

Supporting Information

Green Chain–Shattering Polymers Based on a Self-Immolative Azobenzene Motif

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A. Experimental Procedures:

A.1. Chemicals: 10-undecen-1-ol (99 %, Alfa Aesar), 1,1'-carbonyldiimidazole for synthesis (CDI, Merck), anhydrous THF (99.5 %, extra dry over molecular sieves, Acros Organics), 4-aminobenzyl alcohol for synthesis (Acros Organics), potassium peroxymonosulfate (Oxone®, Sigma-Aldrich), 4-nitrobenzyl alcohol (99 %, Alfa Aesar), D(+)-glucose (anhydrous, Carl Roth), sodium hydroxide (NaOH, VWR Chemicals), ethanol (absolute, EtOH_{absolute}, Sigma-Aldrich), acetic acid glacial (AcOH, Merck), *N,N*-dimethylacetamide (99 % extra pure, DMAc, Acros Organics), potassium hydroxide (≥85 % technical grade, KOH, Sigma-Aldrich), phosphate-buffered saline powder (pH 7.4, Sigma-Aldrich), enzyme azoreductase under the brand name of DT-diaphorase human (D1315-1MG, Sigma-Aldrich), β-nicotinamide adenine dinucleotide phosphate reduced tetra(cyclohexylammonium) salt (NADPH, Sigma-Aldrich), sodium dithionite (85 % technical grade, Na₂S₂O₄, Acros Organics), [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxy-phenylmethylene)ruthenium (97 %, second generation Hoveyda-Grubbs catalyst, HGII, Aldrich) were used without further purification. The (*E*) icos-10-ene-1,20-diol was prepared according to the procedure reported by Meier and co-workers.¹ Solvents for chromatography were technical grade. Polyethylene glycol (PEG) methyl ether acrylate ($M_n = 480$ Da, containing 100 ppm BHT as inhibitor, Aldrich) was purified by passing through a short basic Al₂O₃ column, prior to use to remove the stabilizer. The purified comonomer was stored in the freezer, at -20 °C. Phosphate-buffered saline solution pH 7.4 (PBS) was prepared by dissolving one pouch of phosphate-buffered saline powder in one liter of distilled water.

A.2. Synthesis of undec-10-enyl imidazole-1-carboxylate.² CDI (4.28 g, 26.4 mmol) was dissolved in 15 mL anhydrous THF (1.5 M) under continuous inert gas stream. 10-undecen-1-ol (2.96 g, 13.4 mmol) was dissolved in the smallest amount of anhydrous THF and added in a drop-wise manner with continuous stirring to the reaction mixture under an inert gas flow. After 4 h at 23 °C, the mixture was diluted with Et₂O (~80 mL) and washed with H₂O

(3 × 75 mL). The organic layer was dried over MgSO₄ and rotary evaporated to afford 1-imidazolecarboxylate of 10-undecen-1-ol (3.02 g, 11.4 mmol, 85.3 % yield) as a colourless oil. ¹H NMR (500 MHz, CDCl₃, δ in ppm) 8.13 (s, 1H), 7.42 (t, *J* = 1.3 Hz, 1H), 7.07 (s, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.15 – 4.69 (m, 2H), 4.40 (t, *J* = 6.7 Hz, 2H), 2.09 – 1.99 (m, 2H), 1.82 – 1.72 (m, 2H), 1.50 – 1.22 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, δ in ppm) 148.75, 139.13, 137.07, 117.08, 114.15, 68.51, 33.75, 29.36, 29.32, 29.09, 29.03, 28.86, 28.44, 25.68. MS (EI) *m/z* calculated for C₁₅H₂₄N₂O₂ [M+H]⁺: 265.2, found 265.1.

A.3. Synthesis of 4-nitrobenzyl alcohol.³ According to a modified procedure from the literature, 4-aminobenzyl alcohol (1.0 g, 8.12 mmol) was dissolved in 100 mL of CHCl₃:MeOH (2:1) at 0 °C. A cooled solution of Oxone® (4.99 g, 812 mmol) dissolved in 100 mL of distilled water was added. The mixture was stirred under an inert gas stream at ambient temperature until TLC monitoring indicated no further conversion of the starting material. After separation of the layers, the aqueous layer was extracted with dichloromethane twice. The combined organic layers were washed with 1N HCl, saturated sodium bicarbonate solution, followed with water and brine. The washed organic layers were dried over MgSO₄ and evaporated to dryness. The crude solid residue was used without further purification (quantitative yield). The ¹H and ¹³C NMR spectra were in accordance with the already reported ones. ¹H NMR (500 MHz, DMSO-*d*₆, δ in ppm) 8.20 (d, *J* = 8.6 Hz, 2H), 8.13 – 7.86 (m, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 5.54 (t, *J* = 5.7 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 2H), 4.64 (d, *J* = 5.6 Hz, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ in ppm) 150.80, 146.31, 127.02, 123.30, 61.99.

