Supporting information for the manuscript;

Synthesis, kinetics, and characterization of biobased thermosets obtained through polymerization of a 2,5-furandicarboxylic acid based bis(2oxazoline) with sebacic acid.

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KEYWORDS: Renewable polymer glasses, 2,5-furandicarboxylic acid, 2-oxazoline.

### Characterization methods.

Cross polarization total sideband suppression (CP/TOSS) <sup>13</sup>C NMR experiments were performed at room temperature on a 300 MHz Bruker AVANCE-III spectrometer. These experiments utilized a rotational frequency of 5.0 kHz. Experiments were performed using a <sup>1</sup>H 90° pulse, followed by a contact time of 1000  $\mu$ s, and a TOSS sequence to remove sidebands. The 90° pulse was 4  $\mu$ s and the 180 ° pulse was 8  $\mu$ s. The pulse power used during contact was 4 dB (1000  $\mu$ s) and 1 dB during decoupling (2.5  $\mu$ s). The number of scans and recycle delay were 2000 and 2 s, respectively.

Thermal stability of the materials synthesized in this study was evaluated using thermogravimetric analysis (TGA). Experiments were performed on a TA Instruments TGA Q500 in a nitrogen rich atmosphere. Samples were heated from 20 to 800 °C, at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC Q100. Two heating and cooling runs were performed -50 °C to 220 °C at 10 °C/min and the glass transition temperatures were determined from the second heating run.

Dynamic mechanical thermal analysis (DMTA) was performed using a TA Instruments Q800. Samples were prepared by mixing and grinding the desired ratio of 2,5-FDCAox to SeA powder prior to the addition of 5 wt% TPP and 1 wt% Irganox 1330. The mixtures were heated to 160 °C until a clear casting liquid was obtained (generally 30 seconds to 1 minute under mild stirring). The obtained liquid was poured on a Teflon film and cured in an oven at 200 °C for 10 minutes to one hour under a nitrogen atmosphere. The obtained polymer films were reshaped into rectangles of 20 mm x 5 mm and were measured in the DMTA from - 50 °C to 225 °C at a heating rate of 2 °C/min, a frequency of 1 Hz, and an amplitude of 10 µm. If required, the samples were kept under isothermal conditions at 200 °C to follow the

curing process of the sample. Glass transition temperatures were calculated from the maximum in the tan  $\delta$  trace obtained during heating of the sample.

# Conversion calculation based on <sup>1</sup>H NMR data.

The 2-oxazoline conversion was calculated from the <sup>1</sup>H NMR spectra of the products obtained after polymerization for varying  $t_r$  (1 to 15 minutes). First, the fraction of unreacted 2-oxazoline groups was obtained after dividing the value of the integral of the CH<sub>2</sub>N resonance (4.35 ppm) by the value of the integral of the resonance of the furanic protons (7.13 ppm). Next, the conversion was calculated via subtraction of the 2-oxazoline fraction from 1.00 and converted to percentages. A correction for the number of protons was performed prior to the subtraction. Similarly, the fraction of unreacted 2-oxazoline groups in the IAox polymerization was calculated using the resonance of CH<sub>2</sub>N proton at 4.35 ppm and the aromatic proton at 8.30 ppm. The 2-oxazoline conversion as a function of reaction time was used for data fitting with differential equations (1) – (3). The data fitting was performed using non-linear regression, yielding reaction constants  $k_1$  and  $k_2$ , shown in Figure 1 of the original document.

### Thermal properties of poly(ester amide)s

The thermal properties of the polymers obtained after one hour of polymerization were evaluated using DSC analysis. The samples were measured at a heating and cooling rate of 10 °C / min and the second heating runs are depicted in Figure S1. It is observed that the glass transition temperature ( $T_g$ ) of the 2,5-FDCA based polymer is roughly 5 °C higher than the  $T_g$  of the IA based polymer. This difference in  $T_g$  is attributed to the cross-linked nature of the 2,5-FDCA based polymer, as is confirmed by the broad temperature range of the glass transition. Furthermore, the 2,5-FDCA based polymer shows no melting transitions prior to

degradation, similar to other 2,5-FDCA based polyamides and poly(ester amide)s. It should be noted that, even though 2,5-FDCA based polyamides generally do not exhibit crystallization or melting, the cross-linked nature of the 2,5-FDCA based poly(ester amide) synthesized in this study is expected to limit crystallization and melting even further. In contrast, the IAox based polymer shows a peak melting temperature at 105 °C, which is in relatively good agreement with the melting range between 110 to 115 °C reported in literature.<sup>i</sup>



**Figure S1.** Second heating DSC curves of the polymers obtained after one hour of polymerization of 2,5-FDCAox and SeA and and IAox and SeA at 160 °C. The broad glass transition observed for the 2,5-FDCAox based polymer is characteristic for branched and cross-linked polymers.

