

# Supporting Information

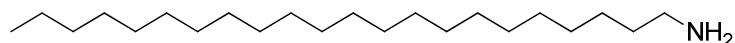
for *Macromol. Chem. Phys.*, DOI: 10.1002/macp.201700302

## Phase Segregation in Supramolecular Polymers Based on Telechelics Synthesized via Multicomponent Reactions

Ansgar Sehlinger, Nikolai Bartnick, Ilja Gunkel, Michael A. R. Meier\* and Lucas Montero de Espinosa\*

### 1. Synthesis

#### 1-Aminodocosane

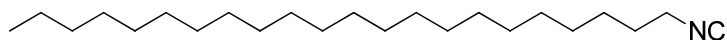


A mixture of 1-bromodocosane (5.17 g, 13.3 mmol), hexadecyltrimethylammonium bromide (0.484 g, 1.33 mmol), sodium azide (2.16 g, 33.3 mmol), and water (10 mL) was sonicated at 60 °C for 4 h. The resulting emulsion was refluxed (85 °C) for 4 days. The milky reaction mixture was treated with hexane and the aqueous layer separated. After drying over sodium sulfate, the solvent was removed and 1-azidodocosane was obtained as a sticky white solid (3.36 g, 72 %). TLC (hexane)  $R_f$  = 0.44;  $^1\text{H}$  NMR analysis showed a conversion of 90 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) = 0.88 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ), 1.18 – 1.48 (m, 38 H, 19  $\text{CH}_2$ ), 1.60 (m, 2 H,  $\text{N}_3\text{CH}_2\text{CH}_2$ ), 3.25 (t,  $J$  = 6.9 Hz, 2 H,  $\text{N}_3\text{CH}_2$ ).

To a solution of 1-azidodocosane (3.36 g, 9.56 mmol) in 50 mL hexane was added 10% Pd/C (0.168 g, 5 wt%). The resulting mixture was hydrogenated at 10 bar and ambient temperature overnight. The reaction mixture was hot filtered over Celite and the filtrate was put in the freezer for 2 hours. The pure product was collected by filtration and dried under high vacuum (2.75 g, 88 %). TLC (hexane)  $R_f$  = 0.10;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) = 0.88 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ), 1.06 – 1.52 (m, 42 H, 20  $\text{CH}_2$ ,  $\text{NH}_2$ ), 2.67 (t,  $J$  = 6.9 Hz, 2 H,  $\text{CH}_2\text{NH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) = 14.24, 22.83, 27.05, 29.50, 29.66, 29.80, 29.84, 32.07, 34.07, 42.45; FAB of  $\text{C}_{22}\text{H}_{47}\text{N}$  ( $\text{M}+\text{H}^+$  = 326.4); HRMS (FAB) of  $\text{C}_{22}\text{H}_{47}\text{N}$  [ $\text{M}+\text{H}$ ] $^+$  calc.

326.3781, found 326.3780; IR (ATR)  $\nu$  = 3330.0, 3165.8, 2952.9, 2914.3, 2846.3, 1609.8, 1471.6, 1461.2, 1364.5, 1058.5, 1031.4, 1007.5, 983.4, 968.7, 930.6, 918.4, 892.6, 730.0, 718.9, 521.3, 429.5  $\text{cm}^{-1}$ ;  $T_m$  = 66 °C.

### 1-Isocyanodocosane

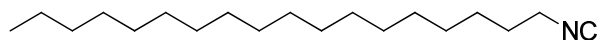


50 mL (46.0 g, 621 mmol) of ethyl formate were added to 1-aminodocosane (2.75 g, 8.45 mmol) and the reaction mixture was refluxed overnight. Then, the solvent was evaporated to obtain the product as white solid (2.93 g, 98 %). TLC (hexane)  $R_f$  = 0.05;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, mixture of *cis/trans*-amide bonds, ratio = 1:5):  $\delta$  (ppm) = 0.87 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ), 1.16 – 1.40 (m, 38 H, 19  $\text{CH}_2$ ), 1.42 – 1.59 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{NH}$ ), 3.21, 3.29 (2q,  $J$  = 6.8 Hz, 2 H,  $\text{CH}_2\text{NH}$ , *cis/trans*), 5.50 (br, 1 H, NH), 8.04 (d,  $J$  = 12.0 Hz, 1 H,  $\text{NHCHO}$ , *cis*), 8.16 (s, 1 H,  $\text{NHCHO}$ , *trans*);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) = 14.23, 22.82, 26.52 ( $\text{CH}_2$ , *cis*), 26.98 ( $\text{CH}_2$ , *trans*), 29.27, 29.37, 29.49, 29.62, 29.66, 29.70, 29.83, 31.39 ( $\text{CH}_2$ , *cis*), 32.05 ( $\text{CH}_2$ , *trans*), 38.34 ( $\text{CH}_2$ , *trans*), 41.89 ( $\text{CH}_2$ , *cis*), 161.25 ( $\text{CHO}$ , *trans*), 164.69 ( $\text{CHO}$ , *cis*); FAB of  $\text{C}_{23}\text{H}_{47}\text{NO}$  ( $\text{M}+\text{H}^+$  = 354.4); HRMS (FAB) of  $\text{C}_{23}\text{H}_{47}\text{NO}$  [ $\text{M}+\text{H}$ ] $^+$  calc. 354.3730, found 354.3729; IR (ATR)  $\nu$  = 3294.6, 2953.0, 2914.3, 2846.4, 1643.8, 1534.2, 1468.6, 1378.4, 1235.3, 1220.8, 1211.4, 778.5, 718.7, 667.4, 445.8  $\text{cm}^{-1}$ ;  $T_m$  = 79 °C.

