

Supporting Information

Mechanical and morphological properties of lignin-based thermosets

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Lignin fractionation

The fractionation procedure developed by Duval et al.^[1] yields 5 fractions from the parent lignin used.

In this work a SEC using THF as the mobile phase was used to analyze the molecular weight of the fractions.

Though SEC analysis for lignin samples suffers from the ominous, heterogeneous structure combined with the lack of representative standards, SEC still allows for indicating a relative size difference between the fractions in comparison to each other.

THF was efficient for the fractions used in this this work but the last insoluble fraction could not be solubilized in this medium and thus, neither the parent lignin. The solvent fractionation method has however been used in earlier work on the same batch of LignoBoost lignin with other SEC-systems using DMSO^[2] and DMF^[3] as solvents. The parent lignin was then determined to have M_n of 1100 and 2400 g/mol, a M_w of 6800 and 19000 g/mol, and a dispersity, $\bar{D}$, of 6.1 and 7.9 respectively.

³¹P-NMR sample preparation

Internal standard preparation. *Endo-n*-Hydroxy-5-Norbornene-2,3-dicarboxylic acid imide, eHNDI, (30 mg) and chromium (III) acetyl acetonate (2.5 mg) was added to a vial. They were thoroughly dissolved in 500 µl of pyridine and used as a stock solution for the internal standard used in the NMR runs.

Sample preparation. 30-35 mg of lignin sample were dissolved in a 200 µl pyridine/DMF (50-50 vol%) mixture. 50 µl of the internal standard stock solution was added to the mixture. 150 µl of the derivatisation agent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, was added to the solution and stirred thoroughly. A white precipitate formed under exothermic conditions. Everything was again dissolved in 400 µl of deuterated chloroform and left to rest for 30 min before the NMR measurement.

NMR

NMR spectra of the lignin fractions (KL_{Fraction}) and the allylated product (A-KL_{Fraction}).

