Supporting information

Optimized synthesis of a High Oleic Sunflower Oil derived Polyamine and its Lignin-based NIPUs

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Materials

Organosolv beech wood lignin was kindly donated by the Fraunhofer Center for Chemical-Biotechnological Processes CBP (Leuna, Germany). High oleic sunflower oil (Rapunzel), high oleic sunflower oil (Alnatura), 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate, 90%, BLDPharm), 2,2-dimethoxy-2-phenylacetophenone (DMAP, 99%, Thermo Scientific), ethyl(2,4,6-trimethylbenzoyl)-phenyl phosphinate (TPO-L, >95%, TCI), *N*-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (NHND, 97%, Alfa Aesar), Chromium(III) acetylacetonate (99.99% trace metal basis, Sigma Aldrich), meso-erythritol (99%, Alfa Aesar), dimethyl carbonate (anhydrous, > 99%, Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, > 98%, Fluorochem), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, > 98%, TCI Chemicals), pyridine (≥99%, Sigma Aldrich), *N*,*N*-dimethylacetamide (99.5%, anhydrous, dried over molecular sieves, Thermo Scientific), dichloromethane (DCM ≥99%, Fisher Chemicals), chloroform (≥99.8%, Fisher Chemicals), 1,4-dioxane (Fluka Chemicals, 99.5%), ethanol (>99.8%, Fisher Chemicals), and propan-2-ol (>99.5%, Fisher Chemical) were used without further purification. Deuterated solvents (DMSO-d_6 and $CDCl_3$) were purchased from Eurisotop.

Experimental part

Infrared (IR) Spectroscopy

Infrared spectra were recorded using a Bruker ALPHA attenuated total reflection (ATR) IR spectrometer in the range of ν = 400–4000 cm^{-1} at ambient temperature with 24 scans per measurement.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H NMR spectra were recorded using a Bruker Ascend 400 MHz or a Bruker Avance DRX 500 MHz spectrometer, with 16 to 128 scans, a delay time d_1 ranging from 1 to 5 s, at 298 K. The chemical shift was reported in parts per million (ppm) and referenced to characteristic signals of deuterated solvents, e.g. DMSO-d_6 at 2.50 ppm or chloroform-d_1 at 7.26 ppm. ^{13}C NMR spectra were recorded using a Bruker Avance DRX spectrometer at 126 MHz with 1024 to 32768 scans, with delay time d_1 of 1 to 4 s at 298 K. The chemical shift was reported in parts per million (ppm) and referenced to characteristic signals of deuterated solvents, e.g. DMSO-d_6 at 39.52 ppm or chloroform-d_1 at 77.16 ppm. Peak deconvolution was performed applying the GSD (Global Spectrum Deconvolution) method with refinement level 3 (10 fitting cycles) and 10 improvement cycles.

Quantitative ^{13}C-NMR

Quantitative ^{13}C analysis was performed according to the procedure described from Meier and Over.[1] A weighed, dry lignin sample (95.0 mg) was dissolved in 500 µL DMSO-d_6. 100 µL of a solution of the internal standard (IS) 1,3,5-trioxane (65 mg/mL) and chromium(III) acetylacetonate (24.9 mg/mL) as relaxation agent in DMSO-d_6 were added. Measurements were performed with inverse gated decoupling, 32768 scans, delay time d_1 of 4 s at 298 K.

Calculations were performed by first determining the mole quantity of IS in the IS solution:

$$trioxane\ in\ IS\ solution\ (mmol) = \frac{mass\ of\ trioxane\ added\ to\ the\ IS\ solution\ (g)}{M\ of\ trioxane\ (90.08 \frac{g}{mol})} * purity\ of\ trioxane\ (\%) * 1000$$

Afterwards, the mole quantity of the IS (trioxane) in the NMR sample was calculated:

$$trioxane\ in\ NMR\ sample\ (mmol) = \frac{trioxane\ in\ IS\ solution\ (mmol)}{total\ mass\ of\ IS\ solution\ (g)} * mass\ of\ 0.1\ mL\ of\ IS\ solution\ (g)$$

The integral ratio (I_{ratio}) between the spectral region of interest and the IS integration peak ($I_{Trioxane}$) is determined:

$$I_{ratio} = \frac{integral\ of\ the\ region\ of\ interest}{integral\ of\ IS\ peak} = \frac{I_{OH}}{I_{trioxane}}$$

Finally, to calculate the amount of carbonyl groups in lignin, which is expressed in mmol carbonyl / g lignin:

$$mmol\ of\ carbonyl\ groups\ per\ g\ of\ lignin = \frac{I_{ratio} * mmol\ of\ trioxane\ in\ NMR\ sample}{dry\ weight\ of\ lignin}$$

Quantitative ^{31}P-NMR

For quantitative determination of hydroxyl values, an exact amount of 28-32 mg of lignin sample (previously dried under vacuum at 70 °C) was weighed. Subsequently, 100 µL of a solution of chromium(III) acetylacetonate (5 mg/ml) as relaxation agent and the internal standard (IS) endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (NHND, 18 mg/ml) in $CDCl_3$:pyridine (1 : 1.6 v/v) are added to the lignin sample, and 450 µL of solvent mixture $CDCl_3$:pyridine (1 : 1.6 v/v) are added to aid solubilization. After a homogeneous solution was obtained, 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP, 70 µL) was added and the solution was stirred for an additional 15 minutes. Afterwards, it was transferred into a NMR tube for subsequent measurement using a Bruker Ascend instrument at 162 MHz with 512 scans and a delay time d_1 of 10 seconds at 298 K and a spectral width of 100 ppm (190–90 ppm).[2,3]

The chemical shifts are reported relative to the reaction product of 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane with water, at 132.2 ppm. Integrals are assigned to the functional groups as followed: δ = 152.5 – 151.7 (NHND), 149.5 – 145 (aliphatic hydroxyl groups), 145 - 141.2 (syringyl hydroxyl groups), 140.8 – 137.7 (guaiacyl hydroxyl groups), 135.7 – 134 (carboxylic acids).

Calculations were performed by first determining the mole quantity of IS in the IS solution:

$$NHND\ in\ IS\ solution\ (mmol) = \frac{mass\ of\ NHND\ added\ to\ the\ IS\ solution\ (g)}{M_w\ of\ NHND\ (179.17\frac{g}{mol})} * purity\ of\ NHND\ (\%) * 1000$$

Afterwards, the mole quantity of IS (NHND) in the NMR sample was calculated:

$$NHND\ in\ NMR\ sample\ (mmol) = \frac{NHND\ in\ IS\ solution\ (mmol)}{total\ mass\ of\ IS\ solution\ (g)} * mass\ of\ 0.1\ mL\ of\ IS\ solution\ (g)$$

I_{ratio} between the spectral region of interest (I_{OH}) over the IS integration peak (I_{NHND}) is determined:

$$I_{ratio} = \frac{integral\ of\ the\ region\ of\ interest}{integral\ of\ IS\ peak} = \frac{I_{OH}}{I_{NHND}}$$

Finally, to calculate the amount of different hydroxyl groups in lignin, i.e. OH / g lignin:

$$mmol\ of\ \ OH\ groups\ per\ g\ of\ lignin = \frac{I_{ratio} * mmol\ of\ NHND\ in\ NMR\ sample}{dry\ weight\ of\ lignin}$$

Size Exclusion Chromatography

SEC measurements were performed on an Agilent Technologies 1260 Infinity II system equipped with a Mixed-C and Mixed-E Agilent column, and a differential refractive index detector. The used eluent

was DMAc containing 0.034wt% LiBr. The number average molar mass (M_n), the weight average molar mass (M_w), and the dispersity ($Đ = M_w/M_n$) of the samples were determined using a calibration of polystyrene (PS) standards with M_p ranging from 370 to 2.52×10^6 Da. The samples were dissolved in the eluent at a concentration of 2 mg / mL and filtered over a 0.2 µL filter.

Mass Spectrometry (MS)

Electrospray ionization (ESI) experiments were recorded on a Q-Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific) equipped with a HESI II probe to record high resolution. The spectra were evaluated by molecular signals $[M - H]^+$ and indicated with their mass-to-charge ratio (m/z).

Continuous Flow reactor

Photo reactions in flow were conducted using an E-series flow reactor from Vapourtec with photochem equipment. As irradiation source, a 365 nm LED with 16 W power was used. The inner volume of the reactor capillary is 10 mL. A flow rate ranging from 1 to 9 mL/min was applied. Total irradiation time was up until 6 hours.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a Mettler Toledo DSC 3 STARe system. Aluminum crucibles (40 µL) were used to weigh a precise amount of each sample, between 3 and 7 mg. The samples were measured in two heating cycles to remove any thermal history: from 25 to 200, 200 to −50, and −50 to 200 °C. DSC curves presented are relative to the second heating cycle. A heating or cooling rate of 10 – 30 K min^{-1} was applied.

Thermogravimetric Analysis (TGA)

Thermogravimetric measurements were performed using a TGA Q5500 instrument from TA Instruments. The samples were dried under vacuum (10 mbar) at 70 °C overnight before measurement. The samples (5 – 6 mg) were heated in a Pt crucible from 25 to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. $T_{d,5\%}$ is defined as the temperature at which 5% weight loss of the sample occurred, while $T_{d,50\%}$ is defined as the temperature at which 50% of the weight loss of the sample occurred. Residue (%) is defined as the weight percentage of residual mass at the end of the analysis.

DMA

A Discovery DMA 850 from TA instruments was used to modulate from -50 °C to 200 °C at a heating rate of 3 K min^{-1}. The measurements were performed with tensile geometry at a frequency of 1 Hz, an initial force of 0.1 N and a strain sweep of 0.02%. Analyses were carried out in triplicate to ensure sample homogeneity and reproducibility.

WCA

Contact angle measurements were performed with a DSA25S contact angle goniometer (Krüss) using the sessile drop technique. A water droplet with a size of 5 µL was slowly added onto the thermoset samples by a micrometer syringe and contact angles between the surface of the thermoset against the water droplet were measured. The average value of five measurements was calculated for each sample with a standard deviation of less than 5°.

Gel content and swelling percentage determination

Weighed bar samples of the cured thermosets were immersed in THF for 24 hours. Afterwards, the swollen samples were dried gently between paper sheets and weighed again. Then, the samples were dried at 60 °C for 24 h, and their final weight was recorded.

The gel content of the samples is defined as:

$$Gel\ content\ (\%) = \frac{m_d}{m_i} \times 100\%$$

where:

m_d is the final weight of the sample after drying at 60 °C for 24 hours

m_i is the initial weight of the sample

The swelling percentage is defined as:

$$Swelling\ (\%) = \frac{m_{sw} - m_d}{m_d} \times 100\%$$

where:

m_d is the weight of the sample after drying at 60 °C for 24 hours

m_{sw} is the weight of the swollen sample after drying between paper sheets

UV-systems and reaction setups

1) A UV lamp of 365 nm of 45 W was used. Details of the distances between lamp and sample are shown in the figures below (**Fig. S1**).

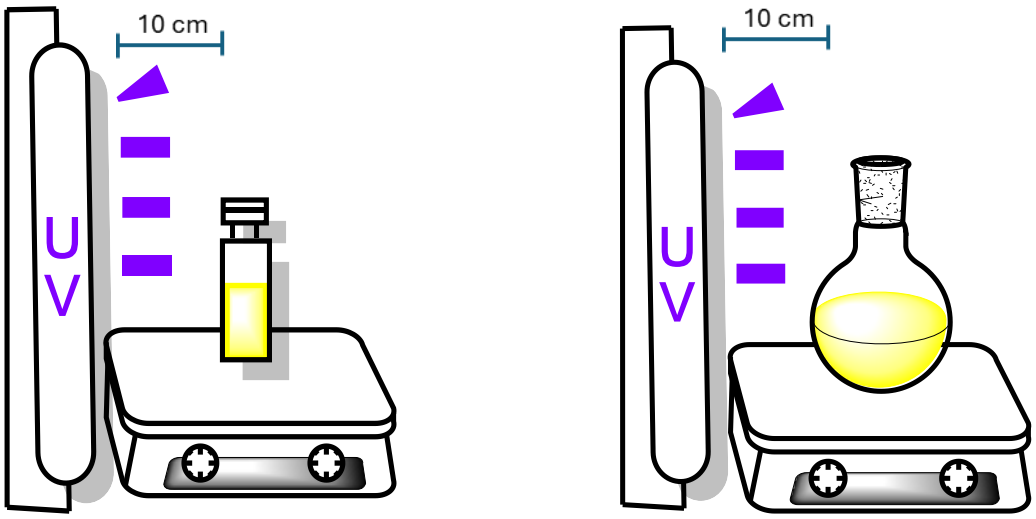


Fig. S1 – UV system (lamp 365 nm, 45 W) for small-scale reactions (left) and for larger-scale reactions (right).

2) A system consisting of five LEDs (1 cm x 1 cm) placed in a circle and installed on a metallic plate was used. Typically, the vial containing the reaction mixture was placed directly on one LED. When a round bottom flask was used, this was centered in the middle circle of LEDs (**Figs. S2 and S3**).

