

Polymer Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Santos Correa, S. Leidenheimer and M. A. R. Meier, *Polym. Chem.*, 2024, DOI: 10.1039/D4PY01358A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

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

View Article Online
DOI: 10.1039/D4PY01358A

Received 00th January 20xx,
Accepted 00th January 20xx

Luis Santos Correa,^a Silas Leidenheimer,^b and Michael A. R. Meier^{*a,b}

DOI: 10.1039/x0xx00000x

Tricarboxylic acids are molecules of interest for the synthesis of cross-linked polymers. Herein, a recently established route to a tricarboxylic acid from high oleic sunflower oil was utilized to synthesize renewable cross-linked polymers *via* the Passerini three-component reaction. Ten different polymers were synthesized by variation of the diisocyanide and monoaldehyde components and subsequently characterized *via* infrared spectroscopy, swelling tests, thermogravimetric analysis, differential scanning calorimetry, and tensile tests. The characterization of the insoluble polymeric networks was complemented by the synthesis of model compounds to enable analysis in solution *via* nuclear magnetic resonance spectroscopy. Due to the fast curing of all polymers at room temperature, adhesive tests were performed to demonstrate their potential application as glues. At last, one Passerini polymer was chemically reused by transesterification with methanol and catalytic amounts of sulfuric acid to establish a proof-of-concept of the circularity of these materials. Azelaic acid dimethyl ester, an industrially relevant compound used for the synthesis of polyamides, and a difunctional α -hydroxyamide were recovered in a yield of 75%. Repolymerization of the α -hydroxyamide to a polyurethane was performed to demonstrate a potential second life cycle of these compounds.

Introduction

The development and production of new polymeric materials from renewable resources is of paramount importance to reduce humanity's high dependency on depleting fossil resources. For instance, in 2022, a concerningly small share of less than 1% of the worldwide plastic production of >400 Mt was bio-based.^[1] Plant oils and fatty acids are the most important renewable feedstock of the chemical industry for polymer applications. In 2019, approximately 25% of the annual global production of 208 Mt vegetable oils were already used industrially for the production of biodiesel, oleochemicals, and other applications to substitute fossil-resources.^[2] In polymer chemistry, fatty acids are either functionalized at the carboxylic acid moiety by esterification or at their double bonds *via* oxidations, thiol-ene reaction, olefin metathesis or isomerizing functionalization to synthesize difunctional monomers that can be polymerized.^[3, 4] Polyfunctional derivatives can be obtained from oils by functionalization of the triglyceride double bonds.^[5] Alternatively, cross-linked polymers can be synthesized from triglycerides by direct polymerization of the double bonds *via* acyclic triene metathesis polymerization or cationic/radical polymerization.^[3]

Besides the use of renewable feedstocks, chemical reactions must adhere as much as possible to the 12 Principles of Green Chemistry, as established by Anastas and Warner in 1998.^[6, 7] These principles act as guidelines to develop more sustainable processes and address topics such as waste production, atom economy, toxicity of the involved chemicals, the design of inherently safer chemistry, utilization of renewable resources,

and the development of catalysts to reduce energy consumption.

Multicomponent reactions (MCRs) align with many of the 12 Principles of Green Chemistry and are defined as reactions that combine at least three different starting compounds in a single one-pot reaction, in which most of the atoms of the starting materials are incorporated in the final product.^[8, 9] Hence, waste generation is kept to a minimum due to the high atom economy of these reactions, and usually only benign by-products such as water, alcohols or amines are formed.^[10] The isocyanide based Passerini three-component reaction (P-3CR) was discovered in 1921 and describes the addition reaction between a carboxylic acid, an aldehyde, and an isocyanide to form an α -acyloxy amide.^[11, 12] The high versatility of this reaction enables its use in step economic syntheses of several natural products and active pharmaceutical ingredients.^[12, 13, 14]

Although the Passerini reaction is known to achieve near quantitative conversions at room temperature, its utilization as step-growth polymerization reaction was first reported 90 years after its discovery.^[15] Meier *et al.* reported polyesters with high molecular weights of up to 56 kDa that were obtained by combination of a dicarboxylic acid, a dialdehyde, and a monoisocyanide at reaction temperatures of only 40 °C. Shortly after, several syntheses of new poly(ester-amide)s,^[16] polyamides,^[17] and polyesters^[18] were achieved by simple permutation of the starting materials' functional groups. The multicomponent polymerization approach moreover easily allows the polymers to be grafted onto by introduction of additional functional groups during the MCR step.^[17, 18] So far, the synthesis of cross-linked polymers *via* isocyanide based MCRs has however been reported scarcely. Most studies focused on the synthesis of hydrogels from carboxylic acid group bearing polysaccharides such as alginic acid,^[19, 20, 21, 22] hyaluronic acid,^[22, 23] and carboxymethylcellulose^[22, 24] *via* the P-3CR or the Ugi four-component reaction. Furthermore, the polysaccharide chitosan was used as polyamine component for the synthesis of Ugi-4CR based microgels.^[25] However, in all of

^a Laboratory of Applied Chemistry, Institute of Biological and Chemical Systems - Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

^b Laboratory of Applied Chemistry, Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

† Footnotes relating to the title and/or authors should appear here.

Supplementary Information available: Analytical data of the synthesized compounds, details about the carboxylic acid value determination, and all tensile and adhesive test measurements. See DOI: 10.1039/x0xx00000x



these reports, the cross-linking was only performed with already polymeric starting materials. To the best of our knowledge, so far only one report by Xie *et al.* describes the synthesis of a cross-linked P-3CR polymer from terephthalaldehyde, 1,6-diisocyanohexane, and sebacic acid.^[26] However, due to the high molar excess of 50 mol% terephthalaldehyde, it is most likely that these materials exhibited a low degree of cross-linking and a high share of unreacted aldehyde groups. In addition, both the hydrogel approach and the polymer reported by Xie *et al.* used solvents during the polymerization, which is not desired as this generates additional waste.

Thus, we herein report for the first time the solvent-free synthesis of ten different P-3CR thermosets from a tricarboxylic acid, two diisocyanides, and five monoaldehydes. All components were by design chosen to be liquid to allow the facile preparation of solvent-free formulations. Moreover, isocyanide and aldehyde components were chosen to be at least in principle renewable in order to further increase the sustainability of these new materials. The used tricarboxylic acid is fully renewable and was synthesized from high oleic sunflower oil with a literature reported procedure.^[27]

Experimental

Materials. All starting materials, solvents and reagents were purchased from chemical suppliers and used without further purification unless stated otherwise.

Used Solvents. Cyclohexane (VWR, HPLC grade), ethyl acetate (VWR, HPLC grade), methanol (Thermo Fisher Scientific, HPLC grade) and *tert*-butanol (Acros Organics, 99.5%) were used without further purification. Dichloromethane (OQEMA, technical) was purified by distillation prior to use. DMSO-*d*₆ (<99.8% D) and CDCl₃ (<99.8% D) were purchased from Eurisotop. Trifluoroacetic acid-*d* (99.5% D) was purchased from Sigma-Aldrich.

Used Compounds. High Oleic sunflower Oil was bought at the local supermarket dm in Karlsruhe, Germany. Acetaldehyde (Acros Organics, 99.5%), butanal (Acros Organics, 99%), bromocresol green (TCI, >99%), cerium(IV)sulfate (ChemPUR, 98%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Sigma-Aldrich, 95%), 1,6-diaminohexane (Sigma-Aldrich, ≥97.5%), 1,9-diaminononane (abcr, 98%), 2-ethylbutyraldehyde (Sigma-Aldrich, ≥92%), ethyl formate (Thermo Scientific, ≥98%), formic acid (Acros Organics, 99%), hexanal (Sigma-Aldrich, 98%), hexamethylene diisocyanate (Sigma-Aldrich, for synthesis), *n*-hexylamine (Sigma-Aldrich, 99%), hydrogen peroxide (abcr, 35% aqueous solution), endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (Alfa Aesar, 97%), nonanal (Alfa Aesar, 97%), phosphomolybdic acid (Sigma-Aldrich, >99%), potassium carbonate (Sigma-Aldrich, >99%), potassium permanganate (Sigma-Aldrich, >99%), pyridine (Sigma-Aldrich, >99%), pyridine-2,6-dicarboxylic acid (Acros Organics, 99%), ruthenium(III)acetylacetonate (abcr, 99%), sodium carbonate (Carl Roth, ≥99.5%), sodium chloride (Sigma-Aldrich, >99%), sodium hydroxide (Sigma-Aldrich, >99%), sodium sulfate (Thermo Fisher Scientific, 99%), sulfuric acid

(Sigma-Aldrich, 98%) and *p*-toluenesulfonyl chloride (Sigma-Aldrich, ≥99%) were used without further purification.