The obtained formamide (2.90 g, 8.20 mmol) was dissolved in dichloromethane (25.0 mL) and diisopropylamine (5.79 mL, 4.15 g, 41.0 mmol, 5.00 eq.) was added. Then the reaction mixture was cooled with an ice bath to 0°C and, subsequently, phosphorus oxychloride (1.07 mL, 1.76 g, 11.5 mmol, 1.40 eq.) was dropped to the strongly stirred solution. The mixture was allowed to reach room temperature and stirred for two hours. The reaction was quenched by addition of a sodium carbonate solution (20 %, 25 mL). After thirty additional minutes dichloromethane (100 mL) and water (100 mL) were added. The organic layer was separated, dried over sodium sulfate and then evaporated to dryness. The crude isocyanide was purified

by flash chromatography (hexane/ ethyl acetate 30:1) to obtain a white solid (1.94 g, 71 %). TLC (hexane/ ethyl acetate 30:1)  $R_f$  = 0.38;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) = 0.88 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ), 1.15 – 1.35 (m, 36 H, 18  $\text{CH}_2$ ), 1.37 – 1.52 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NC}$ ), 1.60 – 1.76 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{NC}$ ), 3.32 – 3.42 (m, 2 H,  $\text{CH}_2\text{NC}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) = 14.22, 22.81, 26.44, 28.83, 29.25, 29.49, 29.63, 29.73, 29.82, 32.05, 41.65 (t), 155.82 (t); FAB of  $\text{C}_{23}\text{H}_{45}\text{N}$  ( $\text{M}+\text{H}^+$  = 336.4); HRMS (FAB) of  $\text{C}_{23}\text{H}_{45}\text{N}$  [ $\text{M}+\text{H}$ ] $^+$  calc. 336.3625, found 336.3627; IR (ATR)  $\nu$  = 2911.9, 2847.1, 2149.2, 1470.9, 1350.7, 926.4, 716.1, 549.8  $\text{cm}^{-1}$ ;  $T_m$  = 50  $^\circ\text{C}$ .

### 1-Isocyanooctadecane



20 mL (18.4 g, 248 mmol) of ethyl formate were added to octadecylamine (5.80 g, 21.5 mmol) and the reaction mixture was refluxed overnight. Then, the solvent was evaporated to obtain the product as white solid (6.40 g, quant.). TLC (hexane / ethyl acetate )  $R_f$  = 0.48;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, mixture of *cis/trans*-amide bonds, ratio = 1:4):  $\delta$  (ppm) = 0.87 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ), 1.17 – 1.41 (m, 30 H, 15  $\text{CH}_2$ ), 1.41 – 1.59 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{NH}$ ), 3.20, 3.29 (2q,  $J$  = 6.8 Hz, 2 H,  $\text{CH}_2\text{NH}$ , *cis/trans*), 5.57 (br, 1 H, NH), 8.03 (d,  $J$  = 12.0 Hz, 1 H,  $\text{NHCHO}$ , *cis*), 8.16 (s, 1 H,  $\text{NHCHO}$ , *trans*);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) = 14.10, 22.70, 26.42 ( $\text{CH}_2$ , *cis*), 26.91 ( $\text{CH}_2$ , *trans*), 29.17, 29.29, 29.38, 29.46, 29.51, 29.58, 29.62, 29.68, 29.73, 31.16 ( $\text{CH}_2$ , *cis*), 31.95 ( $\text{CH}_2$ , *trans*), 38.28 ( $\text{CH}_2$ , *trans*), 42.07 ( $\text{CH}_2$ , *cis*), 161.64 ( $\text{CHO}$ , *trans*), 163.62 ( $\text{CHO}$ , *cis*), 165.16 ( $\text{CHO}$ , *cis*); FAB of  $\text{C}_{19}\text{H}_{39}\text{NO}$  ( $\text{M}+\text{H}^+$  = 298.4); HRMS (FAB) of  $\text{C}_{19}\text{H}_{39}\text{NO}$  [ $\text{M}+\text{H}$ ] $^+$  calc. 298.3104, found 298.3106; IR (ATR)  $\nu$  = 3292.4, 2952.9, 2913.9, 2866.9, 2846.5, 1709.1, 1643.2, 1534.9, 1467.9, 1377.4, 1249.2, 1230.7, 1215.5, 1204.8, 778.0, 718.9, 666.4, 483.5, 421.5  $\text{cm}^{-1}$ ;  $T_m$  = 68  $^\circ\text{C}$ .

