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Electronic Supplementary Information

Microphase Separation of Carbohydrate-Based Star-Block Copolymers with Sub-10 nm Periodicity

Takuya Isono,[†,*] Nao Kawakami,[‡] Kodai Watanabe,[‡] Kohei Yoshida,[‡] Issei Otsuka,[§] Hiroaki Mamiya,[∥] Hajime Ito,[†,¶] Takuya Yamamoto,[†] Kenji Tajima,[†] Redouane Borsali,[§] Toshifumi Satoh[†,*]

[†]*Faculty of Engineering and* [‡]*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan.*

[§]*Univ. Grenoble Alps, CNRS, CERMAV, 38000 Grenoble, France.*

[∥]*National Institute for Materials Science, Ibaraki 305-0047, Japan.*

[¶]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo 060-8628, Japan.*

*(T.I.) E-mail: isono.t@eng.hokudai.ac.jp

*(T.S.) E-mail: satoh@eng.hokudai.ac.jp

Experimental

Materials. 6-Azido-1-hexanol[1], 6-azidohexanoic acid[2], and *N*-maltotriosyl-3-acetamido-1-propyne (MT-C≡CH)[3] were prepared in accordance with reported methods. 4-Dimethylaminopyridine (DMAP; >99.0%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC; >98.0%), and *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA; >99.0%) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI), and used as received. Trimethylolpropane (>98.0%), pentaerythritol (>98.0%), dipentaerythritol (>80.0%), and diphenyl phosphate (DPP; >99.0%) were purchased from TCI and were dried under high vacuum prior to use. Copper(I) bromide (CuBr; 99.999% trace metals basis) was purchased from Sigma-Aldrich Chemicals Co., and used as received. ε-Caprolactone (CL; >99.0%) was purchased from TCI and was purified by distillation over CaH_2 under reduced pressure. Dry dichloromethane (CH_2Cl_2; >99.5%) was purchased from Kanto Chemical Co., Inc., and was used as received.

Instruments. ^{1}H NMR spectra (400 MHz) were recorded on a JEOL JNM-ECS400 instrument. Size exclusion chromatography (SEC) analysis was performed in DMF (containing 0.01 M LiCl) at 40 °C with a JASCO HPLC system (PU-980 Intelligent HPLC pump, CO-965 Column oven, and RI-930 Intelligent reflective index detector) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm x 300 mm; pore size, 20 nm; bead size, 5 μm; exclusion limit, 4 x 10^4) and a Shodex Asahipak GF-7 M HQ column (linear, 7.6 mm x 300 mm; pore size, 20 nm; bead size, 9 μm; exclusion limit, 4 x 10^7) at a flow rate of 0.60 mL min^{-1}. The number-average molecular weight

($M_{n,SEC}$) and dispersity (M_w/M_n) of the polymer were calculated based on polystyrene standards. The FT-IR spectra were obtained in the attenuated total reflection (ATR) mode using a Perkin-Elmer Frontier MIR spectrometer. Thermogravimetric analysis (TGA) was performed up to 500 °C using a Bruker AXS TG-DTA 2010 instrument under a nitrogen atmosphere at the heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) analysis was carried out using a Bruker AXS DSC 3100 instrument under a nitrogen atmosphere at the heating rate of 10 °C min^{-1} and cooling rate of -20 °C min^{-1} (scan range: -50 – 150 °C). Atomic force microscopy (AFM) observations were performed in tapping mode with a PicoPlus atomic force microscope using a silicon cantilever (Mikromash HQ: NSC16/Al). The thin film sample for the AFM measurements were prepared by spin-coating the BCP solution (5 wt% in DMF) onto an oxygen plasma-treated silicon substrate. The film thickness was in the range of ca. 20 – 50 nm, as determined by spectroscopic ellipsometry analysis with a JASCO M-500S instrument. Small angle X-ray scattering (SAXS) experiments were carried out on the BM02 beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) or on the BL-6A beamline at the Photon Factory (PF, Tsukuba, Japan). The BCP samples for the SAXS measurements were put into a glass capillary with an inner diameter of 1.5 mm. In the ESRF, the SAXS profiles of the BCPs were obtained by 5 °C step during the continuous heating process from 30 to 200 °C (heating rate, ca. 2.5 °C min^{-1}; λ = 0.689 Å; acquisition time, 10 sec). In the PF, the SAXS profiles of the BCPs were obtained by 20 °C step during the step-by-step cooling process from the molten state (140 °C) to -20 °C (cooling rate, 5 °C min^{-1}; λ = 1.50 Å; acquisition time, 30

sec), in which each scan was started just after holding the desired temperature for 1 min. Grazing incidence small angle X-ray scattering experiments were carried out on the BL-6A beamline at the PF (λ = 1.50 Å; acquisition time, 10 sec).

Synthesis of PCL_L-N_3. The typical procedure polymerization procedure is as follows (method A). In a glovebox, 6-azido-1-hexanol (215 mg, 1.50 mmol), CL (1.37 g, 12.0 mmol), and DPP (18.8 mg, 75.0 μmol) were placed in a reaction vessel. The vessel was sealed with a septum and taken out from the glovebox. The mixture was stirred at 80 °C for 1 h, and the polymerization was quenched by adding Amberlyst A21 and CH_2Cl_2. The mixture was filtered and concentrated, and the residue was purified by reprecipitation using CH_2Cl_2 as the good solvent and cold MeOH as the poor solvent to give PCL_L-N_3 as a white solid (649 mg). Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.05 (t, -C*H*$_2$-O-C(=O)-), 3.64 (q, -C*H*$_2$-OH), 3.26 (t, -C*H*$_2$-N_3), 2.29 (t, -O-C(=O)C*H*$_2$-), 1.71-1.51 (m, -C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$-O-), 1.48-1.30 (m, -C(=O)CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$-O-). $M_{n,SEC}$ = 3170 g mol^{-1}; $M_{n,NMR}$ = 1460 g mol^{-1}; M_w/M_n = 1.03.

Synthesis of PCL_H-N_3. Method A was used for the polymerization of CL (1.83 g, 16.0 mmol) with 6-azido-1-hexanol (143 mg, 1.00 mmol) and DPP (12.5 mg, 50.0 μmol) for 1.5 h to give PCL_H-N_3 as a white solid (1.39 g). Yield: 82%. $M_{n,SEC}$ = 3790 g mol^{-1}; $M_{n,NMR}$ = 1980 g mol^{-1}; M_w/M_n = 1.04.

Synthesis of $(PCL_L\text{-}OH)_3$. Method A was used for the polymerization of CL (1.83 g, 16.0 mmol) with trimethylolpropanene (85.9 mg, 640 μmol) and DPP (8.01 mg, 32.0 μmol) for 1.5 h to

give (PCL_L-OH)$_3$ as a white solid (1.67 g). Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.05 (t, -C*H*$_2$-O-C(=O)-), 4.00 (s, $CH_3CH_2C(CH_2$-O-)$_3$), 3.64 (q, -C*H*$_2$-OH), 2.35-2.26 (m, -C(=O)C*H*$_2$-), 1.73-1.56 (m, CH_3CH_2-, -C(=O)$CH_2CH_2CH_2CH_2CH_2$-O-), 1.49-1.31 (m, -C(=O)$CH_2CH_2CH_2CH_2CH_2$-O-), 0.87 (C*H*$_3$-). $M_{n,SEC}$ = 4110 g mol^{-1}; $M_{n,NMR}$ = 3260 g mol^{-1}; M_w/M_n = 1.09.

Synthesis of (PCL_H-OH)$_3$. Method A was used for the polymerization of CL (1.83 g, 16.0 mmol) with trimethylolpropaneme (42.9 mg, 320 μmol) and DPP (4.00 mg, 16.0 μmol) for 2.5 h to give (PCL_H-OH)$_3$ as a white solid (1.49 g). Yield: 88%. $M_{n,SEC}$ = 7390 g mol^{-1}; $M_{n,NMR}$ = 5750 g mol^{-1}; M_w/M_n = 1.11.

Synthesis of (PCL_L-OH)$_4$. Method A was used for the polymerization of CL (1.83 g, 16.0 mmol) with pentaerythritol (62.2 mg, 457 μmol) and DPP (5.72 mg, 22.9 μmol) for 1.5 h to give (PCL_L-OH)$_4$ as a white solid (1.28 g). Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.11 (s, C(C*H*$_2$-O-)$_4$), 4.06 (t, -C*H*$_2$-O-C(=O)-), 3.65 (t, -C*H*$_2$-OH), 2.37-2.26 (m, -C(=O)C*H*$_2$-), 1.71-1.54 (m, -C(=O)CH_2C*H*$_2$$CH_2$C*H*$_2$$CH_2$-O-), 1.45-1.32 (m, -C(=O)CH_2CH_2C*H*$_2$$CH_2CH_2$-O-). $M_{n,SEC}$ = 5460 g mol^{-1}; $M_{n,NMR}$ = 4700 g mol^{-1}; M_w/M_n = 1.10.

Synthesis of (PCL_H-OH)$_4$. Method A was used for the polymerization of CL (1.83 g, 16.0 mmol) with pentaerythritol (31.1 mg, 229 μmol) and DPP (2.86 mg, 11.4 μmol) for 3.5 h to give (PCL_H-OH)$_4$ as a white solid (1.33 g). Yield: 80%. $M_{n,SEC}$ = 13000 g mol^{-1}; $M_{n,NMR}$ = 6800 g mol^{-1}; M_w/M_n = 1.09.

Synthesis of (PCL_L-OH)$_6$. Method A was used for the polymerization of CL (1.71 g, 15.0 mmol) with dipentaerythritol (76.3 mg, 300 μmol) and DPP (7.51 mg, 30 μmol) for 1.0 h to give (PCL_L-OH)$_6$ as a white solid (1.25 g). Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.10-4.04 (m, -C*H*$_2$-O-C(=O) -, -O-CH$_2$C(C*H*$_2$-O-C(=O)-)$_3$), 3.65 (t, -C*H*$_2$-OH), 3.38 (d, -C*H*$_2$-O-C*H*$_2$-), 2.34-2.20 (m, -C(=O)C*H*$_2$-), 1.80-1.55 (m, -C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$-O-), 1.49-1.21 (m, -C(=O)CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$-O-). $M_{n,SEC}$ = 10900 g mol^{-1}; $M_{n,NMR}$ = 6550 g mol^{-1}; M_w/M_n = 1.11.

Synthesis of (PCL_H-OH)$_6$. Method A was used for the polymerization of CL (1.71 g, 15.0 mmol) with dipentaerythritol (38.1 mg, 150 μmol) and DPP (3.75 mg, 15.0 μmol) for 2.5 h to give (PCL_L-OH)$_6$ as a white solid (1.16 g). Yield: 83%. $M_{n,SEC}$ = 15400 g mol^{-1}; $M_{n,NMR}$ = 9980 g mol^{-1}; M_w/M_n = 1.10.

Synthesis of (PCL_L-N_3)$_3$. The typical end functionalization reaction procedure is as follows (method B). 6-Azidohexanoic acid (173 mg, 1.10 mmol) was added a stirred solution of (PCL_L-OH)$_3$ (1.00 g, 306 μmol), DMAP (168 mg, 1.38 mmol), and EDC (264 mg, 1.38 mmol) in dry CH_2Cl_2 (20 mL) under an argon atmosphere. After stirring at room temperature for 72 h, the reaction mixture was concentrated and poured into cold MeOH to give (PCL_L-N_3)$_3$ as a white solid (1.00 g). Yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.14-4.03 (t, -C*H*$_2$-O-C(=O)-), 4.01 (s, CH$_3$CH$_2$C(C*H*$_2$-O-)$_3$), 3.28 (t, -C*H*$_2$-N$_3$), 2.40-2.21 (m, -C(=O)C*H*$_2$-), 1.79-1.53 (m, CH$_3$C*H*$_2$-, -C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$-O-), 1.53-1.20 (m, -C(=O)CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$-O-). $M_{n,SEC}$ = 6670 g mol^{-1}; $M_{n,NMR}$ = 3550 g mol^{-1}; M_w/M_n = 1.10.

Synthesis of (PCL_H-N_3)$_3$. Method B was used for the reaction of (PCL_H-OH)$_3$ (1.00 g, 174 μmol) and 6-azidohexanoic acid (98.4 mg, 626 μmol) with DMAP (95.6 mg, 783 μmol) and EDC (150 mg, 783 μmol) in dry CH_2Cl_2 (20 mL) to give (PCL_H-N_3)$_3$ as a white solid (1.00 g). Yield: 91%. $M_{n,SEC}$ = 11500 g mol^{-1}; $M_{n,NMR}$ = 6330 g mol^{-1}; M_w/M_n = 1.08.