Methods. **Thin-Layer Chromatography (TLC).** Aluminum plates coated with fluorescent silica gel of the type F₂₅₄ obtained from Sigma-Aldrich were used for TLC measurements. TLC plates with the applied samples were placed in a glass chamber filled with eluent (filling height ca. 0.5 cm). The plates were removed once the eluent front had reached a height of ~3 cm and cautiously dried with a heat gun. The compounds on the plates were visualized either by potassium permanganate stain (solution of 1.5 g potassium permanganate, 10 g potassium carbonate, 1.25 ml of 10 wt% sodium hydroxide solution, 200 ml water), Seebach stain (2.0 g cerium(IV)sulfate, 5.0 g phosphomolybdic acid, 16 ml sulfuric acid, 200 ml water) or bromocresol green stain (40 mg bromocresol green in 100 ml ethanol and subsequent addition of 0.1 M sodium hydroxide solution until a persistent blue color appears).

Flash Column Chromatography. The purification of compounds by flash column chromatography was conducted according to the publication of W.C. Still *et al.*^[28] Silica gel, obtained from Sigma Aldrich, with a pore size of 60 Å, a mesh size of 230–240, and a particle size of 40–63 μm was used as stationary phase.

Distillation. A Büchi Labortechnik Kugelrohr model B-585 was used for distillations of volumes smaller than 5 ml.

Addition of Liquids with a Syringe Pump. The slow addition of liquids over time was performed with a Landgraf Laborsysteme syringe pump model LA-30.

Instruments. **Infrared (IR) Spectroscopy.** Infrared spectra of all compounds were recorded on a Bruker Alpha Fourier transform infrared spectrometer with attenuated total reflection technology in the range from 4000 to 400 cm⁻¹. The resulting absorbance spectra are averaged over 24 scans per measurement. By convention, the signals are noted from large to small wavenumbers. Characterization of the absorption bands was done in dependence of the absorption strength with the following abbreviations: vs (very strong), s (strong), m (medium), w (weak), vw (very weak).

Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H NMR spectra were recorded either on a Bruker Ascend™ 400 spectrometer at 400 MHz with 16 scans and a delay time D₁ of 1 s at 298 K or on a Bruker Avance DRX spectrometer at 500 MHz with 16 scans and a delay time D₁ of 1 s at 298 K. The chemical shift δ is reported in parts per million and referenced to the solvent signal of DMSO-*d*₅ at 2.50 ppm, CHCl₃ at 7.26 ppm, or trifluoroacetic acid at 11.5 ppm. Additionally, gradient selected correlation spectroscopy (COSY) was carried out for signal assignment of protons. The following abbreviations are used to describe the proton splitting pattern: s = singlet, d = doublet, t = triplet, m = multiplet. All coupling constants *J* are given in Hz and decreasing order. ¹³C NMR spectra were recorded either on a Bruker Ascend™ 400 spectrometer at 101 MHz with 1024 scans and a delay time D₁ of 2 s at 298 K or on a Bruker Avance DRX spectrometer at 126 MHz with 1024 scans and a delay time D₁ of 2 s at 298 K. The chemical shift δ is reported in parts per million and referenced to the solvent signal of DMSO-*d*₆ at 39.52 ppm,



CDCl₃ at 77.16 ppm, or trifluoroacetic acid-*d* at 164.2 ppm. Furthermore, phase-edited heteronuclear single quantum coherence (HSQC_{ed}) and heteronuclear multiple bond correlation (HMBC) spectroscopy were carried out for signal assignment of carbon atoms and structure elucidation. Signals of carbon atoms were specified as follows: C_q = quaternary carbon atom, CH, CH₂, or CH₃. Quantitative ³¹P NMR spectra were recorded on a Bruker Avance DRX spectrometer at 202 MHz with an inverse gated decoupling pulse program, 1024 scans and a delay time D₁ of 10 s at 298 K.

Mass Spectrometry (MS). Electrospray ionization (ESI) experiments were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific) equipped with a HESI II probe to record high resolution. The spectra of most compounds were evaluated by molecular signals [M]⁺, signals of protonated molecules [M+H]⁺, and characteristic fragment peaks and indicated with their mass-to-charge ratio (*m/z*). Moreover, spectra of carboxylic acids were evaluated by signals of deprotonated molecules [M-H]⁻.

Melting Point. The Melting point of diol **6** was recorded on a Stanford Research Systems OptiMelt – Automated Melting Point System with Digital Image Processing Technology. The measurement was performed from 25 °C to 200 °C with a heating rate of 10 K min⁻¹.

Size Exclusion Chromatography (SEC). SEC analyses were performed on one of the two following systems. **System I (Oligo THF SEC):** A PSS SECcurity² SEC system based on Agilent Infinity 1260 II hardware was used for the measurements. The system is equipped with a refractive index detector SECcurity² RI, a column oven (Bio)SECcurity² column compartment TCC6500, a standard SECcurity² autosampler, and an isocratic pump SECcurity² isocratic pump. Anhydrous tetrahydrofuran stabilized with 250 ppm butylated hydroxytoluene (BHT, ≥99.9%) was used at a flow rate of 1.0 ml min⁻¹ and at 30 °C as mobile phase. The analysis was performed on the following column system: PSS SDV analytical precolumn (3 μm, 8 mm × 50 mm) with two PSS SDV analytical columns (3 μm, 8 mm × 300 mm, 1000 Å). For the calibration, narrow linear poly(methyl methacrylate) standards (Polymer Standards Service, PSS, Germany) ranging from 102 to 62200 Da were used. **System II (DMAc SEC):** A PSS SECcurity² SEC system based on Agilent Infinity 1260 II hardware was used for the measurements. The system is equipped with a refractive index detector. DMAc with 0.03 wt% lithium bromide was used at a flow rate of 1.0 ml min⁻¹ and at 35 °C as mobile phase. The analysis was performed on the following column system: Agilent Mixed-C column and Agilent Mixed-E column. For the calibration, polystyrene standards ranging from 370 to 2520000 Da were used. For sample preparation, 2.00 mg of analyte was dissolved in 1.50 ml of the solvent used in the respective system. All samples were filtered by syringe filter prior to use, to avoid plugging of the injection setup or the column.

Differential Scanning Calorimetry (DSC). DSC measurements were recorded on a Mettler Toledo DSC3 STAR^e system. All experiments were carried out under nitrogen atmosphere using 40 μl aluminum crucibles and a sample mass of 4–7 mg. The

samples were measured using the following program: first heating from 25 °C to 250 °C, then cooling from 250 °C to -70 °C and a final heating step from -70 °C to 250 °C with a heating/cooling rate of 10 K min⁻¹. The glass transition temperature (*T_g*) was determined from the second heating run to eliminate possible interference from the polymer's thermal history.

Thermogravimetric Analysis (TGA). TGA measurements were performed on a TA Instruments TGA 5500 under a nitrogen atmosphere using platinum TGA sample pans and a heating rate of 10 K min⁻¹ over a temperature range from 25 °C to 600 °C. *T_{d,5%}* is defined as the temperature of 5% weight loss.

Tensile Strength Measurements. Tensile strength measurements were performed on an Inspect table 10kN from Hegewald & Peschke equipped with a 1.5 kN load cell. Tensile strength measurements and adhesive tests were performed with an elongation of 5 mm min⁻¹ and 1 mm min⁻¹, respectively.

Oxidative cleavage of high oleic sunflower oil. In a 100 ml three-necked flask, high oleic sunflower oil (39.8 g, 45.0 mmol (based on the molecular weight of triolein (885.5 g/mol)), 1.00 equiv.), ruthenium(III) acetylacetonate (359 mg, 900 μmol, 2.00 mol%) and pyridine-2,6-dicarboxylic acid (3.01 g, 18.0 mmol, 40.0 mol%) were dissolved in a mixture of *tert*-butanol (405 ml) and water (135 ml). The reaction mixture was stirred magnetically (400 rpm with a cross shaped stirring bar) at 80 °C for 24 h. After the reaction temperature reached 80 °C, hydrogen peroxide (35% aq. sol., 92.9 ml, 1.08 mol, 24.0 equiv.) was added slowly to the reaction solution by a syringe pump with a flow rate of 77.4 μl min⁻¹ over a period of 20 h. After the entire reaction time passed, the reaction solution was diluted with water (200 ml) and *tert*-butanol was removed under reduced pressure to ensure easier phase separation during extraction. The aqueous phase was extracted with ethyl acetate (3 × 150 ml) and the combined organic layers were washed with saturated sodium chloride solution (3 × 100 ml), dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The reaction was conducted twice. Both reactions were combined and distilled in a Zinke apparatus *in vacuo* (100 °C, 0.1 mbar) to remove the cleavage product nonanoic acid (29.2 g, 185 mmol, 90%). The residue of the distillation was purified by flash column chromatography (cyclohexane/ethyl acetate, 4:1 + 1% formic acid, then 2:1 + 1% formic acid, then 2:1 without formic acid) to obtain three fractions (Fraction 1: residual nonanoic acid (2.50 g, 15.8 mmol, 8%), Fraction 2: side product with low carboxylic acid content (18.0 g, 31%), Fraction 3: sunflower oil-based triacid (20.8 g, 36%)) after removal of solvent and formic acid under reduced pressure. Analytical data for sunflower oil-based triacid: ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ = 11.95 (s, 3H), 5.18 (tt, *J* = 6.9, 3.7 Hz, 1H), 4.25 (dd, *J* = 12.0, 3.7 Hz, 2H), 4.12 (dd, *J* = 12.0, 6.5 Hz, 2H), 2.34–2.22 (m, 6H), 2.17 (t, *J* = 7.4 Hz, 6H), 1.49 (ddd, *J* = 14.6, 9.6, 5.5 Hz, 12H), 1.25 (d, *J* = 3.8 Hz, 18H), 0.89–0.78 (m, 0.17H); ¹³C NMR (126 MHz, DMSO-*d*₆, ppm): δ = 174.5 (C_q, CO₂H), 174.4 (C_q, CO₂H), 172.5 (C_q, C_{Ester}), 172.2 (C_q, C_{Ester}), 68.8 (CH, C_{Glycerol}), 61.8 (CH₂, C_{Glycerol}), 33.6 (CH₂), 33.5 (CH₂), 33.3 (CH₂), 28.4 (CH₂), 28.3 (CH₂), 28.2 (CH₂), 24.4 (CH₂), 24.4 (CH₂), 24.3 (CH₂);



