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Supporting information

Reversible hetero-Diels-Alder amine hardener as drop-in replacement for healable epoxy coatings

Sinu C. Rajappan[‡a], Brad J. Davis[‡a],Isaiah T. Dishner[a], Travis L. Thornell[b], John J. Peyrefitte[a], and Yoan C. Simon[a]*

*Corresponding authors

[a]118 College Dr. Hattiesburg Mississippi, 39406, USA
Email: yoan.simon@usm.edu
[b]Environmental Laboratory, U.S. Army Engineer Research and Development Center, 3909 Halls Ferry Road, Vicksburg, MS 39180, USA

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‡ These authors contributed equally to this work

Contents

I. Materials and methods

Tetrahydrofuran (THF) and chloroform were purchased from Fisher Scientific and collected from a solvent purification system (PureSolv MD 5, INERT Technology). Anhydrous solvents: methanol (Alfa Aesar), ethyl acetate (Sigma Aldrich), and dichloromethane (ACS grade Fisher) were dried over activated 4-Å molecular sieves. The following reagents: (1-(3-dimethyl aminopropyl)-3-ethyl carbodiimide) hydrochloride (EDC·HCl) (Oakwood, 99%), *N,N*-dimethyl-4-aminopyridine (DMAP) (Acros), sodium sulfate (Fisher Chemical)), Methyl ricinoleate (TCI chemicals, >75%), triethylenetetramine (TETA) (60%, Huntsman Petroleum), potassium hydroxide (Fisher Chemical), Methanol (Fisher Chemical, ACS grade), ethanol (Decon laboratories, 200 proof), hexanes (Fisher Chemical), ethyl acetate (Fisher Chemical), dichloromethane (Fisher Chemical, ACS grade), and chloroform (Fisher Chemical, ACS grade) were used as received. HCl (0.1 N) in isopropanol was purchased from Fisher chemical for titration. Food grade castor oil (Humco) was purchased from Walmart. The epoxy resins were obtained from Hexion Inc., USA. Hydrogenated dimer acid (C-36 fatty acid, CAS 68783-41-5, average Mn ~570), ethylenediamine (>99%), and benzyl alcohol (99.8%) were purchased from Sigma Aldrich. 4-((((Diethoxyphosphoryl)carbonothioyl) thio)methyl)-benzoic acid (PDTMBA) was synthesized according to the previous literature procedure.[1] Type II Millipore deionized (DI) water was used throughout the process. Aluminum sheets (multipurpose 6061) were purchased from McMaster-Carr Supply Company and cut into 6” x 3” x 0.025” rectangles.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance AVANCE III spectrometer at 600 MHz (^{1}H) and 151 MHz (^{13}C), respectively. All chemical shifts were referenced to TMS at 0 ppm or $CDCl_3$ at 7.26 ppm. ^{1}H NMR and ^{13}C NMR spectra were recorded at 298 K. For many of our synthesis, we utilized crude products which also contained multiple isomers. Not all of the potential isomers are depicted or assigned. Our NMR assignments may refer to a single isomer with tentative peak assignments in the case of the crude product being a a mixture of compounds. High-resolution mass spectra were recorded on the Waters Synapt XS instrument.

Thermogravitric analysis (TGA) was performed on a TGA 500 (TA Instruments, USA). Polymer coating was removed from aluminum substrate post-cure and heated to 600°C under a nitrogen atmosphere at 10°C min^{-1} from ambient using platinum pans. Differential scanning calorimetry (DSC) was performed on a Discovery DSC 250 (TA Instruments, USA). Differential scanning calorimetry measurements were carried out under N_2 on a DSC Q100 (TA Instruments, USA) at a heating and cooling rate of 10 C min^{-1} and 5°C min^{-1}, respectively, in sealed, hermetic aluminum pans. Coating sample was heated from 40°C to 125°C, cooled to -50°C, and then reheated to 125°C.

II. Synthesis

*Sulfonylation of castor oil (**1**)*

An oven-dried 500-mL round-bottom flask (RBF) was charged with castor oil (20 g, 21.4 mmol, 1 equiv.) and dry chloroform (100 mL). Triethylamine (9 mL, 64.7 mmol, 3 equiv.) was added and the solution was cooled in an ice bath. Methane sulfonyl chloride (5 mL, 64.7 mmol, 3 equiv.) in chloroform (20 mL) was slowly added, and the reaction mixture was stirred for 2 h at room temperature. Upon completion, the reaction mixture was diluted with DCM (50 mL), followed by HCl (1 N, 15 mL), and water (100 mL). The product was extracted with additional DCM (2 x 50 mL). The combined organic layers were washed with water (2 x 75 mL) and then dried over anhydrous sodium sulfate; upon filtration, the solvent was removed by rotary evaporation. The crude product obtained was used for the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.57 – 5.48 (m, –CHC*H*CH_2O–, 3H), 5.42 – 5.33 (m, –C*H*CHCH_2O–, 3H), 5.27 – 5.21 (m, –C*H*OCO_2–, 1H), 4.72 – 4.63 (m, –C*H*OSO_2–, 3H), 4.32 – 4.26 (dd, J = 11.9, 4.4 Hz, –CH_2OCO–, 2H), 4.16 – 4.12 (dd, J = 11.9, 5.9 Hz, –CH_2OCO–, 2H), 3.01 – 2.97 (s, –SO_3CH_3, 9H), 2.54 – 2.47 (dt, J = 13.9, 6.8 Hz, –CHC*H*HCHO–, 3H), 2.47 – 2.40 (m, –CHCH*H*CHO–, 3H), 2.34 – 2.28 (td, J = 7.6, 3.4 Hz, –CO_2C$H_2$$CH_2$–, 6H), 2.06 – 1.99 (m, –CHCHCH_2–, 6H), 1.74 – 1.64 (m, –CO_2CH_2CH_2–, 4H), 1.64 – 1.56 (m, –CO_2CH_2CH_2–, 4H), 1.45 – 1.25 (m, –CH_2C$H_2$$CH_2$– 52H), 0.92 – 0.85 (t, J = 7.0 Hz, –CH_3, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.32 (CO), 172.91(CO), 133.87, 133.84, 123.21, 123.20, 83.69, 83.67, 69.04, 62.22, 60.48, 38.80, 34.37, 34.28, 34.12, 32.68, 31.76, 29.55, 29.54, 29.29, 29.27, 29.25, 29.23, 29.17, 29.13, 29.11, 27.55, 25.17, 24.97, 24.93, 22.67, 21.14, 14.32, 14.15.

*Conjugated linoleic acid synthesis (**2**)*

In a 500-mL RBF, potassium hydroxide (16 g, 5285.2 mmol, 30 equiv.) was taken in absolute ethanol (200 mL) and stirred for 5 minutes at 80 °C under a nitrogen atmosphere. This solution was then cooled to room temperature and pre-dissolved **1** (11 g, 9.4mmol, 1 equiv.) in ethanol (100 mL) was added. The flask was then equipped with a reflux condenser and the reaction mixture was continued stirring overnight with refluxing at 100 °C. We observed the formation of a yellow waxy solid after 5 minutes of mixing. Upon completion, the reaction mixture was cooled to room temperature and distilled water (200 mL) added to form a clear brown solution. The solution was acidified with HCl (6 N, until pH ~2) and then the organic layer was extracted with hexanes (2 x 75 mL). The combined organic layers were washed with water and then with brine solution (50 mL). The organic layer were dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation. The ^{1}H NMR showed the disappearance of methanesulfonyl (4.62 ppm) and glycerol units (4.28 and 4.13 ppm). The crude material (~8.3 g) obtained in this step was used for the next synthesis without further purification.

*Esterification of conjugated linoleic acid (**3**)*

A 100-mL RBF equipped with a reflux condenser was charged with **2** (8.3 g, 29.6 mmol) and methanol (40 mL). Concentrated sulfuric acid (6 drops) was added to the solution and the reaction was refluxed for 3 h. The completion was monitored by TLC (10 vol % ethyl acetate in hexanes) and the reaction mixture was allowed to cool to room temperature. The solution was then diluted with distilled water (50 mL) and extracted with hexanes (3 x 30 mL). The combined hexanes layers were washed with water (2 x 75 mL) and then brine (25 mL) and dried over anhydrous sodium sulfate. The solvent was then removed by rotary evaporation and the crude was purified by flash chromatography. A gradient of 0 - 3 vol % ethyl acetate in hexanes was used as the eluting mixture and a yellow liquid was isolated (~5.8 g), which contained an isomeric mixture of conjugated linoleic acid methyl esters. The formation of the methyl ester is evidenced by the peak appearing at 3.68 ppm corresponding to 3 protons of the C(O)OCH$_2$C*H$_3$* end group.

1H NMR (600 MHz, CDCl3) δ 6.35 – 5.22 (m, 9-,10-,11-,12-H, 4H), 3.73 – 3.60 (s, C*H*$_3$OC(O)–, 3H), 2.36 – 2.24 (t, –OC(O)C*H*$_2$–, 2 H), 2.22 – 1.95 (m, 8- and 13- *H*$_2$, 4 H), 1.68 – 1.55 (t, –OC(O)CH$_2$C*H*$_2$, 2 H), 1.52 – 1.12 (m, –CH$_2$C*H*$_2$CH$_2$–, 18 H), 0.93 – 0.82 (t, –C*H*$_3$, 3 H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.24, 165.69, 138.91, 132.82, 130.58, 130.08, 129.27, 124.15, 74.92,

64.86, 64.82, 51.43, 39.98, 34.11, 33.75, 32.06, 31.75, 29.52, 29.21, 29.16, 29.12, 29.11, 27.39, 25.42, 24.97, 22.60, 16.35, 16.31, 14.07.

Synthesis of PDTBMA

The PDTMBA was synthesized based on a modified literature procedure.[1] A oven dried 1-L RBF was charged with sodium hydride (3.1 g, 125 mmol, 1.5 equiv.) and dry THF (100 mL) to form a suspension. A solution of diethylphosphite (11 mL, 83.3 mmol, 1 equiv.) in dry THF (125 mL) was slowly added to the RBF. Upon completion of the hydrogen gas evolution at room temperature, the solution was refluxed for 15 min. Subsequently, the solution was cooled to -90 °C using a LN_2/acetone bath and carbon disulfide (24.5 mL, 416.4 mmol, 5 equiv.) was added dropwise through an addition funnel. The mixture was then stirred for 2 h still within the cooling bath, where it began to turn brown. Dry THF (750 mL) was then added and the reaction was transferred to an oven-dried 2-L RBF. A solution of 4-bromomethyl benzoic acid (20.1 g, 91.6 mmol, 1.1 equiv.) in THF (150 mL) was added dropwise through an addition funnel at room temperature. Due to the appearance of a gel-like precipitate, dry THF was occasionally added to the reaction mixture to keep all reagents in solution. The reaction was allowed to stir for 16 h at room temperature. Upon completion, the THF was removed by rotary evaporation. The obtained purple precipitate was dissolved in DCM (150 mL) and washed with water (150 mL). The aqueous layer was washed with additional DCM (2 x 75 mL). The combined organic layers were washed with water (2 x 75 mL) and brine (50 mL). The organic layer was then dried over anhydrous sodium sulfate and filtered. The filtrate was then concentrated by rotary evaporation and purified *via* column chromatography with an increasing gradient of ethyl acetate (20-75%) in hexanes yielding 15.3 g product (51%). ^{1}H NMR (600 MHz, CDCl3) δ 8.08 – 8.03 (d, J = 8.3 Hz, Ar*H*, 2H), 7.44 – 7.39 (d, J = 8.3 Hz, Ar*H*, 2H), 4.56 – 4.53 (s, –ArC*H*$_2$–, 2H), 4.34 – 4.22 (m, –OC*H*$_2$CH$_3$, 4H), 1.41 – 1.34 (m, –OCH$_2$C*H*$_3$–, 3H).

