*Supporting information for*

# Bis(formylpyrrolyl) cobalt complexes as mediators in the Reversible-Deactivation Radical Polymerization of styrene and methyl methacrylate

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# Polymerization reaction data

**Table S1** Polymerization data for the system mediated by **1**/tBiB-Br. $V_{monomer}$:$V_{toluene}$=5:5 mL.

| Monomer | $[M]_0$:[1]:[tBiB-Br] | T (°C) | t (min) | Conv. | $\ln([M]_0/[M])$ | $M_n$ (g/mol) | Đ | $k_p' \times 10^5$ ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| MMA | 500:1:1 | 90 | 20 | 0.487 | 0.667 | 4900 | 1.55 | 18±4 |
| | | | 40 | 0.509 | 0.712 | 6300 | 1.44 | |
| | | | 60 | 0.631 | 0.998 | 6800 | 1.45 | |
| | | | 80 | 0.722 | 1.28 | 6600 | 1.42 | |
| | | | 100 | 0.672 | 1.11 | 7000 | 1.45 | |
| | | 70 | 60 | 0.398 | 0.508 | 6200 | 1.44 | 15±1 |
| | | | 120 | 0.677 | 1.13 | 5100 | 1.57 | |
| | | | 180 | 0.805 | 1.63 | 5500 | 1.47 | |
| | | 50 | 90 | 0.219 | 0.247 | 7800 | 1.49 | 4.0±0.7 |
| | | | 150 | 0.302 | 0.36 | 9200 | 1.65 | |
| | | | 180 | 0.39 | 0.494 | 8300 | 1.43 | |
| | | | 240 | 0.402 | 0.514 | 10700 | 1.58 | |
| | | | 300 | 0.388 | 0.492 | 11700 | 1.56 | |
| | | 25 | 120 | 0.191 | 0.212 | - | - | 2.4±0.2 |
| | | | 240 | 0.282 | 0.331 | - | - | |
| | | | 360 | 0.411 | 0.529 | - | - | |
| | 1000:1:1 | 90 | 120 | 0.649 | 1.04 | 7600 | 1.35 | 12±2 |
| | | | 180 | 0.695 | 1.18 | 6700 | 1.58 | |
| | | | 240 | 0.55 | 0.8 | 9800 | 1.37 | |
| Sty | 500:1:1 | 90 | 120 | 0.345 | 0.414 | 25600 | 1.35 | 11±2 |
| | | | 180 | 0.339 | 0.428 | 31300 | 1.48 | |
| | | | 240 | 0.348 | 0.49 | 33600 | 1.76 | |
| | | | 300 | 0.387 | 0.235 | 40500 | 1.73 | |
| | | 70 | 120 | 0.108 | 0.114 | 8000 | 1.44 | 3.7±0.5 |
| | | | 240 | 0.197 | 0.22 | 12300 | 1.28 | |
| | | | 360 | 0.255 | 0.295 | 13100 | 1.40 | |
| | | | 480 | 0.258 | 0.298 | 17900 | | |
| | | | 600 | 0.318 | 0.383 | 20200 | 1.30 | |
| | | 50 | 120 | 0.079 | 0.083 | - | - | 1.0±0.1 |
| | | | 240 | 0.103 | 0.109 | 8400 | 1.49 | |
| | | | 360 | 0.124 | 0.132 | 9800 | 1.46 | |
| | | | 480 | 0.125 | 0.134 | 10300 | 1.59 | |
| | | | 600 | 0.144 | 0.155 | 11600 | 1.62 | |
| MMA | 500:1:1 (Copolymerization reaction with PS-Br) | 50 | 90 | 0.066 | 0.068 | 10700 | 1.68 | 1.3±0.1 |
| | | | 150 | 0.110 | 0.117 | 11300 | 1.54 | |
| | | | 180 | 0.131 | 0.141 | 11600 | 1.47 | |
| | | | 240 | 0.174 | 0.192 | 12100 | 1.43 | |
| | | | 300 | 0.128 | 0.137 | 12600 | 1.37 | |

