Supporting Information

Amine-Containing Block Copolymers for Efficient Catalyst-Free Hydroamination and Preparation of Functional Metallopolymers

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Polymers are addressed according to the following table:

Nr.	Polymer
	PS_{797}[a)]
P1	PS_{797}-*b*-(P*t*BAEMA$_{21}$-*co*-PMMA$_{6}$)
P1*	PS_{797}-*b*-(PCoE*t*BAEMA$_{7}$-*co*-PMMA$_{8}$)
	PS_{773} [a)]
P2	PS_{773}-*b*-(P*t*BAEMA$_{45}$-*co*-PMMA$_{13}$)
P2*	PS_{773}-*b*-(PCoE*t*BAEMA$_{31}$-*co*-PMMA$_{12}$)
	PS_{773}[a)]
P3	PS_{773}-*b*-(P*t*BAEMA$_{71}$-*co*-PMMA$_{23}$)
P3*	PS_{773}-*b*-(PCoE*t*BAEMA$_{57}$-*co*-PMMA$_{27}$)
	PS_{776}[a)]
P4	PS_{776}-*b*-(P*t*BAEMA$_{108}$-*co*-PMMA$_{37}$)
P4*	PS_{776}-*b*-(PCoE*t*BAEMA$_{80}$-*co*-PMMA$_{30}$)
P5	P*t*BAEMA$_{406}$-*b*-PMMA$_{133}$
P5*	PCoE*t*BAEMA$_{387}$-*b*-PMMA$_{133}$