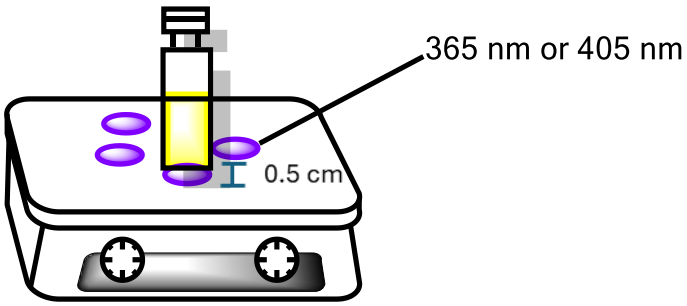


Fig. S2 – LEDs system (365 nm or 405 nm, 2W).

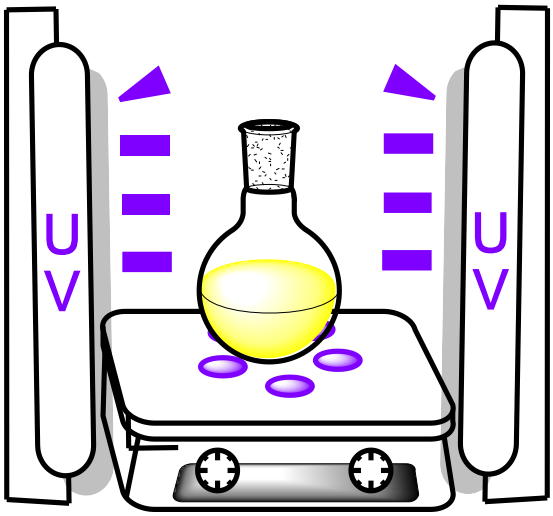


Fig. S3 – Three-side irradiation system. UV lamp 365nm 45 W (left side), UV lamp 365nm 12 W (right side), LEDs 365 nm, 2W (bottom).

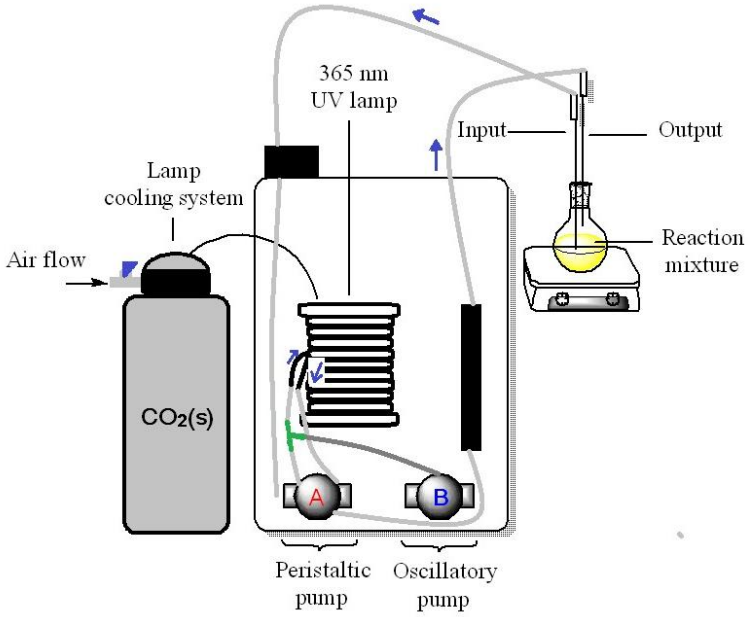


Fig. S4 –Flow reactor setup (closed-loop system).

Lignin modification

Organosolv lignin characterization

Characterization was performed *via* ^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR, SEC (DMAc), FT-IR, DSC, TGA. Data are reported in **Table S1**.

Table S1 – Characterization data of Organosolv lignin.

$OH_{aliphatic}$ [mmol g^{-1}]^a	$OH_{aromatic}$ [mmol g^{-1}]^a	COOH [mmol g^{-1}]^a	OH_{total} [mmol g^{-1}]^a	M_n [Da]	M_w [Da]	*Đ*	T_g [°C]	$T_{d,5\%}$ [°C]
2.42 ± 0.05	1.83 ± 0.04	0.1 ± 0.005	4.35 ± 0.08	5044	13097	2.59	140	267

^{a}: Determined via ^{31}P-NMR. Measurements were performed in triplicates.

ATR-IR: ν = 3443, 2937, 2841, 1722, 1594, 1512, 1456, 1423, 1325, 1216, 1115, 1031 cm^{-1}

^{1}H–NMR (400 MHz, DMSO-d_6) δ_H (ppm) = 7.50 – 6.25 ppm (m, C**H**$_{aryl}$); 4.0 – 3.50 (s, OC**H**$_3$, O**H**); 1.40 – 0-70 (m, C**H**$_{alkyl}$).

^{13}C–NMR (126 MHz, DMSO) δ 152.61, 147.81, 135.32, 115.88, 107.52, 104.08, 93.38, 60.08, 56.38, 15.74.

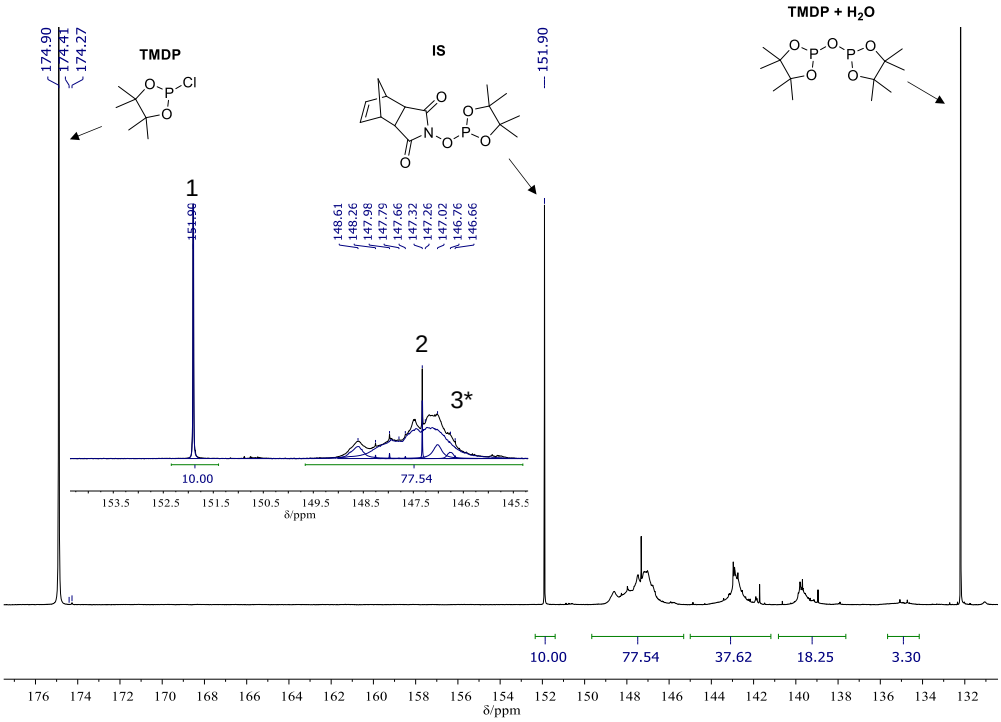


Fig. S5 – ^{31}P–NMR of pristine Organosolv lignin. Residual ethanol (sharp peak at 147.32 ppm) could not be fully removed, even after drying at 60 °C under vacuum (10 mbar) for 5 days, as also reported from Jääskeläinen *et al.*[4] To obtain more accurate results, peak deconvolution was performed and is shown in the expanded view (blue lines in **Figure S5**) and in **Table S2**.

Table S2 – Peak deconvolution data for organosolv lignin

Peak	δ/ppm	Area / arb. unit
1	151.90	199877
2	147.32	20596
3*	149.7-145.3	1549857

*: Area of the integral between 149.7 – 145.3 ppm.

Theoretical yield calculations for lignin modification

A simplified theoretical yield was calculated assuming 100% conversion of the reactive sites towards the main reaction, following Equation S1:

$$m_f = m_i \left(1 + \Delta M_{graft} \left(reactive\ sites\ in \frac{mol}{g}\right)\right) \quad \textbf{Eq. S1}$$

where:

m_f = final mass of the modified lignin (g)

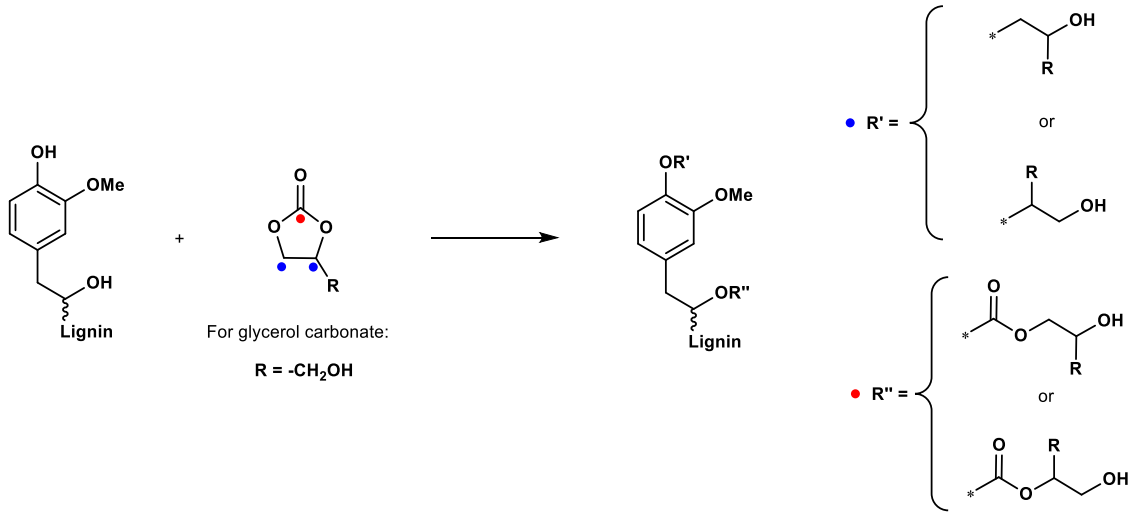
m_i = initial mass of pristine lignin (g)

ΔM_{graft}= increase in the molecular weight caused by the modification (g/mol)

reactive sites = number of moieties participating in the reaction (depending on the reaction type) in mol/g.

Lignin reactivity with organic carbonates

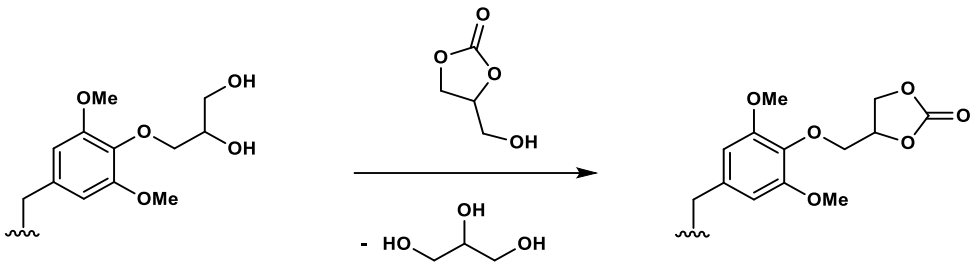
Lignin functionalization was performed following a two-step modification with organic carbonates as benign reactants and solvents. The procedure was adapted and modified from Lehnen *et al.*[5] It is known that the reaction between the hydroxyl groups of and organic carbonates can take place at both the electrophilic sites of the carbonyl and the alkyl carbons of an organic carbonate, generating, respectively, carbonyl and ether linkages (see **Scheme S*1***).[6–8] Regarding cyclic carbonates, several studies have been conducted in order to gain insights on the different reactivities. For instance, in the work of Lehnen *et al.*[7,9] oxyalkylation of beech wood organosolv lignin with propylene carbonate was investigated, showing that the formation of carbonate linkages is favored by longer reaction times, higher catalyst amounts and equivalents of propylene carbonate used. Under optimized conditions, only 0.3% of the total propyl units was grafted *via* carbonate linkages.



Scheme S1 – General scheme illustrating different reactivities for hydroxyl groups of lignin and a general structure of a cyclic carbonate.