*$ZnCl_2$ mediated synthesis of HDA adduct (**4**)*

Adapted from the literature procedure,[2] an oven-dried RBF under a nitrogen atmosphere and equipped with a reflux condenser was charged with PDTBMA (8.3 g, 23.8 mmol, 1 equiv.), conjugated linoleic acid methyl ester (7.37 g, 25.0 mmol, 1.05 equiv.) and anhydrous ethyl acetate (50 mL). Anhydrous $ZnCl_2$ (3.57 g, 26.2 mmol, 1.1 equiv.) was added and the reaction mixture was continued stirring for 24 h at 80 °C. The reaction was monitored by TLC (50 vol % ethyl

acetate in hexanes) and was cooled to room temperature upon completion. The solvent was removed by rotary evaporation. The crude product was taken up in distilled water (30 mL) and transferred to a separating funnel and acidified with 0.5 N HCl (20 mL). The product was extracted with dichloromethane (3 x 25 mL) and the combined organic layers were washed with water (2 x 50 mL) then brine solution (25 mL), and dried over anhydrous sodium sulfate. Upon solvent evaporation using a rotary evaporator, the crude was purified by flash column chromatography with a gradient of ethyl acetate (0-55 vol%) in hexane yielding a yellow liquid (8.9 g, 58%). The product was a mixture of various isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, Ar*H*, 2H), 7.49 – 7.41 (m, Ar*H*, 2H), 5.96 – 5.65 (m, –C*H*C*H*–, 2H), 4.44 – 4.21 (m, –OCH_2CH$_3$, 4H), 4.20 – 4.06 (m, –SCH_2Ar, 2H), 3.69 – 3.65 (s, –OCH_3, 3H), 3.56 – 3.40 (m, –CH$_2$C*H*S–, 1H), 2.75 – 2.68 (m, –CH$_2$C*H*C–, 1H), 2.35 – 2.27 (m, –CH_2CO$_2$–, 2H), 1.79 – 1.67 (m, CH_2CHS-, 2H), 1.65 – 1.59 (m, –CO$_2$CH$_2$CH_2–, 2H), 1.40 – 1.36 (m, –OCH$_2$CH_3 6H), 1.36 – 1.22 (m, –CH$_2$CH_2CH$_2$–, 16H), 0.92 – 0.85 (t, *J* = 9.2 Hz, –OCH_3, 3H). HRMS (ESI) calcd. for $C_{32}H_{51}O_7PS_2Na^+$: m/z = 665.2706 $[M+Na]^+$; found: 665.2712.

*Synthesis of HDA dimer acid ester (**5**)*

An oven-dried RBF, was charged with **4** (5.3 g, 8.3 mmol, 1 equiv.), methyl ricinoleate (3.1 g, 10.0 mmol, 1.2 equiv.), and 4-dimethylaminopyridine (0.57 g, 4.2 mmol, 0.5 equiv.). The compounds were dissolved in dry DCM (50 mL) and stirred for 5 minutes at room temperature. EDC·HCl (1.97 g, 10.0 mmol, 1.2 equiv.) ass added and the mixture continued stirring under nitrogen atmosphere overnight. The progress of the reaction was monitored by TLC (30 vol % ethyl acetate in hexane). Upon completion, the reaction mixture was diluted with DCM (50 mL) and then washed with HCl (0.5 N, 25 mL). The organic layer was extracted and then washed with water (2 x 50 mL), followed by brine solution (25 mL). Upon drying over anhydrous sodium sulfate and solvent evaporation using a rotary evaporator, the crude was purified by flash column chromatography using 35 vol % ethyl acetate in hexane isolating 5.71 g product. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97– 7.92 (m, Ar*H*, 2H), 7.43– 7.36 (m, Ar*H*, 2H), 5.96 – 5.66 (m, –CHC*H*C*H*CHS–, 2H), 5.50 – 5.43 (m, –(O)CH$_2$C*H*CHCH$_2$– 1H), 5.43 – 5.36 (m, –(O)CH$_2$CHC*H*CH$_2$–, 1H), 5.15 – 5.06 (m, –CH$_2$C*H*OC(O)–, 1H), 4.40 – 4.18 (m, –OCH_2CH$_3$, 4H), 4.16 – 4.05 (m, –SCH_2 Ar, 2H), 3.68 – 3.65 (s, –OCH_3, 6H), 3.55 – 3.44 (m, –CH$_2$C*H*S–, 1H), 2.75 – 2.67 (m, –CH$_2$C*H*C–, 1H), 2.49 – 2.35 (m, –CHCH_2CHO–, 2H), 2.32 – 2.27 (m, –

CH_2CO$_2$–, 4H), 2.09 – 1.94 (m, –CH=CHCH_2CH–, 2H), 1.75 – 1.58 (m, –CO$_2$CH$_2$CH_2CH$_2$–, –CH_2CHS–, –CH_2CHO– 8H), 1.54 – 1.42 (m, –CH_2CHC–, 2H), 1.40 – 1.22 (m, 38H), 0.91 – 0.84 (m, 6H). HRMS (ESI) calcd. for $C_{51}H_{85}O_9PS_2Na^+$: m/z = 959.5265 $[M+Na]^+$; found: 959.5270.

*EDC Coupling of PDTMBA and methyl ricinoleate (**6**)*

In an oven-dried 100-mL RBF under nitrogen atmosphere, PDTMBA (0.3 g, 0.86 mmol, 1 equiv.), methyl ricinoleate (0.296 g, 0.95 mmol, 1 equiv.) and DMAP (0.039 g, 0.32 mmol, 0.4 equiv.) were taken into dry DCM (15 mL). EDC·HCl (0.198 g, 1.03 mmol, 1.2 equiv.) was added and the reaction continued stirring under a nitrogen atmosphere. After overnight stirring, the reaction mixture was acidified with HCl (1 N, 5 mL) and then the product was extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with water (2 x 25 mL) and then dried over anhydrous sodium sulfate. After solvent removal via rotary evaporation, the crude was purified by flash chromatography using 30 vol % ethyl acetate in hexanes, isolated a purple-colored liquid (365 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.96 (d, *J* = 8.2 Hz, Ar*H*, 2H), 7.41 – 7.35 (d, *J* = 8.2 Hz, Ar*H*, 2H), 5.50 – 5.44 (m, –CHC*H*CH$_2$CHO–, 1H), 5.42 – 5.36 (m, –C*H*CHCH$_2$CHO–, 1H), 5.15 – 5.10 (m, –CH$_2$C*H*(O)CH$_2$– 1H), 4.56 – 4.50 (s, –SCH_2Ar 2H), 4.33 – 4.21 (m, –OCH_2CH$_3$, 4H), 3.68 – 3.64 (s, –OCH_3, 3H), 2.48 – 2.37 (m, –CH_2CHCO–, 2H), 2.32 – 2.27 (t, *J* = 7.5 Hz, –CH_2CO$_2$–, 2H), 2.06 – 1.99 (m, –CHCHCH_2CH$_2$–, 2H), 1.73 – 1.64 (m, –CH$_2$CH_2CHO–, 2H), 1.64 – 1.57 (m, –CH_2CH$_2$CO$_2$–, 2H), 1.42 – 1.35 (t, J = 7.1 Hz, –OCH$_2$CH_3, 6H), 1.35 – 1.21 (br m, –CH_2–, 16H), 0.88 – 0.84 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.24 (C=O), 165.69 (C=O), 138.91, 132.82, 130.58, 130.08, 129.27, 124.15, 74.92, 64.86, 64.82, 51.43, 39.98, 34.11, 33.75, 32.06, 31.75, 29.52, 29.21, 29.16, 29.12, 29.11, 27.39, 25.42, 24.97, 22.60, 16.35, 16.31, 14.07. HRMS (ESI) calcd. for $C_{32}H_{52}O_7PS_2^+$: m/z = 643.2887 $[M+H]^+$; found: 643.2892.

Synthesis of hydrogenated dimer acid ester (for the **control-coating***)*

A 250-mL RBF equipped with a reflux condenser was charged with 50 g of saturated fatty dimer acid (C-36 fatty acid) and 100 mL methanol. Concentrated sulfuric acid (1 mL) was added and the mixture refluxed overnight at 75 °C. The progress of the reaction was monitored by ^{1}H NMR by the formation of the methyl ester peak at 3.65 ppm. Upon completion, the reaction

mixture was cooled to room temperature, and transferred into a separating funnel, then diluted with water (100 mL) and hexanes (100 mL). The organic layer was separated, and the aqueous layer was washed with hexanes (2 x 75 mL). The combined organic layers were washed with water (2 x 100 mL) and brine (50 mL) and dried over anhydrous sodium sulfate. The filtered organic layers were concentrated by rotary evaporation. The crude obtained was used for the next reaction with ethylene diamine without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.73 – 3.67 (s, –OC*H*$_3$, 6H), 2.32 – 2.27 (t, *J* = 7.5 Hz, –C*H*$_2$CO$_2$–, 4H), 1.70 – 1.61 (m, –CO$_2$CH$_2$C*H*$_2$–, –CHCH*H*CH*H*CH– (cyclohexane), 6H), 1.52 – 1.04 (m, CH$_2$, –CHC*H*HC*H*HCH– (cyclohexane), 50H), 0.88 – 0.84 (t, *J* = 6.9 Hz, 3H).

*Synthesis of hydrogenated dimer diamine (***control-amine***, for* ***control-coating****)*

A 100 mL RBF was charged with the crude dimer product (7.24 g, 12.2 mmol, 1 equiv.) along with ethylene diamine (2.45 mL, 36.6 mmol, 3 equiv.) and allowed to stir at 90 °C overnight under reflux. The solution was cooled to room temperature, and concentrated by rotary evaporation. The crude thus obtained was used for the next reaction without further purification. NMR of the product showed a loss of the methyl ester at 3.69 ppm, and a shift in the CH_2 adjacent to the carbonyl from 2.33 to 2.18 ppm.

Synthesis of ***HDA hardener***

Ethylenediamine (0.822 g, 13.6 mmol, 2 equiv.) was added to the **5** (6.4 g, 6.8 mmol, 1 equiv.) in a RBF equipped with a reflux condenser and heated at 90 °C. After overnight stirring, the byproduct methanol was removed by nitrogen gas flushing, and then the product was dried overnight at 35 °C in a vacuum oven. The crude product was subjected to ^{1}H NMR, and the disappearance of methyl ester protons at 3.66 ppm confirmed the amide formation. This crude material is used for further experiments.

Synthesis of ***TETA-hardener***

Triethylenetetraamine (60%, 5.2 g, 21.3 mmol, 2 equiv.) was added to the **5** (10 g, 10.7 mmol, 1 equiv.) in a RBF equipped with a reflux condenser and heated at 90 °C. After overnight stirring, the byproduct methanol was removed by nitrogen gas flushing, and then the product was dried overnight at 35 °C in a vacuum oven. The crude product was subjected to ^{1}H NMR, and the

disappearance of methyl ester protons at 3.66 ppm confirmed the amide formation. This crude material is used for further experiments.

III. Calculation of the amine hydrogen equivalent weight (AHEW)

Amine values of the hardener calculated according to the ASTM D 2074 method carried out using a Metrohm 905 Titrando. From the titration data, the calculated AHEW for the **HDA hardener** was 304 and 171 for the control hardener.

AHEW = 56100/(Amine Value x Average number of active H's per Nitrogen)

Amine Value (from titration) = (V x N x 56.1)/S

where V = volume of HCl required for titration of the specimen in mL, N = normality of the HCl solution, and S = specimen weight used in grams.

EPON-872 resin provides a EEW range of 625-725 where we opted to use the median value of 675.

