Titin-Mimicking Polycyclic Polymers with Shape Regeneration and Healing Properties

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Electronic Supplementary Information (ESI)

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1. Materials and instrumentation

Materials

Thiazolidine-2,4-dione (TZD) (99%, SIGMA–ALDRICH), maleic anhydride (≥99%, FLUKA), 4-hydroxybenzoic acid (99%, SIGMA-ALDRICH), glycine ethyl ester hydrochloride (99%, SIGMA-ALDRICH), ammonium thiocyanate (97.5 %, SIGMA-ALDRICH), N-ethyl diisopropyl amine (DIPEA, 98 %, FLUKA), sebacic acid (99 %, SIGMA-ALDRICH), dimethyl aminopyridine (DMAP), N,N,N',N',N'-Pentamethyldiethylentriamin (PMDETA, 99%, SIGMA-ALDRICH), ethylene diamine tetraacetate (EDTA) (25 % in water, GRÜSSING), 2-(phenoxymethyl) oxirane (99 %, SIGMA-ALDRICH), thiourea (99.7%; SIGMA-ALDRICH), propylene glycol monomethyl ether acetate (99.5 %, SIGMA-ALDRICH) and 1-N-Methylpyrrolidin-2-one (NMP, anhydrous, 99%, SIGMA-ALDRICH) were used as received. (±)-Epichlorohydrin (99%, FLUKA), 1,1'carbonyl diimidazole (reagent grade, SIGMA-ALDRICH), 3-chloro-1-propanol (98%, SIGMA-ALDRICH) and propargylic alcohol (99%, FLUKA) were stored in the refridgerator at 4 °C. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) was provided by the institute of Organic- and Biomolecular Chemistry (Göttingen) and was stored at -20 °C. Tetrabutylammonium chloride (97%, SIGMA-ALDRICH) was purified by recrystallization from ethanol and stored under dry argon atmosphere at 4 °C. Selected solvents for synthesis and polymerization including dichloromethane (DCM, 99.8 %, ACROS), dimethyl sulfoxide (DMSO, 99.8 %, ACROS) and 1-N-Methylpyrrolidin-2-one (NMP, 99.5 %, ACROS) were stored over molecular sieves and under dry argon atmosphere. Tetrahydrofuran (THF) for synthesis was dried over CaH₂ and distilled prior to use. THF used as the eluent in the SEC (\geq 99.5%, CARL ROTH, stabilized with 2,6-di-tert-butyl-4-methylphenol) was used as received. Unless otherwise specified, all other chemicals were used as available without further purification. The monomer

compound (<u>1</u>) methyl thiirane (96%, SIGMA-ALDRICH) was stored in the refridgerator at 4 °C and was used as received.

Instrumentation

Molar weight distributions were determined by SEC using a JASCO AS-2055-plus auto-sampler, a WATERS 515 HPLC pump, three PSS (Polymer Standards Service) SDV columns with nominal 5 μ m particle size, and pore sizes of 10⁵, 10³, and 10² Å, a WATERS 2410 refractive index detector, a VISCOTEK VE 3210 UV-detector, and THF at 35 °C as the eluent at a flow rate of 1 mL min⁻¹ or an AGILENT 1260 Infinity-System including an autosampler, an isocratic HPLCpump, three PSS (POLYMER STANDARDS SERVICE) SDV columns with nominal 5 µm particle size, and pore sizes of 10^6 , 10^5 , and 10^3 Å and a detector system including a refractive index and a UV-detector. The SEC set-ups were calibrated against polystyrene standards of narrow dispersity from PSS. Mark-Houwink parameters for *ring*-poly(PMT) in THF at 35 °C have been determined previously¹ and were utilized for molar weight estimation of synthesized ring polymers according to the principles of universal calibration. Multi-Gaussian fits of several SECcurves were calculated using the program ORIGIN (version 8.5). NMR spectra were recorded on a VARIAN Mercury 200, VARIAN Mercury 300 or VARIAN Unity 300 spectrometer using CDCl₃ and DMSO- d^6 as solvents. A delay of 15 s between each NMR measurement was applied to allow for complete spin relaxation. Differential scanning calorimetry (DSC) measurements were performed on a METTLER Toledo 820 including a cryostat (LAUDA Kryomat RUK 90) in a temperature range from -40 to 200 ° C and a METTLER Toledo 60 DS-calorimeter cooled by LN2 with a cryostat in a temperature range from -100 to 150 ° C. Measurements on both devices were conducted with a heating rate of 10° C min⁻¹ under a constant nitrogen flow of 4.5 mL min⁻¹ and 20 mL min⁻¹, respectively, to prevent water condensation. Thermogravimetric measurements were carried out on a NETZSCH TG 209F3 thermobalance with a heating rate of 10 °C min⁻¹ up to 1 000 °C under a constant flow of nitrogen (20 ml min⁻¹). The sample was filled in a freshly heat-purged aluminum crucible and measured subsequently after weight constancy was achieved. Tensile-testing was conducted using a Zwicki 2.5 kN testing machine by ZWICK & ROELL (details see chapter 5).