The obtained formamide (6.00 g, 20.2 mmol) was dissolved in dichloromethane (60.0 mL) and diisopropylamine (14.2 mL, 10.2 g, 101 mmol, 5.00 eq.) was added. Then the reaction

mixture was cooled with an ice bath to 0°C and, subsequently, phosphorus oxychloride (2.63 mL, 4.34 g, 28.3 mmol, 1.40 eq.) was dropped to the strongly stirred solution. The mixture was allowed to reach room temperature and stirred for two hours. The reaction was quenched by addition of a sodium carbonate solution (20 %, 60 mL). After thirty additional minutes dichloromethane (250 mL) and water (250 mL) were added. The organic layer was separated, dried over sodium sulfate and then evaporated to dryness. The crude isocyanide was purified by flash chromatography (hexane/ ethyl acetate 10:1) to obtain a white solid (4.69 g, 83 %). TLC (hexane/ ethyl acetate 9:1)  $R_f$  = 0.62;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) = 0.88 (t,  $J$  = 6.6 Hz, 3 H,  $\text{CH}_3$ ), 1.16 – 1.36 (m, 28 H, 14  $\text{CH}_2$ ), 1.36 – 1.53 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NC}$ ), 1.59 – 1.75 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{NC}$ ), 3.33 – 3.42 (m, 2 H,  $\text{CH}_2\text{NC}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) = 14.20, 22.79, 26.43, 28.82, 29.24, 29.47, 29.62, 29.71, 29.80, 32.04, 41.64 (t), 155.85 (t); FAB of  $\text{C}_{19}\text{H}_{37}\text{N}$  ( $\text{M}+\text{H}^+$  = 280.3); HRMS (FAB) of  $\text{C}_{19}\text{H}_{37}\text{N}$  [ $\text{M}+\text{H}$ ] $^+$  calc. 280.2999, found 280.3001; IR (ATR)  $\nu$  = 2910.4, 2846.6, 2151.6, 1470.8, 1447.6, 1337.2, 1350.8, 1141.9, 986.5, 954.7, 889.6, 851.8, 827.5, 716.4, 549.7, 468.0  $\text{cm}^{-1}$ ;  $T_m$  = 35 °C.

## 2. $^1\text{H}$ NMR spectra

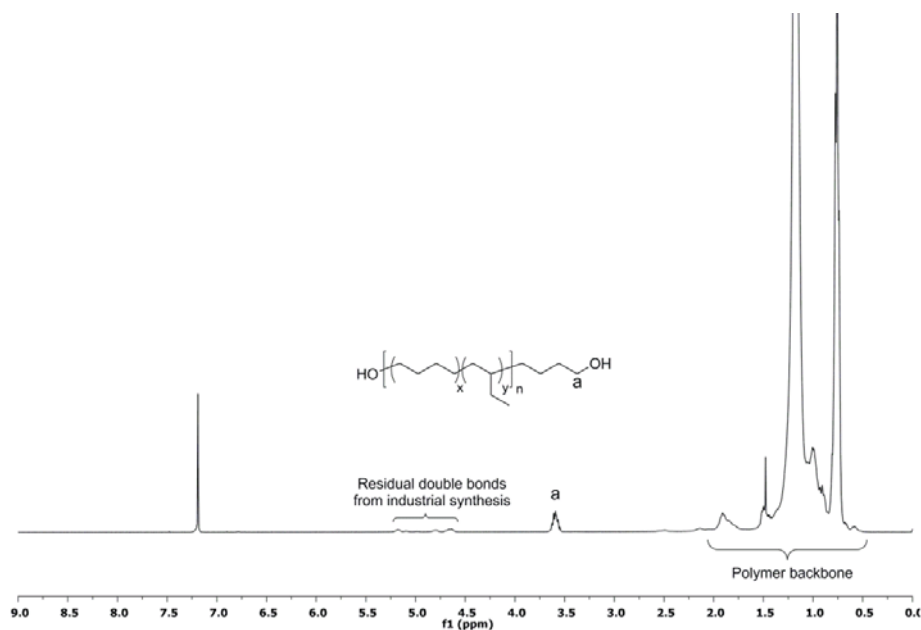


Figure S1.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of the commercial hydroxyl-terminated poly(ethylene-*co*-butylene) telechelic used in this study.

