Controlling molecular weight and polymer architecture during the Passerini three component step-growth polymerization

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SUPPORTING INFORMATION

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1. Materials

The following chemicals were used as received: 10-undecenal (\geq 90%, Aldrich), 3-mercaptopropionic acid (\geq 99%, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich), 10-undecenoic acid (98%, Aldrich), cyclohexyl isocyanide (98%, Aldrich), *tert*-butyl isocyanide (98%, Aldrich), benzyl isocyanide (98%, Aldrich), pentyl isocyanide (98%, Aldrich), trimesic acid (95%, Aldrich), silica gel 60 (0.035–0.070, Aldrich), chloroform-*d* (CDCl₃, 99.8 atom-% D, euriso-top). All solvents used were of technical grade.

2. Characterization

Thin-layer chromatography (TLC) identification of reactants and products was performed on silica-gel-coated aluminum foil (Aldrich, silica gel 60, F 254 with fluorescence indicator). Compounds were visualized by Seebach reagent (mixture of phosphomolybdic acid, cerium(IV) sulfate, water and sulfuric acid).

NMR spectra were recorded on a Bruker AVANCE DPX spectrometer (measuring frequency: ¹H NMR = 300 MHz, ¹³C NMR = 75 MHz) or a Bruker AMX R 500 spectrometer (measuring frequency: ¹H-NMR = 500 MHz, ¹³C NMR = 126 MHz). NMR spectra were obtained using CDCl₃. All ¹H NMR spectra are reported in ppm relative to the solvent signal for CDCl₃ at 7.26 ppm, ¹³C NMR spectra are reported relative to the solvent signal for CDCl₃ at 77.16 ppm. Polymers were characterized on a SEC System LC-20A (Shimadzu) equipped with a SIL-20A autosampler and a RID-10A refractive index detector using THF (flow rate 1 mL/min) at 50 °C. The analysis was performed on the following column system: analytical main-column PSS SDV (5 µm, 300 mm × 8.0 mm, 10,000 Å) with a PSS SDV analytical precolumn (5 µm, 50 mm × 8.0 mm). For the calibration narrow linear poly(methyl methacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1.1 to 981 kDa were used. FAB (fast atom bombardment) mass spectra were recorded on a MAT95 (Finnigan) instrument.

Infrared (IR) spectra were recorded on a Bruker alpha-p instrument applying KBr- as well as ATR-technology.

The thermal properties of the prepared polymers were studied *via* DSC (differential scanning calorimetry) with a Mettler Toledo DSC star system, operating under nitrogen atmosphere and using about 5 mg of the respective polymer for the analysis. The glass transition temperature (T_g) was recorded on the second heating scan by using the following method: heating from -70 to 150 °C at 10 °C min⁻¹, cooling from 150 to -70 °C at 10 °C min⁻¹, and heating from -70 to 150 °C at 10 °C min⁻¹.

Size exclusion chromatography-electrospray ionization-mass spectra (SEC-ESI-MS) were recorded on a O Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74– 1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.6 kV, a dimensionless sheath gas of 8, and a dimensionless auxiliary gas flow rate of 2 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a thermostated column department (TCC 3000SD). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250×4.6 mm, particle diameter 3 μ m) with precolumn (Mesopore 50 \times 4.6 mm) operating at 30 °C. THF at a flow rate of 0.30 mL min⁻¹ was used as eluent. The mass spectrometer was coupled to the column in parallel to a RI-detector (RefractoMax520, ERC, Japan). 0.27 mL min⁻¹ of the eluent were directed through the RI-detector and 30 μ L min⁻¹ infused into the electrospray source after postcolumn addition of a 100 μ M solution of sodium iodide in methanol at 20 μ L min⁻¹ by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 20 µL aliquot of a polymer solution with a concentration of 2 mg mL^{-1} was injected onto the HPLC system.