# CP/TOSS <sup>13</sup>C NMR analysis of the 2,5-FDCAox based polymers.

CP/TOSS <sup>13</sup>C NMR spectroscopy was performed on the product obtained after polymerization of 2,5-FDCAox with SeA for 60 minutes at 200 °C in the presence of 5 wt% TPP and confirmed that polymerization had successfully taken place. The obtained CP/TOSS spectra of the reaction mixture before and after polymerization are shown in Figure S2a and S2b, respectively. It is observed that resonance  $O_a$  (69.2 ppm), corresponding to the methylene carbon next the oxygen atom in the unreacted 2-oxazoline ring, has decreased significantly after one hour of reaction. This confirms that the 2-oxazoline concentration has obtained. Furthermore, the presence of resonances  $C_a$  (ester carbonyl carbon, 173.5 ppm),  $F_a$  (the furan C-H carbon, 120.7 ppm),  $O_c$  (methylene carbon next to the secondary amide group, 38.5 ppm), and  $O_d$  (methylene carbon next to the ester group, 65.0 ppm) indicates that the ring-opening addition reaction between the 2-oxazoline rings and the carboxylic acid groups has successfully taken place. The presence of the tertiary amides formed during the branching reaction can be detected by the presence of resonances  $O_e$  (methylene carbon next to the tertiary amide group, 46.9 ppm) and  $F_e$ , (furan carbon of a furan ring connected to a tertiary amide group, 115.9 ppm).



**Figure S2.** CP/TOSS <sup>13</sup>C NMR spectra obtained a) after and b) before polymerization of 2,5-FDCAox with SeA (ratio = 2.25 : 1) containing 5 wt% TPP for one hour at 200 °C.

As can be seen in Figure S2, the area of the resonance  $O_e$  (46.9 ppm) is larger than the resonances  $O_d$  (65.0 ppm) +  $O_f$  (62.1 ppm) and  $O_g$  +  $O_c$  (38.5 ppm), indicating that the

concentration of tertiary amides is larger than that of the secondary amides. Although the obtained CP/TOSS spectra do not allow for quantitative analysis of the signals, such an excess of tertiary amides groups is expected for polymerizations using a large excess of 2,5-FDCAox. According to differential equations (1) to (3), polymerization will continue until all 2-oxazoline groups have reacted, indicating that, at full conversion, all oxazoline groups have reacted into secondary or tertiary amide groups. Therefore, the concentration of tertiary amides at full conversion should be equal to the excess of 2-oxazoline groups added at the start of the reaction, since the maximum concentration of amide groups is equal to the starting concentration of carboxylic acid groups.

Overall, based on the CP/TOSS NMR data shown in Figure S2, it can be concluded that both the expected secondary and tertiary amides are present in the system, thus, polymerization in the presence of TPP yields the expected cross-linked product.

#### FTIR and NMR data fitting procedure

For the data fitting process described in the sections "Polymerization of 2,5-FDCAox and IAox with Sebacic acid" and "Influence of the reaction temperature and TPP loading on the branching reaction" in the original manuscript, a Matlab script was used containing the differential equations (1) to (3) as described in the original manuscript. The starting bulk concentrations of the reactive groups at  $t_r = 0$  min were calculated in mol/kg by taking the monomer ratio and molar masses of the 2,5-FDCAox and SeA into account. For the equimolar systems of 2,5-FDCAox and SeA and IAox and SeA, the starting concentrations of the reactive groups were 4.89 mol/kg and 4.78 mol/kg, respectively. For the 2,5-FDCAox and SeA polymerization in a ratio of 2.25 to 1, the used starting concentrations were 6.75 mol/kg (2,5-FDCAox) and 3.00 mol/kg (SeA). The concentration of the ester, amide and tertiary amide groups were set to 0 mol/kg at the start of the reaction. Next, the experimental data,

either the oxazoline concentration obtained from <sup>1</sup>H NMR analysis or the tertiary amide concentration obtained from FTIR analysis, was loaded into the program and fitted to the differential equations (1) to (3) through a non-linear regression.

In order to fit the data obtained from FTIR analysis, the intensity of the vibration bands has to be converted to concentration in mol/kg. However, since the extent of the reaction is unknown after 60 minutes of reaction, no information on the exact concentration is available and thus the concentration of the reactive groups cannot be calculated. Therefore, in order to obtain a value for the bulk concentration, the authors have used a conversion factor to linearly convert the intensity to bulk concentrations. The conversion factor is defined as the normalized intensity signal divided by the bulk concentration, assuming that the correlation between the intensity observed in FTIR spectroscopy and the bulk concentration is linear.

