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A Systematic Study on Biobased Epoxy-Alcohol Networks: Highlighting the Advantage of Step-Growth Polyaddition over Chain-Growth Cationic Photopolymerization

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A systematic study on bio-based epoxy-alcohol networks: highlighting the advantage of step-growth polyaddition over chain-growth cationic photopolymerization

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Table of contents

Synthesis of 2-[(2-Methoxy-4-{[(2-oxiranyl)methoxy]methyl}phenoxy)methyl]-oxirane (DGEVA)

The synthesis was conducted according to a modified procedure by Fache *et al.*[1] The reaction was performed in inert atmosphere. Vanillyl alcohol (9.98 g, 65.0 mmol, 1 eq) was stirred with epichlorohydrin (51 mL, 650 mmol, 10 eq) and tetrabutylammonium chloride (1.52 g, 6.12 mmol, 0.1 eq) at room temperature for 4 h using a mechanical stirrer. The clear pink solution was cooled to 0 °C with an ice bath and an aqueous solution of NaOH (33 wt%, 38.9 g, 973 mmol, 15 eq) was added dropwise over 30 min. The ice bath was left to melt over time and the white suspension stirred for 18 h. Thereafter, 250 mL of deionized water were added and the aqueous layer was washed three times with 200 mL of ethyl acetate. Pooled organic extracts were washed with water (100 mL) and brine (100 mL) and consequently dried over Na_2SO_4 and dried *in vacuo*. After purification *via* column chromatography (petroleum ether:ethyl acetate = 1:3), the desired compound was obtained as a white solid (14.23 g, 82 % of theory).

m.p.: 52.7 – 53.1 °C (lit.: 53 °C[1])

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 6.95 – 6.82 (m, 3H), 4.52 (d, 2H), 4.24 (dd, 1H), 4.04 (dd, 1H), 3.88 (s, 3H), 3.76 (dd, 1H), 3.42– 3.34 (m, 2H), 3.19 (m, 1H), 2.89 (m, 1H), 2.81 (dd, 1H), 2.74 (dd, 1H), 2.61 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 149.9, 147.8, 131.8, 120.5, 114.1, 111.8, 73.3, 70.8, 70.5, 56.1, 51.0, 50.3, 45.1, 44.4.

Co-reactivity study *via* ^{1}H-NMR

For the model study on the co-polymerization epoxy and alcohol moieties, photo-DSC was combined with ^{1}H-NMR spectroscopy. The model epoxy monomer PGE was polymerized with *n*-hexanol as chain transfer agent (co-monomer). Formulations contained equimolar ratios (of functional groups) of epoxy and alcohol monomers. 1 wt% of UVI6976 was added as photoinitiator. After varying the irradiation time from 5-240 s in the photo-DSC, the respective conversion of each functional group was followed by the decrease of the corresponding peaks in the proton NMR spectra (Figure S2).

Figure S1 shows the chemical structure of PGE and *n*-hexanol. Additionally, the relevant molecular fragments for the proton NMR analysis are marked. Glycidyl ether peaks *-CH_2-* (2.84-2.69 ppm) are labelled blue and the hydroxyl groups *-OH* (4.31 ppm) of *n*-hexanol are highlighted in red. For PGE, the aromatic protons were used as reference (7.21 and 6.87 ppm, green) and for *n*-hexanol, the -CH_3 signal at 0.86 ppm (yellow) was chosen as reference. Decrease of characteristic signals were followed over time and are depicted in Figure S2.

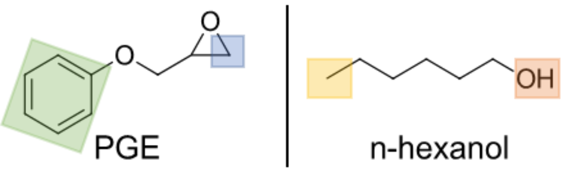

Figure S 1: Chemical structure of the monomers used in this study: phenyl glycidyl ether (PGE) and *n*-hexanol. Molecular fragments for the analysis are labelled.