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); *ESI-MS* ($[\text{M}-\text{H}]^-$, $\text{C}_{30}\text{H}_{49}\text{O}_{12}$): calcd.: 601.3230, found: 601.3229.

Quantitative ^{31}P NMR spectroscopy. The amount of carboxylic acids and hydroxyl groups per mg of sample was determined by derivatization of the sunflower oil-based triacid sample using the phosphitylation agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP), according to a modified procedure of the one published by Kilpeläinen *et al.*^[29, 30] First, the internal standard solution was prepared by dissolving endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (550 mg, 3.07 mmol) in pyridine (15 ml) and CDCl_3 (10 ml). This results in a final concentration of 22 mg ml^{-1} or 123 mmol l^{-1} . Then, under standard atmosphere (no argon box), 28–32 mg of the analyte were weighed into a 10 ml screw-cap vial. CDCl_3 (1 ml), pyridine (200 μl , 2.48 mmol) and the internal standard solution of endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (650 μl) were added and the mixture was agitated with a vortex mixer until the sample was fully dissolved (approximately 1 min). At last, 2-Cl-TMDP (200 μl , 1.26 mmol) was added and the mixture was agitated for 1 min. Then, 1.0 ml of the solution was transferred to an NMR tube. ^{31}P NMR measurements were performed immediately after the sample had been prepared. The carboxylic acid and hydroxyl content was calculated according to Equations (S3) and (S4), Supporting Information.

Synthesis of formamides and isocyanides. The syntheses of all formamides and isocyanides were conducted according to a literature reported procedure for the synthesis of aliphatic isocyanides.^[31] All syntheses and their analytical data are described in detail in the Supporting information.

General Procedure for the synthesis of model compounds M1 to M5. Sunflower oil-based triacid (200 mg, 990 μmol , 1.00 equiv. of carboxylic acids), *n*-hexylisocyanide (165 mg, 1.49 mmol, 1.50 equiv. based on carboxylic acids), and the respective aldehyde (1.50 equiv. based on carboxylic acids) were weighed into a glass vial and the vial was sealed. 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 by flash column chromatography (cyclohexane/ethyl acetate) to obtain the respective model compound. Exemplary analytical data for **M4** (data of all other model compounds can be found in the Supporting Information): ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 6.10–5.89 (m, 3H, NH), 5.23 (p, J = 5.0 Hz, 1H, H_{Glycerol}), 5.13 (t, J = 6.0 Hz, 3H), 4.27 (dd, J = 11.9, 4.4 Hz, 2H, H_{Glycerol}), 4.12 (dd, J = 11.9, 5.9 Hz, 2H, H_{Glycerol}), 3.34–3.13 (m, 6H), 2.36 (t, J = 7.5 Hz, 6H, $\alpha\text{-H}_{\text{Ester}}$), 2.29 (t, J = 7.4 Hz, 6H, $\alpha\text{-H}_{\text{Ester}}$), 1.89–1.72 (m, 6H), 1.69–1.54 (m, 12H, $\beta\text{-H}_{\text{Ester}}$), 1.48 (p, J = 7.0 Hz, 6H), 1.34–1.00 (m, 72H), 0.95–0.78 (m, 18H); ^{13}C NMR (101 MHz, CDCl_3 , ppm): δ = 173.2 (C_q , C_{Ester}), 172.8 (C_q , C_{Ester}), 172.5 (C_q , C_{Ester}), 169.9 (C_q , C_{Amide}), 74.1 (CH), 69.0 (CH, $\text{C}_{\text{Glycerol}}$), 62.2 (CH_2 , $\text{C}_{\text{Glycerol}}$), 39.3 (CH_2), 34.3 (CH_2 , $\alpha\text{-C}_{\text{Ester}}$), 34.2 (CH_2 , $\alpha\text{-C}_{\text{Ester}}$), 34.0 (CH_2 , $\alpha\text{-C}_{\text{Ester}}$), 32.0 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 28.9 (CH_2),

26.6 (CH_2), 24.9 (CH_2), 24.8 (CH_2), 24.8 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.2 (CH_3), 14.1 (CH_3); *IR* (ATR, cm^{-1}): 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-MS* ($[\text{M}+\text{H}]^+$, $\text{C}_{78}\text{H}_{144}\text{N}_3\text{O}_{15}$): calcd.: 1363.0592, found: 1363.0494.

General procedure for Passerini three component polymerization. Sunflower oil-based triacid (600 mg, 1.00 equiv. of carboxylic acids) and the respective diisocyanide component (0.50 equiv. of carboxylic acids) were weighed into a 10 ml screw-cap vial and cooled to -20°C with a sodium chloride ice cooling bath. The aldehyde component (1.00 equiv. of carboxylic acids) was freshly distilled and then weighed into the cooled vial. All compounds were mixed while cooling was maintained. The mixture was then poured into a poly(tetrafluoroethylene) form to produce bone shaped samples for tensile strength measurements (Supporting Information chapter 2.5.5). Polymers **P1a** to **P3b** were first cured at 5°C for 30 minutes to prevent evaporation of the volatile aldehyde components, while polymers **P4a** to **P5b** were cured at room temperature for 30 minutes. All polymers were further cured at 50°C for 24 h to guarantee full conversion of functional groups.

Swelling tests for gel content determination. Each polymer sample (50–100 mg) was weighed and immersed in tetrahydrofuran for 3 days at room temperature. The sample was then removed from the solvent, dried at 70°C and 10 mbar, and weighed again to determine the gel content (Equation (1)).

Lap shear force adhesive tests. Testing samples were prepared by cutting each substrate material (aluminum alloy, stainless-steel, wood, poly (methyl methacrylate), glass) into rectangular pieces (Supporting Information chapter 2.5.6). For sample preparation, the respective monomers were premixed at 0°C and then applied onto two rectangular pieces of the same substrate (gluing area of 2.25 cm^2). The two surfaces were pressed together and cured at room temperature for 2 h. Afterwards, the two pieces were pulled apart in a tensile measurement to determine the ultimate tensile strength.

Chemical recycling of P-3CR polymer. Polymer **P4a** (3.00 g, 14.6 mmol ester groups, 1.00 equiv.) was suspended in methanol (120 ml, 2.96 mol, 203 equiv.) and sulfuric acid (96%, 286 mg, 2.91 mmol, 0.20 equiv.) was added. The reaction mixture was stirred for 5 h at 65°C until **P4a** dissolved completely due to depolymerization. While cooling to room temperature, the diol compound **6** precipitated. The reaction volume was reduced to 60 ml and then filtrated to isolate the diol (1.23 g, 2.69 mmol, 74%). The solvent methanol was removed from the filtrate and ethyl acetate (60 ml) was added. The organic phase was washed with water (3 \times 40 ml) to remove glycerol and sulfuric acid, dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was then distilled in a Kugelrohr oven *in vacuo* (10 mbar, 150°C) to isolate azelaic acid dimethyl ester (1.18 g, 5.45 mmol, 75%). At last, the aqueous phase from the washing step before was neutralized with sodium hydroxide (116 mg, 2.91 mmol, 0.20 equiv.) and distilled in a Kugelrohr oven to obtain glycerol (68 mg, 738 μmol , 30%).