**Table S2** Polymerization data for the system mediated by **1**/AIBN. $V_{monomer}$:$V_{toluene}$=5:5 mL.

| Monomer | T (ºC) | $[M]_0$:[1]:[AIBN] | t (min) | Conv. | $\ln([M]_0/[M])$ | $M_n$ (g/mol) | Đ | $k_p' \times 10^5$ ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| MMA | 50 | 500:1:1 | 90 | 0.041 | 0.042 | 8700 | 1.34 | 0.7±0.1 |
| | | | 180 | 0.062 | 0.064 | 12700 | 1.46 | |
| | | | 240 | 0.093 | 0.098 | 12900 | 1.54 | |
| | | | 300 | 0.113 | 0.120 | 13300 | 1.56 | |
| | | 500:1:0 | 90 | 0.052 | 0.054 | 278000 | 1.66 | 1.2±0.1 |
| | | | 180 | 0.095 | 0.100 | 270000 | 1.64 | |
| | | | 270 | 0.198 | 0.220 | 254000 | 1.68 | |
| | | | 360 | 0.247 | 0.284 | 248000 | 1.65 | |

**Table S3** Polymerization data for the system mediated by **2**. $V_{monomer}$:$V_{1,2\text{-dichloroethane}}$=5:10 mL.

| Monomer | $[M]_0$:[2] | T (ºC) | t (min) | Conv. | $\ln([M]_0/[M])$ | $M_n$ | Đ | $k_p' \times 10^5$ ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| MMA | 500:1 | 90 | 120 | 0.163 | 0.177 | 54100 | 1.64 | 2.4±0.1 |
| | | | 210 | 0.266 | 0.31 | 49500 | 1.63 | |
| | | | 300 | 0.357 | 0.442 | 46800 | 1.68 | |
| | | | 390 | 0.445 | 0.588 | 45800 | 1.68 | |
| | 1000:1 | 70 | 90 | 0.216 | 0.243 | 35500 | 1.73 | 2.9±0.4 |
| | | | 180 | 0.348 | 0.428 | 31200 | 1.93 | |
| | | | 270 | 0.472 | 0.639 | 32900 | 1.51 | |
| | | | 450 | 0.543 | 0.782 | 33600 | 1.74 | |
| | | 50 | 120 | 0.088 | 0.092 | 92300 | 2.07 | 1.7±0.1 |
| | | | 300 | 0.263 | 0.306 | 87100 | 1.93 | |
| | | | 390 | 0.336 | 0.409 | 85700 | 1.98 | |
| | | | 480 | 0.366 | 0.456 | 92600 | 1.81 | |
| | | | 180 | 0.143 | 0.154 | 109000 | 2.03 | |
| | | | 260 | 0.215 | 0.241 | 107000 | 2.05 | |
| | | | 360 | 0.264 | 0.308 | 123000 | 1.94 | |
| | | | 450 | 0.313 | 0.375 | 130000 | 1.94 | |
| Sty | 250:1 | 70 | 90 | 0.066 | 0.068 | 11500 | 1.54 | 1.2±0.1 |
| | | | 180 | 0.125 | 0.134 | 21700 | 1.59 | |
| | | | 270 | 0.167 | 0.182 | 29500 | 1.79 | |
| | | | 360 | 0.222 | 0.25 | 30500 | 2.00 | |
| | | | 450 | 0.296 | 0.351 | 31900 | 1.85 | |
| | 500:1 | | 90 | 0.045 | 0.046 | - | - | 0.84±0.06 |
| | | | 270 | 0.113 | 0.12 | 36400 | 1.66 | |
| | | | 360 | 0.153 | 0.166 | 43100 | 1.89 | |
| | | | 450 | 0.213 | 0.24 | 41100 | 1.98 | |
| | 1000:1 | | 90 | 0.045 | 0.046 | - | - | 1.3±0.2 |
| | | | 270 | 0.113 | 0.12 | 39100 | 1.70 | |
| | | | 360 | 0.153 | 0.166 | 42600 | 1.90 | |
| | | | 450 | 0.213 | 0.24 | 46300 | 2.01 | |

**Table S4** Polymerization data for the system mediated by **2**/AIBN. $V_{monomer}$:$V_{1,2\text{-dichloroethane}}$=5:10 mL.

