Electronic Supplementary Information (ESI)

A facile route to segmented copolymers by fusing ambient temperature step-growth and RAFT polymerization

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Contents

1. Materials

11-Bromo-1-undecanol (Alfa Aesar, 97%), *tert*-butyldimethylsilyl chloride (TBDMSCl, TCI, >98%), 1-methylimidazole (Aldrich, 99%), 4-(*N,N*-dimethylamino) pyridine (DMAP, Aldrich, >99%), 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC, Carl Roth, >99%), sodium sulfide (Aldrich, ≥98%), carbon disulfide (VWR, 99.9%), ethylene glycol (Alfa, 99%), diethyl fumarate (Alfa, 98%; monofunctional, **F**) 2-bromo-propionic acid (Aldrich, ≥99%), sodium cyclopentadienyl (NaCp, Aldrich, 2 M in THF), 1,10-dibromodecane (Acros, 97%) and monoethyl fumarate (Aldrich, 95%), were used as received. Azobisisobutyronitrile (AIBN, Aldrich, 98%) was recrystallized from methanol. Styrene (TCI, >99%) was destabilized before the polymerization by running the monomer through an Alox B column. The solvents dichloromethane (DCM, Fischer, p.a.), *n*-hexane (Fischer, p.a.), ethyl acetate (Fischer, p.a.), cyclohexane (Fischer, p.a.), *N,N*-dimethylformamide (DMF, Fischer, p.a.), and tetrahydrofuran (THF, Fischer, HPLC grade) were used as received. The anhydrous solvents DCM (Acros, ≥99.9%) and DMF (Acros, ≥99.9%) were used as received. Deuterated solvents CD_2Cl_2 (DCM-d_2), $CDCl_3$, toluene-d8 and dimethylsulfoxide-d6 (DMSO-d_6) for NMR spectroscopy were purchased from Eurisotop and Aldrich, respectively. (*S,S*-dipropionic acid) trithiocarbonate (DTC) was synthesized according to literature procedure.[1]

2. Instrumentation

2.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR measurements were carried out on a Bruker Avance III 400 spectrometer (^{1}H: 400 MHz, ^{13}C{^{1}H}: 101 MHz). The δ scale was referenced to deuterated solvents, indicated in the respective measurement. Evaluation was performed by TopSpin 7.1 PL7.

2.2. Size Exclusion Chromatography (SEC)

SEC measurements were carried out on an Agilent 1200 system, comprising an auto-sampler, a PLgel 5 µm bed-size guard column (50 × 7.5 mm), one PLgel 5 µm Mixed E column (300 × 7.5 mm), three PLgel 5 µm Mixed C columns (300 × 7.5 mm) and a differential refractive index detector as well as an UV detector using THF as eluent at 35 °C with a flow rate of 1 mL min^{-1}. For all measurements, the RI detector signal is reported. The SEC system was calibrated using linear polystyrene standards ranging from $1.6 \cdot 10^2$ to $6 \cdot 10^6$ $g \cdot mol^{-1}$.

2.3. Electrospray Ionization Mass Spectrometry (ESI-MS)

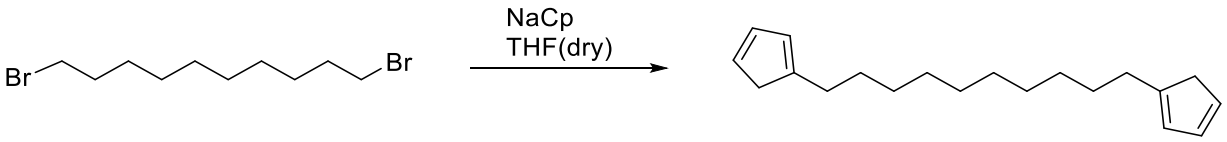
High-resolution mass spectra (HRMS) were obtained using a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument calibration was carried out in the *m*/*z* range 74 – 1822, using calibration solutions from Thermo Scientific. A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62, respectively. The samples were dissolved in a THF:MeOH mixture (volume ratio 3:2) containing 100 µmol of sodium trifluoroacetate and injected with a flow of 5 to 10 $\mu L \cdot min^{-1}$, respectively. The higher-energy collisional dissociation (HCD) measurements were performed with a collision energy of 10 eV. The concentration of the injected samples was in the range of 0.1 and 0.3 $mg \cdot mL^{-1}$.

2.4. UV VIS Spectroscopy

The UV/VIS spectra were recorded on OceanOptics USB4000 spectrometer coupled to an USB-ISS-UV-Vis detecting unit. The measurements were conducted in DCM at ambient temperature, using quartz glass cuvettes (Starna GmbH, 10 mm). The concentrations were varying, in order to keep the absorbance below the value of 2.

3. Synthesis Protocols

Synthesis of 1,10-di(cyclopentadienyl)-decane (AA monomer)



Scheme S1. Synthesis of 1,10-di(cyclopentadienyl)-decane monomer **AA**.

According to literature,[2] in a dry round bottom flask 30.01 g (0.10 mol, 1 eq.) 1,10-dibromo-decane was dissolved in dry THF in an inert gas atmosphere. The solution was cooled to 0 °C and 100 mL of a 2 M solution of sodium cyclopentadienyl in THF (0.20 mol, 2 eq.) were added dropwise. After addition, the brown solution was stirred for 1 h and the reaction mixture was allowed to warm to ambient temperature to stir for 16 h. The suspension was filtered over silica using ethyl acetate. After removal of the solvent, the brown oil was dissolved in *n*-hexane and filtered over silica using *n*-hexane. After the evaporation of the solvent the product was obtained as a colorless oil (23.66 g, 87 % yield) that was stored at -20 °C. ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C): δ (ppm): 6.43 – 5.98 (m, 6H, Cp **H**C=C**H**), 2.88 (d, 4H, C**H$_2$**,Cp), 2.40 - 2.31 (m, 4H, $(CH_2)_3$-CH_2-C**H**$_2$-Cp), 1.55 – 1.46 (m, 4H, $(CH_2)_3$-C**H**$_2$-CH_2-Cp), 1.36 – 1.21 (m, 12H, (C**H**$_2$)$_3$-CH_2-CH_2-Cp). ^{13}C-NMR (101 MHz, $CDCl_3$, 25 °C): δ(ppm): 150.2 (CH_2CH_2**C**$_{Cp}$), 147.5 (CH_2CH_2**C**$_{Cp}$), 135.0 (C_{Cp}), 133.6 (C_{Cp}), 132.6 (C_{Cp}), 130.4 (C_{Cp}), 126.3 (C_{Cp}), 125.7 (C_{Cp}), 43.4 (C_{Cp}), 41.3 (C_{Cp}), 30.9 (CH_2**C**H_2Cp), 30.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.0 (CH_2).

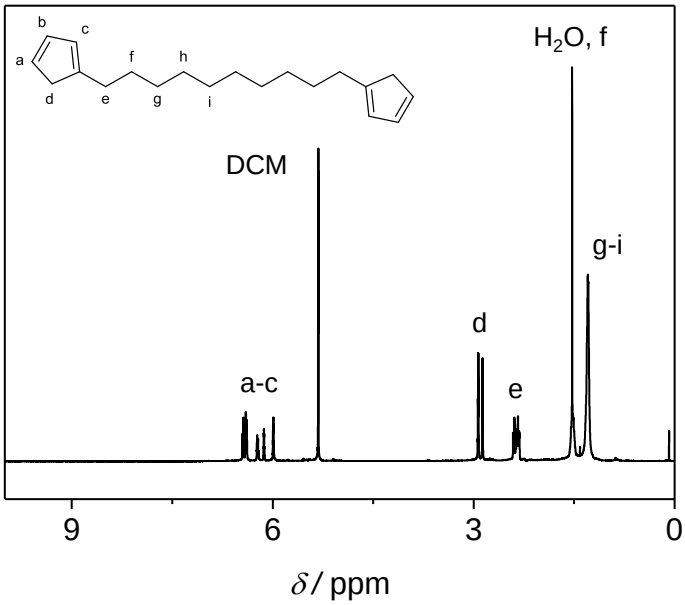


Figure S1. ^{1}H-NMR spectrum of 1,10-di(cyclopentadienyl)-decane (**AA**). Spectrum was recorded in CD_2Cl_2.

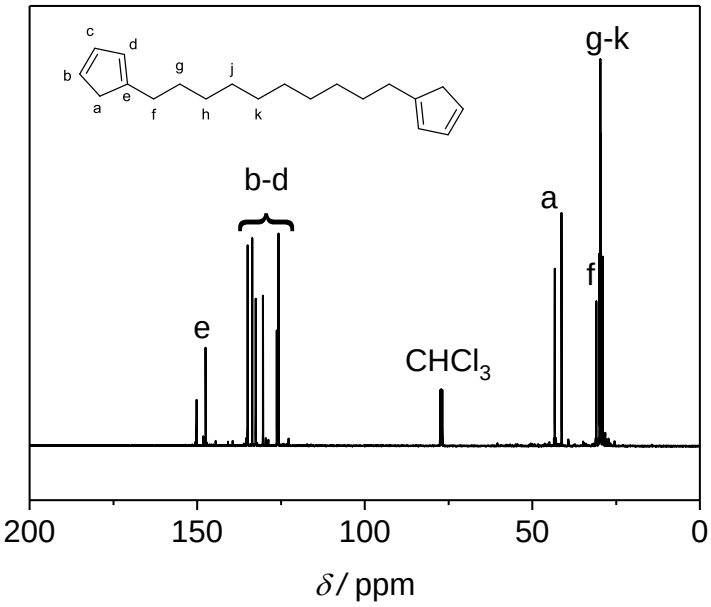
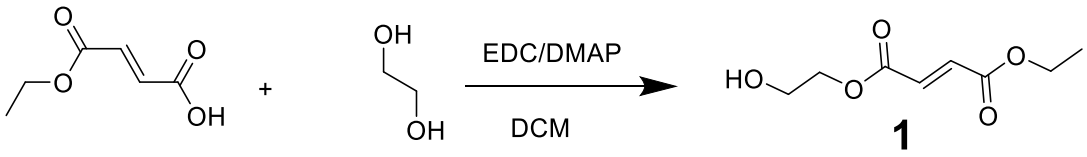


Figure S2. ^{13}C-NMR spectrum of 1,10-di(cyclopentadienyl)-decane (**AA**). Spectrum was recorded in $CDCl_3$.