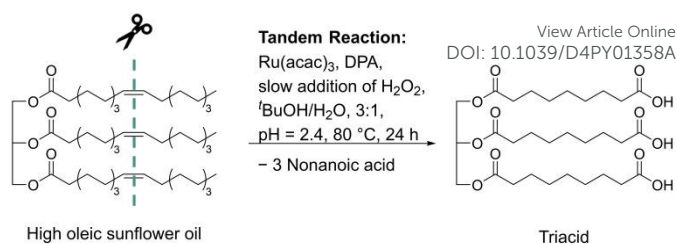


Analytical data for diol **6**: T_m : 162 °C; 1H NMR (500 MHz, TFA-*d*, ppm): δ = 4.63 (dd, J = 8.7, 3.5 Hz, 2H), 3.44 (t, J = 7.3 Hz, 4H), 1.96–1.83 (m, 2H), 1.81–1.68 (m, 2H), 1.68–1.56 (m, 4H), 1.48–1.39 (m, 4H), 1.39 (s, 4H), 1.34–1.15 (m, 20H), 0.79 (t, J = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, TFA-*d*, ppm): δ = 180.7 (C_q , C_{amide}), 73.8 (CH), 43.4 (CH_2), 35.9 (CH_2), 33.6 (CH_2), 31.1 (CH_2), 30.9 (CH_2), 30.8 (CH_2), 29.9 (CH_2), 27.9 (CH_2), 26.7 (CH_2), 24.3 (CH_2), 14.7 (CH_3); 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), 802 (w), 722 (m), 704 (w), 679 (s), 552 (w), 480 (w), 466 (w); ESI-MS ($[M+H]^+$, $C_{26}H_{53}N_2O_4$): calcd.: 457.4000, found: 457.3996.

Repolymerization. Diol **6** (200 mg, 438 μ mol, 1.00 equiv.) and hexamethylene diisocyanate (70.8 μ l, 73.7 mg, 438 μ mol, 1.00 equiv.) were added into a 1.5 ml screw-cap vial. The mixture was heated to 160 °C until a homogeneous solution formed and was then stirred for another 1 h. After cooling to room temperature, the reaction mixture was dissolved in hexafluoroisopropanol and precipitated into cold methanol. The precipitate was filtrated, washed with methanol and dried at 70 °C and 10 mbar to obtain 125 mg of polymer (46%).

Results and discussion

A literature known ruthenium catalyzed oxidative cleavage was used to synthesize the tricarboxylic acid glyceryl triazolate from high oleic sunflower oil (Scheme 1).^[32] The catalytic reaction was first reported by Behr *et al.* in 2013 for the oxidative cleavage of methyl oleate and was further optimized for the oxidative cleavage of high oleic sunflower oil (Scheme 1) by Meier *et al.*^[27] Key features are the use of hydrogen peroxide as greener oxidant, use of the benign solvents *tert*-butanol and water, and the tolerance towards ester groups as they remain uncleaved during this transformation. The successful isolation of the sunflower oil-based tricarboxylic acid was confirmed by 1H NMR, ^{13}C NMR, and IR spectroscopy as well as mass spectrometry (Supporting Information). In the 1H NMR spectrum, a minor methyl proton integral is visible at 0.85 ppm (Figure S3). It was assumed that this signal corresponds to the formation of a dicarboxylic acids due to the presence of saturated fatty acid residues in the used sunflower oil, which are inert to the performed reaction. This is reasonable, since the used sunflower oil contained 7% saturated palmitic acid and stearic acid. The small integral of 0.17 corresponds to approximately 5% dicarboxylic acids. Hence, the isolated compound is practicably a tricarboxylic acid and will therefore be referred to as “triacid” in the following. The amount of carboxylic acid groups per gram of sample was determined quantitatively by ^{31}P NMR spectroscopy according to a procedure introduced by Kilpeläinen *et al.*^[29, 30] In this method, carboxylic acid and hydroxyl groups of the sample are first transformed to their corresponding phosphite esters by reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and then quantified by ^{31}P NMR spectroscopy using an internal standard. The determined carboxylic acid value of 4.95 μ mol CO_2H per mg of sample is almost identical to



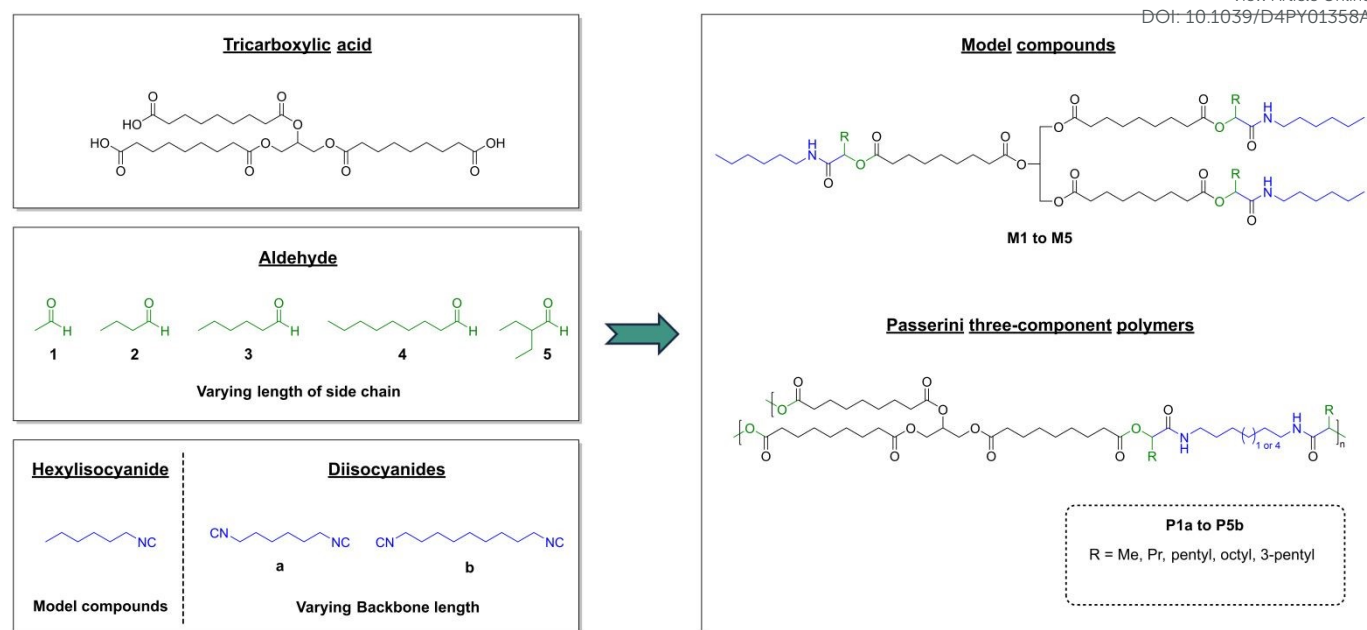
Scheme 1: Ruthenium catalyzed oxidative cleavage of high oleic sunflower oil (DPA: pyridine-2,6-dicarboxylic acid, Ru(acac)₃: ruthenium(III)acetylacetonate).

the carboxylic acid value of glyceryl triazolate (4.98 μ mol CO_2H per mg), again confirming the successful synthesis of the desired triacid.

Five model substances (**M1–M5**) were synthesized from the sunflower oil-based triacid, *n*-hexylisocyanide, and the five aldehydes acetaldehyde (**1**), butanal (**2**), hexanal (**3**), nonanal (**4**), and 2-ethylbutyraldehyde (**5**) to investigate the suitability of the triacid for Passerini three-component reactions and to obtain soluble compounds that allow full molecular characterization (Scheme 2). Each model compound was synthesized by stirring all three components for 3 days at room temperature. After purification by flash column chromatography, good yields between 50% and 70% were achieved. All model compounds were fully characterized by 1H NMR, ^{13}C NMR and IR spectroscopy as well as mass spectrometry (Supporting information). Exemplarily, the 1H NMR spectrum of compound **M4** is depicted in Figure 1. Characteristic signals for Passerini products such as amide protons at 6.03 ppm as well as CH protons of the newly formed α -acyloxy amide group at 5.13 ppm were detected.^[17, 18] Moreover, signals of the glyceryl ester moiety at 5.23 ppm and 4.12–4.27 ppm and signals of α -CH₂ protons of ester groups at 2.29 ppm and 2.36 ppm were observed and therefore confirmed the successful isolation of the trifunctional Passerini product as a proof of concept.

The sunflower oil-based triacid was then reacted with aldehydes **1–5** and the two difunctional isocyanides 1,6-diisocyanohexane (**a**) and 1,9-diisocyanononane (**b**) for the synthesis of ten different cross-linked polymers *via* the Passerini three-component reaction (Scheme 2). All aldehyde and isocyanide components were chosen to be aliphatic and at least in principle renewable. For instance, 1,6-diisocyanohexane was synthesized from hexamethylenediamine, which can be produced from adiponitrile by hydrogenation.^[33] Adiponitrile can be synthesized from ammonia and adipic acid, which in turn can be produced biotechnologically from sugars.^[34, 35, 36] Another feasible route to hexamethylenediamine from adipic acid is the reduction of adipic acid ester to 1,6-hexanediol, which is then reacted with ammonia to yield the diamine.^[33] 1,9-Diaminononane, the starting material for 1,9-diisocyanononane, can most likely be produced in the same way from azelaic acid, which is obtained industrially by oxidative cleavage of oleic acid.^[37, 38] A biotechnological route to 1,9-diaminononane starting from oleic acid was recently reported by Park *et al.*^[39] All unbranched aldehydes occur in natural oils and can further be synthesized by dehydrogenation





Scheme 2: Synthesis of model compounds **M1–M5** (top right) and polymers **P1a–P5b** (bottom right) via Passerini three-component reaction from the sunflower oil-based tricarboxylic acid, the five aldehydes acetaldehyde (**1**) butanal (**2**), hexanal (**3**), nonanal (**4**), 2-ethylbutyraldehyde (**5**), and the three isocyanides *n*-hexylisocyanide, 1,6-diisocyanohexane (**a**) and 1,9-diisocyanononane (**b**).