3. Synthetic Procedure

Synthesis of AB-type monomer 3 via thiol-ene reaction^{S1}

10-undecenal **1** (1.68 g, 10.0 mmol) and DMPA (130 mg, 0.50 mmol) were dissolved in 4.0 mL THF. After purging with argon for 10 minutes, the solution was exposed to UV light (365 nm) for 30 s. Subsequently, 3-mercaptopropionic acid **2** (1.17 g, 959 µL, 11.0 mmol) was slowly added and the reaction mixture was stirred for 2 h under UV irradiation. After evaporating the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 3:1 - 1:1) to yield a white solid (2.10 g, 77%). R_f = 0.30 (dichloromethane/methanol = 20:1); ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.21-1.41 (m, 12 H, 6 CH₂), 1.51-1.69 (m, 4 H, 2 CH₂), 2.42 (td, J = 7.3, 1.7 Hz, 2 H, CH₂CHO), 2.53 (t, J = 7.3 Hz, 2 H, CH₂S), 2.61-2.70 (m, 2 H, CH₂COOH), 2.73-2.82 (m, 2 H, SCH₂), 9.76 (t, J = 1.8 Hz, 1 H, CHO); ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) = 22.13, 26.67, 28.88, 29.20, 29.22, 29.37, 29.39, 29.47, 29.56, 32.25, 34.78, 178.12, 203.31; FAB of C₁₄H₂₆O₃S [M+H]⁺ = <math>275.1; HRMS (FAB) of C₁₄H₂₆O₃S [M+H]⁺ calc. 275.1681, found 275.1680; IR (KBr) v = 2914.7, 2847.2, 2742.6, 1708.0, 1684.7, 1466.7, 1407.2, 1338.2, 1263.9, 1197.5, 1064.0, 915.4, 894.3, 761.7, 737.7, 721.1, 696.0, 660.8, 490.5 cm⁻¹; T_m = 70 °C.

Synthesis of homopolymers P1-P4 via Passerini-reaction

General procedure: To a vigorously stirred solution of 10-undecenoic acid **4** (13.3 mg, 0.0722 mmol) and the corresponding isocyanide **5-8** (7.20 mmol), the AB-type monomer **3** (400 mg, 0.36 mmol) in 1.0 mL dichloromethane (DCM) was added slowly. After stirring for 24 hours at room temperature, the polymer was precipitated from diethyl ether.

Homopolymer P1

Following the aforementioned procedure, **P1** was obtained as a white solid (96 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.20–1.32 (m, 280 H, 140 CH₂), 1.35 (m, 196 H, 180 *t*-Bu, 8 CH₂ end group), 1.52–1.62 (m, 40 H, 20 CH₂CH₂S), 1.75–1.88 (m, 40 H, 20 CHCH₂), 2.53 (t, J = 7.4 Hz, 40 H, 20 CH₂S), 2.69 (t, J = 6.5 Hz, 40 H, 20 SCH₂), 2.81 (t, J = 6.2 Hz, 40 H, 20 CH₂COO), 4.87–5.00 (m, 2 H, CH₂ double bond), 5.07 (t, J = 6.2 Hz, 20 H, OCH(CO)), 5.93–6.03 (m, 1 H, CH double bond), 6.09 (s, 20 H, NH); $T_g = 3$ °C.

Homopolymer P2

Following the aforementioned procedure, **P2** was obtained as sticky yellow solid (81 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 0.84–0.92 (m, 60 H, 20 CH₃), 1.23–1.38 (m, 379 H, 180 CH₂, 8 CH₂ end group), 1.45–1.61 (m, 80 H, 20 CH₂CH₂S, 20 NHCH₂CH₂), 1.75–1.91 (m, 40 H, 20 CHCH₂), 2.53 (t, *J* = 7.4 Hz, 40 H, 20 CH₂S), 2.67–2.75 (m 40 H, 20 SCH₂), 2.79–2.91 (m, 40 H, 20 CH₂COO), 3.18–3.29 (m, 40 H, 20 CHCH₂), 4.92–4.97 (m, 2 H, CH₂ double bond), 5.16–5.23 (m 20 H, OCH(CO)), 5.98–6.07 (m, 1 H, CH double bond), 6.57 (t, J = 6.2 Hz, 20 H, NH); *T_g* = –18 °C.