Synthesis of (PCL_L-N_3)$_4$. Method B was used for the reaction of (PCL_L-OH)$_4$ (1.00 g, 213 μmol) and 6-azidohexanoic acid (160 mg, 1.02 mmol) with DMAP (156 mg, 1.28 mmol) and EDC (245 mg, 1.28 mmol) in dry CH_2Cl_2 (20 mL) to give (PCL_L-N_3)$_4$ as a white solid (1.02 g). Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.11 (s, C(C*H*$_2$-O-)$_4$), 4.06 (t, -C*H*$_2$-O-C(=O)-), 3.28 (t, -C*H*$_2$-N_3), 2.35-2.20 (m, -C(=O)C*H*$_2$-), 1.55-1.81 (m, -C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$-O-), 1.45-1.22 (m, -C(=O)CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$-O-). $M_{n,SEC}$ = 8330 g mol^{-1}; $M_{n,NMR}$ = 4860 g mol^{-1}; M_w/M_n = 1.08.

Synthesis of (PCL_H-N_3)$_4$. Method B was used for the reaction of (PCL_H-OH)$_4$ (1.00 g, 147 μmol) and 6-azidohexanoic acid (111 mg, 706 μmol) with DMAP (108 mg, 882 μmol) and EDC (169 mg, 882 μmol) in dry CH_2Cl_2 (20 mL) to give (PCL_H-N_3)$_4$ as a white solid (978 mg). Yield: 98%. $M_{n,SEC}$ = 13500 g mol^{-1}; $M_{n,NMR}$ = 7480 g mol^{-1}; M_w/M_n = 1.10.

Synthesis of (PCL_L-N_3)$_6$. Method B was used for the reaction of (PCL_L-OH)$_6$ (1.00 g, 153 μmol) and 6-azidohexanoic acid (173 mg, 1.10 mmol) with DMAP (167 mg, 1.37 mmol) and EDC (263 mg, 1.37 mmol) in dry CH_2Cl_2 (20 mL) to give (PCL_L-N_3)$_6$ as a white solid (903 mg). Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.17-3.93 (m, -C*H*$_2$-O-C(=O) -, -O-CH$_2$C(C*H*$_2$-O-C(=O)-)$_3$), 3.43-3.32 (m, -C*H*$_2$-O-C*H*$_2$-), 3.28 (t, -C*H*$_2$-N_3), 2.34-2.20 (m, -C(=O)C*H*$_2$-), 1.81-1.51 (m,

-C(=O)CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$-O-), 1.49-1.18 (m, -C(=O)CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$-O-). $M_{n,SEC}$ = 11400 g mol^{-1}; $M_{n,NMR}$ = 7200 g mol^{-1}; M_w/M_n = 1.11.

Synthesis of (PCL$_H$-N$_3$)$_6$. Method B was used for the reaction of (PCL$_H$-OH)$_6$ (1.00 g, 100 μmol) and 6-azidohexanoic acid (113 mg, 722 μmol) with DMAP (110 mg, 902 μmol) and EDC (173 mg, 902 μmol) in dry CH_2Cl_2 (20 mL) to give (PCL$_H$-N$_3$)$_6$ as a white solid (980 mg). Yield: 98%. $M_{n,SEC}$ = 14500 g mol^{-1}; $M_{n,NMR}$ = 10400 g mol^{-1}; M_w/M_n = 1.10.

Synthesis of PCL$_L$-*b*-MT. The typical click reaction procedure is as follows (method C). PCL$_L$-N$_3$ (400 mg, 275 μmol), MT-C≡CH (192 mg, 330 μmol), and CuBr (55.1 mg, 385 μmol) were placed in a Schlenk flask and dried under vacuum. PMDETA (66.7 mg, 385 μmol) in DMF (20 mL) was degassed by the argon bubbling, then the mixture was transferred into the Schlenck flask under an argon atmosphere. After stirring at 60 °C for 72 h, the reaction mixture was passed through a pad of alumina and eluted with THF. After removing the solvent by evaporation, the crude product was purified by reprecipitation using DMF as the good solvent and cold MeOH as poor solvent to give PCL$_L$-*b*-MT as white solid (128 mg). Yield: 23%. $M_{n,SEC}$ = 6,540 g mol^{-1}; $M_{n,NMR}$ = 2,040 g mol^{-1}; M_w/M_n = 1.10. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.06, 7.88 (rotamers, triazole methine), 5.67 – 5.32 (br, OH^{MT}), 5.08 – 4.73 (br, H-1^{MT}), 4.59 – 4.38 (br, OH^{MT}), 4.35 – 4.22 (br, -NAc-C*H*$_2$-), 3.99 (t, J = 6.4 Hz, -C(=O)-(CH$_2$)$_4$-C*H*$_2$-O-), 3.75 –2.99 (br, H-2, 3, 4, 5, 6^{MT}), 2.27 (t, J = 7.4 Hz, -C(=O)-C*H*$_2$-(CH$_2$)$_4$-O-), 2.09, 1.96 (rotamers, -N-(C=O)C*H*$_3$), 1.61 – 1.47 (m, -C(=O)-CH$_2$-C*H*$_2$-CH$_2$-C*H*$_2$CH$_2$-O-), 1.30 (m, -C(=O)-(CH$_2$)$_2$-C*H*$_2$-(CH$_2$)$_2$-O-).

Synthesis of PCL_H-*b*-MT. Method C was used for the click reaction of PCL_H-N_3 (300 mg, 151 μmol) and MT-C≡CH (106 mg, 182 μmol) in DMF (15 mL) with CuBr (30.4 mg, 212 μmol) and PMDETA (36.7 mg, 212 μmol) to give PCL_H-*b*-MT as white solid (42 mg). Yield: 11%. $M_{n,SEC}$ = 8530 g mol^{-1}; $M_{n,NMR}$ = 2560 g mol^{-1}; M_w/M_n = 1.08.

Synthesis of $(PCL_L$-*b*-MT$)_3$. Method C was used for the click reaction of $(PCL_L$-$N_3)_3$ (500 mg, 141 μmol) and MT-C≡CH (296 mg, 508 μmol) in DMF (20 mL) with CuBr (84.8 mg, 592 μmol) and PMDETA (103 mg, 592 μmol) to give $(PCL_L$-*b*-MT$)_3$ as white solid (301 mg). Yield: 40%. $M_{n,SEC}$ = 20300 g mol^{-1}; $M_{n,NMR}$ = 5300 g mol^{-1}; M_w/M_n = 1.14. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.06, 7.87 (rotamers, triazole methine), 5.71 – 5.27 (br, OH^{MT}), 5.09 – 4.71 (br, H-1^{MT}), 4.57 – 4.38 (br, OH^{MT}), 4.35 – 4.22 (br, -NAc-CH_2-), 3.98 (t, J = 6.4 Hz, -C(=O)-$(CH_2)_4$-CH_2-O-), 3.76 – 3.00 (br, H-2, 3, 4, 5, 6^{MT}), 2.27 (t, J = 7.3 Hz, -C(=O)-CH_2-$(CH_2)_4$-O-), 2.09, 1.96 (rotamers, -N-(C=O)CH_3), 1.60 – 1.46 (m, -C(=O)-CH_2-CH_2-CH_2-CH_2CH_2-O-), 1.30 (m, -C(=O)-$(CH_2)_2$-CH_2-$(CH_2)_2$-O-), 0.83 (t, J = 7.8 Hz, -CH_2CH_3).

Synthesis of $(PCL_H$-*b*-MT$)_3$. Method C was used for the click reaction of $(PCL_H$-$N_3)_3$ (500 mg, 103 μmol) and MT-C≡CH (99.5 mg, 171 μmol) in DMF (15 mL) with CuBr (28.5 mg, 199 μmol) and PMDETA (34.5 mg, 199 μmol) to give $(PCL_H$-*b*-MT$)_3$ as white solid (146 mg). Yield: 38%. $M_{n,SEC}$ = 23000 g mol^{-1}; $M_{n,NMR}$ = 8080 g mol^{-1}; M_w/M_n = 1.10.

Synthesis of $(PCL_L$-*b*-MT$)_4$. Method C was used for the click reaction of $(PCL_L$-$N_3)_4$ (500 mg, 103 μmol) and MT-C≡CH (288 mg, 494 μmol) in DMF (20 mL) with CuBr (82.5 mg, 576

μmol) and PMDETA (99.8 mg, 576 μmol) to give (PCL_L-*b*-MT)$_4$ as white solid (261 mg). Yield: 35%. $M_{n,SEC}$ = 24900 g mol^{-1}; $M_{n,NMR}$ = 7190 g mol^{-1}; M_w/M_n = 1.09. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.06, 7.88 (rotamers, triazole methine), 5.68 – 5.31 (br, OH^{MT}), 5.05 – 4.77 (br, H-1^{MT}), 4.57 – 4.40 (br, OH^{MT}), 4.34 – 4.23 (br, -NAc-CH_2-), 4.06 (s, C(CH_2-O-)$_4$), 3.98 (t, J = 6.8 Hz, -C(=O)-(CH$_2$)$_4$-CH_2-O-), 3.76 – 3.02 (br, H-2, 3, 4, 5, 6^{MT}), 2.27 (t, J = 7.3 Hz, -C(=O)-CH_2-(CH$_2$)$_4$-O-), 2.09, 1.96 (rotamers, -N-(C=O)CH_3), 1.61 – 1.47 (m, -C(=O)-CH$_2$-CH_2-CH$_2$-CH_2CH$_2$-O-), 1.30 (m, -C(=O)-(CH$_2$)$_2$-CH_2-(CH$_2$)$_2$-O-).

Synthesis of (PCL_H-*b*-MT)$_4$. Method C was used for the click reaction of (PCL_H-N$_3$)$_4$ (270 mg, 36.1 μmol) and MT-C≡CH (101 mg, 173 μmol) in DMF (15 mL) with CuBr (28.9 mg, 202 μmol) and PMDETA (35.0 mg, 202 μmol) to give (PCL_H-*b*-MT)$_4$ as white solid (111 mg). Yield: 31%. $M_{n,SEC}$ = 30600 g mol^{-1}; $M_{n,NMR}$ = 9810 g mol^{-1}; M_w/M_n = 1.11.

Synthesis of (PCL_L-*b*-MT)$_6$. Method C was used for the click reaction of (PCL_L-N$_3$)$_6$ (250 mg, 34.7 μmol) and MT-C≡CH (146 mg, 25.0 μmol) in DMF (15 mL) with CuBr (41.8 mg, 292 μmol) and PMDETA (50.6 mg, 292 μmol) to give (PCL_L-*b*-MT)$_6$ as white solid (107 mg). Yield: 29%. $M_{n,SEC}$ = 33200 g mol^{-1}; $M_{n,NMR}$ = 10600 g mol^{-1}; M_w/M_n = 1.13. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.04, 7.85 (rotamers, triazole methine), 5.56 – 5.19 (br, OH^{MT}), 5.07 – 4.62 (br, H-1^{MT}), 4.58 – 4.21 (br, OH^{MT}, -NAc-CH_2-), 3.99 (t, J = 6.9 Hz, -C(=O)-(CH$_2$)$_4$-CH_2-O-), 3.76 –3.03 (br, H-2, 3, 4, 5, 6^{MT}), 2.27 (t, J = 7.8 Hz, -C(=O)-CH_2-(CH$_2$)$_4$-O-), 2.10, 1.97 (rotamers, -N-(C=O)CH_3), 1.61 – 1.46 (m, -C(=O)-CH$_2$-CH_2-CH$_2$-CH_2CH$_2$-O-), 1.31 (m, -C(=O)-(CH$_2$)$_2$-CH_2-(CH$_2$)$_2$-O-).

Synthesis of (PCL_H-*b*-MT)$_6$. Method C was used for the click reaction of (PCL_H-N_3)$_6$ (250 mg, 24.0 μmol) and MT-C≡CH (101 mg, 173 μmol) in DMF (15 mL) with CuBr (28.9 mg, 202 μmol) and PMDETA (35.0 mg, 202 μmol) to give (PCL_H-*b*-MT)$_6$ as white solid (166 mg). Yield: 50%. $M_{n,SEC}$ = 35800 g mol^{-1}; $M_{n,NMR}$ = 13800 g mol^{-1}; M_w/M_n = 1.15.