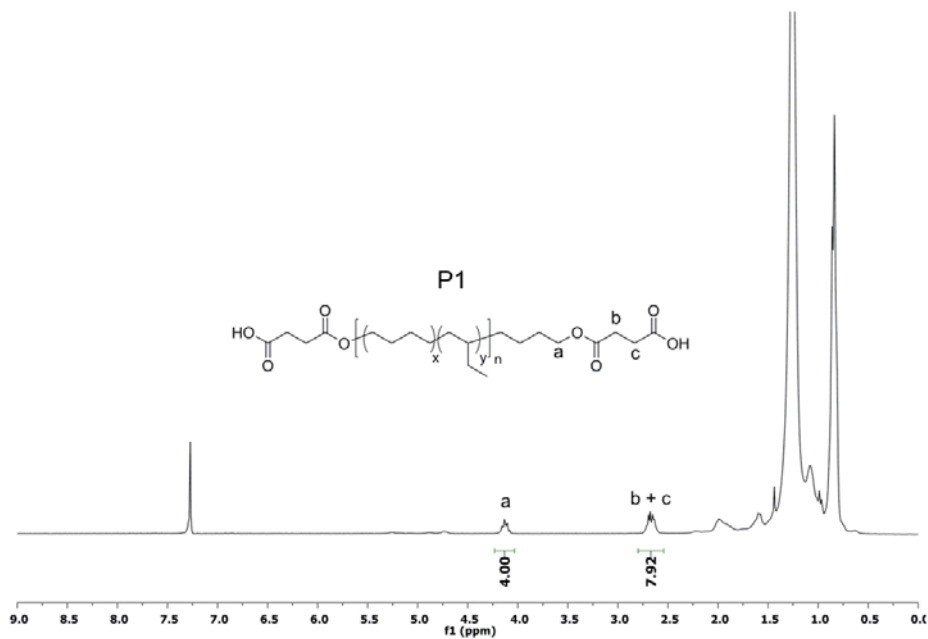


Figure S2.  $^1\text{H}$  NMR spectrum of **P1** ( $\text{CDCl}_3$ ).

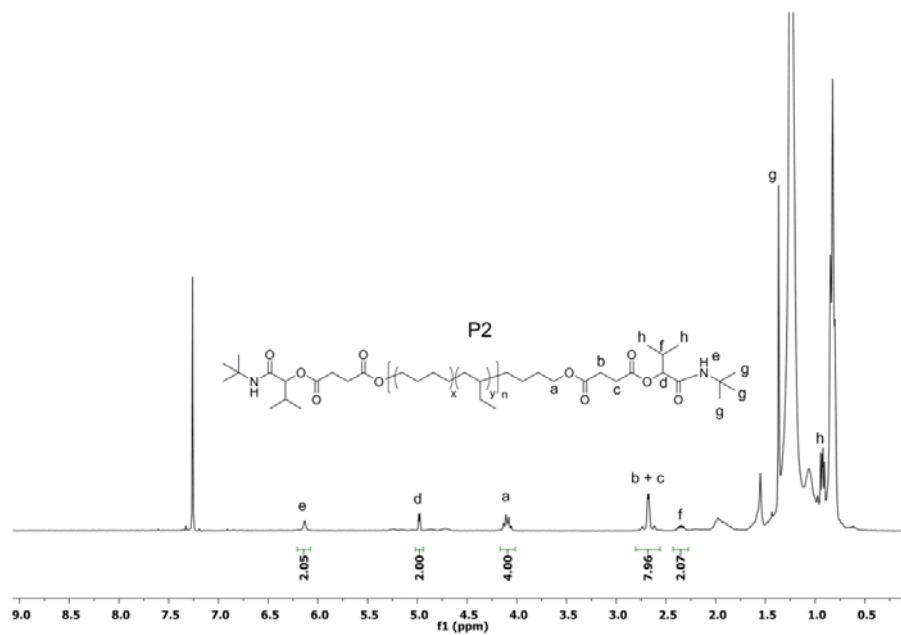


Figure S3.  $^1\text{H}$  NMR spectrum of **P2** ( $\text{CDCl}_3$ ).

