Supporting Information

Sunflower oil-based thermosets *via* the Passerini three-component reaction

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1 Fatty acid content of high oleic sunflower oil and double bonds per triglyceride

The fatty acid (FA) content of the used high oleic sunflower oil in this project was already determined and described in a former publication (note: in the former publication, this oil is labeled "HOSO04").^[1] Here, the outcome of the previous analysis is summarized, as it is important for this study (Table S1).

Fatty Acid		% FA <i>via</i> GC-MS	% FA supplemented by ¹ H NMR spectroscopy
Myristic	C14:0	0.02	0.02
Palmitic	C16:0	3.89	3.89
Stearic	C18:0	3.43	3.43
Arachidic	C20:0	0.02	0.02
Oleic and	C18:1 cis (ω-9)	88.93	88.69
linolenic	C18:3 cis (ω-3)		0.24
Elaidic	C18:1 trans (ω-9)	-	_
Linoleic	C18:2 cis (ω-6)	3.71	3.71
SFAs	C14:0, C16:0, C18:0, C20:0	7.36	7.36
UFAs	C18:1, C18:2, C18:3	92.64	92.64

Table S1: Fatty acid content determination of high oleic sunflower oil *via* GC-MS and supplemented by ¹H NMR spectroscopy.

The fatty acid content was used to calculate the number of double bond protons per triglyceride with Equation (S1).

$$\frac{\text{double bond protons}}{\text{triglyceride}} = \text{oleic acid} \times 2 + \text{linoleic acid} \times 4 + \text{linolenic acid} \times 6 = 5.81$$
(S1)

This number will be used to calculate the yield of the employed oxidative cleavage on high oleic sunflower oil (SI chapter 2.1). For one double bond cleavage, two carboxylic acids form. Hence, for a yield of 100%, the integral of α -CH₂ protons of carboxylic acids (2.18 ppm) in the ¹H NMR spectrum should duplicate. The conversion of double bonds into carboxylic acids, that is, the yield estimated by ¹H NMR spectroscopy, can be calculated with Equation (S2) by division of the integral of α -CH₂ protons of carboxylic acids by 2 and the calculated number of vinylic protons inside the oil (5.81), after normalizing the spectrum relative to the signal of the glyceryl moiety.

NMR-Yield (%) =
$$\frac{\text{integral}(\alpha - \text{CO}_2\text{H})}{2 \times 5.81} \times 100$$
 (S2)

2 Experimental procedures and spectral data

2.1 Oxidative cleavage of high oleic sunflower oil



The oxidative cleavage of high oleic sunflower oil was performed according to a literature reported procedure.^[1] The procedure is described in the main text of the publication.

Analytical data will be listed here for the three fractions that were obtained by flash column chromatography.

Fraction 1: Nonanoic acid



M = 158.24 g/mol

R_f (Fraction 1) = 0.69 (cyclohexane/ethyl acetate, 2:1 + 1% formic acid).

¹**H NMR** (400 MHz, CDCl₃, ppm): *δ* = 11.95 (s, 1H, H¹), 2.18 (t, *J* = 7.4 Hz, 2H, H²), 1.54–1.42 (m, 3H, H³), 1.24 (s, 10H, H⁴), 0.95–0.76 (m, 3H. H⁵).



Figure S1: ¹H NMR spectrum of the isolated nonanoic acid by flash column chromatography in DMSO-d₆.

Fraction 2: Sunflower oil-based carboxylic acid with low carboxylic acid content

Representative Structures:



R_f (Fraction 2) = 0.26 (cyclohexane/ ethyl acetate, 2:1 + 1% formic acid).

¹**H NMR** (400 MHz, DMSO-*d*₆, ppm): δ = 11.99 (s, 3H, H¹), 5.18 (tt, *J* = 7.0, 3.7 Hz, 1H, H²), 4.25 (dd, *J* = 12.0, 3.7 Hz, 2H, H³), 4.12 (dd, *J* = 12.0, 6.5 Hz, 2H, H³), 3.97 (d, *J* = 5.4 Hz, not further oxidized OH group), 2.30–2.24 (m, 6H, H⁴), 2.18 (td, *J* = 7.4, 3.7 Hz, 6H, H⁵), 1.57–1.42 (m, 16H, H⁶), 1.31–1.14 (m, 45H, H⁷), 0.85 (t, *J* = 6.8 Hz, 5H, H⁸).



Figure S2: ¹H NMR spectrum of fraction 2 isolated by flash column chromatography in DMSO-d₆.

Fraction 3: Sunflower oil-based tricarboxylic acid

Representative Structures:



R_f (Fraction 3) = 0.14 (cyclohexane/ ethyl acetate, 2:1 + 1% formic acid).

¹**H NMR** (400 MHz, DMSO-*d*₆, ppm): δ = 11.95 (s, 3H, H¹), 5.18 (tt, *J* = 6.9, 3.7 Hz, 1H, H²), 4.25 (dd, *J* = 12.0, 3.7 Hz, 2H, H³), 4.12 (dd, *J* = 12.0, 6.5 Hz, 2H, H³), 2.34–2.22 (m, 6H, H⁴), 2.17 (t, *J* = 7.4 Hz, 6H, H⁵), 1.49 (ddd, *J* = 14.6, 9.6, 5.5 Hz, 12H, H⁶), 1.25 (d, *J* = 3.8 Hz, 18H, H⁷), 0.89–0.78 (m, 0.17H, H⁸).

¹³**C NMR** (126 MHz, DMSO-*d*₆, ppm): δ = 174.5 (C_q, CO₂H, C¹), 174.4 (C_q, CO₂H, C¹), 172.5 (C_q, C_{Ester}, C²), 172.2 (C_q, C_{Ester}, C²), 68.8 (CH, C_{Glyceryl}, C³), 61.8 (CH₂, C_{Glyceryl}, C⁴), 33.6 (CH₂, C⁵), 33.5 (CH₂, C⁵), 33.3 (CH₂, C⁵), 28.4 (CH₂, C⁶), 28.3 (CH₂, C⁶), 28.2 (CH₂, C⁶), 24.4 (CH₂, C⁶), 24.4 (CH₂, C⁶), 24.3 (CH₂, C⁶).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3223 (vw), 2929 (m), 2857 (w), 1738 (vs), 1703 (vs), 1456 (w), 1413 (w), 1378 (w), 1232 (m), 1160 (vs), 1133 (s), 1094 (m), 1033 (w), 938 (w), 728 (w) cm⁻¹.

