Supporting information

Experimental Section

Materials and methods

All solvents and reagents were purchased from Alfa Aesar, Sigma Aldrich, Fisher Scientific, ABCR and used as received unless otherwise stated. Deuterated solvents were purchased from Deutero GmbH, Kastellaun, Germany. Tetrahydrofuran (THF), *n*-hexane, and toluene were distilled from sodium/benzophenone. Cu^ICl and Cu^IBr were washed five times with glacial acetic acid and ethanol. Methyl methacrylate (MMA) was destabilized by passing through an Al_2O_3 column. MMA, *N,N,N',N*'-tetramethylethylendiamine (TMEDA), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), anisole, and 2-bromoisobutyric *tert*-butyl ester (*t*BbiB) were degassed and stored under an argon atmosphere or in a glovebox. All syntheses were carried out under an atmosphere of argon using Schlenk techniques or a glovebox. Tris(triphenylphosphine)cobaltchloride was synthesized from cobalt(II)chloride hexahydrate and triphenylphosphine on a 60 g scale (yield 80 %) as described elsewhere.[1]

Synthesis of (η^5-cyclopentadienyl-4-hydroxybutan-1-on)cobalt(η^4-tetraphenyl-cyclobutadiene)

In argon atmosphere, γ-butyrolactone (1.9 mL, 24.8 mmol) is added to a solution of cyclopentadienyl sodium (50.0 mL, 25 mmol, 0.5 M, CpNa) in THF over a time of 10 minutes. After stirring for 2 hours under reflux and cooling down to room temperature, neat toluene (100 mL), diphenylacetylene (8.9 g, 50.0 mmol) and *tris*(triphenylphosphine)cobaltchloride (18.8 g, 21.3 mmol) are added. The mixture is stirred for 24 hours under reflux, cooled down to room temperature and filtered. The filtered organic fraction is evaporated under reduced pressure and the residue is purified by column chromatography (*n*-hexane/THF 2/1). 5.41 g (45 %) of (η^5-cyclopentadienyl-4-hydroxybutan-1-on)cobalt(η^4-tetraphenyl-cyclobutadiene) is obtained as orange solid.
^{1}H NMR (300.0 MHz, $CDCl_3$) δ 7.45-7.40 (m, 8 H; Ph); 7.28-7.22 (m, 12 H; Ph); 5.25 (t, 2 H; Cp); 4.79 (t, 2 H; Cp); 3.41 (q, J = 6.0 Hz, 2 H; CH_2); 2.13 (t, J = 7.0 Hz, 2 H; CH_2); 1.97 (t, J = 6.0 Hz, 1 H; OH); 1.51-1.45 ppm (m, 2 H; CH_2)
^{13}C-NMR (75.44 MHz, $CDCl_3$) δ 199.60, 164.61, 135.21, 128.88, 128.37, 127.05, 87.80, 83.19, 62.63, 36.87, 26.58 ppm
ESI-MS [M-H$^+$] for $C_{37}H_{31}O_2Co$: calculated 566 g mol^{-1}, found 566 g mol^{-1}.

Synthesis of [η^5-(1-oxo-4-methacryloyloxy-butyl)-cyclo-pentadienyl]cobalt(η^4-tetraphenylcyclobutadiene) (CpCoCbMA)

Methacrylic acid (0.63 mL, 7.4 mmol), 4-(dimethylamino)pyridine (0.91 g, 7.4 mmol) and (η^5-cyclopentadienyl-4-hydroxybutane-1-on)cobalt(η^4-tetraphenyl-cyclobutadiene) (3.50 g, 6.2 mmol) are dissolved in dichloromethane (170 mL) and cooled with an ice bath. Over a time of 10 minutes, a solution of *N,N'*-dicyclohexylcarbodiimide (1.40 g, 6.8 mmol) in dichloromethane (20 mL) is added via syringe at 0°C. After stirring overnight at room temperature, the reaction mixture is concentrated under reduced pressure and the residue is purified via flash chromatography with an elution mixture consisting of *n*-hexane/ethyl acetate (10/1 per volume) yielding a yellow solid (2.50 g, 64 %).
^{1}H NMR (300.0 MHz, $CDCl_3$) δ 7.45-7.40 (m, 8 H; Ph); 7.29-7.21 (m, 12 H; Ph); 6.05 (bs, 1 H; $=CH_2$); 5.55-5.51 (m, 1 H; $=CH_2$); 5.24 (t, 2 H; Cp); 4.80 (t, 2 H; Cp); 3.92 (t, J = 7.0 Hz, 2 H; CH_2); 2.04 (t, J = 7.0 Hz, 2 H; CH_2); 1.92 (s, 3 H; CH_3); 1.60 ppm (p, J = 7.0 Hz, 2 H; CH_2)
^{13}C-NMR (75.44 MHz, $CDCl_3$) δ 197.94, 167.45, 135.22, 128.85, 128.36, 127.06, 125.43, 93.74, 87.54, 83.14, 64.24, 36.10, 22.80, 18.48 ppm
ESI-MS [M-H$^+$] for $C_{41}H_{35}O_3Co$: calculated 634 g mol^{-1}, found 634 g mol^{-1}.