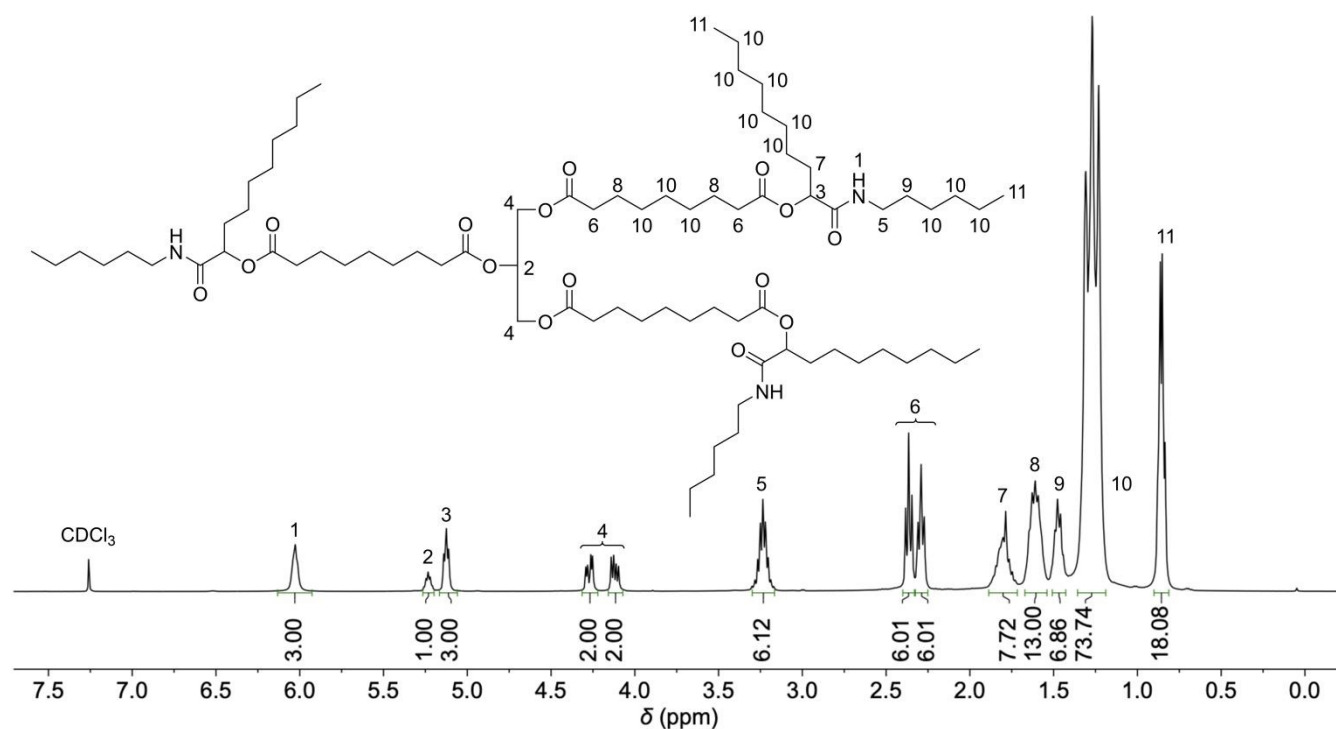


Figure 1: ^1H NMR spectrum of **M4** in CDCl_3 . Integrals are referenced to protons **4** of the glycerol moiety.

of the primary alcohols.^[40, 41, 42] 2-Ethylbutyraldehyde is obtained by aldol condensation of butanal with acetaldehyde and subsequent hydrogenation.^[42]

All polymerizations were performed in bulk, as all compounds were liquid at room temperature. First, the three

components were mixed at $-20\text{ }^\circ\text{C}$ to guarantee a homogeneous mixture of all compounds before the polymerization started, as very rapid curing was observed in bulk. Then, the mixture was casted into a poly(tetrafluoroethylene) form to produce bone shaped



samples for tensile strength measurements. Polymers **P1a** to **P3b** (please see Scheme 1 for compound labeling) were cured at 5 °C for 30 minutes to prevent evaporation of the volatile aldehyde components, while polymers **P4a** to **P5b** were cured at room temperature for 30 minutes. All polymers were further cured at 50 °C for 24 h to guarantee full conversion of functional groups. For polymers **P4a** and **P4b**, a fast reaction was observed as the samples completely solidified after 5 minutes of curing at room temperature, while polymers **P5a** and **P5b** with the sterically more demanding 2-ethylbutyraldehyde took longer to solidify (10 minutes). It is therefore potentially possible to further increase the curing time by incorporating sterically more demanding and/or less reactive substrates into the polymer formulation. The reaction completeness was investigated qualitatively *via* infrared spectroscopy. IR spectra of the sunflower-oil based triacid, nonanal (**4**), 1,6-diisocyanohexane (**a**), model compound **M4**, and polymer **P4a** are exemplarily depicted in Figure 2. Characteristic IR signals of the starting materials, such as the C=O stretching vibration of carboxylic acids at 1703 cm⁻¹, the COH combination band of aldehydes at 2823 cm⁻¹ and 2714 cm⁻¹, and the stretching vibration of isocyanides at 2146 cm⁻¹ were neither visible in the IR spectra of model compound **M4** nor for polymer **P4a**. In the IR spectrum of **M4**, characteristic signals for amide groups, such as the N–H stretching vibration (3305 cm⁻¹), the C=O stretching vibration (1655 cm⁻¹), and N–H deformation vibration (1537 cm⁻¹) were observed. The IR spectrum of polymer **P4a** was identical to the one of **M4**, thereby confirming the successful P-3CR polymerization with near quantitative conversion of all functional groups.

Swelling tests of all polymers were performed to further evaluate the degree of cross-linking. Each polymer was weighed and immersed in tetrahydrofuran for 3 days at room temperature to allow the complete solubilization of residual unreacted monomeric and oligomeric compounds inside the

material. The polymer was then removed from the solvent, dried at 70 °C and 10 mbar, and weighed again. The gel content is the percentage of mass that is insoluble in THF and is therefore calculated by division of the dried sample's mass m_1 by the initial sample's mass m_0 (Equation (1)).

$$\text{Gel content (\%)} = \frac{m_1}{m_0} \times 100 \quad (1)$$

The determined values for the gel content of all polymers were between 96% and 99% (Table 1). Hence, both the results obtained from IR spectroscopy and the high gel contents from the swelling tests show that the P-3CR polymerization is suitable for thermosetting applications, as very high conversions and high degrees of cross-linking are achieved.

The thermal stability of all materials was analyzed using thermogravimetric analysis (TGA). The obtained values for the temperature of 5 wt% loss ($T_{d,5\%}$) of polymers **P1a**–**P5b** ranged from 340 °C to 365 °C and were approximately 20 °C higher than the $T_{d,5\%}$ values of model compounds **M1**–**M5** (321 °C to 344 °C). Variation of aldehyde and isocyanide components had almost no influence on the thermal stability, as all polymers as well as all model compounds decomposed in a temperature range of 10 °C, respectively. Studies by Li *et al.* reported a $T_{d,5\%}$ value of 335 °C for a P-3CR polymer synthesized from adipaldehyde, 1,6-diisocyanohexane, and undecanoic acid as well as $T_{d,5\%}$ values ranging from 291 °C to 316 °C for polycaprolactone derivatives synthesized *via* P-3CR from 6-oxohexanoic acid and aliphatic isocyanides.^[17, 18] For aliphatic poly(ester-amides), $T_{d,5\%}$ values ranging from 267 °C to 290 °C were reported.^[43] A degradation temperature of 313 °C was reported for renewable isosorbide containing P-3CR polymers.^[44] The herein synthesized cross-linked polymers therefore exhibit an improved thermal stability compared to many linear P-3CR polymers.