ESI-HRMS ([M–H][–], C₃₀H₄₉O₁₂, deprotonated triacid): calcd.: 601.3230, found: 601.3229.



Figure S3: ¹H NMR spectrum of sunflower oil-based triacid in DMSO-*d*₆.



Figure S4: ¹³C NMR spectrum of sunflower oil-based triacid in DMSO-d₆.

2.2 ³¹ P NMR spectroscopy of sunflower oil based triacid

2.2.1 Calculation of carboxylic acid and hydroxyl content

The amount of carboxylic acids and hydroxyl groups in the samples was calculated in analogy to the calculation reported by ARGYROPOULOS *et al.*^[2] The carboxylic acid and hydroxyl group content was then calculated using Equations (S3) and (S4). The first term in the numerator corresponds to the amount of IS in mmol and the second term corresponds to the molar ratio of carboxylic acids (or hydroxyl groups) to internal standard.

	mass of IS solution (in mg) \times wt% (IS solution) \rightarrow Integral CO ₂ H	
mmol CO ₂ H	$- 179.18 \frac{g}{mol} \text{ (Molar mass of IS)} \qquad \uparrow \text{ Integral IS}$	(S3)
mg sample	mass of sample (in mg)	
	mass of IS solution (in mg) × wt% (IS solution) _ Integral OH	
mmol OH _	$179.18 \frac{g}{mol}$ (Molar mass of IS) ^ Integral IS	(S4)
mg sample	mass of sample (in mg)	

The final evaluation of the synthesized sunflower oil-based triacid is summarized in Table S2.

Table S2: Carboxylic acid and hydroxyl group content of sunflower oil-based triacid determined *via* ³¹P NMR spectroscopy.

Sample	μmol CO ₂ H mg sample	µmol OH mg sample
Sunflower oil-based triacid (flash column Fraction 3)	4.952 ± 0.036	0.078 ± 0.005

2.2.2 ³¹P NMR spectrum of phosphitylated sunflower oil-based triacid



 δ (ppm)

Figure S5: Quantitative ³¹P NMR spectrum of phosphitylated sunflower oil-based triacid (measurement 1 as example).

- Measurement 1: 30.2 mg sample, 813.8 mg IS solution (1.652 wt%); alkoxy integral: 0.03, carboxy integral: 2.065; result: 4.977 µmol CO₂H per mg sample; 0.0745 µmol OH per mg sample.
- Measurement 2: 28.5 mg sample, 813.4 mg IS solution (1.652 wt%); alkoxy integral: 0.031, carboxy integral: 1.93; result: 4.926 µmol CO₂H per mg sample; 0.0816 µmol OH per mg sample.

2.3 Isocyanides

All isocyanides were synthesized according to the procedure published by Meier et al.[3]

2.3.1 *n*-Hexylisocyanide:

n-Hexylformamide:



C₇H₁₅NO M = 129.20 g/mol

Hexyl amine (20.4 g, 200 mmol, 1.00 eq.) and ethyl formate (322 mL, 296 g, 4.00 mol, 20.0 eq.) were stirred at 54 °C for 16 h. Afterwards, the remaining ethyl formate and ethanol were removed under reduced pressure and the crude product (21.7 g, 168 mmol, 84%) was used without further purification.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 8.20 –7.58 (m, 2H, H¹), 3.05 (q, *J* = 6.6 Hz, 2H, H²), 1.39 (p, *J* = 7.0 Hz, 2H, H³), 1.33–1.16 (m, 6H, H⁴), 0.86 (t, *J* = 6.3 Hz, 3H, H⁵).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 164.4 (CHO, C¹), 160.8 (CHO, C¹), 40.8 (CH₂, α-C_{Formamide}, C²), 37.0 (CH₂, α-C_{Formamide}, C²), 30.9 (CH₂, C³), 30.9 (CH₂, C³), 29.0 (CH₂, C³), 26.0 (CH₂, C³), 25.5 (CH₂, C³), 22.0 (CH₂, C³), 13.9 (CH₃, C⁴).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3276 (w), 3055 (vw), 2956 (w), 2928 (m), 2857 (m), 1656 (vs), 1536 (m), 1466 (w), 1381 (s), 1306 (vw), 1241 (w), 1200 (w), 812 (vw), 762 (w), 724 (w), 652 (vw).

ESI-HRMS ([M+H]⁺, C₇H₁₆NO) calcd.: 130.1226; found: 130.1227.



Figure S6: ¹H NMR spectrum of *n*-hexylformamide in DMSO-*d*₆.



Figure S7 ¹³C NMR spectrum of *n*-hexylformamide in DMSO-*d*₆.

n-Hexylisocyanide:



C₇H₁₃N M = 111.19 g/mol

n-Hexylformamide (5.17 g, 40.0 mmol, 1.00 equiv.) was dissolved in dichloromethane (60 ml, 666 mmol/l) and pyridine (9.71 ml, 120 mmol, 3.00 equiv.) was added. Subsequently, *p*-toluenesulfonyl chloride (11.4 g, 60.0 mmol, 1.50 equiv.) was added under cooling with a water bath. The cooling was removed, and the reaction mixture was stirred for 24 h at room temperature. Afterwards, aqueous saturated sodium carbonate solution (40 ml) was added, and the biphasic mixture was stirred for another 60 minutes. Water (80 ml) and dichloromethane (80 ml) were added, and the organic phase was separated. The aqueous phase was extracted with dichloromethane (3 × 40 ml), the organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by vacuum distillation in a Kugelrohr oven (70 °C, 60 mbar) to obtain the title compound (2.50 g, 22.5 mmol, 56%).

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 3.36 (tt, J = 6.7, 2.1 Hz, 2H, H¹), 1.74–1.57 (m, 2H, H²), 1.42 (p, J = 7.0 Hz, 2H, H³), 1.36–1.23 (m, 4H, H⁴), 0.89 (t, J = 6.9 Hz, 3H, H⁵).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 155.65 (t, J = 6.1 Hz, C¹), 41.62 (t, J = 6.1 Hz, CH₂, C²), 30.9 (CH₂, C³), 29.1 (CH₂, C³), 26.0 (CH₂, C³), 22.5 (CH₂, C³), 14.0 (CH₃, C⁴).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2956 (m), 2929 (s), 2860 (m), 2146 (vs), 1456 (m), 1380 (w), 1351 (w), 892 (w), 727 (w).

HRMS (ESI, [M+H]⁺, C₇H₁₄N) calcd.: 112.1121; found: 112.1123.



Figure S8: ¹H NMR spectrum of *n*-hexylisocyanide in CDCl₃.