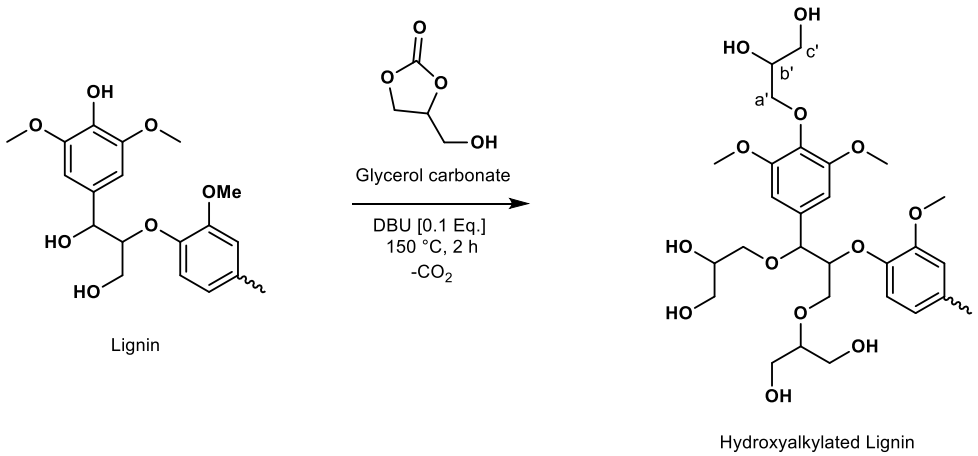
In another study from Avérous *et al.*,[6] oxyalkylation of lignin was investigated with four different cyclic carbonates. Among them, also glycerol carbonate (GC) was tested. For all other derivatives, a new peak between 1728 and 1743 cm^{-1} is forming, corresponding to the C=O stretching band of linear carbonate linkages. Interestingly, in the case of oxyalkylation with GC, this peak is shifted to higher wavenumbers (1786 cm^{-1}, 1789 cm^{-1} in this work) in the range of cyclic carbonates, suggesting a competing reaction between the formed 1,2-diols and GC, as can be seen in **Scheme S2**. This was further confirmed in the same study *via* hydrolysis of the aforementioned carbonates. Complete hydrolysis was confirmed *via* IR spectroscopy, while *via* ^{31}P-NMR spectroscopy it was possible to distinguish that 1,2-diols structures substantially increased after hydrolysis, while the content of 1,3-diols was unaltered, confirming the presence of five-membered cyclic carbonate structures prior to hydrolysis. These results were also in accordance with the findings from Lehnen *et al.*,[9] where cyclic carbonates structures could also be observed after oxyalkylation with GC.

Based on these considerations, it can be assumed that the etherification pathway will be the preferred one in the reaction with GC and some cyclic carbonate structures will already be present after the first step of the modification. However, since this reaction does not reach completion (a high amount of hydroxyl groups is still present, as can be observed from ^{31}P-NMR), the second step of the modification is necessary to achieve a high degree of functionalization with cyclic carbonate structures.



Scheme S2 – Side reaction between newly inserted 1,2-diols and excess glycerol carbonate, leading to cyclic carbonate structures and generating glycerol as by-product, as reported from Duval and Avérous and Lehnen *et al.*[6,9]

General procedure for the synthesis of hydroxyalkylated lignin with glycerol carbonate



Scheme S3 – General reaction scheme for the synthesis of hydroxyalkylated lignin. Only isomers of the etherification pathway with GC are shown, leading to 1,2-diols and 1,3-diols structures. For a comprehensive overview of all the possible structures, see **Scheme S1** and **Scheme S2**.

10 g of lignin (Organosolv lignin: 4.35 mmol OH per g dry lignin) was suspended in glycerol carbonate (10 equiv., 435 mmol, 51.33 g, 36.7 ml) and DBU (0.1 equiv., 4.35 mmol, 0.662 g, 0.65 ml) was added. The reaction mixture was allowed to react at 150 °C for 2 hours under Argon flow. After reaching 100 °C, strong evolution of CO_2 was observed. After completion of the reaction, the crude product was dissolved in a minimum amount of DMSO and the product was recovered by precipitation in a tenfold amount of acidified deionized water (pH =2). After filtration and washing with water (5 x 50 ml), the isolated product was dried at 60 °C under vacuum. (yield: 11.0183 g, 83 % theoretical yield, see **Eq. S1**).

SEC (DMAc, PS standards): M_n = 13800 Da; M_w= 65800 Da; Đ = 4.76

DSC: T_g = 99 °C

TGA: $T_{d,5\%}$ = 267 °C

^{1}H–NMR (400 MHz, DMSO-d_6) δ_H (ppm) = 7.50 – 6.25 ppm (m, C**H**$_{aryl}$); 5.30 - 4.10 (m, C**H**$_{a,b,c}$); 4.0 – 3.50 (s, OC**H$_3$**, O**H**); 1.40 – 0-70 (m, C**H**$_{alkyl}$).

^{13}C–NMR (126 MHz, DMSO) δ 154.97, 152.14, 92.90, 75.58, 72.94, 70.51, 68.59, 66.01, 63.09, 60.01, 55.84, 15.29.

ATR-IR: ν = 3425, 2933, 2871, 1790, 1590, 1504, 1456, 1417, 1327, 1224, 1121, 1031, 843 cm^{-1}.

Hydroxyl content: 4.66 mmol OH per g dry sample, calculated from ^{31}P–NMR.

Degree of substitution (DS) calculations:

DS phenolic hydroxyl groups: 1 (^{31}P – NMR shows no aromatic hydroxyl groups left after the reaction; therefore, the DS is set to one for complete substitution).

DS aliphatic hydroxyl groups: 0.75, determined from ^{13}C – NMR, according to the procedure established by Lehnen *et al.* [9] Signal of the installed hydroxyl terminated carbon (*b'*) is correlated to the total amount of aliphatic carbon atoms next to hydroxyls (60.01 ppm) according to Eq. S2:

$$DS_{aliphatic} = \frac{I_{b'}}{I_{b'} + I_{C-OH}}$$ Eq. S2

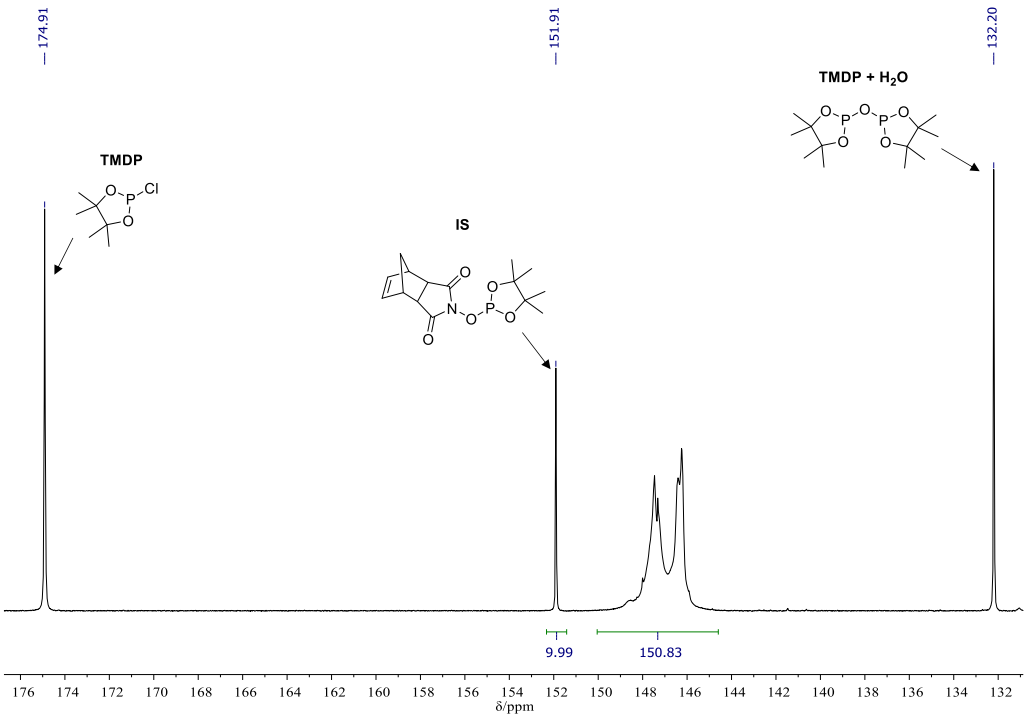


Fig. S6 – ^{31}P–NMR of hydroxyalkylated lignin.

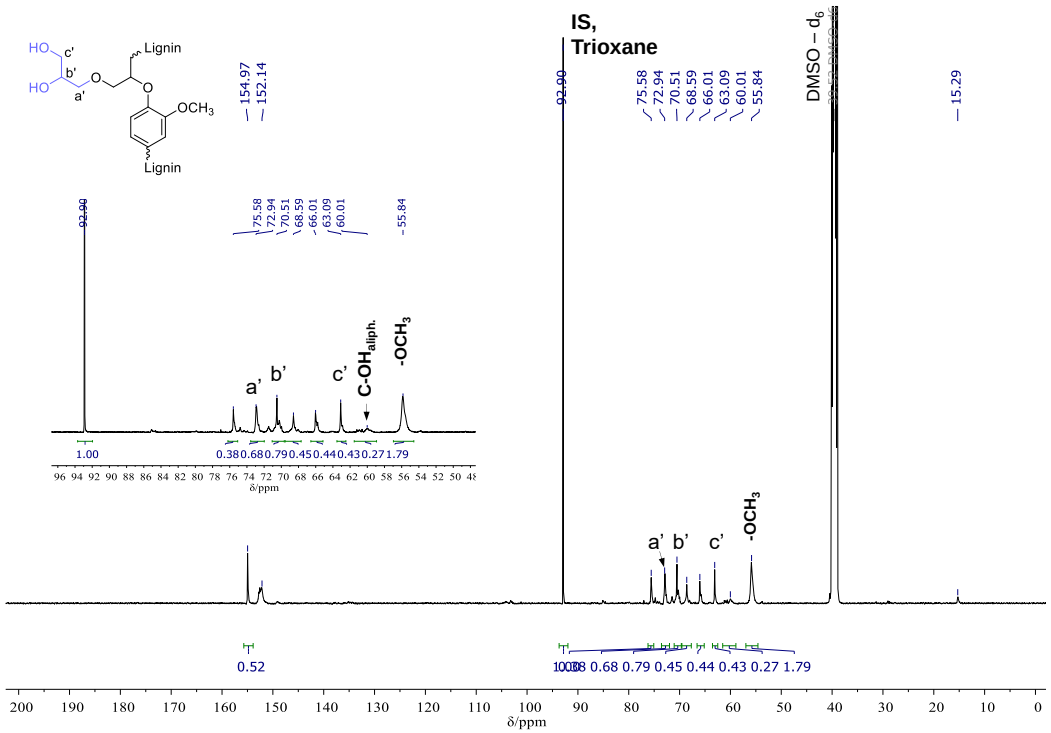
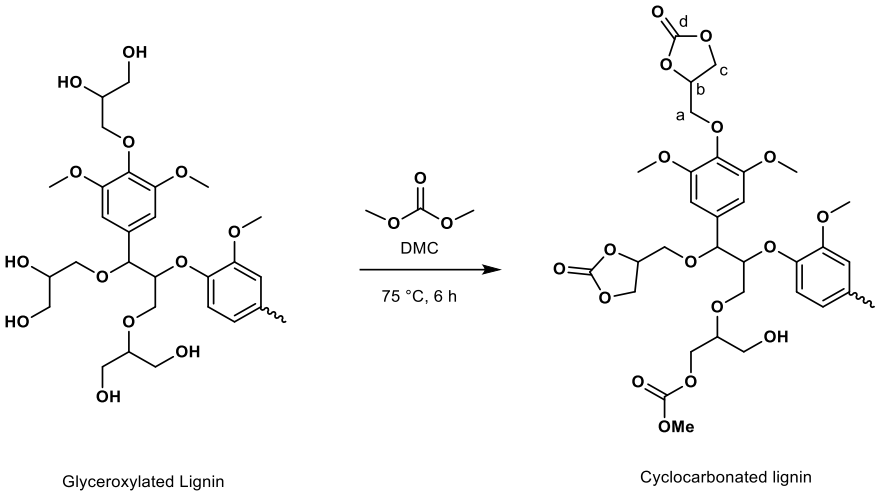


Fig. S7 – ^{13}C–NMR of hydroxyalkyated lignin, peak assignment was conducted based on literature data.[5]

Table S3 – Quantitative ^{13}C–NMR data for hydroxyalkylated lignin

mmol IS in the sample	I_{ratio} Carbonyl peak	Carbonyl content [mmol g^{-1}]
0.06169	0.52	0.34

General procedure for the synthesis of cyclic carbonate functionalized lignin with dimethyl carbonate



Scheme S4 – General reaction scheme for the synthesis of cyclic carbonate functionalized lignin. The main reaction leading to the formation of cyclic carbonate structures is shown, as well as the formation of linear carbonates due to the reaction of hydroxyl groups with only one side of DMC. Both possible isomers deriving from etherification with GC are shown (forming 1,2-diols and 1,3-diols).

Solventless procedure:

In a crimp vial, 1 gram of previously synthesized hydroxyalkylated lignin (4.66 mmol OH per g) was suspended in DMC (anhydrous, 5 equiv., 23.3 mmol, 2.09 g, 2.00 ml). The catalyst DBU (0.4 equiv., 1.86 mmol, 284 mg, 278 µL) was added to the reaction vessel, and this was flushed with a gentle Argon flow for 5 to 10 minutes. Afterwards, the desired temperature was applied and the reaction was stirred for 6 h at 75 °C. After completion of the reaction, the crude product was recovered by precipitation in a tenfold amount of acidified deionized water (pH =2). After filtration and washing with water (5 x 50 ml), the isolated product was dried at 60 °C under vacuum.

Hydroxyl content: 1.68 mmol OH per g, calculated from ^{31}P–NMR.

Procedure with solvent:

6 grams of previously synthesized hydroxyalkylated lignin (4.66 mmol OH per g) was dissolved in DMAc (anhydrous, 15 ml) with gentle heating. Afterwards, DMC was added (anhydrous, 5 equiv., 140 mmol, 12.6 g, 11.8 ml) as well as the catalyst TBD (0.4 equiv., 11.2 mmol, 1.56 g), and the vessel was flushed with a gentle Argon flow for 5 to 10 minutes. Afterwards, the desired temperature was applied, and the reaction was stirred for 6 h at 75 °C. After completion of the reaction, the crude product is recovered by precipitation in a tenfold amount of acidified deionized water (pH = 2). After filtration and washing with water (5 x 50 ml), the isolated product was dried at 60 °C under vacuum. (yield: 5.83 g, 86 % theoretical yield, see **Eq. S1**).