A.4. Synthesis of 4,4'-bis(hydroxymethyl)-azobenzene. The reaction was performed by adopting a modified procedure from the literature in the following way: 4-Nitrobenzyl alcohol (6.0 g, 0.04 mol) was dissolved in 60 mL EtOH_{absolute} and added to a sodium hydroxide solution (25 g, 0.625 mol, in 150 mL distilled H₂O) at 50 °C in a 3-necked round bottom flask

equipped with stirring bar and reflux condenser. The mixture was stirred for 30 min under a continuous inert gas flow. Subsequently, a 50 mL of glucose solution (75 g, 0.42 mol) was added drop-wise (within 90 min) at 50 °C with continuous stirring under an inert gas flow. The reaction mixture was subsequently aerated for 3 h at 50 °C and then cooled to ambient temperature, and aerated additionally over night with vigorous stirring. The final mixture was acidified with a dilute acetic acid (50 %) until pH>5. The generated solid was filtered off, washed with water and dissolved in boiling water to obtain an orange-yellow colored solution. This solution was let to stand for a day for crystal formation and then filtered. The crude product was purified by recrystallization from ethanol to give 5.62 g (58 %). ¹H NMR (500 MHz, DMSO-*d*₆, δ in ppm) 7.86 (d, *J* = 8.3 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 4H), 5.38 (s,-OH), 4.60 (s, 4H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ in ppm) 151.10, 146.44, 127.43, 122.62, 62.68. MS (EI) *m/z* calculated for C₁₄H₁₄N₂O₂ [M+H]⁺: 243.1, found 242.9.

A.5. Synthesis of monomer M1, (*E*)-(diazene-1,2-diylbis(4,1-phenylene))bis(methylene) di(undec-10-en-1-yl) bis(carbonate). A 250 mL round-bottomed flask, with a stir bar, was charged with 4,4'-bis(hydroxymethyl)-azobenzene (0.95 g, 3.92 mmol) and 70 mL dry DMAc. Subsequently, undec-10-enyl imidazole-1-carboxylate (2.18 g, 8.26 mmol) dissolved in 5 mL dry DMAc was added drop-wise under inert atmosphere at room temperature. KOH (219.5 mg, 3.92 mmol) was then added, and the resulting mixture was allowed to stir for additional 17 h at room temperature under inert atmosphere. The formed clear solution was diluted by addition of CH₂Cl₂ (200 mL) and extracted with H₂O (3 × 200 mL). The collected organic phase was dried over MgSO₄ and filtered. The filtrate was concentrated on a rotary evaporator and the crude product was purified *via* recrystallization using 40 mL of EtOH:EtOAc (1:1) to give 2.25 g (90.4 %) isolated product. ¹H NMR (500 MHz, CDCl₃, δ in ppm) 7.92 (d, *J* = 8.4 Hz, 3.5H_{trans}), 7.53 (d, *J* = 8.4 Hz, 3.5H_{trans}), 7.27 (d, *J* = 8.4 Hz, 0.5H_{cis}), 6.84 (d, *J* = 8.4 Hz, 0.5H_{cis}), 5.80 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 2H), 5.23 (s, 3.5H_{trans}), 5.08 (s, 0.5H_{cis}), 5.06 – 4.85 (m, 4H), 4.25 – 4.06 (m, 4H_{87.5% trans+12.5% cis}), 2.11 –

1.98 (m, 4H), 1.74 – 1.61 (m, 4H), 1.46 – 1.19 (m, 24H). ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm) 155.15, 155.07, 153.08, 152.41, 139.14, 139.10, 138.32, 134.61, 128.79, 128.67, 123.07, 120.67, 114.16, 114.10, 68.75, 68.58, 68.47, 33.75, 29.37, 29.32, 29.14, 29.03, 28.85, 28.60, 25.63. MS (ESI) m/z calculated for $\text{C}_{38}\text{H}_{54}\text{N}_2\text{O}_6$ $[\text{M}+\text{Na}]^+$: 657.3982, found 657.4167.

A.6. Example of acyclic diene metathesis (ADMET) homopolymerization of **M1**.

Homopolymers of (*E*)-(diazene-1,2-diylbis(4,1-phenylene))bis(methylene) di(undec-10-en-1-yl) bis(carbonate) (**M1** in Scheme 1) were synthesized by ADMET in *o*-chlorobenzene as solvent. The procedure illustrated here corresponds to the entry 1 in Table S1. 255 mg (0.40 mmol) of monomer **M1** was dissolved in 670.0 μL *o*-chlorobenzene (0.6 M) in a 10 mL flask which was attached to a vacuum (under 200 mbar vacuum and 65 $^\circ\text{C}$). After 10 min, 5.0 mg **HGII** ($\sim 8.02 \cdot 10^{-3}$ mmol, 2.0 mol% / molecule, *i.e.* 1.0 mol% / double bonds) were added, and the reaction was started at 65 $^\circ\text{C}$ under 200 mbar pressure with 500 rpm rotating rate. For the first 30 min the pressure was kept at 200 mbar and the following 90 min at 100 mbar. The reaction was stopped after 120 min reaction time via dilution with 5 mL CH_2Cl_2 :*o*-chlorobenzene (1:1), and quenched via the addition of ethyl vinyl ether. Subsequently, the mixture was concentrated and precipitated in ice-cold methanol. The precipitate was collected by filtration, washed with ice-cold MeOH, and dried at ambient temperature. 190 mg of polymer was isolated (75% yield). $M_{n,\text{SEC}} = 24.9$ kDa, $D = 2.00$. ^1H NMR (500 MHz, CDCl_3 , δ in ppm) 7.91 (d, $J = 8.3$ Hz), 7.53 (d, $J = 8.4$ Hz), 6.69 (d, $J = 15.9$ Hz), 6.25 – 6.12 (m), 5.42 – 5.32 (m), 5.21 (s), 4.21 – 4.09 (m), 2.05 – 1.88 (m), 1.73 – 1.61 (m), 1.58 (m), 1.32 (m), 0.95 (m), 0.88 (m). ^{13}C NMR (125 MHz, CDCl_3 , δ in ppm) 155.18, 152.44, 138.34, 130.31, 129.85, 128.80, 123.10, 68.78, 68.51, 32.56, 29.81 – 25.66 (aliphatic region).