Figure S9: ¹³C NMR spectrum of *n*-hexylisocyanide in CDCl₃.

2.3.2 1,6-Diisocyanohexane:

1,6-diformamidohexane:

H H N _N _H

C₈H₁₆N₂O₂ M = 172.23 g/mol

1,6-Diaminohexane (15.0 g, 129 mmol, 1.00 eq.) and ethyl formate (209 ml, 191 g, 2.58 mol, 20.0 eq.) were stirred at 54 °C for 16 h. Afterwards, the remaining ethyl formate and ethanol were removed under reduced pressure and the crude product (21.5 g, 125 mmol, 97%) was used without further purification.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 8.04–7.63 (m, 4H, H¹), 3.05 (q, *J* = 6.7 Hz, 4H, H²), 1.39 (p, *J* = 6.5 Hz, 4H, H³), 1.30–1.20 (m, 4H, H⁴).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 164.4 (CHO, C¹), 160.9 (CHO, C¹), 40.7 (CH₂, C²), 37.0 (CH₂, C²), 30.8 (CH₂, C³), 28.9 (CH₂, C³), 26.0 (CH₂, C³), 25.5 (CH₂, C³).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3275 (s), 3182 (vw), 3030 (vw), 2943 (w), 2913 (w), 2863 (w), 2853 (w), 1641 (vs), 1627 (vs), 1528 (vs), 1475 (m), 1460 (w), 1442 (w), 1386 (vs), 1236 (s), 1212 (s), 1082 (w), 778 (s), 740 (w), 708 (vs), 461 (w).

ESI-HRMS ([M+H]⁺, C₈H₁₇N₂O₂) calcd.: 173.1285; found: 173.1283.



Figure S10: ¹H NMR spectrum of 1,6-diformamidohexane in DMSO-*d*₆.



Figure S11: ¹³C NMR spectrum of 1,6-diformamidohexane in DMSO-d₆.

1,6-diisocyanohexane:

C⁻_×N⁺ `N<u>*</u> ℃

C₈H₁₂N₂ M = 136.20 g/mol

1,6-Diformamidohexane (30.0 mmol, 5.17 g, 1.00 eq.) was dissolved in dimethyl carbonate (60 ml) and pyridine (14.6 ml, 180 mmol, 6.00 eq.) was added. Subsequently, *p*-toluenesulfonyl chloride (17.2 g, 90.0 mmol, 3.00 eq.) was added under water bath cooling and the reaction mixture was stirred for 18 h at room temperature. Afterwards, aqueous saturated sodium carbonate solution (60 ml) was added, and the biphasic mixture was stirred for another 30 minutes. Water (100 ml) and dimethyl carbonate (100 ml) were added, and the organic phase was separated. The aqueous phase was extracted with dimethyl carbonate (3 × 60 ml), the organic extracts were combined and washed with water (2 × 50 ml) and saturated sodium chloride solution (2 × 50 mL). The organic extract was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 2:1) to obtain the title compound (4.30 g, 25.0 mmol, 83%).

 $R_{\rm f}$ (cyclohexane/ethyl acetate, 2:1) = 0.36.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 3.49 (tt, *J* = 6.6, 1.9 Hz, 4H, H¹), 1.72–1.53 (m, 4H, H²), 1.43–1.30 (m, 4H, H³).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 155.45 (t, *J* = 5.6 Hz, C¹), 41.02 (t, *J* = 5.5 Hz, C²), 28.2 (CH₂, C³), 24.9 (CH₂, C⁴).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2944 (w), 2863 (vw), 2146 (vs), 1453 (w), 1351 (w), 958 (vw), 935 (vw), 820 (vw), 728 (vw).

ESI-HRMS ([M+H]⁺, C₈H₁₃N₂) calcd.: 137.1073; found: 137.1073.



Figure S12: ¹H NMR spectrum of 1,6-diisocyanohexane in DMSO-*d*₆.



Figure S13: ¹³C NMR spectrum of 1,6-diisocyanohexane in DMSO-*d*₆.

2.3.3 1,9-Diisocyanononane:

1,9-diformamidononane:

н ⊢_И

 $C_{11}H_{22}N_2O_2$ M = 214.31 g/mol

1,9-Diaminononane (20.0 g, 124 mmol, 1.00 eq.) and ethyl formate (200 mL, 184 g, 2.48 mol, 20.0 eq.) were stirred at 54 °C for 16 h. Afterwards, the remaining ethyl formate and ethanol were removed under reduced pressure and the crude product (26.4 g, 123 mmol, 99%) was used without further purification.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 8.06–7.59 (m, 4H, H¹), 3.05 (q, *J* = 6.6 Hz, 4H, H²), 1.38 (p, *J* = 6.8 Hz, 4H, H³), 1.24 (s, 10H, H⁴).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 164.4 (CHO, C¹), 160.8 (CHO, C¹), 40.8 (CH₂, C²), 37.0 (CH₂, C²), 30.9 (CH₂, C³), 29.0 (CH₂, C³), 28.9 (CH₂, C³), 28.6 (CH₂, C³), 28.6 (CH₂, C³), 26.3 (CH₂, C³), 25.8 (CH₂, C³).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3278 (m), 2928 (m), 2891 (w), 2874 (w), 2850 (w), 1628 (vs), 1520 (s), 1476 (w), 1463 (m), 1384 (s), 1313 (w), 1276 (w), 1245 (w), 1215 (s), 1198 (m), 1064 (w), 779 (m), 748 (w), 731 (w), 687 (s), 398 (w)

ESI-HRMS ([M+H]⁺, C₁₁H₂₃N₂O₂) calcd.: 215.1754; found: 215.1754.



Figure S14: ¹H NMR spectrum of 1,9-diformamidononane in DMSO-d₆.



Figure S15: ¹³C NMR spectrum of 1,9-diformamidononane in DMSO-d₆.

1,9-diisocyanononane:

 $C_{11}H_{18}N_2$ M = 178.28 g/mol

1,9-Diformamidononane (5.36 g, 25.0 mmol, 1.00 eq.) was dissolved in dimethyl carbonate (75 ml) and pyridine (12.1 ml, 150 mmol, 6.00 eq.) was added. Subsequently, *p*-toluenesulfonyl chloride (14.3 g, 75.0 mmol, 3.00 eq.) was added under cooling with a water bath. The cooling was removed, and the reaction mixture was stirred for 24 h at room temperature. Afterwards, aqueous sodium carbonate solution (30 ml, 20 wt%) was added and the biphasic mixture was stirred for another 60 minutes. Water (60 ml) and dimethyl carbonate (60 ml) were added, and the organic phase was separated. The aqueous phase was extracted with dimethyl carbonate (3×30 ml), the organic extracts were combined and washed with water (2×50 ml) and saturated sodium chloride solution (50 ml). The organic extract was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 10:1 until 5:1) to obtain the title compound (4.20 g, 23.6 mmol, 94%) as a colorless liquid.