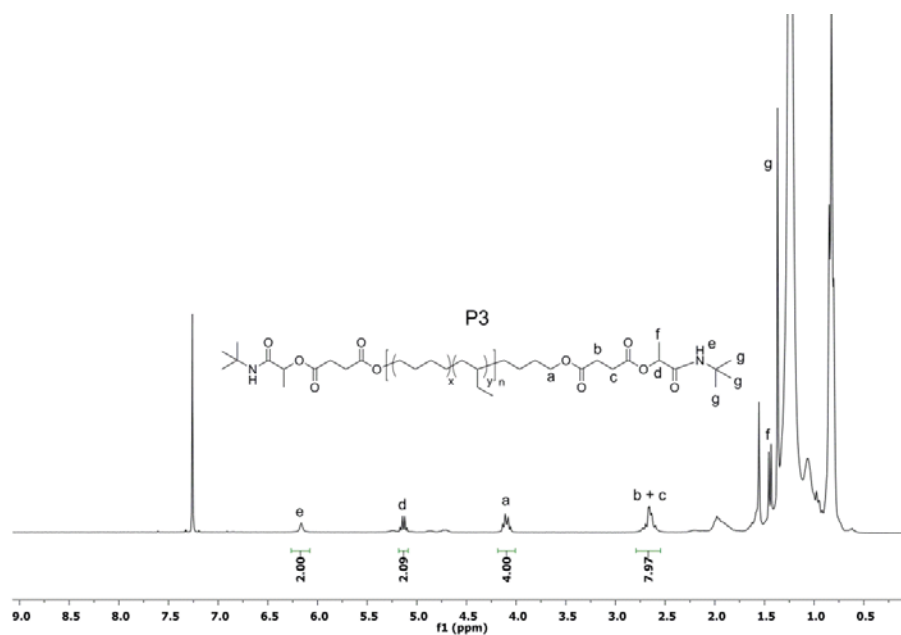


Figure S4. <sup>1</sup>H NMR spectrum of **P3** (CDCl<sub>3</sub>).

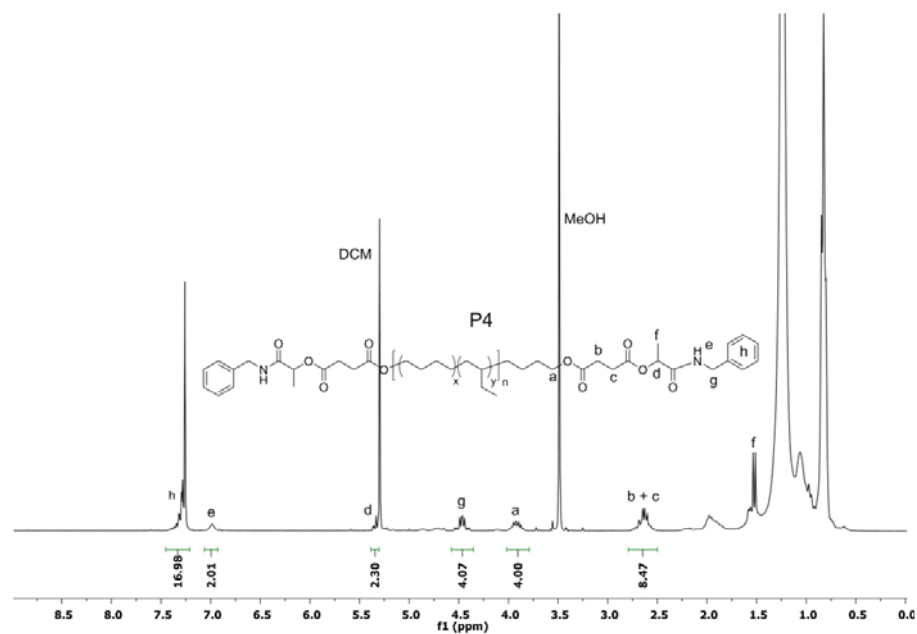


Figure S5. <sup>1</sup>H NMR spectrum of **P4** (CDCl<sub>3</sub>).

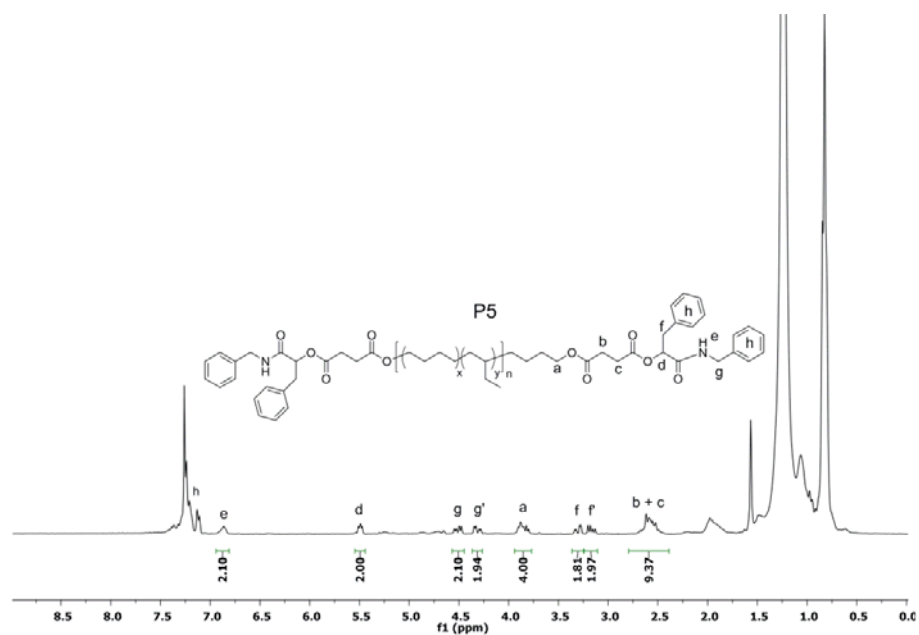


Figure S6.  $^1\text{H}$  NMR spectrum of **P5** ( $\text{CDCl}_3$ ).

