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Supporting Information for Publication in RSC Advances

Allylation of a lignin model phenol: A highly selective reaction under benign conditions towards a new thermoset resin platform†

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Characterizations

2D HSQC NMR

The 2D-NMR spectra were recorded on a Sensitivity improved with gradient (e/a TAPPI) 2D HSQC NMR. Experiments were carried out with the Bruker pulse program 'hsqcetgpsi' where the spectra were acquired with the following parameters: size of FID 1024, pulse 9.2 µm, number of dummy scan 16, spectral width 13 ppm and the relaxation delay of 1.5 seconds. The number of scans was set to 4 for the pure monomer which lead to a run time of 30 minutes while it was set to 35 scans for the thermally formed product, resulting in a 4 hours run time. Data were processed with MestreNova (Mestrelab Research) using 90° shifted square sine-bell apodization window; baseline and phase correction was applied in both directions.

2D HSQC NMR spectra of CAAE model compounds before (Figure S1) and after (Figure S2) thermal treatment in DSC, Figure S1 and S2. Figure S3 shows the Claisen rearrangement mechanism.

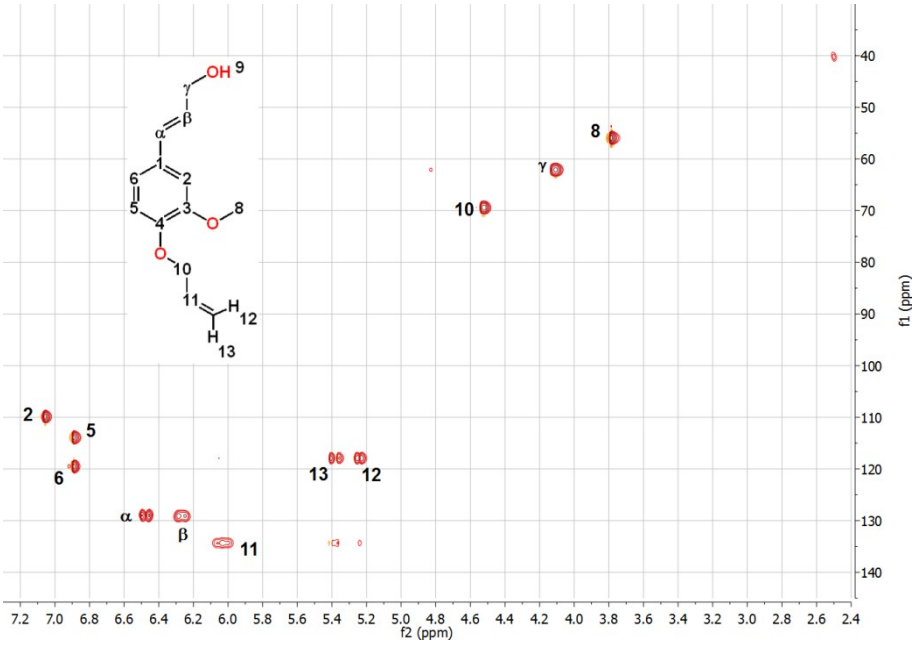

Figure S1

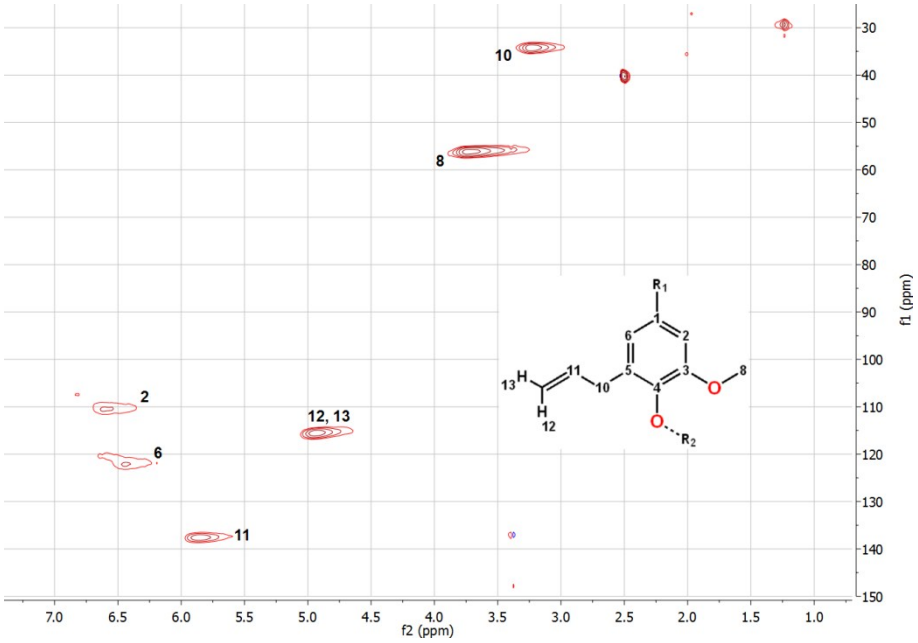

Figure S2

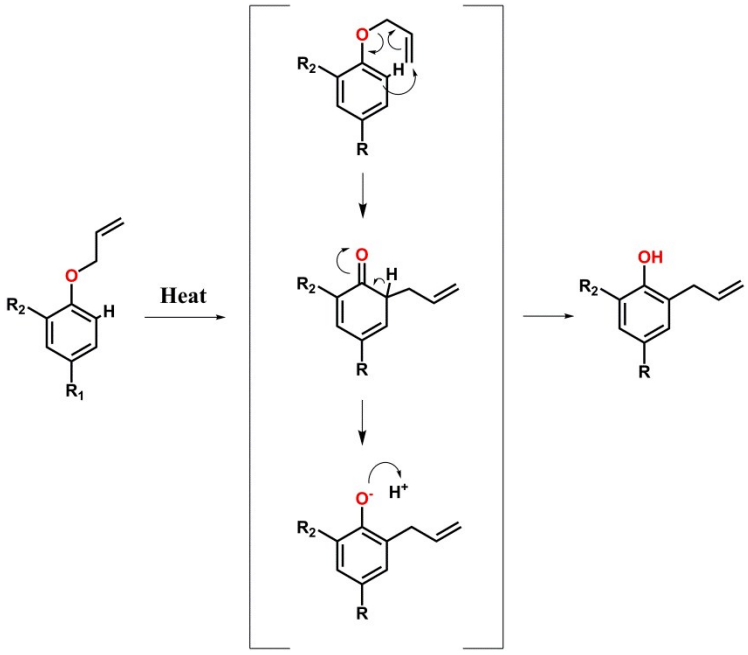

Figure S3

Full spectras of FT-IR and FT-Raman

Full spectra, 4000-600 cm^{-1}, from FT-IR (Figure S4) and FT-Raman (Figure S5) analysis are provided below.