SEC (DMAc, PS standards): M_n = 12600 Da; M_w= 49660 Da; Đ = 3.93

DSC: T_g = 117 °C

TGA: $T_{d,5\%}$ = 222 °C

^{1}H–NMR (400 MHz, DMSO-d$_6$) δ_H (ppm) = 7.6 – 5.9 ppm (m, C**H**$_{aryl}$); 5.3 - 4 (m, C**H**$_{a,b,c}$); 4.0 – 3.4 (s, OC**H**$_3$, O**H**); 1.40 – 0-70 (m, C**H**$_{alkyl}$).

^{13}C–NMR (126 MHz, DMSO) δ 155.43, 153.03, 149.54, 135.63, 103.37, 93.36, 76.04, 73.33, 71.92, 70.70, 66.46, 63.55, 60.39, 56.25, 55.10, 15.69.

ATR-IR: ν =3493, 2937, 1792, 1748, 1592, 1506, 1456, 1329, 1267, 1125, 1051, 847, 771 cm^{-1}.

Hydroxyl content: 1.64 mmol OH per g, calculated from ^{31}P–NMR.

Carbonyl content: 0.91 mmol per g, calculated from ^{13}C–NMR.

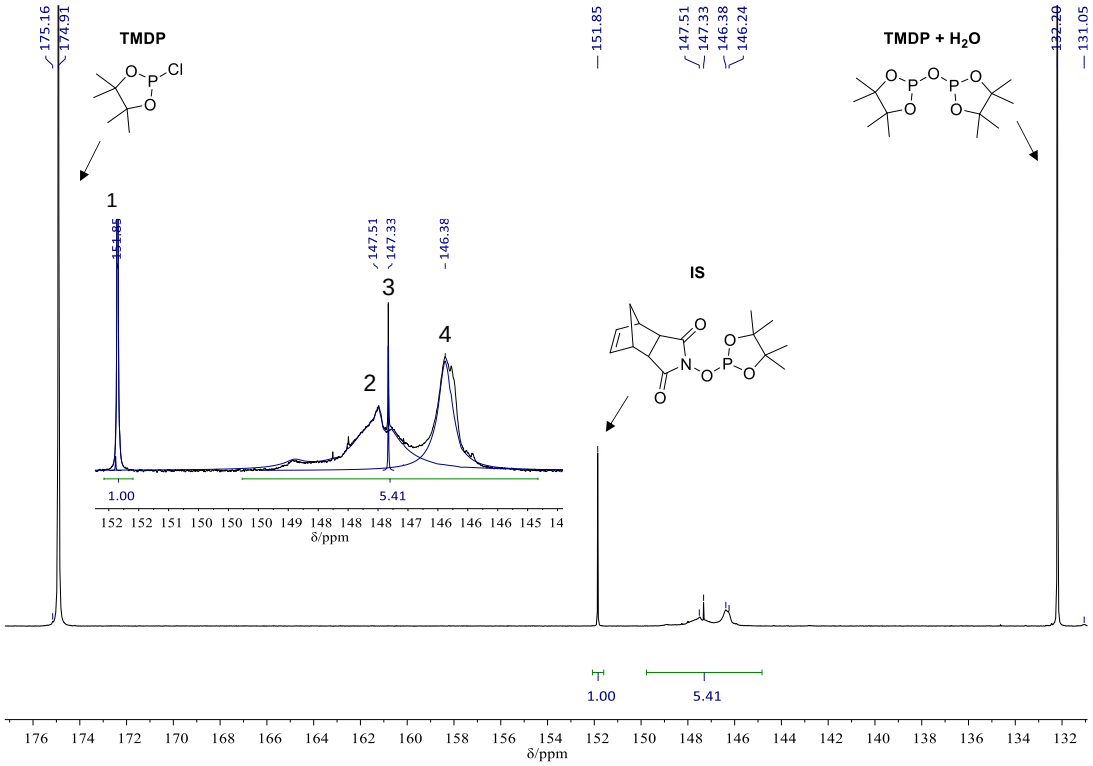


Fig. S8 – ^{31}P–NMR of cyclic carbonate functionalized lignin. Residual ethanol (sharp peak at 147.32 ppm) could not be removed, even after drying at 60 °C under vacuum (10 mbar) for 5 days, as also reported from Jääskeläinen *et al.*[4] To obtain more accurate results, peak deconvolution was performed and is shown in the expanded view (blue lines).

Table S4 – Peak deconvolution data for cyclic carbonate functionalized lignin

Peak	δ/ppm	Area / arb.unit
1	151.85	47648669
2	147.51	169196204
3	147.33	4115611
4	146.38	120457654

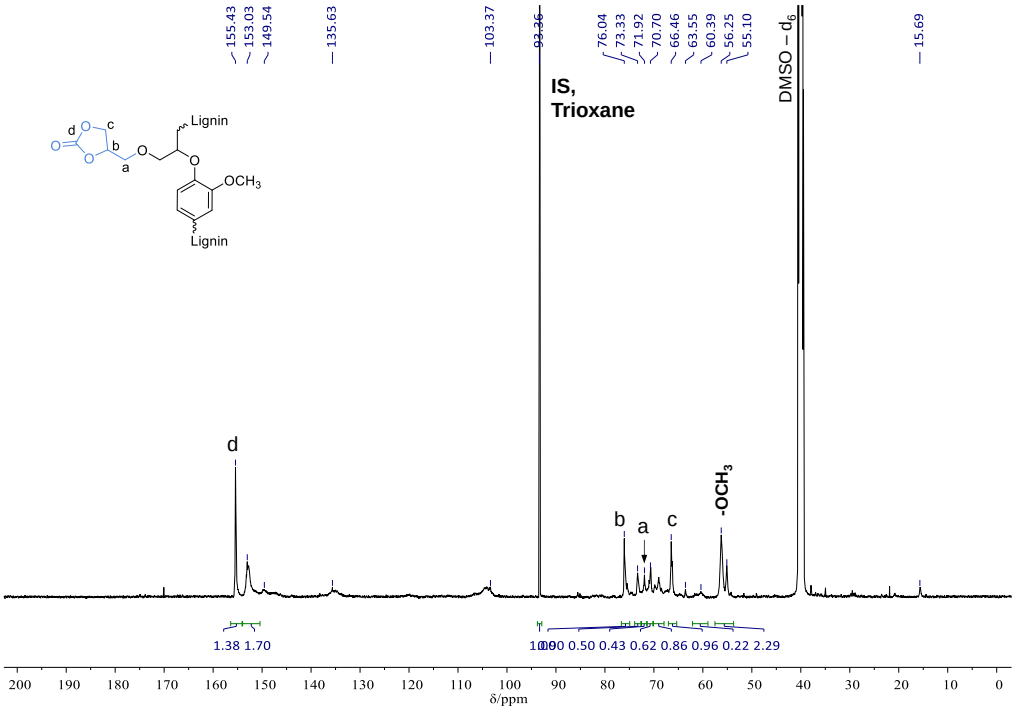


Fig. S9 – ^{13}C–NMR of cyclic carbonate functionalized lignin, peak assignment was conducted based on literature data.[5]

Table S5 – Quantitative ^{13}C–NMR data for cyclic carbonate functionalized lignin

mmol IS in the sample	I_{ratio} Carbonyl peak	Carbonyl content [mmol g^{-1}]
0.06289	1.38	0.91

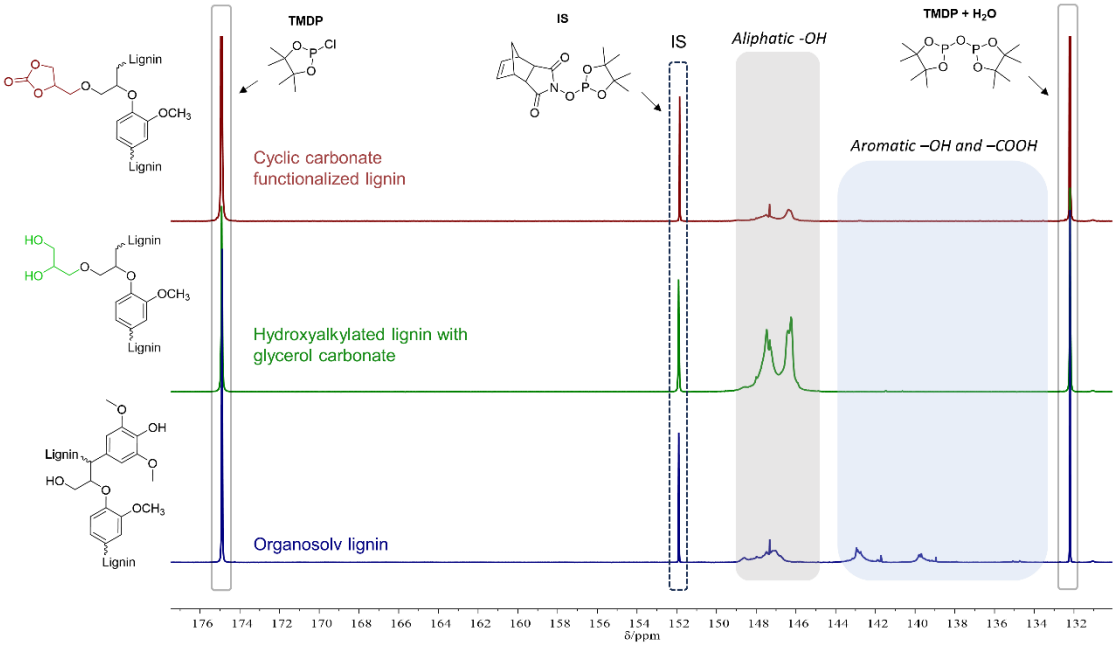


Fig. S10 – Overlay of ^{31}P–NMR spectra for Organosolv lignin (blue), hydroxyalkylated lignin (green) and cyclic carbonate functionalized lignin (red). After hydroxyalkylation, a complete conversion of aromatic hydroxyl groups is observed, as well as a concomitant increase of aliphatic hydroxyl groups. Two signals are visible, due to the primary and secondary alcohols formed at the end of the grafted chain.[9] After subsequent reaction with dimethyl carbonate, a strong decrease in aliphatic hydroxyl groups is observed, as a consequence of cyclic carbonate moieties formation.

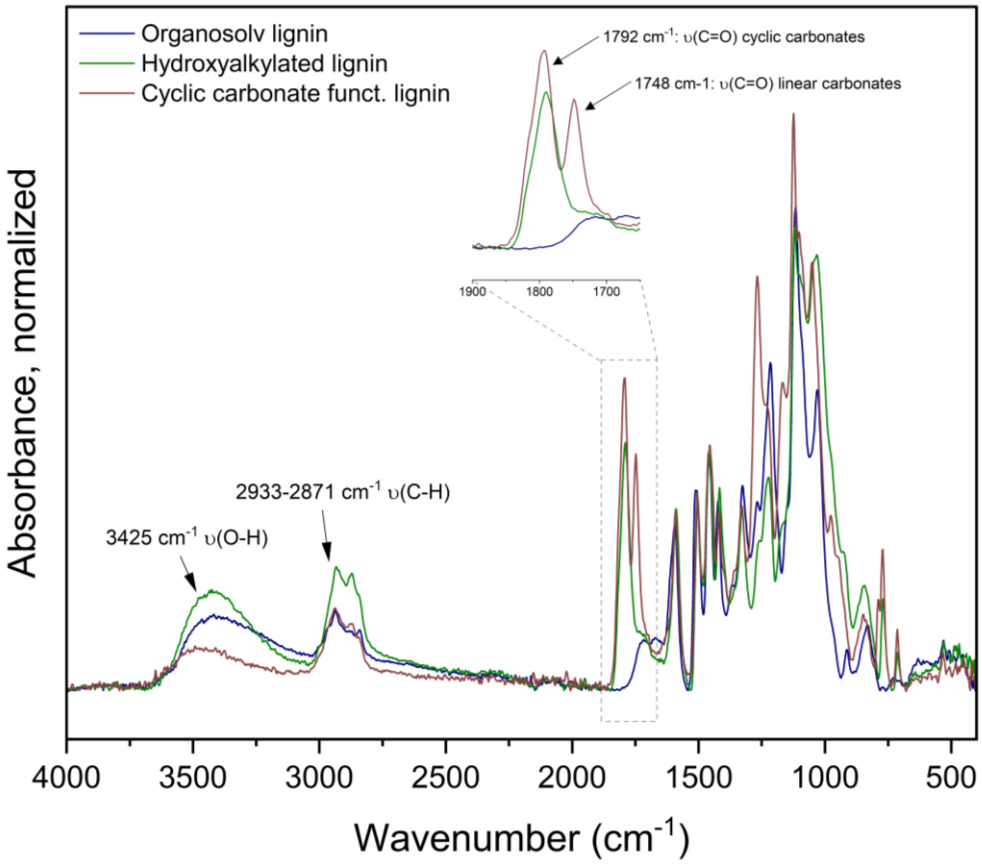


Fig. S11 – Overlay of IR spectra for organosolv lignin (black), hydroxyalkylated lignin (red) and cyclic carbonate functionalized lignin (blue); all spectra are normalized to the signal at 1504 cm^{-1}, ascribed to the C=C aromatic stretching vibration that is not affected during the modifications. After hydroxyalkylation, an expected increase in the stretching vibration of hydroxyl groups is observed (3425 cm^{-1}), as well as an increase in the C-H stretching vibration (2933-2871 cm^{-1}). Interestingly, a C=O stretching vibration band appeared at 1790 cm^{-1}, suggesting the presence of cyclic carbonate structures. These structures form due to the side reaction between the newly formed 1,2 diols and excess of GC (see **Scheme S2**), as already reported from Lehnen *et al.*[9] and Duval and Avérous.[6] This is also confirmed by ^{13}C – NMR analysis, that shows a carbonyl peak ("*d*") forming after hydroxyalkylation. (**Fig. S13**). Nevertheless, after reaction with DMC, the signal of cyclic carbonate stretching vibration increases further, and a new signal appears at 1746 cm^{-1}, due to the formation of linear carbonates between alcohols and one functionality of DMC.