³¹P-NMR

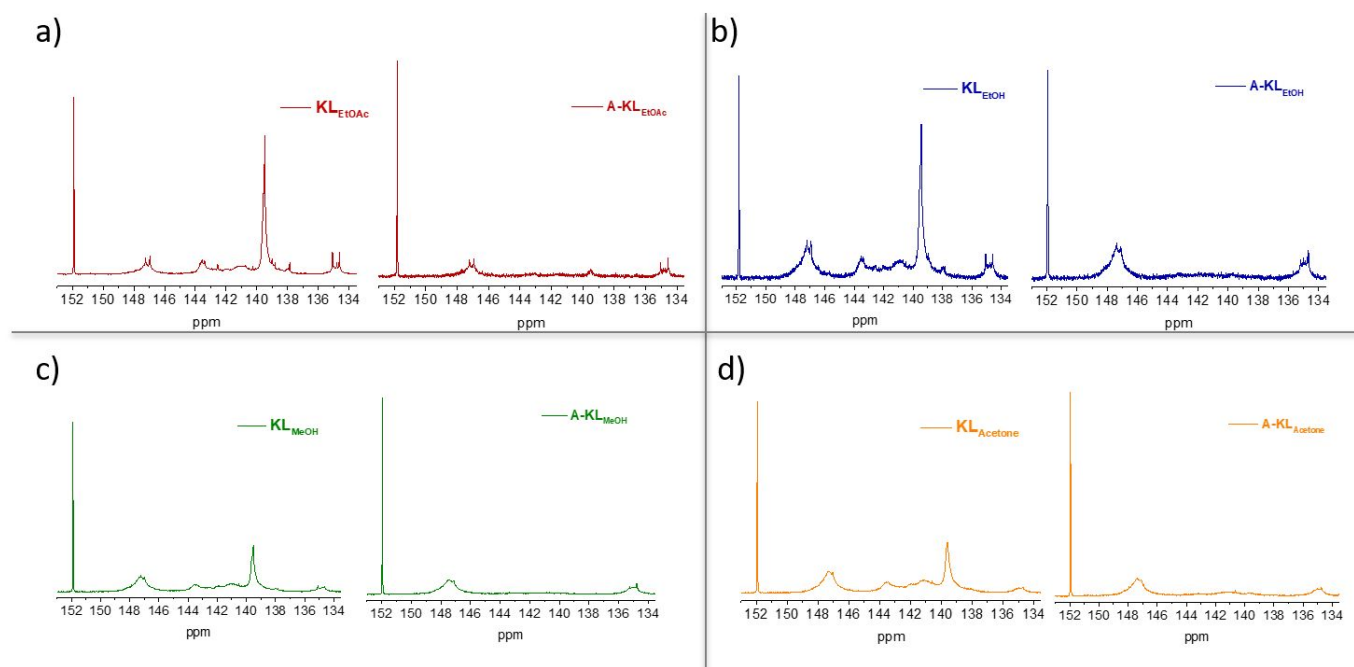


Figure S1: ³¹P-NMR before and after allylation of all the soluble fractions with *endo-n*-hydroxy-5-norbornene-2,3-dicarboxylic acid imide, eHNDI, as an internal standard. KL_{EtOAc} & A-KL_{EtOAc}, a), KL_{EtOH} & A-KL_{EtOH}, b), KL_{MeOH} & A-KL_{MeOH}, c), KL_{Acetone} & A-KL_{Acetone}, d).

¹H-NMR

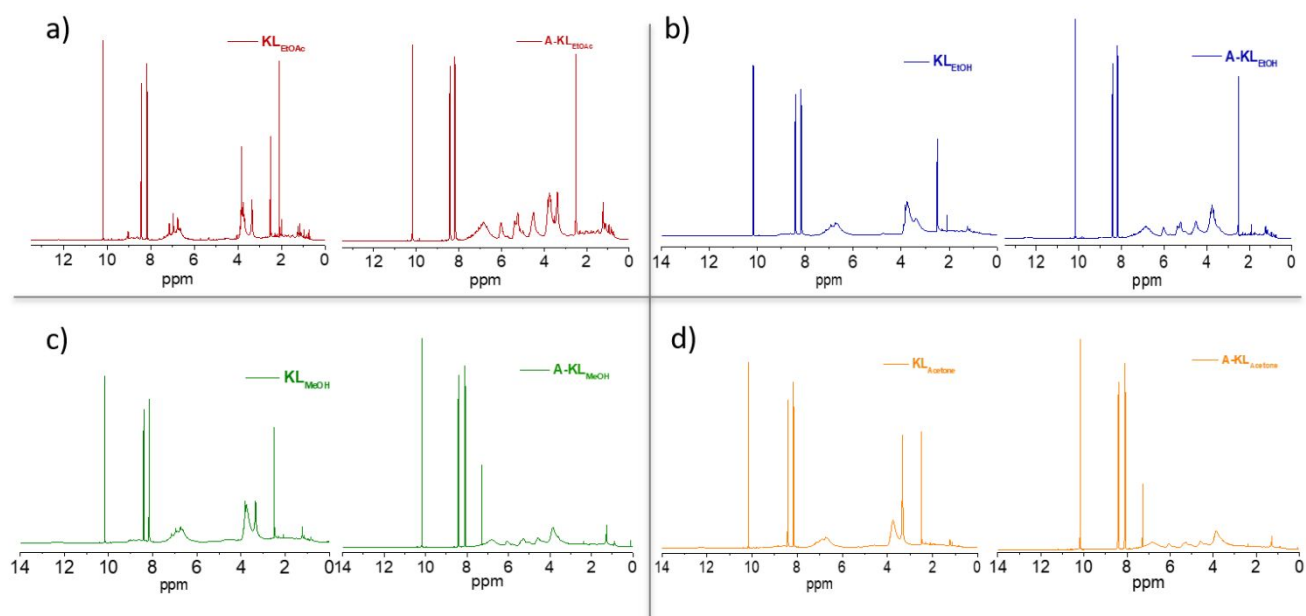


Figure S2: ¹H-NMR before and after allylation of all the soluble fractions with *p*-nitro benzaldehyde as an internal standard. KL_{EtOAc} & A-KL_{EtOAc}, a), KL_{EtOH} & A-KL_{EtOH}, b), KL_{MeOH} & A-KL_{MeOH}, c), KL_{Acetone} & A-KL_{Acetone}, d).

Table S1: Degree of allylation in mmol/g as calculated from ³¹P- and ¹H-NMR signal integrals.