Homopolymer P3

Following the aforementioned procedure, **P3** was obtained as sticky colorless solid (81 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.20–1.43 (m, 412 H, 198 CH₂, 8 CH₂ end group), 1.56–1.75 (m, 132 H,66 CH₂), 1.80–1.89 (m, 88 H, 22 CH₂CH₂S, 22 CHCH₂), 2.54 (t, *J* = 7.4 Hz, 44 H, 22 CH₂S), 2.65–2.74 (m, 44 H, 22 SCH₂), 2.77–2.88 (m, 44 H, 22 CH₂COO), 3.69–3.82 (m, 22 H, NCH) 4.89–4.94 (m, 2 H, CH₂ double bond), 5.11–5.20 (m, 22 H, OCH(CO)), 5.29–5.34 (m, 1 H, CH double bond), 6.35 (d, J = 8.2 Hz, 22 H, NH); *T₈* = 3 °C.

Homopolymer P4

Following the aforementioned procedure, **P4** was obtained as sticky brown solid (92 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.15–1.46 (m, 304 H, 144 CH₂, 8 CH₂ end group), 1.81–1.95 (m, 36 H, 18 CHC*H*₂), 2.34 (t, *J* = 7.3 Hz,, 36 H, 18 CH₂S), 2.63–2.72 (m, 36 H, 18 SCH₂), 2.74–2.84 (m, 36 H, 18 CH₂COO), 4.41–4.49 (m, 36 H, 18 NCH₂) 4.95–4.99 (m, 2 H, CH₂ double bond), 5.23–5.31 (m, 18 H, OCH(CO)), 5.73–5.84 (m, 1 H, CH double bond), 6.96–7.04 (m, 18 H, NH), 7.11–7.24 (m, 36 H, 36 Ar-H), 7.28–7.39 (m, 54 H, 54 Ar-H); *T_g* = 1 °C.

Synthesis of homopolymers P5-P7 via Passerini-reaction

General procedure: To a vigorously stirred solution of 10-undecenoic acid **4** (1.00 equiv.) and isocyanide **5** (50, 150, 200 equiv.), the AB-type monomer **3** (10, 30, 40 equiv.) in 1.50 mol/L dichloromethane (DCM) was added slowly. After stirring for 24 hours at room temperature, the polymer was precipitated from diethyl ether.

Homopolymer P5

Following the aforementioned procedure, **P5** was obtained as a white solid (93 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.20–1.32 (m, 140 H, 70 CH₂), 1.35 (m, 106 H, 90 *t*-Bu, 8 CH₂ end group), 1.52–1.62 (m, 20 H, 10 CH₂CH₂S), 1.75–1.88 (m, 20 H, 10 CHCH₂), 2.53 (t, *J* = 7.3 Hz, 20 H, 10 CH₂S), 2.69 (m, 20 H, 10 SCH₂), 2.81 (m, 20 H, 10 CH₂COO), 4.87–5.00 (m, 2 H, CH₂ double bond), 5.07 (m, 10 H, OCH(CO)), 5.93–6.03 (m, 1 H, CH double bond), 6.09 (s, 10 H, NH); $T_g = 3$ °C.

Homopolymer P6

Following the aforementioned procedure, **P6** was obtained as a white solid (95 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.20–1.32 (m, 420 H, 210 CH₂), 1.35 (m, 286 H, 270 *t*-Bu, 8 CH₂ end group), 1.52–1.62 (m, 60 H, 30 CH₂CH₂S), 1.75–1.88 (m, 60 H, 30 CHCH₂), 2.53 (t,

J = 7.5 Hz, 60 H, 30 CH₂S), 2.69 (m, 60 H, 30 SCH₂), 2.81 (m, 60 H, 30 CH₂COO), 4.87–5.00 (m, 2 H, CH₂ double bond), 5.07 (m, 30 H, OCH(CO)), 5.93–6.03 (m, 1 H, CH double bond), 6.09 (s, 30 H, NH); *T_g* = 3 °C.