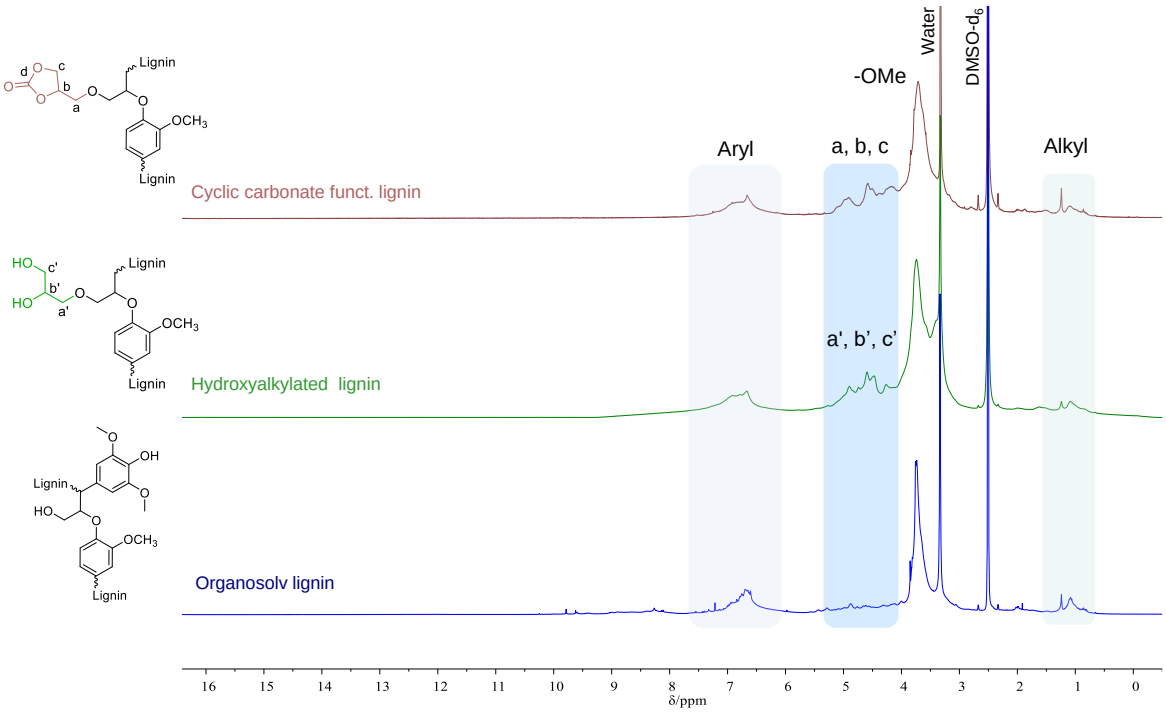


Fig. S12 – Overlay of ^{1}H–NMR spectra for organosolv lignin (bottom), hydroxyalkylated lignin (middle) and cyclic carbonate functionalized lignin (top).

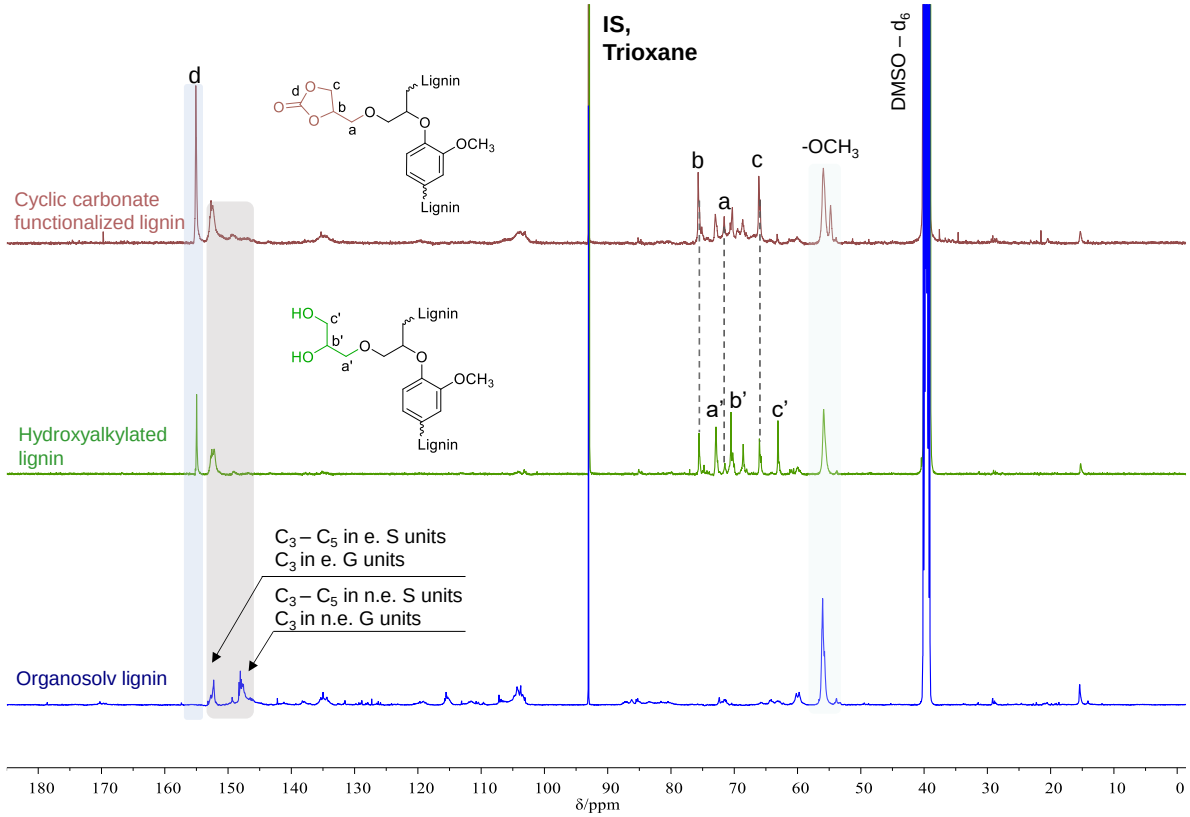


Fig. S13 – Overlay of ^{13}C–NMR spectra for organosolv lignin (bottom), hydroxyalkylated lignin (middle) and cyclic carbonate functionalized lignin (top). Peak assignment was performed based on literature values.[5] The increasing signal ascribed to the carbonyl of cyclic carbonates structures is already present after hydroxyalkylation step, due to the side reaction shown in **Scheme S2Scheme S2**. Additionally, the signal attributed to the C_3-C_5 of etherified syringyl and guaiacyl units increases, while the signal for the C_3-C_5 of non-etherified syringyl and guaiacyl units decreases, providing further confirmation of a successful reaction (both highlighted in gray).

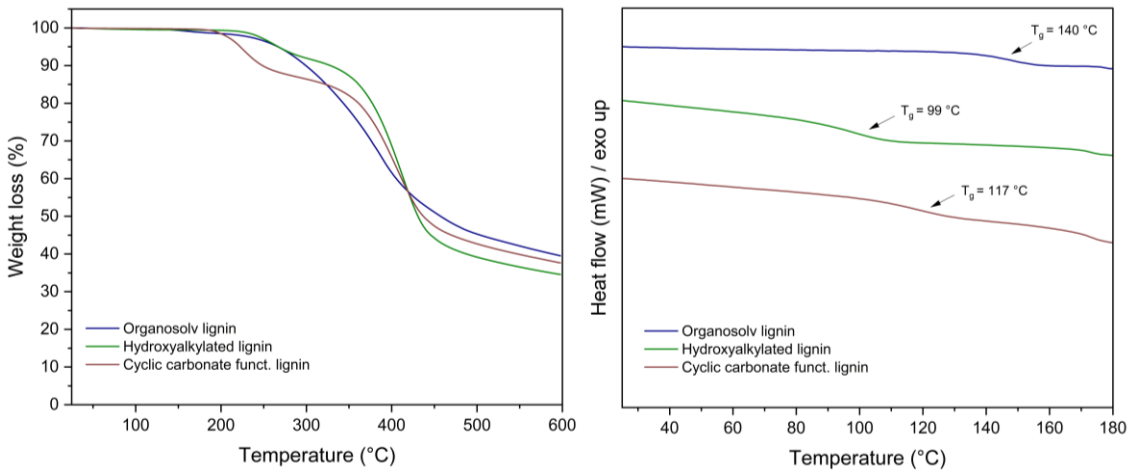


Fig. S14 – TGA (left) and DSC (right) thermograms of organosolv lignin (black), hydroxyalkylated lignin (red) and cyclic carbonate functionalized lignin (blue). Values are shown in **Table S6**.

Table S6 – Values obtained from thermal analyses TGA and DSC for unmodified Organosolv lignin, hydroxyalkylated lignin, and cyclic carbonate functionalized lignin.

Sample	$T_{d,5\%}$ [°C]	$T_{d,30\%}$ [°C]	Residues [%]	T*g* [°C]
Organosolv lignin	267	376	45	140
Hydroxyalkylated lignin	267	398	35	99
Cyclic carbonate funct. lignin	222	391	38	117

Triglyceride modification

Calculation of triglycerides unsaturation by ^{1}H-NMR

Equations system:[10]

$$Vinylic\ hydrogens\ integral = 2A + 4B + 6C$$

$$Linoleic\ bisallylic\ hydrogens\ integral = 2B$$

$$Linolenic\ bisallylic\ hydrogens\ integral = 4C$$

$$A + B + C + D = 3$$

A = oleic chain (monounsaturated)

B = linoleic chain (diiunsaturated)

C = linolenic chain (triunsaturated)

D = saturated chain

High oleic sunflower oil (Rapunzel)

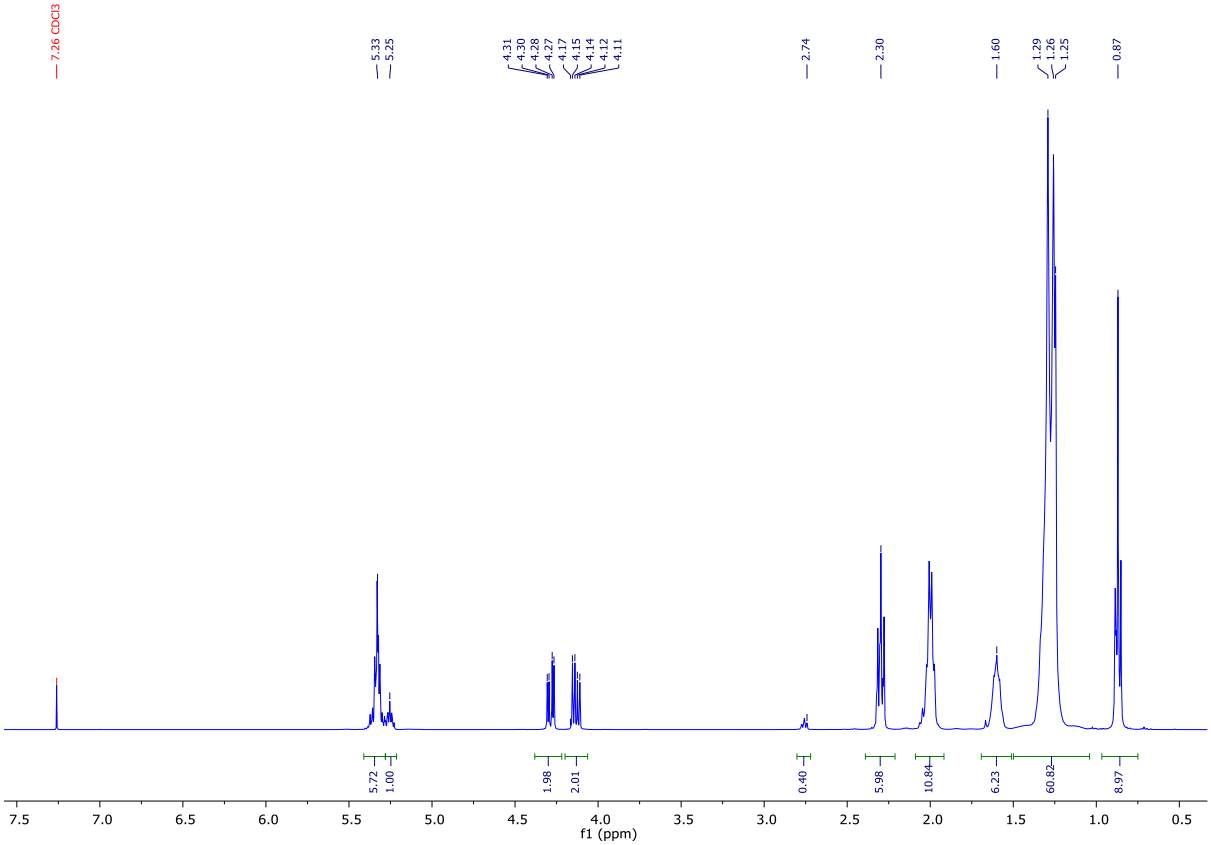


Fig. S15 – ^{1}H–NMR of the employed HOSO during experiments.