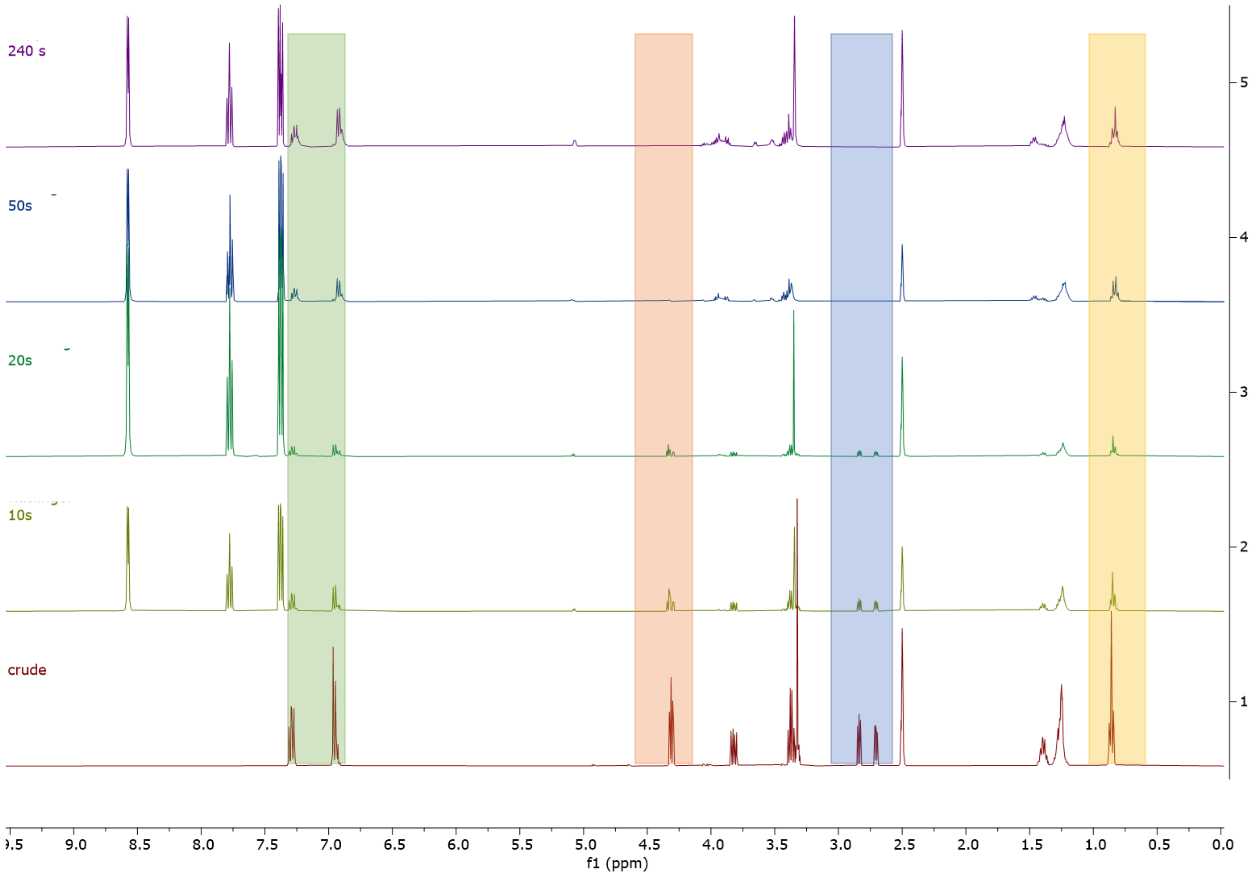

Figure S 2: NMR study of the polymerization between epoxy monomer PGE and CTA *n*-hexanol. The corresponding peaks (Figure S1) are allocated.

Dynamic mechanical thermal analysis (DMTA)

Figure S3 displays the results of the DMTA of specimens cured at 90 °C or 100 °C.