Homopolymer P7

Following the aforementioned procedure, **P7** was obtained as a white solid (91 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.20–1.32 (m, 560 H, 280 CH₂), 1.35 (m, 376 H, 360 *t*-Bu, 8 CH₂ end group), 1.52–1.62 (m, 80 H, 40 CH₂CH₂S), 1.75–1.88 (m, 80 H, 40 CHCH₂), 2.53 (t, J = 7.4 Hz, 80 H, 40 CH₂S), 2.69 (m, 80 H, 40 SCH₂), 2.81 (m, 80 H, 40 CH₂COO), 4.87–5.00 (m, 2 H, CH₂ double bond), 5.07 (m, 40 H, OCH(CO)), 5.93–6.03 (m, 1 H, CH double bond), 6.09 (s, 40 H, NH); $T_g = 3 \,^{\circ}$ C.

Synthesis of copolymers P8 and P9 via Passerini reaction

To a vigorously stirred solution of homopolymer **P1** (100 mg, 0.0137 mmol) and benzyl isocyanide **8** (1.37 mmol, 0.685 mmol,) in 1.50 mL DCM, the AB-type monomer **3** (0.274 mmol, 0.137 mmol,) in 1.50 mol/L DCM was added slowly. After stirring for 24 hours at room temperature, the polymer was precipitated from diethyl ether.

Following the aforementioned procedure **P8** was obtained as sticky brown solid (87%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.14–1.29 (m, 560 H, 280 CH₂), 1.31–1.40 (m, 196 H, 180 *t*-Bu, 8 CH₂ end group), 1.50–1.64 (m, 80 H, 40 CH₂CH₂S), 1.75–1.93 (m, 80 H, 40 CHCH₂), 2.28–2.34 (m, 40 H, 20 CH₂S), 2.53 (t, *J* = 7.3 Hz, 40 H, 20 CH₂S), 2.63–2.65 (m, 80 H, 40 SCH₂), 2.77–2.89 (m, 80 H, 40 CH₂COO), 4.32–4.52 (m, 40 H, 20 NCH₂), 4.91–4.97 (m, 2 H, CH₂ double bond), 5.03–5.11 (m, 20 H, OCH(CO)) 5.16–5.36 (m, 20 H, OCH(CO)), 5.78–5.85 (m, 1 H, CH double bond), 6.10 (s, 20 H, NH), 6.95–7.07 (m, 20 H, NH), 7.11–7.23 (m, 40 H, 40 Ar-H), 7.29–7.41 (m, 60 H, 60 Ar-H); *T_g* = 5 °C.

Following the aforementioned procedure **P9** was obtained as sticky brown solid (88 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.14–1.29 (m, 420 H, 210 CH₂), 1.31–1.40 (m, 196 H, 180 *t*-Bu, 8 CH₂ end group), 1.50–1.64 (m, 60 H, 30 CH₂CH₂S), 1.75–1.93 (m, 60 H, 30 CHCH₂), 2.28–2.34 (m, 20 H, 10 CH₂S), 2.53 (t, *J* = 7.3 Hz, 40 H, 20 CH₂S), 2.63–2.65 (m, 60 H, 30 SCH₂), 2.77–2.89 (m, 60 H, 30 CH₂COO), 4.32–4.52 (m, 20 H, 10 NCH₂), 4.91–4.97 (m, 2 H, CH₂ double bond), 5.03–5.11 (m, 20 H, OCH(CO)) 5.16–5.36 (m, 10 H, OCH(CO)), 5.78–5.85 (m, 1 H, CH double bond), 6.10 (s, 20 H, NH), 6.95–7.07 (m, 10 H, NH), 7.11–7.23 (m, 20 H, 20 Ar-H), 7.29–7.41 (m, 30 H, 30 Ar-H); *T_g* = 5 °C.

Synthesis of star-shaped homopolymer P10 via Passerini reaction

To a vigorously stirred solution of trimesic acid **9** (5.12 mg, 0.024 mmol) and *tert*-butyl isocyanide **5** (606 mg, 7.30 mmol) in 0.5 mL THF, the AB-type monomer **3** (400 mg, 1.46 mmol) in 0.5 mL DCM was added slowly. After stirring for 24 hours at room temperature, the polymer was precipitated from diethyl ether.