A.7. Example of acyclic diene metathesis (ADMET) triblock copolymerization of **M1**.

Amphiphilic blockpolymers of (*E*)-(diazene-1,2-diylbis(4,1-phenylene))bis(methylene) di(undec-10-en-1-yl) bis(carbonate) (**M1** in Scheme 1) by ADMET polymerization. A typical procedure is described below. This particular example corresponds to Entry 2 in Table S1. 119.0 mg (0.188 mmol) of monomer **M1** was dissolved in 310.0 μ L *o*-chlorobenzene (0.6 M) in 10 mL flask to which 1.8 mg ($3.76 \cdot 10^{-3}$ mmol, 2.0 mol% / molecule) PEG methyl ether acrylate ($M_n=480$ Da) was added. Finally, the flask was attached to a vacuum (under 200 mbar pressure and 65 °C). After 10 min, ~2.4 mg HGII ($3.76 \cdot 10^{-3}$ mmol, 2.0 mol% / molecule, *i.e.* 1.0 mol% / double bonds) was added, and the reaction was started at 65 °C at 200 mbar pressure with stirring at 500 rpm. During the first 30 min the pressure was kept at 200 mbar and for the next 90 min at 100 mbar. The reaction was stopped after 120 min reaction time. The reaction was quenched via dilution with 5 mL CHCl_3 and the addition of ethyl vinyl ether. Subsequently, the mixture was concentrated and precipitated in ice-cold methanol. The precipitate was collected by filtration, washed with ice-cold MeOH and dried at ambient temperature, yielding 80 mg of polymer (85% yield). $M_{n,SEC} = 9.7$ kDa, $D = 2.22$.

$^1\text{H NMR}$ (500 MHz, CDCl_3 , δ in ppm) 7.91 (d, $J = 7.9$ Hz), 7.53 (d, $J = 7.8$ Hz), 7.03 – 6.93 (m), 6.84 (d, $J = 7.9$ Hz) 5.82 (dd, $J = 18.8, 11.5$ Hz), 5.59 – 5.22 (m), 5.22 – 5.17 (m, 5H), 5.08 (s), 5.04 – 4.87 (m), 4.35 – 4.23 (m), 4.16 (t, $J = 6.5$ Hz), 3.65 (d, $J = 5.1$ Hz), 3.55 (d, $J = 4.6$ Hz), 3.38 (s, 1H), 2.18 (d, $J = 7.0$ Hz), 2.09 – 1.86 (m), 1.78 – 1.54 (m), 1.49 – 1.08 (m). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , δ in ppm) 155.13, 152.38, 138.29, 130.28, 129.82, 128.71, 123.06, 120.74, 120.65, 114.09, 70.49, 69.20, 68.74, 68.47, 32.53, 28.59-29.55 (aliphatic region), 27.14, 25.65.

A.8. Example of reductive degradation of **M1** with sodium dithionite. Azobenzene **M1**

(0.4–2.1 mmol) was added to a mixture of H_2O (165 mL/mmol of **M1**), MeOH (165 mL/mmol of **M1**), and CH_2Cl_2 (25 mL/mmol of **M1**). The resulting mixture was stirred and

heated to reflux, after which an excess of sodium dithionite (see the Main Text) was added. After stirring at reflux for a specified time (as mentioned in the Main Text), the product mixture was poured into ice and extracted with Et₂O (3 × 100 mL). The combined extracts were dried (MgSO₄) and filtered. Subsequently, the solvent was removed under reduced pressure to give a residue, which was analysed further without any purification.

A.9. Example of enzymatic degradation of amphiphilic acyclic diene metathesis (ADMET) triblock copolymer. The amphiphilic triblock copolymer **P4** containing 10 % PEG methyl ether acrylate as chain stopper, (1.1 mg) was first suspended in 1 mL PBS buffer (pH 7.4) under an inert atmosphere. Then, 1 mL of DTD solution in PBS (1 mg/mL, pH 7.4) was added. The enzymatic reaction was initiated by the addition of 1 mL NADPH solution in PBS (20 mg/mL) and the mixture was incubated under an inert atmosphere at 37 °C with continuous stirring for 12, 24 and 36 h, respectively. A yellowish suspension formed and was heated to 60 °C for 5 h. The reaction mixture was subsequently dialyzed against deionized water for 1 day to remove NADPH and the buffer salts. The purified aqueous solution was filtered with a PTFE (0.45 µm pore size) filter and extracted with chloroform. The organic phase was dried over MgSO₄, filtered, and the solvent was removed under reduced pressure to give a residue, which was analysed further without any purification.