In general, once normalised to integral = 2, the peaks of the glycerol -CH_2-CH-CH_2- unit (4.28 ppm), the integrals of the vinylic hydrogen (5.33 ppm), linoleic bisallylic hydrogens (2.74 ppm) and linoleic bisallylic hydrogen (~2.80 ppm) were evaluated and evaluated according to the above shown equation system. In the specific case of this HOSO sample, no tri-unsaturated chains were present (no 2.80 ppm peak, see **Fig. S15**).

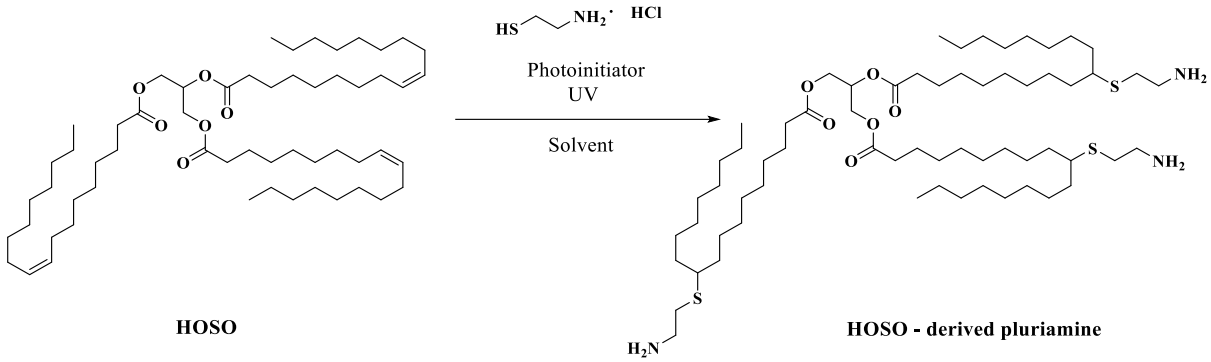
$$5.93 = 2A + 4B + 6C$$
$$0.41 = 2B$$
$$0 = 4C$$
$$A + B + C + D = 3$$

This equation resulted in: A = 2.55, B = 0.205, C = 0, D = 0.245. TOT= 3.

Peak	**Percentage**
A = monounsatured, oleic chain	85%
B = diunsatured, linoleic chain	6.83%
C= triunsatured	0
D=satured	8.16%

The average double bond per triglyceride is the weighted average of double bonds per chain = 0.986, which was approximated to 1 double bond per chain or approximately 3 per triglyceride.

Synthesis of High Oleic Sunflower Oil (HOSO) – derived polyamine (PA) – *Batch with DMPA*



Scheme S5 – General reaction scheme for the synthesis of HOSO-derived polyamine (PA).

The procedure was adapted and modified from Stemmelen *et al*.:[11] 500 mg (0.56 mmol) of High Oleic Sunflower oil (**HOSO**, 85 % of monounsaturated fatty acid chains, average 3 double bonds per triglyceride, calculated by ^{1}H-NMR as shown above, from Rapunzel)[10] were placed in a glass vial, together with cysteamine hydrochloride (**CAHC**, 3 equiv. per double bond, 5.08 mmol, 577.14 mg) and the correct amount of the solvent mixture chosen (depending on the concentration, see **Table 1**). The mixture was stirred for 30 min. Afterwards, 0.3 equivalents of 2,2-dimethoxy-2-phenylacetophenone (DMPA, 0.1 equiv. per double bond, 0.169 mmol, 43.42 mg) were added. The reaction was stirred for the chosen time at room temperature and irradiated by UV light (see different setups in **Fig. S1, Fig. S2, Fig. S3**). At the end of the reaction, the solvent was removed using a rotary evaporator. Subsequently, 20 mL of chloroform were added to the dried crude. The organic phase was therefore washed with saturated sodium carbonate solution and multiple times with distilled water until neutral pH was observed. Afterwards, the residual traces of water were removed with anhydrous sodium sulfate. After filtration of the Na_2SO_4, the solvent was removed using a rotary evaporator. The product appeared as a slightly yellow oil.

Synthesis of High Oleic Sunflower Oil (HOSO) – derived polyamine (PA) – *Batch with TPO-L*

The procedure was adapted and modified from Stemmelen *et al*.:[11] 500 mg (0.56 mmol) of High Oleic Sunflower oil (**HOSO**, 85 % of monounsaturated fatty acid chains, average 3 double bonds per triglyceride, calculated via ^{1}H-NMR as shown above, from Rapunzel)[10] were placed in a glass vial, together with cysteamine hydrochloride (**CAHC**, 3 equiv. per double bond, 5.08 mmol, 577.14 mg) and the correct amount of the solvent mixture chosen (Dioxane: EtOH,7:3 or Isopropanol: EtOH, 1:1), with a concentration of 0.28 g/mL of oil. The mixture was stirred for 30 min. Afterwards, a 2 wt% TPO-L solution was prepared in the solvent mixture chosen. The weight percentage was calculated considering the total weight of HOSO and CAHC in the concentration of 1 mg/35 µL of oil. The reaction was stirred for 48 h at room temperature and irradiated by 405 nm LEDs (see setup in **Fig. S2**). At the end of the reaction, the solvent was removed using a rotary evaporator. Subsequently, 20 mL of chloroform were added to the dried crude. The organic phase was therefore washed with saturated sodium carbonate solution and multiple times with distilled water until neutral pH was observed. Afterwards, the residual traces of water were removed with anhydrous sodium sulfate. After filtration of the Na_2SO_4, the solvent was removed using a rotary evaporator. The product was obtained as a slightly yellow oil.

Synthesis of High Oleic Sunflower Oil (HOSO) – derived polyamine (PA) - *Batch, aliquots addition*

The procedure was adapted and modified from Rios *et al.*:[12] Briefly, 1 g of High Oleic Sunflower oil (**HOSO**, 87% of oleic fatty acid chains, average 3 double bonds per triglyceride, calculated from ^{1}H−NMR, from Alnatura) was placed in a glass vial, together with the necessary amount of 2,2-dimethoxy-2-phenylacetophenone (**DMPA**, 0.1 equiv. per double bond, 0.339 mmol, 87 mg) and 4.5 ml of iPrOH. The mixture was stirred until homogeneous. Cysteamine hydrochloride (**CAHC**, 3 equiv. per db, 10.16 mmol, 1.15 g) was added in three aliquots, according to **Table S7**. The reaction was stirred for 24 h at RT and irradiated with 365 nm UV-light (45 W + 12 W lamps, see **Fig. S16**). At the end of the reaction, the solvent was removed using a rotary evaporator. Subsequently, 20 mL of chloroform were added to the dried crude. The organic phase was washed with saturated sodium carbonate solution and multiple times with distilled water until neutral pH was observed. Afterwards, the residual traces of water were removed with anhydrous sodium sulfate. After filtration of the Na_2SO_4, the solvent was removed using rotary evaporator. The product resulted was obtained as slight yellow oil.

Table S7 – Multistep addition of CAHC, aliquot weights and distribution

Cysteamine HCl aliquot	**1**	**2**	**3**
Weight (g)	0.575	0.2875	0.2875
Time (h)[a]	0	1.5	4

[a]Time from the start of the reaction

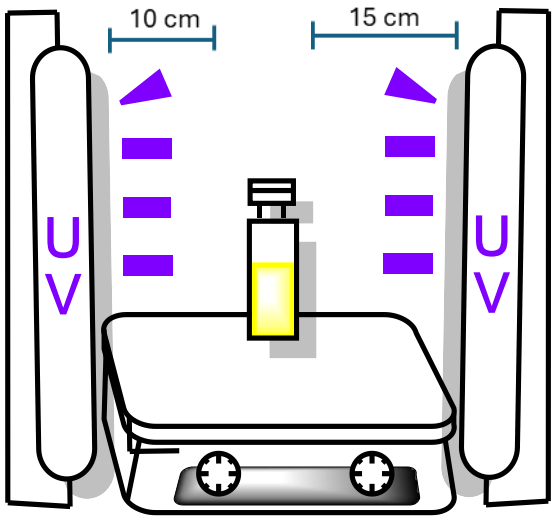


Fig. S16 – General reaction set-up: two-side irradiation system. UV lamp 365nm 45 W (left side), UV lamp 365nm 12 W (right side).

Synthesis of High Oleic Sunflower Oil (HOSO) – derived polyamine (PA) – Continuous flow

2 g of high oleic sunflower oil (**HOSO**, 87% of monounsaturated fatty acid chains, average 3 double bonds per triglyceride, calculated from ^{1}H-NMR, from Alnatura) and 2.31 g (20.3 mmol, 9 eq) of cysteamine hydrochloride were dissolved in 12 mL isopropanol and stirred for 30 min. Subsequently, 2,2-dimethoxy-2-phenylacetophenone DMPA (174 mg, 0.3 eq) and more solvent (2 mL) were added. The reaction mixture (under stirring) was fed to the flow reactor in a closed-loop mode. A scheme of the flow reactor is represented above (**Fig. S4**).

Characterization of High Oleic Sunflower Oil (HOSO) – derived polyamine (PA)

^{1}H–NMR (400 MHz, $CDCl_3$) δ 5.37 (m, -C**H** from unreacted double bonds), 5.25 (q, -C**H** from glycerol backbone), 4.08 – 4.34 (m, -C**H₂** from glycerol backbone), 2.77 – 2.92 (t, -C**H₂**NH_2), 2.47–2.71 (m, - C**H**SC**H₂**), 2.22 – 2.38 (t, -COC**H₂**), 1.65 – 1.83 (s, -N**H₂**), 1.08 – 1.65 (m, -C**H₂** from fatty acid chains), 0.87 (t, -C**H₃**).

^{13}C–NMR (101 MHz, $CDCl_3$) δ 173.25, 68.89, 62.09, 45.90, 41.72, 35.07, 34.71, 34.02, 31.90, 29.67, 29.62, 29.31, 29.10, 26.85, 24.82, 22.68, 14.13.

ATR-IR: ν = 2923, 2853, 1740, 1650, 1604, 1462, 1275, 1158, 755 cm^{-1}

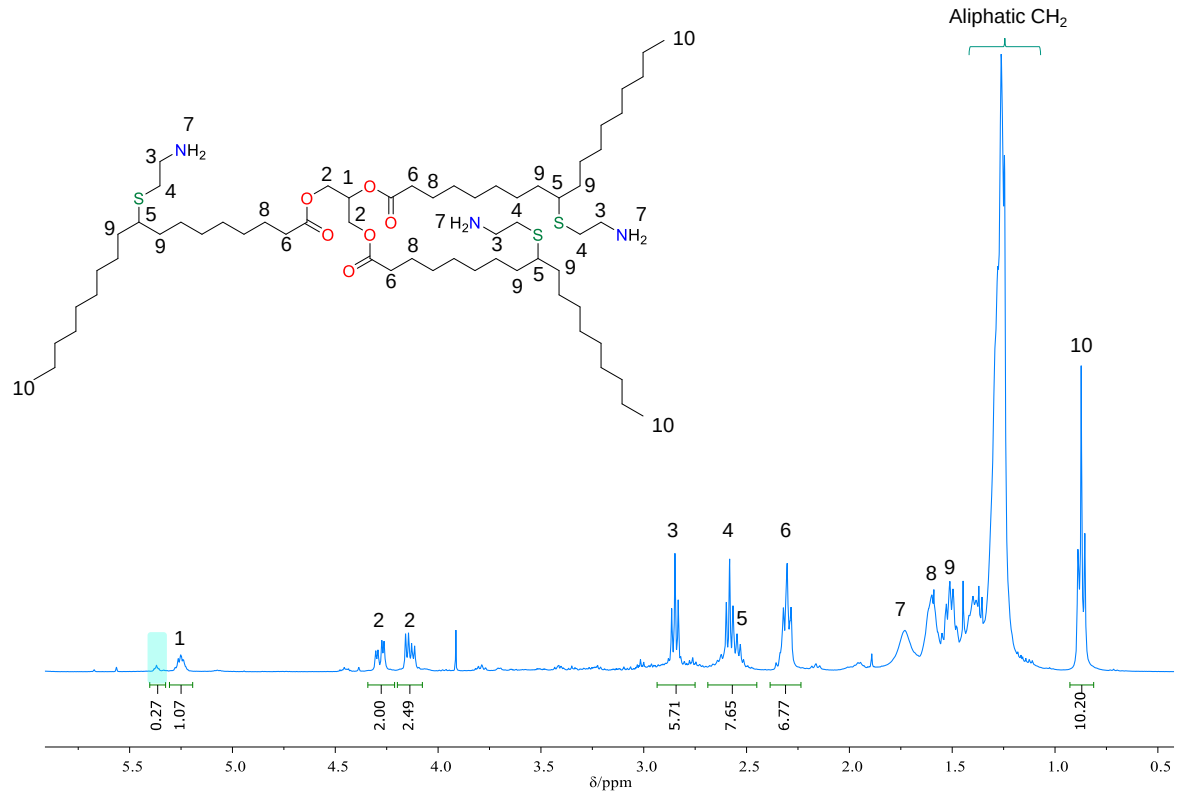


Fig. S17 – ^{1}H–NMR spectrum of **PA** with a conversion of 95 %. Peak assignation was performed *via* 2D – NMR spectroscopy techniques (HMBC, HSQC, COSY), DEPT – 135 and according to literature values.