IV. Coatings preparation

A 1:1 epoxy to hardener stochiometric mixing ratio was calculated using the AHEW and EEW of the **HDA hardener**. The **HDA-coating** was formulated by combinging EPON-872 resin (1500 mg), **HDA hardener** (675 mg), 4-nonylphenol (10 wt % to epoxy, 150 mg), and 2-heptanone (10 wt % to epoxy, 150 mg) in a FlackTeck Max 20 jar and hand mixing with a metal spatula. Further mixing was completed using FlackTeck Speedmixer (2 m, 2500 rpm cycles until uniform). An eight wet mills thickness coat was developed on a 15 x 7.5 cm aluminum alloy (A6061) panel with a drawdown bar. The coatings were allowed to cure at room temperature for 2 days and then completed the curing by heating the panels at 60 °C for 1 hour in a pre-heated oven. The **control-coating** was formulated similarly using the **control-amine** (763 mg), EPON-872 resin (3000 mg), 4-nonylphenol (300 mg), and 2-heptanone (300 mg).

The TETA-based hardener (**TETA-hardener**, AHEW 301) was used to make coatings with and without $ZnCl_2$. The TETA-based coatings without $ZnCl_2$ were made with **TETA-hardener** (297 mg), EPON 1007 (EEW 1866, 5455 mg) and 4-nonylphenol (545 mg). Additionally a TETA-based coating was also made with $ZnCl_2$ by combining the **TETA-hardener** (297 mg), EPON 1007 (EEW 1866, 5455 mg) and 4-nonylphenol (545 mg) and $ZnCl_2$ (33 mg, 1%

of the epoxy+amine). Note that EPON 1007 is 55% epoxy in solvent and the weights above are recorded as the mixture weight, not epoxy content.

V. Thermal scratch healing test procedure

For the thermal healing test, the cured coatings were scribed with a craft knife, and an ink mark was drawn to identify the scratch. The scratch images were recorded using Keyence VHS 600 microscope at 200x magnification. The scribed panels were then heated to 95 °C in a pre-heated oven. After heating for the desired time, the images of the scratches were taken again.

VI. Hardness test procedure

The pendulum hardness test was used for determining the effect of heating on coating hardness. A TQC Pendulum hardness tester was used in Konig mode, and the time required for the pendulum amplitude to decrease from 6° to 3° was recorded. **HDA-Coating** and **control-coating** hardness was measured in triplicate after heating to 95°C for 30 min in a preheated oven.

VII. NMR spectra of compounds synthesized

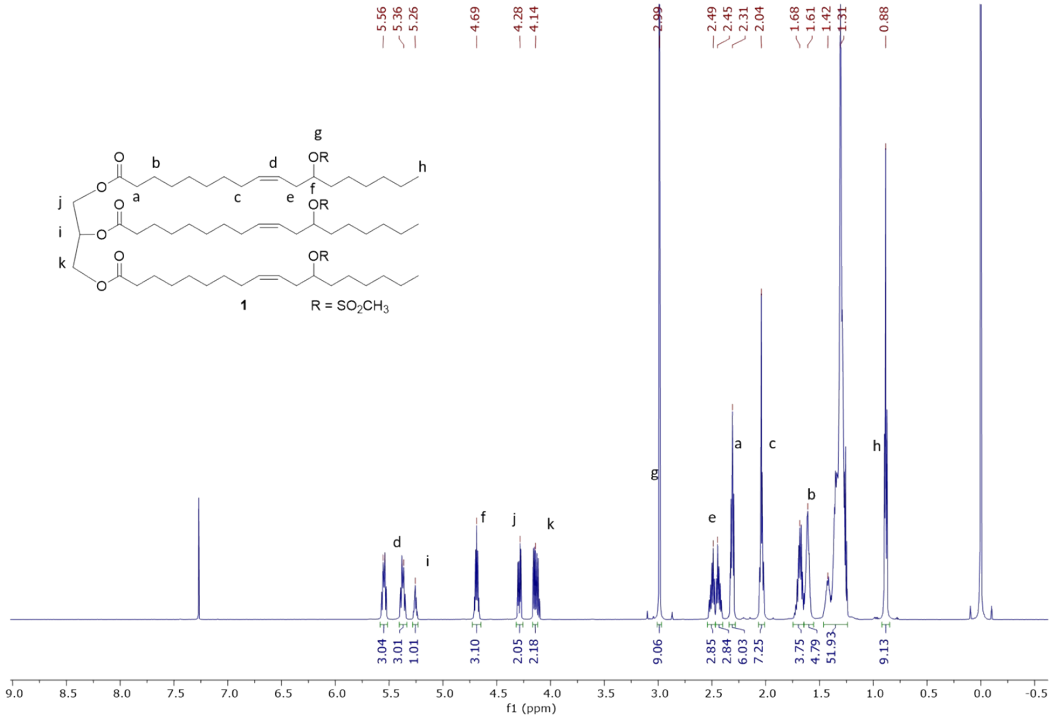


Figure S1. ^{1}H NMR spectrum of **1** (600 MHz, $CDCl_3$).

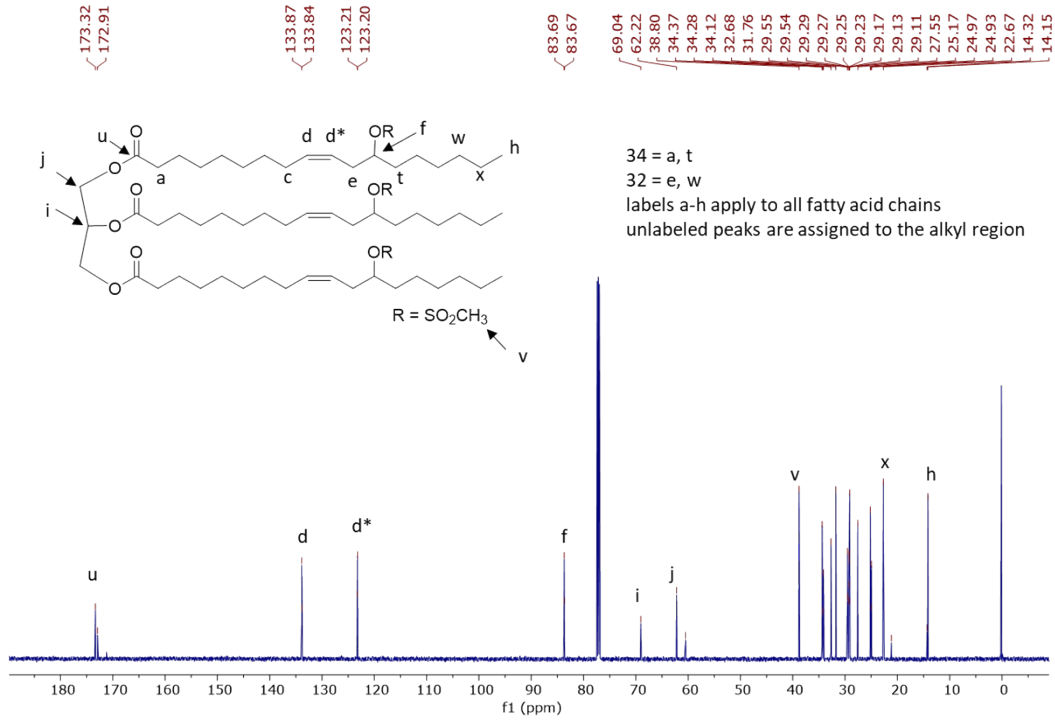


Figure S2. ^{13}C NMR spectrum of **1** (151 MHz, $CDCl_3$).

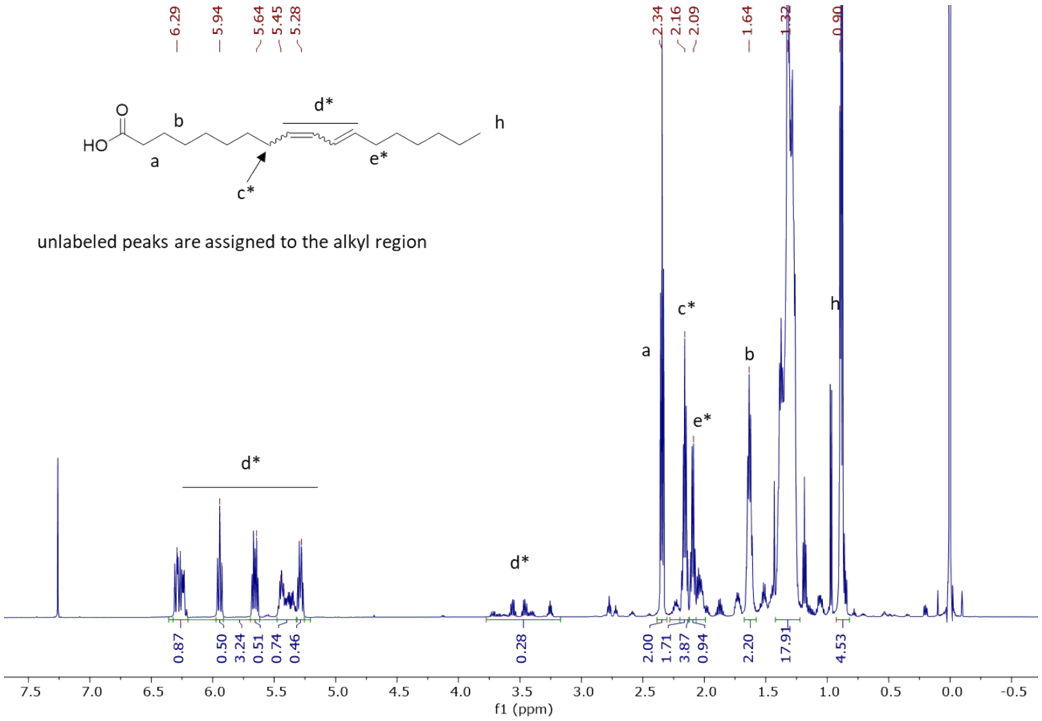


Figure S3. ^{1}H NMR spectrum of **2** (600 MHz, $CDCl_3$).

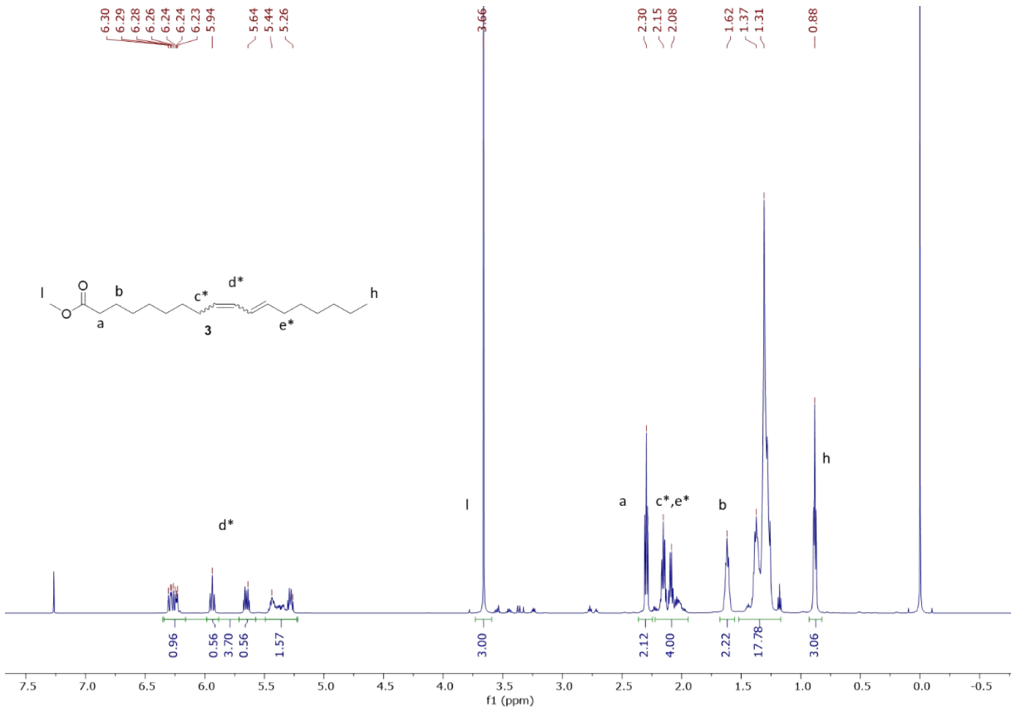


Figure S4. ^{1}H NMR spectrum of **3** (600 MHz, $CDCl_3$).