| Monomer | $[M]_0$:[2]:[AIBN] | T (ºC) | t (min) | Conv. | $\ln([M]_0/[M])$ | $M_n$ (g/mol) | Đ | $k_p' \times 10^5$ ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| MMA | 500:1:0.5 | 90 | 90 | 0.132 | 0.142 | 68900 | 2.20 | 4.0±0.2 |
| | | | 180 | 0.285 | 0.335 | 49300 | 2.14 | |
| | | | 270 | 0.43 | 0.561 | 43100 | 2.23 | |
| | | | 360 | 0.565 | 0.833 | 41400 | 2.04 | |
| | | | 450 | 0.648 | 1.043 | 37500 | 2.09 | |
| | 1000:1:0.5 | 70 | 90 | 0.3 | 0.357 | 37800 | 1.58 | 7.6±0.3 |
| | | | 180 | 0.527 | 0.748 | 34100 | 1.59 | |
| | | | 270 | 0.7136 | 1.250 | 35500 | 1.55 | |
| | | | 360 | 0.798 | 1.599 | 35900 | 1.56 | |
| | | 50 | 90 | 0.071 | 0.074 | 135000 | 2.07 | 1,7±0.1 |
| | | | 180 | 0.175 | 0.192 | 106000 | 2.07 | |
| | | | 270 | 0.244 | 0.279 | 102000 | 1.99 | |
| | | | 360 | 0.297 | 0.353 | 96700 | 2.03 | |
| | | | 450 | 0.369 | 0.46 | 100000 | 1.97 | |
| | 2000:1:0.5 | 50 | 90 | 0.076 | 0.079 | 95100 | 2.17 | 1.3±0.1 |
| | | | 270 | 0.204 | 0.229 | 83500 | 2.01 | |
| | | | 360 | 0.234 | 0.266 | 80300 | 2.07 | |
| | | | 450 | 0.294 | 0.348 | 81200 | 2.13 | |
| Styrene | 250:1:0.5 | 70 | 90 | 0.173 | 0.19 | 13500 | 1.41 | 4.3±0.3 |
| | | | 270 | 0.465 | 0.625 | 19600 | 1.61 | |
| | | | 360 | 0.614 | 0.952 | 21200 | 1.66 | |
| | 500:1:0.5 | | 90 | 0.081 | 0.084 | 17100 | 1.62 | 0.84±0.06 |
| | | | 270 | 0.221 | 0.25 | 24800 | 1.64 | |
| | | | 360 | 0.306 | 0.366 | 26500 | 1.70 | |
| | | | 450 | 0.35 | 0.43 | 26900 | 1.69 | |

# Crystallographic data

**Table S5** Crystallographic data for complexes **2**, **3a** and **3b**.

| | **2** | **3a** | **3b** |
|---|---|---|---|
| Formula | $C_{16}H_{26}CoN_2O_2P_2Br{\cdot}H_2O$ | $C_{16}H_{26}BF_4CoN_2O_2P_2Br$ | $C_{41}H_{48}BCoN_2O_2P_2{\cdot}CH_2Cl_2$ |
| M | 497.18 | 486.07 | 803.39 |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 |
| T (K) | 150 | 150 | 150 |
| Crystal system | Orthorhombic | Monoclinic | Triclinic |
| Space group | $P2_12_12_1$ | C 2/c | P -1 |
| a (Å) | 12.521(3) | 20.429(8) | 11.2435(5) |
| b (Å) | 9.249(2) | 12.230(5) | 11.6245(5) |
| c (Å) | 18.569(4) | 10.184(4) | 16.9612(8) |
| α (Å) | 90 | 90 | 92.816(2) |
| β (Å) | 90 | 117.496(12) | 90.895(2) |
| γ (Å) | 90 | 90 | 112.274(2) |
| V ($Å^3$) | 2150.42 | 2257.03 | 2047.53 |
| Z | 4 | 4 | 2 |
| $\rho_{calc}$ ($g.cm^{-3}$) | 1.536 | 1.430 | 1.303 |
| μ ($mm^{-1}$) | 2.821 | 0.948 | 0.664 |
| Crystal size | 0.04×0.06×0.12 | 0.20×0.26×0.44 | 0.10×0.10×0.20 |
| $\theta_{max}$ (°) | 25.69 | 25.35 | 28.885 |
| Total data | 12648 | 22833 | 16446 |
| Unique data | 4018 | 2070 | 6908 |
| $R_{int}$ | 0.0616 | 0.0493 | 0.0598 |
| R [$I > 2\sigma(I)$] | 0.0382 | 0.0543 | 0.0624 |
| $R_w$ | 0.0584 | 0.1537 | 0.1403 |
| Goodness of fit | 1.013 | 1.117 | 0.954 |
| $\rho_{min}$ | -0.264 | -0.449 | -0.427 |
| $\rho_{max}$ | 0.447 | 0.882 | 0.828 |