Table S1. Synthesis of star-shaped PCLs by the DPP-catalyzed ring-opening polymerization of CL with polyol initiators [a]

	$[CL]_0/[I]_0/[DPP]$	time (h)	conv. [b] (%)	$M_{n,NMR}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	M_w/M_n [c]	yield (%)
$(PCL_L\text{-}OH)_3$	25/1/0.05	1.5	98.6	3300	4100	1.09	89
$(PCL_H\text{-}OH)_3$	50/1/0.05	2.5	90.9	5800	7400	1.11	88
$(PCL_L\text{-}OH)_4$	35/1/0.05	1.5	94.4	4700	5500	1.10	72
$(PCL_H\text{-}OH)_4$	70/1/0.05	3.5	89.9	6800	13000	1.09	80
$(PCL_L\text{-}OH)_6$	50/1/0.10	1.0	92.5	6600	10900	1.11	75
$(PCL_H\text{-}OH)_6$	100/1/0.10	2.0	79.8	10000	15400	1.10	83

[a] Polymerization condition: Ar atmosphere; in the bulk; temp., 80 °C; initiator, trimethylolpropane for $(PCL\text{-}OH)_3$, pentaerythritol for $(PCL\text{-}OH)_4$, and dipentaerythritol for $(PCL\text{-}OH)_6$. [b] Determined by ^1H NMR in $CDCl_3$. [c] Estimated by SEC in DMF containing 0.01 M LiCl with polystyrene standards.

Table S2. Synthesis of azido-functionalized star-shaped PCLs [a]

	$M_{n,NMR}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	M_w/M_n [c]	extent of reaction (%)	yield (%)
$(PCL_L\text{-}N_3)_3$	3,600	6,700	1.10	96.1	92
$(PCL_H\text{-}N_3)_3$	6,300	11,500	1.08	94.3	91
$(PCL_L\text{-}N_3)_4$	4,900	8,300	1.08	89.2	99
$(PCL_H\text{-}N_3)_4$	7,500	13,500	1.10	>99	98
$(PCL_L\text{-}N_3)_6$	7,200	11,400	1.11	>99	83
$(PCL_H\text{-}N_3)_6$	10,400	14,500	1.10	88.8	94

[a] Reaction condition: Ar atmosphere; temp., 80 °C; solvent, CH_2Cl_2; $[\text{-}N_3]_0/[6\text{-azidohexanoic acid}]_0/[EDC]_0/[DMAP]_0 = 1/1.2/1.5/1.5$. [b] Determined by ^1H NMR in $CDCl_3$. [c] Estimated by SEC in DMF containing 0.01 M LiCl with polystyrene standards.

Table S3. Thermal properties of (PCL-*b*-MT)$_x$s (x = 1, 3, 4, and 6)

	$T_{d,5\%}$ [a] (°C)	$T_{d,10\%}$ [a] (°C)	first heating T_m [b] (°C)	first cooling T_c [b] (°C)	second heating T_m [a] (°C)
PCL_L-*b*-MT	289	314	54	2	39
PCL_H-*b*-MT	301	329	55, 60	2	42
$(PCL_L\text{-}b\text{-}MT)_3$	273	298	61	-	-
$(PCL_H\text{-}b\text{-}MT)_3$	296	319	54, 59	-	-
$(PCL_L\text{-}b\text{-}MT)_4$	290	312	70	-	-
$(PCL_H\text{-}b\text{-}MT)_4$	304	322	54	-	-
$(PCL_L\text{-}b\text{-}MT)_6$	282	302	57	-	-
$(PCL_H\text{-}b\text{-}MT)_6$	267	301	63	-	-

[a] 5% and 10% weight-loss temperatures ($T_{d,5\%}$ and $T_{d,10\%}$, respectively) were determined by TGA analysis under nitrogen atmosphere. [b] Melting temperature (T_m) and crystallization temperature (T_c) were determined by DSC analysis under nitrogen atmosphere.

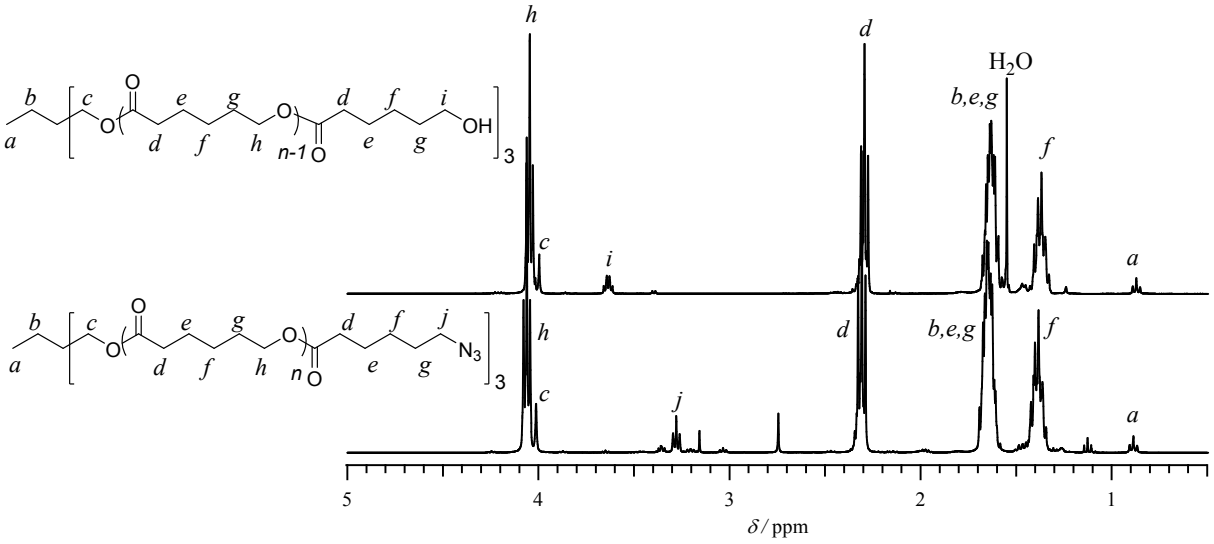

Figure S1. ^{1}H NMR spectra of $(PCL_L\text{-}OH)_3$ (upper) and $(PCL_L\text{-}N_3)_3$ (lower) in $CDCl_3$ (400 MHz).

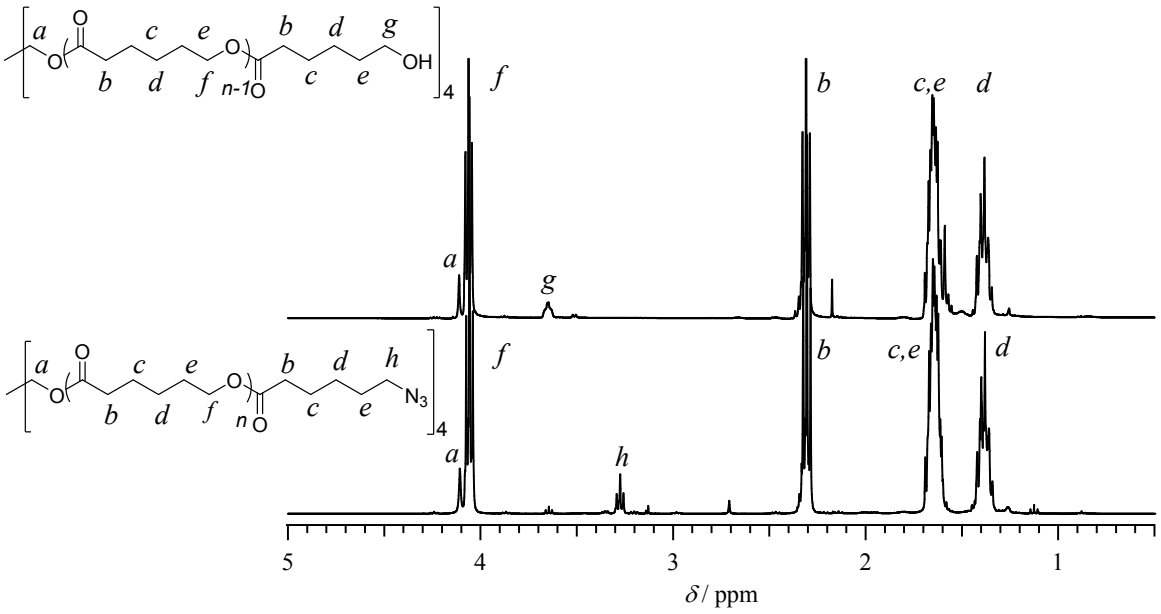

Figure S2. ^{1}H NMR spectra of $(PCL_L\text{-}OH)_4$ (upper) and $(PCL_L\text{-}N_3)_4$ (lower) in $CDCl_3$ (400 MHz).

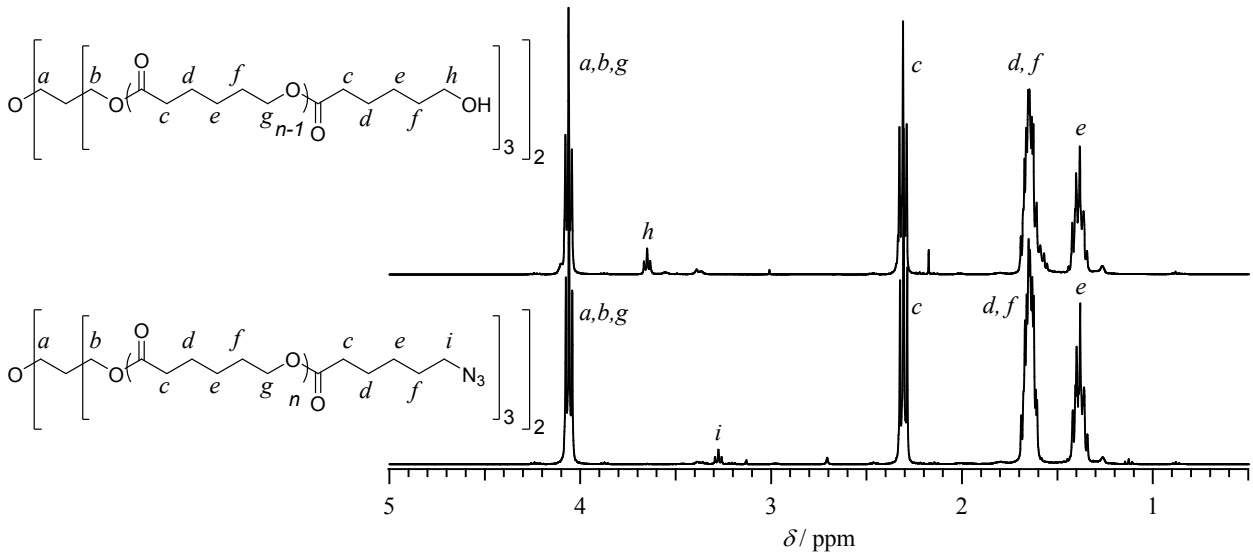

Figure S3. ^{1}H NMR spectra of $(PCL_L\text{-}OH)_6$ (upper) and $(PCL_L\text{-}N_3)_6$ (lower) in $CDCl_3$ (400 MHz).

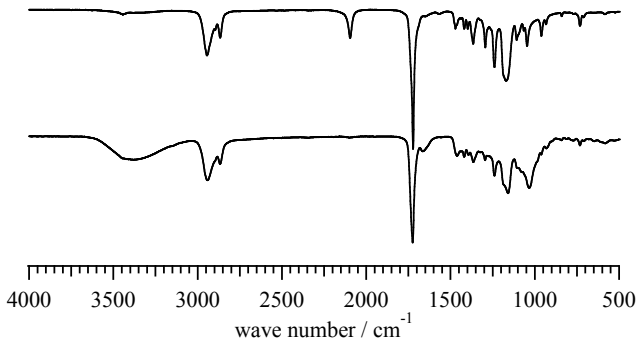

Figure S4. FT-IR spectra of $(PCL_L\text{-}N_3)_3$ (upper) and $(PCL_L\text{-}b\text{-}MT)_3$.

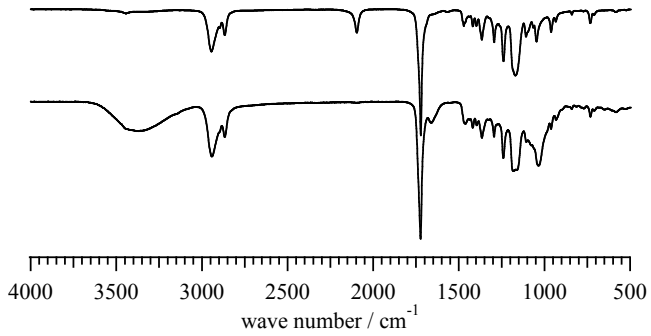

Figure S5. FT-IR spectra of $(PCL_L\text{-}N_3)_4$ (upper) and $(PCL_L\text{-}b\text{-}MT)_4$.