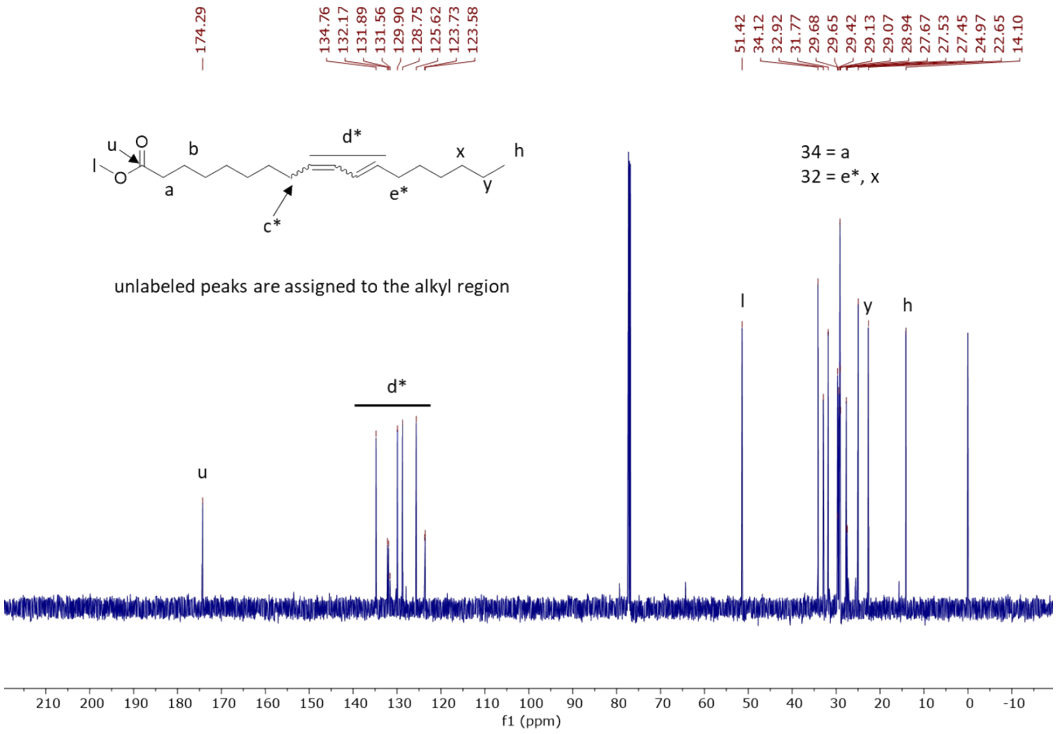


Figure S5. ^{13}C NMR spectrum of **3** (151 MHz, $CDCl_3$).

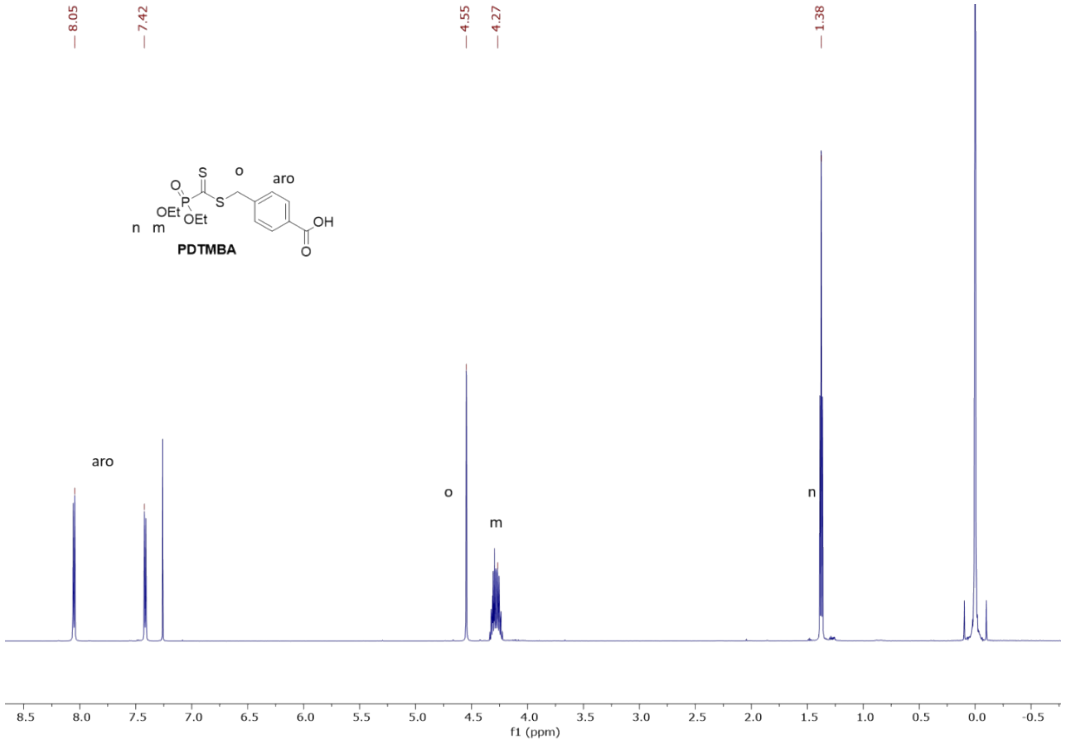


Figure S6. ^{1}H NMR spectrum of **PDTMBA** (600 MHz, $CDCl_3$).

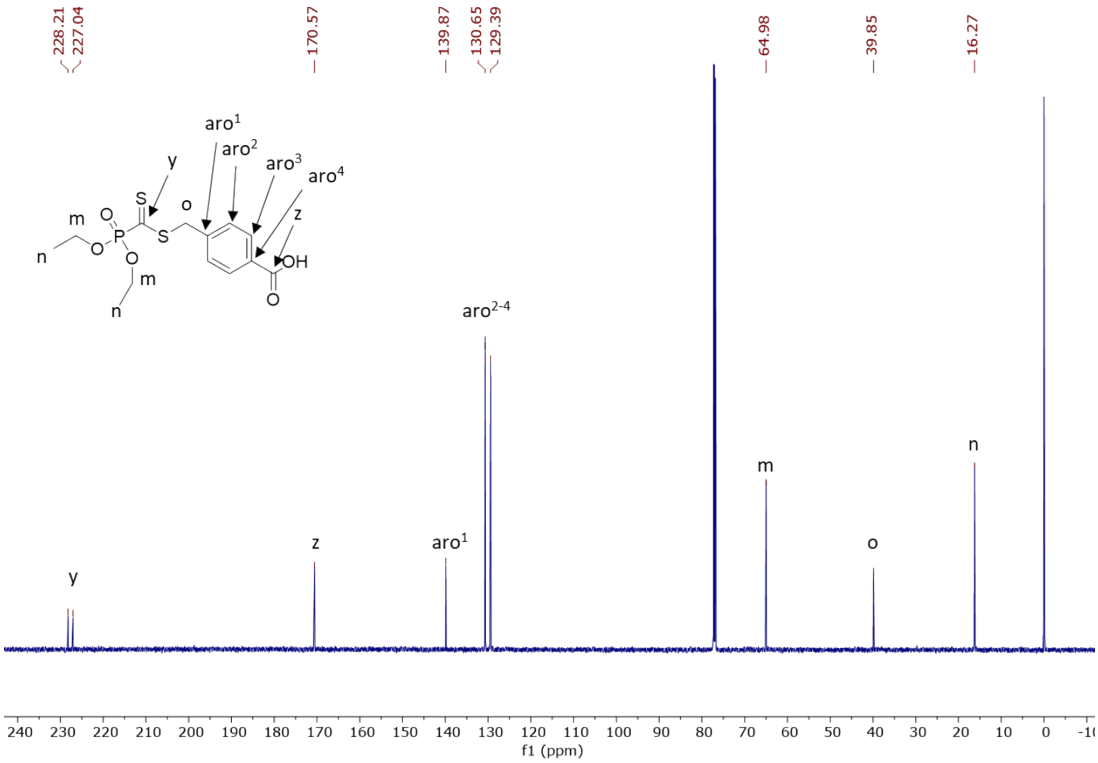


Figure S7. ^{13}C NMR spectrum of **PDTMBA** (600 MHz, $CDCl_3$).

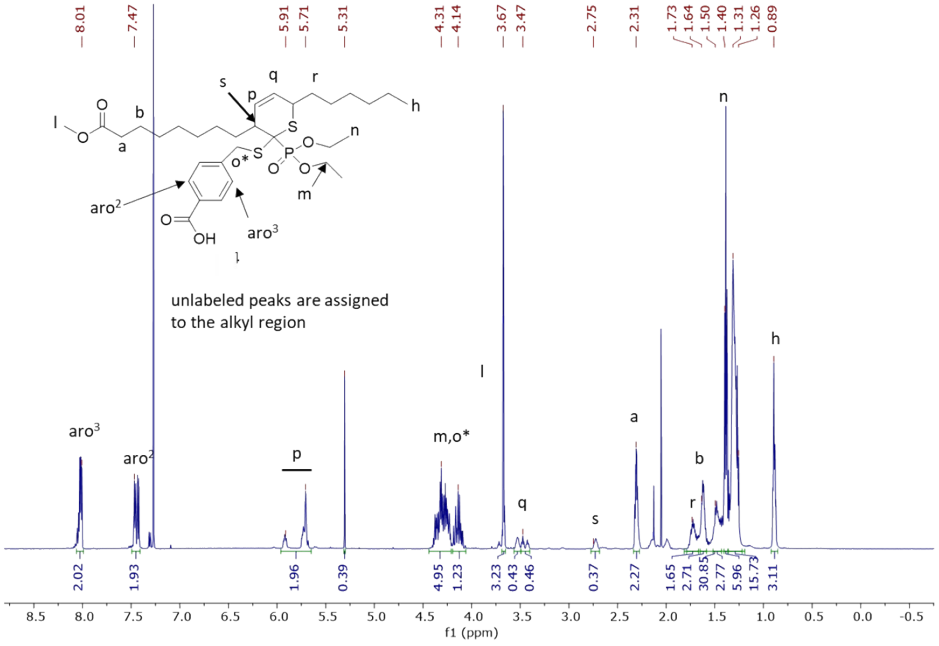


Figure S8. ^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$).

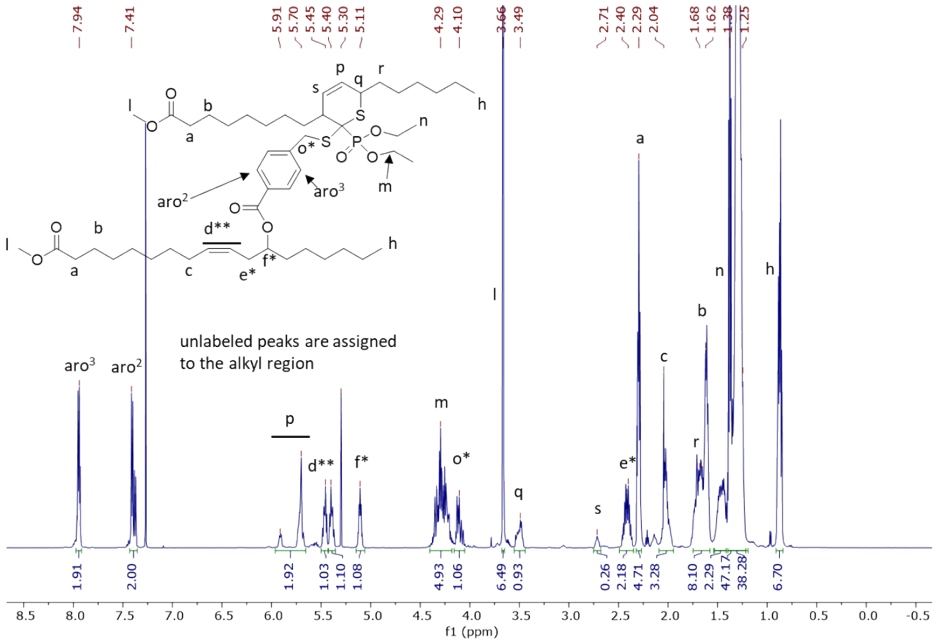


Figure S9. ^{1}H NMR spectrum of **5** (600 MHz, $CDCl_3$).