Synthesis of 2-hydroxyethyl-ethyl fumarate (1)



Scheme S2. Synthesis of 2-hydroxyethyl-ethyl fumarate for **BB** synthesis.

In a round bottom flask 2.00 g (13.88 mmol, 1.0 eq.) monoethyl fumarate, 8.61 g (138.77 mmol, 10.0 eq.) ethylene glycol, and 339 mg (2.78 mmol, 0.2 eq.) 4-(*N,N*-dimethylamino) pyridine (DMAP) were dissolved in a mixture of 24 mL dry DCM and 9 mL dry THF. The solution was cooled to 0 °C and 3.19 g (16.65 mmol, 1.2 eq.) 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC) was added. The solution was allowed to reach ambient temperature and left to stir overnight. After the reaction, the solvent was evaporated under reduced pressure. Subsequently, the crude product was dissolved in DCM and washed with 5% hydrochloric acid, saturated $NaHCO_3$ solution and brine. The combined organic phase was dried over Na_2O_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate, 1/1 v/v) to obtain 2.01 g of a colorless oil (yield 77%). ^{1}H-NMR (400 MHz, DMSO-d6, 25 °C): δ (ppm): 6.89 (m, 2H, **H**C=C**H**), 4.88 (t, ^3J = 6.04 Hz, 1H, O**H**), 4.22-4.15 (m, 4H, C**H**$_2$O), 3.64-3.60 (m, 2H, C**H**$_2$O), 1.25 (t, ^3J = 7.19 Hz, 3H, -C**H**$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 25 °C): δ(ppm): 165.3 (H**C**=CH), 165.0 (HC=**C**H), 134.5 (**C**=O), 133.1, (**C**=O), 67.0 (HOCH$_2$-**C**H$_2$-C=O), 61.6 (CH$_3$-**C**H$_2$-C=O), 61.1 (HO**C**H$_2$-CH$_2$-C=O), 14.2 (**C**H$_3$-CH$_2$-C=O). ESI-MS: *m/z* $[M+Na]^+_{exp}$: 211.0578, $[M+Na]^+_{calc}$: 211.0577.

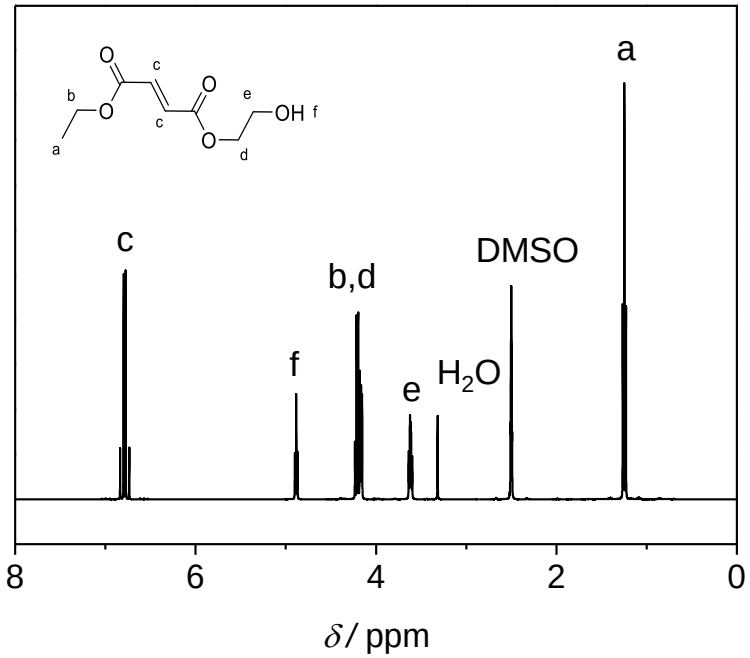


Figure S3. ^{1}H-NMR spectrum of 2-hydroxyethyl-ethyl fumarate (**1**). The spectrum was recorded in DMSO-d_6.

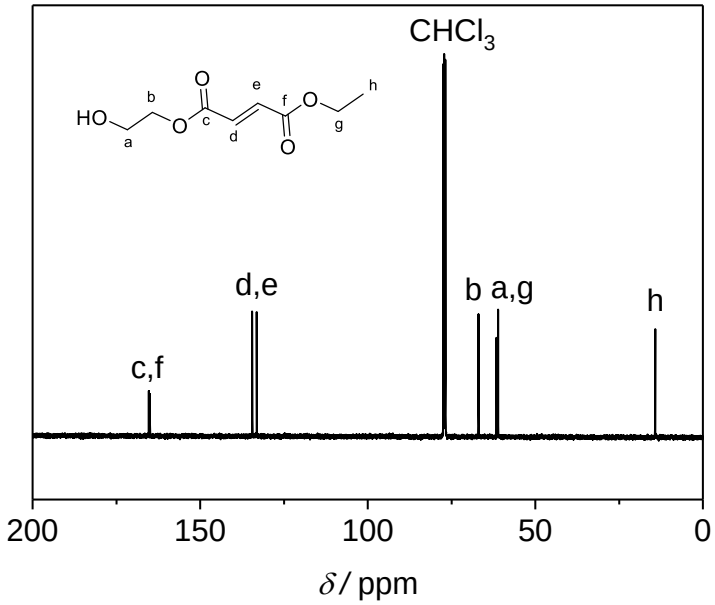


Figure S4. ^{13}C-NMR spectrum of 2-hydroxyethyl-ethyl fumarate (**1**). Spectrum was recorded in $CDCl_3$.

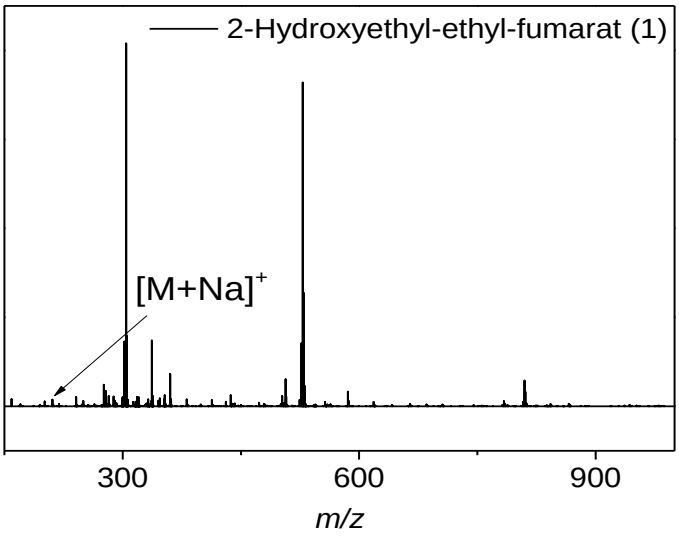
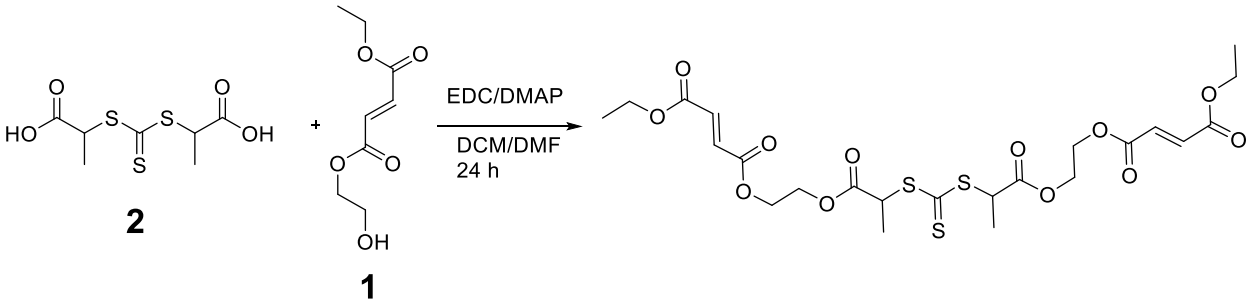


Figure S5. ESI-MS spectrum of 2-hydroxyethyl-ethyl fumarate (**1**). The spectrum was recorded in a direct-infusion experiments using a solvent mixture of THF/MeOH (3/2 v/v) by doping with sodium trifluoroacetate.

Synthesis of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate (BB monomer)



Scheme S3. Synthesis of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate **BB**.