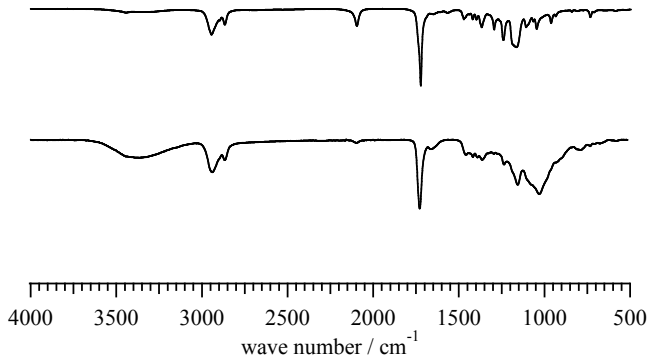

Figure S6. FT-IR spectra of $(PCL_L\text{-}N_3)_6$ (upper) and $(PCL_L\text{-}b\text{-}MT)_6$.

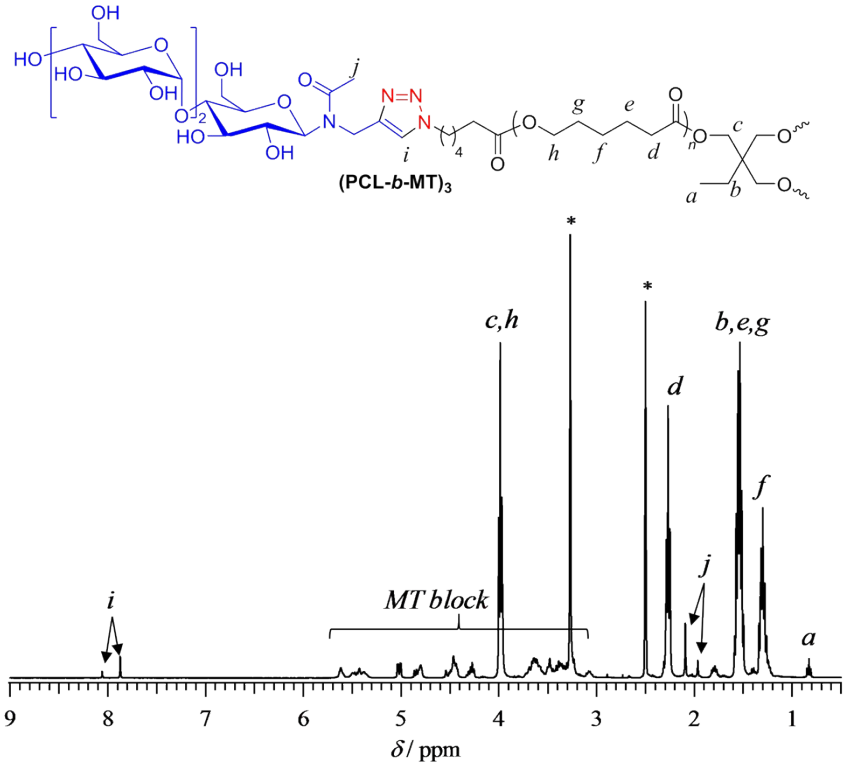

Figure S7. ^{1}H NMR spectrum of $(PCL_L\text{-}b\text{-}MT)_3$ in DMSO-d_6 (400 MHz). The asterisks represent residual solvents (water and DMSO).

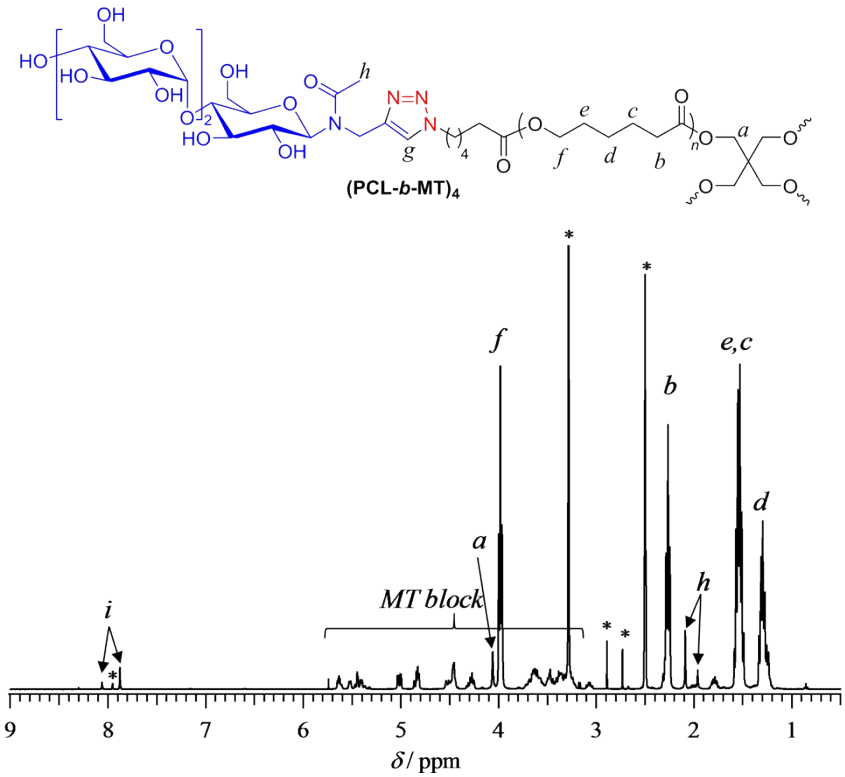

Figure S8. ^{1}H NMR spectrum of $(PCL_L\text{-}b\text{-}MT)_4$ in DMSO-d_6 (400 MHz). The asterisks represent residual solvents (water, DMF, and DMSO).

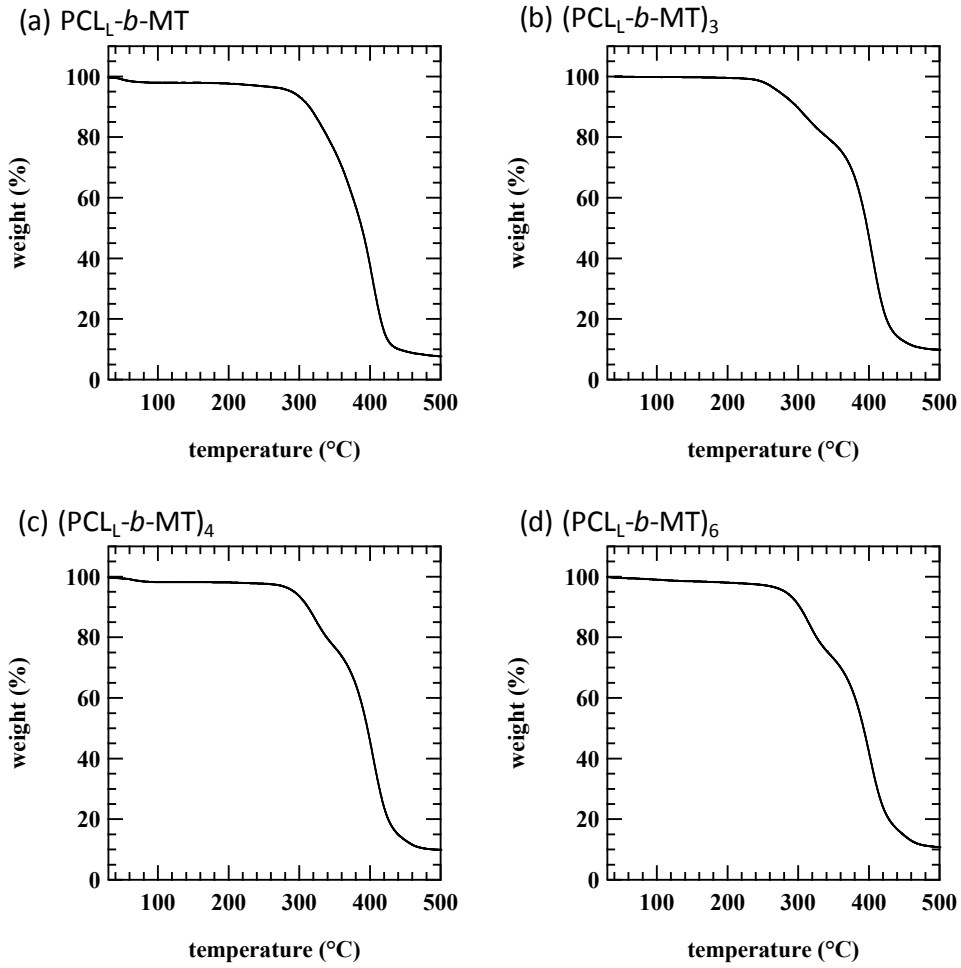

Figure S9. TGA traces of PCL$_L$-*b*-MT, (PCL$_L$-*b*-MT)$_3$, (PCL$_L$-*b*-MT)$_4$, and (PCL$_L$-*b*-MT)$_6$ (see **Table S3**).

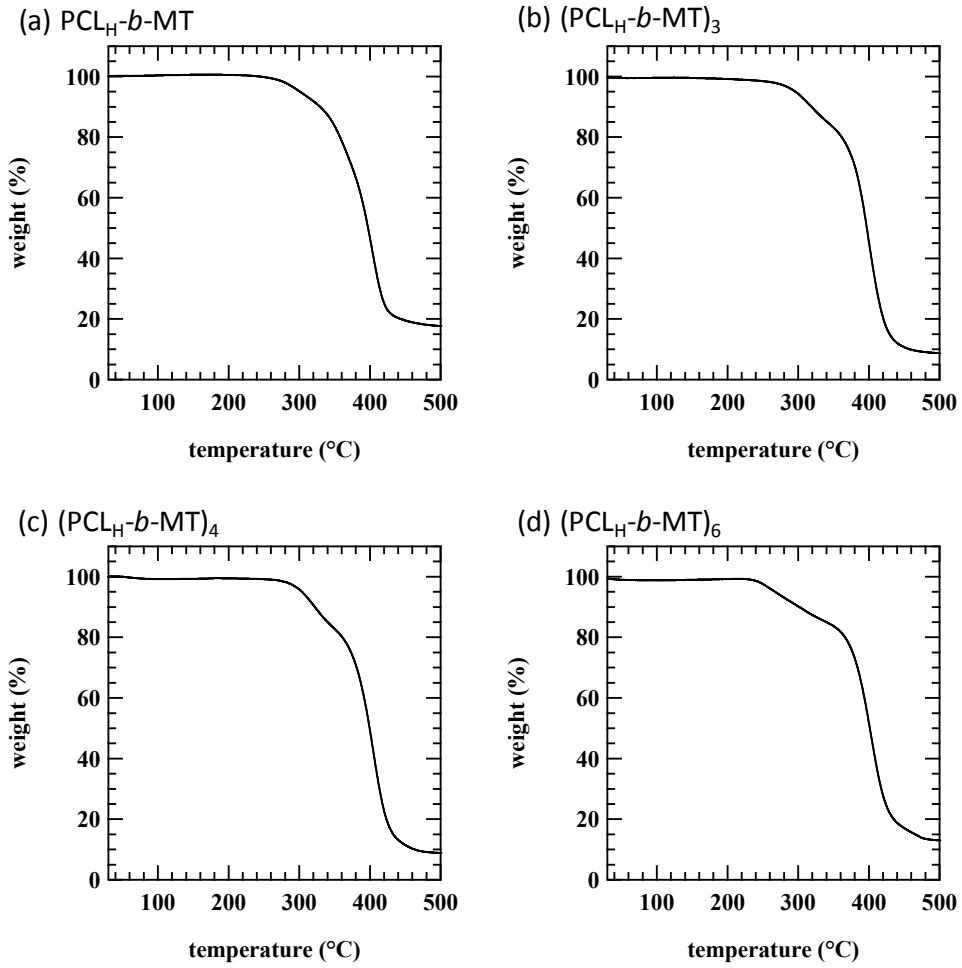

Figure S10. TGA traces of PCL$_H$-*b*-MT, (PCL$_H$-*b*-MT)$_3$, (PCL$_H$-*b*-MT)$_4$, and (PCL$_H$-*b*-MT)$_6$ (see **Table S3**).