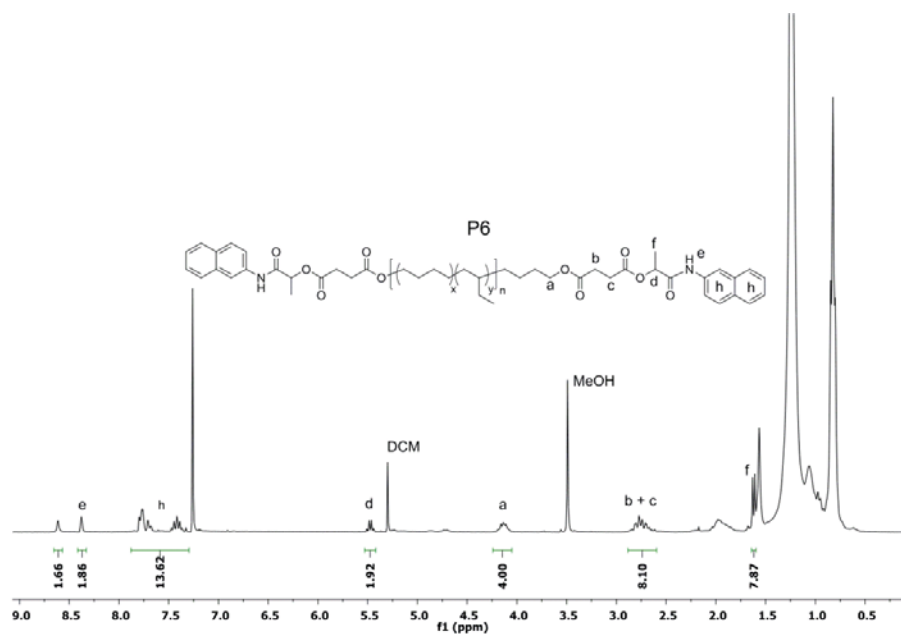


Figure S7.  $^1\text{H}$  NMR spectrum of **P6** ( $\text{CDCl}_3$ ).

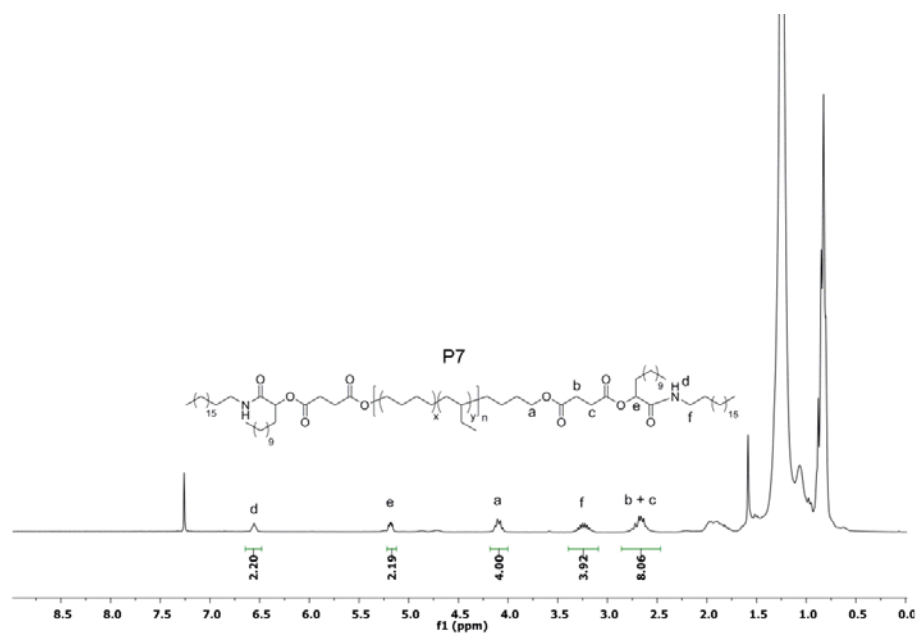


Figure S8.  $^1\text{H}$  NMR spectrum of **P7** ( $\text{CDCl}_3$ ).