Free radical polymerization of CpCoCbMA

The cobalt-containing methacrylate CpCoCbMA **5** (100 mg, 0.16 mmol, 1 equiv.) is dissolved in a solution of AIBN (0.016 mmol, 0.1 equiv.) in toluene (0.65 mL) and stirred at 60°C for 24 hours. The polymer is precipitated by pouring the solution into 25 mL methanol, collected by centrifugation, dissolved in DCM and precipitated in methanol again. The obtained polymer is dried in vacuum yielding a yellow solid (10 mg, 10 %).
M_n: 8900 g mol^{-1}, M_w: 18600 g mol^{-1} (SEC vs. PS standards)
PDI: 2.09
M_w: 56000 g mol^{-1} (SEC-MALLS)

^{1}H NMR (300.0 MHz, $CDCl_3$) δ 7.35 (b, 8 H; Ph); 7.12 (b, 12 H; Ph); 5.11 (b, 2 H; Cp); 4.61 (b, 2 H; Cp); 3.60 (b, 2 H; CH_2); 1.88 (b, 2 H; CH_2); 1.42 (b, 2 H; CH_2); 0.78 ppm (b, 3 H; α-CH_3)

Free radical copolymerization of CpCoCbMA with methyl methacrylate

The cobalt-containing methacrylate **5** (100 mg, 0.16 mmol) and methyl methacrylate (80 mg, 0.80 mmol) are dissolved in a solution of AIBN (0.016 mmol, 0.1 equiv. with respect to **5**) in toluene (0.65 mL) and stirred for 24 hours at 60°C. The polymer was precipitated in 25 mL methanol, collected by centrifugation, dissolved in DCM and precipitated in methanol again. The obtained polymer was dried in vacuum (70 mg, 39 %).
M_n: 13100 g mol^{-1}, M_w: 25700 g mol^{-1} (SEC vs. PS standards)
PDI:1.96
^{1}H NMR (300.0 MHz, $CDCl_3$) 7.40 (b, 8 H; Ph); 7.25 (b, 12 H; Ph); 5.27 (b, 2 H; Cp); 4.79 (b, 2 H; Cp); 3.66 (b, 2 H; CH_2); 3.59 (b, 3 H; OCH_3); 2.00-0.84 Alkyl/Backbone.

Atom Transfer Radical Polymerization (ATRP) of CpCoCbMA

Exemplary synthesis of poly(CpCoCbMA) featuring a molar mass of 5800 g mol^{-1} (M_w)

In an argon atmosphere the cobalt-containing methacrylate **5** (300 mg, 0.48 mmol) and 2-bromo*iso*butyric *tert*-butyl ester (7.7 µL, 0.04 mmol) are dissolved in degassed anisole (0.32 mL) and heated to 80°C. The polymerization is initiated by adding a solution of [Cu^I(PMDETA)Br] (0.2 M, 0.24 mL, 0.048 mmol in anisole) via syringe. After 4 days of reaction time, the solution is cooled and passed through an Al_2O_3 column to remove the copper catalyst. The polymer is precipitated by repeated pouring in a ten-fold excess of methanol, collected and dried in vacuum (117 mg, 39 %).
M_n: 4600 g mol^{-1}, M_w: 5800 g mol^{-1} (SEC vs. PS standards)
PDI: 1.26
M_w: 12800 g mol^{-1} (SEC-MALLS)