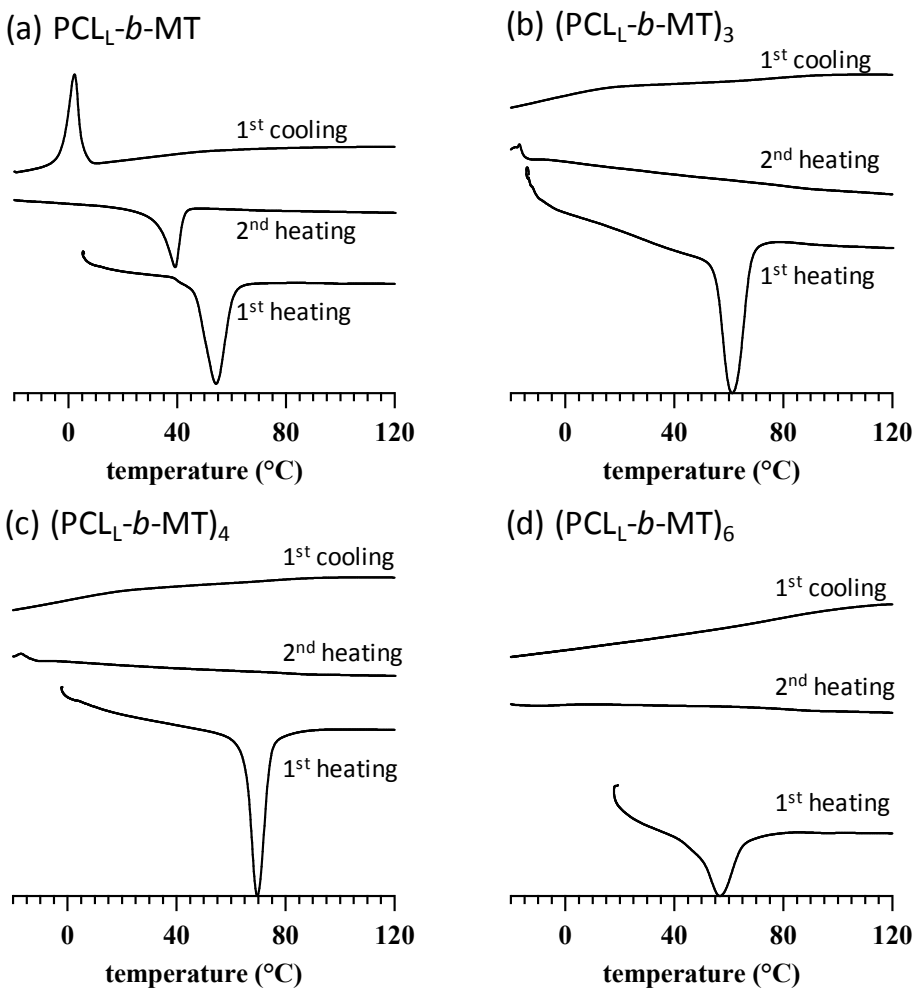

Figure S11. DSC traces of PCL$_L$-*b*-MT, (PCL$_L$-*b*-MT)$_3$, (PCL$_L$-*b*-MT)$_4$, and (PCL$_L$-*b*-MT)$_6$ (see **Table S3**).

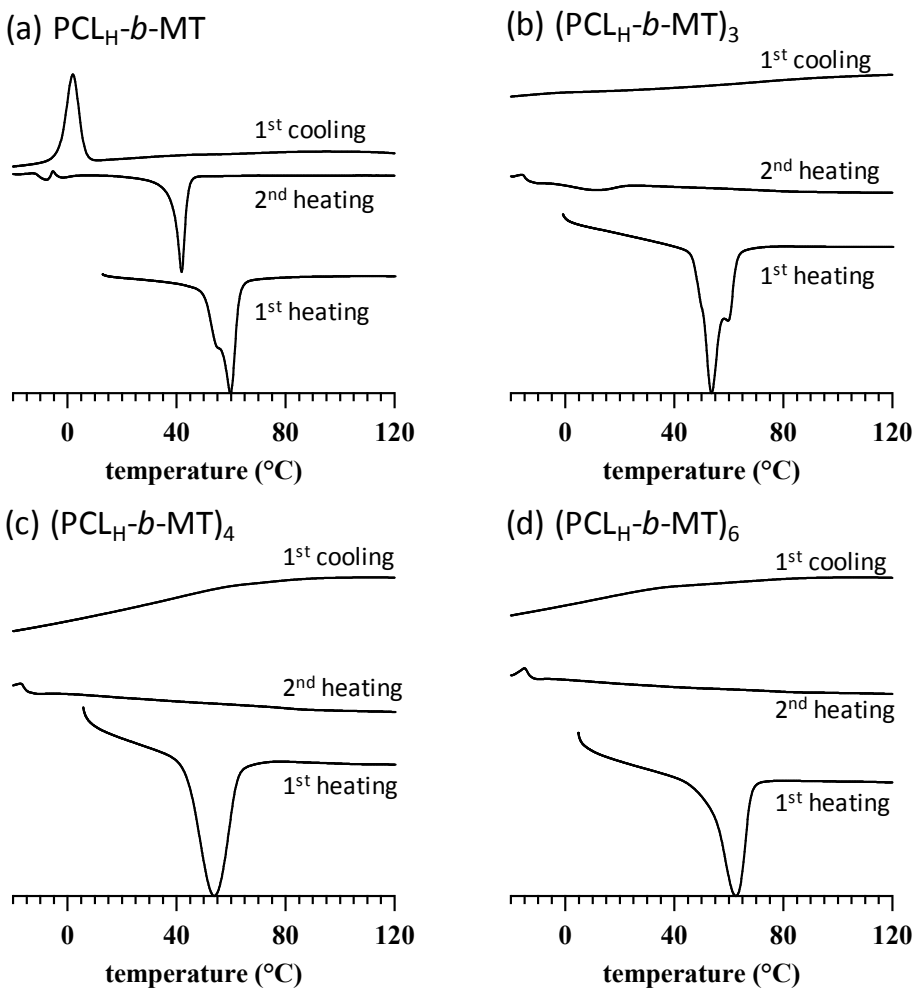

Figure S12. DSC traces of PCL$_H$-*b*-MT, (PCL$_H$-*b*-MT)$_3$, (PCL$_H$-b-MT)$_4$, and (PCL$_H$-*b*-MT)$_6$ (see **Table S3**).

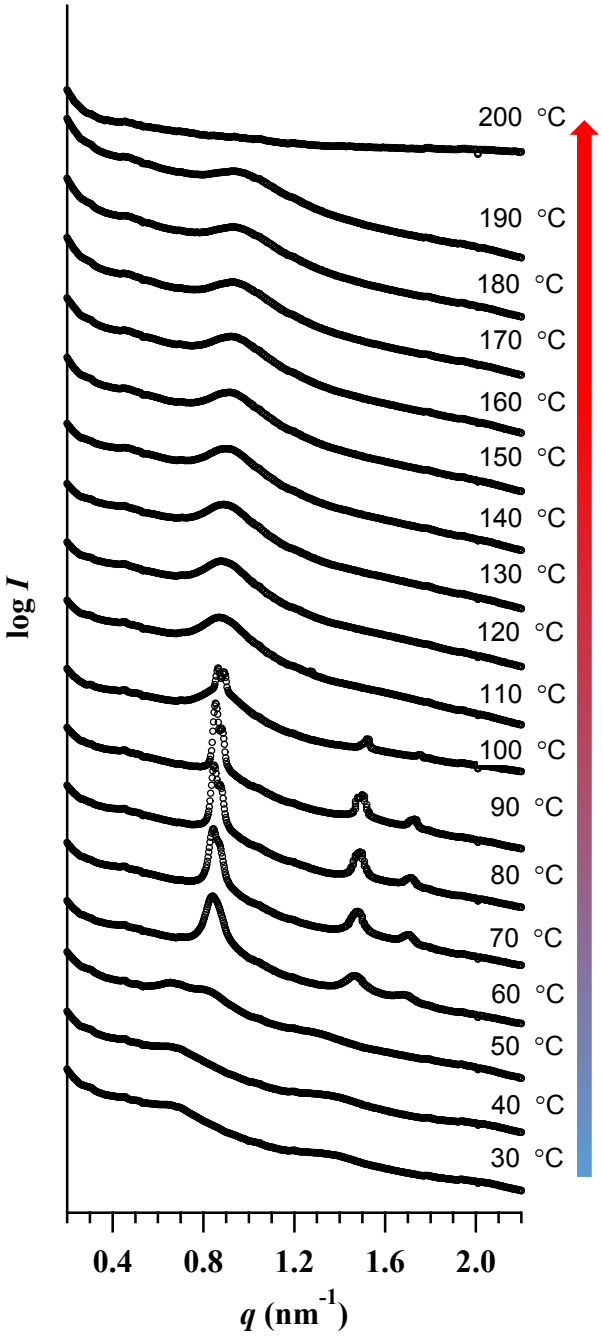

Figure S13. SAXS profiles of PCL_L-*b*-MT during the continuous heating from 30 to 200 °C.

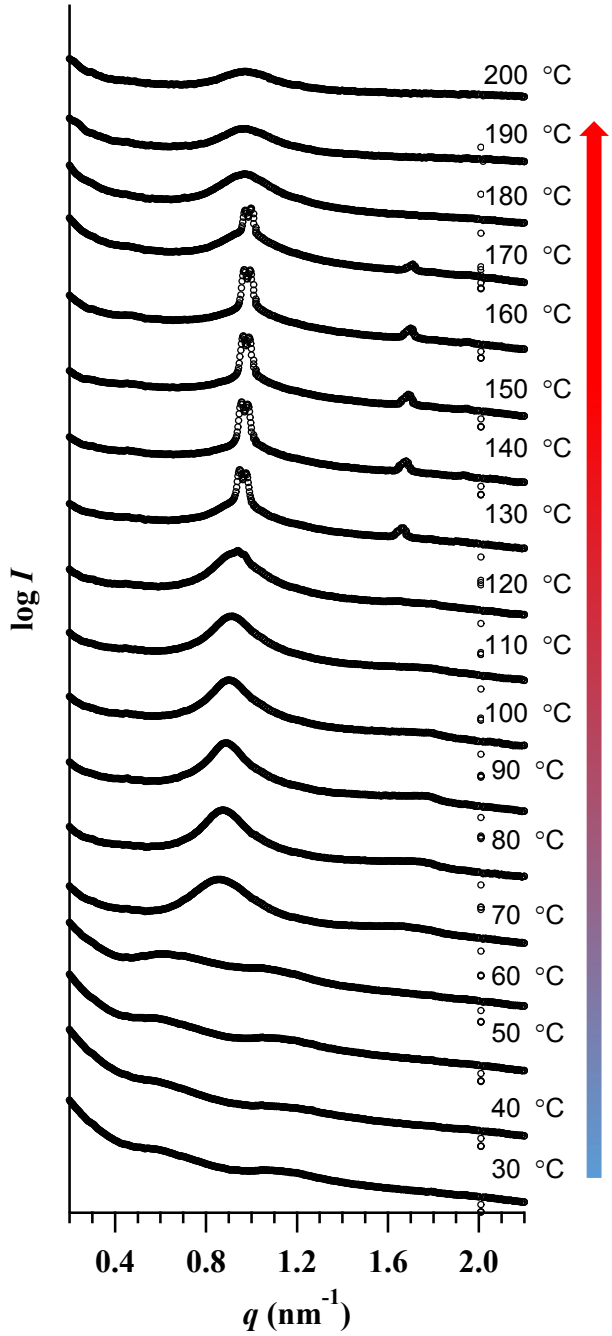

Figure S14. SAXS profiles of $(PCL_L\text{-}b\text{-}MT)_3$ during the continuous heating from 30 to 200 °C.

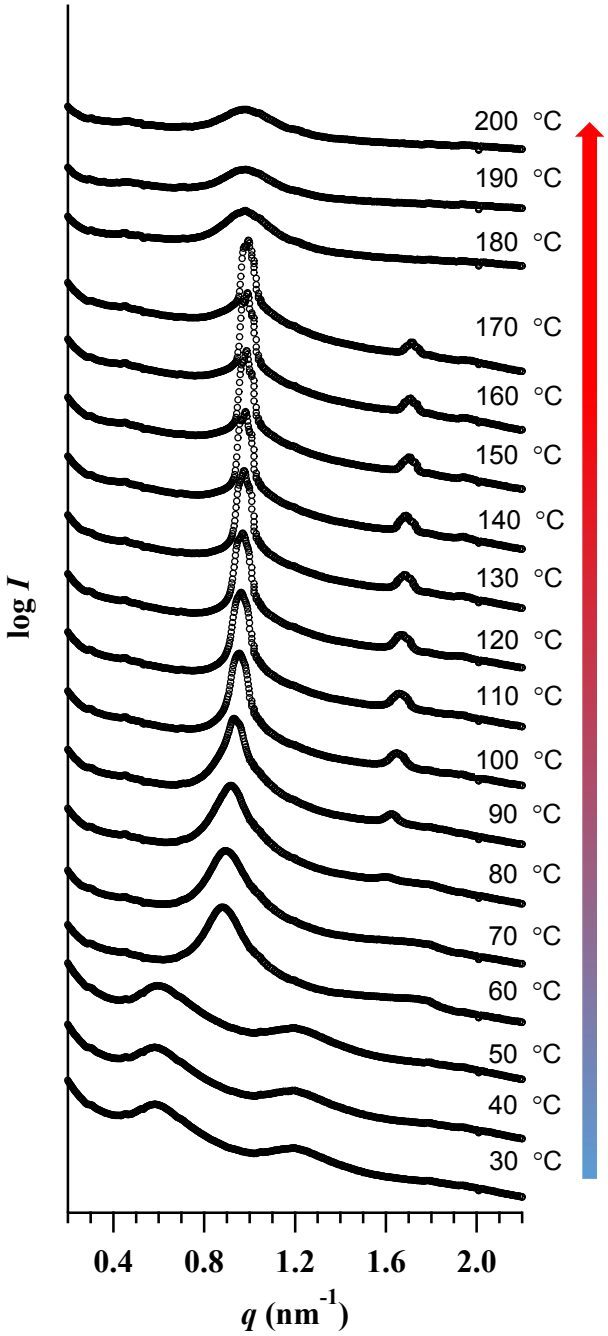

Figure S15. SAXS profiles of $(PCL_L\text{-}b\text{-}MT)_4$ during the continuous heating from 30 to 200 °C.