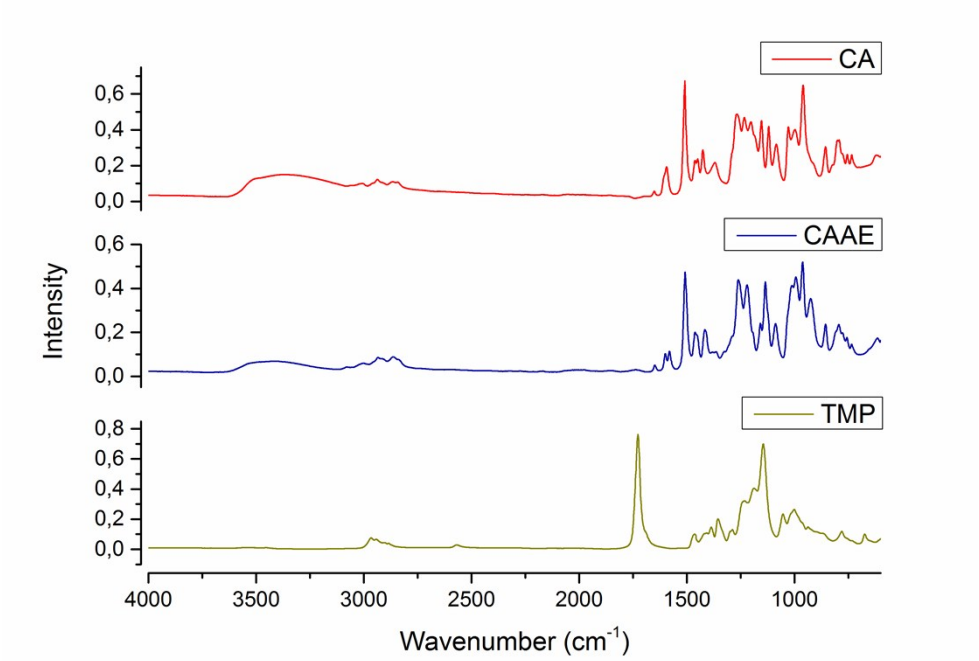

Figure S4

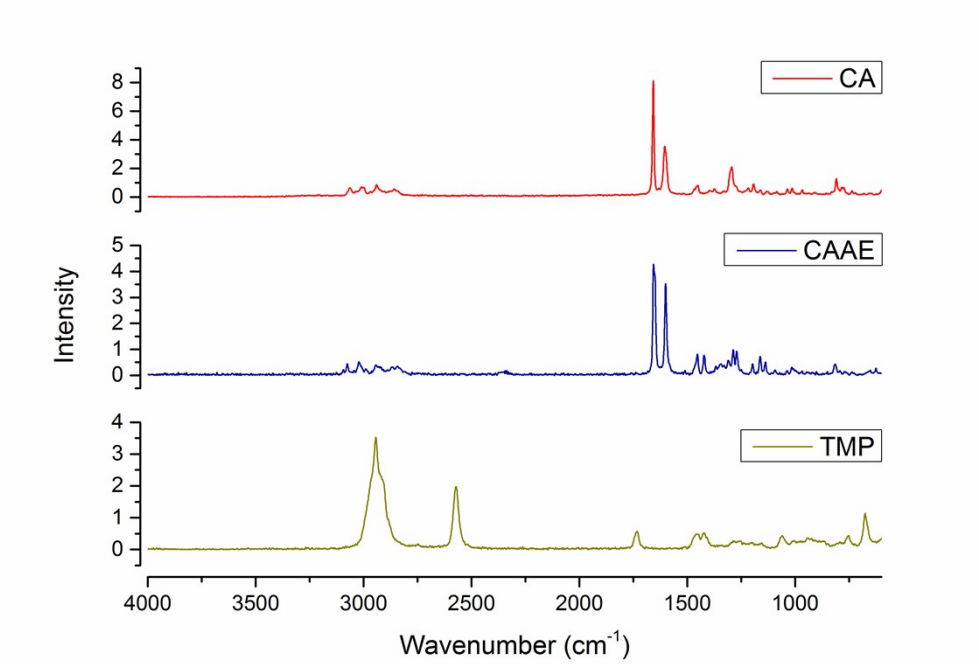

Figure S5

Tables of calculated conversion values

The calculated values from 1H-NMR integrals are presented in the tables below as well as mean values and standard deviations, Table S1 and S2.

Table S1 Calculated conversions over time at 55 ^{0}C.

Time (h)	Conv.$_{\text{Methoxy group}}$	Conv.$_{\gamma\text{-protons}}$	Conv.$_{\text{Mean}}$	Standard dev.
0.17	1.2	1.2	1.2	0
0.42	13.0	12.9	13.0	0.05
0.67	19.6	19.7	19.7	0.05
1	21.9	22.4	22.2	0.25
1.5	32.9	33.1	33.0	0.10
2	40.3	40.7	40.5	0.20
17	89.3	89.8	89.6	0.25
20	91.2	90.5	90.9	0.35
26	91.5	92.1	91.8	0.30
42	93.8	95.7	94.8	0.95

Table S2 Calculated conversions for temperature reactions.

T[°C]$_{t[h]}$	Conv.$_{\text{Methoxy group}}$	Conv.$_{\gamma\text{-protons}}$	Conv.$_{\text{Mean}}$	Standard dev.
25$_6$	9.5	10.6	10.1	0.57
25$_{24}$	29.2	30.0	29.6	0.37
35$_6$	25.0	26.0	25.5	0.54
35$_{24}$	54.2	55.0	54.7	0.41
45$_6$	38.9	39.7	39.3	0.39