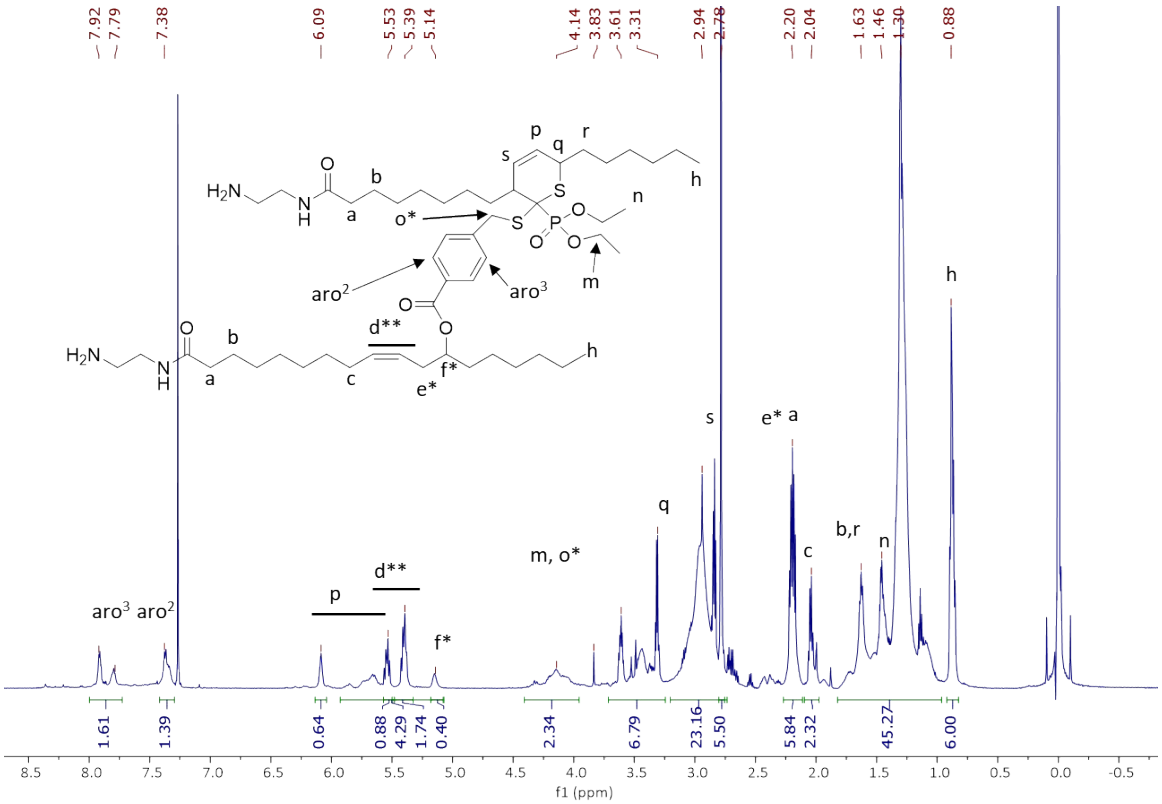


Figure S10. ^{1}H NMR spectrum of **HDA hardener** (600 MHz, $CDCl_3$).

VIII. Thermal reversion test

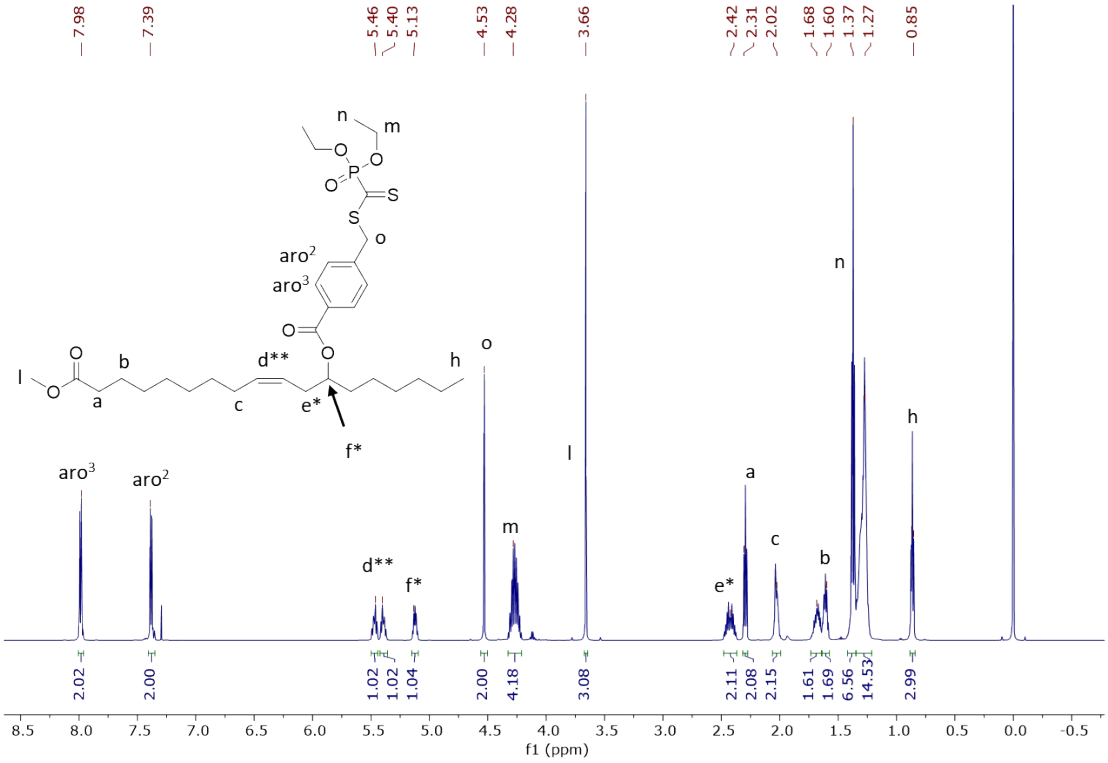


Figure S11. ^{1}H NMR spectrum of **6** (600 MHz, $CDCl_3$).

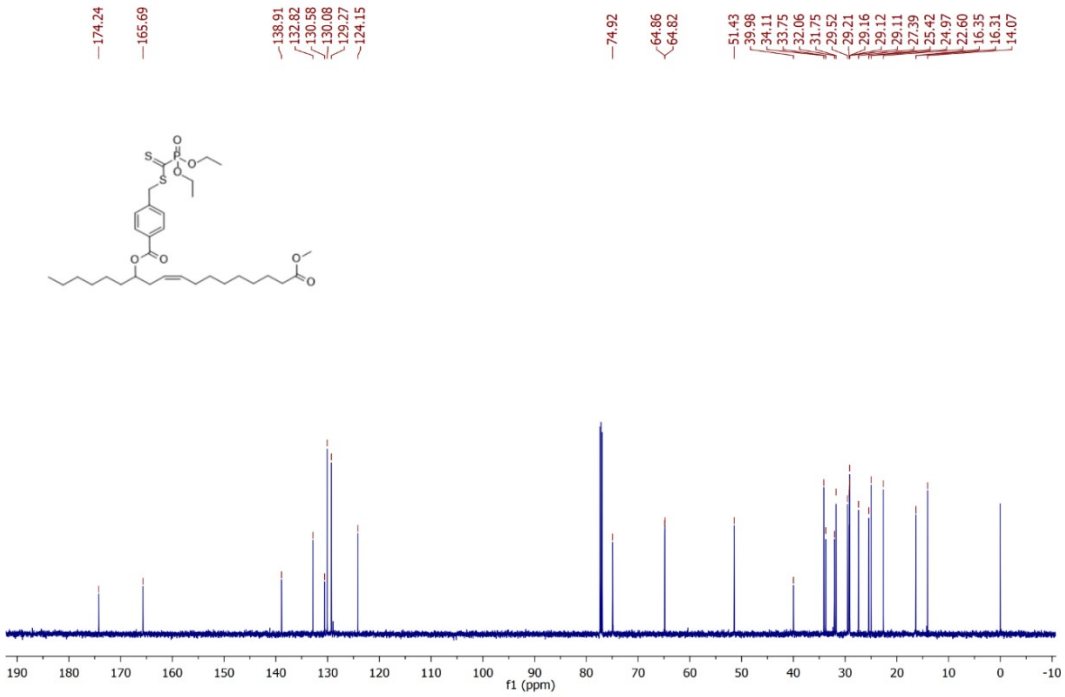


Figure S12. ^{13}CNMR spectrum of **6** (151 MHz, $CDCl_3$).

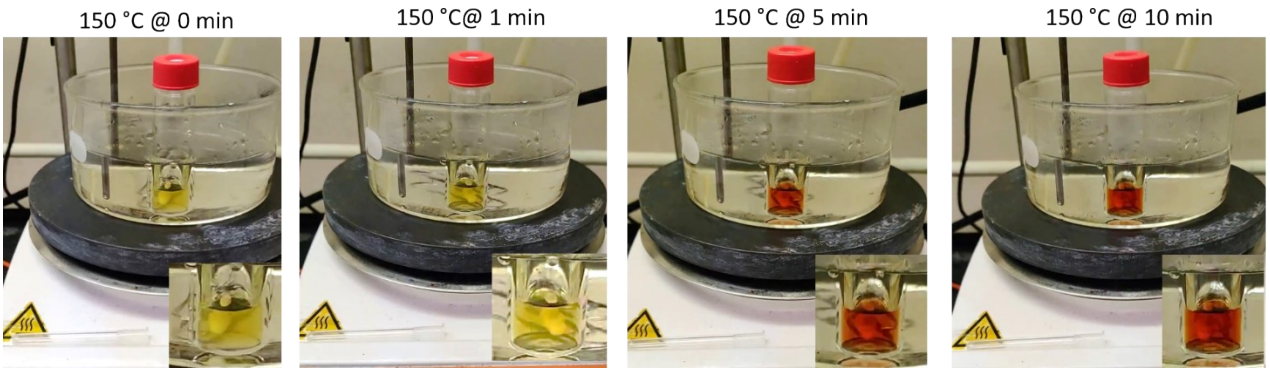


Figure S13. Visual color change of **5** during the heating process.