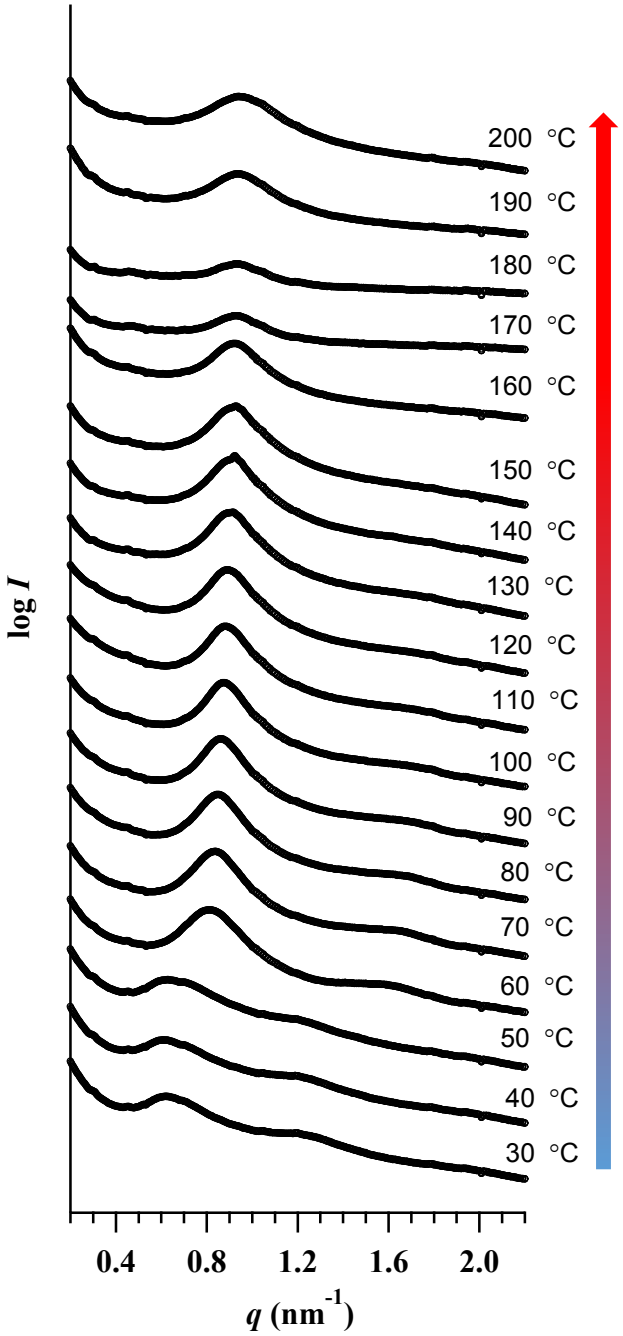

Figure S16. SAXS profiles of $(PCL_L\text{-}b\text{-}MT)_6$ during the continuous heating from 30 to 200 °C.

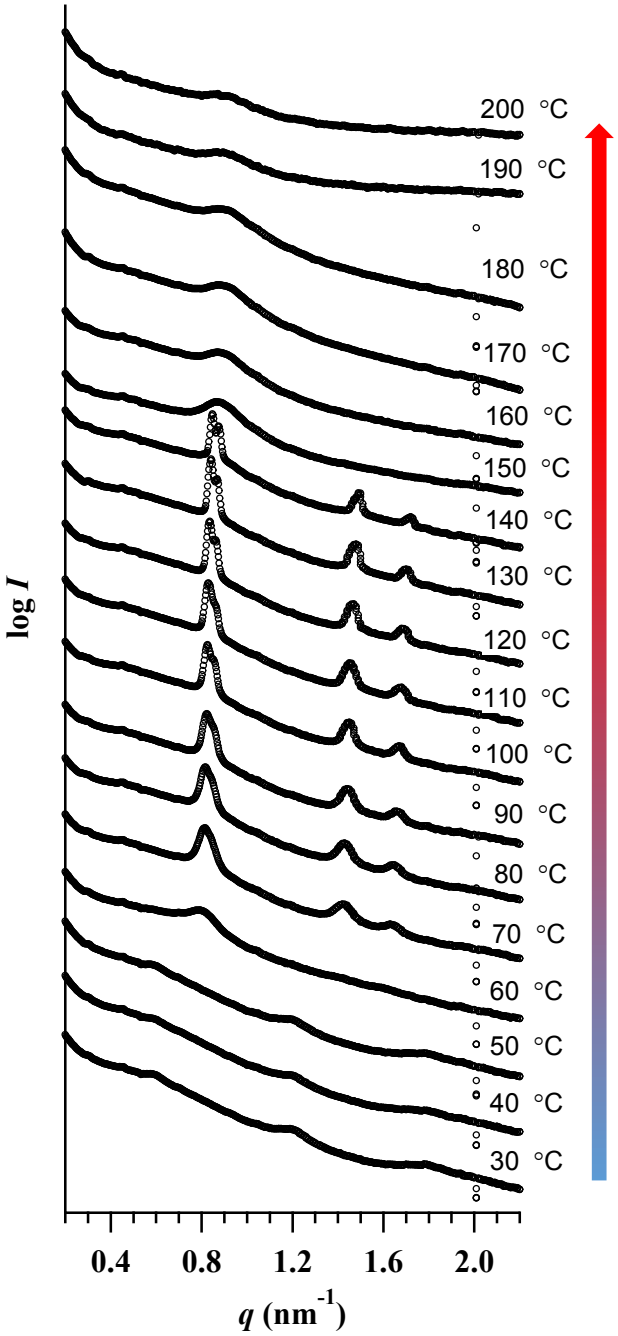

Figure S17. SAXS profiles of PCL_H-*b*-MT during the continuous heating from 30 to 200 °C.

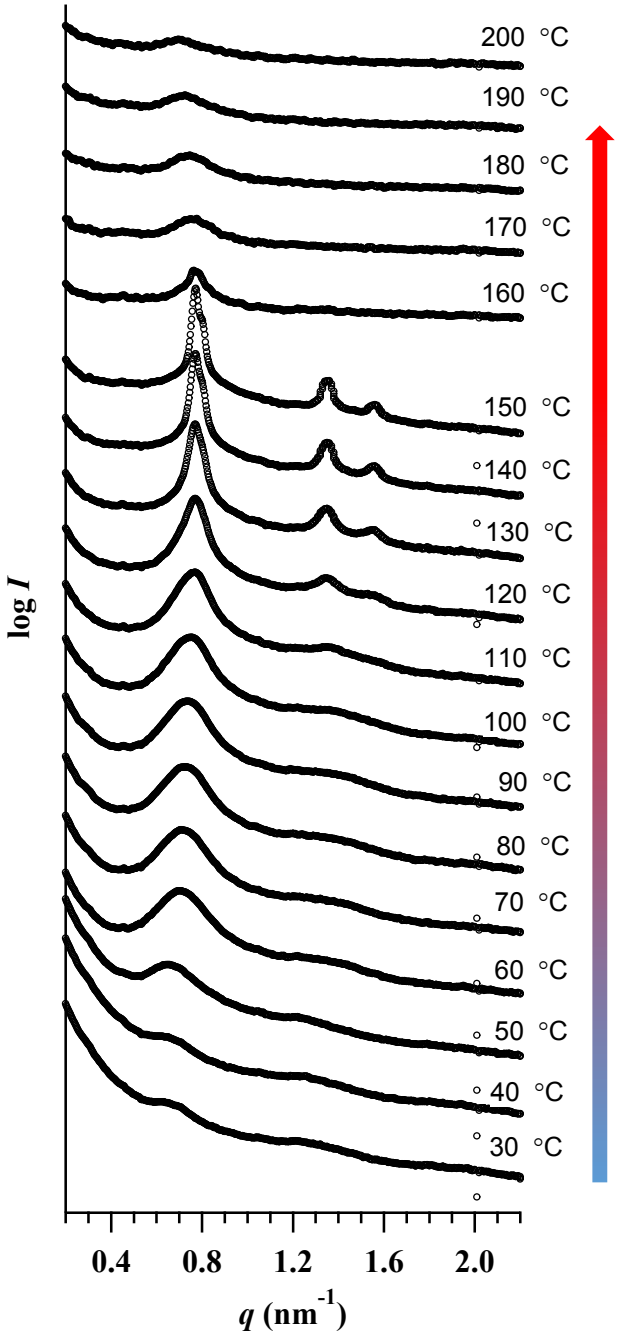

Figure S18. SAXS profiles of $(PCL_H\text{-}b\text{-}MT)_3$ during the continuous heating from 30 to 200 °C.

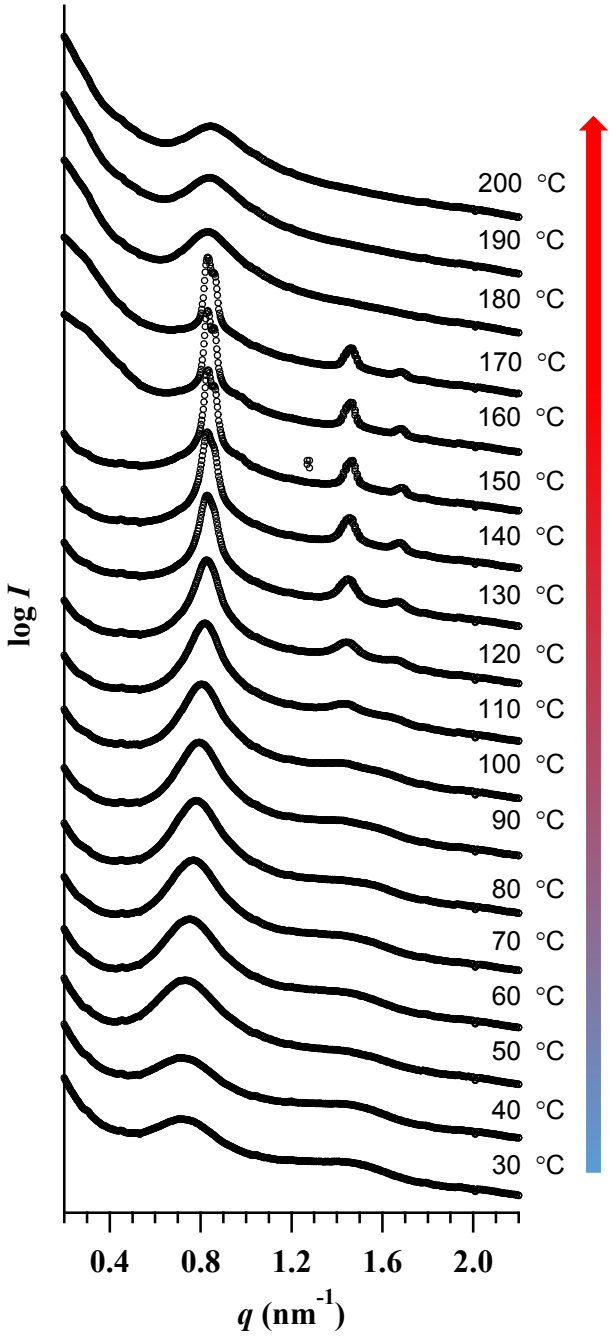

Figure S19. SAXS profiles of $(PCL_H\text{-}b\text{-}MT)_4$ during the continuous heating from 30 to 200 °C.