B. Measurements and analysis:

B.1. Nuclear Magnetic Resonance (NMR) spectroscopy. ¹H NMR spectra were recorded in CDCl₃ on a Bruker Avance 500 MHz spectrometer equipped with Ultrashield magnets. ¹H NMR chemical shifts are reported in ppm relative to the solvent's residual ¹H signal. All NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet), coupling constant(s) in Hertz (Hz) and integration. Multiplets (m) were reported over the range (ppm) where they appeared at the indicated field strength. In order to calculate the degree of polymerization (DP) and the number average molecular weight (*M_n*) of the ADMET polymers obtained with and without chain stopper, we took advantage of the

ratio of the proton resonances in the ^1H NMR associated with the end groups (\mathbf{E}_1 - \mathbf{E}_4) compared to the proton resonances of the methylene units $-\text{OC}(\text{O})\text{O}-\text{CH}_2-(\text{CH}_2)_{7-}$ of the polymer chain in the ^1H NMR spectra shown in Fig. 3 and 4 (in the Main Text).⁴ Three types of end group can be detected in the final ADMET homopolymer polymer as a result of the olefin isomerization of the terminal double bonds:

\mathbf{E}_1 : CH_3 - end-group signals at 1.60 ppm ($-\text{CH}_2=\text{CH}-\text{CH}_3$),

\mathbf{E}_2 : CH_3 - end-group at 0.88 ppm ($-\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$),

\mathbf{E}_3 : CH_3 - end-group at 0.96 ppm ($-\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{CH}_3$ with $n \geq 2$).

Thus, the degree of polymerization (n , DP) was calculated using the integrals of the proton resonances of each end group: \mathbf{A} , \mathbf{B} and \mathbf{C} are respectively the integral values of the resonances associated with end groups \mathbf{E}_1 , \mathbf{E}_2 and \mathbf{E}_3 . Additionally, \mathbf{P} is the integral value associated with the proton resonances of the methylene units $-\text{OC}(\text{O})\text{O}-\text{CH}_2-(\text{CH}_2)_{7-}$ of the polymer chain in the ^1H NMR spectra (compare Fig. 3 in the Main Text):

$$\mathbf{n} = DP = (3 \cdot \mathbf{P}) / [(\mathbf{A} + \mathbf{B} + \mathbf{C}) \cdot 2] \quad \text{Formula 1}$$

In the case of the amphiphilic triblock copolymers synthesized with PEG methyl ether acrylate as chain stopper (polymers $\mathbf{P2-P5}$ in Table S1 as well as Fig. 3 and 5 in the Main Text), we observed four types of end groups in the polymers resulting from the end-group of the chain stopper \mathbf{E}_4 (see Fig. 5), $\text{CH}_3\text{O}-$ (\mathbf{D} representing the integral value for the respective end-group), along the groups arising from the isomerization of the terminal vinyl groups.

\mathbf{E}_4 : CH_3 - end-group at 3.38 ppm ($\text{CH}_3\text{O}-(\text{CH}_2\text{OCH}_2)_n-$)

$$\mathbf{n} = DP = (3 \cdot \mathbf{P}) / [(\mathbf{A} + \mathbf{B} + \mathbf{C} + \mathbf{D}) \cdot 2] \quad \text{Formula 2}$$

All theoretical and experimental molecular weights for the amphiphilic polymers collated in Table S1 were calculated using the following equation (where $M_{M1} = 634.86$ Da, $M_{CS} = 482.57$ Da and $M_{ethylene} = 28.05$ Da are the molecular weights of **M1**, the chain stopper PEG methyl ether acrylate **CS** and ethylene, respectively):

$$M_{n, theor} = M_{n, NMR} = n \cdot M_{M1} + 2M_{CS} - (n + 1) \cdot M_{ethylene} \quad \text{Formula 3}$$

B.2. Size Exclusion Chromatography (SEC). Molecular weights and molecular weight distribution were determined using a SEC system equipped with Shimadzu LC20AD pump, Wyatt Optilab rEX refractive index detector and four PLgel 5 μ Mixed-C columns. The characterization was performed at 30 °C in THF with a flow rate of 1 mL \cdot min⁻¹. The molecular weight calibration was based on sixteen narrow molecular weight linear polystyrene standards from PSS, Mainz.

B.3. Electrospray Ionization-Mass Spectrometry (ESI-MS). Mass spectra were recorded on a Q 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 4.7 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 62.0 V, respectively. The samples were dissolved with a concentration of 0.05 mg \cdot mL⁻¹ in a mixture of THF:MeOH (3:2) (or CH₂Cl₂:MeOH=3:1) containing 100 μ mol of sodium trifluoroacetate (NaTFA) and infused with a flow of 5, 10 and 20 μ L \cdot min⁻¹.

B.4. UV-Vis Spectroscopy. UV-Vis spectra were measured on a Varian Cary 100 Bio spectrometer including a temperature control unit. All measurements were carried out in THF in quartz glass cuvettes (Starna) with a thickness of 2 mm at a temperature of 20 °C.