Content

1. ^{1}H-NMR spectra of synthesized polymers

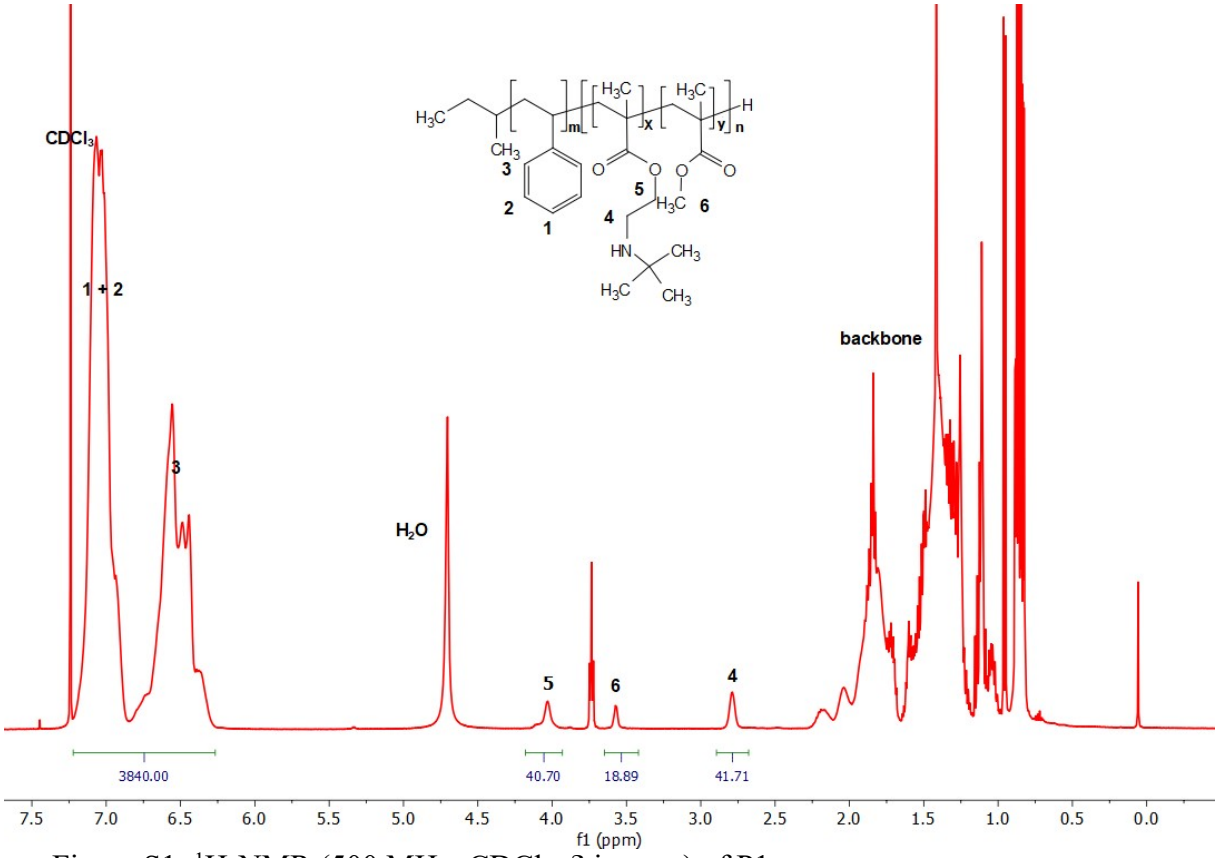


Figure S1: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of P1

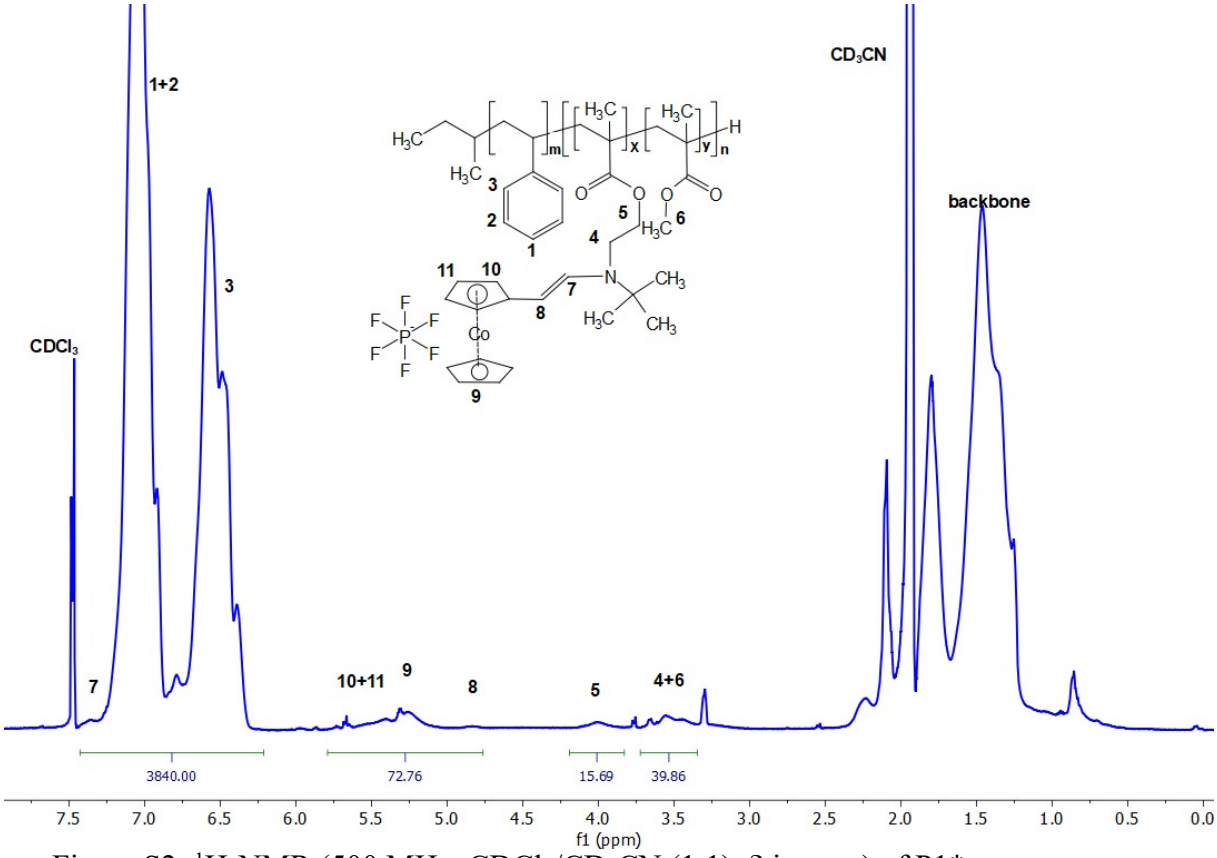


Figure S2: ^{1}H-NMR (500 MHz, $CDCl_3$/CD_3CN (1:1), δ in ppm) of P1*

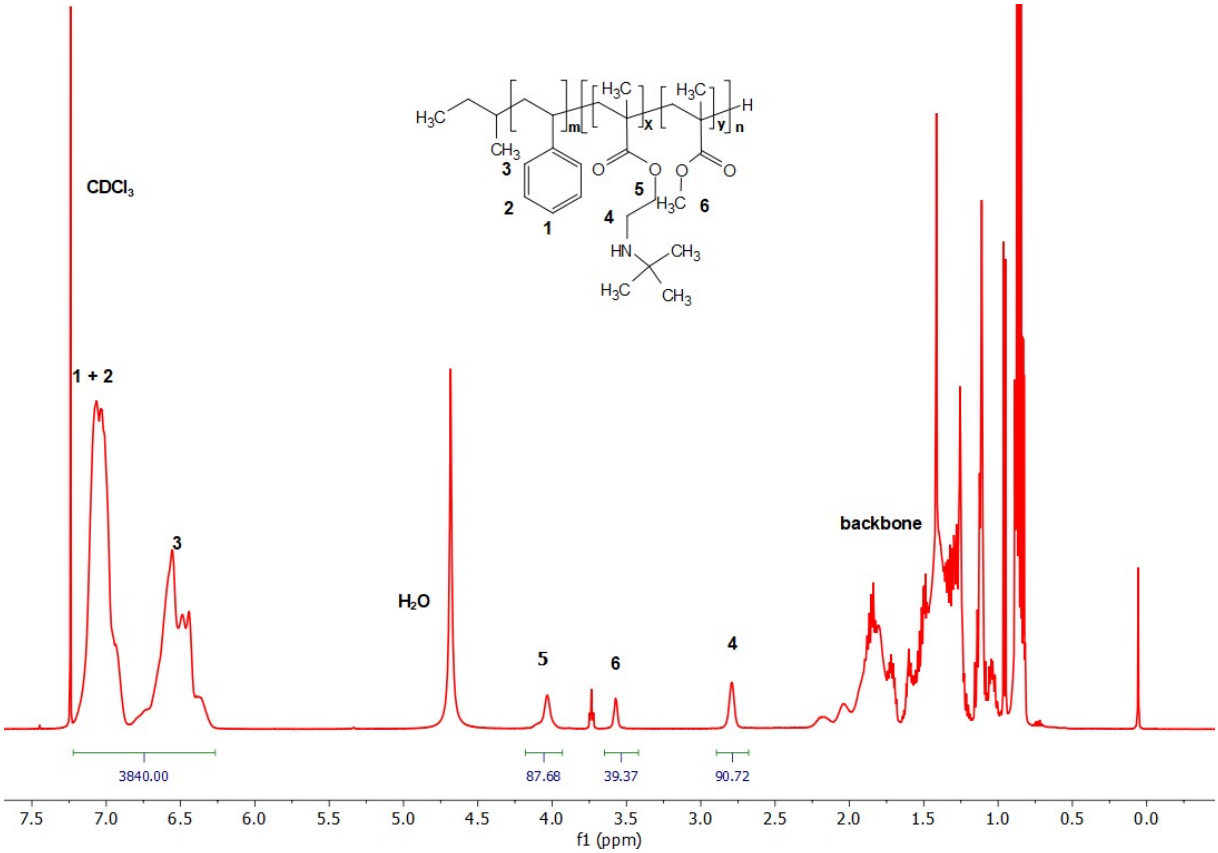


Figure S3: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of P2

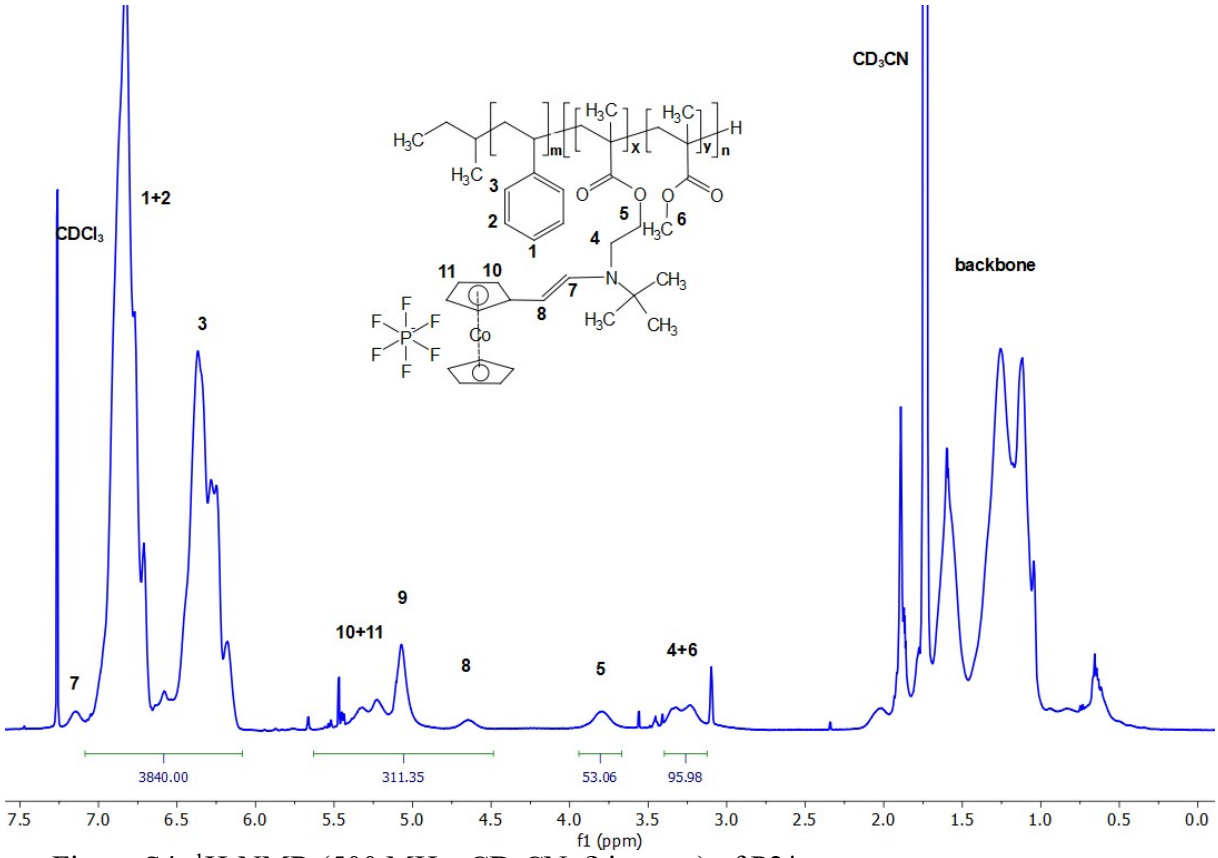


Figure S4: ^{1}H-NMR (500 MHz, CD_3CN, δ in ppm) of P2*

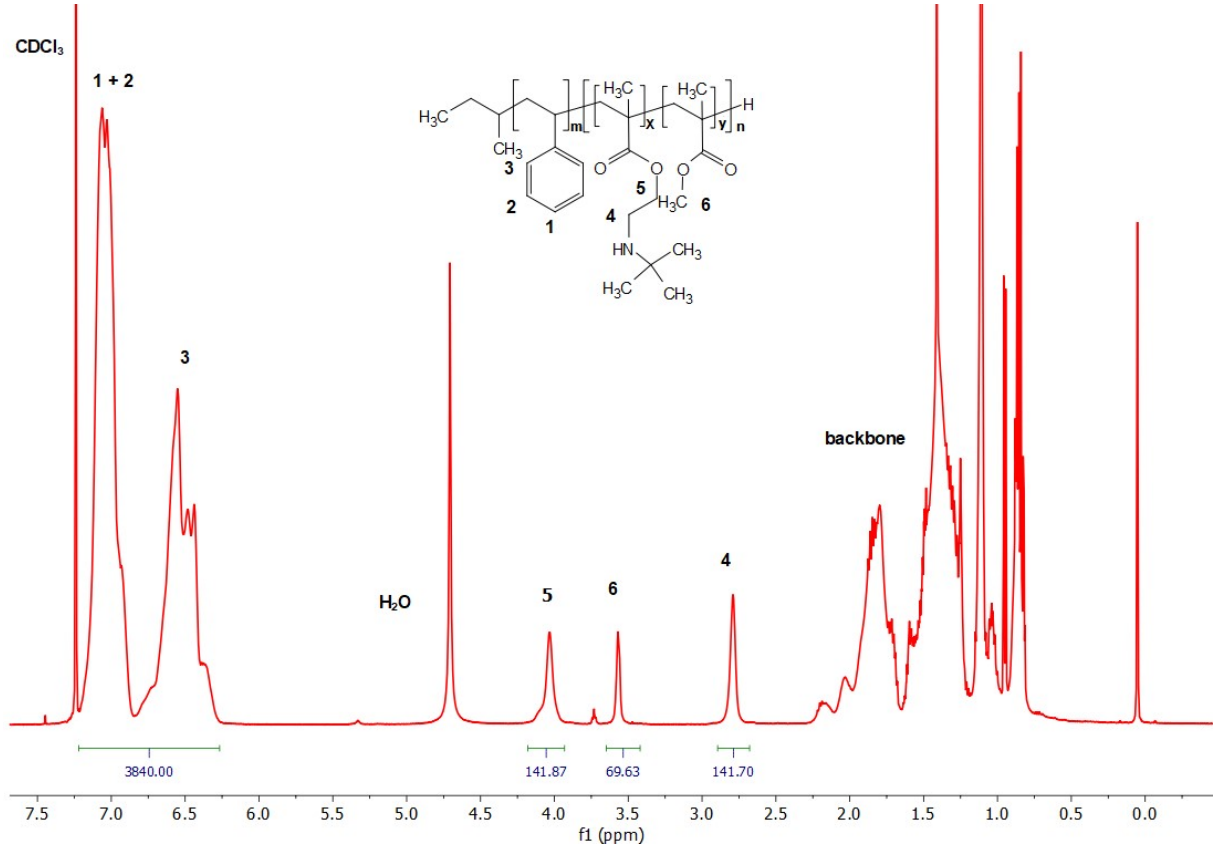


Figure S5: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of P3

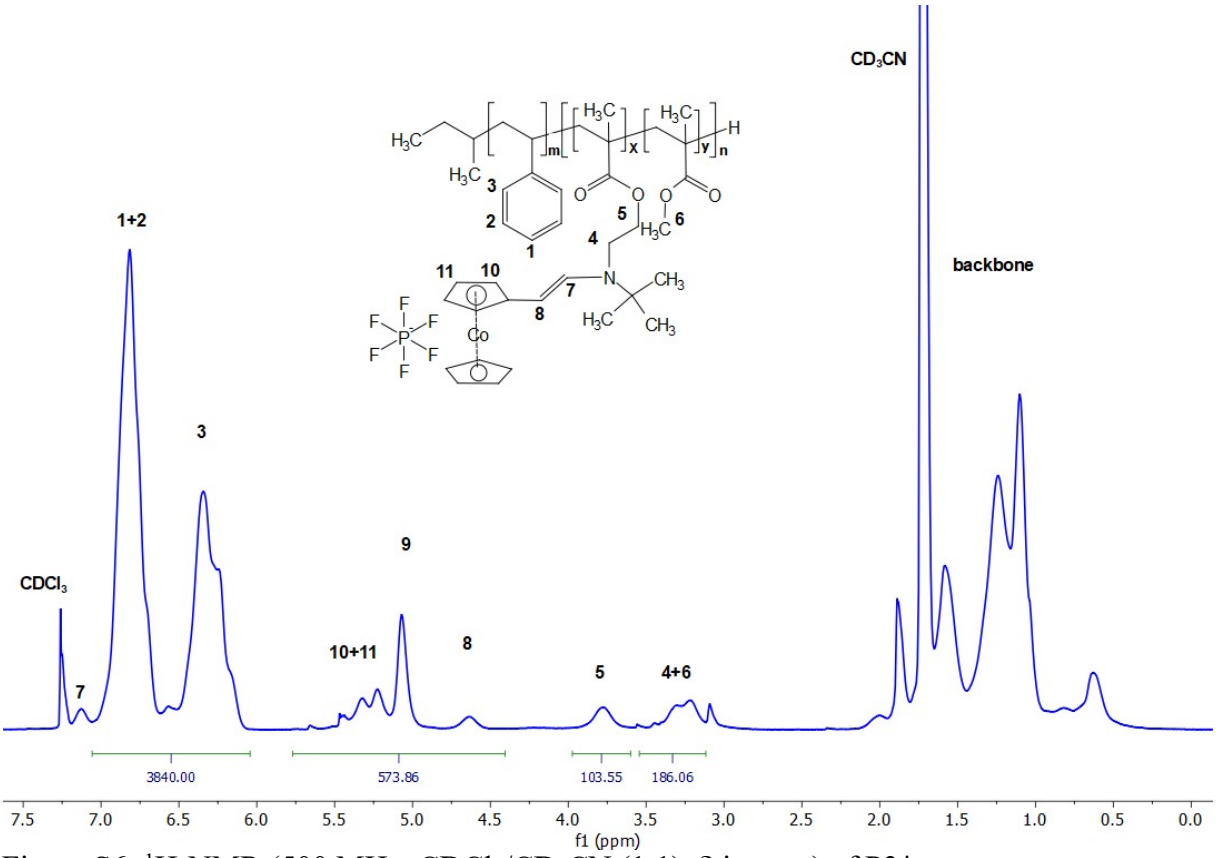