2. Synthesis of the precursor compounds

Synthesis of 2-(phenoxymethyl)thiirane PMT (2)

Compund $\underline{2}$ was synthesized according to a previously given procedure.¹



Synthesis of self-complementary hydrogen bonding monomer ETBAA (3)

Methyl 4-hydroxybenzoate (6)

To a solution of 4-hydroxybenzoic acid (27.6 g, 200 mmol, 1.00 eq) in methanol (120 mL) conc. sulfuric acid (12 mL, 200 mmol, 1.00 eq) was added and the mixture was refluxed for 24 h. After cooling to rt and addition of ice water a white precipitate was filtered off, rinsed with another portion of ice water and dried *in vacuo*. The obtained white solid (25.5 g, 168 mmol, 84 %) was used in the next step without further purification.

¹H NMR (300 MHz, DMSO-*d*⁶) δ = 10.25 (br, 1 H, COO*H*), 7.85–7.76 (m, 2 H, Ar-*H*), 6.88–6.80 (m, 2 H, Ar-*H*), 3.78 (s, 3H, O–C*H*₃).

Methyl (4-Oxiranylmethoxy)benzoate (7)

The synthesis was conducted after an altered literature procedure.² Potassium carbonate (37.2 g, 269 mmol, 2.00 eq) was added to a solution of **6** (20.5 g, 135 mmol, 1.00 eq) and epichlorohydrin (24.9 g, 269 mmol, 2.00 eq) in acetone (100 mL) which was refluxed for 48 h afterwards. After cooling down to rt the acetone was removed under reduced pressure and the residue was treated with diethyl ether (150 mL) and water (100 mL). After separation of the organic phase, the aqueous phase was extracted two more times with diethyl ether (150 mL, respectively). The united organic phases were dried over sodium sulfate and after removal of the solvent, were dried *in vacuo*. After purification by column chromatography (silica, dichloromethane, $R_f = 0.3$) the product was obtained as a white solid (20.5 g, 98 mmol, 73 %). ¹H NMR (300 MHz, CDCl₃) $\delta = 8.10-7.91$ (m, 2 H, Ar-*H*), 7.02–6.86 (m, 2 H, Ar-*H*), 4.30 (dd, J = 11.0, 3.0 Hz, 1 H, CH_aH_b –O–Ar), 4.00 (dd, J = 11.1, 5.8 Hz, 1 H, CH_aH_b –O–Ar), 3.89 (s, 3 H, O– CH_3), 3.38 (ddd, J = 6.9, 5.7, 2.8 Hz, 1 H, epoxy-CH), 2.93 (dd, J = 4.9, 4.2 Hz, 1 H, epoxy- CH_aH_b).

¹³C NMR (75 MHz, CDCl₃) δ = 166.66 (*C*=O), 162.04 (Ar-*C*), 131.58 (Ar-*C*), 123.04 (Ar-*C*), 114.10 (Ar-*C*), 68.69 (*C*H₂-O-Ar), 51.83 (epoxy-*C*H), 49.83 (O-*C*H₃), 44.52 (epoxy-*C*H₂).

(4-Oxiranylmethoxy)benzoic acid (8)

The synthesis was conducted after a literature procedure.³ To a solution of 7 (20.0 g, 96.1 mmol, 1.00 eq) in acetone (480 mL) a 0.4 M sodium hydroxide solution (480 mL, 192 mmol, 2.00 eq) was added and stirred at rt for approx. 4.5 h under TLC-monitoring of the reaction. After consumption of the reactant the mixture was extracted with ethyl acetate (2×250 mL) and the residual aqueous phase was acidified with 1 M hydrochloric acid until a pH of 4 was reached. The resulting suspension was extracted with ethyl acetate again (3×250 mL) and the united organic phases were dried over sodium sulfate. After removal of the solvent the residue was dried *in vacuo* overnight and yielded the pure product (14.1 g, 72.6 mmol, 80 %) as a white powder.