 $R_{\rm f}$ (cyclohexane/ethyl acetate, 4:1) = 0.34.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 3.37 (tt, *J* = 6.7, 2.0 Hz, 4H, H¹), 1.73–1.58 (m, 4H, H²), 1.48–1.38 (m, 4H, H³), 1.36–1.27 (m, 6H, H⁴).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 155.7 (t, J = 5.8 Hz, C¹), 41.62 (t, J = 6.6 Hz, C²), 29.2 (CH₂, C³), 29.1 (CH₂, C³), 28.6 (CH₂, C³), 26.3 (CH₂, C³).

IR (ATR, cm⁻¹): \tilde{v} = 2928 (m), 2857 (w), 2146 (vs), 1455 (w), 1351 (w), 939 (vw), 836 (vw), 722 (vw), 534 (vw).

ESI-HRMS ([M+H]⁺, C₁₁H₁₉N₂) calcd.: 179.1543; found: 179.1543.



Figure S16: ¹H NMR spectrum of 1,9-diisocyanononane in CDCI₃.



Figure S17: ¹³C NMR spectrum of 1,9-diisocyanononane in CDCI₃.

2.4 Model compounds M1 to M5

Model Compound M1: Passerini reaction of triacid, acetaldehyde, and n-hexylisocyanide



M = 1068.44 g/mol

Sunflower oil-based triacid (200 mg, 990 μ mol CO₂H, 1.00 equiv.) and *n*-hexylisocyanide (132 mg, 1.19 mmol, 1.20 equiv. based on CO₂H) were weighed into a glass vial. The vial was then cooled to -20°C and acetaldehyde (87.3 mg, 1.98 mmol, 2.00 equiv. based on CO₂H) was weighed into the vial and the vial was sealed. Then, dichloromethane (1 ml) was added, and the reaction was stirred at room temperature for 2 days. The solvent was removed under reduced pressure and the crude product was purified *via* flash column chromatography (cyclohexane/ethyl acetate, 2:1, then 1:1) to obtain the title compound as colorless oi (229 mg, 214 μ mol, 64%).

 $R_{\rm f}$ (cyclohexane/ethyl acetate, 1:1) = 0.2.

*T*_{d,5%}: 342 °C.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 6.12 (t, *J* = 6.0 Hz, 3H, H¹), 5.23 (p, *J* = 5.3 Hz, 1H, H²), 5.17 (q, *J* = 6.8 Hz, 3H, H³), 4.27 (dd, *J* = 11.9, 4.4 Hz, 2H, H⁴), 4.12 (dd, *J* = 11.9, 5.9 Hz, 2H, H⁴), 3.24 (q, *J* = 6.7 Hz, 6H, H⁵), 2.35 (t, *J* = 7.5 Hz, 6H, H⁶), 2.29 (td, *J* = 7.6, 2.2 Hz, 6H, H⁶), 1.67–1.54 (m, 12H, H⁷), 1.52–1.46 (m, 6H, H⁸), 1.43 (d, *J* = 6.8 Hz, 9H, H⁹), 1.36–1.21 (m, 36H, H¹⁰), 0.86 (d, *J* = 6.4 Hz, 9H, H¹¹).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 173.2 (C_q, C_{Ester}, C¹), 172.8 (C_q, C_{Ester}, C¹), 172.3 (C_q, C_{Ester}, C¹), 170.4 (C_q, C_{Amide}, C²), 70.6 (CH, C³), 69.0 (CH, C_{Glyceryl},C⁴), 62.2(CH₂, C_{Glyceryl}, C⁵), 39.3 (CH₂, C⁶), 34.3 (CH₂, C⁷), 34.2 (CH₂, C⁷), 34.0 (CH₂, C⁷), 31.5 (CH₂, C⁸), 29.6 (CH₂, C⁸), 29.0 (CH₂, C⁸), 28.9 (CH₂, C⁸), 28.9 (CH₂, C⁸), 26.6 (CH₂, C⁸), 24.9 (CH₂, C⁸), 24.8 (CH₂, C⁸), 24.8 (CH₂, C⁸), 22.6 (CH₂, C⁸), 18.1 (CH₃, C⁹), 14.1 (CH₃, C¹⁰).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3308 (vw), 2929 (s), 2857 (w), 1738 (vs), 1657 (vs), 1537 (m), 1456 (w), 1418 (w), 1371 (w), 1300 (w), 1238 (m), 1160 (vs), 1132 (vs), 1094 (vs), 1040 (w), 725 (w), 645 (vw).

ESI-HRMS ([M+H]⁺, C₅₇H₁₀₂N₃O₁₅): calcd.: 1068.7305, found: 1068.7312.







Figure S19: ¹³C NMR spectrum of M1 in CDCl₃.



Model Compound M2: Passerini reaction of triacid, butanal, and n-hexylisocyanide

Sunflower oil-based triacid (200 mg, 990 μ mol CO₂H, 1.00 equiv.) and *n*-hexylisocyanide (165 mg, 1.49 mmol, 1.50 equiv. based on CO₂H) were weighed into a glass vial. The vial was then cooled to 0 °C and butanal (107 mg, 1.49 mmol, 1.50 equiv. based on CO₂H) was weighed into the vial and the vial was sealed. Then, dichloromethane (1 ml) was added, and the reaction was stirred at room temperature for 3 days. Then, the solvent was removed under reduced pressure and the crude product was purified *via* flash column chromatography (cyclohexane/ethyl acetate, 2:1, then 1:1) to obtain the title compound as colorless oil (230 mg, 200 μ mol, 60%).

 $R_{\rm f}$ (cyclohexane/ethyl acetate, 2:1) = 0.2.