Block Copolymerization by ATRP of MMA and CpCoCbMA

Exemplary synthesis of PMMA-b-PCpCoCbMA featuring a molar mass of 30.1 kg mol^{-1} (weight ratio PMMA/PCpCoCbMA is 73/27) (block 1):

In an argon atmosphere methyl methacrylate (2500 mg, 24.97 mmol, MMA) and 2-bromo*iso*butyric *tert*-butyl ester (15 µL, 0.08 mmol) are dissolved in degassed anisole (2.7 mL) and heated up to 88°C. The polymerization is initiated by adding a solution of [$Cu^I(TMEDA)_2Br$] (0.2 M, 0.4 mL, 0.08 mmol in anisole) by syringe. After 3.5 hours of reaction time, the solution is cooled in an ice bath and passed through an Al_2O_3 column to remove the copper catalyst. The polymer is precipitated in 50 mL *n* hexane, collected and dried in vacuum (1125 mg, 45 %). In an argon atmosphere PMMA-macroinitiator (437 mg, 0.022 mmol) and the cobalt-containing methacrylate **5** (163 mg, 0.26 mmol) are dissolved in degassed anisole (2 mL) and heated up to 80°C. The polymerization was initiated by adding a solution of [$Cu^I(PMDETA)_2Br$] (0.2 M, 0.2 mL, 0.04 mmol in anisole) by syringe. After 5 days of reaction time, the solution is passed through an Al_2O_3 column to remove the copper catalyst. The polymer is precipitated in methanol, collected and dried in vacuum (433 mg, 72 %).

Exemplary synthesis of PMMA-b-PCpCoCbMA featuring a molar mass of 15 kg mol^{-1} (weight ratio PMMA/PCpCoCb is 57/43) (block 2)

In an argon atmosphere methyl methacrylate (1970 mg, 19.68 mmol, MMA) and 2-bromo*iso*butyric *tert*-butyl ester (15 µL, 0.08 mmol) are dissolved in degassed anisole (2 mL) and heated up to 88°C. The polymerization is initiated by adding a solution of [$Cu^I(TMEDA)_2Br$] (0.2 M, 0.8 mL, 0.16 mmol in anisole) by syringe. After 2 hours of reaction time, the solution is cooled in an ice bath and passed through an Al_2O_3 column to remove the copper catalyst. The polymer is precipitated in 50 mL *n*-hexane, collected and dried in vacuum (952 mg, 48 %). In an argon atmosphere PMMA-macroinitiator (340 mg, 0.036 mmol) and the cobalt-containing methacrylate **5** (267 mg, 0.42 mmol) are dissolved in degassed anisole (2 mL) and heated up to 80°C. The polymerization was initiated by adding a solution of [$Cu^I(PMDETA)_2Br$] (0.2 M, 0.36 mL, 0.072 mmol in anisole) by syringe. After 5 days of reaction time, the solution is passed through an Al_2O_3 column to remove the copper catalyst. The polymer is precipitated in methanol, collected and dried in vacuum (362 mg, 60 %).

TEM sample preparation for PMMA-*block*-PCpCoCbMA (block 1) for chemical oxidation and reduction

PMMA-*b*-P(CpCoCb)MA (block 1; 1 mg, 4.0 mmol Co units) is dissolved in filtered $CHCl_3$ (1 mL). A yellow solution is obtained that is utilized for characterization in TEM by adding a drop on a carbon-coated copper grid followed by drying under ambient conditions. In order to oxidize the cobalt-containing block copolymer, PMMA-*b*-PCpCoCbMA (block 1; 10 mg, 4.0 mmol Co units) and $NOBF_4$ (0.5 mg, 4.3 mmol) are dissolved in filtered $CHCl_3$ (0.67 mL) and stirred for 24 h. For TEM investigations, the solution was diluted with the 5-fold volume of filtered chloroform and drop-casted on a carbon-coated copper grid, followed by drying.