¹H NMR (300 MHz, DMSO-*d*⁶) δ = 12.60 (br, 1 H, COO*H*), 7.99–7.79 (m, 2 H, Ar-*H*), 7.16– 6.95 (m, 2H, Ar-*H*), 4.42 (dd, *J* = 11.5, 2.6 Hz, 1 H, CH_aH_b–O–Ar), 3.91 (dd, *J* = 11.4, 6.6 Hz, 1 H, CH_aH_b–O–Ar), 3.46–3.29 (m, 1 H, epoxy-C*H*), 2.86 (t, *J* = 4.7 Hz, 1 H, epoxy-CH_aH_b), 2.73 (dd, *J* = 5.0, 2.6 Hz, 1 H, epoxy-CH_aH_b).

¹³C NMR (75 MHz, DMSO-*d*⁶) δ = 166.92 (COOH), 161.78 (Ar-*C*), 131.34 (Ar-*C*), 123.30 (Ar-*C*), 114.35 (Ar-*C*), 69.17 (*C*H₂–O–Ar), 49.52 (epoxy-*C*H), 43.75 (epoxy-*C*H₂).

ESI-MS (Q⁺): m/z = 195.1 ([M+H]⁺), 217.1 ([M+Na]⁺), 411.1 ([2M+Na]⁺), 581.3 ([2M+Na]⁺).

(Ethyl-2-(4-(oxiran-2-ylmethoxy)benzamido)acetate (9)

The synthesis was conducted after an altered literature procedure.⁴ **8** (1.17 g, 8.80 mmol, 1.00 eq) was suspended in anhydrous DCM (8 mL) and stirred at 0 °C under argon atmosphere. After addition of 1,1-carbonyl diimidazole (1.50 g, 9.24 mmol, 1.05 eq) the mixture was stirred for approx. 5 min at this temperature under vigorous gas formation and was then stirred another 30 min until gas formation had ceased and the suspension dissolved completely. Afterwards glycine ethyl ester hydrochloride (1.28 g, 9.24 mmol, 1.05 eq) was added to the solution which was stirred for another 1 h until it was quenched with water. After separation of the organic phase it was rinsed with water once more and dried over sodium sulfate. After removal of the solvent the viscous raw product was put to column chromatography (silica, DCM/methanol 40:1 vol-%, $R_f = 0.5$) and the product was obtained as a white crystalline solid (1.41 g, 5.04 mmol, 57 %).

¹H NMR (300 MHz, CDCl₃) δ = 7.85–7.71 (m, 2 H, Ar-*H*), 7.02–6.86 (m, 2 H, Ar-*H*), 6.61 (br, 1 H, N–*H*), 4.37–4.14 (m, 5 H, COO–*CH*₂, NH–*CH*₂, O–*CH*_aH_b), 3.98 (dd, *J* = 11.1, 5.8 Hz, 1 H, O–CH_aH_b), 3.36 (ddt, *J* = 5.6, 4.0, 2.8 Hz, 1 H, epoxy-*CH*), 2.92 (dd, *J* = 4.9, 4.1 Hz, 1 H, epoxy-*CH*_aH_b), 2.77 (dd, *J* = 4.9, 2.6 Hz, 1 H, epoxy-*CH*_aH_b), 1.31 (t, *J* = 7.1 Hz, 3 H, *CH*₃). ESI-MS (Q⁺): *m*/*z* = 280.1 ([M+H]⁺), 302.1 ([M+Na]⁺), 581.3 ([2M+Na]⁺).

(Ethyl-2-(4-(thiiran-2-ylmethoxy)benzamido)acetate (3)

To a suspension of **9** (1.41 g, 5.04 mmol, 1.00 eq) in water/ethanol (20 mL, 1:1 vol-%) ammonium thiocyanate (1.10 g, 14.5 mmol, 2.87 eq) was added and stirred for approx. 5 h under TLC-monitoring. After complete consumption of the reactant the mixture was extracted with ethyl acetate (3×50 mL) and the united organic phases were dried over sodium sulfate. After

removal of the solvent the raw product was instantly purified by column chromatography (silica, DCM/methanol 40:1 vol-%, $R_f = 0.62$) in order to prevent premature polymerization. The pure product was obtained as a white crystalline solid (843 mg, 2.85 mmol, 57 %) and stored immediately in the freezer.

