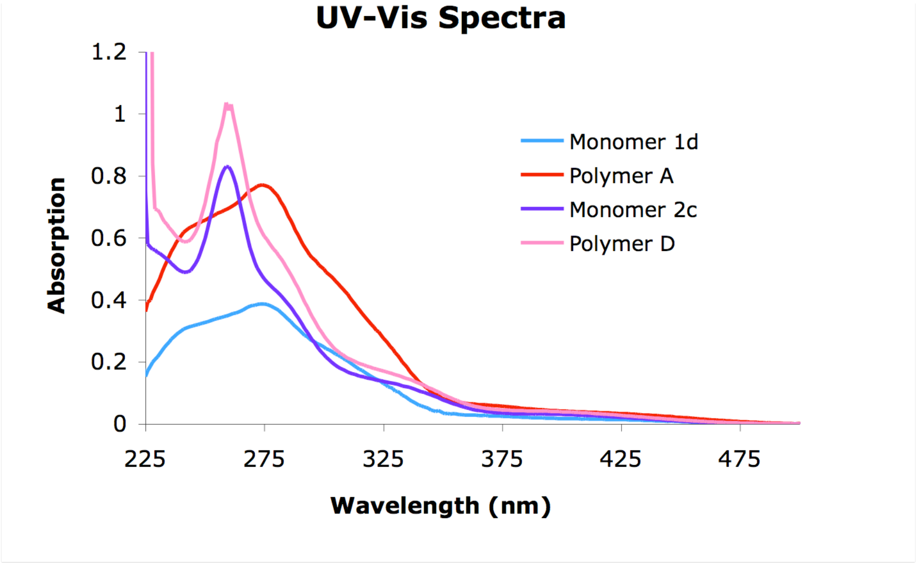
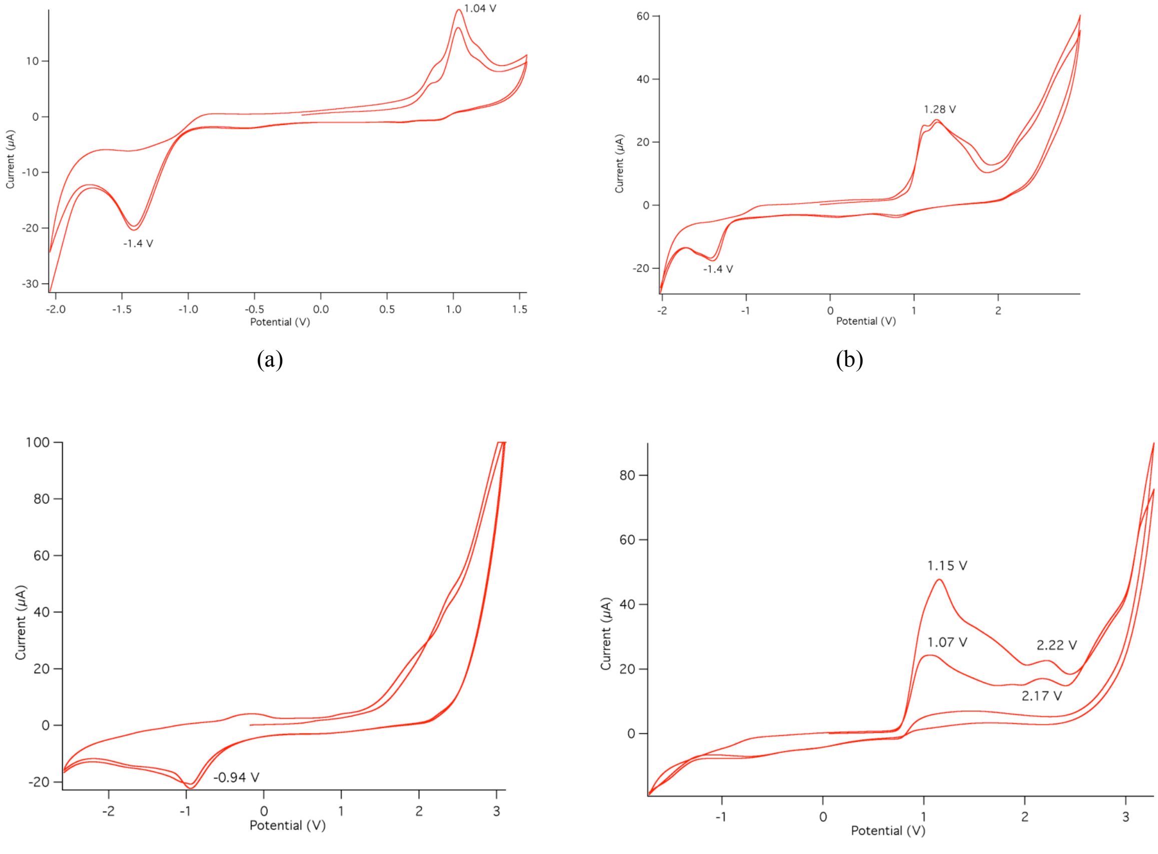