Figure S6: ^{1}H-NMR (500 MHz, $CDCl_3$/CD_3CN (1:1), δ in ppm) of P3*

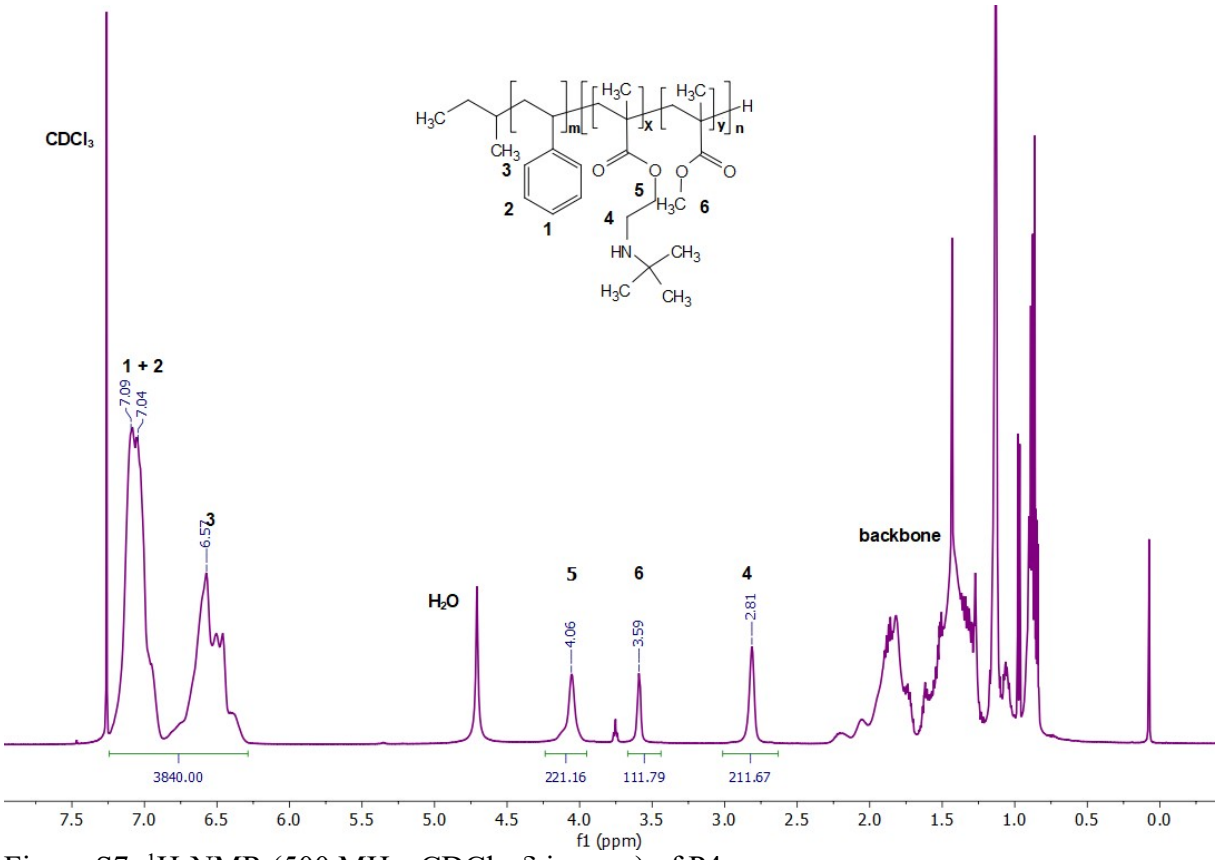


Figure S7: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of P4

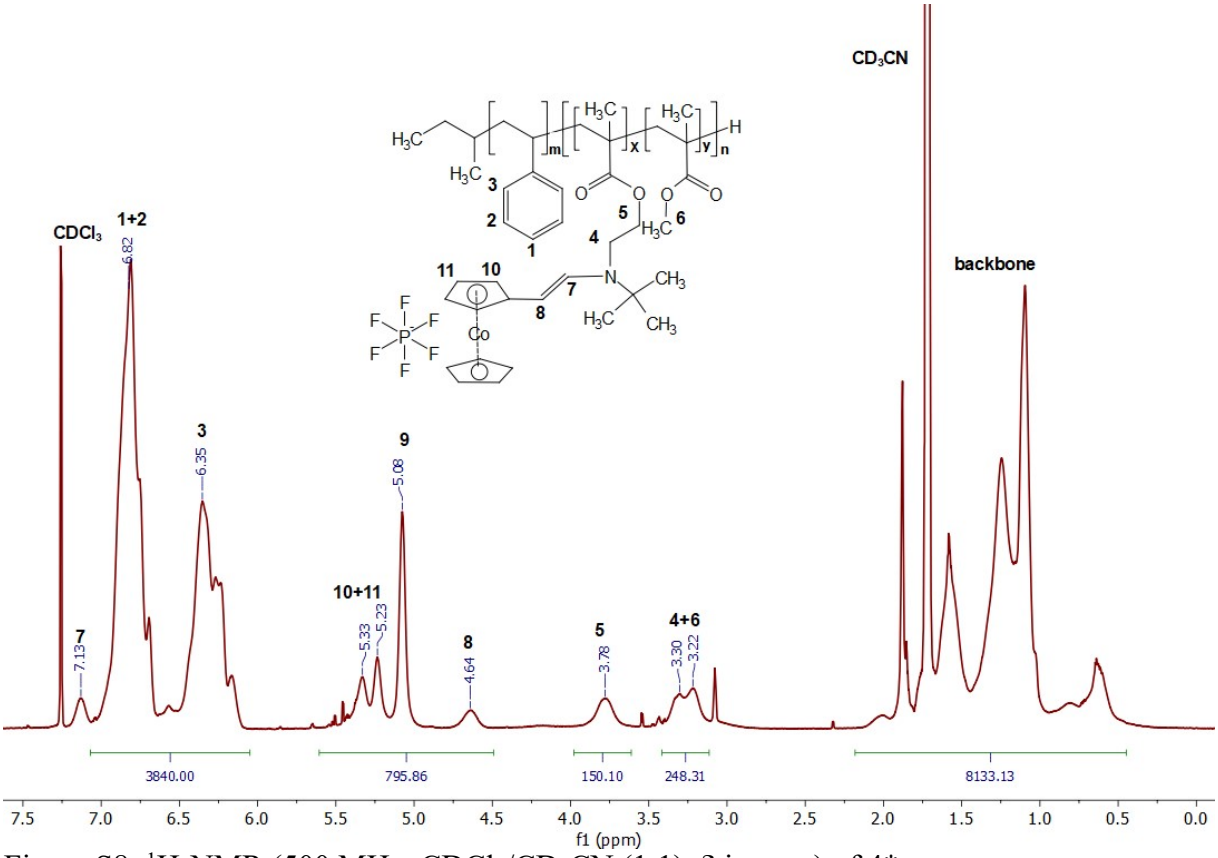


Figure S8: ^{1}H-NMR (500 MHz, $CDCl_3$/CD_3CN (1:1), δ in ppm) of 4*

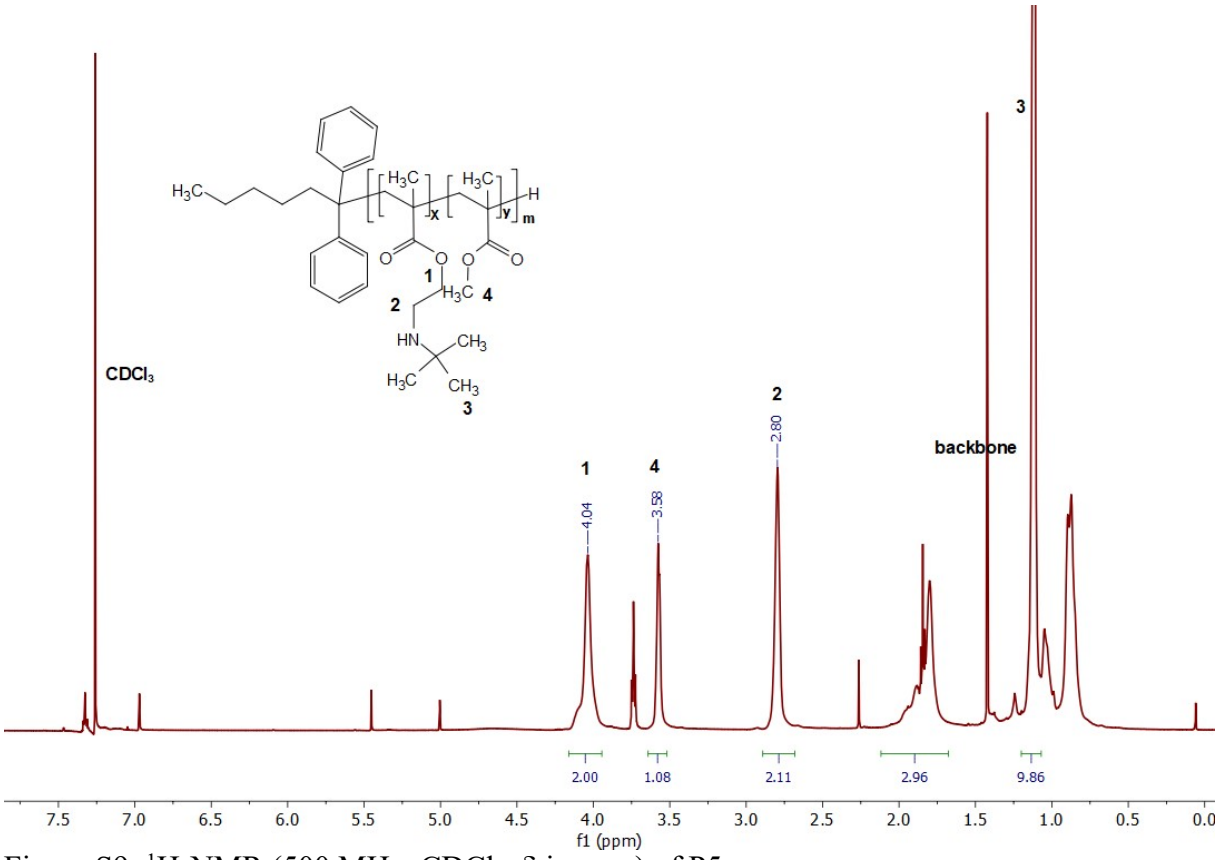


Figure S9: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm) of P5

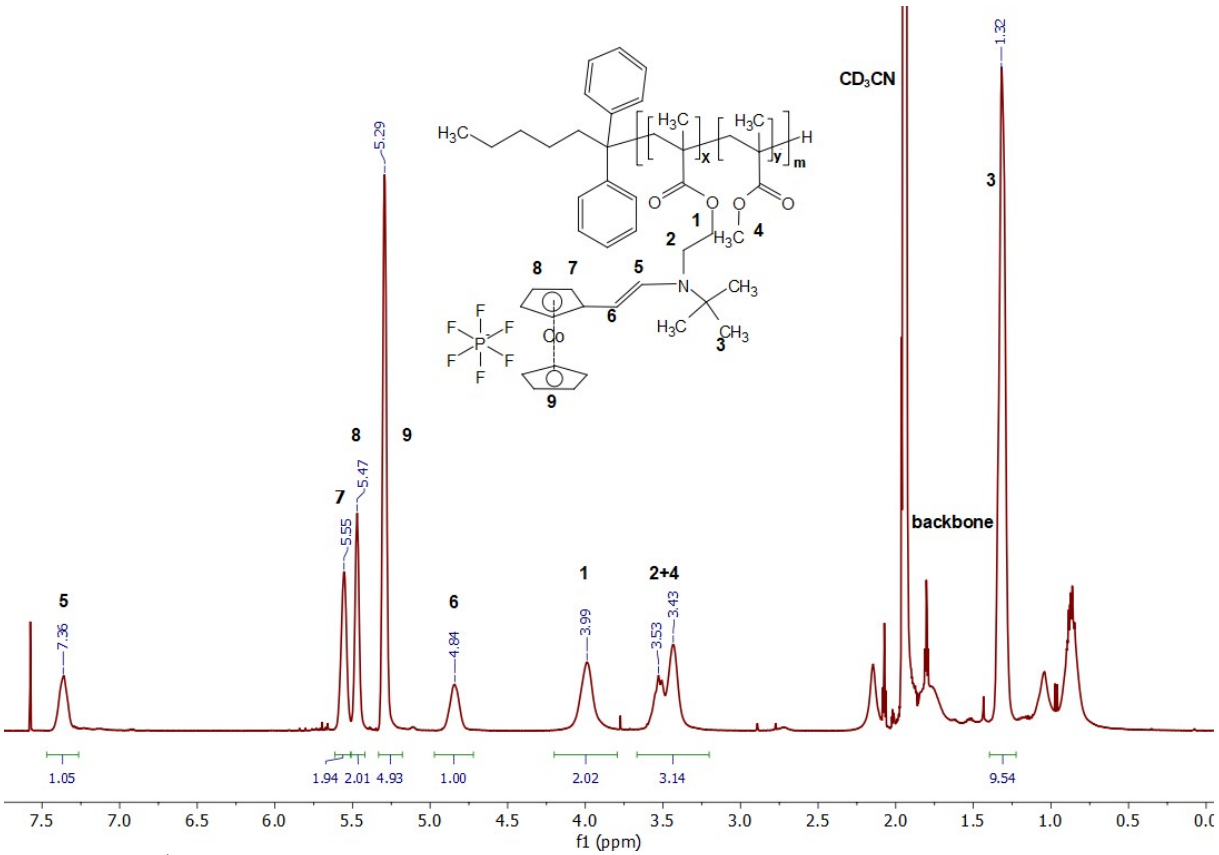


Figure S10: ^{1}H-NMR (500 MHz, CD_3CN, δ in ppm) of P5*

2. Composition calculation using ^{1}H-NMR spectroscopy data