C. Additional Data and Figures:

Table S1. Properties (after precipitation) of ADMET homo- and amphiphilic triblockpolymers of **M1**.^a

	CS (mol%)	$M_{n,theor}$ ^b (kDa)	$M_{n,SEC}$ ^c (kDa)	$M_{n,NMR}$ ^d (kDa)	D^d (M_w/M_n) ^b
P1	-	30.3	24.9	25.5	2.0
P2	2	30.1	23.4	25.1	2.2
P3	5	25.2	16.6	9.2	2.1
P4	10	13.4	9.7	8.9	2.0
P5	20	7.0	6.1	2.9	1.7

^a All homo and copolymerizations were performed in the presence of 2 mol% Hoveyda-Grubbs second generation metathesis catalyst in 0.6 M *o*-chlorobenzene under continuous vacuum. ^b $M_{n,theor} = n \cdot M_{M1} + 2M_{CS} - (n + 1) \cdot M_{ethylene}$, where $M_{M1} = 634.86$ Da, $M_{CS} = 482.57$ Da and $M_{ethylene} = 28.05$ Da are the molecular weights of **M1**, the chain stopper PEG methyl ether acrylate **CS** and ethylene, respectively (n = the degree of polymerization). ^c Number average molecular weight (M_n) and dispersity (D) were determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards. ^d Determined by ¹H NMR (500 MHz) in CDCl₃ at ambient temperature, $M_{n,NMR} = n \cdot M_{M1} + 2M_{CS} - (n + 1) \cdot M_{ethylene}$.

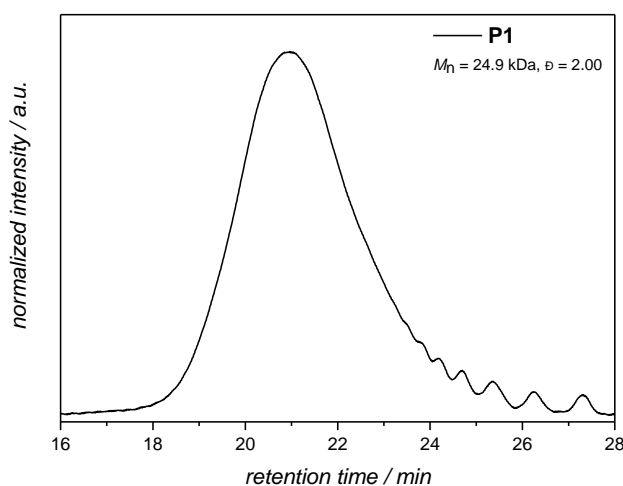


Fig. S1. SEC trace of **P1** synthesized via ADMET polymerization. The chromatogram was recorded in THF at 30 °C.

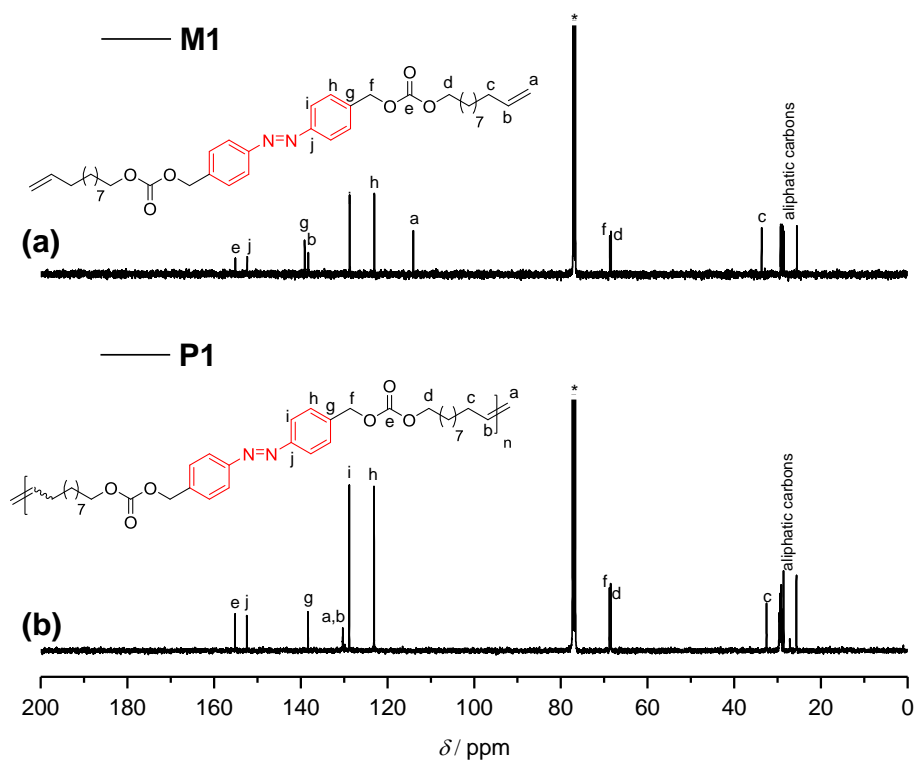


Fig. S2. ^{13}C NMR (125 MHz) spectra of (a) azo derivative α,ω -diene monomer **M1** and (b) representative polymer **P1** in CDCl_3 at ambient temperature.