Figure S5. UV-Vis Spectra of monomer **1d**, polymer **A**, monomer **2c** and polymer **D**.

Cyclic Voltammetric traces of selected examples are shown in **Figure S6**. All traces show an electrochemically irreversible behaviour.



(a) (b)

(c) (d)

Figure S6. (a) Cyclic voltamogram of monomer **1d**, (b) Polymer **A**, (c) monomer **2c** and (d) Polymer **D**.

Size exclusion chromatography (SEC) traces of the polymers **A-D** are shown below.

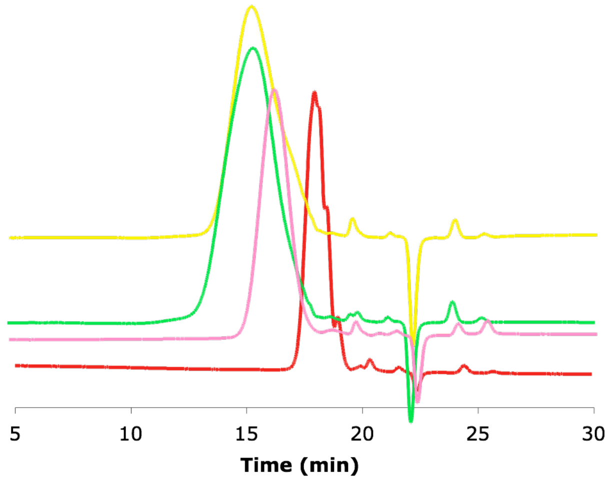


Figure S7. Stack plot of SEC traces of polymers **A-D** (red – Polymer **A**, green – Polymer **B**, yellow – Polymer **C**, pink - Polymer **D**).