Following the aforementioned procedure, **P10** was obtained as white solid (93 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.22–1.30 (m, 840 H, 420 CH₂), 1.32–1.36 (m, 540 H, *t*-Bu), 1.53–1.61 (m, 120 H, 60 CH₂CH₂S), 1.75–1.87 (m, 120 H, 60 CHCH₂), 2.53 (t, *J* = 7.5 Hz, 120 H, 60 CH₂S), 2.66–2.72 (m, 120 H, 60 SCH₂), 2.77–2.85 (m, 120 H, 60 CH₂COO), 5.04–5.11 (m, 60 H, OCH(CO)), 6.06–6.16 (m, 60 H, NH), 8.89–8.91 (m, 3 H, Ar-H); *T_g* = 6 °C.

Synthesis of star-shaped copolymer P11 via Passerini reaction

To a vigorously stirred solution of star-shaped homopolymer **P10** (100 mg, 0.0046 mmol) and benzyl isocyanide **8** (162 mg, 1.38 mmol) in 0.1 mL DCM, the AB-type monomer **3** (76 mg, 0.276 mmol) in 0.1 mL DCM was added slowly. After stirring for 24 hours at room temperature, the polymer was precipitated from diethyl ether.

Following the aforementioned procedure, **P11** was obtained as sticky brown solid (82 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.06–1.28 (m, 1320 H, 660 CH₂), 1.32–1.39 (m, 540 H, *t*-Bu), 1.48–1.64 (m, 180 H, 90 CH₂CH₂S), 1.72–1.91 (m, 180 H, 90 CHC*H*₂), 2.26–2.35 (m, 60 H, 30 CH₂S), 2.52 (t, *J* = 7.4 Hz, 120 H, 60 CH₂S), 2.63–2.74 (m, 180 H, 60 SCH₂), 2.76–2.85 (m, 180 H, 60 CH₂COO), 4.31–4.50 (m, 60 H, 30 NCH₂), 5.01–5.09 (m, 60 H, OCH(CO)) 5.18–5.31 (m, 30 H, OCH(CO)), 6.11 (s, 60 H, NH), 6.98–7.09 (m, 30 H, NH), 7.17–7.25 (m, 60 H, 60 Ar-H), 7.27–7.35 (m, 90 H, 90 Ar-H), 8.87–8.92 (m, 3 H, Ar-H); *T_g* = 8 °C.

Esterification of the star-shaped homopolymer P12 with CDI^{S2}

To a vigorously stirred solution of CDI **10** (32.4 mg, 0.20 mmol) in dry CH_2Cl_2 (0.60 mL), the star polymer **P10** (average MW 21.8 kDa) (200 mg, 0.01 mmol) in dry CH_2Cl_2 (0.90 mL) was added slowly under nitrogen. After stirring for 24 h at room temperature, the solution was precipitated in diethyl ether.

Following the aforementioned procedure, **P12** was obtained as white solid (90 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 1.16–1.29 (m, 840 H, 420 CH₂), 1.31–1.36 (m, 540 H, *t*-Bu), 1.53–1.59 (m, 120 H, 60 CH₂CH₂S), 1.74–1.86 (m, 120 H, 60 CHCH₂), 2.52 (t, *J* = 7.4 Hz, 120 H, 60 CH₂S), 2.67–2.70 (m, 120 H, 60 SCH₂), 2.76–2.84 (m, 120 H, 60 CH₂COO), 5.03–5.10 (m, 60 H, OCH(CO)), 6.06–6.13 (m, 60 H, NH), 7.09–7.12 (m, 3 H, OCNCHC*H*), 7.46–7.49 (m, 3 H, OCNCH), 8.16–8.19 (m, 3 H, NCHN), 8.88–8.91 (m, 3 H, Ar-H); *T_g* = 6 °C.

4. Tables

Polymer	M_n	M_n	M_n SEC	Ð	Tg
TOTYMET	calc.	NMR	[g/mol]	M_w/M_n	[°C]
	[g/mol]	[g/mol]			
P1	7335	7377	12000	1.51	5
P2	7616	7950	11800	1.51	-11
P3	7856	8884	12000	1.67	3
P4	8016	7052	11000	1.46	1

Table S1: Molecular weights of polyesters **P1-P4** synthesized with different isocyanides **5-8** (ratio monomer **3**:isocyanide **5-8**:10-undecenoic acid **4** of 20:100:1).