¹H NMR (300 MHz, CDCl₃) δ = 7.86–7.71 (m, 2 H, Ar-*H*), 7.00–6.88 (m, 2 H, Ar-*H*), 6.58 (br, 1 H, N–*H*), 4.31–4.16 (m, 5 H, COO–*CH*₂, NH–*CH*₂, O–*CH*_aH_b), 3.97 (dd, *J* = 10.1, 6.9 Hz, 1 H, O–*C*H_aH_b), 3.27 (quint, *J* = 6.0 Hz, 1 H, S–*CH*), 2.62 (d, *J* = 6.1 Hz, 1 H, S–*CH*_aH_b), 2,34 (dd, *J* = 5.2, 1.5 Hz, 1 H, S–*C*H_aH_b), 1.31 (t, *J* = 7.2 Hz, 3 H, *CH*₃). ESI-MS (Q⁺): *m*/*z* = 296.1 ([M+H]⁺), 318.1 ([M+Na]⁺), 613.2 ([2M+Na]⁺).

Synthesis of the TZD-based alkyne-group bearing initiator PTZDA (5)



2-(2,4-Dioxothiazolidin-5-yl)acetic acid (10)

The synthesis was conducted after a literature procedure.⁵ Maleic anhydride (4.94 g, 50.3 mmol, 1.00 eq) and thiourea (3.84 g, 50.4 mmol, 1.00 eq) were dissolved in conc. hydrochloric acid and refluxed for 20 h. After cooling to 0 °C in an ice bath the precipitate was filtered off, rinsed with ice water and dried overnight *in vacuo*. The pure product was yielded as small white crystals (6.84 g, 39.1 mmol, 78 %).

¹H NMR (300 MHz, DMSO-*d*⁶) δ = 12.75 (br, 1 H, COO*H*), 12.01 (br, 1 H, N–*H*), 4.66 (dd, J = 5.1, 7.2 Hz, 1 H, C*H*), 3.03 (m, 2 H, C*H*₂).

Propin-1-yl-2-(thiazolidindionyl)acetate (4)

A solution of **10** (3.50 g, 20.0 mmol, 1.00 eq) in propargylic alcohol (11.6 mL, 200 mmol, 10 eq) was stirred in a round bottom flask with a connected reflux condenser at 60 °C for 20 h. The mixture was allowed to cool down to rt and diluted with water afterwards. After extraction with DCM (3×50 mL) the united organic phases were dried over sodium sulfate. After removal of the solvent the brown raw product was purified by column chromatography (silica, DCM/methanol 20:1, $R_f = 0.4$) and recrystallized from water/ethanol (1:1 vol-%) in order to yield the product as slightly brownish crystals (2.89 g, 13.6 mmol, 68 %).

¹H NMR (300 MHz, CDCl₃) δ = 8.44 (br, 1 H, N–*H*), 4.75 (d, *J* = 2.5 Hz, 2 H, HC=CH₂–O), 4.56 (dd, *J* = 8.8, 3.8 Hz, 1 H, S–C*H*), 3.28 (dd, *J* = 17.8, 3.8 Hz, 1 H, CH_aH_b–COOR), 3.07 (dd, *J* = 17.8, 8.8 Hz, 1 H, CH_aH_b–COOR), 2.52 (t, *J* = 2.5 Hz, 1 H, *H*C=CH₂).

¹³C NMR (75MHz, CDCl₃) δ = 173.55 (NH–CO), 170.27 (O–CO), 169.03 (S–CO), 77.73 (C=CH), 75.93 (C=CH), 53.23 (O–CH₂), 46.40 (S–CH), 36.85 (CH₂).

ESI-MS (Q⁺): *m*/*z* =236.0 ([M+Na]⁺), 449.0 ([2 M+Na]⁺), 471.0 ([2M+2 Na-H]⁺).