V. Proton NMR spectra of new compounds:

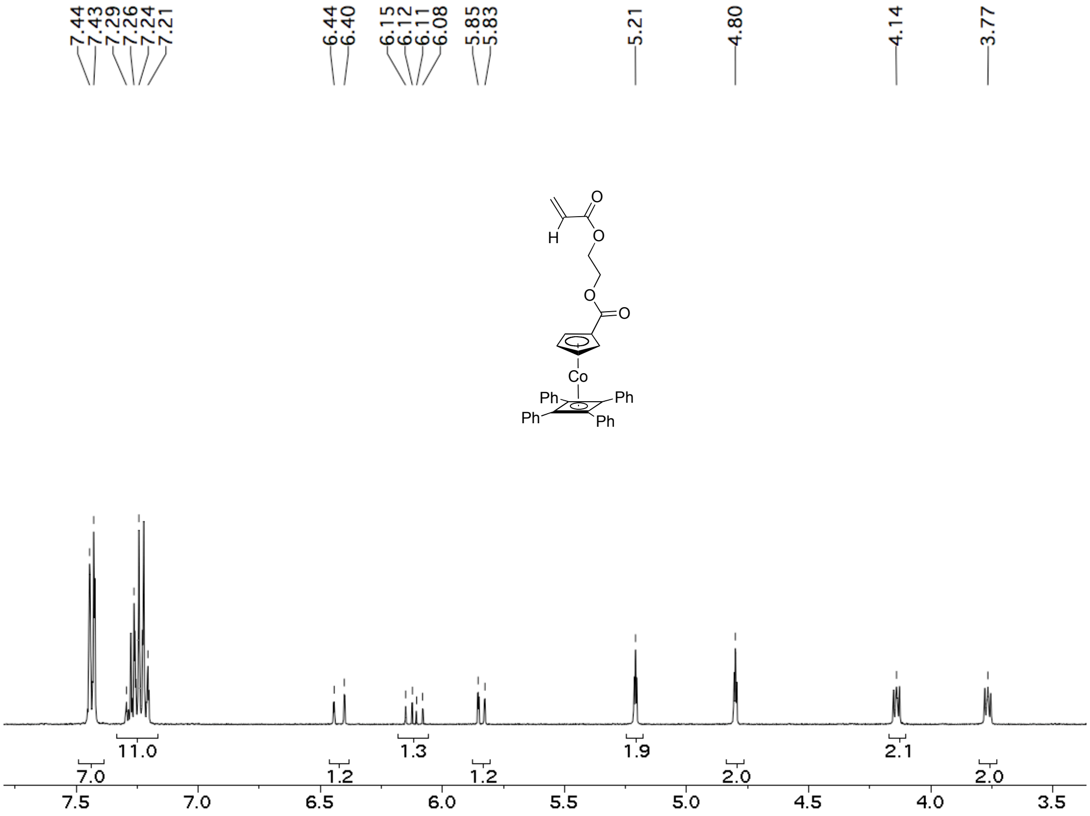


Figure S8. ^{1}H NMR spectra of **1d**.

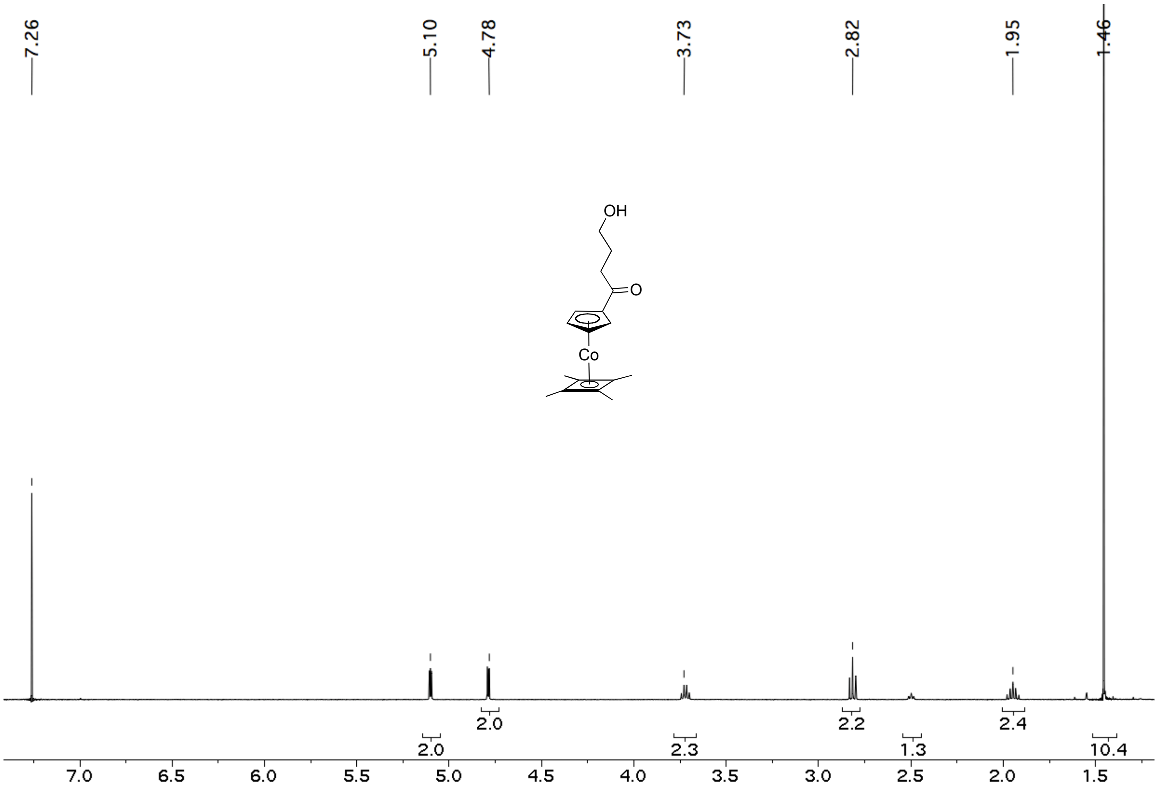


Figure S9. ^{1}H NMR spectra of **2a**.