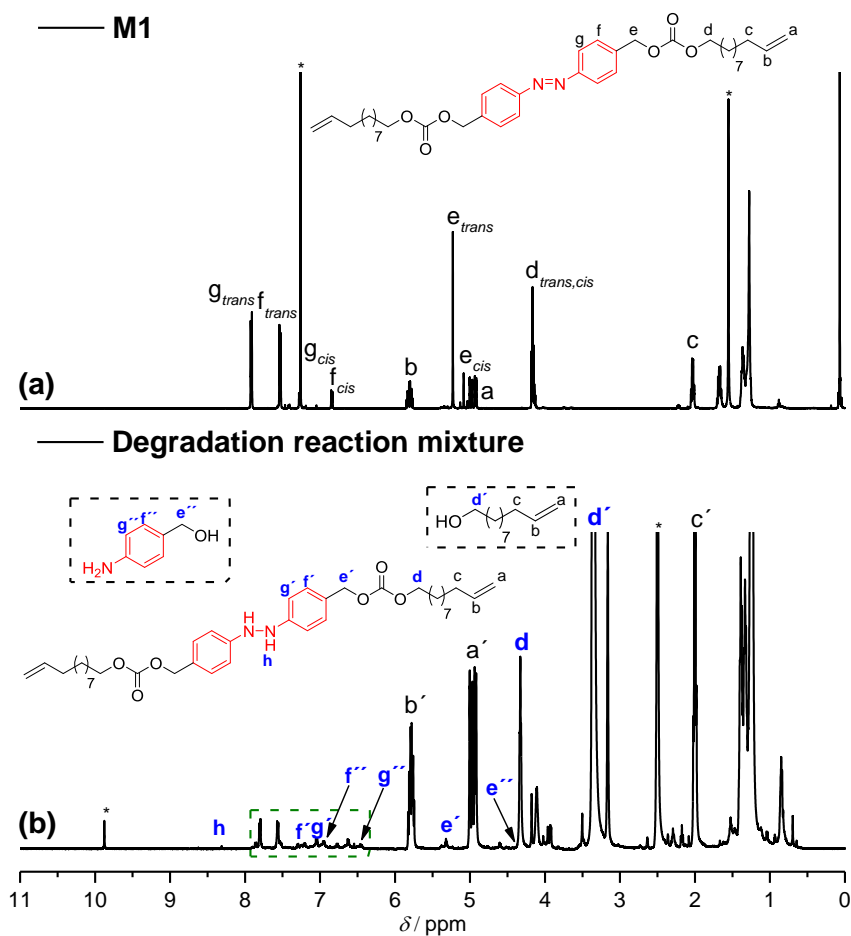


Fig. S3. ¹H NMR (400 MHz) spectra of azo derivative α,ω -diene monomer **M1** (a), along and the representative degradation mixture of **M1** (reaction time of 40 min, spectra (b)) as described in Section A.8 in the Supporting Information. The spectrum (a) was recorded in CDCl₃ and spectrum (b) in DMSO-*d*₆, respectively, at ambient temperature.

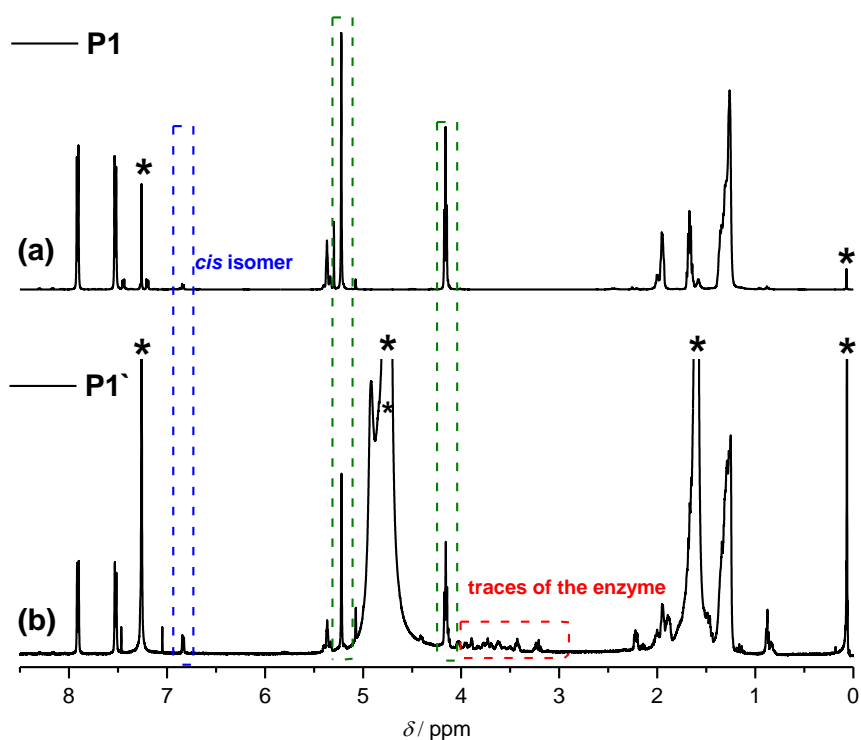


Fig. S4. ¹H NMR traces for ADMET polymer **P1** (a, presented in Table S1, entry 1) and resulting mixture after treatment of **P1** with enzyme for 12 h – **P1'** (b), respectively. Refer to Fig. 3 and 5 as well as S3, respectively in the Main Text and the Supporting Information for the assignment of key resonances associated with the polymer. The ¹H NMR traces were measured in CDCl₃ at ambient temperature.