Synthesis of the bifunctional linker (5)



3-Azidopropanol (11)

The synthesis was conducted after an altered literature procedure.⁶ To a solution of 3chloropropanol (10 g, 106 mmol, 1.00 eq) in DMSO (160 mL) sodium azide (13.8 g, 212 mmol, 2.00 eq) was added and the mixture was stirred for 20 h at rt. Afterwards the reaction mixture was extracted with diethyl ether (3 × 50 mL) and the united organic phases were rinsed with brine and dried over sodium sulfate. After cautious removal of the solvent at 30 °C the raw product was left drying overnight at rt under a continuous airstream. The product was obtained as a colorless liquid (8.5 g, 84.4 mmol, 80 %) and used in the next step without further purification. ¹H NMR (300 MHz, CDCl₃) δ = 3.72 (t, *J* = 6.1 Hz, 2 H), 3.42 (t, *J* = 6.6 Hz, 2 H), 2.15 (br, 1 H), 1.88–1.73 (m, 2 H).

EI-MS (70 eV): m/z = 72.0 (58, [M-N2]⁺⁺), 101.0 (100, [M]⁺⁺), 102.0 (17, [M+H]⁺⁺).

Bis(3-azidopropyl)decandioate (5)

To a suspension of sebacic acid (1.01 g, 5.00 mmol, 1.00 eq) in anhydrous DCM (20 mL) under argon atmosphere **11** (1.11 g, 11.0 mmol, 2.20 eq) and DMAP (61.1 mg, 0.50 mmol, 10 mol-%) was added and cooled to 0 °C afterwards. EDC (2.11 g, 11.0 mmol, 2.20 eq) was added in one portion to the suspension under vigorous stirring and left at this temperature for further 20 min. After warming to rt the mixture was stirred for 20 h until completion of the reaction. The mixture was diluted with DCM and rinsed with water (2 × 50 mL) and brine. After re-extraction of the aqueous phase with DCM (3 × 50 mL) the united organic phases were dried over sodium sulfate. After removal of the solvent the raw product was dried *in vacuo* overnight and obtained as a colorless liquid (1.32 g, 3.57 mmol, 71 %) with a purity > 95 %.

¹H NMR (300 MHz, CDCl3 δ = 4.14 (t, *J* = 6.5 Hz, 4 H, O–C*H*₂), 3.37 (t, *J* = 6.5 Hz, 4 H, N₃– C*H*₂), 2.28 (t, *J* = 7.5 Hz, 4 H, C*H*₂–COOR), 1.89 (quint, *J* = 6,5 Hz, 4 H, CH₂–C*H*₂–CH₂), 1.69– 1.51 (m, 4 H, C*H*₂–CH₂–COOR) 1.28 (s, 8 H, (C*H*₂)₈). ¹³C NMR (75 MHz, CDCl3) δ = 173.55 (COOR), 61.03 (COO–CH₂), 48.17 (N₃–CH₂), 34.11 (CH₂–COOR), 28.96 (CH₂–CH₂–CH₂), 28.12 ((CH₂)₈), 24.80 (CH₂–CH₂–COOR).

ESI-MS (Q⁺): *m*/*z* =369.2 ([M+H]⁺), 386.2 ([M+NH₄]⁺), 391.2 ([M+Na]⁺) 759.4 ([2M+Na]⁺).

3. Synthesis of the cyclic multiblock-copolymers

General procedure for the synthesis of cyclic (AB)_n- or (ABC)_n-multiblock-copolymers

In a typical stepwise polymerization for the synthesis of $(ABC)_n$ -multiblockcopolymer, initiator PTZDA (213.2 mg, 1.00 mmol, 1.00 eq), tetrabutylammonium chloride (27.8 mg, 0.10 mmol, 10 mol-%) and ETBAA (1.48 g, 5.00 mmol, 5.00 eq) were weighed in a 10 mL volumetric flask which was filled with *N*-methylpyrrolidinone (NMP) in order to reach a monomer concentration of 0.5 mol L⁻¹. After determination of the total weight the solution was degassed via three *freeze-pump-thaw*-cycles and put directly into a glove-box (Lab Master 130) for further treatment. The solution was transferred into a round bottom flask equipped with a stirring bar which was then sealed with a rubber septum and used for immediate polymerization in a heated oil-bath (see table 2 or S1 for conditions). In certain intervals small portions of the solution (approx. 100 μ L) were extracted via syringe and put to SEC-measurement in order to determine the monomer conversion (see Figure 2a). After complete conversion the next monomer MT (1.85 g, 25.0 mmol, 20.0 eq) and additional NMP (12.5 mL) was added. After bubbling of the solution with argon for 10 min the polymerization was continued (see table 2 or S1 for conditions). After