The demonstrated calculations here are using Figures S1 and S2. Respective integrals are numbered as described in the spectra. For composition analysis, SEC results of the initial polystyrene block were used. From the measured Mn, the degree of polymerization (Dp) was calculated for styrene. The Dp was multiplied by the number of expected protons (N =5) visible in the aromatic region, and the respecting integral (1+2+3) was set to the resulting value. The degree of polymerization of all other components was calculated by comparing to the number of expected protons per unit (N):

$$DP(MMA) = \frac{I(6)}{N_{MMA}}$$

The molar composition of tBAEMA or MMA was now calculated using the respective integrals (tBAEMA: 4+5; MMA: 6) and expected protons per unit using the following equation:

$$x(PMMA) = \frac{I(6) \cdot \frac{1}{N_{MMA}}}{I(6) \cdot \frac{1}{N_{MMA}} + \frac{I(4)+I(5)}{2} \cdot \frac{1}{N_{tBAEMA}} + I(1-3) \cdot \frac{1}{N_S}}$$

For the functionalized polymers, again, the polystyrene value was used to set the initial integral. The molar composition of the functionalized monomer CoEtBAEMA was now calculated using the integral over 7 to 10 according to the following equation. The overlapping MMA and CoEtBAEMA signals were differentiated by comparison with the integral of signal 5.