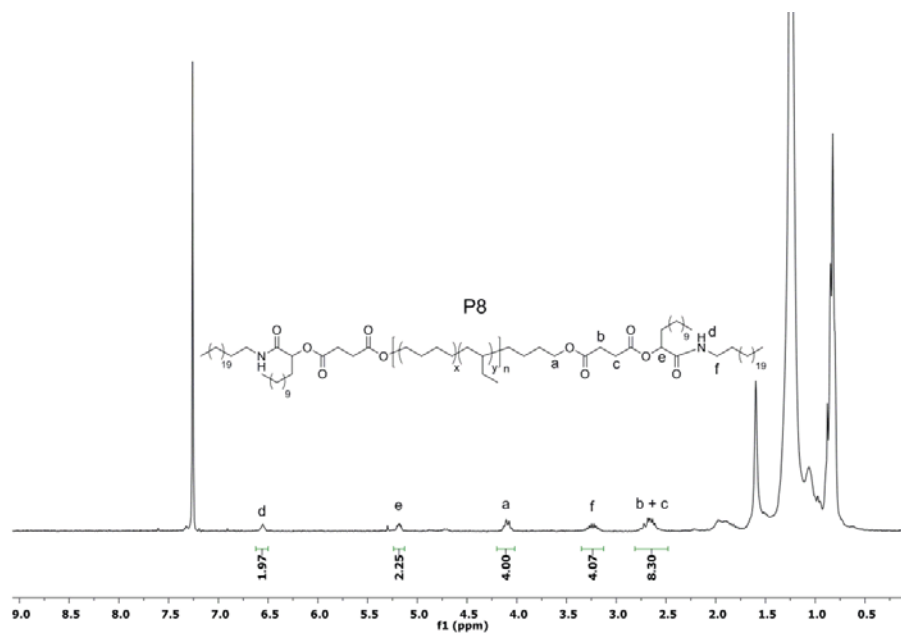
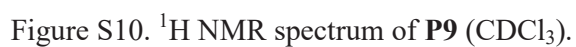


Figure S9.  $^1\text{H}$  NMR spectrum of **P8** ( $\text{CDCl}_3$ ).





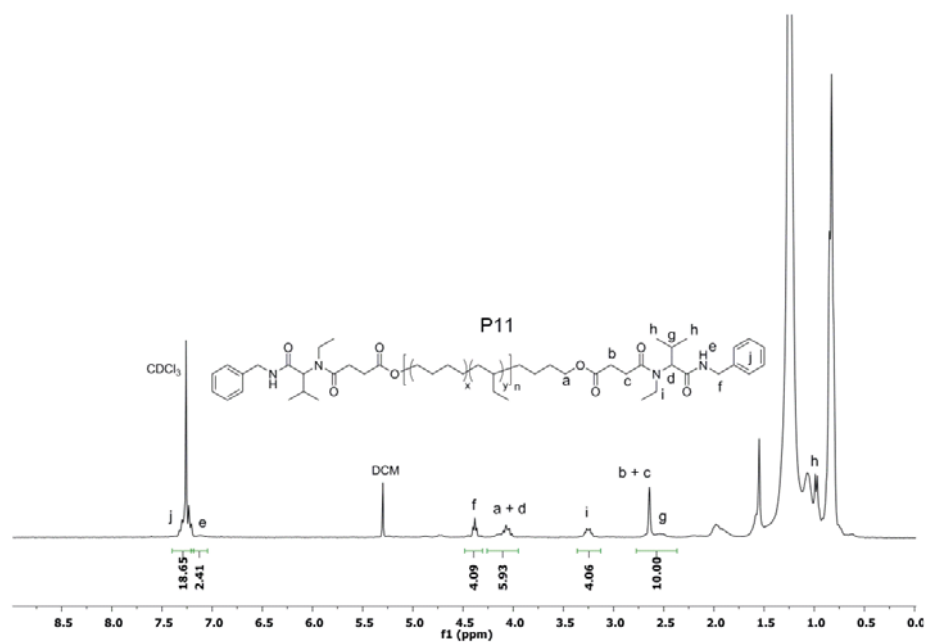


Figure S12.  $^1\text{H}$  NMR spectrum of **P11** ( $\text{CDCl}_3$ ).