45$_{24}$	72.3	71.1	71.7	0.57
55$_6$	65.6	65.9	65.8	0.14
55$_{24}$	91.2	90.7	90.9	0.26
65$_6$	84.2	83.4	83.8	0.43
65$_{24}$	95.2	95.2	95.2	0
75$_6$	89.8	89.0	89.4	0.39
75$_{24}$	98.4	97.5	97.9	0.45
85$_6$	89.3	88.6	88.9	0.34
85$_{24}$	90.6	91.4	91.0	0.36

GS-MS Spectra of CAAE

Gas Chromatography Mass spectroscopy, GC-MS, was performed with a TRACE™2000 GC with Agilent J&W DB-5MS column (30 m, 320 mm I.D., 0.25 mm thickness) and coupled with a Finnigan Trace MS operated at an impact energy of 70 eV. The initial temperature was set to 120 °C and ramp 1 had a heating rate of 15 °C up to 200 °C .The inlet temperature was set to 150 °C and the split ratio 80. The injection volume was 1 microliter.

To further prove the purity of the purified product a GC-MS measurement was performed. In Figure S6 the mass spectra from GC is shown. The single peak at the retention time of 9.46 minutes testifies of a pure product. The calculated molecular weight is 220 g/mol which correspond to the retrieved product in the spectra.