5. SEC figures



Figure S1: SEC results of polymerization with varying ratio of AB-type monomer **3** and 10-undecenoic acid **4** (a = 10:1, b = 20:1, c = 30:1, d = 40:1).



Figure S2: SEC results of diblock copolymer **P9** (b) synthesized from homopolymer **P1** (a) in ratios of the two different blocks of 20:10 (*tert*-butyl side group:benzyl side group).



Figure S3: SEC results of star-shaped homopolymer P10 (a) and star-shaped copolymer P11 (b).



Figure S4: Integrated ¹H NMR spectrum of AB-type monomer **3**.



Figure S5: Integrated ¹H NMR spectrum of homopolymer P1.



Figure S6: Integrated ¹H NMR spectrum of homopolymer P2.



Figure S7: Integrated ¹H NMR spectrum of homopolymer P3.



Figure S8: Integrated ¹H NMR spectrum of homopolymer P4.



Figure S9: Integrated ¹H NMR spectrum of copolymer **P9**.



Figure S10: Integrated ¹H NMR spectrum of star-shaped homopolymer P10.



Figure S11: Integrated ¹H NMR spectrum of star-shaped copolymer P11.



Figure S12: Integrated ¹H NMR spectrum of esterified star-shaped homopolymer P12.



Figure S13: Comparison of the ¹H NMR spectra of AB-type monomer **3** and crude polyester **P1** after 2 hours of reaction time with 5.00 equivalents of monomer **3** indicating full monomer (aldehyde) conversion.

7. Relevant mass spectra



Figure S14: Mass spectra of homopolymer **P1** with n repeating units and a calculated mass of 357.234 g/mol per repeating unit (a = retention time of 13.14 min, b = retention time of 11.84-14.05 min, c = calculated isotope pattern, d = experimental isotope pattern at a retention time of 13.14 min).



Figure S15: Mass spectra of homopolymer **P2** with n repeating units and a calculated mass of 371.580 g/mol per repeating unit (a = retention time of 13.17 min, b = retention time of 11.94-13.93 min, c = calculated isotope pattern, d = experimental isotope pattern at a retention time of 13.17 min).



Figure S16: Mass spectra of homopolymer **P3** with n repeating units and a calculated mass of 383.249 g/mol per repeating unit (a = retention time of 13.16 min, b = retention time of 11.74-13.83 min, c = calculated isotope pattern, d = experimental isotope pattern at a retention time of 13.16 min).



Figure S17: Mass spectra of homopolymer **P5** with n repeating units and a calculated mass of 357.234 g/mol per repeating unit (a = retention time of 14.27 min, b = retention time of 12.76-14.28 min, c = calculated isotope pattern, d = experimental isotope pattern at a retention time of 14.27 min).



Figure S18: Mass spectra of homopolymer **P6** with n repeating units and a calculated mass of 357.234 g/mol per repeating unit (a = retention time of 12.61 min, b = retention time of 11.79-14.73 min, c = calculated isotope pattern, d = experimental isotope pattern at a retention time of 12.61 min).



Figure S19: Mass spectra of homopolymer **P7** with n repeating units and a calculated mass of 357.234 g/mol per repeating unit (a = retention time of 12.37 min, b = retention time of 11.76-14.39 min, c = calculated isotope pattern, d = experimental isotope pattern at a retention time of 12.37 min).

8. Notes and References

$$M_n = M_n$$
 (Monomer **3** + Isocyanide) * n + M_n (ITCA **4**)

Formula S1: Formula to calculate the molecular weight of the homopolymers by the number of monomer units n.

Representative example for **P1**:

$$M_n = \left(274.42\frac{\text{g}}{\text{mol}} + 83.13\frac{\text{g}}{\text{mol}}\right) * 20 + 184,27\frac{\text{g}}{\text{mol}} = 7335\frac{\text{g}}{\text{mol}}$$

References

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- S2 H. A. Staab, Angew. Chem. Int. Ed., **1962**, 1, 351.