Differential scanning calorimetry experiments revealed that all polymers showed glass transition temperatures (T_g) below

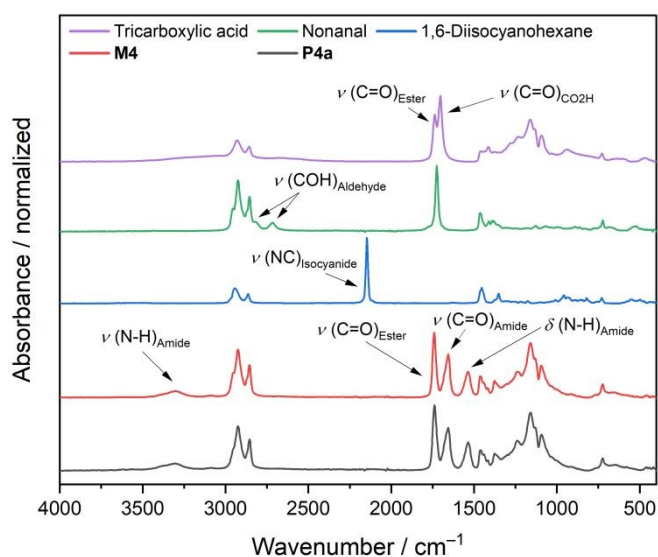


Figure 2: Stacked IR spectra of sunflower oil-based tricarboxylic acid, nonanal (**4**), 1,6-diisocyanohexane (**a**), model compound **M4**, and polymer **P4a**. Each IR spectrum is normalized to the strongest absorbance vibration.

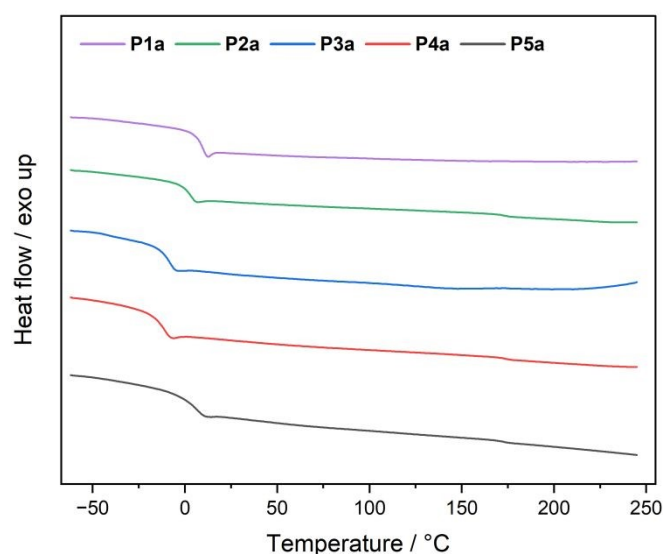


Figure 3: Differential scanning calorimetry measurements of polymers series **a**.



room temperature (Table 1). Exemplarily, all DSC measurements of the polymer series **a** are depicted in Figure 3.

The glass transition temperature decreased gradually with an increasing aldehyde side chain length from

acetaldehyde (**P1a**) with 9 °C to nonanal (**P4a**) with -12 °C. The T_g of **P5a** was identical to **P2a**, presumably due to the similar steric hindrance of 2-ethylbutyraldehyde and butanal.

Table 1: Polymers **P1a** to **P5b** with their gel content in tetrahydrofuran, temperature of 5 weight% loss ($T_{d,5\%}$), glass transition temperature (T_g), Young's modulus, ultimate tensile strength, and their elongation at break. The given error values are standard deviations calculated from three measurements.

Polymer	Gel content in THF / %	$T_{d,5\%}$ / °C	T_g / °C	Young's Modulus / MPa	Ultimate Tensile Strength / MPa	Elongation at break / %
P1a	98 ± 2	363	9	2.16 ± 0.41	1.64 ± 0.29	104 ± 8
P1b	96 ± 2	362	4	1.78 ± 0.40	1.34 ± 0.31	101 ± 2
P2a	96 ± 1	346	3	1.84 ± 0.10	1.45 ± 0.20	105 ± 10
P2b	98 ± 1	365	1	2.11 ± 0.08	1.68 ± 0.21	109 ± 13
P3a	97 ± 2	357	-8	1.86 ± 0.08	1.24 ± 0.03	84 ± 4
P3b	96 ± 2	363	-12	1.44 ± 0.09	0.92 ± 0.14	81 ± 16
P4a	97 ± 1	362	-12	1.24 ± 0.02	0.85 ± 0.01	91 ± 1
P4b	97 ± 1	364	-18	1.27 ± 0.04	0.87 ± 0.05	90 ± 6
P5a	98 ± 1	333	3	1.35 ± 0.04	2.20 ± 0.33	214 ± 26
P5b	99 ± 1	343	0	1.95 ± 0.05	1.98 ± 0.23	146 ± 14

The same relationship between T_g and side chain length is observed for the polymer series **b** (Table 1, Figure S31). Interestingly, every **a** polymer had a slightly higher T_g than the respective polymer from the **b** series. 1,9-Diisocyanononane (series **b**) is three carbon atoms longer than 1,6-diisocyanohexane (series **a**), resulting, on the one hand, in a lower density of amide groups per repeating unit and thus in less hydrogen bonding and on the other hand in a larger mesh size. Both factors contribute to a higher T_g in the **a** series.

Tensile strength measurements were performed to evaluate the mechanical properties of all samples. The manufactured samples as well as one exemplary measurement of **P4a** are depicted in Figure 4a. All samples behaved flexible and could be bent by 180 °C without breaking. Moreover, linear elastic regions of at least 20% were observed for each measurement (Figure S33–S42). The determined Young's moduli are in the region on rubber-like materials and ranged from 1.24 MPa to 2.16 MPa (Table 1).

Ultimate tensile strengths were in the range of the 0.85 MPa to 2.20 MPa and the determined elongations at break ranged from 81% up to a maximum of 214%. It was observed that the Young's modulus decreases slightly but gradually with an increasing side chain length from **P1a** to **P4b**. Polymers **P2a** to **P5b** showed great reproducibility in preparation of samples and had standard deviations between 1% to 5% for the Young's modulus and a maximum of 15% for the ultimate tensile strength. The high standard deviations of approximately 20% for **P1a** and **P1b** are attributed to the low boiling point of acetaldehyde and hence a more difficult reproducibility.

Due to the fast curing of all polymers at room temperature, a potential application as "three component glues" was imagined. For this proof of concept, polymer **P5a** was chosen since the sterically more demanding 2-ethylbutyraldehyde significantly increased the curing time and enabled a

reproducible manufacturing of adhesive test samples. The substrates to be glued together were prepared by cutting aluminum alloy, stainless-steel, wood, poly(methyl methacrylate), and borosilicate glass into rectangular pieces. Polymer **P5a** was freshly prepared and applied onto two pieces of the same substrate. The two surfaces were then pressed together and cured at room temperature for 2 h. Afterwards, each substrate was measured in triplicate to determine the ultimate tensile strength. The prepared samples and the measurements performed with stainless-steel as substrate are depicted in Figure 4b.

The adhesion of **P5a** ranged from 0.94 MPa to 1.17 MPa for all surfaces expect for stainless-steel, for which a stronger adhesion of 1.88 MPa was accomplished. In further experiments, wood surfaces were glued together and measured after 30 minutes, 60 minutes, and 120 minutes had passed (Figure S46). Already after 60 minutes of curing at room temperature, no further increase of the tensile strength could be detected, indicating a fully cured glue. These results prove that a multicomponent approach can be used to manufacture new thermosetting glues and that different substrates can be glued efficiently.

At last, chemical degradation of polymer **P4a** was investigated to demonstrate a possible way to reutilize all components in a second life cycle after the materials have reached their end of life. It was assumed that transesterification of **P4a** with methanol yields the three products glycerol, azelaic acid dimethyl ester, and the difunctional α -hydroxyamide **6** (Scheme 3).