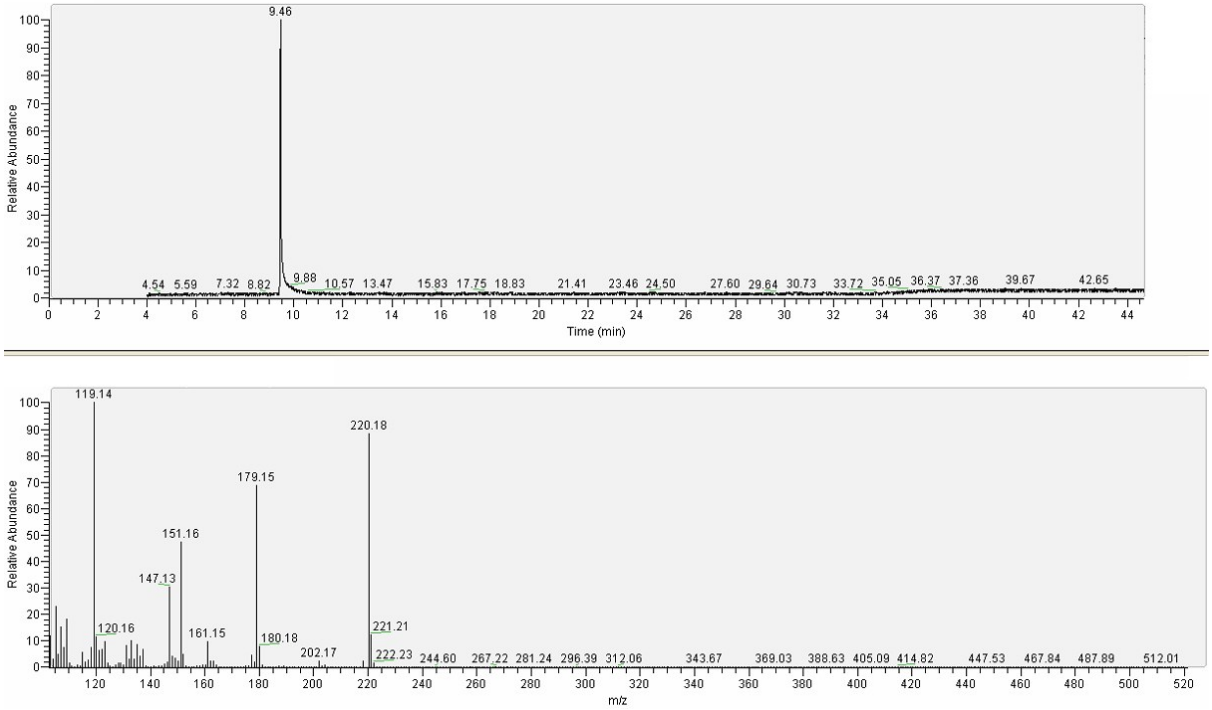

Figure S6

DSC curves of thiol-ene films

In Figure S7 to S9 the DSC curves of the formed thiol-ene films are shown with -10%, 0% and +10% excess of thiol groups. The cooling cycle after the first heating where 4 coolings and 4 heatings. A clear glass transition can be seen for each film.