Sample	³¹ P-NMR [mmol/g]	¹ H-NMR [mmol/g]
A-KL _{EtOAc}	4.7 (91% conv.)	4.9
A-KL _{EtOH}	4.5 (90% conv.)	4.6
A-KL _{MeOH}	4.5 (90% conv.)	4.0
A-KL _{Acetone}	3.4 (78% conv.)	3.2

Thermoset compositions

The final compositions of the thermoset samples are presented in **Table 1**.

Table S2: Final thermoset compositions after mixing 1:1 ratio with regards to reactive groups.

Thermoset	wt% _{Allylated lignin}
T-KL _{EtOAc}	61 ± 1
T-KL _{EtOH}	61 ± 2
T-KL _{MeOH}	56 ± 2
T-KL _{Acetone}	57 ± 4

FT-IR

Curing of the different resin mixtures ($R\text{-KL}_{\text{Fraction}}$) to form thermosets ($T\text{-KL}_{\text{Fraction}}$) confirmed by FT-IR.

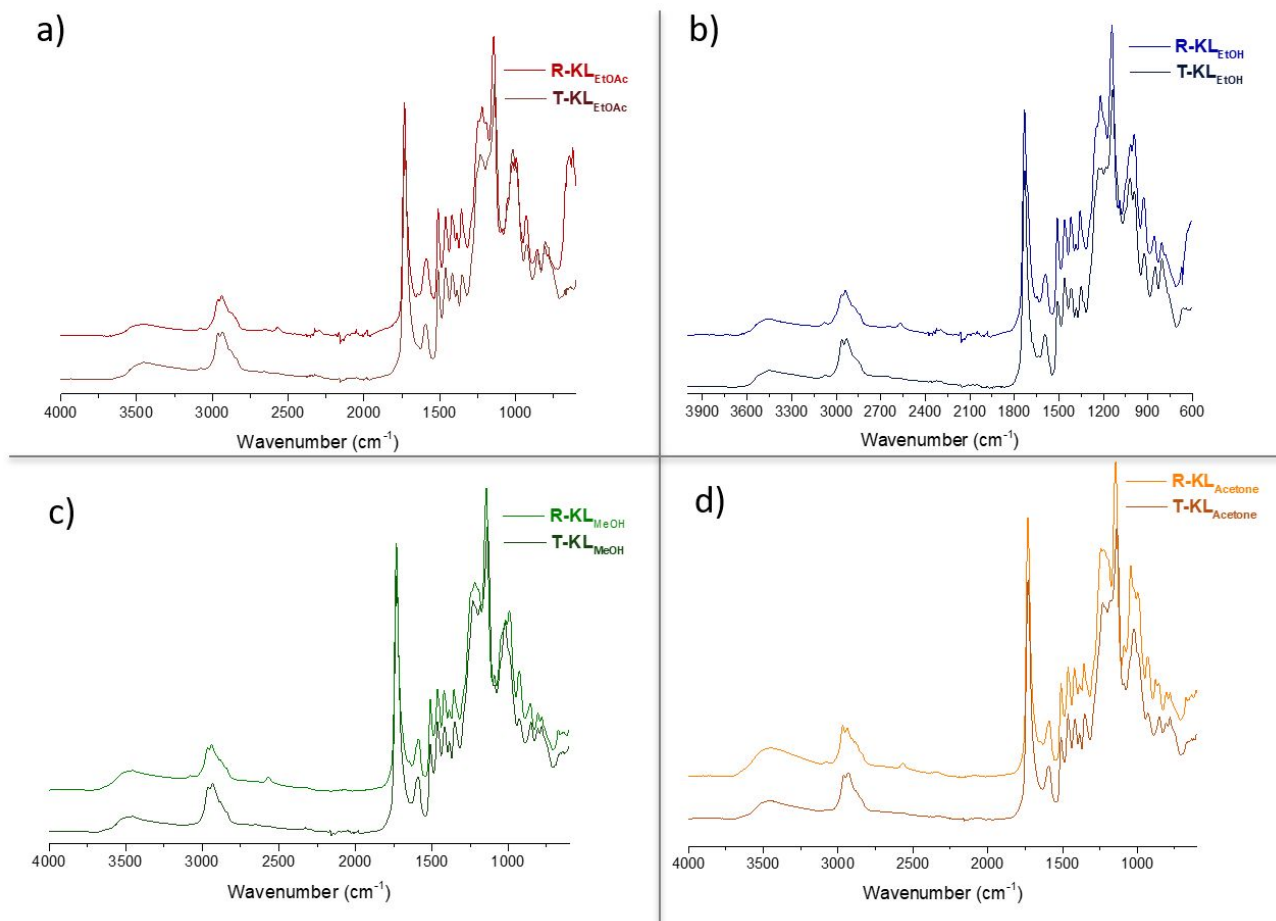


Figure S3: FT-IR before and after curing of the modified lignin/crosslinker mixtures. KL_{EtOAc} based resin and thermoset, a), KL_{EtOH} based resin and thermoset, b), KL_{MeOH} based resin and thermoset, c), $\text{KL}_{\text{Acetone}}$ based resin and thermoset, d).

DMA

Dynamical mechanical analysis curves for each different thermoset (T-KL_{Fraction}). Storage and loss modulus as well as Tan δ as a function of temperature between -50 and 200°C.