*T*d,5%: 337 °C.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 6.21–6.08 (m, 3H, H¹), 5.22–5.12 (m, 1H, H²), 5.07 (dd, *J* = 7.1, 5.1 Hz, 3H, H³), 4.22 (dd, *J* = 11.8, 4.3 Hz, 2H, H⁴), 4.06 (dd, *J* = 11.9, 5.9 Hz, 2H, H⁴), 3.24–3.07 (m, 6H, H⁵), 2.31 (t, *J* = 7.5 Hz, 6H, H⁶), 2.23 (td, *J* = 7.5, 2.1 Hz, 6H, H⁶), 1.81–1.64 (m, 6H, H⁷), 1.61–1.48 (m, 12H, H⁸), 1.41 (p, *J* = 7.1 Hz, 6H, H⁹), 1.34–1.14 (m, 42H, H¹⁰), 0.88–0.75 (m, 18H, H¹¹).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 173.0 (C_q, C_{Ester}, C¹), 172.6 (C_q, C_{Ester}, C¹), 172.3 (C_q, C_{Ester}, C¹), 169.8 (C_q, C_{Amide}, C²), 73.7 (CH, C³), 68.9 (CH, C_{Glyceryl}, C⁴), 62.0 (CH₂, C_{Glyceryl}, C⁵), 39.1 (CH₂, C⁶), 34.1 (CH₂, C⁷), 34.0 (CH₂, C⁷), 33.9 (CH₂, C⁷), 33.8 (CH₂, C⁷), 31.4 (CH₂, C⁷), 29.4 (CH₂, C⁷), 28.8 (CH₂, C⁷), 28.8 (CH₂, C⁷), 28.7 (CH₂, C⁷), 26.4 (CH₂, C⁷), 24.8 (CH₂, C⁷), 24.7 (CH₂, C⁷), 24.6 (CH₂, C⁷), 22.5 (CH₂, C⁷), 18.1 (CH₂, C⁷), 13.9 (CH₃, C⁸), 13.7 (CH₃, C⁸).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3305 (w), 2956 (m), 2929 (s), 2857 (m), 1740 (vs), 1656 (vs), 1536 (m), 1460 (w), 1441 (w), 1418 (w), 1377 (w), 1299 (w), 1234 (m), 1160 (vs), 1132 (vs), 1109 (s), 1094 (s), 1026 (w), 977 (w), 727 (w), 656 (vw).

ESI-HRMS ([M+H]⁺, C₆₃H₁₁₄N₃O₁₅) calcd.: 1152.8245; found: 1152.8242.







Figure S21: ¹³C NMR spectrum of M2 in CDCl₃.



Model Compound M3: Passerini reaction of triacid, hexanal, and n-hexylisocyanide

Sunflower oil-based triacid (200 mg, 990 μ mol CO₂H, 1.00 equiv.), *n*-hexylisocyanide (165 mg, 1.49 mmol, 1.50 equiv. based on CO₂H) and hexanal (149 mg, 1.49 mmol, 1.50 equiv. based on CO₂H) were weighed into a glass vial. Then, dichloromethane (1 ml) was added and the reaction was stirred at room temperature for 3 days. The solvent was removed under reduced pressure and the crude product was purified *via* flash column chromatography (cyclohexane/ethyl acetate, 2:1, then 1:1) to obtain the title compound as colorless oil (282 mg, 0.228 mmol, 69%).

 $R_{\rm f}$ (cyclohexane/ethyl acetate, 2:1) = 0.36.

*T*d,5%: 344 °C.

¹**H NMR** (400 MHz, CDCl₃, ppm): $\delta = 6.09-5.93$ (m, 3H, H¹), 5.24 (p, J = 5.1 Hz, 1H, H²), 5.13 (t, J = 6.0 Hz, 3H, H³), 4.27 (dd, J = 11.9, 4.4 Hz, 2H, H⁴), 4.12 (dd, J = 11.9, 5.9 Hz, 4H, H⁴), 3.32-3.15 (m, 6H, H⁵), 2.37 (t, J = 7.5 Hz, 6H, H⁶), 2.29 (td, J = 7.5, 2.2 Hz, 6H, H⁶), 1.89-1.71 (m, 6H, H⁷), 1.62 (dq, J = 15.4, 7.5 Hz, 12H, H⁸), 1.48 (p, J = 7.0 Hz, 6H, H⁹), 1.37-1.19 (m, 54H, H¹⁰), 0.86 (td, J = 6.6, 3.8 Hz, 18H, H¹¹).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 173.2 (C_q, C_{Ester}, C¹), 172.8 (C_q, C_{Ester}, C¹), 172.5 (C_q, C_{Ester}, C¹), 169.9 (C_q, C_{Amide}, C²), 74.1 (CH, C³), 69.0 (CH, C_{Glyceryl}, C⁴), 62.2 (CH₂, C_{Glyceryl}, C⁵), 39.3 (CH₂, C⁶), 34.3 (CH₂, C⁷), 34.2 (CH₂, C⁷), 34.0 (CH₂, C⁷), 32.0 (CH₂, C⁸), 31.5 (CH₂, C⁸), 31.5 (CH₂, C⁸), 29.6 (CH₂, C⁸), 29.0 (CH₂, C⁸), 29.0 (CH₂, C⁸), 28.9 (CH₂, C⁸), 26.6 (CH₂, C⁸), 24.9 (CH₂, C⁸), 24.8 (CH₂, C⁸), 24.5 (CH₂, C⁸), 22.6 (CH₂, C⁸), 22.5 (CH₂, C⁸), 14.1 (CH₃, C⁹), 14.1 (CH₃, C⁹).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3306 (vw), 2953 (m), 2927 (s), 2857 (m), 1740 (vs), 1656 (vs), 1537 (m), 1459 (w), 1418 (w), 1377 (w), 1299 (w), 1235 (m), 1160 (vs), 1132 (vs), 1094 (s), 1062 (w), 1021 (w), 725 (w)

ESI-HRMS ([M+H]⁺, C₆₉H₁₂₆N₃O₁₅) calcd.: 1236.9184; found: 1236.9183.



Figure S22: ¹H NMR spectrum of M3 in CDCl₃.



Figure S23: ¹³C NMR spectrum of M3 in CDCl₃.



Model Compound M4: Passerini reaction of triacid, nonanal, and n-hexylisocyanide

C₇₈H₁₄₃N₃O₁₅ M = 1363.01 g/mol

Sunflower oil-based triacid (300 mg, 1.49 mmol CO₂H, 1.00 equiv.) and hexylisocyanide (248 mg, 2.23 mmol, 1.50 equiv. based on CO₂H) were dissolved in dichloromethane (1.5 ml). Then, nonanal (95% purity, 404 μ l, 334 mg, 2.23 mmol, 1.50 equiv. based on CO₂H) was added and the solution was stirred for 72 h at room temperature. Afterwards, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate) to obtain the title compound (358 mg, 263 mmol, 53%).

R_f (cyclohexane/ethyl acetate, 2:1): 0.29.

*T*d,5%: 338 °C.