It should be noted that this approach of P-3CR reaction and subsequent transesterification has already been utilized in literature for the targeted synthesis of α -hydroxyamides.^[45, 46] Hence, three grams of **P4a** were suspended in methanol and catalytic amounts of sulfuric acid were added. Intriguingly, the



thermoset had completely dissolved after heating the reaction mixture to 65 °C for 5 h. Diol **6** precipitated as a white powder from the reaction mixture while cooling to room temperature and was thus easily isolated by filtration in a yield of 74% (1.26 g). The compound had a high melting point of 162 °C and was poorly soluble in common organic solvents due to the

vacuum distillation of the organic phase in a yield of 75% (1.18 g) and glycerol was isolated by vacuum distillation of the aqueous phase in a yield of 30% (68 mg). The low glycerol yield is attributed to the small scale of recycling as 227 mg of glycerol corresponded to 100% yield. The chemical recycling of **P4a** was therefore successful with a simple transesterification

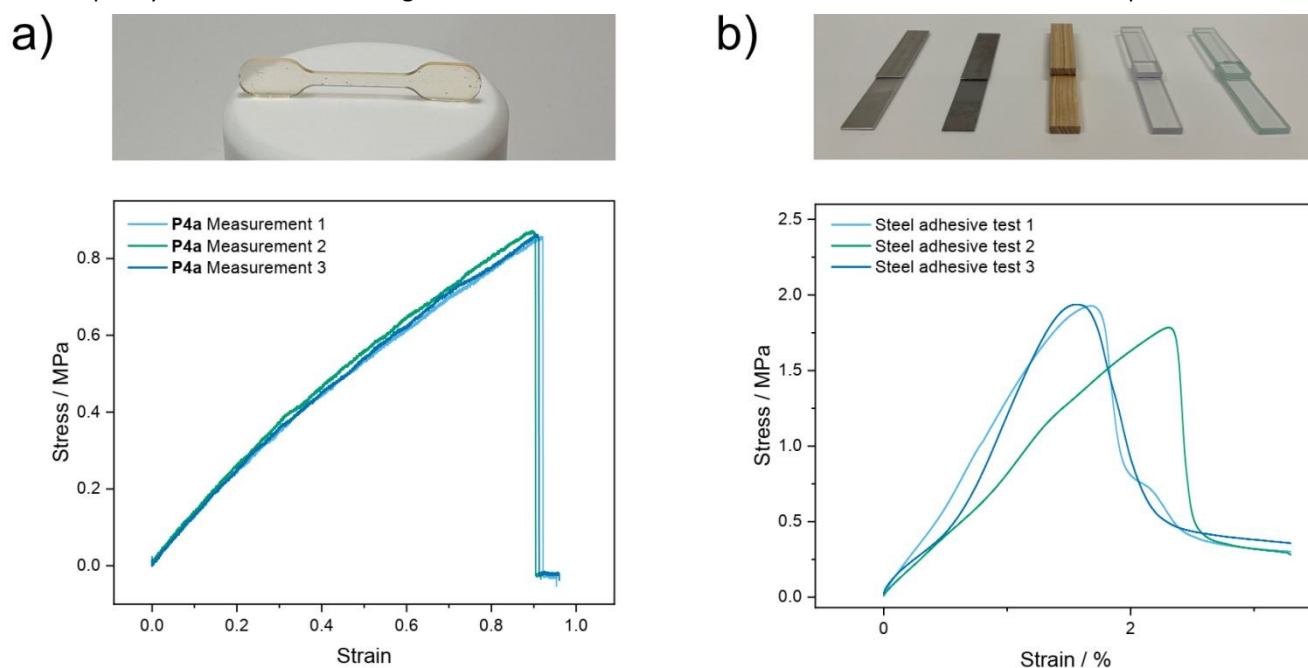
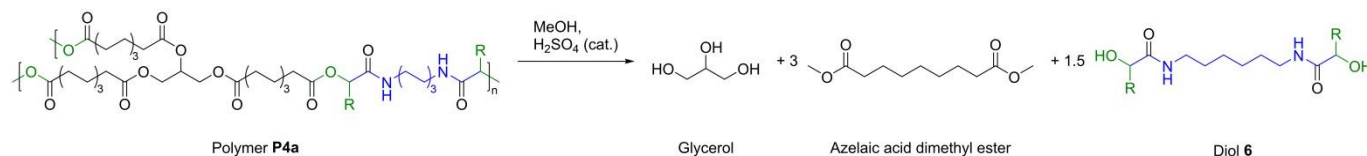


Figure 2: Dog bone sample of polymer **P4a** with the associated tensile strength measurements (a) and adhesive test samples prepared from polymer **P5a** and different substrates (aluminum, stainless, wood, PMMA, borosilicate glass) with the adhesive tests of stainless-steel after 2 h of curing at room temperature (b).

strong hydrogen bonding that originates from its amide groups. The molecular structure was confirmed by mass spectrometry and by NMR spectroscopy in deuterated trifluoroacetic acid (Figures S49–50). In the ^1H NMR spectrum, the alpha amide proton signal is shifted downfield to 4.63 ppm due to the electron withdrawing effect of the hydroxy group. This was further confirmed by heteronuclear multiple bond correlation (HMBC) spectroscopy that showed correlation between this signal and the quaternary carbon atom of the amide at 180.7 ppm (Figure S51). Moreover, characteristic signals of the amide functionality such as the C=O stretching vibration at 1638 cm^{-1} , the N–H stretching vibration at 3243 cm^{-1} , and the N–H deformation vibration at 1543 cm^{-1} were observed in IR spectroscopy.

Methanol was then removed from the filtrate under reduced pressure. The residue that still contained a mixture of azelaic acid dimethyl ester and glycerol was extracted with ethyl acetate and washed with water to separate both compounds. Azelaic acid dimethyl ester was obtained in high purity by

approach. Noteworthy, azelaic acid dimethyl ester is an industrially relevant compound, which is used for cosmetic applications and the manufacture of polymers such as polyamides and polyesters.^[47, 48, 49] It was desired to repolymerize diol **6** with azelaic acid dimethyl ester to show that the recycled compounds can directly be incorporated into a new material. However, several polymerization efforts in bulk at 160 °C under 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalysis yielded only oligomeric compounds with an average molecular weight of 1900 Da (Figure S54). Unfortunately, also other catalysts (i.e. KOtBu or Sb_2O_3) did not lead to successful polymerization. The apparently low reactivity of **6** towards transesterification renders this diol with secondary hydroxyl groups impractical for poly(ester-amide) synthesis. Alternatively, it was discovered that diol **6** reacted readily with isocyanates in bulk. A reaction with hexamethylene diisocyanate yielded a poly(amide-urethane) with an average molecular weight of 17 kDa already after one hour of reaction time at 160 °C (Figure S55). The polymer structure was further



Scheme 3: Chemical recycling of polymer **P4a** by transesterification with methanol and catalytic amounts of sulfuric acid.



elucidated *via* NMR spectroscopy (Figures S56–57). In the ^1H NMR spectrum, characteristic amide and urethane protons were visible at 6.89 ppm and 5.85 ppm, respectively. The corresponding quaternary carbon signals were observed at 171.5 ppm and 155.8 ppm in the ^{13}C NMR spectrum. Although the use of isocyanates is rather unsustainable, we have demonstrated one possible way to reuse this difunctional α -hydroxyamide. Apart from this polymer application, α -hydroxyamides are found in pharmaceutical, and natural products.^[50, 51]

Conclusions

A multicomponent polymerization approach for the synthesis of thermosets from a sunflower oil-derived tricarboxylic acid is presented. The triacid was produced from commercial sunflower oil *via* a ruthenium catalyzed oxidative cleavage, which uses hydrogen peroxide as greener oxidant.^[27, 32] As proof of concept for the multicomponent approach, five model compounds were synthesized *via* the Passerini three-component reaction (P-3CR) and fully characterized *via* ^1H NMR, ^{13}C NMR, and IR spectroscopy and mass spectrometry. Afterwards, a set of ten P-3CR thermosets was synthesized from the triacid in combination with five monoaldehydes and two diisocyanides. The polymerization proceeds readily at room temperature and was performed without any additional solvents, rendering this process more sustainable. IR spectroscopy of the cured thermosets indicated a quantitative conversion of all aldehyde and isocyanide groups. Gel contents between 96% and 99% in THF point towards high degrees of cross-linking in all materials. Differential scanning calorimetry experiments revealed structure property relationships, it was possible to fine-tune the glass transition temperature in a range from $-18\text{ }^\circ\text{C}$ to $9\text{ }^\circ\text{C}$ by variation of aldehyde and diisocyanide components. With increasing side chain length as well as increasing length of the diisocyanide, a gradual decrease of the T_g was observed. In tensile strength measurements, Young's moduli ranging from 1.24 MPa to 2.16 MPa, and elongations at break between 81% and 214% were determined. The presented system can be used as a "three component glue" since all compounds are liquid and no additional heating was required for curing. After 60 minutes of curing at room temperature, the adhesive exhibited ultimate tensile strengths between 0.94 MPa and 1.88 MPa on aluminum, steel, wood, PMMA, and glass surfaces. At last, chemical reuse of polymer **P4a** was achieved by transesterification with methanol and catalytic amounts of sulfuric acid. The difunctional α -hydroxyamide **6** precipitated during recycling and was isolated in a good yield of 74%, while azelaic acid dimethyl ester was obtained by vacuum distillation in a yield of 75%. Eventually, a new polyurethane was synthesized from diol **6** and hexamethylene diisocyanate to exemplify a second life cycle of the recycled compound.

Author contributions

Luis Santos Correa: Conceptualization, data curation, formal analysis, investigation (synthesis and analytics), visualization, writing—original draft; Silas Leidenheimer: Investigation (synthesis); Michael A. R. Meier: Conceptualization, resources, supervision, writing—review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supporting Information.

Acknowledgements

The authors thank Prof. Dr. Manfred Wilhelm and Dr. Valerian Hirschberg for their support with tensile strength measurements and Alexander Jaks for manufacturing the required customized poly(tetrafluoroethylene) forms. Furthermore, the authors thank Prof. Dr. Stefan Bräse, Prof. Dr. Jörg Lahann, Prof. Dr. Patrick Théato, and Birgit Huber for TGA measurements, Lara Hirsch for mass spectrometric measurements, Timo Sehn for fruitful discussions, and Severin Stalter for his help on the synthesis of a few compounds.