$$x(PCoEtBAEMA) = \frac{I(6) \cdot \frac{1}{N_{MMA}}}{(I(4+6) - I(5)) \cdot \frac{1}{N_{MMA}} + I(7-10) \cdot \frac{1}{N_{CoEtBAEMA}} + I(1-3) \cdot \frac{1}{N_S}}$$

From the different molar compositions, the weight composition (wt.%) was calculated using the molar mass M and the following equation:

$$wt\%(CoEtBAEMA) = \frac{x(CoEtBAEMA) \cdot M_{CoEtBAEMA}}{x(PS) \cdot M_S + x(PCoEtBAEMA) \cdot M_{CoEtBAEMA} + x(PMMA) \cdot M_{MMA}}$$

3. Composition calculation using UV-VIS -spectroscopy data

For composition calculation using UV-Vis spectroscopy, first, a calibration curve with the CoEtBAEMA monomeric unit in tetrahydrofuran was done. For all experiments, a cuvette with d=1cm was used. By using the Beer-Lambert equation, an extinction of ε= 9286 L mol^{-1} cm^{-1} was found (**Figure S11**). To calculate the weight percentage (wt%) of CoE*t*BAEMA, first, a 1 mg ml^{-1} polymer solution c^{poly} was prepared and diluted to four concentrations of c^{d} = 0.1, 0.05, 0.025, and 0.0125 mg ml^{-1}. The extinction *example* was measured three times for each concentration. Using the extinction coefficient $\varepsilon_{CoEtBAEMA}$ = 9286 L mol^{-1} cm^{-1}, the concentration of CoE*t*BAEMA $c_{CoEtBAEMA}$ was calculated for each sample like the following:

$$c_{CoEtBAEMA} = \frac{E_{sample}}{\varepsilon_{CoEtBAEMA} \cdot d}$$

The resulting concentration in mmol mL^{-1} was converted to the mass concentration $c_{CoEtBAEMA,\ mg\ ml^{-1}}$ by using the molar mass of CoE*t*BAEMA (M=543.38 mg $mmol^{-1}$) like the following:

$$c_{CoEtBAEMA,\ mg\,mL^{-1}} = c_{CoEtBAEMA,\ mmol\,mL^{-1}} \cdot M_{CoEtBAEMA}$$

The final weight fraction $x_{CoEtBAEMA}$ was now calculated by comparing the mass concentration of the diluted polymer solution c^{d} (0.1, 0.05…. mg mL^{-1}) to the CoE*t*BAEMA concentration $c_{(CoEtBAEMA,\ mg\ mL^{-1})}$:

$$X_{CoEtBAEMA,} = \frac{c_{CoEtBAEMA,\ mg\,mL^{-1}}}{c^{d}_{polymer,\ mg\,mL^{-1}P}}$$

The mean weight percentage overall for concentrations was used as the final result.

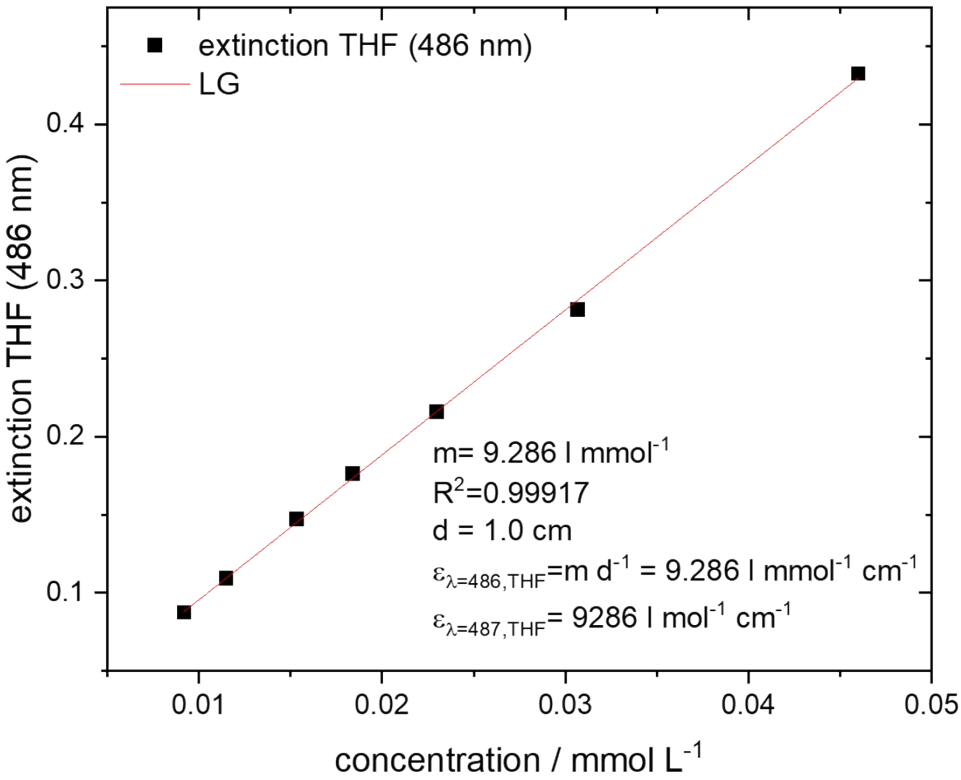
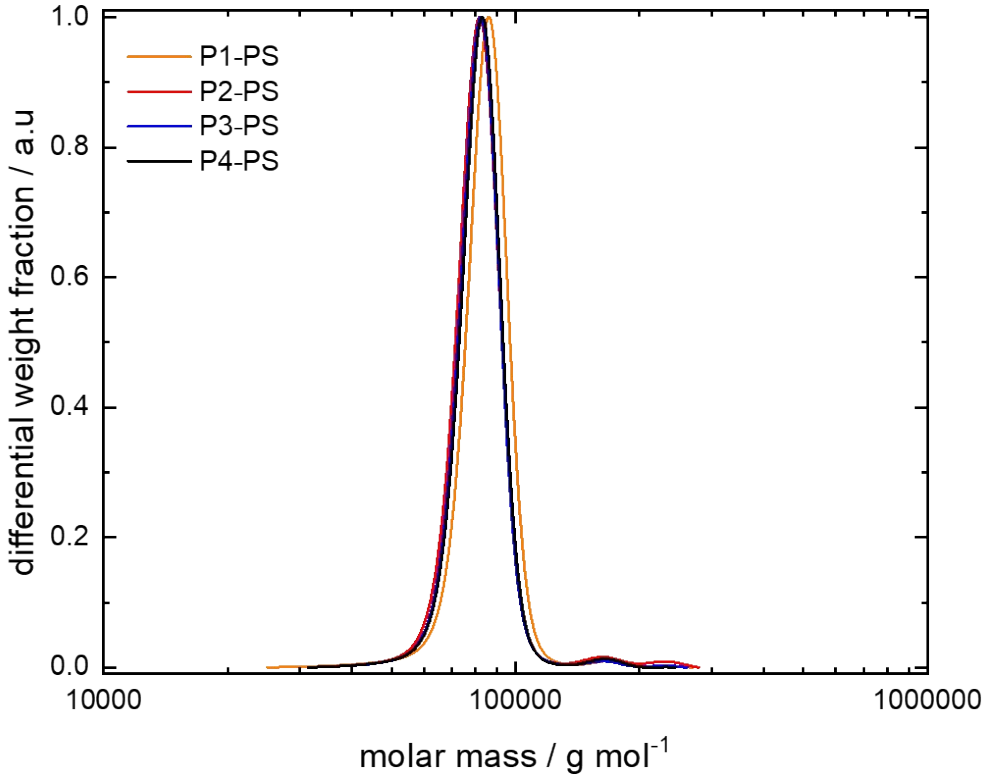