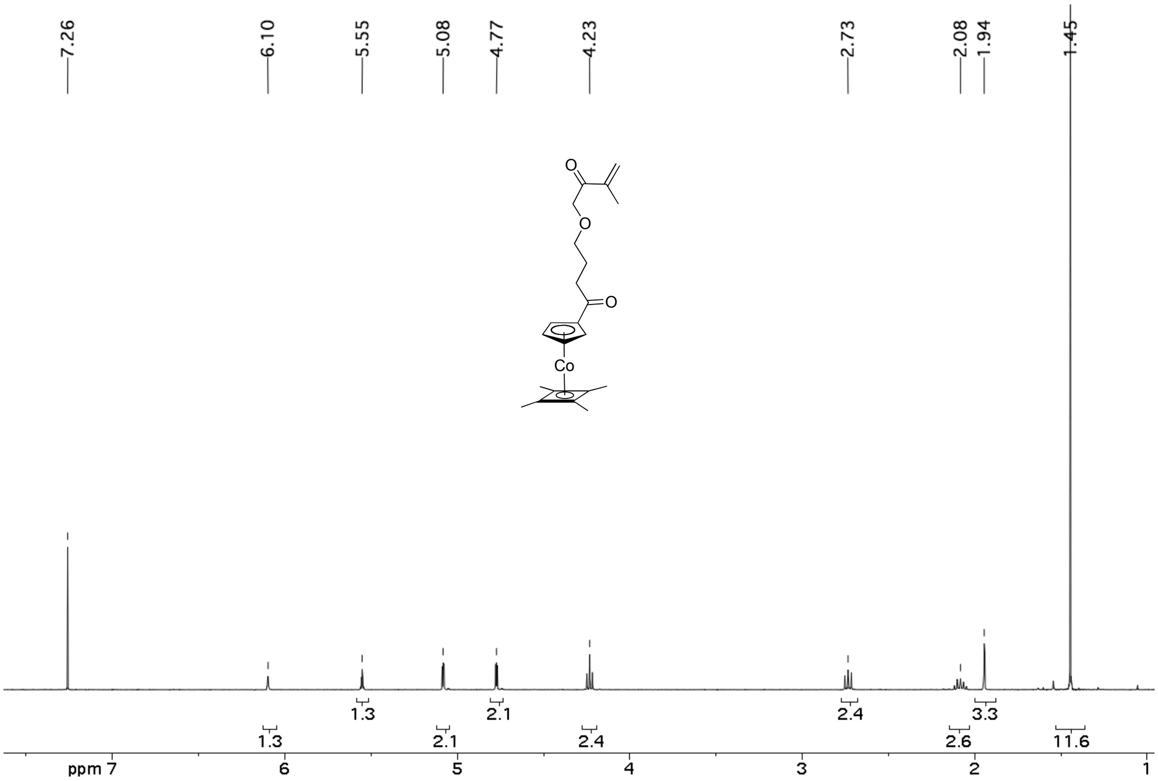


Figure S10. ^{1}H NMR spectra of **2b**.