For reduction of PMMA-*b*-PCpCoCbMA (block 1; 10 mg, 4.0 mmol Co units), decamethylcobaltocene (1.4 mg, 4.3 mmol, Cp^*_2Co) is dissolved in filtered $CHCl_3$ (0.67 mL) and stirred for 24 h. For TEM investigations, the solution was diluted with the 5-fold volume of filtered chloroform and drop-casted on a carbon-coated copper grid, followed by drying.

Characterization

NMR spectra were recorded on a Bruker DRX 500 NMR or on a Bruker DRX 300 spectrometer working at 500 MHz or 300 MHz. NMR chemical shifts are referenced relative to tetramethylsilane or the used deuterated solvent. Electro spray ionization mass spectrometry (ESI-MS) experiments were carried out with an **Esquire LC in a molar mass range of** 40-2200 u using a quadrupole ion trap as analyzer. Standard SEC was performed with THF as the mobile phase (flow rate 1 mL min^{-1}) on a SDV column set from PSS (SDV 1000, SDV 100000, SDV 1000000) at 30°C. Calibration was carried out using PS standards (from Polymer Standard Service, Mainz). For the SEC-MALLS experiments, a system composed of a Waters 515 pump (Waters, Milford, CT), a TSP AS100 autosampler, a Waters column oven, a Waters 486 UV detector operating at 254 nm, a Waters 410 RI-detector, and a DAWN DSP lightscattering detector (Wyatt Technology, Santa Barbara, CA) was used. For data acquisition and evaluation of the light-scattering experiments, Astra version 4.73 (Wyatt Technology, Santa Barbara, CA) was used. The light-scattering instrument was calibrated using pure toluene, assuming a Rayleigh ratio of 9.7810^{-6} cm^{-1} at 690 nm. An injection volume of 118 μL, a sample concentration of 1-2 g L^{-1}, a column temperature of 35 °C, and a THF flow rate of 1 mL min^{-1} have been applied. SEC analysis was performed on a high resolution column set from PSS (SDV 5 μm 10^6 Å, SDV 5 μm 10^5 Å, SDV 5 μm 1000 Å). TEM experiments were carried out on a Zeiss EM 10 electron microscope operating at 60 kV. All shown images were recorded with a slow-scan CCD camera obtained from TRS (Tröndle) in bright field mode. Camera control was computer-aided using the ImageSP software from TRS. For TGA, a Mettler TGA1 was used in the temperature range from 35°C to 800°C with a heating rate of 10 K min^{-1} under oxygen or nitrogen atmosphere. WAXS measurements were conducted using a Stoe Stadi P with Ge_{111} as monochromator and a wavelength of $Mo_{K,\alpha}$=0.7093 Å. A PSD Klein detector was used. For a qualitative analysis the programm Match! from Crystal Impact was used. The corresponding structures were taken from Crystallography Open Database. A quantitative analysis was partially performed by the program Full-Prof using the Rietveld refinement algorithm. Thermal properties of the polymers were characterized using a differential scanning calorimeter (DSC) (Mettler Toledo DSC-1) in the temperature range from -110°C to 220°C with a heating rate of 10 K min^{-1}. Micro-Raman spectra (10 scans, each scan lasting 3 s) were recorded with a Horiba HR800 micro-Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany) equipped with an Ar laser (wavelength 514.5 nm). The excitation line has its own interference filter (to filter out the plasma emission) and a Raman notch filter (for laser light rejection). The measurements were performed by using a grating of 1800 g mm^{-1} and a confocal microscope (magnification 100×, NA 0.5) with a 100 μm aperture, giving a resolution of 2–4 μm. The laser power (20 mW) was attenuated by using neutral density (ND) filters; thus, the power on the sample was in the range of 2 mW 20 μW. Magnetic properties of the cobalt-containing polymethacrylates after thermal treatment were characterized with a SQUID magnetometer from Quantum Design. Samples were placed in a gelatin capsule and brought into the magnetic field with a carbon straw positioning system. The measurements were done in a helium cooled dewar within a temperature range from 5K to 300K at an applied field of 1000 Oersted (Oe) after an equilibration time of 10 min. The temperature dependent susceptibility was measured with a cooling rate of 2.5 K min^{-1}. Cyclic voltammetry (CV) was carried out in dichloromethane (DCM) or acetontrile with tetrabutylammonium hexafluorophosphate (TBAHFP) as electrolyte (0.1 M). Ag/AgCl reference electrode, a glass/carbon electrode as working electrode, and a Pt counter electrode were chosen and a scan rate of 20 mV s^{-1} or 100 mV s^{-1} in a range of -2 to 0 V and 0 to +1.7 V was applied.