**Table S6** Selected bond distances and angles for complexes **2**, **3a** and **3b.**

| | **2** | | **3a** | **3b** | |
|---|---|---|---|---|---|
| | Ligand 1 | Ligand 2 | | Ligand 1 | Ligand 2 |
| *Distances (Å)* | | | | | |
| Co(1)-N(1) | 1.899(4) | 1.901(4) | 1.898(2) | 1.898(2) | 1.898(2) |
| Co(1)-O(1) | 1.921(4) | 1.928(4) | 1.912(2) | 1.9199(19) | 1.9219(19) |
| Co(1)-P(1) | 2.2827(18) | 2.2820(18) | 2.2793(11) | 2.2762(7) | 2.2709(7) |
| O(1)-C(6) | 1.271(6) | 1.262(6) | 1.285(5) | 1.285(4) | 1.282(3) |
| N(1)-C(5) | 1.332(6) | 1.326(6) | 1.327(4) | 1.318(4) | 1.335(4) |
| N(1)-C(2) | 1.390(7) | 1.377(6) | 1.390(4) | 1.401(4) | 1.391(4) |
| C(2)-C(6) | 1.383(7) | 1.395(7) | 1.366(5) | 1.395(4) | 1.378(4) |
| C(2)-C(3) | 1.405(7) | 1.404(7) | 1.410(5) | 1.412(4) | 1.410(4) |
| C(3)-C(4) | 1.357(9) | 1.360(8) | 1.346(7) | 1.380(4) | 1.376(4) |
| C(4)-C(5) | 1.399(8) | 1.392(8) | 1.406(6) | 1.423(4) | 1.413(4) |
| | | | | | |
| *Angles (º)* | | | | | |
| N(1)-Co(1)-O(1) | 83.65(17) | 83.74(18) | 84.18(10) | 84.73(9) | 84.13(9) |
| O(1)-Co(1)-P(1) | 88.38(12) | 88.51(12) | 89.12(9) | 87.83(6) | 87.95(6) |
| N(1)-Co(1)-P(1) | 90.91(14) | 90.17(14) | 90.08(9) | 89.53(7) | 87.73(7) |
| C(5)-N(1)-Co(1) | 141.2(4) | 141.7(5) | 142.1(3) | 141.5(2) | 140.9(2) |
| C(2)-N(1)-Co(1) | 111.7(3) | 111.6(3) | 111.0(2) | 110.96(19) | 111.56(19) |
| C(6)-O(1)-Co(1) | 112.6(3) | 112.3(3) | 111.9(2) | 111.83(19) | 111.79(18) |
| N(1)-C(2)-C(3) | 108.4(5) | 110.7(6) | 108.7(4) | 109.6(3) | 109.2(3) |
| C(5)-N(1)-C(2) | 107.1(5) | 106.0(5) | 106.8(3) | 107.3(3) | 107.5(3) |
| C(6)-C(2)-N(1) | 113.0(5) | 113.4(5) | 113.6(3) | 113.1(3) | 113.2(3) |
| C(6)-C(2)-C(3) | 138.4(6) | 136.4(6) | 137.4(4) | 137.2(3) | 137.6(3) |
| C(4)-C(3)-C(2) | 106.9(6) | 105.4(6) | 106.5(4) | 105.2(3) | 105.8(3) |
| C(3)-C(4)-C(5) | 107.6(6) | 107.9(6) | 108.1(3) | 108.0(3) | 108.1(3) |
| N(1)-C(5)-C(4) | 110.0(6) | 110.7(6) | 109.9(4) | 109.8(3) | 109.3(3) |
| O(1)-C(6)-C(2) | 119.0(5) | 118.9(5) | 119.1(3) | 118.9(3) | 119.5(3) |