In a round bottom flask 420 mg (1.65 mmol, 1.0 eq.) DTC (**2**), 668 mg (3.55 mmol, 2.15 eq.) 2-hydroxyethyl-ethyl fumarate (**1**, see synthesis route above), and 61 mg (0.50 mmol, 0.3 eq.) DMAP were dissolved in a mixture of 10 mL dry DCM and 1 mL dry DMF. The solution was cooled to 0 °C and 665 mg (3.47 mmol, 2.1 eq.) EDC was added. The solution shortly turned intensively red and was allowed to reach ambient temperature, before being stirred for 16 h. Next, the solution mixture was washed with 5% hydrochloric acid, saturated $NaHCO_3$ solution and brine. The combined organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate, 2/1 v/v) to obtain 687 mg of yellowish oil (yield 70%). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm): 6.86 (s, 4H, *H*C=C*H*), 4.77-4.75 (m, 2H, C**H**S), 4.40 (m, 8H, -C**H**$_2$O), 4.27-4.25 (m, 4H, C**H**$_2$O), 1.61-1.59 (m, 6H, C**H**$_2$-CHS), 1.32 (t, ^3J = 7.03 Hz, 6H, -C**H**$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 25 °C): δ(ppm): 219.5 (**C**=S), 170.7 (S-CH(CH_3)-**C**=O) 164.8 (H**C**=**C**H), 134.7 (**C**=O), 132.9, (**C**=O), 63.3 (CH_2-**C**H_2-C=O), 62.8 (CH_2-**C**H_2-C=O), 61.6 (CH_3-**C**H_2-C=O), 48.3 (**C**H(CH_3)-S) 16.7 ((**C**H_3)CH-S), 14.2 (**C**H_3-CH_2-C=O). ESI-MS: *m/z* $[M+Na]^+_{exp}$: 617.0786, $[M+Na]^+_{calc}$: 617.0792.

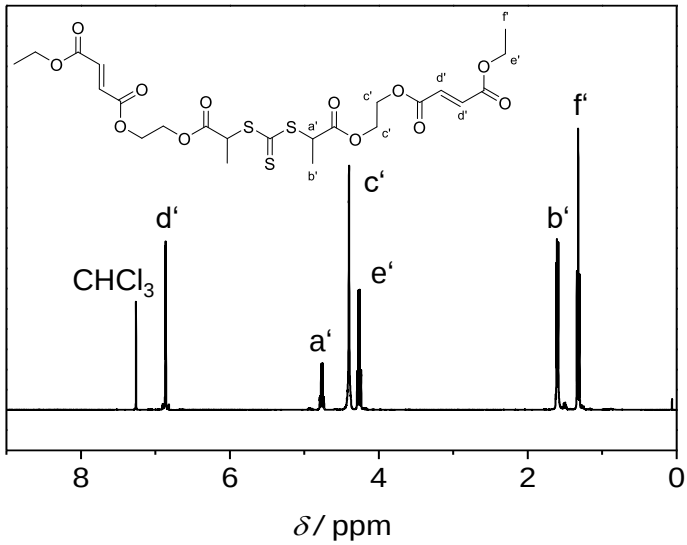


Figure S6. ^{1}H-NMR spectrum of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate (**BB** monomer). The spectrum was recorded in $CDCl_3$.

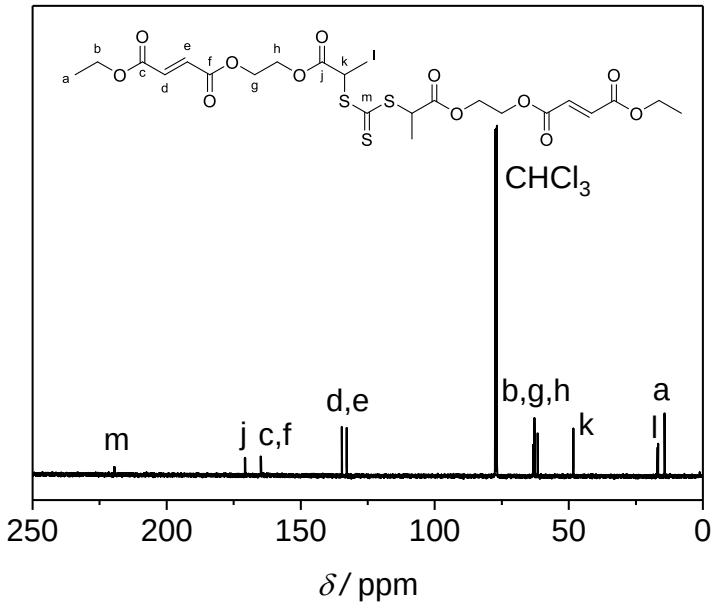


Figure S7. ^{13}C-NMR spectrum of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate (**BB** monomer). Spectrum was recorded in $CDCl_3$.

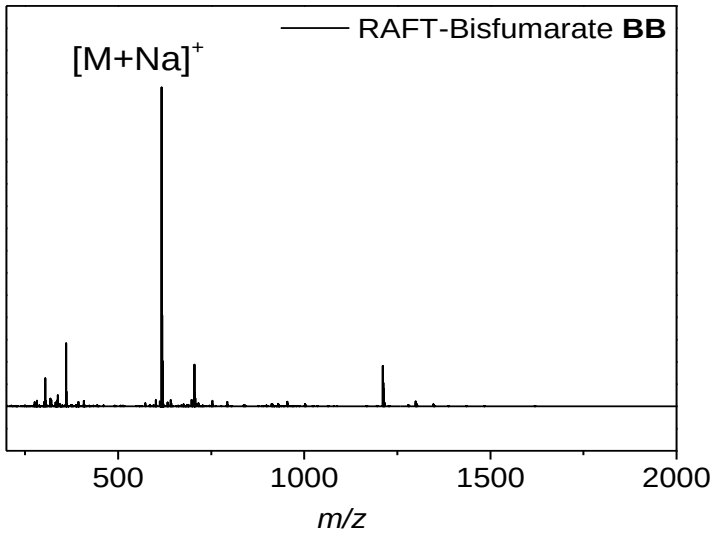
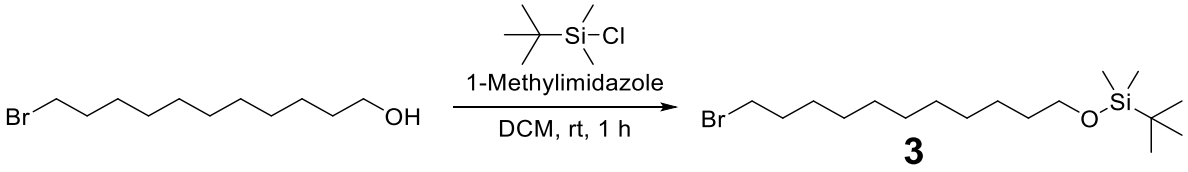


Figure S8. ESI-MS spectrum of the RAFT bisfumarate **BB** monomer. The spectrum was recorded via a direct-infusion experiment in THF/MeOH (3/2 v/v) by doping with sodium trifluoroacetate.

Synthesis of ((11-bromoundecyl)oxy)(tert-butyl)dimethylsilane (3)



Scheme S4. Protection of 11-bromoundecan-1-ol with silyl-ether.

In a 100 mL Schlenk flask 4.00 g 11-bromoundecan-1-ol (15.9 mmol, 1.00 eq) and 2.80 g TBDMSCl (18.5 mmol, 1.20 eq) were dissolved in 15 mL of dry DCM under inert gas atmosphere. Subsequently 3.9 mL 1-methyilmidazole (49.0 mmol, 3.00 eq) was added to the dissolved material. The mixture was stirred for 1 h at ambient temperature under inert gas atmosphere. The reaction was quenched with 20 mL of water, followed by the addition of 90 mL ethyl acetate. The organic layer was washed with saturated aqueous solution of Na_2CO_3 and deionized water, and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate, 93/7 v/v) to obtain a yellow oil (5.15 g, 88 %).^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm): 3.59 (t, ^3J = 6.6 Hz, 2 H, SiO-C**H**$_2$-CH$_2$), 3.40 (t, ^3J = 6.9 Hz, 2 H, Br-C**H**$_2$-CH$_2$), 1.89 – 1.80 (m, 2 H, Br-CH$_2$-C**H**$_2$-CH$_2$), 1.49 (q, ^3J = 6.7 Hz, 2 H, SiO-CH$_2$-C**H**$_2$), 1.46 – 1.37 (m, 2 H, SiO-CH$_2$-CH$_2$-C**H**$_2$), 1.27 (s, 12 H, CH$_2$-C**H**$_2$-CH$_2$), 0.89 (s, 9 H, C-C**H**$_3$), 0.4 (s, 6 H, Si-(C**H**$_3$)$_2$). ^{13}C-NMR (101 MHz, $CDCl_3$, 25 °C): δ(ppm): 63.5 (CH$_2$-**C**H$_2$-O), 34.2 (Br-**C**H$_2$-CH$_2$), 33.0 (CH$_2$-**C**H$_2$-CH$_2$-O), 33.0 (Br-CH$_2$-**C**H$_2$-CH$_2$), 29.7 (Si-**C**-(CH$_3$)$_3$), 29.6 (CH$_2$-**C**H$_2$-CH$_2$), 29.6 (CH$_2$-**C**H$_2$-CH$_2$), 28.9 (CH$_2$-**C**H$_2$-CH$_2$), 28.3 (CH$_2$-**C**H$_2$-CH$_2$), 26.1 (**C**H$_3$), –5.1(Si-(**C**H$_3$)$_2$). ESI-MS: *m/z* [M+Na]$^+_{exp}$: 387.1688, [M+Na]$^+_{calc}$: 387.1695.