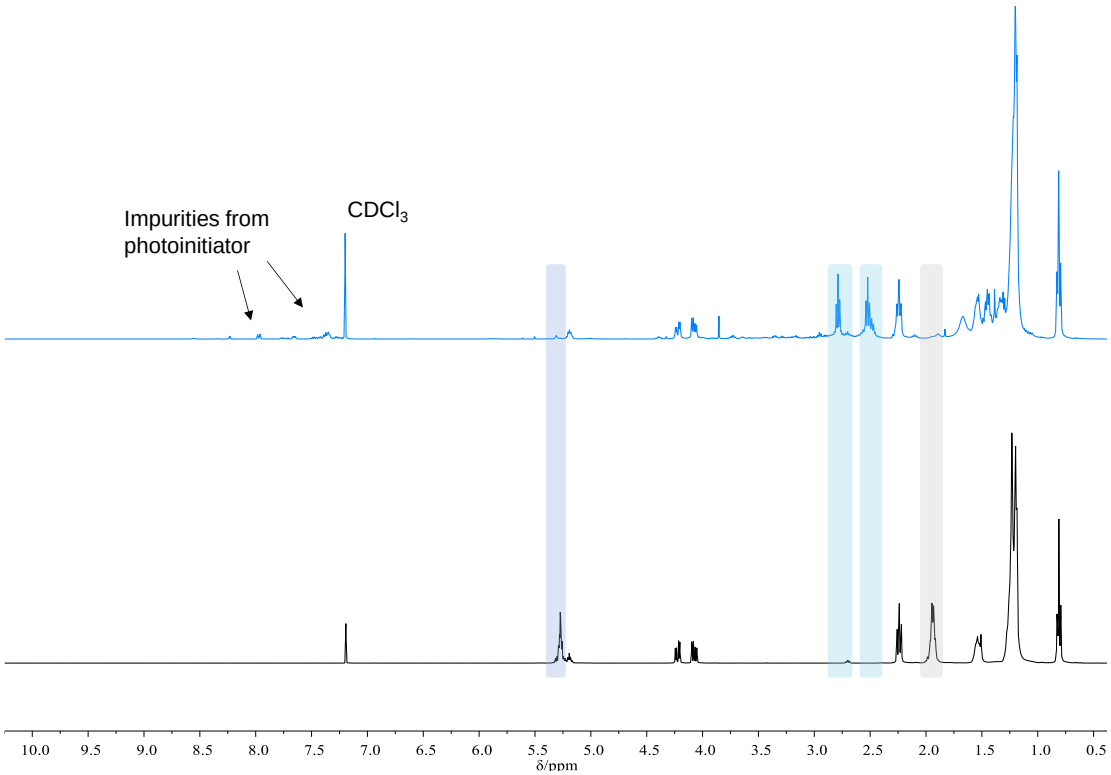


Fig. S18 – Overlay of ^{1}H–NMR spectra for pristine HOSO (black, bottom) and **PA** (top, blue). The disappearance of the signal attributed to the -CH protons of the double bonds (vinylic protons, highlighted in violet) indicates a high conversion (95%), confirming the successful reaction. In the spectrum of the aminated HOSO, two new signals (highlighted in light blue) appear, corresponding to the CH_2 protons directly attached to the -NH_2 and -S groups, respectively. Additionally, the signal for the allylic -CH_2 protons disappears in **PA**.

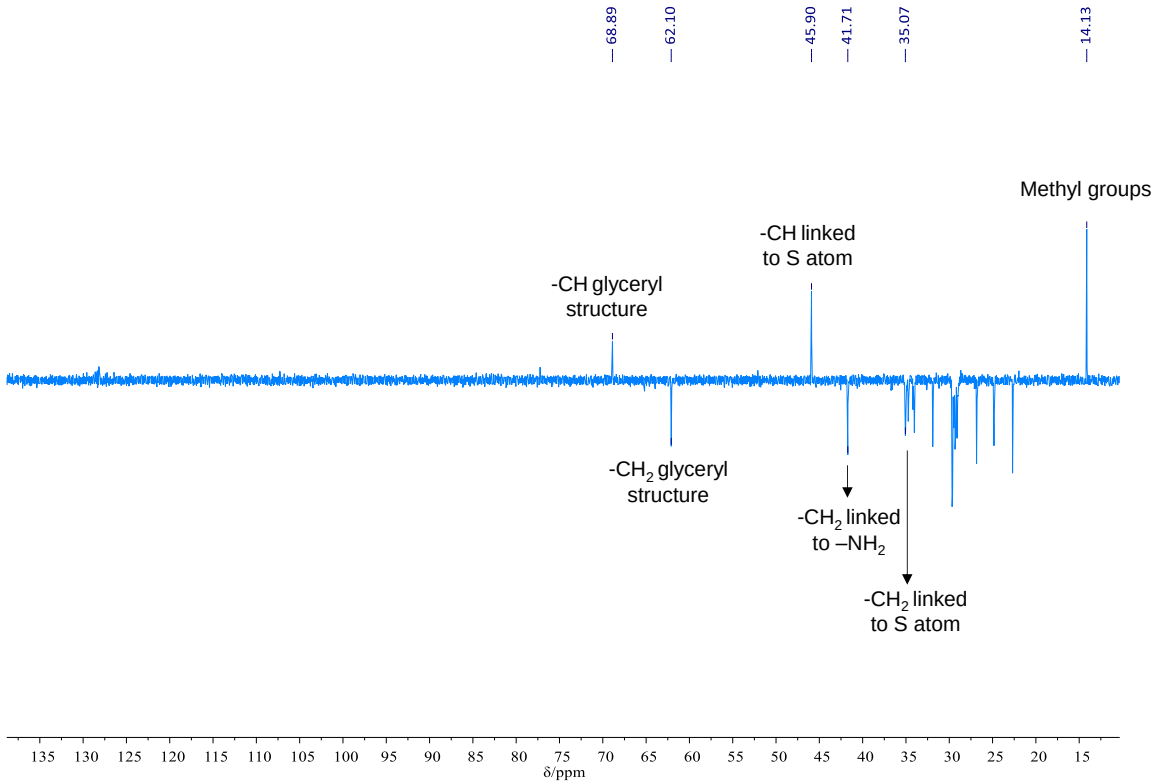


Fig. S19 – DEPT – 135 spectrum of **PA** in $CDCl_3$. CH and CH_3 groups are shown as positive, while CH_2 are negative.

Conversion calculation:

Conversion of the double bonds was calculated based on the normalized integral of the signal ascribed to the double bond protons, both in the pristine HOSO (5.33 ppm, *I* = 5.93) and in the aminated HOSO (5.37 ppm).

$$Conversion\ (\%) = \frac{I_{CH=CH\ HOSO} - I_{CH=CH\ aminated\ HOSO}}{I_{CH=CH\ HOSO}} \times 100$$

Amine functionality calculation:

Introduced functionalities (f) equals to the functional groups of cysteamine introduced to the aminated HOSO per trigyceride. The theoretical maximum equals to 3 (if all three double bonds of HOSO have reacted), which corresponds to 100% conversion. Functionalities are therefore calculated based on the conversion reached, according to the equation:

$$f = \frac{Conversion\ (\%)}{100\ \%} \times 3$$

Molecular weight calculation:

$$MW\ final = MW(HOSO) + (f \times 77.137)$$

Yield calculation:

To calculate the yield of the product, the theoretical mass has to be calculated first, with the final MW obtained in the calculation above. The yield of the product can then be calculated as follows:

$$Yield = \frac{Obtained\ weight\ of\ product}{Theoretical\ mass} \times 100\%$$

Conversion monitoring in flow reactions

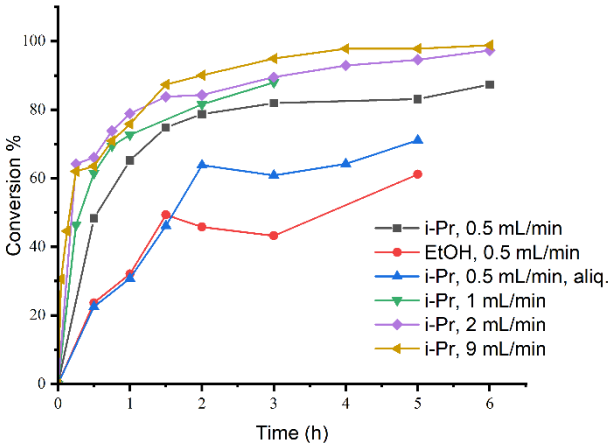


Fig. S20 – Comparison of reaction conversions for flow experiments. To evaluate the conversion, a 100 µL sample was taken at different reaction times and ^{1}H−NMR was recorded. Different flow rates and different solvents were evaluated.

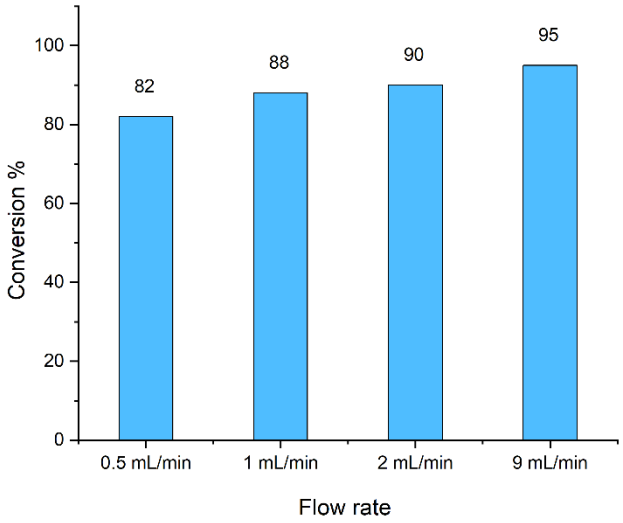


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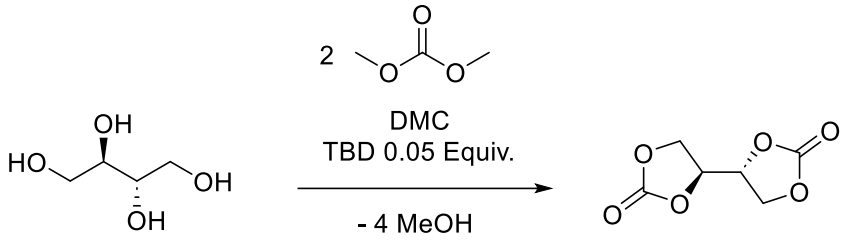
Fig. S21 – Conversion after 3 hours of reaction time in flow experiments.

Thermosets

Synthesis of erythritol bis-cyclic carbonate (EBC)



Scheme S6 – General reaction scheme for the synthesis of erythritol bis-cyclic carbonate.

Procedure:

A procedure described in previous work from Meier *et al*. was applied:[13] In particular, in a 100 mL flask, erythritol (2.00 g, 16.4 mmol, 1.00 eq) and TBD (114 mg, 0.820 mmol, 0.05 eq.) were dispersed in 41 mL DMC (43.87 g, 0.487 mol, solvent and reactant) and heated to 60 °C for 40 min at the rotary evaporator at 320 mbar. The crystalline erythritol dissolved completely after 35 min and after 45 min, a white precipitate was formed. The product was filtered off after the mixture was cooled to room temperature and washed with dimethyl carbonate yielding a white powder (2.53 g, 90%).

^{1}H–NMR (400 MHz, DMSO-d_6) δ 5.22 – 5.06 (m, 2H), 4.71 – 4.54 (m, 2H, diastereotopic signals), 4.49 – 4.32 (m, 2H, diastereotopic signals).

^{13}C–NMR (101 MHz, DMSO) δ 154.62, 75.38, 65.16.