# MALDI-TOF MS of the low molecular weight fractions of selected PMMA samples

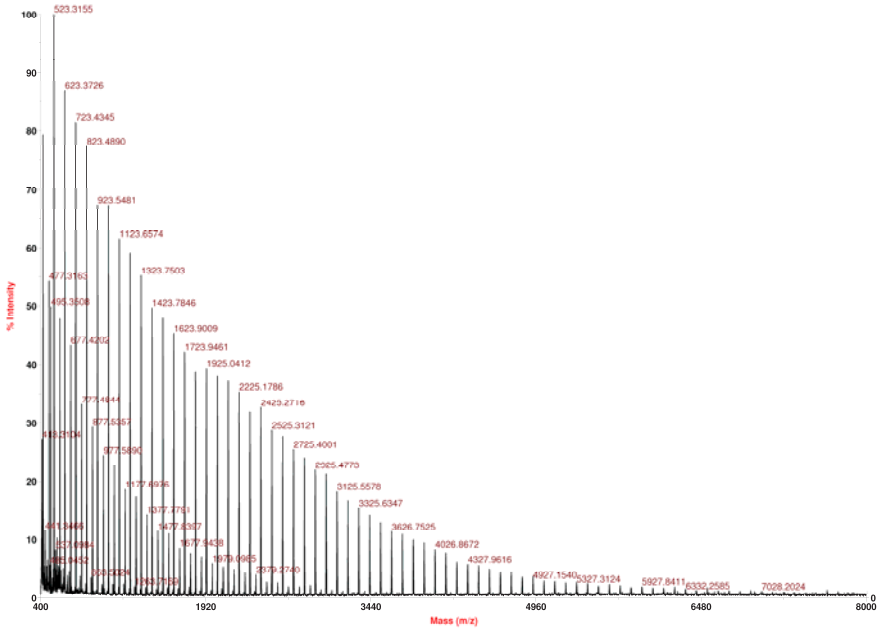



**Figure S1** MALDI-TOF MS spectrum (matrix: 2,5-dihydroxybenzoic acid (DHB) + $NaBF_4$) for the lower molecular weight fractions of the PMMA prepared at 90 ºC; [Monomer]:[**1**]:[tBiB-Br]=500:1:1, $M_n$=7000 g.mol$^{-1}$, Đ=1.45.

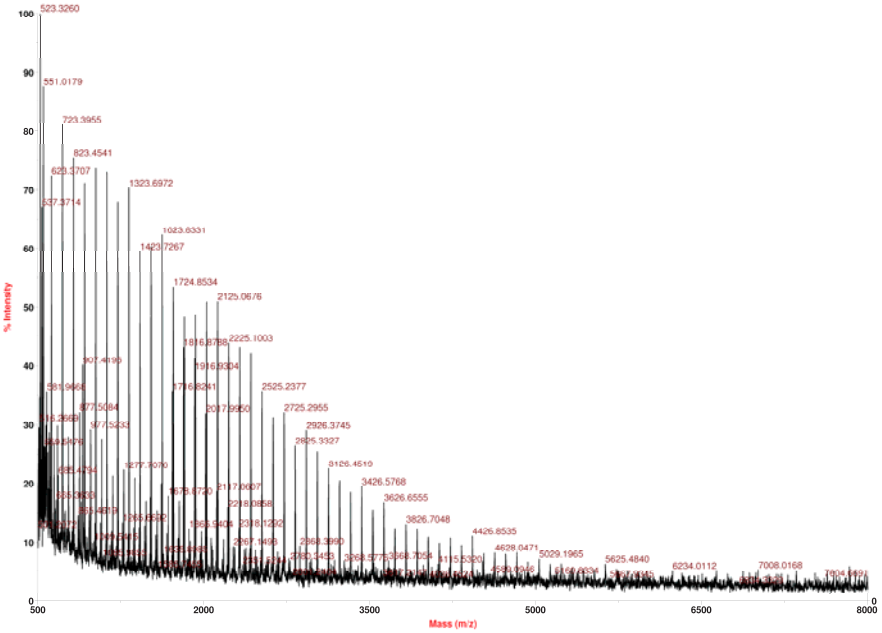



**Figure S2** MALDI-TOF data (matrix: 2,5-dihydroxybenzoic acid (DHB) + $NaBF_4$) for the for the lower molecular weight fractions of the PMMA prepared at 50 ºC; [Monomer]:[**1**]:[tBiB-Br]=500:1:1, $M_n$=10700 g.mol$^{-1}$, Đ=1.58 .