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 6.10–5.89 (m, 3H, N*H*, H¹), 5.23 (p, *J* = 5.0 Hz, CH, *H*_{Glyceryl}, 1H, H²), 5.13 (t, *J* = 6.0 Hz, 3H, CH, H³), 4.27 (dd, *J* = 11.9, 4.4 Hz, 2H, *H*_{Glyceryl}, H⁴), 4.12 (dd, *J* = 11.9, 5.9 Hz, 2H, *H*_{Glyceryl}, H⁴), 3.34–3.13 (m, 6H, CH₂, H⁵), 2.36 (t, *J* = 7.5 Hz, 6H, CH₂, *α*-*H*_{Ester}, H⁶), 2.29 (t, *J* = 7.4 Hz, 6H, CH₂, *α*-*H*_{Ester}, H⁶), 1.89–1.72 (m, 6H, CH₂, H⁷), 1.69–1.54 (m, 12H, CH₂, *β*-*H*_{Ester}, H⁸), 1.48 (p, *J* = 7.0 Hz, 6H, CH₂, H⁹), 1.34–1.00 (m, 72H, CH₂, H¹⁰), 0.95–0.78 (m, 18H, CH₃, H¹¹).

¹³**C NMR** (101 MHz, CDCl₃, ppm): δ = 173.2 (2C, C_q, C_{Ester}, C¹), 172.8 (C_q, C_{Ester}, C¹), 172.5 (3C, C_q, C_{Ester}, C¹), 169.9 (3C, C_q, C_{Amide}, C²), 74.1 (3C, CH, C³), 69.0 (CH, C_{Glyceryl}, C⁴), 62.2 (2C, CH₂, C_{Glyceryl}, C⁵), 39.3 (3C, CH₂, C⁶), 34.3 (3C, CH₂, *α*-C_{Ester}, C⁷), 34.2 (CH₂, *α*-C_{Ester}, C⁷), 34.0 (2C, CH₂, *α*-C_{Ester}, C⁷), 32.0 (CH₂), 31.9 (CH₂), 31.5 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 29.0 (CH₂), 28.9 (CH₂), 26.6 (CH₂), 24.9 (CH₂), 24.8 (CH₂), 24.8 (CH₂), 22.7 (CH₂), 22.6 (CH₂), 14.2 (3C, CH₃, C⁸), 14.1 (3C, CH₃, C⁸).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3303 (w), 2952 (m), 2924 (vs), 2854 (s), 1741 (vs), 1656 (vs), 1537 (m), 1460 (m), 1418 (w), 1377 (w), 1299 (w), 1237 (m), 1159 (vs), 1132 (s), 1094 (s), 724 (w).

ESI-HRMS ([M+H]⁺, C₇₈H₁₄₄N₃O₁₅): calcd.: 1363.0592, found: 1363.0494.



Figure S24: ¹H NMR spectrum of M4 in CDCl₃.





Model Compound M5: Passerini reaction of triacid, 2-ethylbutyraldehyde, and n-hexylisocyanide



M = 1236.77 g/mol

Sunflower oil-based triacid (200 mg, 990 μ mol CO₂H, 1.00 equiv.), *n*-hexylisocyanide (165 mg, 1.49 mmol, 1.50 equiv. based on CO₂H) and 2-ethylbutyraldehyde (149 mg, 1.49 mmol, 1.50 equiv. based on CO₂H) were weighed into a glass vial. Then, dichloromethane (1.0 ml) was added and the reaction was stirred at room temperature for 3 days. The solvent was removed under reduced pressure and the crude product was purified *via* flash column chromatography (cyclohexane/ethyl acetate, 2:1, then 1:1) to obtain the title compound as colorless oil (220 mg, 178 μ mol, 54%).

 $R_{\rm f}$ (cyclohexane/ethyl acetate, 2:1) = 0.36.

*T*_{d,5%}: 313 °C.

¹**H NMR** (400 MHz, CD₂Cl₂, ppm): δ = 6.03 (d, *J* = 6.6 Hz, 3H, H¹), 5.23 (ddd, *J* = 6.0, 5.1, 3.0 Hz, 1H, H²), 5.19 (d, *J* = 3.9 Hz, 3H, H³), 4.26 (dd, *J* = 11.9, 4.5 Hz, 2H, H⁴), 4.13 (dd, *J* = 11.9, 5.9 Hz, 2H, H⁴), 3.31–3.07 (m, 6H, H⁵), 2.44–2.34 (m, 6H, H⁶), 2.30 (t, *J* = 7.5 Hz, 6H, H⁶), 1.85–1.73 (m, 3H, H⁷), 1.69–1.54 (m, 12H, H⁸), 1.52–1.15 (m, 54H, H⁹), 0.97–0.68 (m, 27H, H¹⁰).

¹³**C NMR** (101 MHz, CD₂Cl₂, ppm): δ = 173.6 (C_q, C_{Ester}, C¹), 173.2 (C_q, C_{Ester}, C¹), 172.9 (C_q, C_{Ester}, C¹), 170.0 (C_q, C_{Amide}, C²), 75.5 (CH, C³), 69.4 (CH, C_{Glyceryl}, C⁴), 62.6 (CH₂, C_{Glyceryl}, C⁵), 44.2 (CH, C⁶), 39.6 (CH₂, C⁷), 34.8 (CH₂, C⁸), 34.6 (CH₂, C⁸), 34.4 (CH₂, C⁸), 32.0 (CH₂, C⁸), 30.1 (CH₂, C⁸), 29.5 (CH₂, C⁸), 29.5 (CH₂, C⁸), 29.4 (CH₂, C⁸), 29.4 (CH₂, C⁸), 27.1 (CH₂, C⁸), 25.5 (CH₂, C⁸), 25.3 (CH₂, C⁸), 23.1 (CH₂, C⁸), 22.8 (CH₂, C⁸), 22.4 (CH₂, C⁸), 14.3 (CH₃, C⁹), 12.0 (CH₃, C⁹), 11.9 (CH₃, C⁹).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3323 (vw), 2958 (w), 2929 (s), 2859 (w), 1740 (vs), 1653 (s), 1531 (m), 1460 (w), 1417 (w), 1377 (w), 1237 (m), 1157 (vs), 1126 (vs), 1095 (m), 1047 (w), 1007 (w), 727 (w), 652 (vw).

ESI-HRMS ([M+H]⁺, C₆₉H₁₂₆N₃O₁₅) calcd.: 1236.9184; found: 1236.9180.







Figure S27:¹³C NMR spectrum of M5 in CD₂Cl₂.