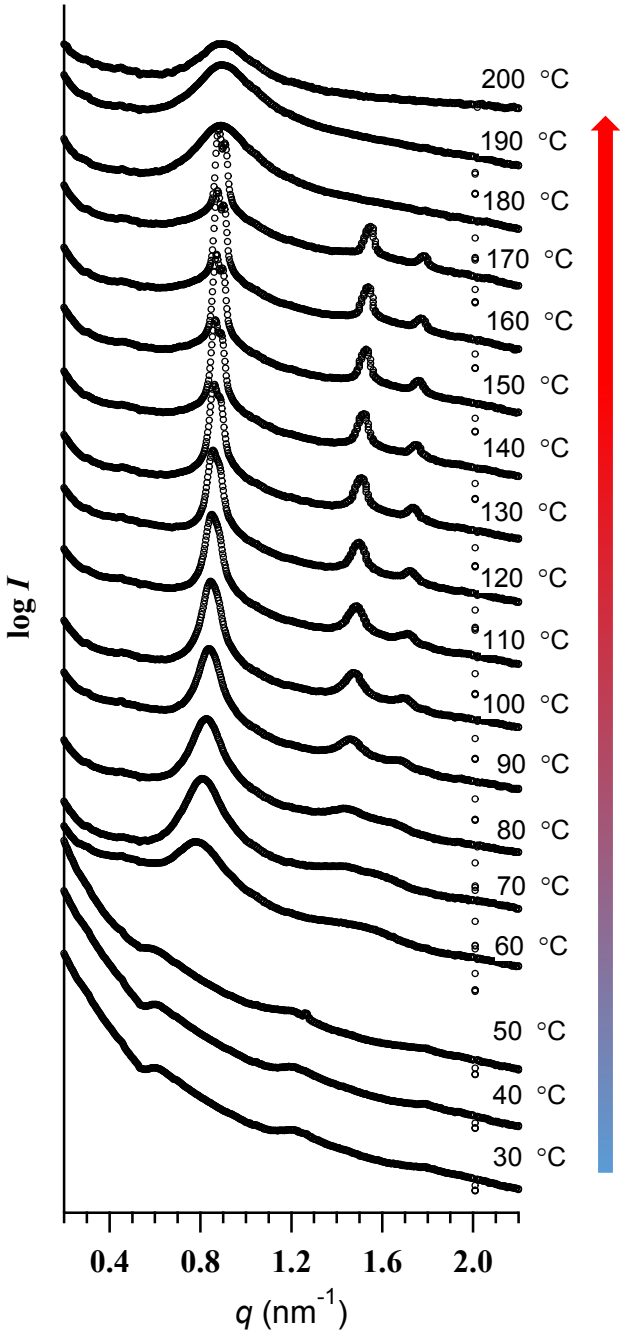

Figure S20. SAXS profiles of $(PCL_H\text{-}b\text{-}MT)_6$ during the continuous heating from 30 to 200 °C.

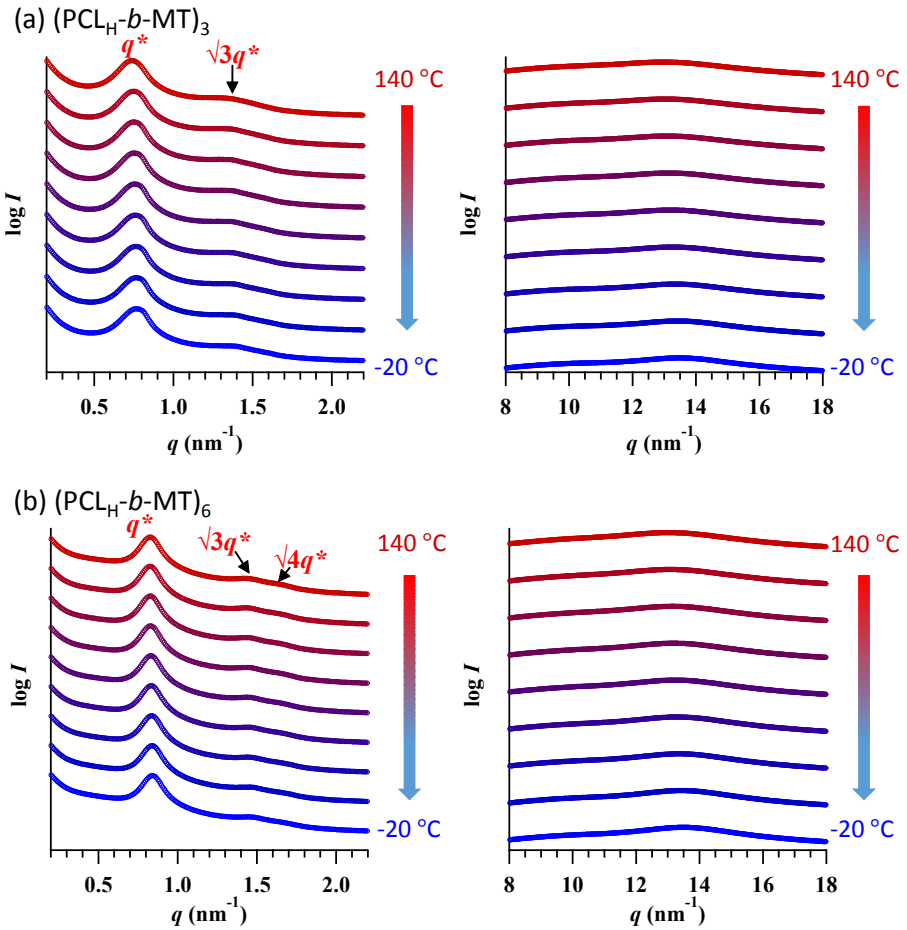

Figure S21. SAXS and WAXS profiles (left and right, respectively) of (a) (PCL$_H$-*b*-MT)$_3$ and (b) (PCL$_H$-*b*-MT)$_6$ acquired during the cooling process from 140 °C to -20 °C by 20 °C step.

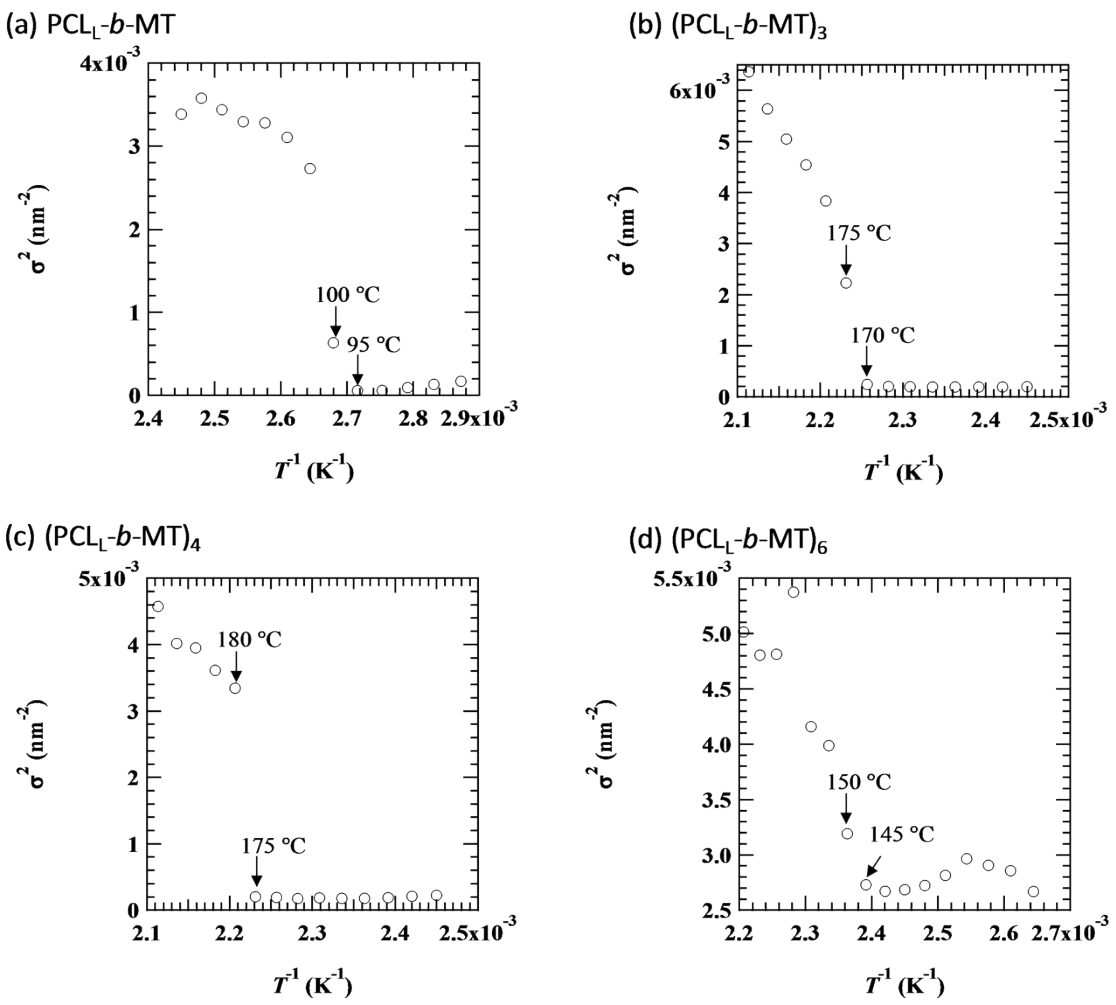

Figure S22. Dependence of the square of half width half maximum (σ^2) of the primary scattering peak on the reciprocal absolute temperature (T^{-1}) for (PCL$_L$-*b*-MT)$_x$. The order-disorder transition temperature (T_{ODT}) was determined as the temperature at which the σ^2 discontinuously increased.

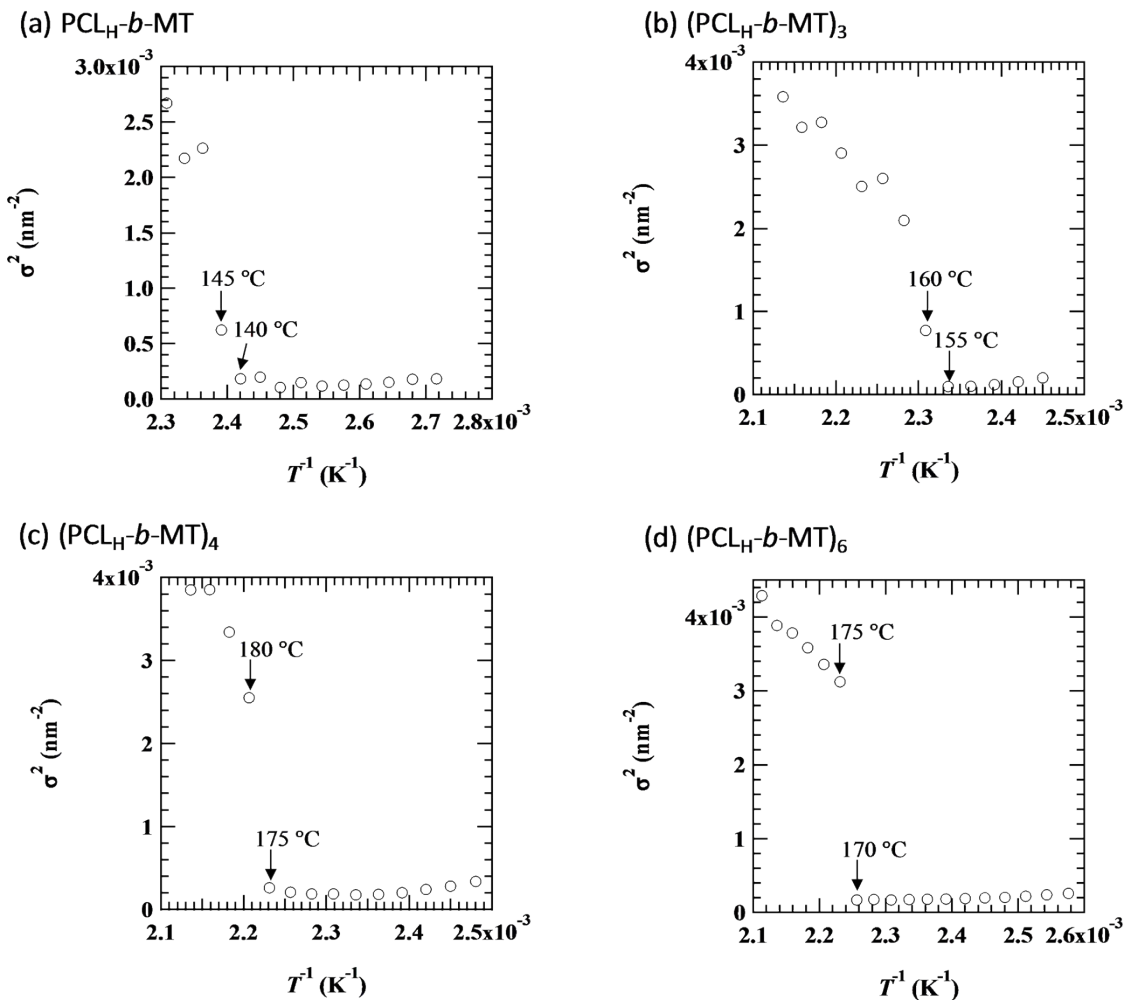

Figure S23. Dependence of the square of half width half maximum (σ^2) of the primary scattering peak on the reciprocal absolute temperature (T^{-1}) for (PCL$_H$-*b*-MT)$_x$. The order-disorder transition temperature (T_{ODT}) was determined as the temperature at which the σ^2 discontinuously increased.