References

1 Y. Watatsuki and H. Yamazaki, *Inorg. Synth.*, 1989, **26**, 189–200.

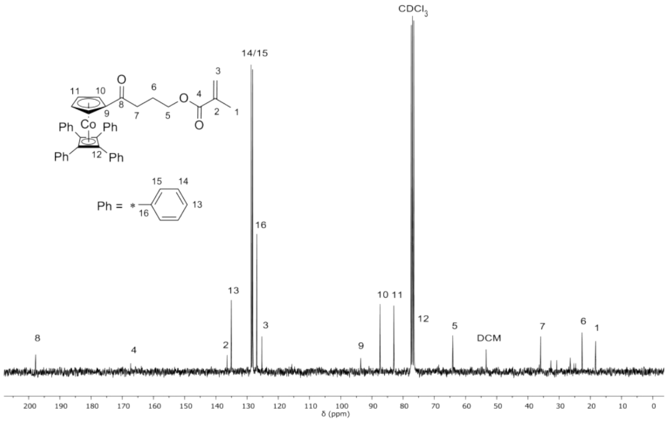

Fig. S1 ^{13}C NMR spectrum of [η5-(1-carboxy-propylmethacrylate)-cyclo-pentadienyl]cobalt(η4-tetra-phenyl-cyclobutadiene) **5** (CpCoCbMA) and signal assignment.

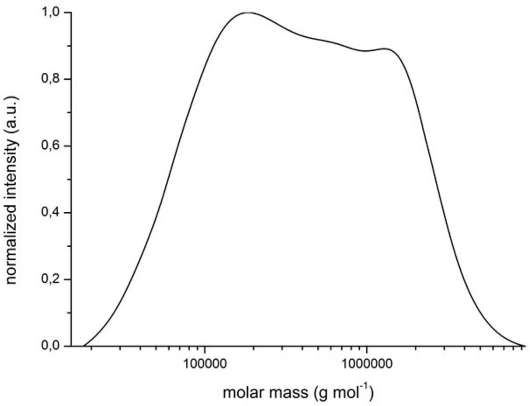

Fig. S2 Molecular weight distribution of poly(CpCoCbMA) homopolymer in THF obtained after thermal polymerization. Obtained values were calibrated against PS as standards.

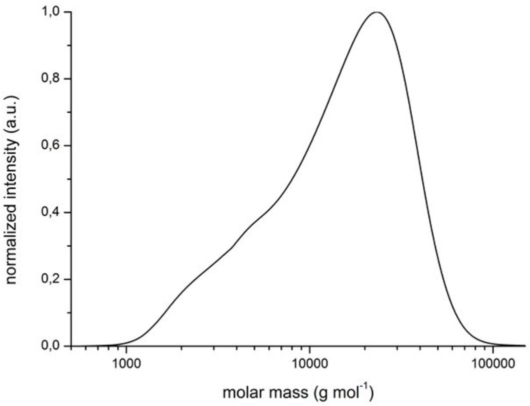

Fig. S3 Molecular weight distribution of poly(CpCoCbMA) homo polymer in THF obtained after free radical polymerization. Obtained values were calibrated against PS as standards.

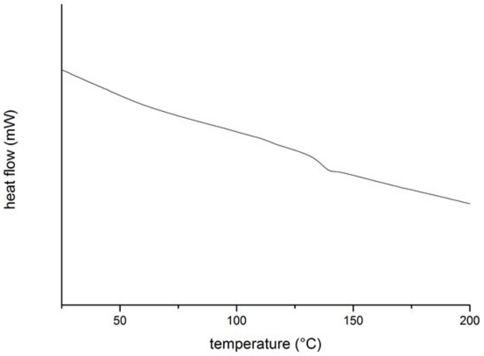

Fig. S4 DSC thermogram on poly(CpCoCbMA) homo polymer obtained by free radical polymerization (heat rate 10 K min^{-1}). The glass transition temperature, T_g, of poly(CpCoCbMA) was determined to be 137°C