TGA of compounds M1 to M5:

The conducted TGA measurements and the determined $T_{d,5\%}$ values of compounds **M1–M5** are depicted in Figure S28 and Table S3, respectively.



Figure S28: TGA Measurements of compounds M1 to M5.

Table S3: Determined degradation temperatures $T_{d,5\%}$ of compounds M1 to M5.

Compound	T d,5%
M1	342
M2	337
M3	344
M4	338
M5	321

2.5 Polymerization of sunflower oil-based triacid

2.5.1 General procedure for P-3CR polymerization

The exact amount of all compounds used for the respective polymers is listed in Table S4. Acetaldehyde and butanal were used in excess due to their low boiling points leading to loss of substance during the curing time.

Polymer Tricarboxylic acid Aldehyde Diisocyanide 600 mg Acetaldehyde 1,6-Diisocyanidohexane P1a (2.97 mmol CO₂H) (170 mg, 3.86 mmol, 1.30 equiv.) (202 mg, 1.49 mmol, 0.50 equiv.) 600 mg Acetaldehyde 1,9-Diisocyanidononane P1b (265 mg, 1.49 mmol, 0.50 equiv.) (2.97 mmol CO₂H) (170 mg, 3.86 mmol, 1.30 equiv.) 1,6-Diisocyanidohexane 600 mg Butanal P2a (236 mg, 3.27 mmol, 1.10 equiv.) (2.97 mmol CO₂H) (202 mg, 1.49 mmol, 0.50 equiv.) 600 mg **Butanal** 1,9-Diisocyanidononane P2b (2.97 mmol CO₂H) (236 mg, 3.27 mmol, 1.10 equiv.) (265 mg, 1.49 mmol, 0.50 equiv.) 550 mg Hexanal 1,6-Diisocyanidohexane P3a $(2.72 \text{ mmol CO}_2\text{H})$ (273 mg, 2.72 mmol, 1.00 equiv.) (186 mg, 1.36 mmol, 0.50 equiv.) 1.9-Diisocyanidononane 550 mg Hexanal P3b (2.72 mmol CO₂H) (273 mg, 2.72 mmol, 1.00 equiv.) (243 mg, 1.36 mmol, 0.50 equiv.) 600 mg Nonanal 1,6-Diisocyanidohexane P4a (2.97 mmol CO₂H) (423 mg, 2.97 mmol, 1.00 equiv.) (202 mg, 1.49 mmol, 0.50 equiv.) 600 mg Nonanal 1,9-Diisocyanidononane P4b (265 mg, 1.49 mmol, 0.50 equiv.) (423 mg, 2.97 mmol, 1.00 equiv.) (2.97 mmol CO₂H) 550 mg 2-Ethylbutyraldehyde 1,6-Diisocyanidohexane P5a (273 mg, 2.72 mmol, 1.00 equiv.) (2.72 mmol CO₂H) (186 mg, 1.36 mmol, 0.50 equiv.) 500 mg 2-Ethylbutyraldehyde 1,9-Diisocyanidononane P5b (2.48 mmol CO₂H) (248 mg, 2.48 mmol, 1.00 equiv.) (221 mg, 1.24 mmol, 0.50 equiv.)

 Table S4: Amount of monomer compounds used for all Passerini-3CR polymerization.

2.5.2 Infrared Spectroscopy (IR)

All P-3CR polymers were characterized via IR spectroscopy. All spectra are depicted in Figure S29.



Figure S29: IR spectra of all P-3CR polymers.

2.5.3 Thermogravimetric analysis (TGA)

TGA measurements of all P-3CR polymers are depicted in Figure S30 and the corresponding $T_{d,5\%}$ values are listed in Table S5.



Figure S30: TGA Measurements of all P-3CR polymers.

Polymer	T d,5%
1a	363
1b	362
2a	348
2b	365
3a	357
3b	363
4a	362
4b	364
5a	340
5b	349

Table S5: Determined degradation temperatures $T_{d,5\%}$ of all polymers.

2.5.4 Differential Scanning Calorimetry (DSC)

DSC measurements of all P-3CR polymers are depicted in Figure S31 and the corresponding T_g values are listed in Table S6.



Figure S31: DSC Measurements of all P-3CR polymers.

Table S6: Determined glass transition temperatures T_g of all P-3CR polymers.

Polymer	<i>T</i> g / °C
1a	9
1b	4
2a	3
2b	1
3a	- 8
3b	- 12
4a	- 12
4b	- 18
5a	3
5b	0

2.5.5 Tensile Strength Measurements

A poly(tetrafluoroethylene) form was manufactured to allow casting of customized tensile test samples. The dimensions of the prepared samples are depicted in Figure S32 and are given in millimeters. For each polymer, three samples were measured to determine the average young's modulus, ultimate tensile strength, elongation at break and their standard deviations. All tensile strength measurements are depicted in Figures S33–S42.



Figure S32: Dimensions of the manufactured tensile test samples (in millimeters). This drawing was made with Autodesk Inventor.



Figure S33: Tensile strength measurements of P1a.



Figure S34: Tensile strength measurements of P1b.



Figure S35: Tensile strength measurements of P2a.



Figure S36: Tensile strength measurements of P2b.



Figure S37: Tensile strength measurements of P3a.



Figure S38: Tensile strength measurements of P3b.



Figure S39: Tensile strength measurements of P4a.



Figure S40: Tensile strength measurements of P4b.



Figure S41: Tensile strength measurements of P5a.



Figure S42: Tensile strength measurements of P5b.

2.5.6 Lap shear force adhesive tests

Testing samples were prepared by cutting each test substrate into rectangular pieces.

- 1. Aluminum alloy (5754, or AIMg₃): 6 cm × 1.5 cm × 0.1 cm
- 2. Stainless-steel (S235JR): 6 cm × 1.5 cm × 0.1 cm
- 3. Wood (common ash): 6 cm × 1.5 cm × 0.5 cm
- 4. Poly(methyl methacrylate): 6 cm × 1.5 cm × 0.4 cm
- 5. Borosilicate glass: 6 cm × 1.5 cm × 0.4 cm

All adhesive test measurements are depicted in Figures S43-S48.



Figure S43: Adhesive test measurements of P5a on aluminum.



Figure S44: Adhesive test measurements of P5a on stainless-steel.



Figure S45: Adhesive test measurements of P5a on wood.



Figure S46: Adhesive test measurements of P5a on wood with different curing times.



Figure S47: Adhesive test measurements of P5a on PMMA.



Figure S48: Adhesive test measurements of P5a on glass.