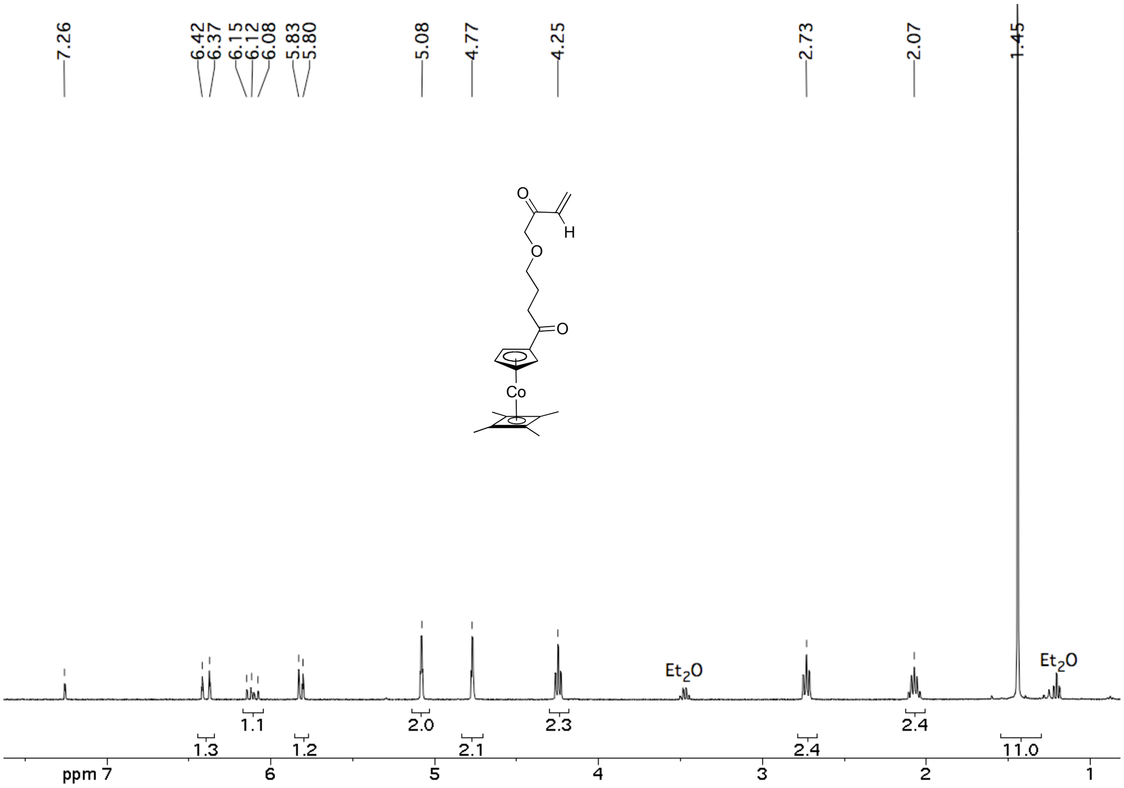


Figure S11. ^{1}H NMR spectra of **2c**.

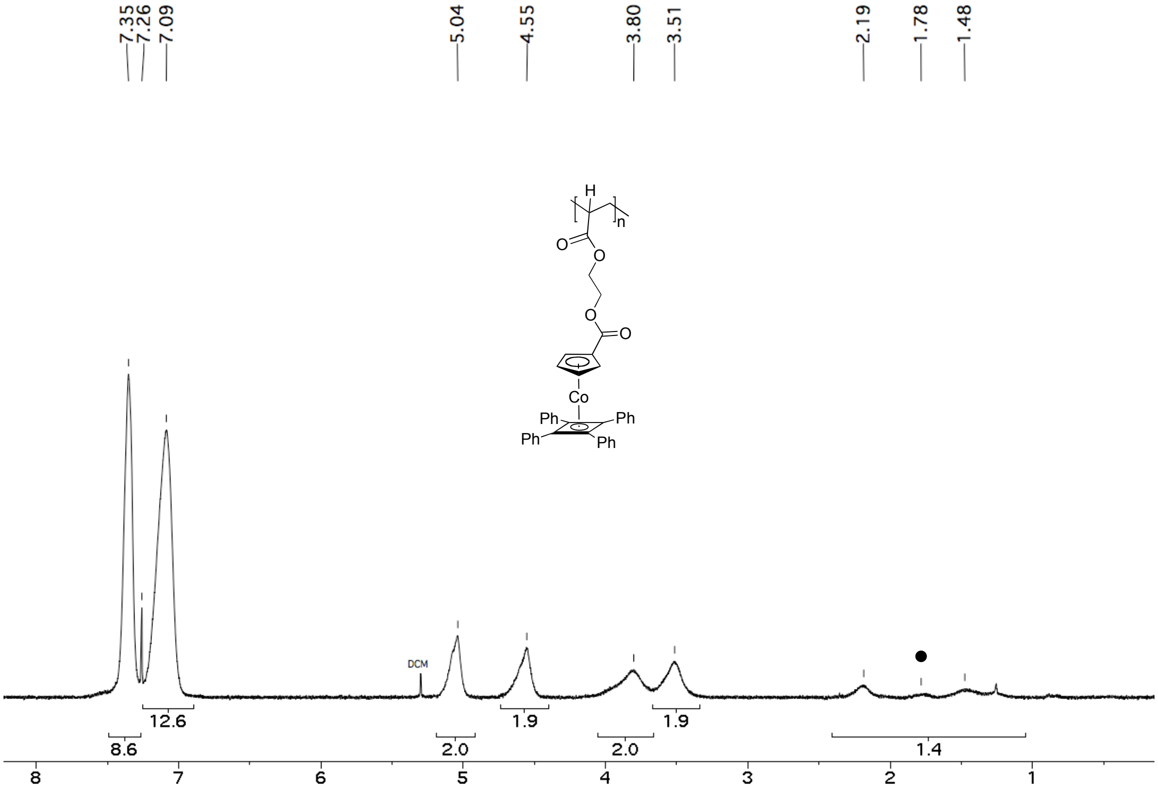


Figure S12. ^{1}H NMR spectra of **Polymers A-C**. ● denotes -CH-CH_2- protons in the polymer backbone. The integration is less than the expected value of 3 due to the broadening.