reaching the maximum conversion (as complete conversion could not be achieved in all cases) the next monomer PMT (1.66 g, 10.0 mmol, 10 eq) along with NMP was added and it was continued as described above. The polymerization was stopped by cooling down to 0 °C, diluted with DCM and precipitated from diethyl ether. The residue was separated by centrifugation (Sigma 2-16PK centrifuge with temperature control) at 0 °C and re-dissolved followed by a repetition of the procedure. The polymer obtained that way was dried *in vacuo* and characterized further.

In case of the $(AB)_n$ -multiblock-copolymers MT was used as the first monomer and PMT as the second one. In some cases additional PMT had to be added after the first portion since the conversion of a higher amount of PMT added at once was insufficient (see table S1).

Determination of distinct ring-species from SEC of the $(AB)_n$ -multiblock-copolymers (see Figure S1) was performed by calculating the theoretical number average molar mass of the ring species from ¹H-NMR data (see chapter 6) by using Equation (2) (see main text) and assigning a maximum or shoulder from the SE-chromatograms which fits the value best. Molar masses were determined via universal calibration of the samples the with calculated Mark-Houwink coefficients from *ring*-polyPMT⁷ (K_{PMT} and a_{PMT}) and linear polyMT¹ at 30 °C (K_{MT} and a_{MT}) due to its good accordance with the molar masses of *ring*-polyMT based on the molar composition of the multiblock-copolymers by the following equations:

$$K_{copo} = x_{PMT} \times K_{PMT} + (1 - x_{PMT}) \times K_{MT} \text{ and}$$
$$a_{copo} = x_{PMT} \times a_{PMT} + (1 - x_{PMT}) \times a_{MT}$$

In order to find the shoulders in the distribution curves the first derivative of all curves was calculated and analyzed on local minima and maxima which correspond to inflection points in the distribution indicating the position of a shoulder. Determination of ring species of the $(ABC)_n$ -multiblock-copolymers was performed by the more accurate multi-gaussian fitting (see main text).

Table S1 Conditions for the synthesis of cyclic (AB)n-multiblock copolymers from MT and PMT.												
Sample	Polymerization time per block (MT+PMT) / h	Т / °С	Initial molar amounts TZD/MT/PMT	Conv. / %	Found molar amounts TZD/MT/PMT ^a	$x_{\rm PMT}{}^a$	${\bar M}_{ m n}$ / g mol ⁻¹	Đ				
pre-1	48+2	60	1:50:50	12.2	1:50:6	0.13	$6~692^{b}$	1.3				
pre-2	48+6	60	1:50:50	29.2	1:50:15	0.27	9 186	1.3				
pre-3	48 + 8	60	1:50:50	43.2	1:50:22	0.35	11 880	1.3				
pre-4	48+18	60	1:50:50	68.5	1:50:34	0.46	14 250	1.3				
pre-5	48+48	60	1:50:50	87.4	1:50:44	0.52	18 500	1.2				
δ	24+47 ^c	70	1:25:25+25 ^c	>90	1:22:50	0.66	9 836	1.4				
3	$+65^{d}$	70	$+50^{d}$	92	1:22:97	0.81	14 820	1.5				
ζ	$+22^{d}$	70	$+50^{d}$	96	1:22:165	0.88	78 390	6.7				

^{*a*}Determined by ¹H NMR spectroscopy.

^bDetermined by means of universal calibration using Mark-Houwink coefficients of pure *ring*-polyPMT. ^cPMT was added two times in order to achieve a greater second block.

^dSample RBP22-50 was polymerized with more PMT in order to obtain samples RBP22-97 and RBP22-165.



Figure S1 SEC curves of MT-homopolymer (black) and copolymers ring-poly(MT-b-PMT) δ (green, molar composition: MT/PMT=22:50), ϵ (blue, MT/PMT=22:97) and ζ (red, MT/PMT=22:165). The numbers and labels indicate the respective ringpolymer species with its denoted degree of ring merging.