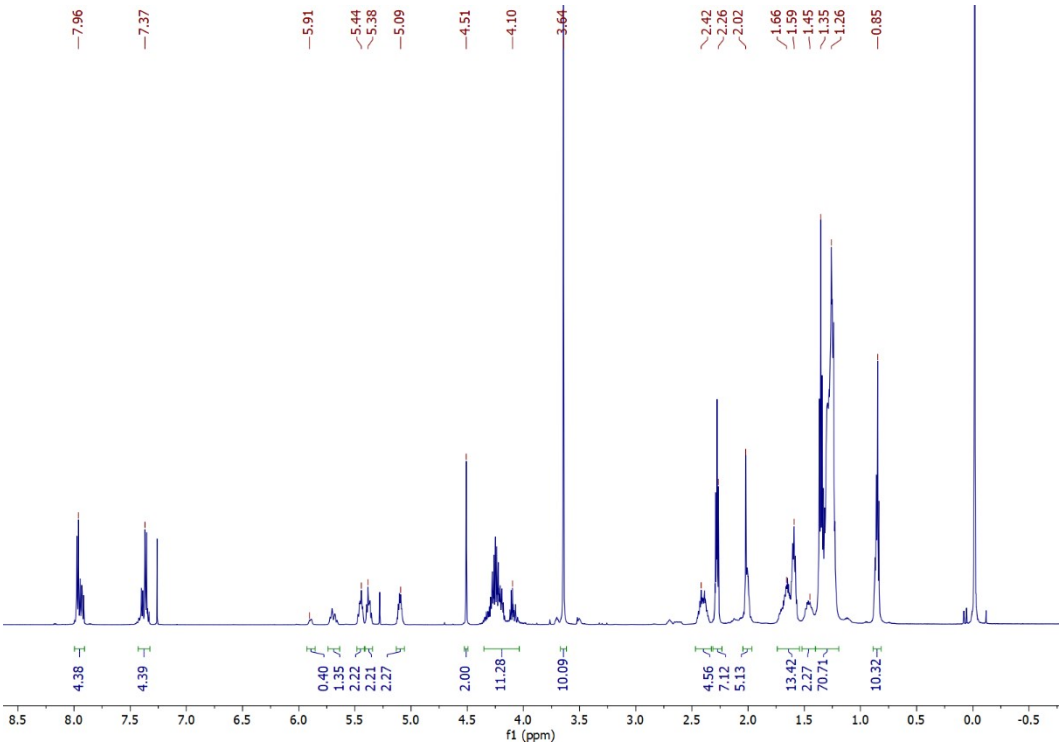


Figure S14. ^{1}H NMR spectrum of the polar fraction of heated HDA ester.

IX. Thermal Characterization.

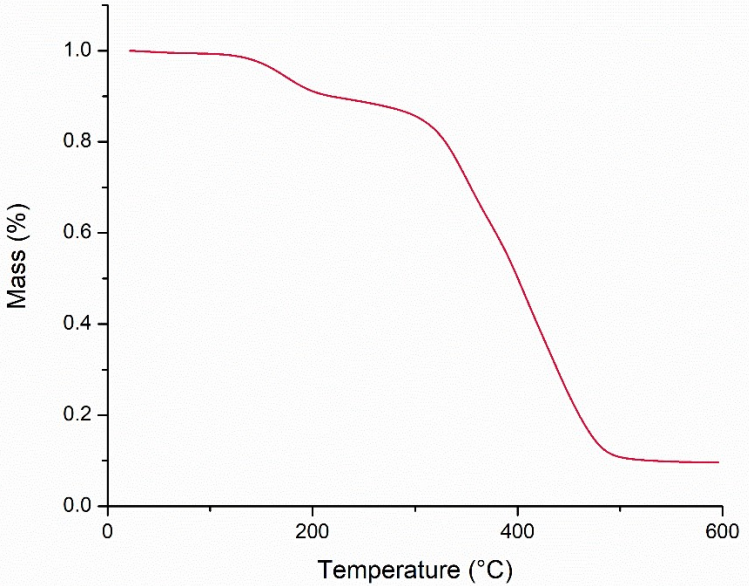


Figure S15. TGA thermogram of **HDA-coating**.

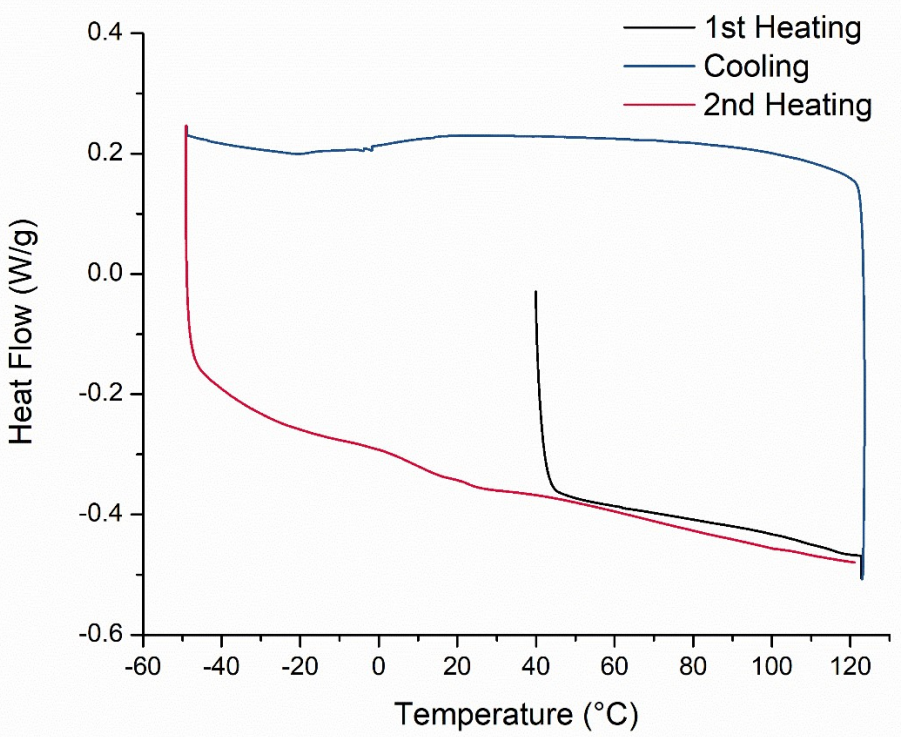
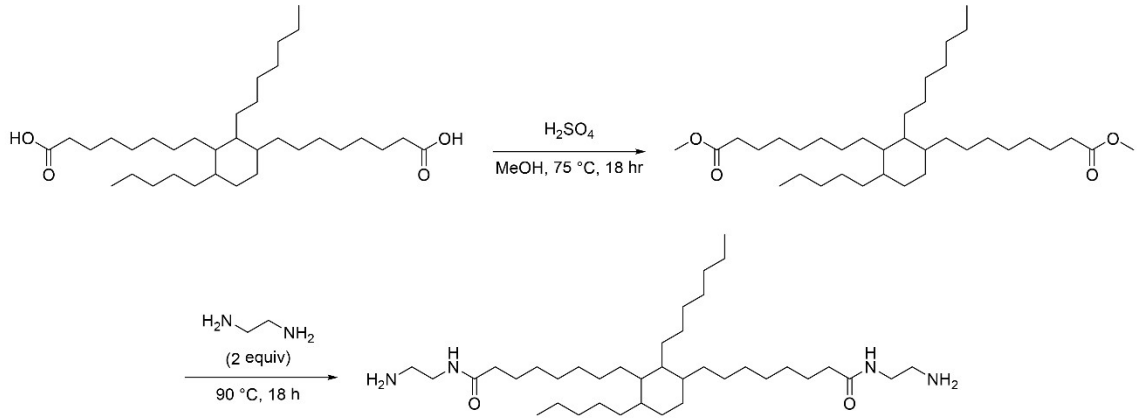


Figure S16. DSC thermogram of **HDA-coating**. T_g of coating was measured at 20°C.

X. Control-amine reaction scheme



Scheme S1. Synthesis of the **control-amine** used for the **control-coating**.

XI. NMR spectra for the control-amine synthesis

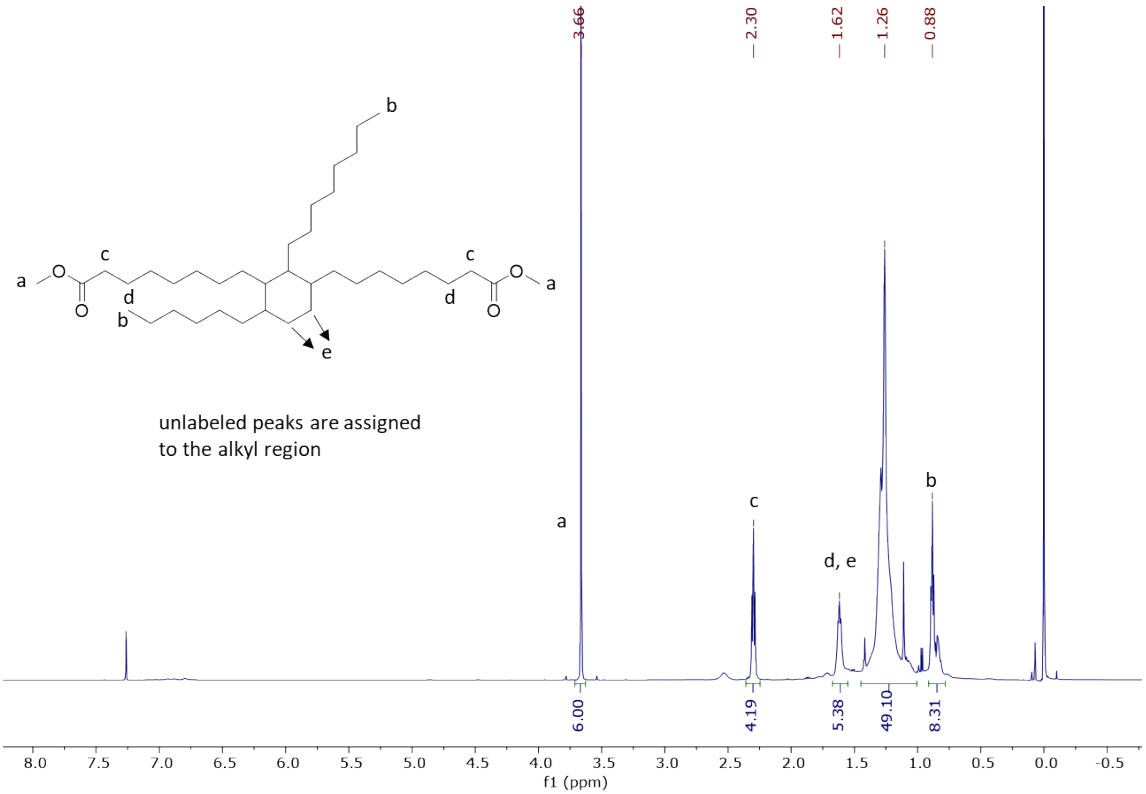


Figure S17. ^{1}H NMR spectrum of **control ester** (600 MHz, $CDCl_3$).

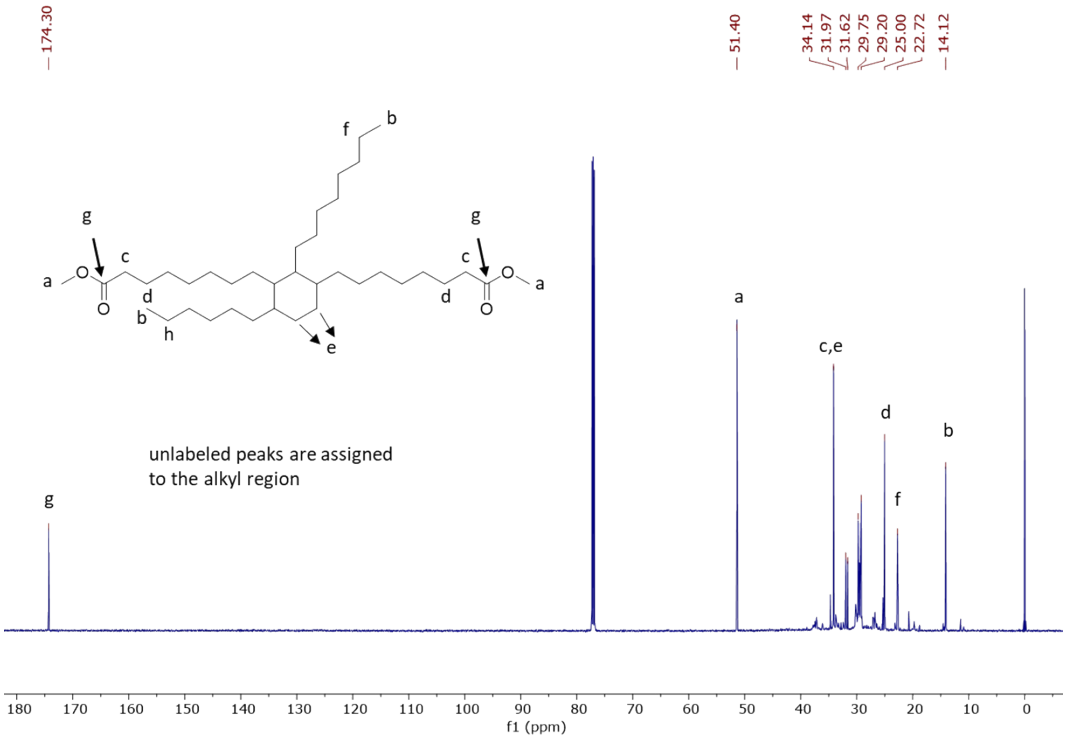


Figure S18. ^{13}C NMR spectrum of **control ester** (600 MHz, $CDCl_3$).