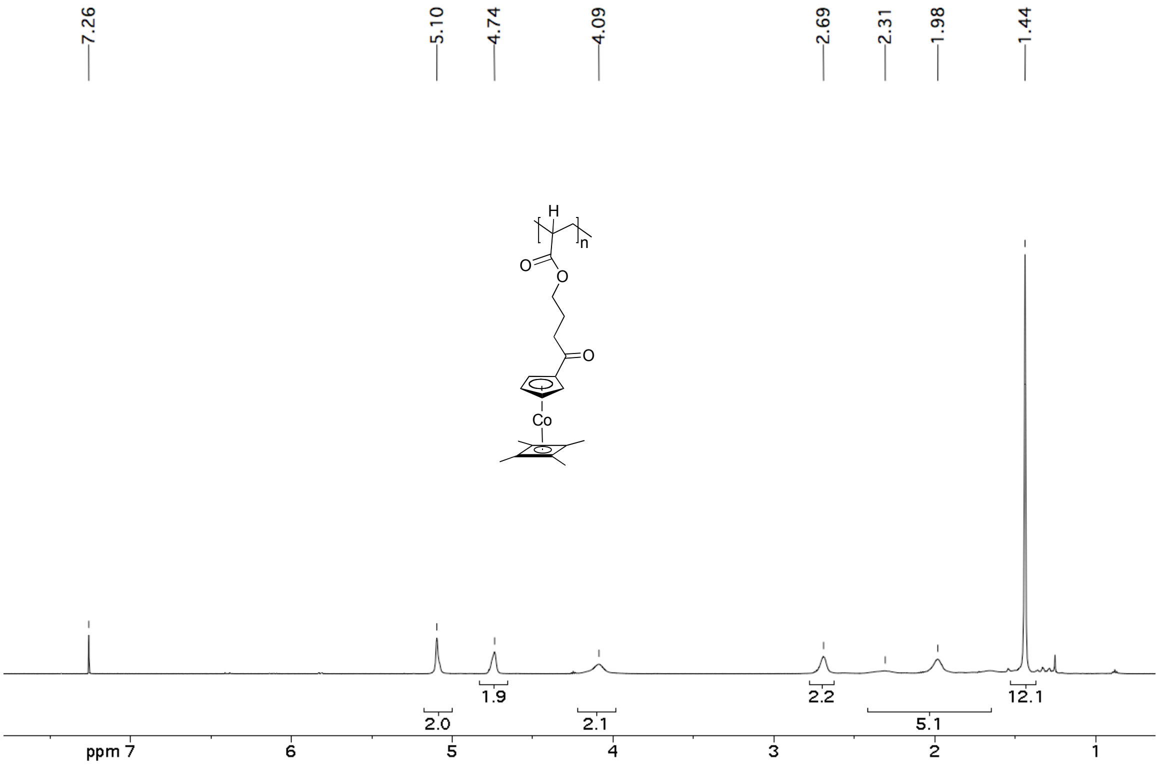


Figure S13. ^{1}H NMR spectra of **Polymer D**.