HRMS (ESI) of $C_6H_6O_6$ $[M + H]^+$ m/z calc. 175.0237, found 175.0237

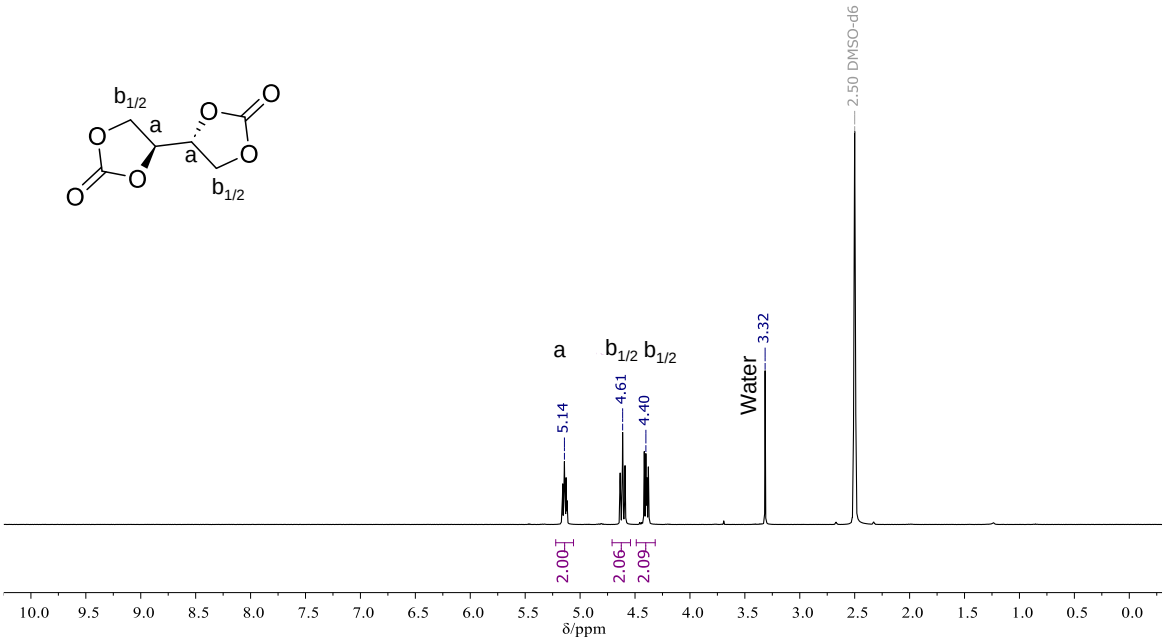


Fig. S22 – ^{1}H–NMR spectrum of erythritol bis-cyclic carbonate.

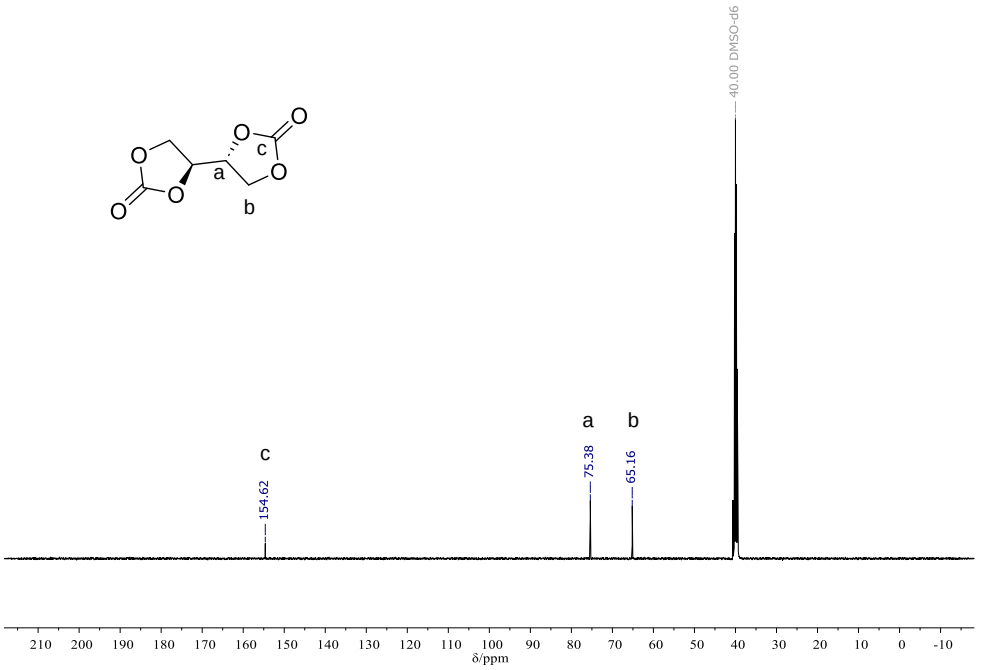


Fig. S23 – ^{13}C–NMR spectrum of erythritol bis-cyclic carbonate.

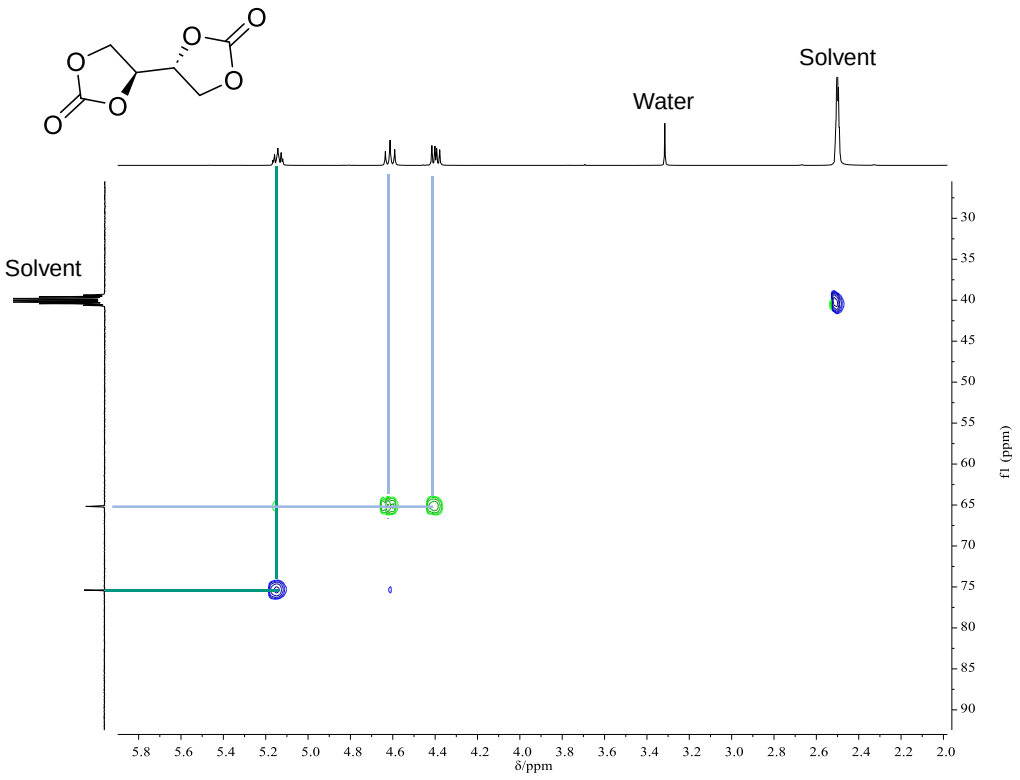


Fig. S24 – HSQC spectrum of erythritol bis-cyclic carbonate

General procedure for the synthesis of lignin-based NIPU thermoset with EBC as a third component

In a 10 ml scintillation vial, the necessary amount of previously synthesized **PA** was weighed. Then, **EBC**, cyclic carbonate functionalized lignin (**CCFL**), and 1,5,7-triazabicyclo[4.4.0]dec-5-en (TBD), were weighed and added to the vial. Dimethylsulfoxide (DMSO) (typically 1 ml for 125 mg CCFL) was added and the solution was vortexed until completely homogeneous (typically 15 to 20 minutes). If necessary, gentle heating was applied to aid the dissolution of all components. The homogeneous solutions were poured into pre-heated teflon molds (40×10×15 mm) at 50 °C. The curing was performed by heating gradually in the oven until the desired temperature (150 °C) was reached. The samples were cured at 150 °C for 2.5 days. Curing performance was followed by IR spectroscopy, monitoring the disappearance of the signal at 1792 cm^{-1} ascribed to the stretching band of carbonyls from cyclic carbonate moieties.

Fig. S25 – Picture of a first batch of thermosets without erythritol bis-cyclic carbonate as third component, with CC:NH_2 ratio of 1:1 (left) and 1:1.5 (right). The material was brittle and broke during IR measurements.

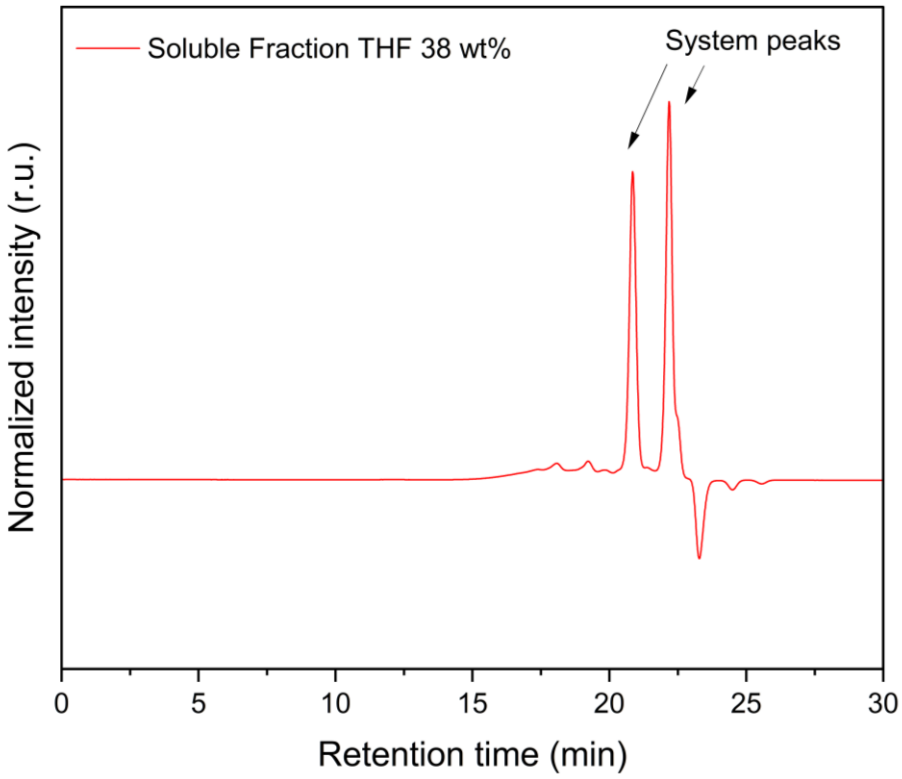


Figure S26 – GPC plot of the soluble fraction of the thermoset containing 38 wt% lignin after gel content determination.

DMA Analyses

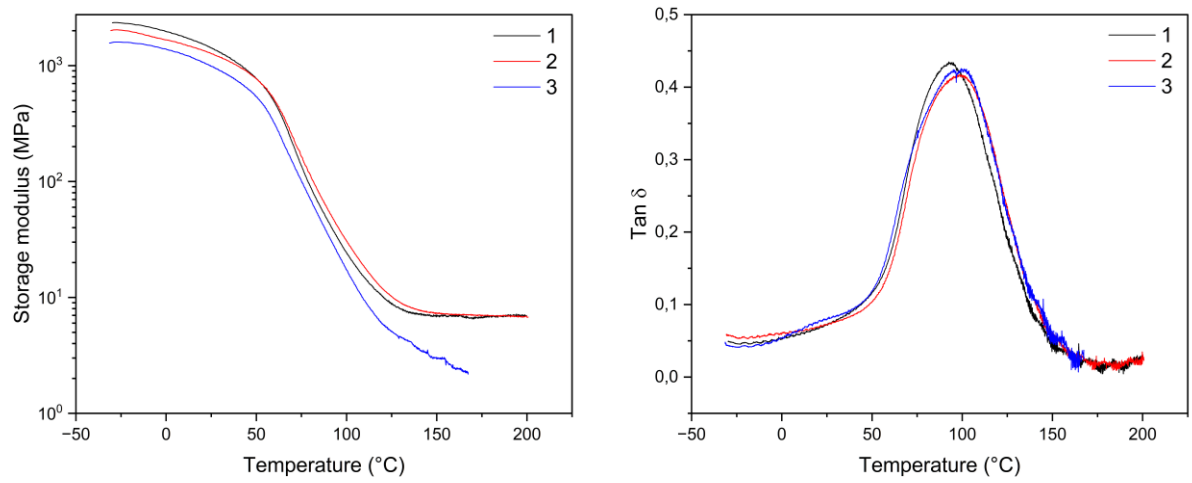


Figure S27 – DMA curves for the thermoset with 38 wt% of lignin. Measurements were performed in triplicates.

Table S8 – Overview of the values of the storage modulus in MPa, E', at different temperatures, and the T*g* values calculated on the onset of E' and at the peak of tan δ for the sample with 38 wt% lignin content. Measurements were performed in triplicates and results for the three entries are shown.

Entry	$E'_{-30°C}$ (MPa)	$E'_{25°C}$ (MPa)	$E'_{150°C}$ (MPa)	T*g* (°C) Onset E'	T*g* (°C) Max tanδ
1	2000	1260	7,30	56,9	99,8 °C
2	2340	1420	6,91	56,3	92,6°C
3	1570	980	2,94	52,5	99,5°C

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