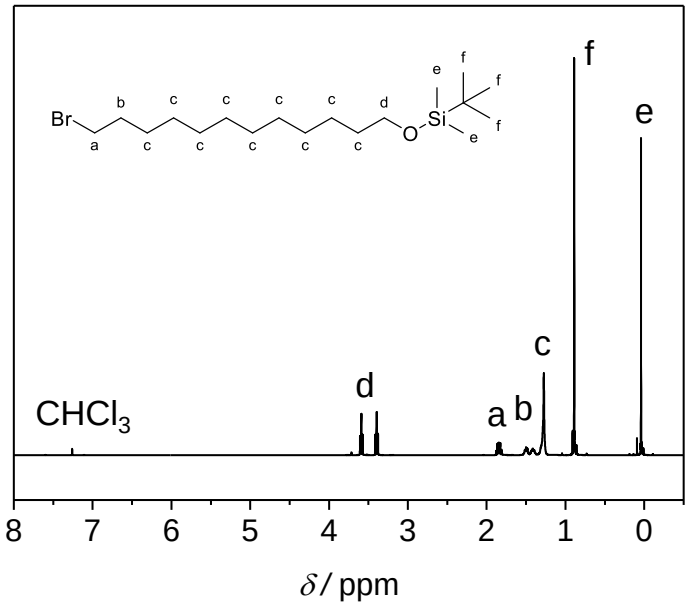


Figure S9. ^{1}H-NMR spectrum of ((11-bromoundecyl)oxy)(tert-butyl)dimethylsilane (**3**, precursor of Mono-Cp). Spectrum was recorded in $CDCl_3$.

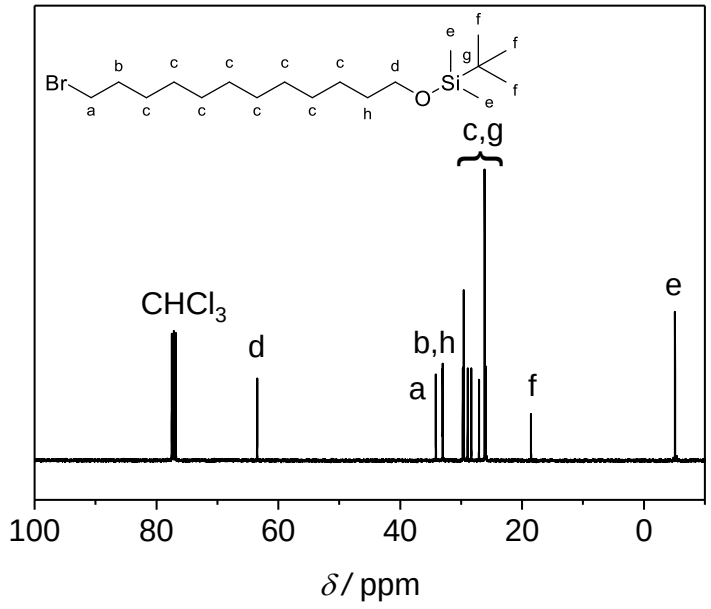
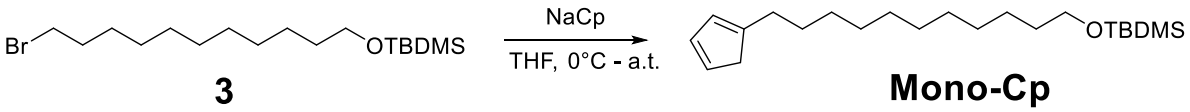


Figure S10. ^{13}C-NMR spectrum of ((11-bromoundecyl)oxy)(tert-butyl)dimethylsilane (**3**, precursor of Mono-Cp). Spectrum was recorded in $CDCl_3$.

Synthesis of *tert*-butyl((11-(cyclopenta-1,3-dien-1-yl)undecyl)oxy)dimethylsilane (Mono-Cp)



3 **Mono-Cp**

Scheme S5. Synthesis of the *tert*-butyl((11-(cyclopenta-1,3-dien-1-yl)undecyl)oxy)dimethylsilane (Mono-Cp).

To a cooled (0 °C) solution of ((11-bromoundecyl)oxy)(*tert*-butyl)dimethylsilane (**3**, 3.60 g, 9.0 mmol, 1.00 eq) in dry THF (25 mL), sodium cyclopentadienyl (5.5 mL of a 2.0 M solution in THF, 11.0 mmol, 1.20 eq) was added. After stirring for 1 h at 0 °C, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The suspension was filtered off and the residual solution was filtered by flash chromatography (silica gel, cyclohexane/ethyl acetate, 93/7 v/v). The crude product was concentrated and isolated by flash chromatography (silica gel, cyclohexane/toluene, 4/1 v/v) to obtain a colourless oil (1.7 g, 54%).

^{1}H- NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm): 6.49 – 5.96 (m, 3 H, CH-C**H**$_{ar}$-CH), 3.60 (t, ^{3}J = 6.6 Hz, 2 H, Si-O-C**H**$_2$-CH$_2$), 2.92 – 2.87 (m, 2 H, CH$_{ar}$-C**H**$_{2,ar}$-CH$_{ar}$), 2.44 – 2.30 (m, 2 H, CH$_2$-C**H**$_2$-CH$_2$), 1.59 – 1.39 (m, 4 H, CH-(C**H**$_2$)$_2$-CH$_{ar}$), 1.27 (s, 14 H, CH-(C**H**$_2$)$_7$-CH$_{ar}$), 0.93 – 0.86 (m, 9 H, Si-C-(C**H**$_3$)$_3$), 0.08 – 0.02 (m, 6 H, Si-(C**H**$_3$)$_2$). ^{13}C-NMR (101 MHz, $CDCl_3$, 25 °C): δ(ppm): 150.5 (CH$_2$CH$_2$**C**$_{Cp}$), 148.6 (CH$_2$CH$_2$**C**$_{Cp}$), 135.0, (C$_{Cp}$), 133.7 (C$_{Cp}$), 132.6 (C$_{Cp}$), 130.5 (C$_{Cp}$), 126.2 (C$_{Cp}$), 125.8 (C$_{Cp}$), 63.5 (CH$_2$-**C**H$_2$-O), 43.4 (Cp-**C**H$_2$), 41.3 (Cp-**C**H$_2$), 33.1 (**C**H$_2$-CH$_2$-O), 30.9 (Si-**C**-(CH$_3$)$_3$), 30.0 (CH$_2$-**C**H$_2$-CH$_2$), 29.8 (CH$_2$-**C**H$_2$-CH$_2$), 29.8 (CH$_2$-**C**H$_2$-CH$_2$), 29.7 (CH$_2$-**C**H$_2$-CH$_2$), 29.6 (CH$_2$-**C**H$_2$-CH$_2$), 29.0 (CH$_2$-**C**H$_2$-CH$_2$), 26.2 (C$_q$-**C**H$_3$), –5.1 (Si-(**C**H$_3$)$_2$). ESI-MS: *m/z* [M+Na]$^+_{exp.}$: 373.2911, [M+Na]$^+_{calc}$: 373.2897.

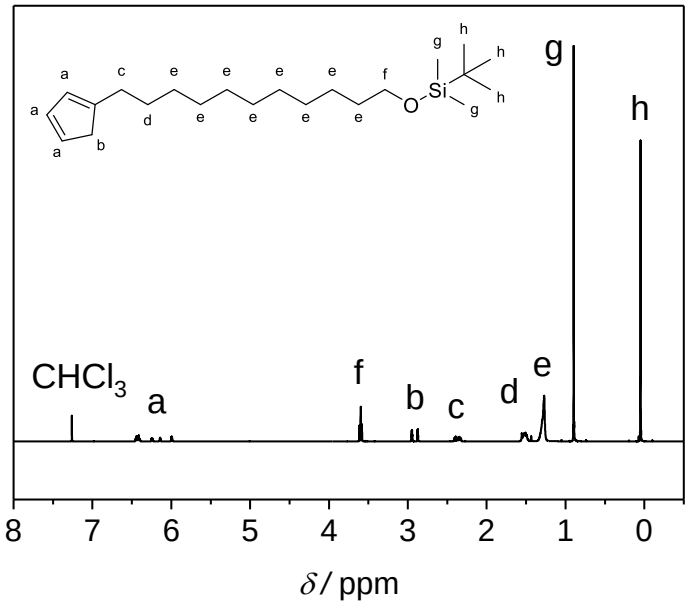


Figure S11. ^{1}H-NMR spectrum of *tert*-butyl((11-(cyclopenta-1,3-dien-1-yl)undecyl)oxy)dimethylsilane (Mono-Cp). Spectrum was recorded in $CDCl_3$.