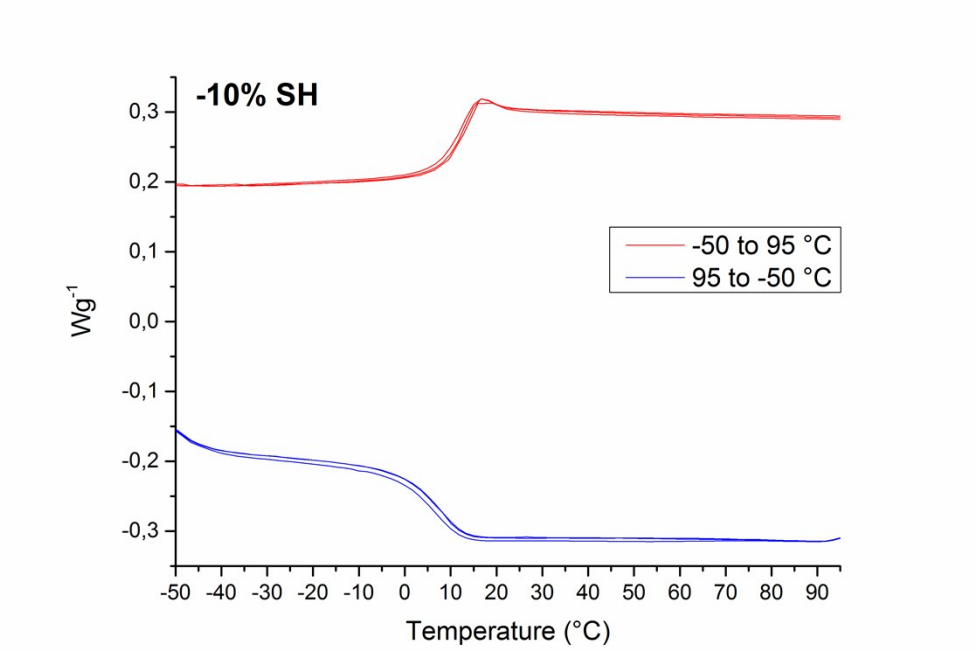

Figure S7: Glass transition can be found at 12 °C while heating and 7 °C while cooling.

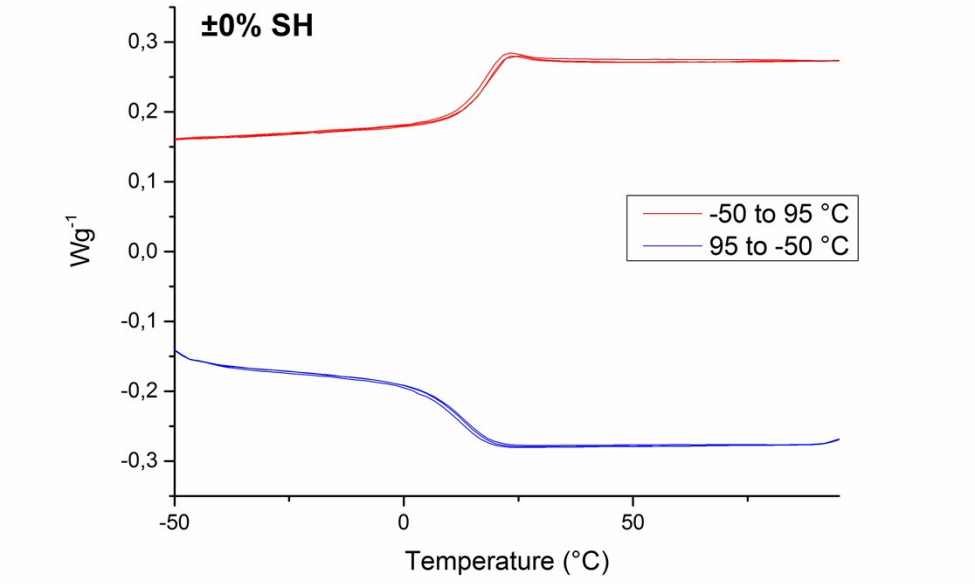

Figure S8: Glass transition can be found at 17 °C while heating and 13 °C while cooling

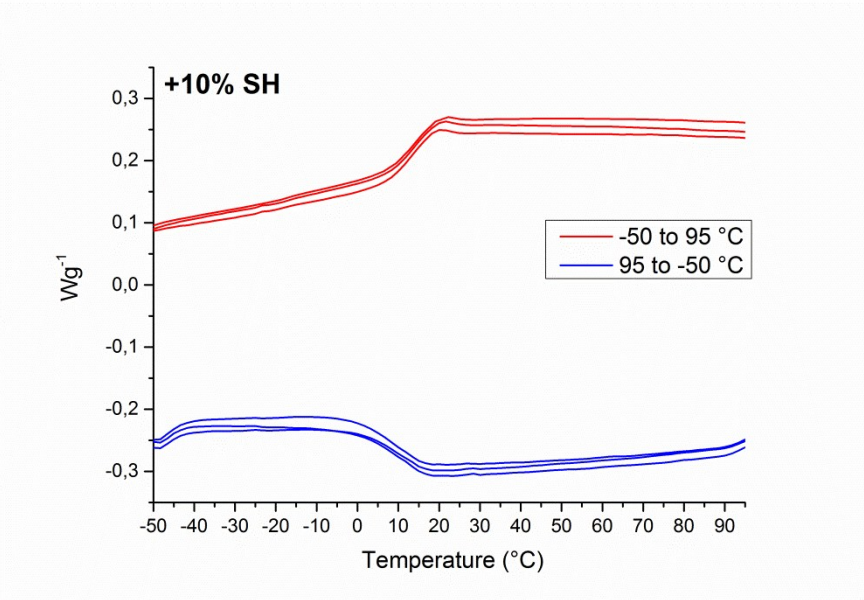

Figure S9: Glass transition can be found at 14 °C while heating and 9 °C while cooling