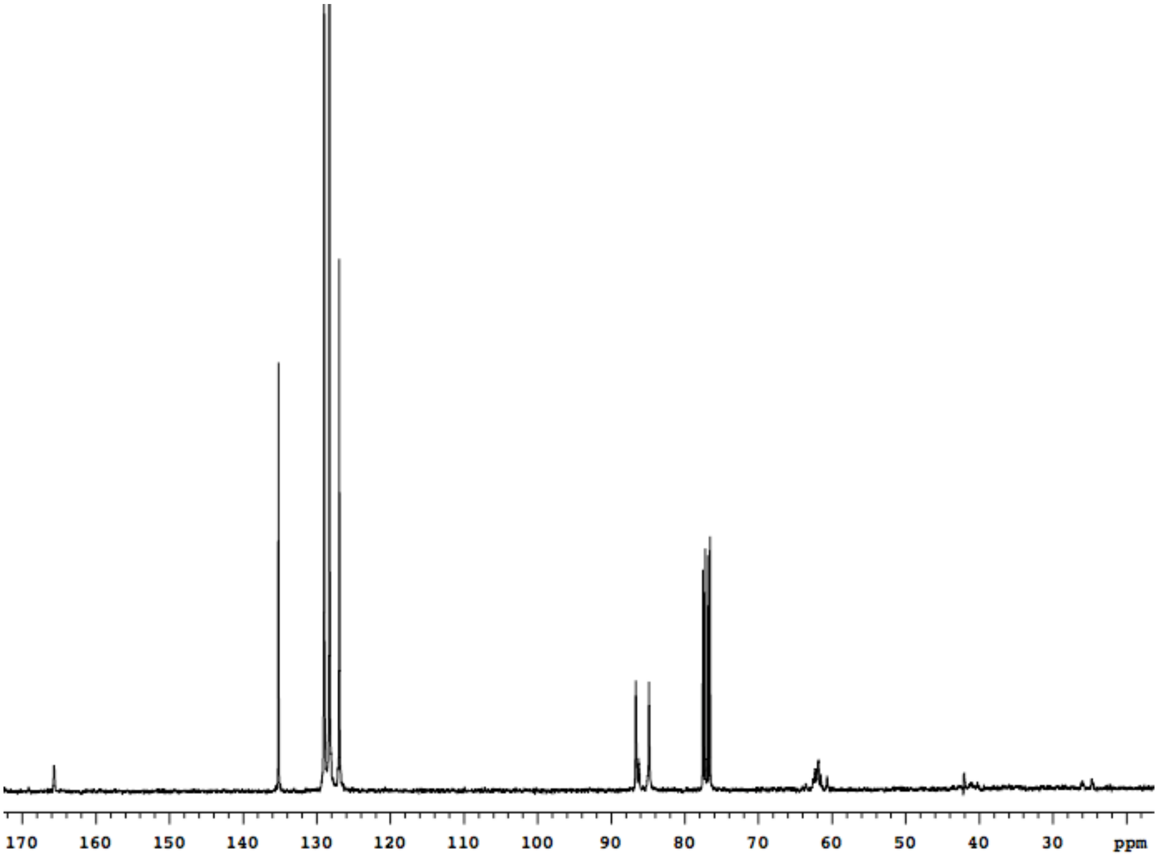


Figure S14. ^{13}C NMR spectra of **Polymers A-C**.

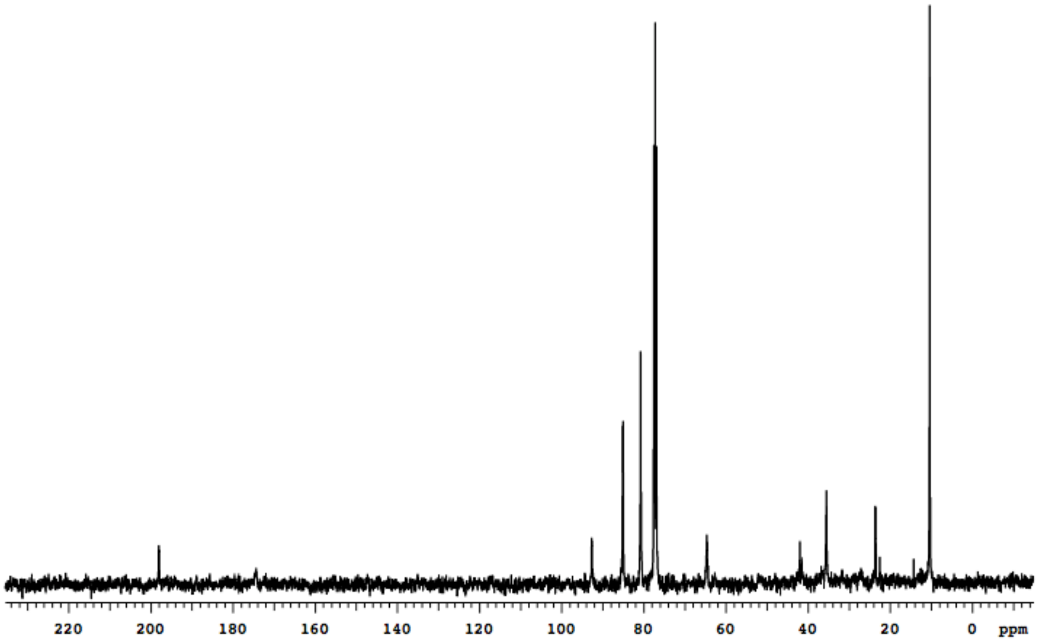


Figure S15. ^{13}C NMR spectra of **Polymer D**.