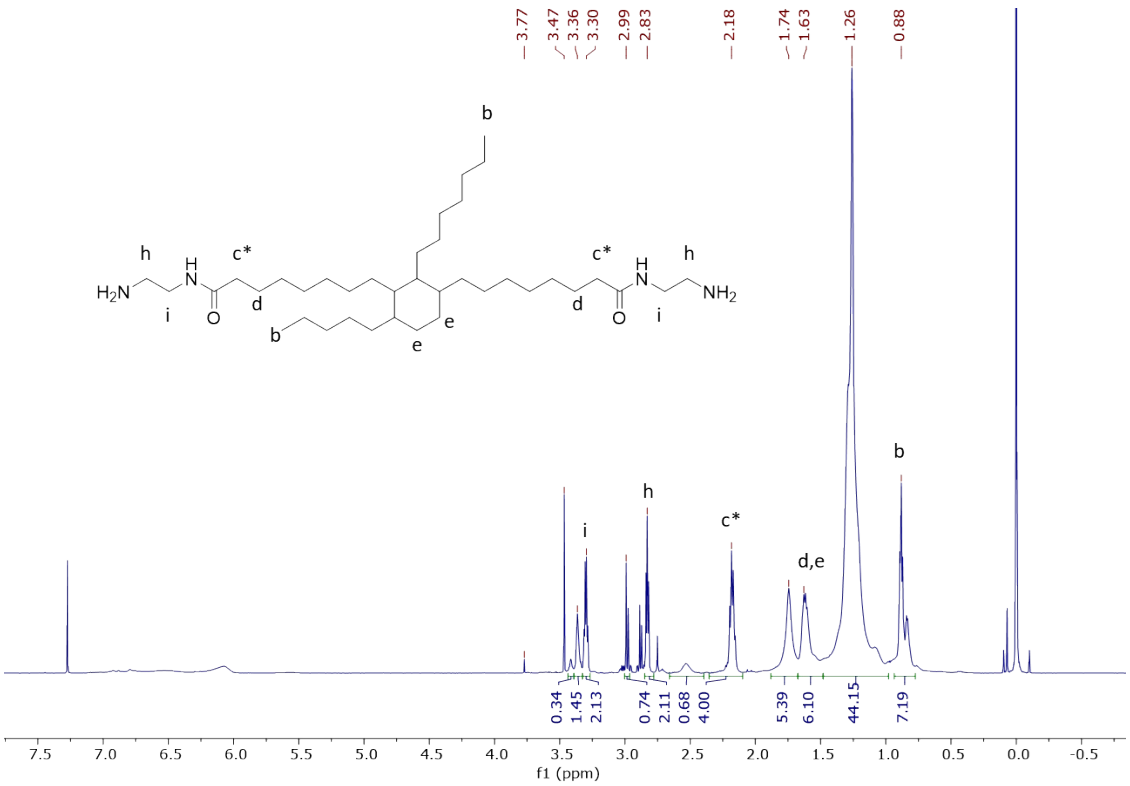


Figure S19. ^{1}H NMR spectrum of **control amine** (600 MHz, $CDCl_3$).

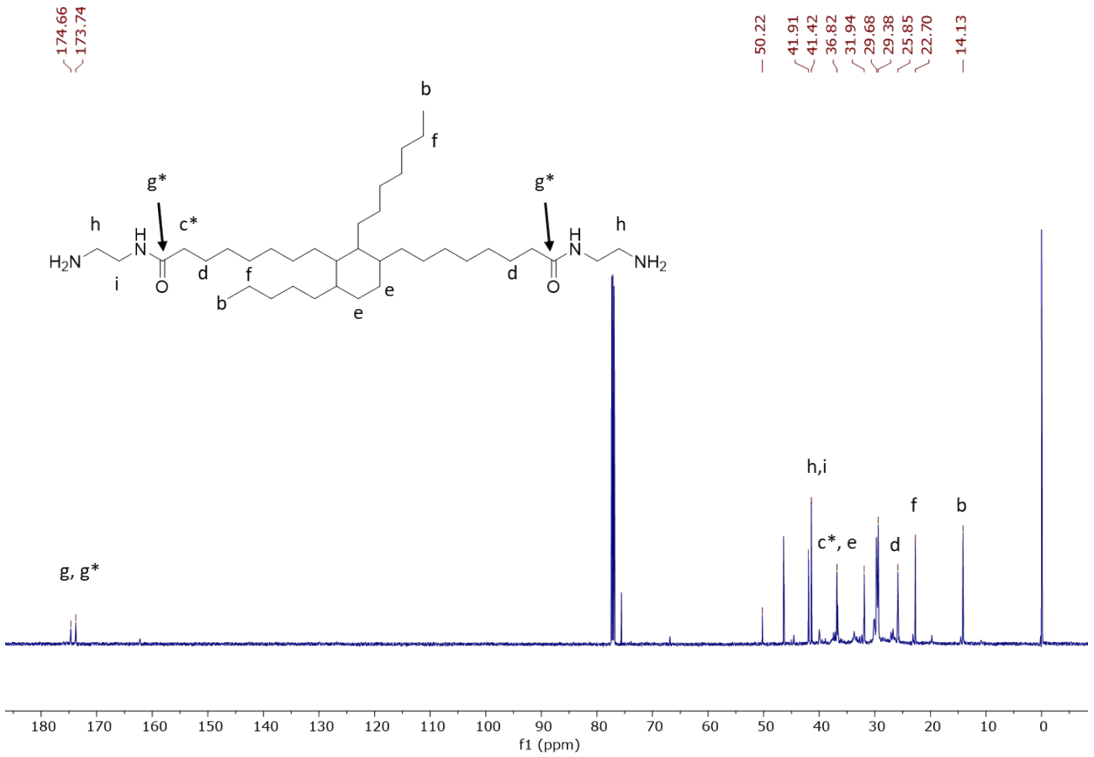


Figure S20. ^{13}C NMR spectrum of **control amine** (600 MHz, $CDCl_3$).

XII. Scratch healing test images

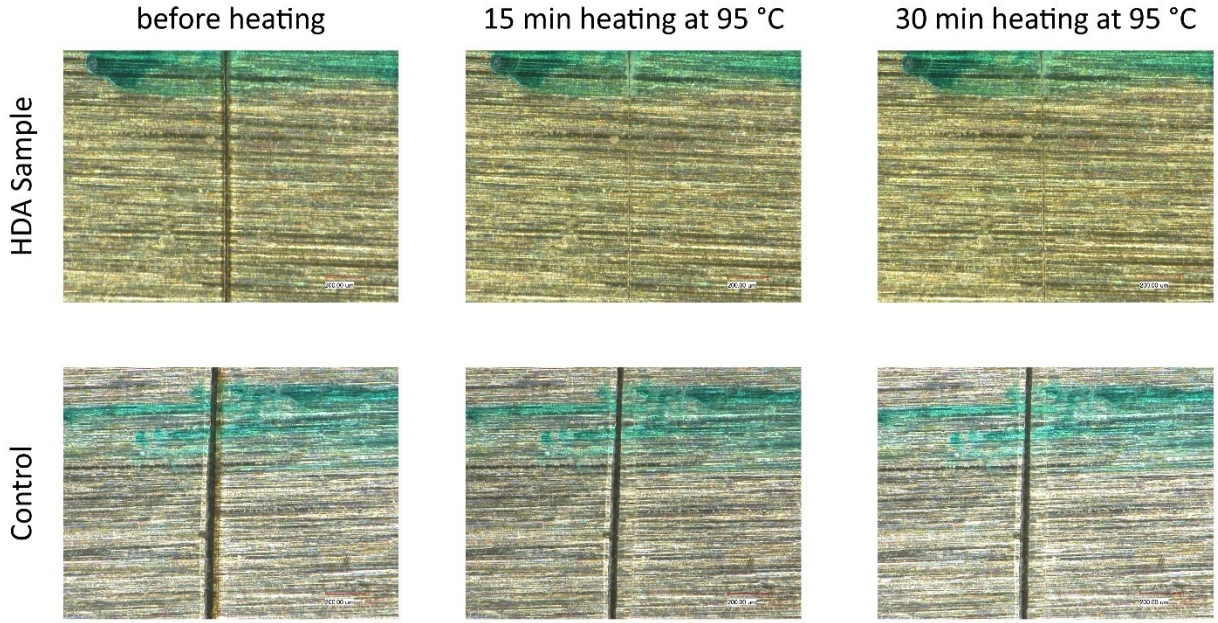


Figure S21. OM image of scratch before and after heating. Top row: healable **HDA-coating**. Bottom row: non-healing **Control-coating**. All images are taken at 200x magnification.

XIII. Solvent resistance.

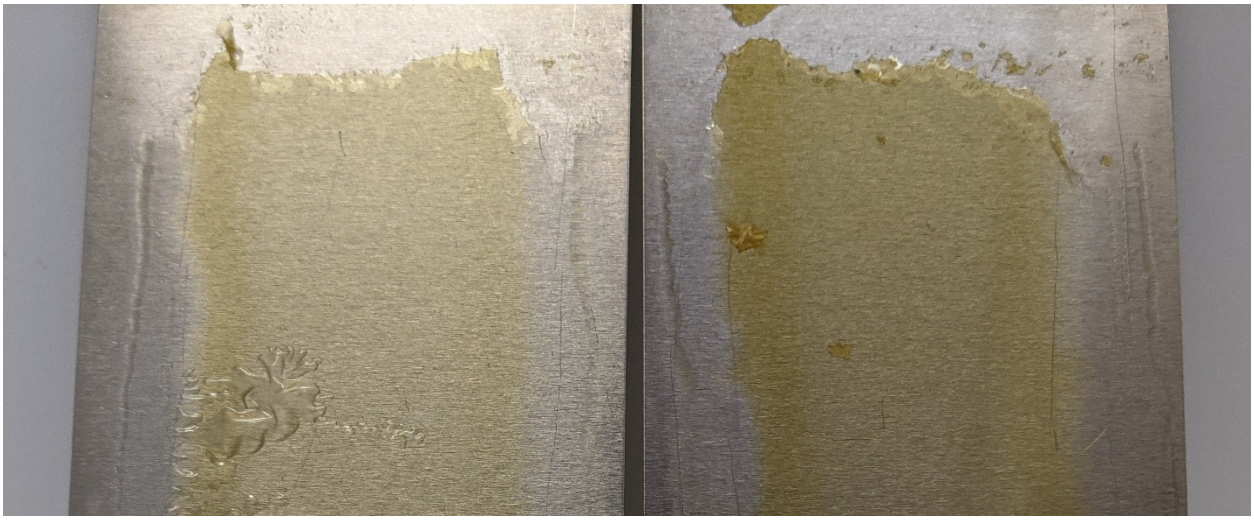


Figure S22. Image of an **HDA-coating** panels after being fully submerged in acetone for 4 days. Left panel was not heated prior to testing whereas the right panel was first heated to 95°C in a preheated oven for 30 min.