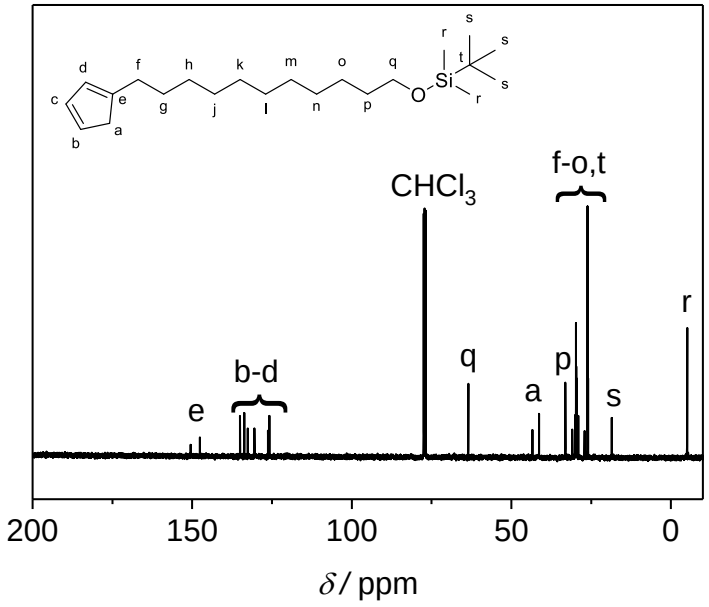


Figure S12. ^{13}C-NMR spectrum of *tert*-butyl((11-(cyclopenta-1,3-dien-1-yl)undecyl)oxy)dimethylsilane (Mono-Cp). Spectrum was recorded in $CDCl_3$

4. Stability Test of Monomer AA

Reaction conditions: **AA** stirring for 24 h in DCM-d_2 (0.2 mol·L^{-1}) at ambient temperature

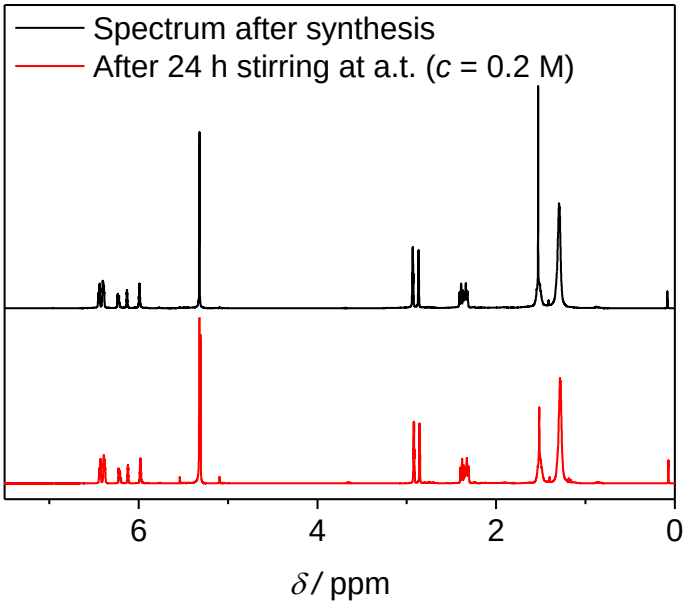


Figure S13. ^{1}H-NMR spectra of the di(cyclopentadienyl)-decane **AA** after stirring at ambient temperature for 24 h in DCM-d_2 (c = 0.2 mol·L^{-1}). Spectrum was recorded in DCM-d_2.

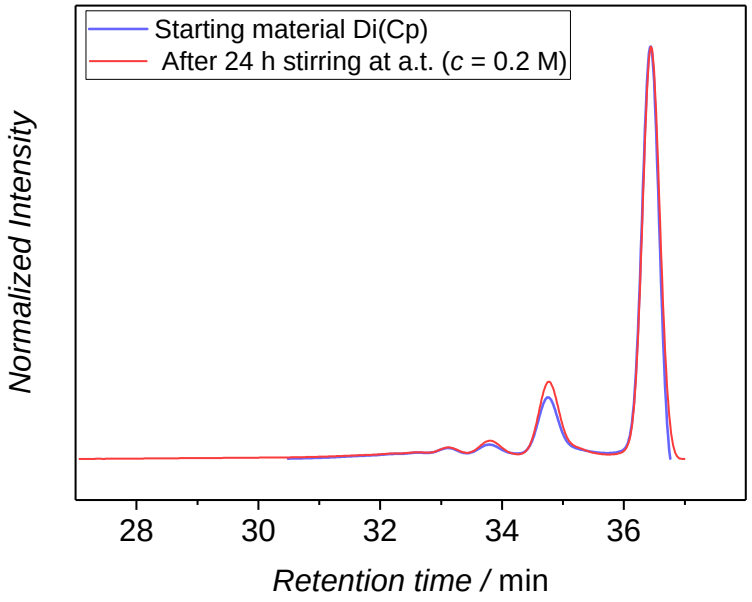
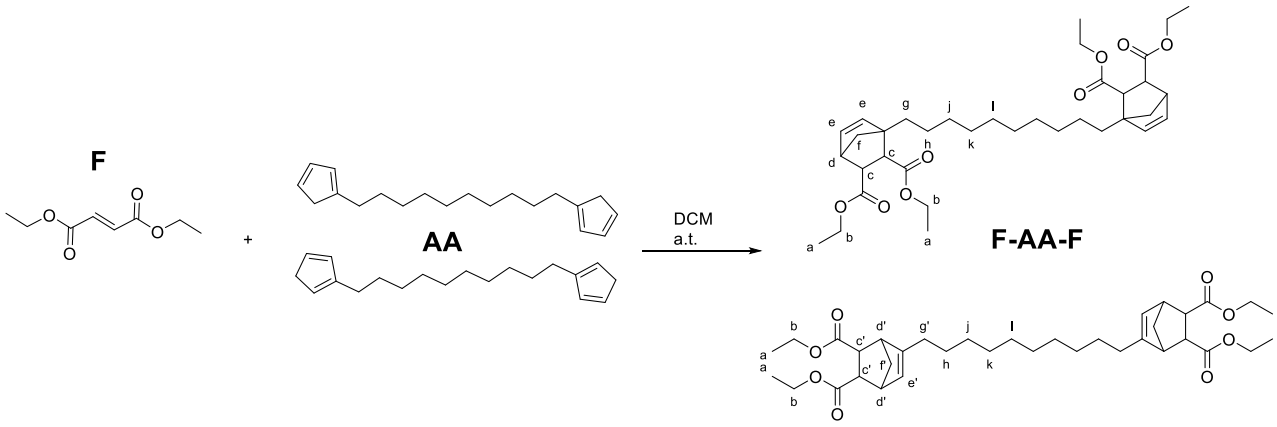


Figure S14. THF-SEC-trace of the di(cyclopentadienyl)-decane **AA** after stirring at ambient temperature for 24 h in DCM-d_2 (c = 0.2 mol·L^{-1}). Detection was carried out by an RI detector.

5. Small Molecule Study



Scheme S6. Small molecule reaction between di(cyclopentadienyl) decane **AA** and diethyl fumarate **F**. Two constitutional isomers of **AA** are shown as well as two possible adducts **F-AA-F**.

In a 5 mL glass vial 115.8 mg 1,10-di(cyclopentadienyl) **AA** (0.428 mmol, 1 eq.) and 196 µL diethyl fumarate **F** (206 mg, 1.20 mmol, 2.8 eq.) were dissolved in 5 mL DCM. The glass vial was sealed and the reaction mixture stirred for 24 h at ambient temperature. The raw product was obtained by removing the solvent under reduced pressure, yielding a colorless oil.

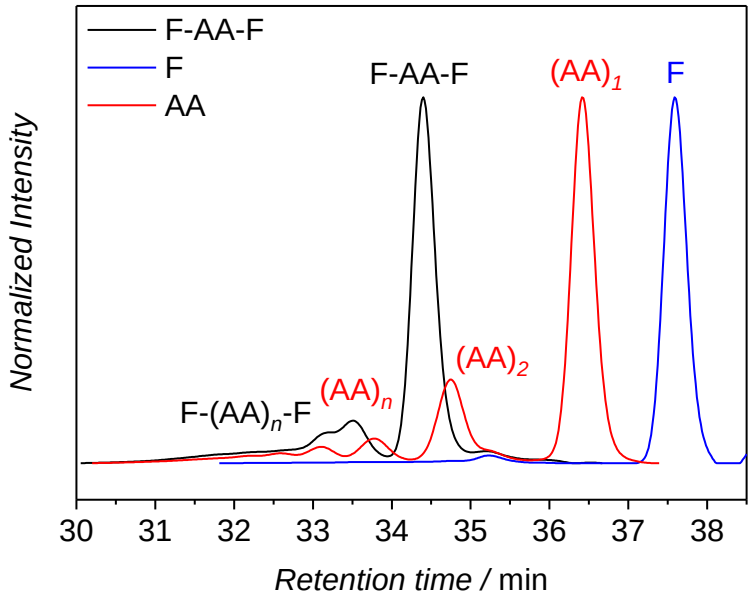


Figure S15. THF-SEC traces of the product **F-AA-F** (black), and the starting materials **AA** (red) and **F** (blue). Detection was carried out by an RI detector.

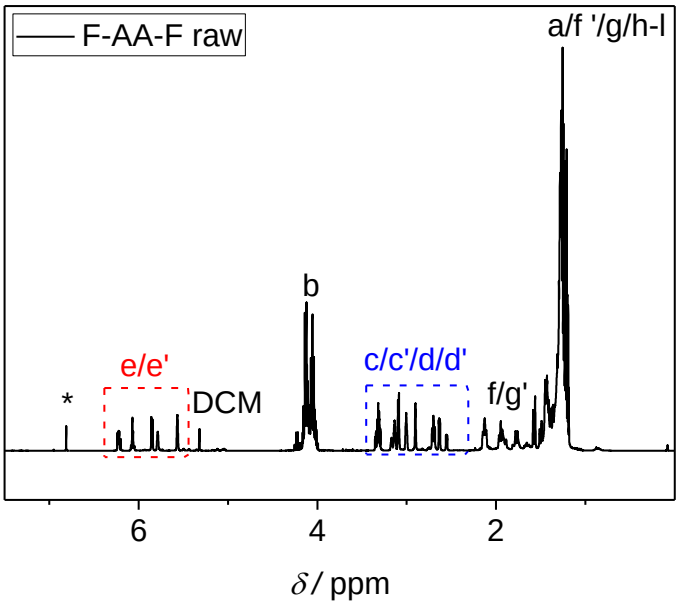


Figure S16. ^{1}H-NMR spectrum of the raw **F-AA-F** product. Spectrum was recorded in CD_2Cl_2. Assignment, as indicated in the plot, according to the two different product structures in Scheme S6. * represents the left-over starting material diethyl fumarate **F**.