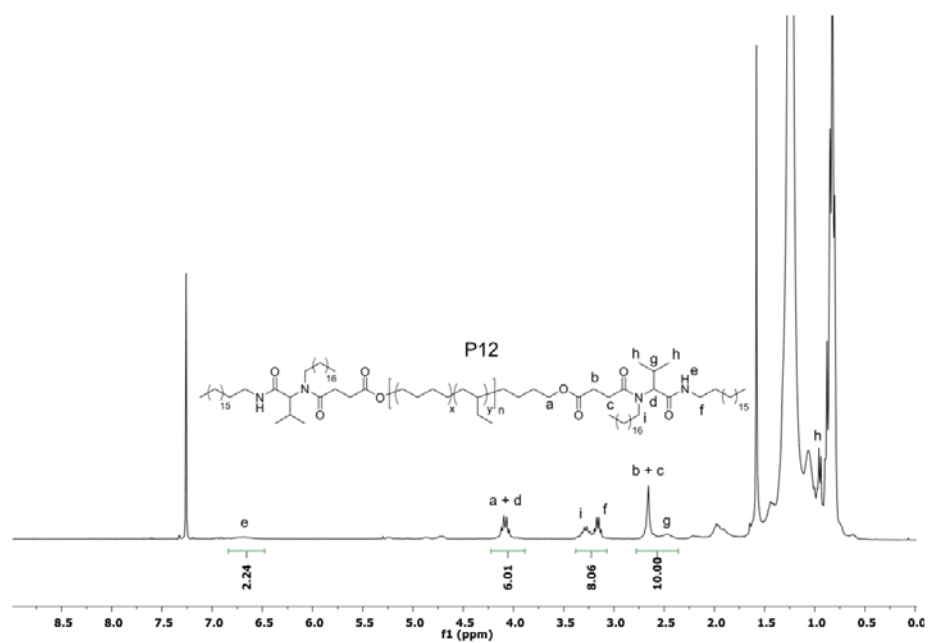


Figure S13.  $^1\text{H}$  NMR spectrum of **P12** ( $\text{CDCl}_3$ ).

### 3. SEC traces

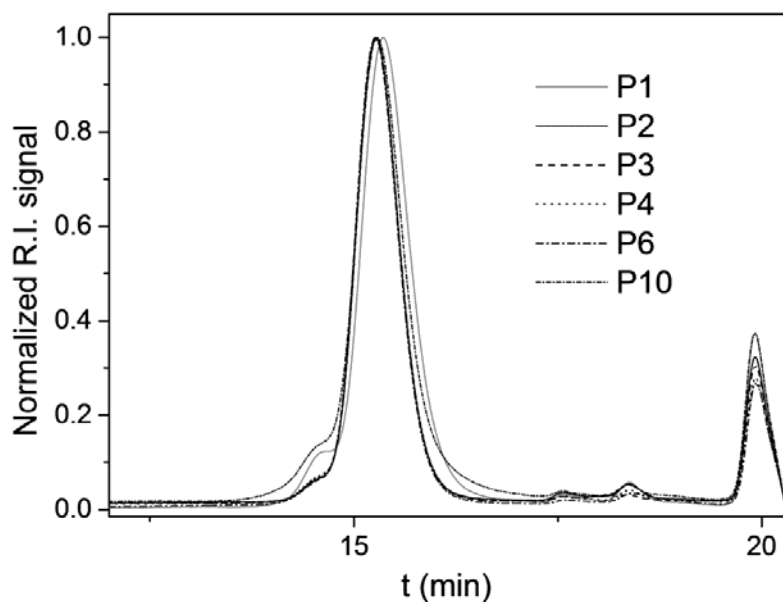


Figure S14. SEC traces of carboxylic acid terminated PEB **P1** and telechelic PEBs synthesized via Passerini and Ugi MCRs.

### 4. AFM

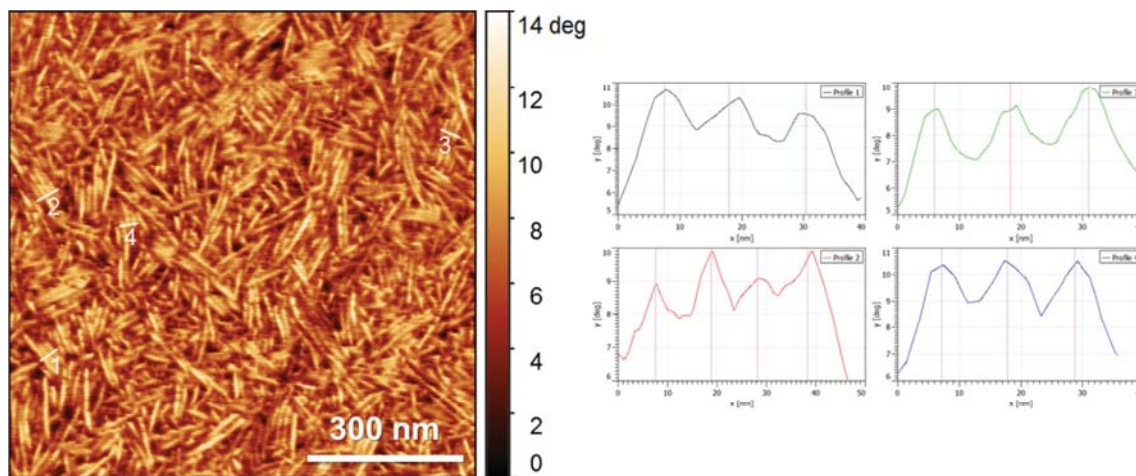


Figure S15. AFM phase image and profiles extracted from the numbered regions (white lines labeled as 1, 2, 3, and 4). Based on the profiles the spacing of the fibril-like features can be estimated to  $\approx 11 \pm 2$  nm.