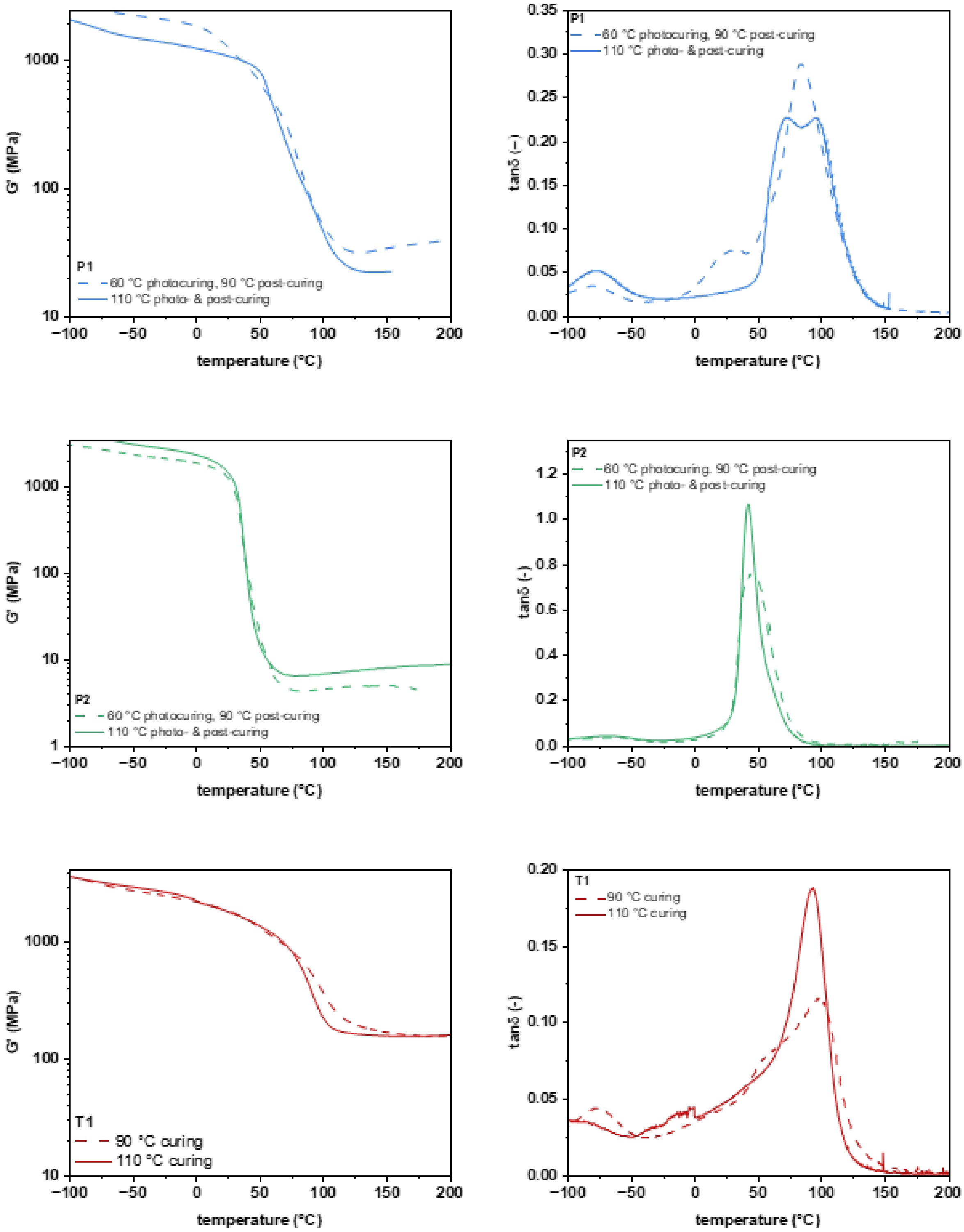

Figure S 3: G’ and tanδ over time for specimens P1, P2 and T1. Curing temperatures were varied from 90 °C (dotted) and 110 °C (solid).

Mechanical Properties

For the calculation of $\Delta\sigma/\Delta\varepsilon$, the slope of the stress-strain curve was assessed in the linear region of the polymer specimens and is displayed in Table S1.

Table S 1: Calculated $\Delta\sigma/\Delta\varepsilon$ for P1, P2, T1 and T2.

polymer	$\Delta\sigma/\Delta\varepsilon$ (MPa)
P1	1783.4 ± 68.9
P2	1668.5 ± 37.1
T1	1971.4 ± 55.1
T2	1924.2 ± 107.4

References

1. Fache, M.; Auvergne, R.; Boutevin, B.; Caillol, S., New vanillin-derived diepoxy monomers for the synthesis of biobased thermosets. European Polymer Journal 2015, 67, 527-538.