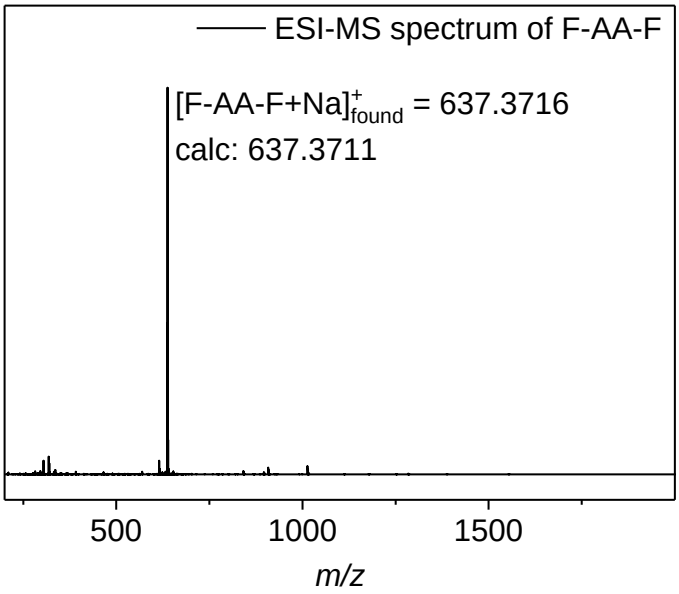


Figure S17. ESI-MS spectrum of the raw material of **F-AA-F**. The spectrum was recorded via a direct-infusion experiment with THF/MeOH 3/2 v/v, doping with sodium trifluoroacetate.

6. Stoichiometry Determination

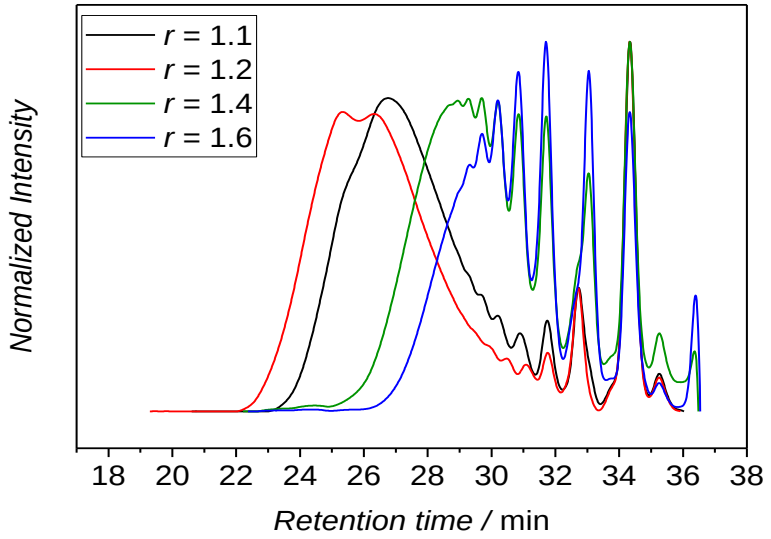
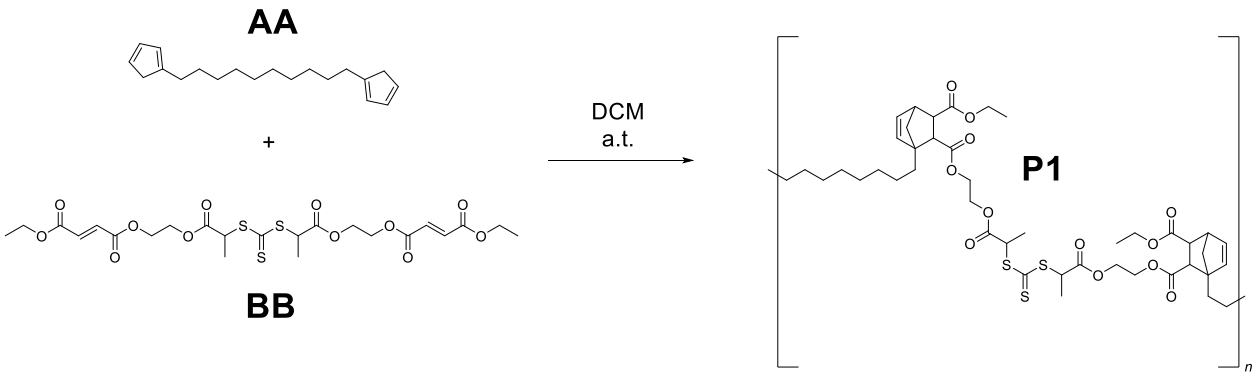


Figure S18. SEC-traces of step-growth polymers, obtained by polymerization with different stoichiometries *r* of **AA/BB**, as indicated in the plot. Reaction conditions: *c* = 0.2 mol·L^{-1} in DCM after 12 h of reaction. Detection was carried out by an RI detector.

Table S1. Results of the step-growth polymerization for stoichiometry determination, obtained by THF-SEC applying a polystyrene calibration, using different stoichiometries *r* of the monomers **AA/BB**, indicating the highest molecular weight for ***r* = 1.2**.

Stoichiometry *r*	M_n / g·mol^{-1}	M_w / g·mol^{-1}	*Đ*
1.1	3,650	23,750	6.49
1.2	**4,150**	**40,000**	**9.67**
1.4	2,100	8,250	3.97
1.6	1,850	5,600	3.00

7. Step-Growth Polymerization



Scheme S7. Step-growth polymerization by Diels-Alder reaction using monomer **AA** and **BB** in DCM at ambient temperature.

In a typical step-growth polymerization procedure, monomer **AA** (0.2 mol·L^{-1}, 1.2 eq.) and monomer **BB** (0.17 mol·L^{-1}, 1.0 eq.) were separately dissolved in DCM and subsequently mixed. The step-growth polymerization was allowed to stir under ambient conditions (T = 25 °C) for the desired time. After the polymerization, the solvent was removed under reduced pressure at ambient temperature to obtain the step-growth polymer as a yellowish rubber-like solid.

Table S2. Molecular results of the step-growth polymers obtained by DA cycloaddition. Conversion was obtained by evaluation of ^{1}H-NMR spectra of the corresponding samples, M_n, M_w and $Đ$ values were obtained by THF-SEC applying a polystyrene calibration.

Reaction time/min	Conversion	M_n / g·mol^{-1}	M_w / g·mol^{-1}	$Đ$
20	0.66	1,200	2,350	1.97
40	0.78	1,650	3,950	2.4
60	0.84	2,050	4,850	2.36
90	0.89	2,500	6,150	2.44
120	0.92	2,800	7,800	2.81
180	0.95	3,150	10,500	3.35
240	0.97	3,250	13,500	4.1
360	0.98	3,650	18,700	5.15
480	0.99	3,900	22,200	5.65
1200	1	3,850	38,960	10.2