Notes and references

- [1] PlasticsEurope Deutschland e. V., *Plastics – the fast Facts 2023*, **2023**, <https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/>; access date: 07.11.2024.
- [2] U. Biermann, U. T. Bornscheuer, I. Feussner, M. A. R. Meier, J. O. Metzger, *Angew. Chem. Int. Ed.*, **2021**, *60*, 20144–20165.
- [3] L. Montero de Espinosa, M. A. R. Meier, *Eur. Polym. J.*, **2011**, *47*, 837–852.
- [4] S. Pandey, B. S. Rajput, S. H. Chikkali, *Green Chem.*, **2021**, *23*, 4255–4295.
- [5] J. C. Ronda, G. Lligadas, M. Galià, V. Cádiz, *Eur. J. Lipid Sci. Technol.*, **2011**, *113*, 46–58.
- [6] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, **1998**.
- [7] H. C. Erythropel, J. B. Zimmerman, T. M. de Winter, L. Petitjean, F. Melnikov, C. H. Lam, A. W. Lounsbury, K. E. Mellor, N. Z. Janković, Q. Tu, L. N. Pincus, M. M. Falinski, W. Shi, P. Coish, D. L. Plata, P. T. Anastas, *Green Chem.*, **2018**, *20*, 1929–1961.
- [8] I. Ugi, A. Dömling, W. Hörl, *Endeavour*, **1994**, *18*, 115–122.
- [9] A. Dömling, W. Wang, K. Wang, *Chem. Rev.*, **2012**, *112*, 3083–3135.
- [10] R. C. Cioc, E. Ruijter, R. V. A. Orru, *Green Chem.*, **2014**, *16*, 2958–2975.
- [11] M. Passerini, *Gazz. Chem. Ital.*, **1921**, *51*, 126–129.
- [12] A. Dömling, I. Ugi, *Angew. Chem. Int. Ed.*, **2000**, *39*, 3168–3210.
- [13] L. Banfi, A. Basso, C. Lambruschini, L. Moni, R. Riva, *Chem. Sci.*, **2021**, *12*, 15445–15472.



- [14] I. Akritopoulou-Zanze, *Curr. Opin. Chem. Biol.*, **2008**, *12*, 324-331.
- [15] O. Kreye, T. Tóth, M. A. R. Meier, *J. Am. Chem. Soc.*, **2011**, *133*, 1790-1792.
- [16] X.-X. Deng, L. Li, Z.-L. Li, A. Lv, F.-S. Du, Z.-C. Li, *ACS Macro Letters*, **2012**, *1*, 1300-1303.
- [17] Y.-Z. Wang, X.-X. Deng, L. Li, Z.-L. Li, F.-S. Du, Z.-C. Li, *Polym. Chem.*, **2013**, *4*, 444-448.
- [18] J. Zhang, M. Zhang, F.-S. Du, Z.-C. Li, *Macromolecules*, **2016**, *49*, 2592-2600.
- [19] S. König, I. Ugi, *Zeitschrift für Naturforschung B*, **1991**, *46*, 1261-1266.
- [20] H. Bu, A.-L. Kjøniksen, K. D. Knudsen, B. Nyström, *Biomacromolecules*, **2004**, *5*, 1470-1479.
- [21] H. Bu, A.-L. Kjøniksen, B. Nyström, *Eur. Polym. J.*, **2005**, *41*, 1708-1717.
- [22] A. E. J. de Nooy, D. Capitani, G. Masci, V. Crescenzi, *Biomacromolecules*, **2000**, *1*, 259-267.
- [23] V. Crescenzi, A. Francescangeli, D. Capitani, L. Mannina, D. Renier, D. Bellini, *Carbohydr. Polym.*, **2003**, *53*, 311-316.
- [24] A. E. J. de Nooy, G. Masci, V. Crescenzi, *Macromolecules*, **1999**, *32*, 1318-1320.
- [25] N. Hauck, N. Seixas, S. P. Centeno, R. Schlüßler, G. Cojoc, P. Müller, J. Guck, D. Wöll, L. A. Wessjohann, J. Thiele, *Polymers*, **2018**, *10*, 1055.
- [26] W. Lin, T. Sun, M. Zheng, Z. Xie, Y. Huang, X. Jing, *RSC Advances*, **2014**, *4*, 25114-25117.
- [27] L. Santos Correa, M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, **2023**, *125*, 2200171.
- [28] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.*, **1978**, *43*, 2923-2925.
- [29] A. W. T. King, J. Jalomäki, M. Granström, D. S. Argyropoulos, S. Heikkinen, I. Kilpeläinen, *Analytical Methods*, **2010**, *2*, 1499-1505.
- [30] X. Meng, C. Crestini, H. Ben, N. Hao, Y. Pu, A. J. Ragauskas, D. S. Argyropoulos, *Nature Protocols*, **2019**, *14*, 2627-2647.
- [31] K. A. Waibel, R. Nickisch, N. Möhl, R. Seim, M. A. R. Meier, *Green Chem.*, **2020**, *22*, 933-941.
- [32] A. Behr, N. Tenhumberg, A. Wintzer, *RSC Advances*, **2013**, *3*, 172-180.
- [33] B. D. Herzog, R. A. Smiley, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2012**.
- [34] M. T. Musser, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2000**.
- [35] J. Rios, J. Lebeau, T. Yang, S. Li, M. D. Lynch, *Green Chem.*, **2021**, *23*, 3172-3190.
- [36] R. A. Sheldon, *J. Mol. Catal. A: Chem.*, **2016**, *422*, 3-12.
- [37] *Chem. Eng. News*, **1959**, *37*, 25-26.
- [38] C. G. Goebel, A. C. Brown, H. F. Oehlschlaeger, R. P. Rolfes, *Method of making azelaic acid*, US 2813113, **1957**.
- [39] S.-Y. Hwang, J.-M. Woo, G. E. Choi, D.-K. Oh, J.-H. Seo, J.-B. Park, *ACS Catalysis*, **2024**, *14*, 4130-4138.
- [40] M. Eckert, G. Fleischmann, R. Jira, H. M. Bolt, K. Golka, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2006**.
- [41] D. K. Raff, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2013**.
- [42] C. Kohlpaintner, M. Schulte, J. Falbe, P. Lappe, J. Weber, G. D. Frey, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2013**.
- [43] Y.-T. Guo, C. Shi, T.-Y. Du, X.-Y. Cheng, F.-S. Du, Z.-C. Li, *Macromolecules*, **2022**, *55*, 4000-4010.
- [44] Z. Söyler, K. N. Onwukamike, S. Grelier, E. Gray, H. Cramail, M. A. R. Meier, *Green Chem.*, **2018**, *20*, 2142-2149. NEW ARTICLE ONLINE
- [45] R. M. Carrillo, A. G. Neo, L. López-García, S. Marcaccini, C. F. Marcos, *Green Chem.*, **2006**, *8*, 787-789. DOI: 10.1039/B5PY01358A
- [46] M. Shiri, Z. Gholami-Koupaei, F. Bandehali-Naeini, M.-S. Tonekaboni, S. Soheil-Moghaddam, D. Ebrahimi, S. Karami, B. Notash, *Synthesis*, **2020**, *52*, 3243-3252.
- [47] A. Fitton, K. L. Goa, *Drugs*, **1991**, *41*, 780-798.
- [48] A. Köckritz, A. Martin, *Eur. J. Lipid Sci. Technol.*, **2011**, *113*, 83-91.
- [49] B. Cornils, P. Lappe, in *Ullmann's Encyclopedia of Industrial Chemistry*, **2014**, pp. 1-18.
- [50] H. A. Schenck, P. W. Lenkowski, I. Choudhury-Mukherjee, S.-H. Ko, J. P. Stables, M. K. Patel, M. L. Brown, *Biorg. Med. Chem.*, **2004**, *12*, 979-993.
- [51] M. R. Wood, K. M. Schirripa, J. J. Kim, S. D. Kuduk, R. K. Chang, C. N. Di Marco, R. M. DiPardo, B.-L. Wan, K. L. Murphy, R. W. Ransom, R. S. L. Chang, M. A. Holahan, J. J. Cook, W. Lemaire, S. D. Mosser, R. A. Bednar, C. Tang, T. Prueksaritanont, A. A. Wallace, Q. Mei, J. Yu, D. L. Bohn, F. C. Clayton, E. D. Adarayn, G. R. Sitko, Y. M. Leonard, R. M. Freidinger, D. J. Pettibone, M. G. Bock, *Bioorganic & Medicinal Chemistry Letters*, **2008**, *18*, 716-720.



The data supporting this article have been included within the article and as part of the Supplementary Information. [View Article Online](#)
DOI: 10.1039/D4PY01358A