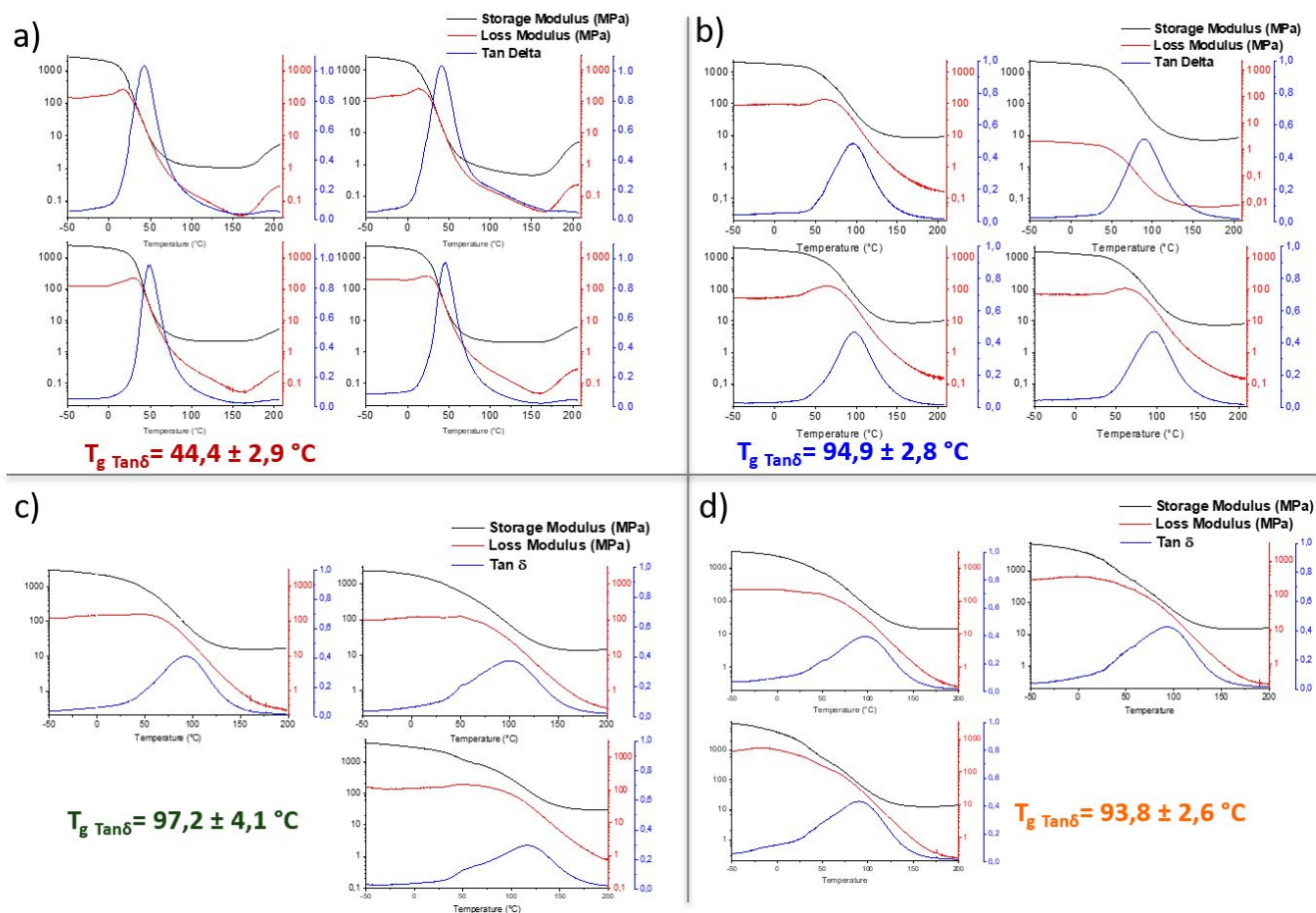


Figure S4: All DMA measurements of all different thermosets including storage modulus (E' , black), loss modulus (E'' , red) and Tan δ (blue). T-KL_{EtOAc}, a), T-KL_{EtOH}, b), T-KL_{MeOH}, c), T-KL_{Acetone}, d).