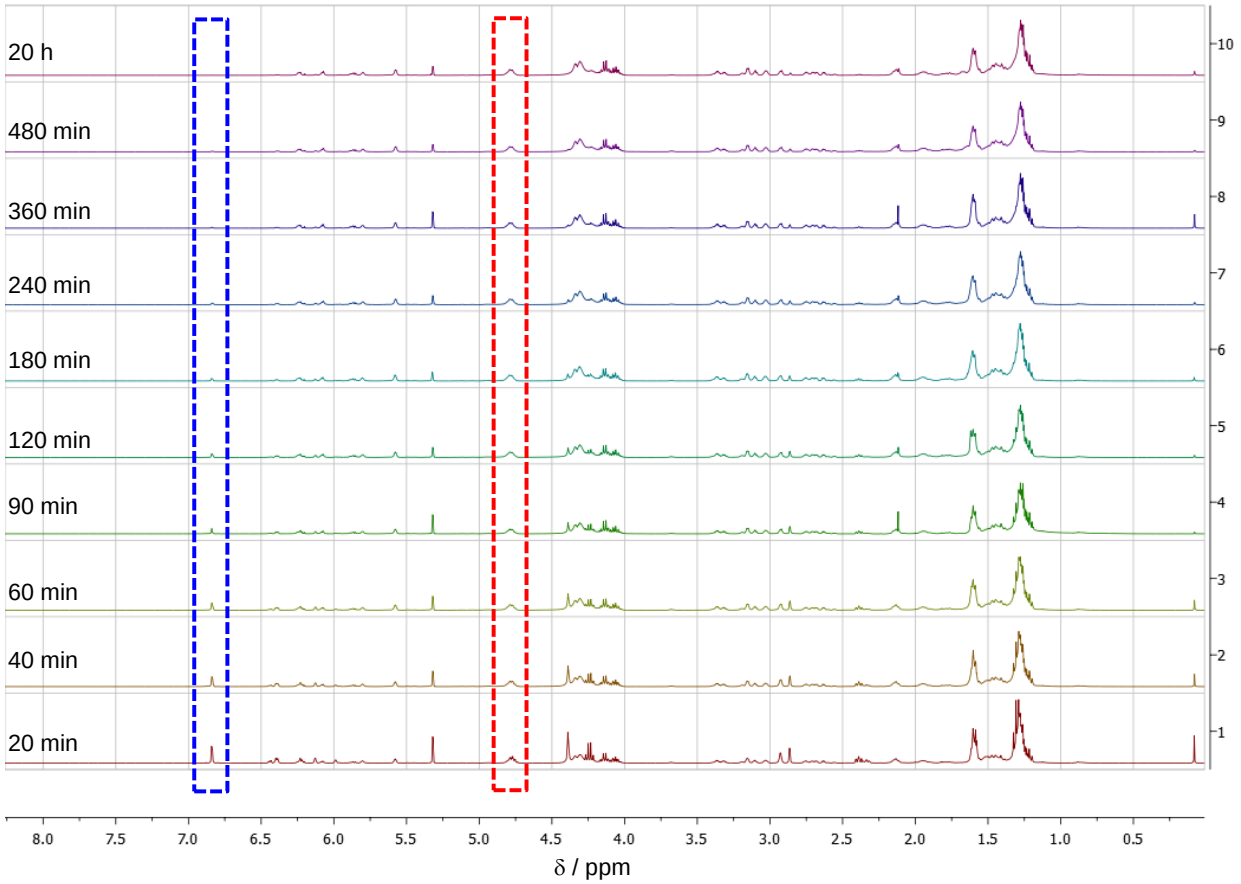


Figure S19. ^{1}H-NMR spectra of the step-growth polymerization kinetics. All measurements were recorded in CD_2Cl_2. The blue box highlights the fumarate resonances, the red box highlights the resonances of the α-proton to the trithiocarbonate.

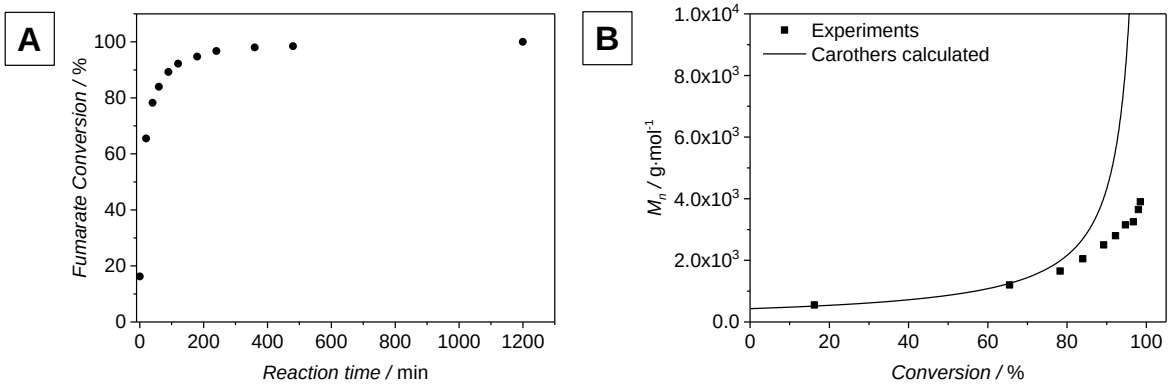


Figure S20. A: Kinetic plot of the step-growth polymerization with a monomer stoichiometry of r = 1.2, ranging from 20 min to 20 h reaction time. Conversion was determined by evaluation of the ^{1}H-NMR spectra, referencing the resonances of the fumarate protons to the α-protons of the trithiocarbonate. **B:** Carothers plots of the step-growth polymerization with a monomer stoichiometry of r = 1.2, M_n *vs. conversion*. Conversion was obtained by evaluation of ^{1}H-NMR spectra of corresponding samples, referencing the integrals of the fumarate resonances to the unchanged α-protons of the trithiocarbonate. M_n and M_w values were determined by THF-SEC applying a polystyrene calibration.

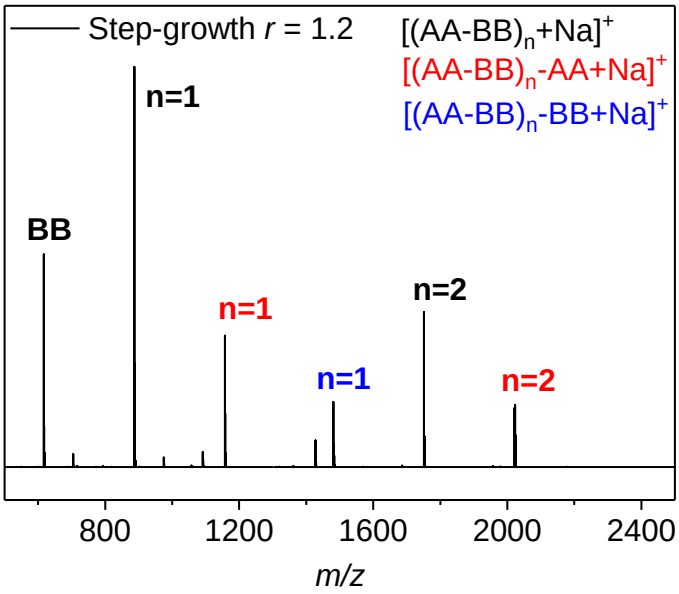


Figure S21. ESI-HCD-MS spectrum of the step-growth polymer with a monomer stoichiometry of *r* = 1.2. Assignment of signals as indicated in the plot. Spectrum was recorded in HCD mode, using an energy of 10 eV fragmenting the species at 2022 Th, triggering the *retro* Diels – Alder reaction to significant extent. The **AA** monomer shows poor ionization, therefore, no signal of the **AA** monomer was detected. A solvent mixture of 3/2 THF/MeOH (v/v) and doping with sodium trifluoroacetate was used.

Table S3. Assignment from ESI-HCD-MS spectrum signals of the SG polymer (*r* = 1.2) in Figure S21.

#	m/z_{found}	$m/z_{calc.}$	$\Delta m/z_{exp}$	$\Delta m/z_{theo}$	R
n = 2	2022.8833	2022.8767	0.0066	0.0417	48,500
n = 2	1751.6455	1751.6386	0.0069	0.0353	49,500
n = 1	1481.406	1481.4039	0.0021	0.0265	55,800
n = 1	1157.5491	1157.5487	0.0004	0.0179	64,600
n = 2	887.3136	887.3139	0.0003	0.0123	71,900
BB	617.0788	617.0792	0.0004	0.0072	85,950

8. Proof of RAFT Group Presence and DA Stability Tests

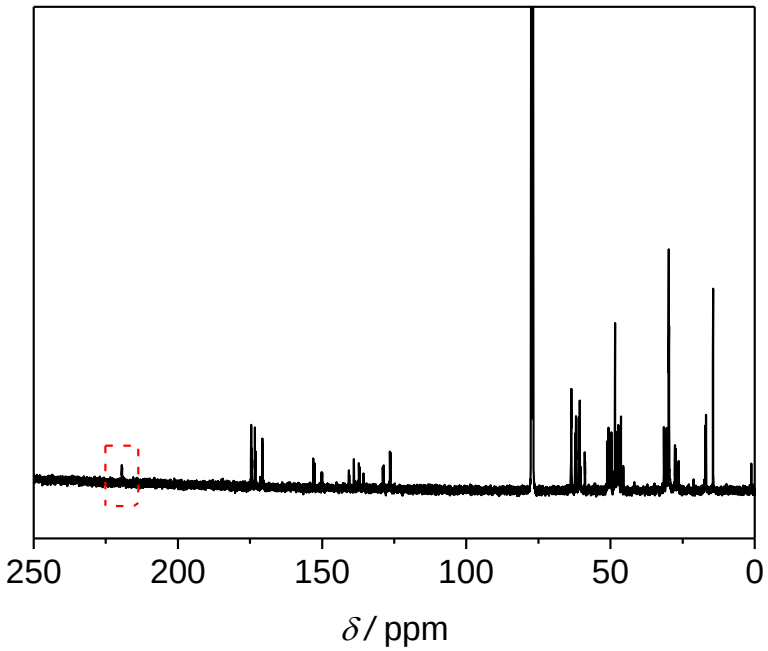


Figure S22. ^{13}C-NMR spectrum of the step-growth polymer **P1** (with monomer stoichiometry *r* = 1.2), showing the presence of the trithiocarbonate resonance at 219 ppm (red box). Spectrum was recorded in $CDCl_3$.