## NMR spectra of the PS-*b*-PMMA block copolymer

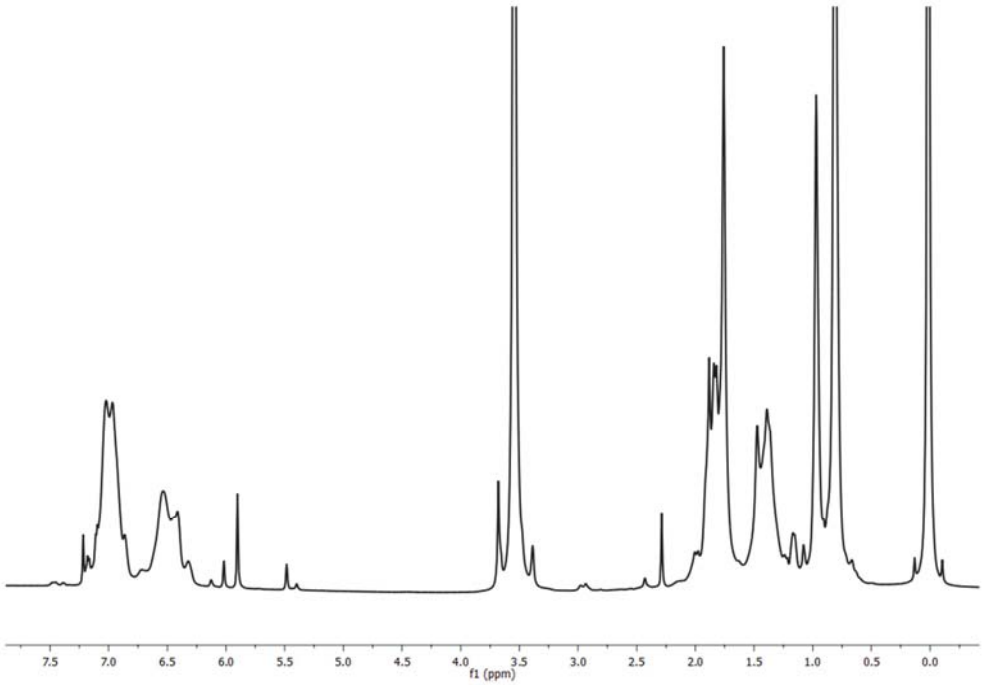



**Figure S3** $^{1}$H NMR spectrum (500 MHz, in 1,1,2,2-tetrachloroethane-$d_4$, at 70 ºC) of the PS-*b*-PMMA copolymer ($M_n$=12600 g mol$^{-1}$, Đ=1.36). [MMA]:[**1**]:[PS-Br]=500:1:1.; reaction temperature: 50 ºC.

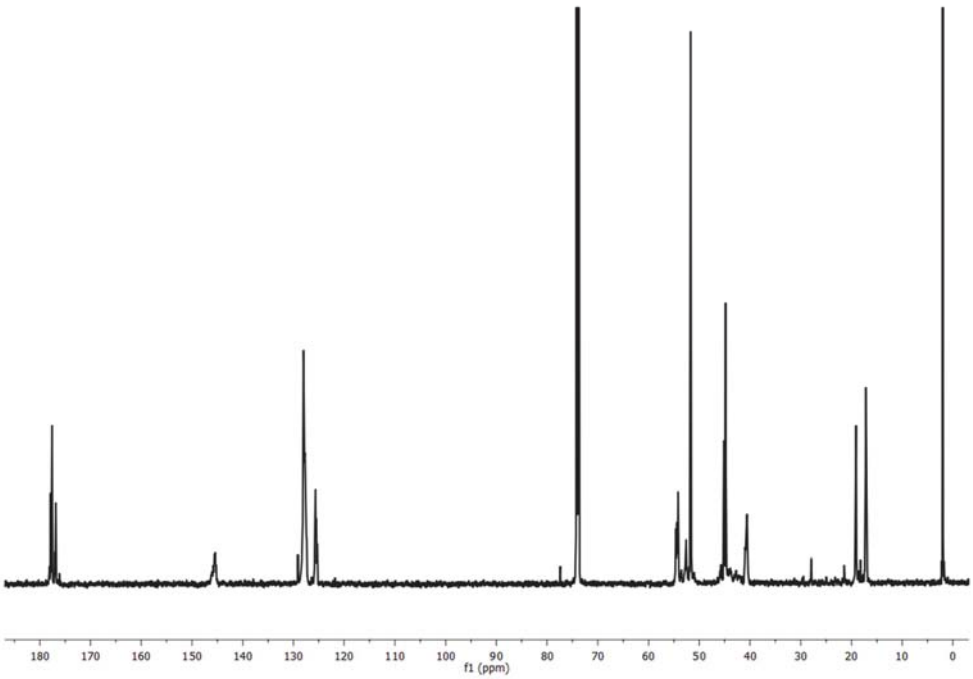



**Figure S4** $^{13}$C{$^{1}$H} NMR spectrum (125 MHz, in 1,1,2,2-tetrachloroethane-$d_4$, at 70 ºC) of the PS-*b*-PMMA copolymer ($M_n$=12600 g mol$^{-1}$, Đ=1.36). [MMA]:[**1**]:[PS-Br]=500:1:1.; reaction temperature: 50 ºC.