Figure S11: Calibration curve for the extinction coefficient of CoETBAEMA



4. Size exclusion chromatography (SEC) Data

Figure S12: SEC in THF vs. PS standard of first polystyrene blocks of P1 to P4

Table S1: SEC data of first polystyrene block for P1-P4 in THF vs. polystyrene standards

Sample (THF)	Mn / kg mol^{-1}	Dp	Mw / kg mol^{-1}	Dispersity
P1-PS	83.0	797	86.3	1.04
P2-PS	80.5	773	84.0	1.04
P3-PS	80.5	773	83.1	1.03
P4-PS	80.9	776	83.5	1.03

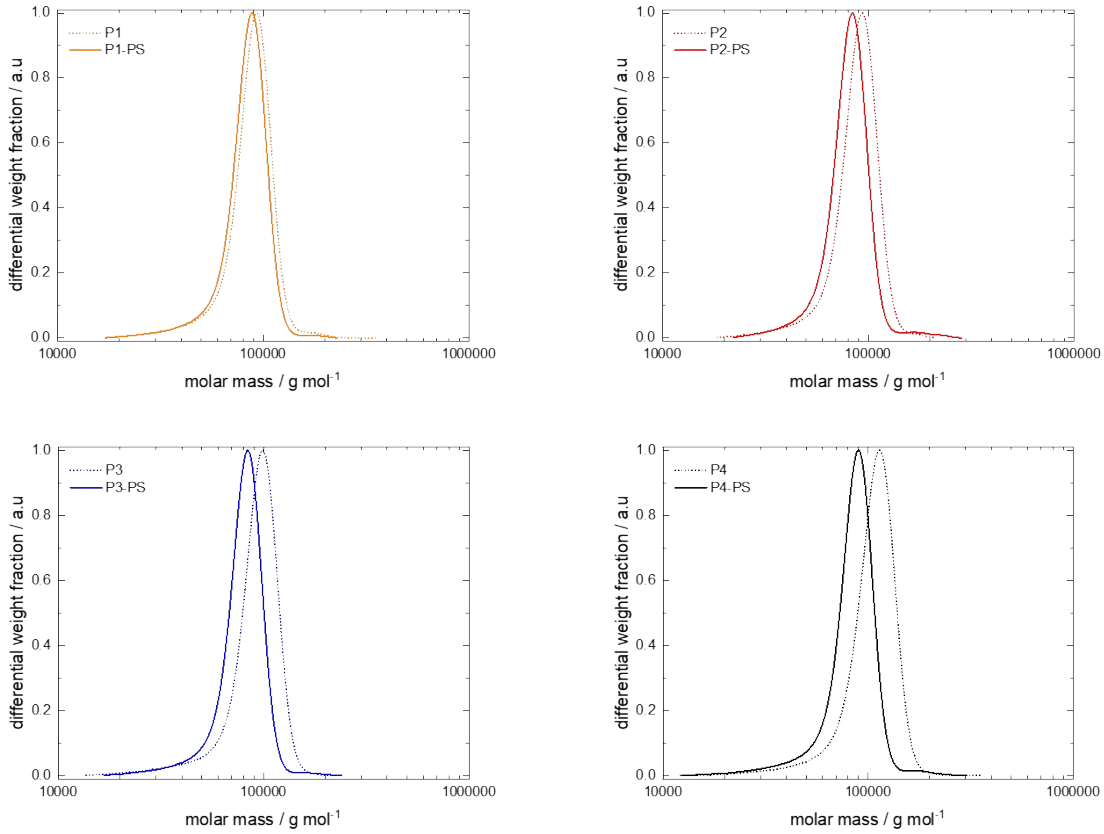
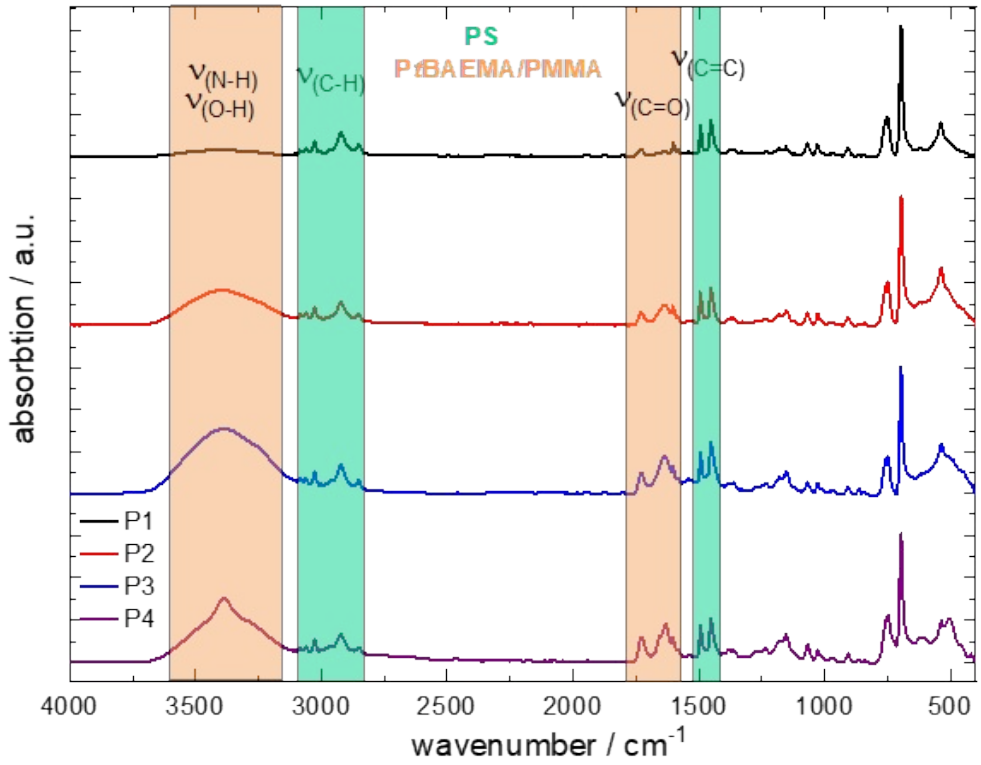


Figure S13: SEC in DMF vs. PMMA standard of first polystyrene blocks and final polymer of P1 to P4 in comparison

Table S2: SEC data of first polystyrene block and final polymer for P1-P4 in DMF vs. PMMA standards