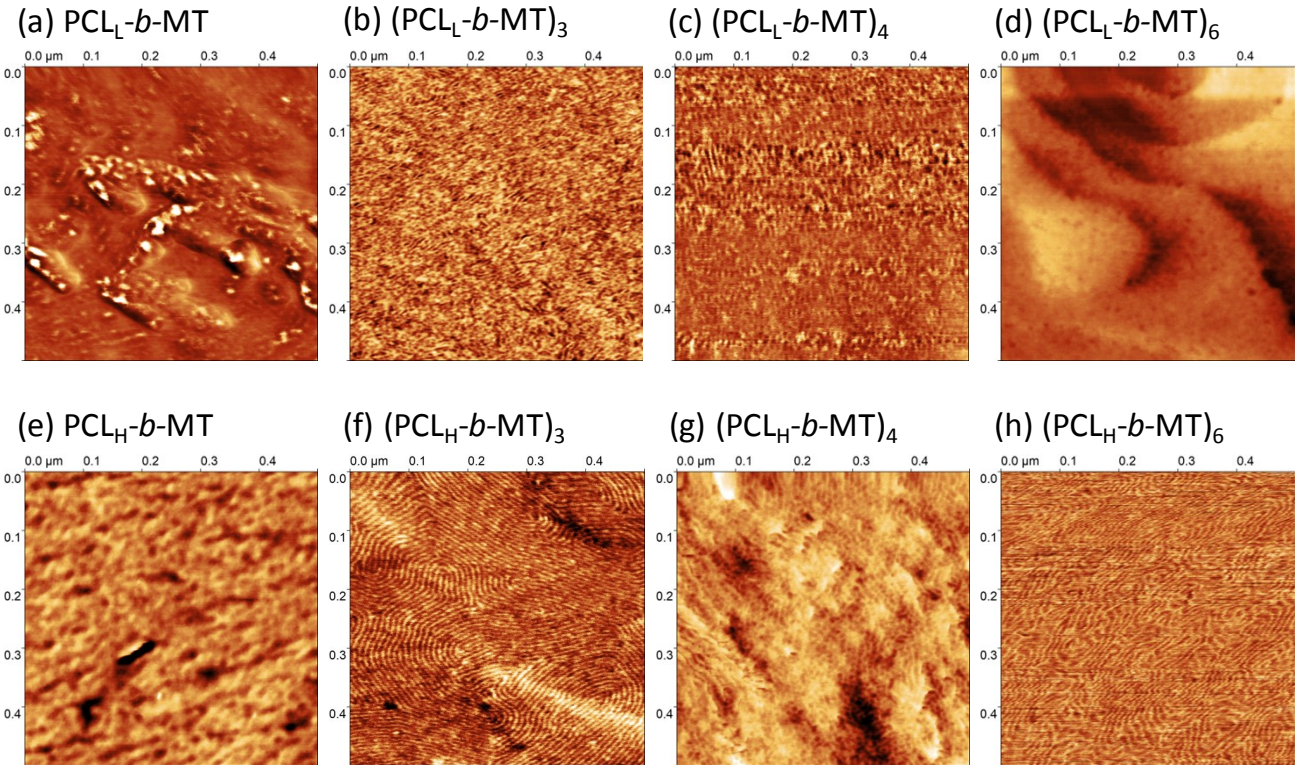

Figure S24. AFM phase images of (a) PCL$_L$-*b*-MT, (b) (PCL$_L$-*b*-MT)$_3$, (c) (PCL$_L$-b-MT)$_4$, (d) (PCL$_L$-*b*-MT)$_6$, (e) PCL$_H$-*b*-MT, (f) (PCL$_H$-*b*-MT)$_3$, (g) (PCL$_H$-*b*-MT)$_4$, and (h) (PCL$_H$-*b*-MT)$_6$ thin films annealed at 80 °C for 30 min.

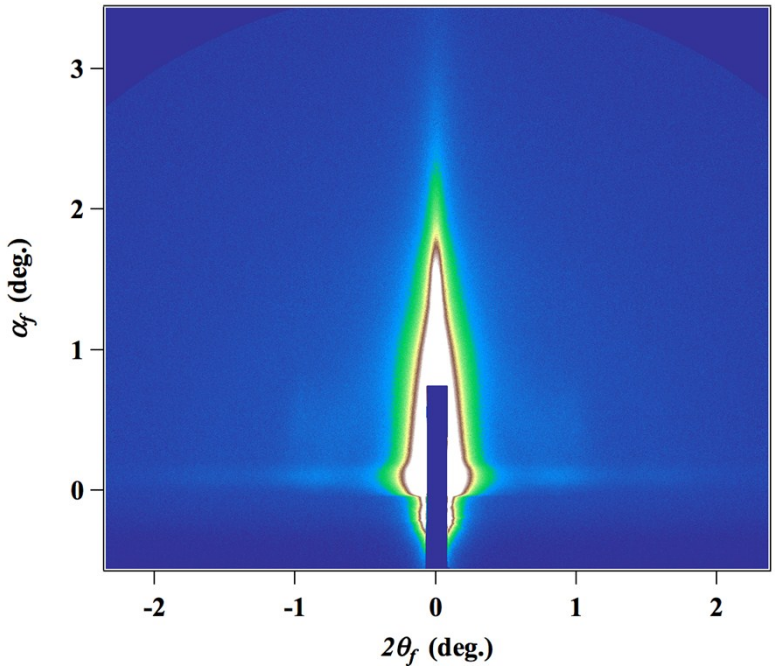

Figure S25. GISAXS profile of the PCL_H-*b*-MT thin film annealed at 130 °C for 30 min.

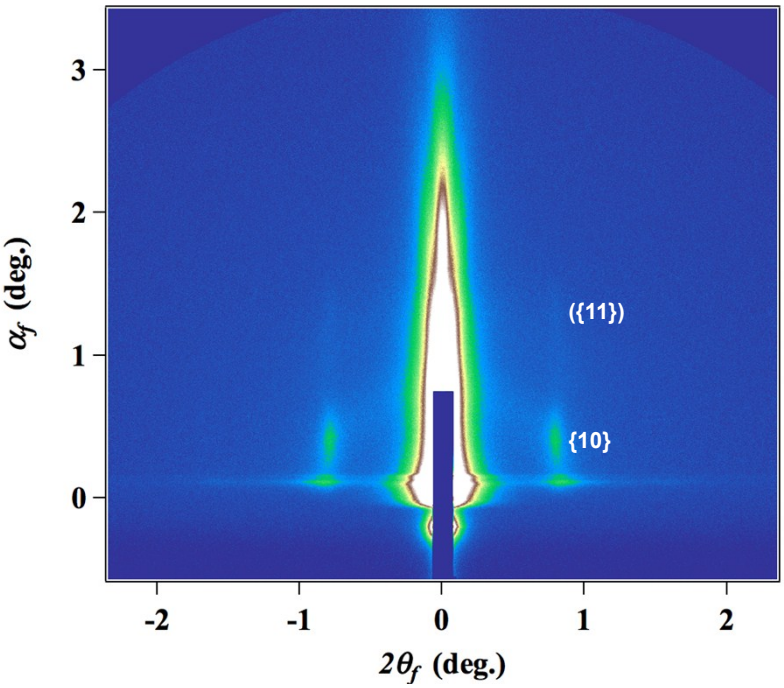

Figure S26. GISAXS profile of the $(PCL_H$-*b*-$MT)_3$ thin film annealed at 130 °C for 30 min.

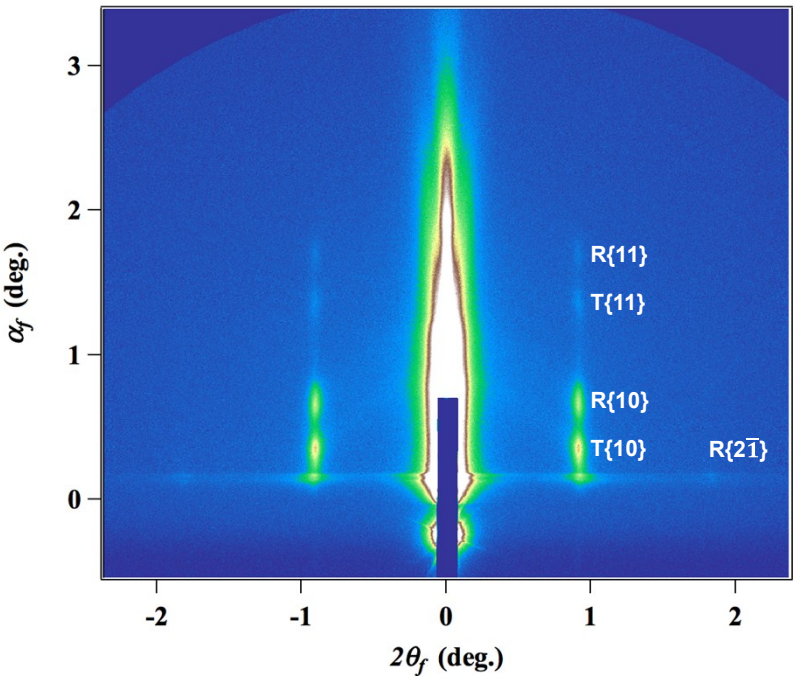

Figure S27. GISAXS profile of the $(PCL_H\text{-}b\text{-}MT)_4$ thin film annealed at 130 °C for 30 min.

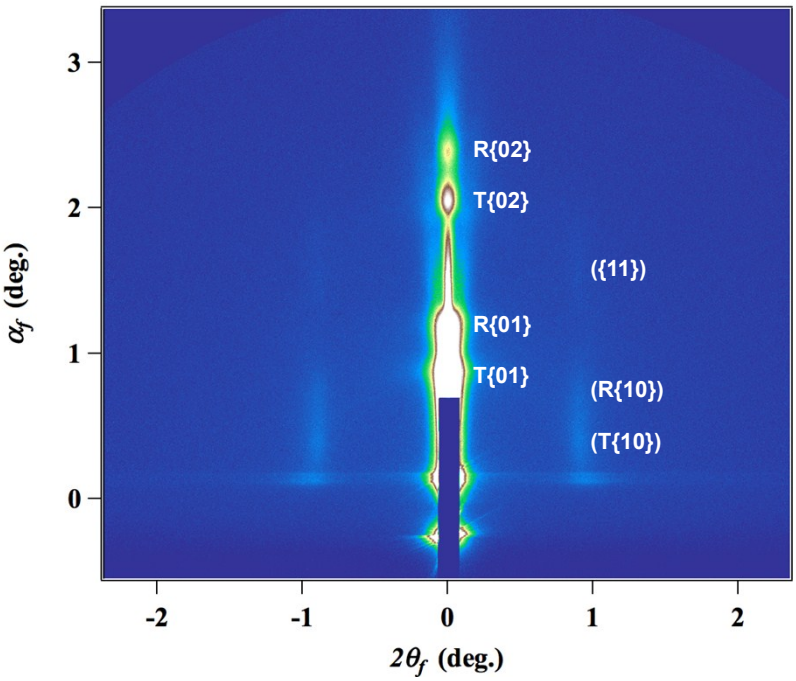

Figure S28. GISAXS profile of the $(PCL_H\text{-}b\text{-}MT)_6$ thin film annealed at 130 °C for 30 min.

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1. M. Malkoch, K. Scheicher, E. Drockenmuller, C. J. Hawker, T. P. Russell, P. Wu, V. V. Fokin, *Macromolecules*, 2005, **38**, 3663-3678.
2. C. Grandjean, A. Boutonnier, C. Guerreiro, J.-M. Fournier, L. A. Mulard, *J. Org. Chem.*, 2005, **70**, 7123−7132.
3. K. Yoshida, S. Tanaka, T. Yamamoto, K. Tajima, R. Borsali, T. Isono, T. Satoh, *Macromolecules*, 2018, **51**, 8870-8877.