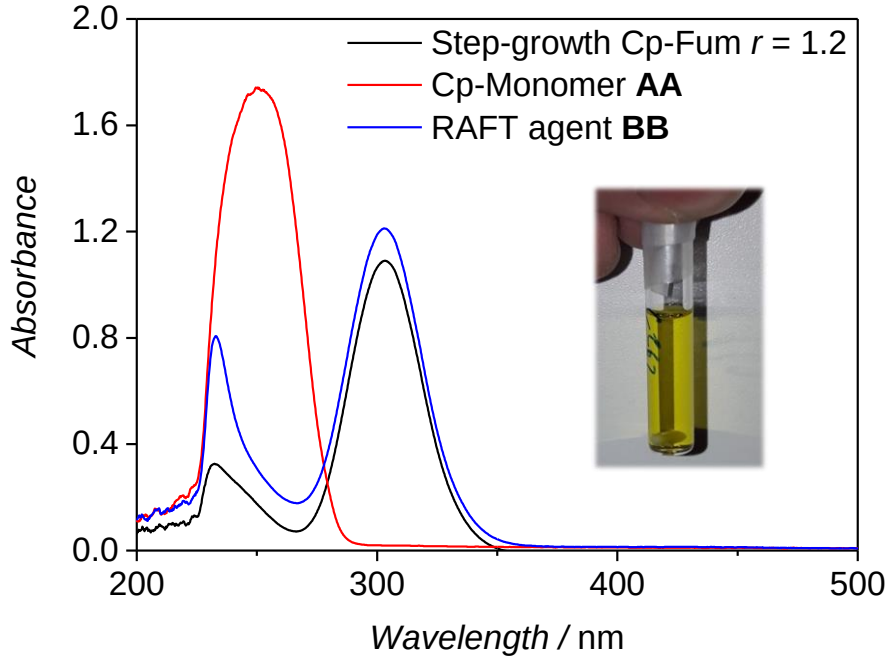
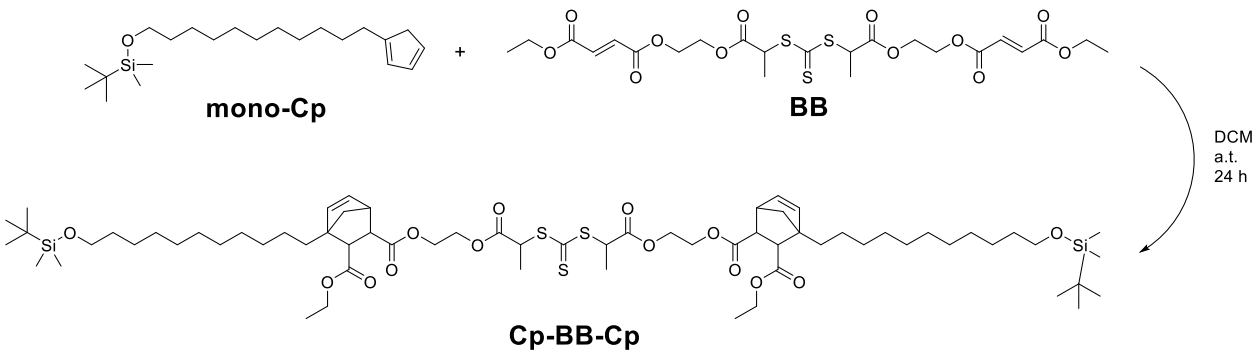


Figure S23. UV/VIS spectra of the step-growth polymer (*r* = 1.2) and the monomers **AA** and **BB**, respectively. Spectra were recorded in DCM, with the following concentrations: *c* (step-growth polymer *r* = 1.2) = 24 µmol·L^{-1}, *c* (**AA**) = 37 mmol·L^{-1}, *c* (**BB**) = 84 µmol·L^{-1}. Absorbance of trithiocarbonate at approx. 303 nm. The inset picture shows the sample after step-growth polymerization in DCM, demonstrating the typical yellow color attributed to the trithiocarbonate group.



Scheme S8. Scheme of the reaction generating the test molecule for the analysis of the *retro*-Diels-Alder reaction by high-temperature NMR at 60 °C. 2.3 eq. of the mono-Cp molecule were employed in the DA reaction.

The **Cp-BB-Cp** molecule was synthesized by mixing 10.0 mg of the **mono-Cp** (0.029 mmol, 2.3 eq.) and 7.4 mg **BB** monomer (0.012 mmol, 1 eq.) in 1 mL DCM for 24 h at ambient temperature. The stability test was carried out with the unpurified **Cp-BB-Cp** in toluene-d8 at 60 °C in a sealed NMR tube inside the NMR instrument.

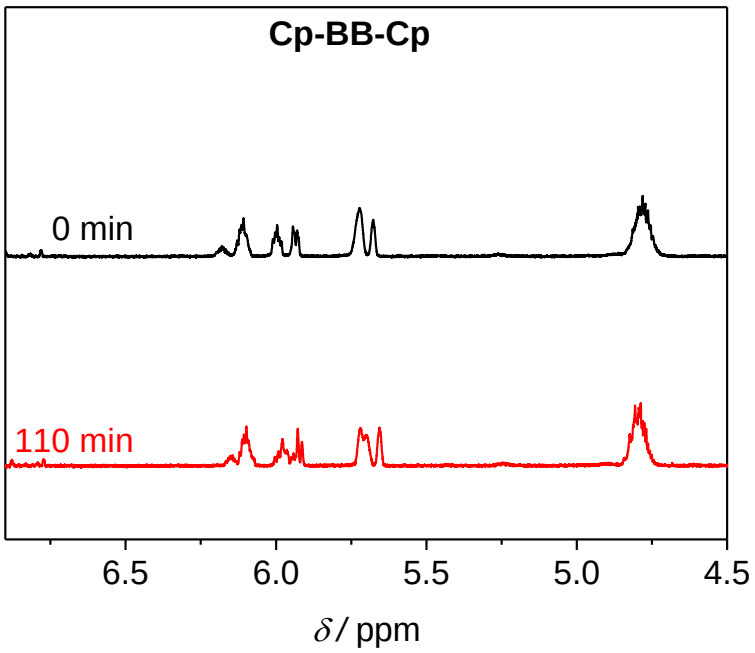


Figure S24. ^{1}H-NMR spectra of the **Cp-BB-Cp** stability test, monitoring no *retro* Diels-Alder products. The reaction scheme is shown in Scheme S8. Spectra were recorded in toluene-d8 at 60 °C. The NMR tube was permanently kept in the instrument during the stability test.

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9. Chain Extension via RAFT Polymerization

In a typical RAFT procedure 1.8 mg (0.012 mmol, 3 eq.) AIBN and 50 mg of the step-growth precursor polymer **P1** (*n*(RAFT) = 5 mmol, 15 Eq.) were dissolved in 10.50 g (100.9 mmol, 8727 eq.) of styrene. The stock solution was split into different headspace vials (*V* = 1.2 mL per vial), sealed and nitrogen was percolated through the solutions for 10 min. Subsequently, the vials were placed in a pre-heated sample holder at 60 °C and stirred for the predefined polymerization time. To terminate the polymerization, the solution was quenched in liquid nitrogen and exposed to air. The crude polymerization solution was exposed to reduced pressure in order to remove any volatile components to obtain the polymer without precipitation.

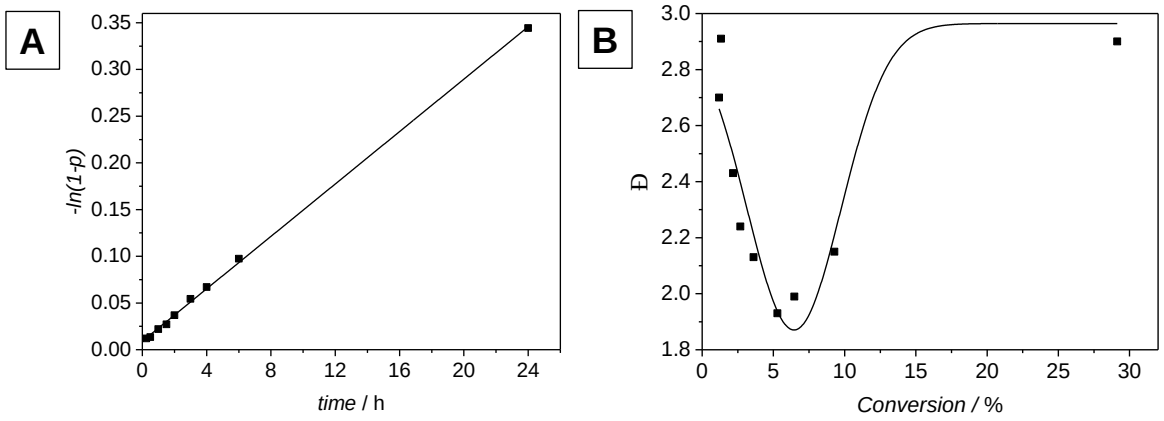

Figure S25. A: *–ln(1-p)* vs. reaction time of the RAFT polymerization. Data was obtained by gravimetric evaluation. **B:** Evolution of Đ with conversion. The line is only for guiding the eye.

Table S4. Molecular results of the polystyrene obtained by RAFT polymerization. Conversion was obtained by gravimetric evaluation, M_n, M_w and $Đ$ values were obtained by THF-SEC applying a polystyrene calibration.

Reaction time/min	Conversion	M_n / g·mol^{-1}	M_w / g·mol^{-1}	$Đ$
15	0.012	30,900	83,400	2.7
30	0.013	37,000	107,800	2.91
60	0.022	44,500	107,800	2.43
90	0.027	50,700	113,200	2.24
120	0.036	68,000	145,000	2.13
180	0.053	92,300	178,300	1.93
240	0.065	101,100	218,700	1.99
360	0.093	145,000	311,200	2.15
1440	0.291	333,500	965,800	2.9

10. Calculation of the molecular weight using the Carothers Equation[3]

Eq. S1 $$M_n = \frac{\left(M/2\right)}{1-p}$$

Eq. S2 $$M_w = \frac{\left(M/2\right)\left(1+p\right)}{1-p}$$

With p: conversion, M: molecular weight of the repeating unit.

11. References

1 D. Nguyen, H. S. Zondanos, J. M. Farrugia, A. K. Serelis, C. H. Such and B. S. Hawkett, *Langmuir*, 2008, **24**, 2140–2150.

2 A. M. Schenzel, C. Klein, K. Rist, N. Moszner and C. Barner-Kowollik, *Adv. Sci.*, 2016, **3**, 1500361.

3 G. Odian, *Principles of polymerization*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 4th edn., 2004.