VI. Crystal data for compounds 2c

Empirical formula	**$C_{20}H_{25}CoO_3$ (2c)**
Formula weight	372.33
Crystal system	Triclinic
Space group	P-1
a (Å)	8.3122(4)
b (Å)	10.9110(5)
c (Å)	11.2874(5)
α (deg)	82.551(2)
β (deg)	68.949(2)
γ (deg)	75.849(3)
V (Å^3)	925.40(7)
Z	2
D_c (Mg m^{-3})	1.336
μ (mm^{-1})	0.941
Observed reflections	38362
Independent reflections	5983 (R_{int} = 0.0737)
Data-restraints-parameters	5983/0/225
Temp (K)	150(2)
R [I>2σ(I)]	0.0428, $wR_2(F^2)$ = 0.0819
R_1 (all data)	0.0776, wR_2 (all data) = 0.0941
CCDC	812213

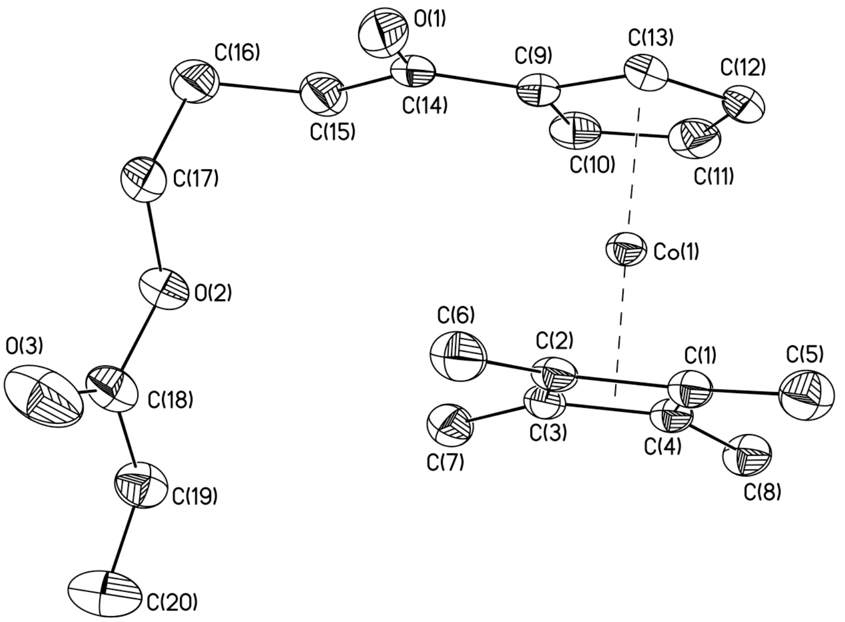


Figure S16. Solid-state structure of compound **2c**. Ellipsoids are drawn to 50% probability and hydrogen atoms are omitted for clarity. Co-Cb = 1.973(2) – 1.987(2) Å, Co-Cb$_{\text{(centroid)}}$ = 1.692 Å, Co-Cp = 2.054(2) – 2.098(2) Å, Co-Cp$_{\text{(centroid)}}$ = 1.682 Å, Cp$_{\text{(centroid)}}$Co-Cb$_{\text{(centroid)}}$ = 179.0º, C(14)-O(1) = 1.221(3) Å, C(18)-O(2) = 1.343(3) Å, C(18)-O(3) = 1.203(3) Å, O(2)-C(18)-O(3) = 123.4(2)º, C(19)-C(20) = 1.316(3) Å.

VII. References:

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7. The lithium salt generated ($LiC_5H_4CO(CH_2)_3OH$) could not be generated in a pure form as compared with the reported Na salt and thereofore, a 5 fold excess was used. Use of $NaC_5H_4CO(CH_2)_3OH$ resulted in reduced selectivity for the formation of the alcohol and other byproducts were generated which were very difficult to separate from the desired compound. So, use of the lithium salt is the more preferred route.

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