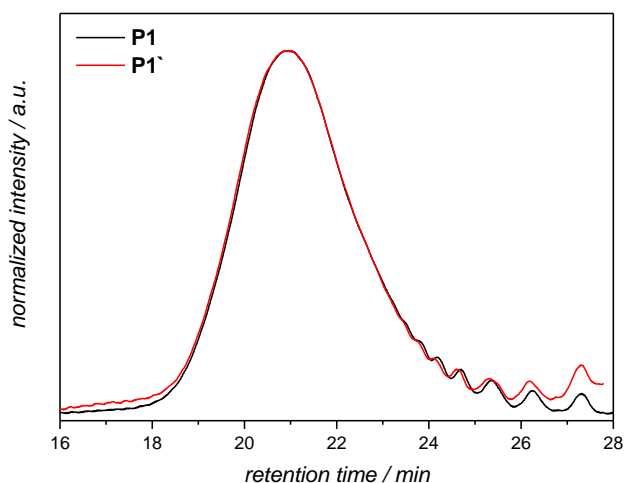


Fig. S5. SEC traces for ADMET polymer **P1** (black line, presented in Table S1, entry 1) and resulting mixture after treatment of **P1** with enzyme for 12 h – **P1'** (red line), respectively. The SEC traces were measured in THF at 30 °C.

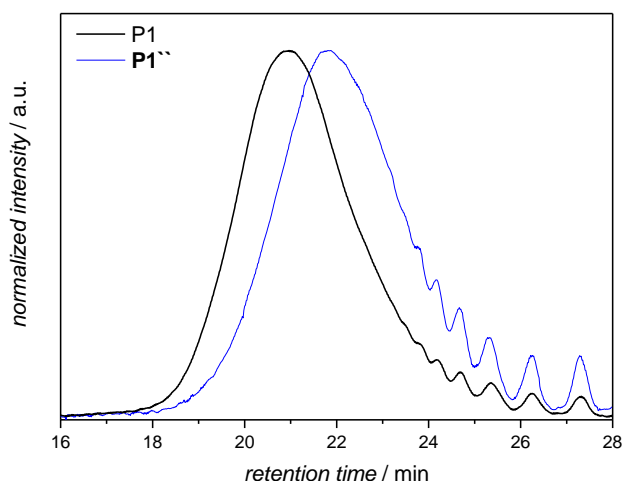


Fig. S6. SEC traces for ADMET polymer **P1** (black line, presented in Table S1, entry 1) and resulting mixture after treatment of **P1** with enzyme for 11 days – **P1''** (blue line), respectively. The SEC traces were measured in THF at 30 °C.

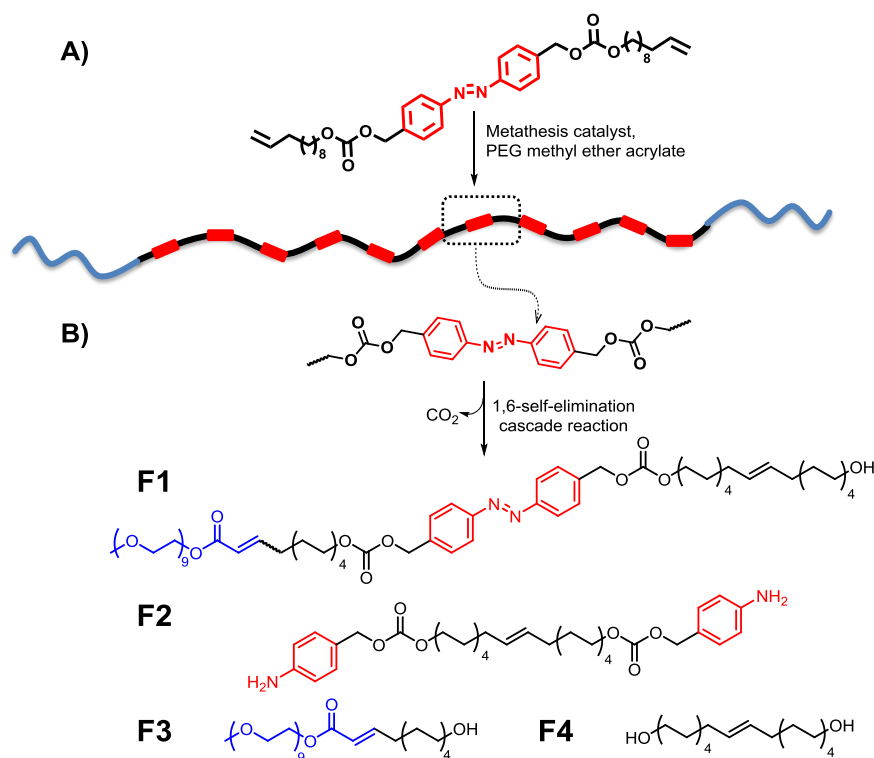


Fig. S7. **A)** Synthesis of the amphiphilic ABA triblock copolymers in a one-step, one-pot procedure using the selectivity of olefin cross-metathesis between acrylates and terminal olefins. This particular example corresponds to Entry 4 in Table S1. Copolymer synthesized in the presence of 10 mol% chain stopper, a monofunctional PEG methyl ether acrylate (average $M_n = 480$ Da). **B)** The plausible cleavage of azobenzene linkages in the amphiphilic triblock copolymer upon enzymatic action and subsequent 1,6-self elimination to smaller molecular weight species **F1-F4**.