## NMR spectra of complexes 2, 3a and 3b

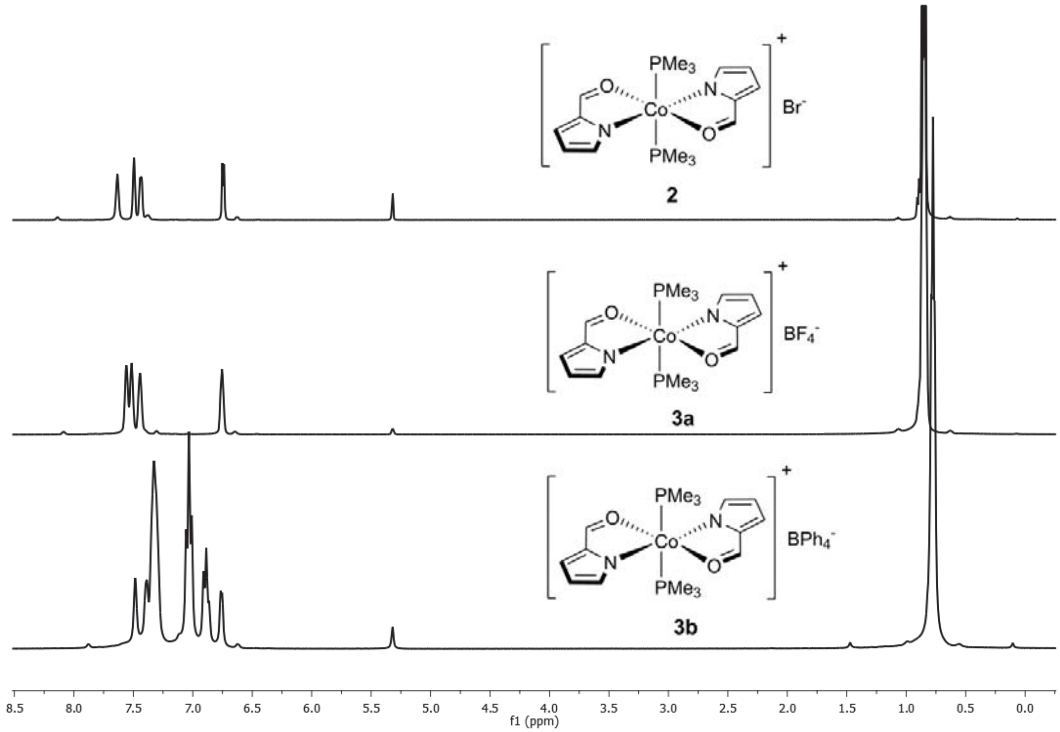
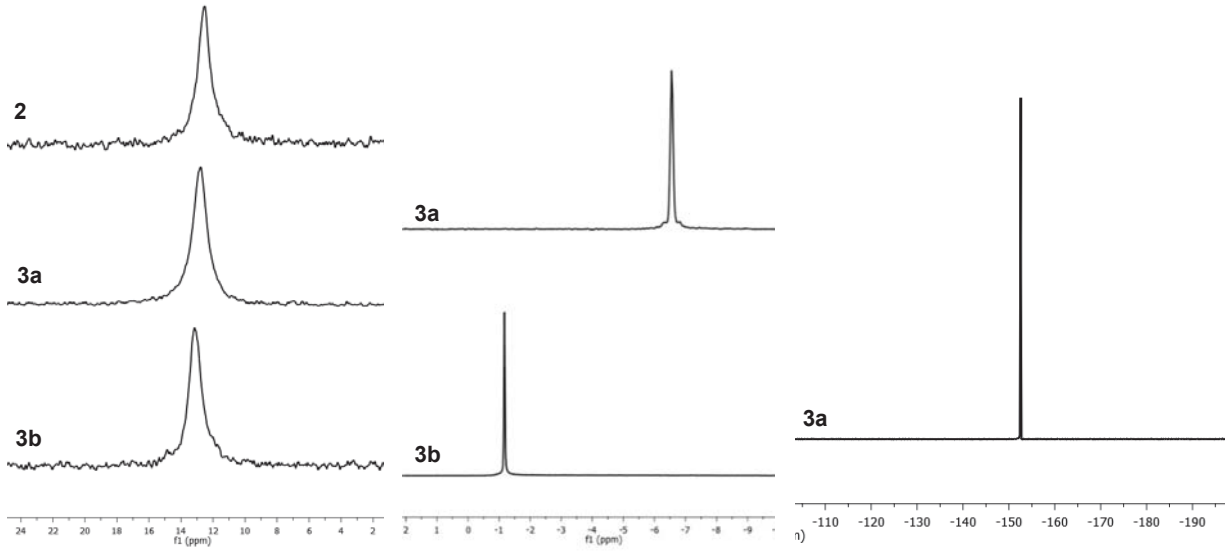



**Figure S5** Stacking of the $^{1}H$ NMR spectra (300 MHz, in $CD_2Cl_2$) of complexes **2**, **3a** and **3b**.




(a) (b) (c)

**Figure S6** Stacking of the (a) $^{31}P\{^{1}H\}$ NMR spectra (121.4 MHz) of complexes **2**, **3a** and **3b**, (b) $^{11}B\{^{1}H\}$ spectra (96.3 MHz) of complexes **3a** and **3b**, and the (c) $^{19}F\{^{1}H\}$ spectrum (282.2 MHz) of complex **3a**, in $CD_2Cl_2$.