Diol 6:

T_m: 162 °C

¹**H NMR** (500 MHz, TFA-*d*, ppm): δ = 4.63 (dd, *J* = 8.7, 3.5 Hz, 2H, H¹), 3.44 (t, *J* = 7.3 Hz, 4H, H²), 1.96–1.83 (m, 2H, H³), 1.81–1.68 (m, 2H, H³), 1.68–1.56 (m, 4H, H⁴), 1.48–1.39 (m, 4H, H⁵), 1.39 (s, 4H, H⁶), 1.34–1.15 (m, 20H, H⁷), 0.79 (t, *J* = 6.6 Hz, 6H, H⁸).

¹³**C NMR** (126 MHz, TFA-*d*, ppm): δ = 180.7 (C_q, C_{Amide}, C¹), 73.8 (CH, C²), 43.4 (CH₂, C³), 35.9 (CH₂, C³), 33.6 (CH₂, C³), 31.1 (CH₂, C³), 30.9 (CH₂, C³), 30.8 (CH₂, C³), 29.9 (CH₂, C³), 27.9 (CH₂, C³), 26.7 (CH₂, C³), 24.3 (CH₂, C³), 14.7 (CH₃, C⁴).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3242 (s), 2953 (m), 2918 (vs), 2873 (w), 2849 (vs), 1638 (vs), 1622 (vs), 1543 (vs), 1468 (s), 1441 (w), 1373 (s), 1334 (m), 1327 (m), 1268 (w), 1176 (w), 1136 (w), 1082 (vs), 1034 (w), 815 (w), 802 (w), 722 (m), 704 (w), 679 (s), 552 (w), 507 (w), 480 (w), 466 (w).

ESI-HRMS ([M+H]⁺, C₂₆H₅₃N₂O₄): calcd.: 457.4000, found: 457.3996.

Dimethyl azelate:

¹**H NMR** (400 MHz, CDCl₃, ppm): δ = 3.65 (s, 6H, H¹), 2.29 (t, *J* = 7.5 Hz, 4H, H²), 1.61 (qd, *J* = 7.6, 4.1 Hz, 4H, H³), 1.31 (d, *J* = 4.5 Hz, 6H, H⁴).

Glycerol:

¹**H NMR** (400 MHz, DMSO-*d*₆, ppm): δ = 4.45 (d, *J* = 4.7 Hz, 1H, H¹), 4.38 (t, *J* = 5.6 Hz, 2H, H²), 3.49–3.17 (m, 5H, H³).



Figure S49: ¹H NMR spectrum of 6 in TFA-d.



Figure S50: ¹³C NMR spectrum of 6 in TFA-d.



Figure S51: HMBC NMR spectrum of 6 in TFA-d.



Figure S52: ¹H NMR spectrum of distilled dimethyl azelate in CDCl₃.



Figure S53: ¹H NMR spectrum of pure glycerol (top) and distilled glycerol (bottom) in DMSO-d₆.

2.7 Repolymerization of diol 6

2.7.1 Polymerization attempt with azelaic acid dimethyl ester



Repeating unit: $C_{35}H_{64}N_2O_6$ M = 608.91 g/mol

Diol **6** (200 mg, 438 µmol, 1.00 equiv.), dimethyl azelate (94.7 mg, 438 µmol, 1.00 equiv.) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (3.05 mg, 21.9 µmol, 5 mol%) were added into a 1.5 ml screw cap vial. The mixture was heated to 160 °C for 16 h and the pressure was reduced to 800 mbar to remove the condensation product methanol. Afterwards, the pressure was further reduced to 10 mbar and the reaction was stirred for another 6 h at 160 °C. After cooling to room temperature, the residue was dissolved in tetrahydrofuran and precipitated into cold methanol. The precipitate was filtrated, washed with methanol and dried at 70 °C and 10 mbar to obtain the oligomer.

SEC (DMAc): *M*_n = 1900 Da, *M*_w = 3600 Da, *Đ* = 1.90.



Figure S54: SEC (THF) after precipitation of polymerization attempt of diol 6 with azelaic acid dimethyl ester and TBD catalysis.

2.7.2 Polymerization with hexamethylene diisocyanate



 $C_{34}H_{64}N_4O_6$ M = 624.91 g/mol

SEC (DMAc): *M*_n = 16700 Da, *M*_w = 53000 Da, *Đ* = 3.17.

¹**H NMR** (500 MHz, CDCl₃, ppm): δ = 7.09–6.27 (m, 2H, H¹), 6.02–5.33 (m, 2H, H²), 5.09–4.91 (m, 2H, H³), 3.33–3.18 (m, 4H, H⁴), 3.18–3.00 (m, 4H, H⁴), 1.88–1.78 (m, 2H, H⁵), 1.74 (m, 2H, H⁵), 1.49 (s, 8H, H⁶), 1.39–1.09 (m, 32H, H⁷), 0.86 (t, *J* = 6.8 Hz, 6H, H⁸).

¹³**C NMR** (126 MHz, CDCl₃, ppm): δ = 171.5 (C_q, C_{Amide}, C¹), 155.8 (C_q, C_{Carbamate}, C²), 74.4 (CH, C³), 41.0 (CH₂, C⁴), 38.3 (CH₂, C⁴), 32.5 (CH₂, C⁵), 32.0 (CH₂, C⁵), 29.8 (CH₂, C⁵), 29.6 (CH₂, C⁵), 29.5 (CH₂, C⁵), 29.4 (CH₂, C⁵), 29.3 (CH₂, C⁵), 26.3 (CH₂, C⁵), 26.1 (CH₂, C⁵), 25.6 (CH₂, C⁵), 25.1 (CH₂, C⁵), 22.8 (CH₂, C⁵), 14.2 (CH₃, C⁶).

IR (ATR, cm⁻¹): $\tilde{\nu}$ = 3302 (w), 2922 (vs), 2853 (m), 1700 (vs), 1656 (vs), 1530 (vs), 1465 (m), 1438 (w), 1375 (w), 1306 (w), 1252 (vs), 1181 (w), 1136 (s), 1102 (w), 1074 (w), 1037 (w), 982 (w), 781 (w), 721 (w), 650 (w), 595 (w).

TGA (*T*_{d,5%}): 280 °C.



Figure S55: SEC (DMAc) of polyurethane made from diol 6 and hexamethylene diisocyanate.



Figure S56: ¹H NMR spectrum of polyurethane made from diol 6 and hexamethylene diisocyanate in CDCl₃.



Figure S57: ¹³C NMR spectrum of polyurethane made from diol 6 and hexamethylene diisocyanate in CDCl₃.

A References

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