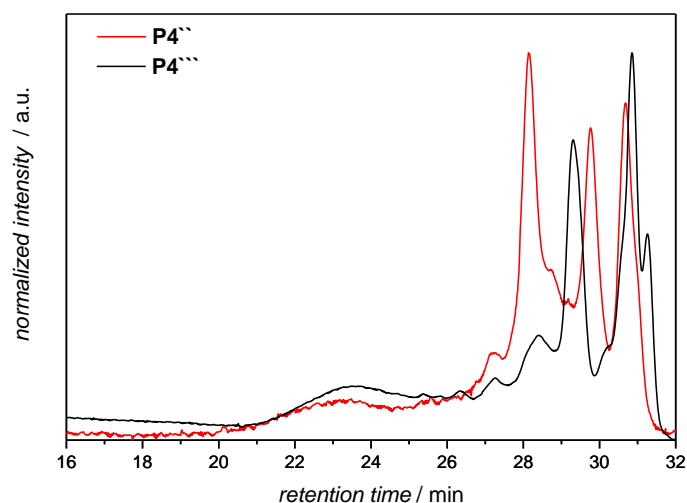


Fig. S8. SEC chromatograms for ADMET polymer **P4**, presented in Table S1, entry 4) and resulting mixture after treatment with enzyme for 24 and 36 h, respectively, isolated polymer mixtures **P4^{24h}** (red line) and **P4^{36h}** (black line). The SEC traces were measured in THF at 30 °C.

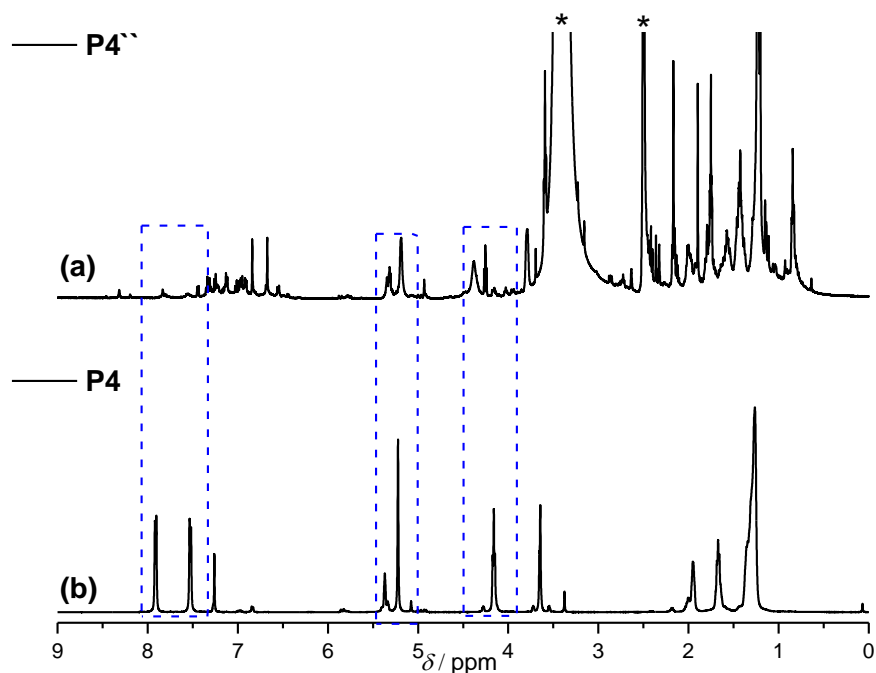


Fig. S9. ¹H NMR traces for enzymatic degradation reaction mixture **P4^{24h}** with polymer **P4** (Table S1). Refer to Fig. 3, 5 and S3, respectively in the Main Text and the Supporting Information for the assignment of key resonances associated with the polymer and the degradation mixture. Spectra recorded in DMSO and CDCl₃ at ambient temperature, respectively for (a) and (b).

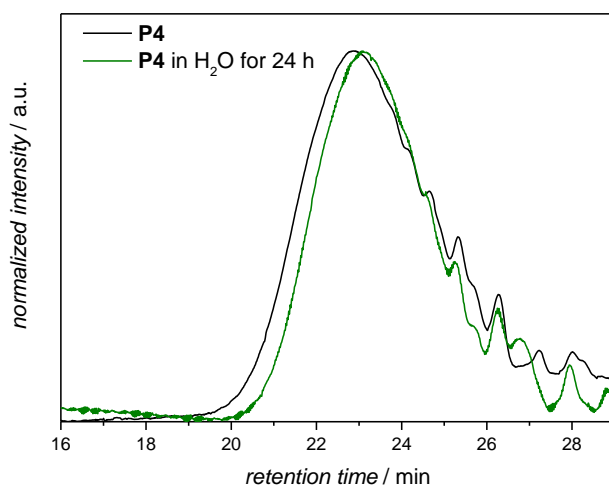


Fig. S10. SEC chromatograms for ADMET polymer **P4** (black line), presented in Table S1, entry 4 and resulting mixture after the control reaction for **P4** performed in water without any reducing agent (chemical or enzymatic) for a period of 24 h (green line), respectively. The SEC traces were measured in THF at 30 °C.

D. References

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