XIV. Hardness test results

Table S1. Results of pendulum hardness test for **HDA-coating** and **control-coating** coating after heating to 95°C for 30 min.

Konig Hardness (s)		
Replicate	**HDA-coating**	**Control-coating**
1	44.9	23.8
2	43.5	23.7
3	42.1	23.8
Average	43.5±1.4	23.8±0.1

XV. TETA-hardener NMR

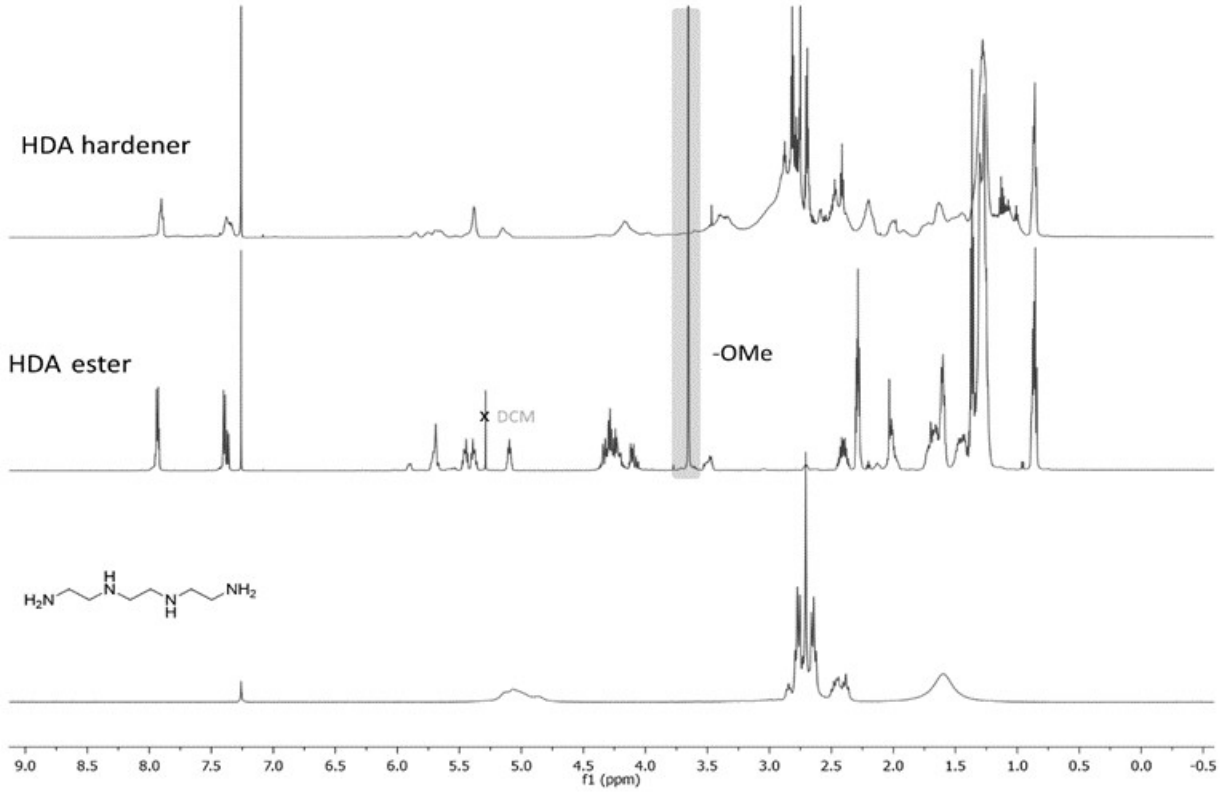


Figure S23. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of the **TETA-hardener** amine (top), the HDA ester (**5**, middle) and TETA (bottom).

XVI. Scratch healing of TETA-based coatings

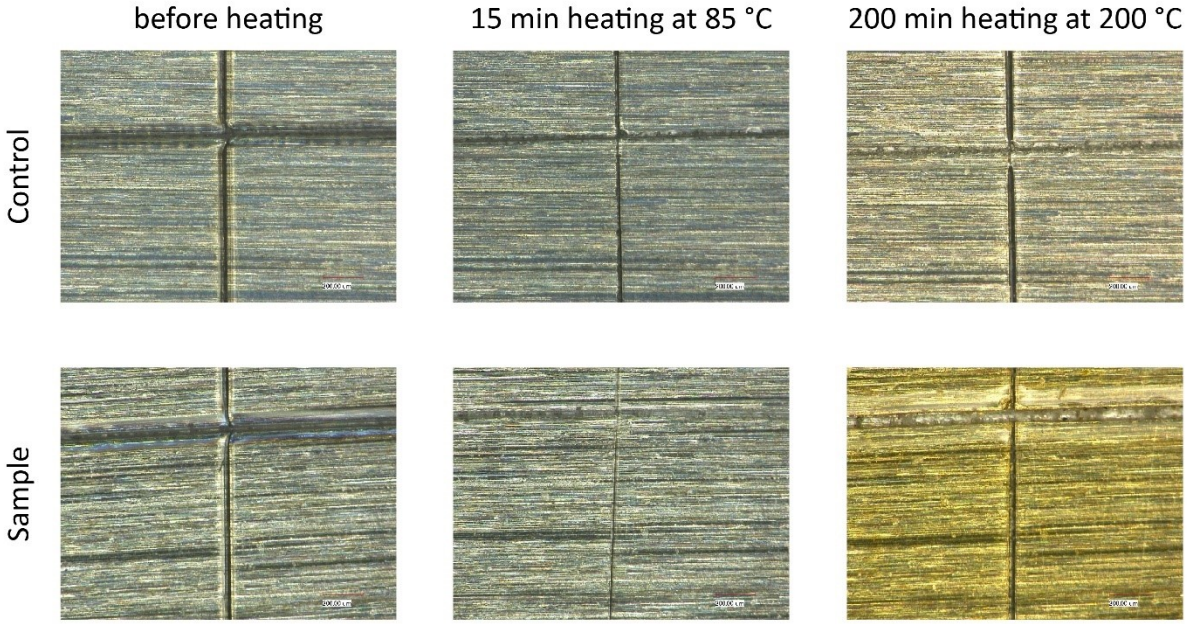


Figure S24. OM image of scratch before and after heating. Top row: non-healing control-coating. Bottom row: **TETA-hardener** coating. All images are taken at 200x magnification.

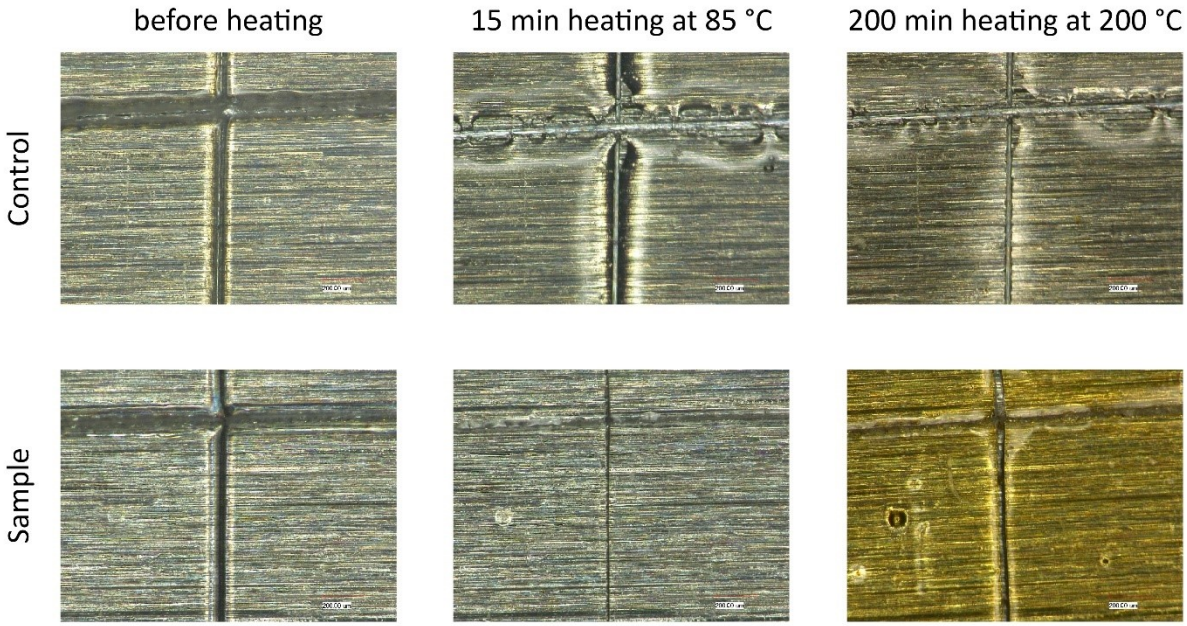


Figure S25. OM image of scratch before and after heating. Top row: non-healing control-coating. Bottom row: **TETA-hardener** coating with $ZnCl_2$. All images are taken at 200x magnification.

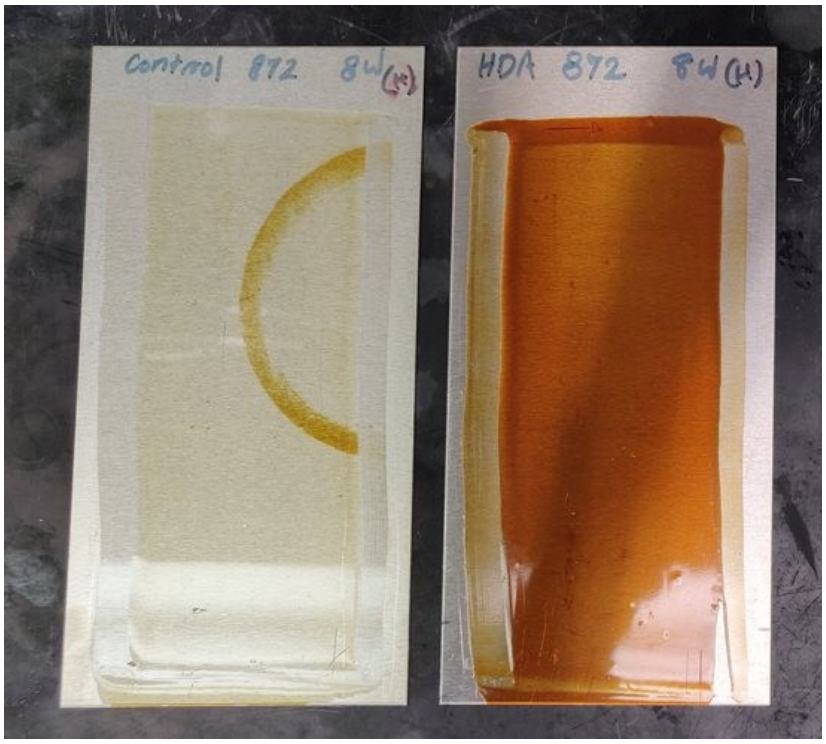


Figure S26. Image of a (left) control film made with Ancamide 2445 and (right) **TETA-hardener** after heating at 200 °C. Both films were made with EPON 872.

XVII. References

1 A. M. Schenzel, C. Klein, K. Rist, N. Moszner and C. Barner-Kowollik, *Adv. Sci.*, 2016, **3**, 1500361.

2 J. Steinkoenig, M. M. Zieger, H. Mutlu and C. Barner-Kowollik, *Macromolecules*, 2017, **50**, 5385–5391.