4. Synthesis of poly(ring-polymers)

General procedure for the synthesis of poly(ring-polymers) via Huisgen click reaction

A stock solution of copper(I) bromide (68.8 mg, 0.48 mmol) and PMDETA (91.5 mg, 52.8 mmol) in anhydrous and oxygen-free THF (5 mL) was prepared and stored under argon in order to form the [Cu(PMDETA)]Br complex (0.1 mol L⁻¹). A solution of cyclic prepolymer (CP-01 to CP-03, 1.00 eq of alkyne groups) and the linker **5** (1.00 eq of azide groups) in anhydrous THF (10 mL) was degassed by bubbling with argon for 10 min. Afterwards a specified volume of the stock solution (approx. 0.50 eq Cu¹ per functional group) was added (for details of the specific amounts see Table S2) and the solution was degassed another 5 min and stirred for a specified time and temperature afterwards (see Table 3 in main text). The reaction was quenched by exposure to air, diluted with DCM (20 mL) and rinsed with 0.25 M EDTA-solution (2×75 mL). The organic phase was treated with diethylether in order to precipitate the polymeric product which was separated by centrifugation. After dissolution in DCM the last step was repeated once. The obtained target compound was dried in vacuo and characterized afterwards by SEC, DSC, ¹H-NMR and thermogravimetry (see chapter S6).

cyclic prepolymer	m _{cyclic prepolymer} / mg	n̄ _{alkyne} ∕ mmol	m _{linker} / mg	n _{azide} / mmol	V _{stock} / mL	n _{Cu} I / mmol
CP-01	1779	0.4797	88.3	0.480	2.50	0.250
CP-02	1924	0.1766	32.5	0.177	0.85	0.085
CP-03	1967	0.4204	77.3	0.420	2.10	0.210

Table S2 Net weights of cyclic prepolymers, volumes of stock solution applied and molar amounts of Cu^I, alkyne and azide groups.

5. Formation of test specimens and tensile testing

Preparation of test specimens

The test specimens were prepared in special PTFE moulds (see Figure S2, upper part) which were made according to ISO 527-2:1996 specification (type 1BA moulds) with a smaller mould depth of 1 mm instead of 2 mm in order to save sample material. The specimens (see Figure S2, lower part) were obtained via drop casting from PGMEA. For this purpose PGMEA and polymer were mixed in a ratio of 2:1 (wt-%) until the polymer was dissolved completely. The viscous solution was divided onto three moulds which were filled completely. After pre-drying in the vacuum oven at 80 °C and 250 to 400 mbar for 1 h it was dried in fine vacuum for another hour after formation of bubbles ceased completely. Afterwards another portion of solution was added and the previous steps were repeated until the mould was filled completely with polymeric material. Afterwards the samples were dried overnight *in vacuo* and were carefully unhinged from the moulds, turned around and dried overnight again. If necessary, this step was repeated until the specimens exhibited no more stickiness from either side.

Tensile testing procedure

After preparation of the test specimens, their cross sections in the bridge area were determined prior to the testing procedure (see Figure S2, lower part). Afterwards a single specimen was fixed in a centered and tensionless position between two pressurized clamps having a distance of 50 mm in the testing machine. Afterwards they were pulled with a rate of 20 mm min⁻¹ until fracture of the specimen. For cyclic testing procedures the specimens were loaded until a defined tensile length was reached and then, unless otherwise stated, unloaded at the same rate until the

original deflection was restored and left at this position for one minute until beginning of the next cycle (see main text for details and obtained data).



Figure S2 Pictures of the PTFE mould (upper part) and a test specimen along with its dimensions (lower part).

6. NMR-, DSC- and thermogravimetric measurements

a) ¹H-NMR-spectra of cyclic homopolymers, (AB)_n- and (ABC)_n-multiblockcopolymers and poly(ring-polymer)

ring-poly(MT)







20

ring-poly(ETBAA-b-MT-b-PMT) (sample CP-01)



21

Poly(ring-polymer) (sample PC-01)



b) DSC measurements



Figure S3 DSC diagrams of *ring*-poly(MT-b-PMT) pre-1 to pre-5 with different PMT-block lengths (see table S1) and MT-homopolymer (RPMT).



Figure S4 DSC diagram of polycyclic polymers PC-02 and PC-03.

c) Thermogravimetric measurements of polymers CP-03 and PC-03.



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