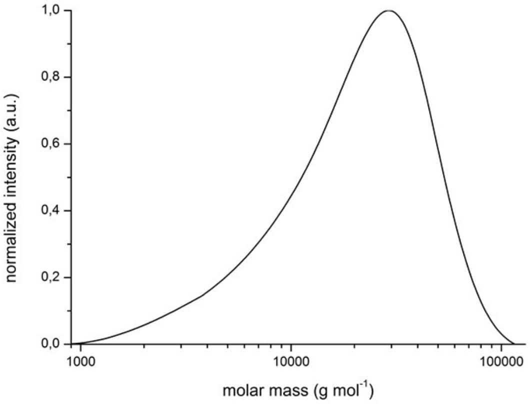

Fig. S5 Molecular weight distribution of poly(CpCoCbMA-*co*-MMA) copolymer in THF obtained by free radical polymerization of CpCoCbMA and MMA. Obtained values were calibrated against PS as standards.

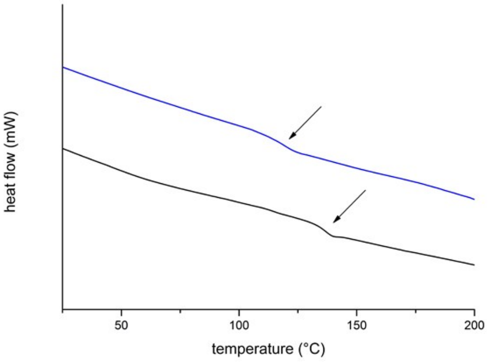

Fig. S6 DSC thermogram on poly(CpCoCbMA-*co*-MMA) copolymer obtained after free radical copolymerization of CpCoCbMA **5** and MMA (heat rate 10 K min^{-1}) (blue line). For comparison, the corresponding poly(CpCoCbMA) homopolymer is given below (black line).

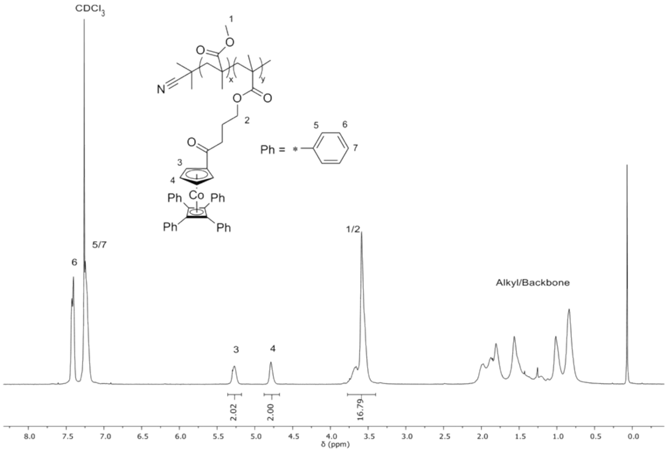

Fig. S7 ^{1}H NMR spectrum in $CDCl_3$ of poly(CpCoCbMA-*co*-MMA) copolymer obtained by free radical copolymerization of CpCoCbMA **5** and MMA.

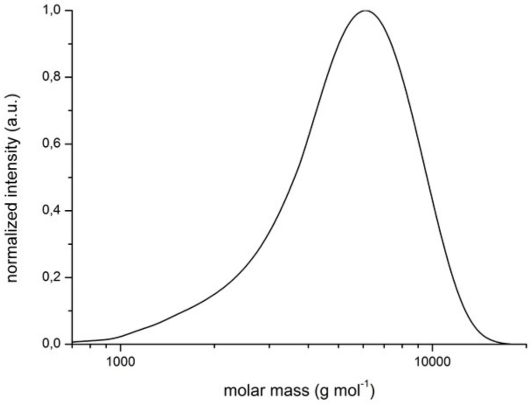

Fig. S8 Molecular weight distribution of poly(CpCoCbMA) in THF obtained by ATRP. Obtained values were calibrated against PS as standards.