SCATTERING TECHNIQUES, SAXS & WAXS

SAXS diffraction patterns and 1d-plots including linear fits are found in Figure S5-S6.

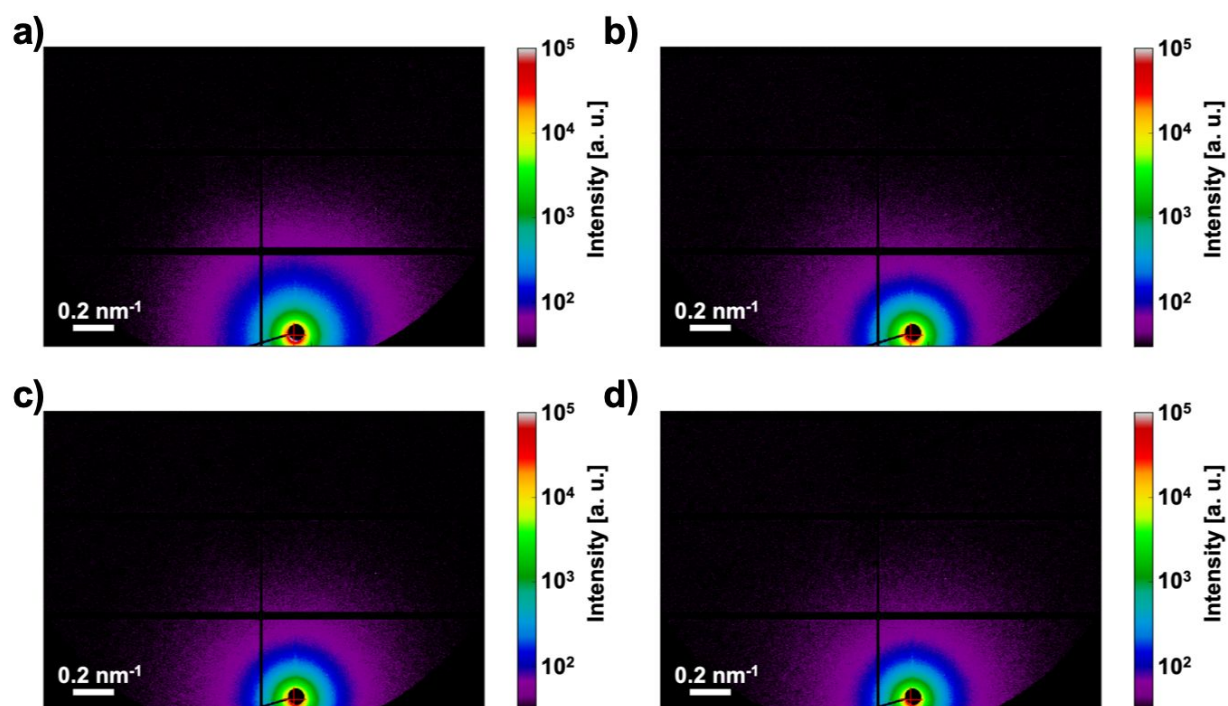


Figure S5: SAXS pattern for lignin thermosets a) T-KL_{EtOAc}, b) T-KL_{EtOH}, c) T-KL_{MeOH}, and d) T-KL_{Acetone}.