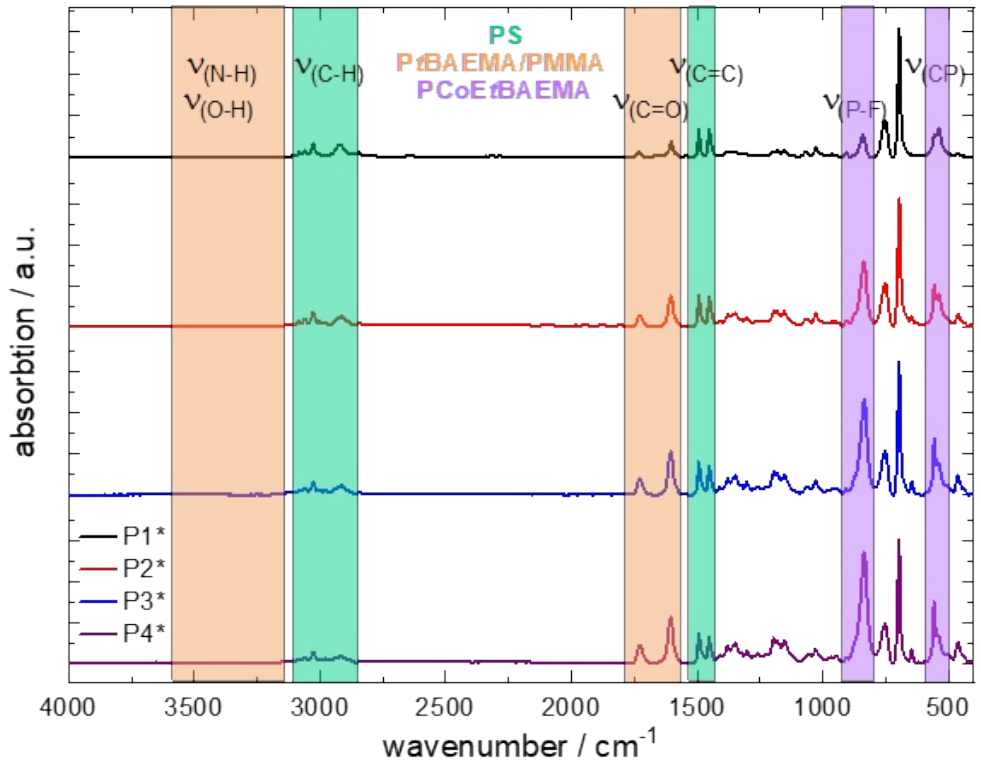
Sample (DMF)	**Mn / kg mol^{-1}**	**Mw / kg mol^{-1}**	**Dispersity**
P1-PS	77.8	84.6	1.08
P1	82.8	89.6	1.08
P2-PS	76.6	82.6	1.07
P2	82.6	89.7	1.08
P3-PS	74.2	80.6	1.08
P3	83.7	93.2	1.11
P4-PS	78.4	86.2	1.09
P-4	97.2	107.1	1.10

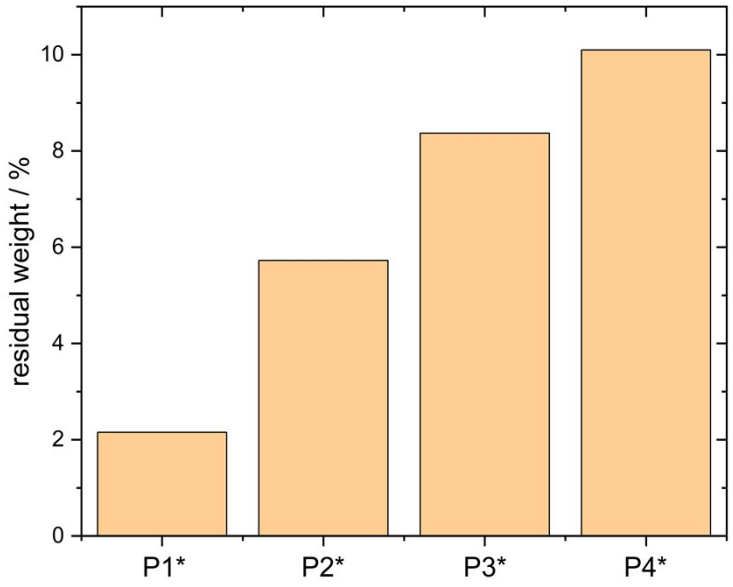


5. Infrared-Spectroscopy (IR) Data

Figure S14: IR spectra of P1 to P4 in comparison

Figure S15: IR spectra of P1* to P4* in comparison





6. Thermogravimetric Analysis (TGA) Data

Figure S16: Residual weight after TGA from 30 to 590 °C in nitrogen with 10 K min^{-1}

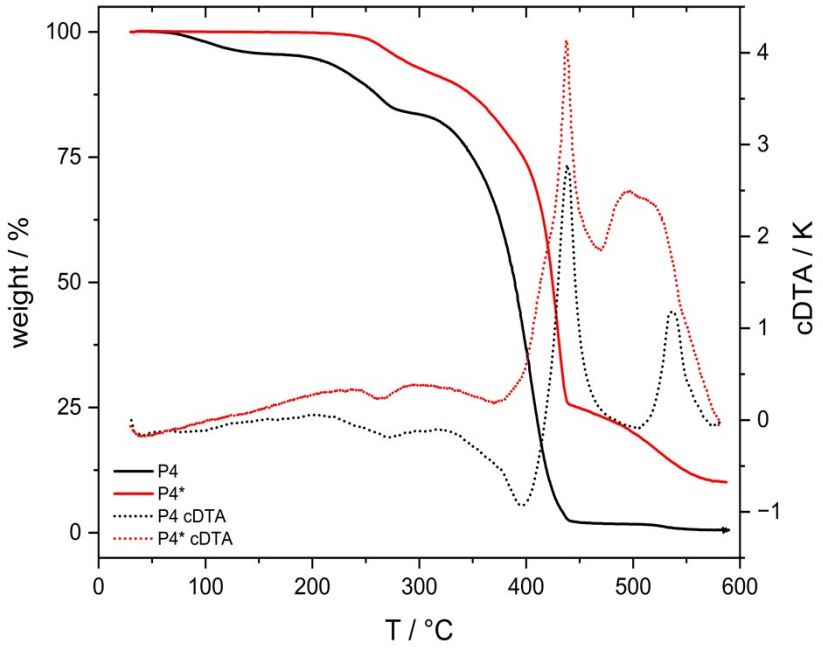
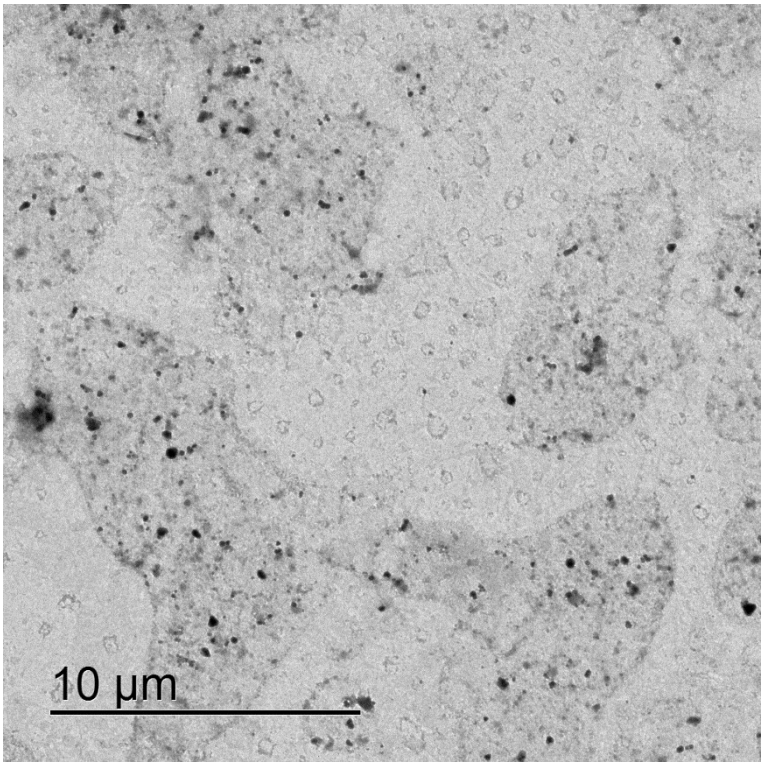


Figure S17: Calculated differential thermogravimetric analysis (cDTA) of P4 and P4* from 30 to 590 °C in nitrogen with 10 K min^{-1}



7. Transmission electron microscopy (TEM)

Figure S18: **TEM** image of P2* micelles formed in chloroform