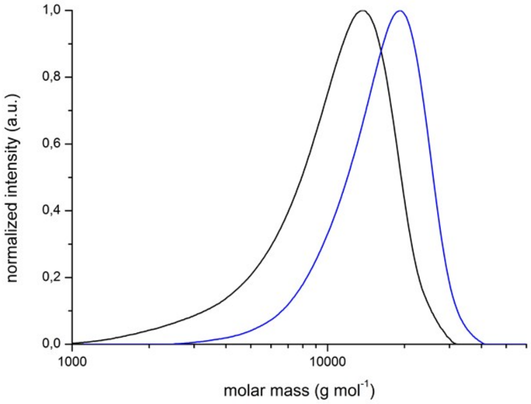

Fig. S9 Molecular weight distribution of poly(CpCoCbMA-*block*-MMA) (blue curve, block 2) in THF obtained by ATRP of PMMA-Br macro initiator (black curve) with CpCoCbMA. Obtained values were calibrated against PS as standards.

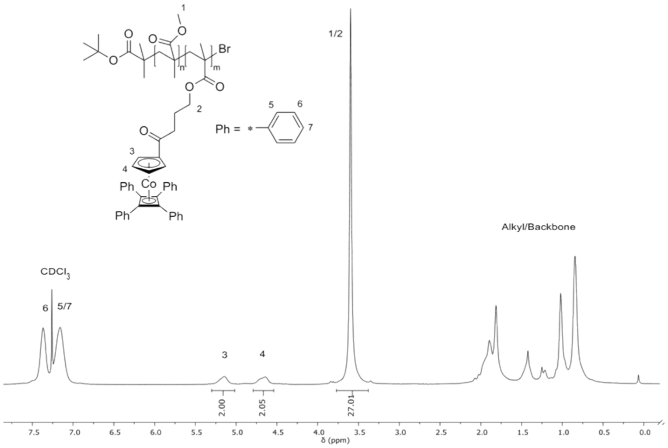

Fig. S10 ^{1}H NMR spectrum in $CDCl_3$ of poly(CpCoCbMA-*block*-MMA) (block 1 corresponding to Table 2).

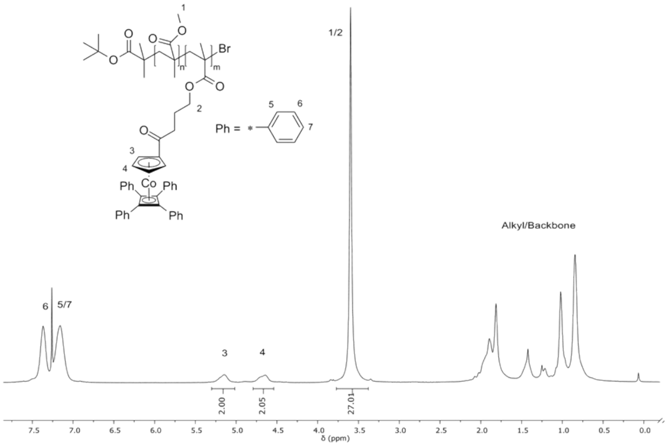

Fig. S11 ^{1}H NMR spectrum in $CDCl_3$ of poly(CpCoCbMA-*block*-MMA) (block 2 corresponding to Table 2).

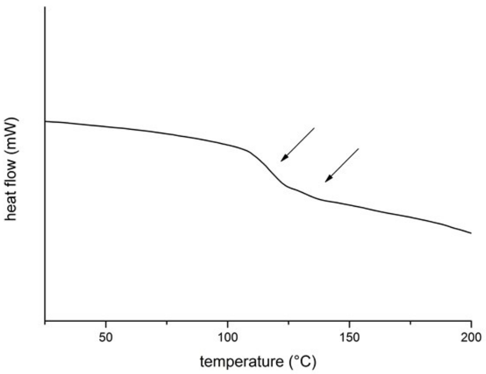

Fig. S12 DSC thermogram on poly(CpCoCbMA-*block*-MMA) (block 1 corresponding to Table 2) obtained by sequential ATRP using a PMMA-Br macro initiator and CpCoCbMA **5** as second monomer (heat rate 10 K min^{-1}). The arrows indicate glass transition temperatures T_g at 116°C and 134°C, which can be assigned to PMMA and PCpCoCbMA, respectively.