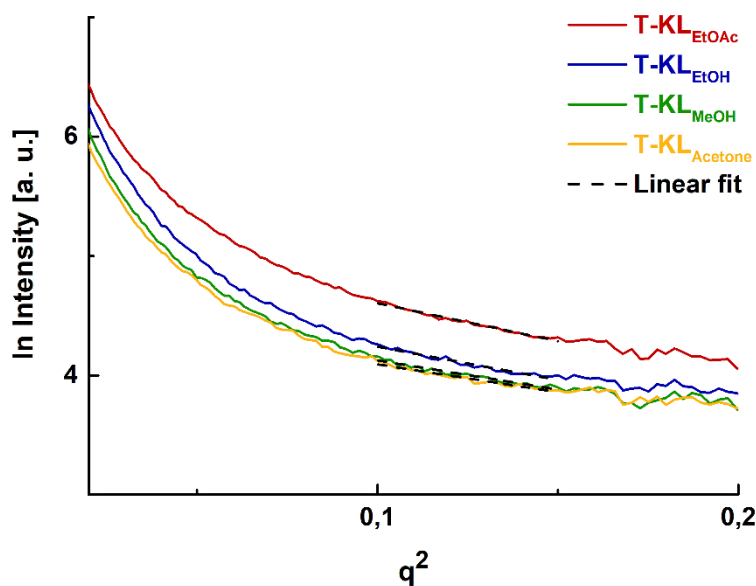


Figure S6: One-dimensional intensity integration from Figure S5. The intensity is plotted $\ln I(q)$ vs q^2 and fitted in the linear region for Guinier radius, R_g , extraction.

WAXS diffraction patterns and 1d intensity integration are presented in Figure S7-S8. In Figure S8 the Gaussian fits that are used to determine the relative amount of different π - π stackings are presented.

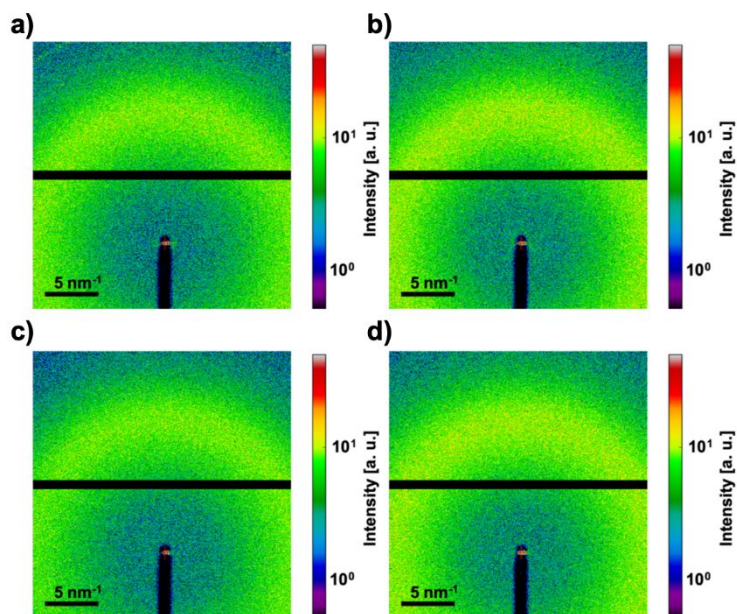


Figure S7: WAXS pattern for lignin thermosets a) T-KL_{EtOAc}, b) T-KL_{EtOH}, c) T-KL_{MeOH}, and d) T-KL_{Acetone}.