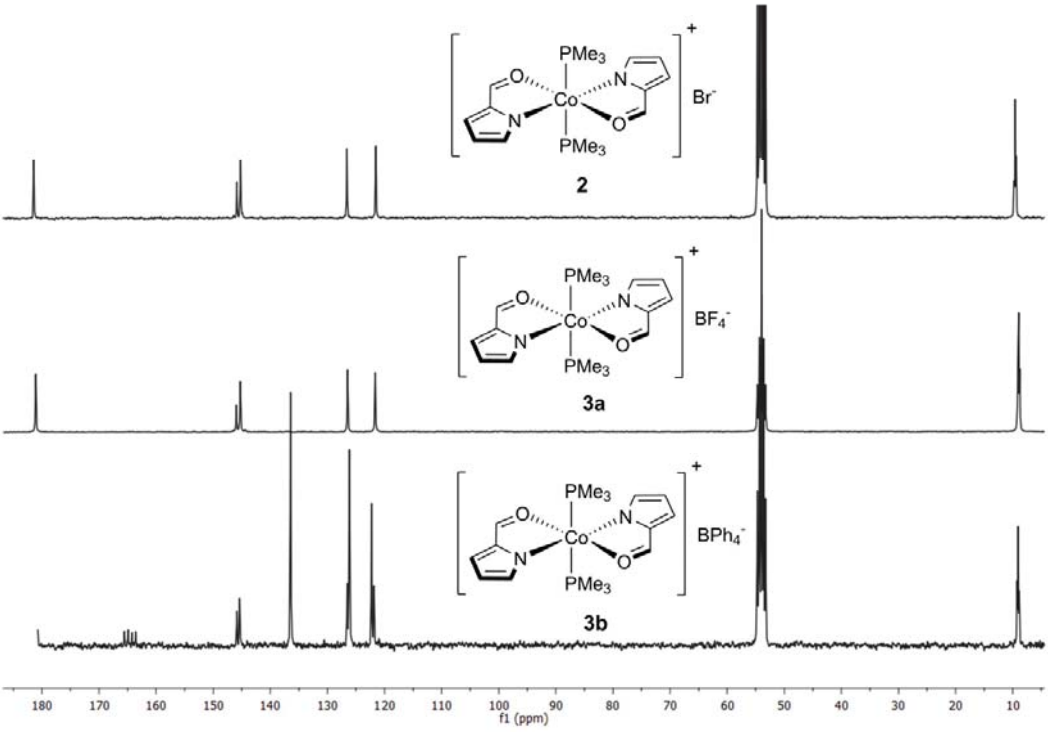



**Figure S7** Stacking of the $^{13}C\{^{1}H\}$ NMR spectra (75.4 MHz, in $CD_2Cl_2$) of complexes **2**, **3a** and **3b**.

# Additional cyclic voltammetry data

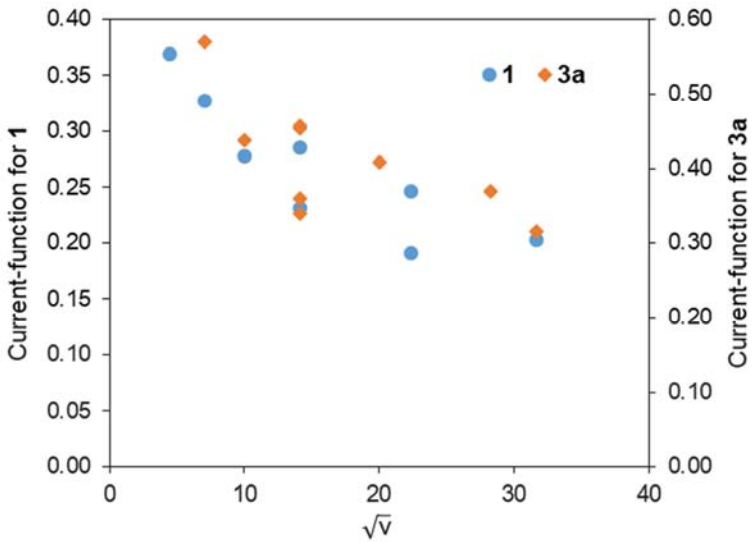



**Figure S8** Current-function *vs* $\sqrt{v}$, with v being the scan rate, for complexes **1** and **3a**.