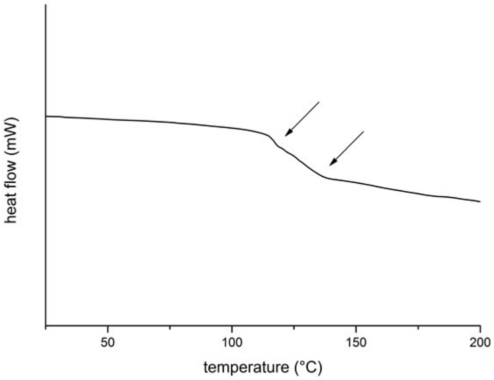

Fig. S13 DSC thermogram on poly(CpCoCbMA-*block*-MMA) (block 2, corresponding to Table 2) obtained by sequential ATRP using a PMMA-Br macro initiator and CpCoCbMA **5** as second monomer (heat rate 10 K min^{-1}). The arrows indicate glass transition temperatures T_g at 116°C and 133°C which can be assigned to PMMA and PCpCoCbMA, respectively.

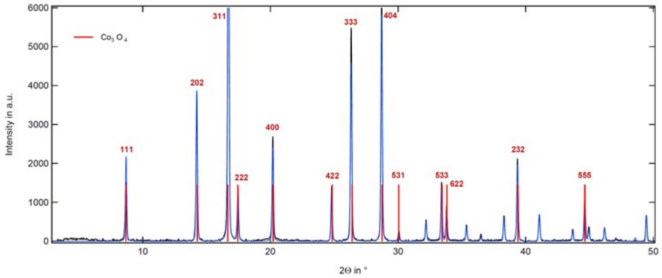

Fig. S14 XRD pattern on the magnetic material obtained by thermal treatment of poly(CpCoCbMA) samples in oxygen atmosphere at 800°C (see text)

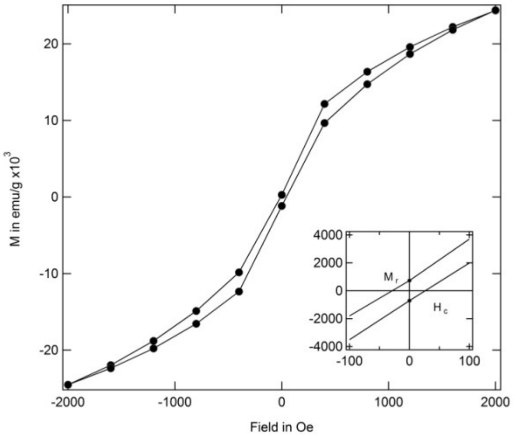

Fig. S15 Results on SQUID measurements on the ferromagnetic susceptibility of the cobalt oxide sample as obtained by thermal treatment at 800°C in nitrogen atmosphere. The average remanence magnetisation was M_r = 722 emu g^{-1}. The corresponding coercive field featured a strength of H_c = 30 Oe for the upper and the lower curve. Due to the high single strength, a saturation magnetisation could not be determined

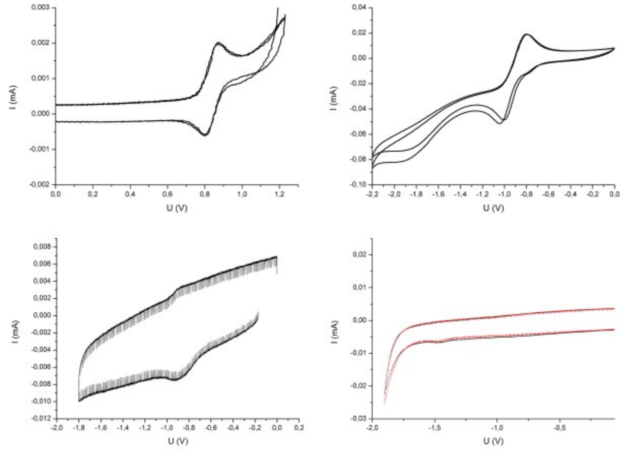

Fig. S16: CV curves of: CpCoCb in 0.1 M TBAHFP in CH_2Cl_2 (top left), CpCoCb in 0.1 M TBAHFP in MeCN solution (middle right), CpCoCbMA in 0.1 M TBAHFP in CH_2Cl_2 (bottom left) and poly(CpCoCbMA) in 0.1 M TBAHFP in CH_2Cl_2 (bottom right).