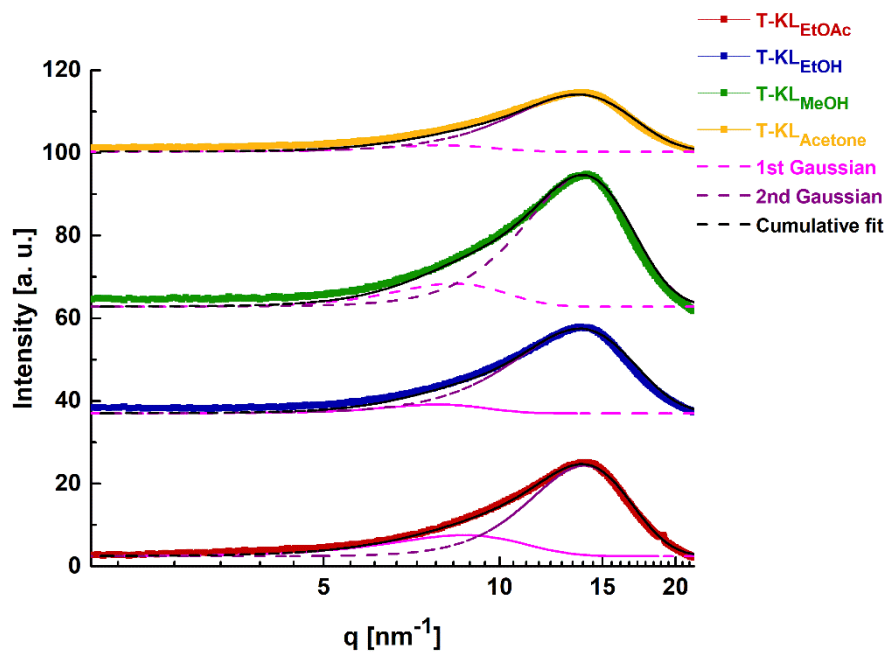


Figure S8: One-dimensional intensity integration from Figure S7. The intensity is plotted I/q and fitted using two Gaussian functions describing π - π stacking (parallel and T-shape). The graphs are shifted and stacked in y-axis for better visualization.

Thermal Degradation

TGA measurements and the thermal stability of the different samples reveals that the thermosets starts to degrade between 250 and 280 °C. After full pyrolysis, when only char and ash remain, there are between 50 and 35wt% of residues left, **Figure 8**. The residue could be thought of as a representation of the oxygen content of the material since the measurement were performed under nitrogen atmosphere and no other oxygen than the inherent content could participate in the combustion. This would mean that T-KL_{EtOAc} contains the least amount of oxygen and T-KL_{MeOH} the most, while there would be no significant difference between the two others in between. The total amounts of functional groups give a partial explanation of the TGA results. However, ³¹P-NMR only shows oxygen as part of different hydroxyl functionalities and does not reveal how much oxygen is present in the form of, e.g., ketones, aldehydes, esters, or ethers.

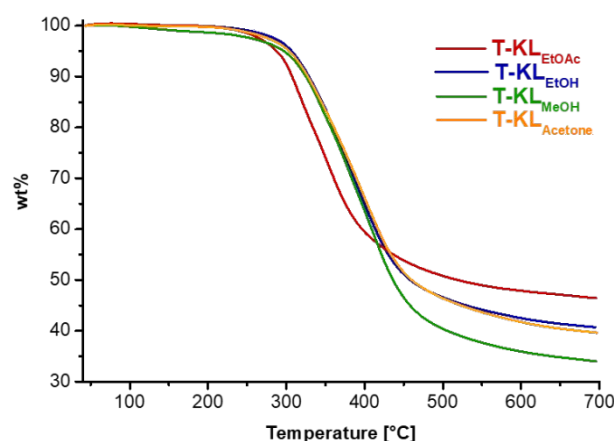


Figure S9: TGA curves of the different thermosets. The ash content can be considered an indication of oxygen content of the thermosets since the analysis was performed under nitrogen atmosphere.

- [1] F. V. Antoine Duval, Claudia Crestini, Martin Lawoko, *Solvent screening for the fractionation of industrial kraft lignin*, *Holzforschung* **2015**, 70, 11-20.
- [2] M. Jawerth, M. Johansson, S. Lundmark, C. Gioia, M. Lawoko, *Renewable Thiol-Ene Thermosets Based on Refined and Selectively Allylated Industrial Lignin*, *Acs Sustainable Chemistry & Engineering* **2017**, 5, 10918-10925.
- [3] P. Olsén, M. Jawerth, M. Lawoko, M. Johansson, L. A. Berglund, *Transforming technical lignins to structurally defined star-copolymers under ambient conditions*, *Green Chemistry* **2019**, 21, 2478-2486.