It was observed that the signal corresponding to the vibration of the unreacted 2-oxazoline ring at 922 cm<sup>-1</sup> was very small or not detectable in systems polymerized at 200 °C in the presence of >5 wt% of TPP. This indicates that the polymerization was close to full conversion. For this reason, it was assumed that 100% conversion was reached in these systems, and the theoretical bulk concentration of tertiary amides (3.75 mol/kg) was used to calculate the conversion factor (yielding a value of 0.95). Nonetheless, to ensure that the FTIR data was interpreted correctly, other conversion factors were also taken into account. Figure S3 shows the obtained  $k_1$  and  $k_2$  reaction constants as a function of various conversion factors.



**Figure S3**. Effect of the conversion factor on the k1 (left) and k2 (right) reaction constants found after data fitting of polymerizations containing different TPP concentrations.

From the data in Figure S3 it can be seen that both the  $k_1$  and  $k_2$  reaction constants vary with one order of magnitude as a function of the conversion factor. Furthermore, from the data shown in Figure S3 it is clear that, independently of the chosen conversion factor, the  $k_1$ constant does not vary significantly as a function of TPP loading. In contrast, the  $k_2$  reaction constant varies with at least one order of magnitude as a function of the TPP loading. As is shown in Figure S4 the  $k_2$  reaction constant increases roughly at least with one order of magnitude when increasing the TPP loading from 0.5 wt% to 7 wt%, and increases even further with decreasing conversion factors. From this data it is concluded that TPP can be used to selectively enhance the branching reaction occurring between amide groups and 2oxazoline rings.



**Figure S4**. Ratio of the k1 and k2 reaction constants after increasing the TPP content from 0.5 wt% to 7 wt%, as a function of the conversion factor.

The residuals obtained after data fitting of the experimental data using different conversion factor were evaluated to determine the accuracy of the obtained fits. The residuals of these fits can generally be used to evaluate the ability of the fit to describe the experimental data. To be more specific, a residual of 0.00 is obtained when the fit describes the experimental data data perfectly. Similarly, a high residual indicates that the found fit is poor and deviates drastically from the experimental data.

Figure S5 shows the residuals obtained after data fitting the experimental data using different conversion factors. It can be seen that the residuals are lowest at conversion factors between 0.9 and 0.95, indicating that these conversion factor yield the most accurate fit. For this reason, and for the reasons described earlier, the authors use 0.95 as conversion factor for the data analysis described in the main article.



Figure S5. Residual of the fit as a function of the conversion factor and the TPP concentration.

## Thermal properties of the cured thermosets.

In order to investigate the thermal properties of the polymer synthesized via this route, DMTA analysis was performed on cured glasses and the glass transition temperatures were determined from the peak in the tan( $\delta$ ) trace. Figure S6 shows the characteristic behavior of systems of a) IAox : SeA (2.25 : 1) and b) 2,5-FDCAox : SeA (2.25 : 1) containing 5 wt%



TPP. The samples were cured for 10 minutes in an oven preheated to 200 °C prior to the DMTA analysis to prevent breaking of the samples above  $T_g$  during the DMTA experiment.

**Figure S6.** Variation of the temperature,  $tan(\delta)$ , E', and E'' during a heating (2 °C / min) and isothermal curing (200 °C, 60 min) as observed in the DMTA analysis in TPP (5 wt%) catalyzed systems of a) IAox : SeA (ratio = 2.25 : 1) and b) 2,5-FDCAox : SeA (ratio = 2.25 : 1). *N.B.* both systems were heated until a clear casting liquid was obtained, which was poured on a Teflon film and cured at 200 °C for 10 minutes prior to DMTA analysis.

From the data shown in Figure S6, it can be concluded that the IAox based polymer obtained after 10 minutes of curing is slightly cross-linked, as is indicated by the low storage modulus (E') of 0.53 MPa above the  $T_g$  (59.6 °C) corresponding to a high molecular weight between entanglements. As expected, the curing process continues after heating to temperatures of 120 °C and higher at a heating rate of 2 °C, as is indicated by the gradual increase of both storage and loss moduli. No changes of the storage and loss modulus are observed after 30 minutes of curing (thus after 90 minutes of the DMTA experiment), indicating that the cross-linking reaction is complete.

Interestingly, the DMTA analysis of the polymer obtained after heating, casting and curing the 2,5-FDCAox and SeA mixture (ratio = 2.25 : 1) for 10 minutes in the presence of 5 wt% TPP shows a  $T_g$  at 143.2 °C and a plateau modulus (E') of 22.01 MPa. This increased glass transition temperature, compared to the glass transition temperature of the IAox based polymer obtained after 10 minutes of curing, indicates that the 2,5-FDCAox based polymer is more densely cross-linked. Furthermore, no significant increase of the plateau modulus is observed upon further heating to temperatures above the  $T_g$  followed by curing under isothermal conditions for 60 minutes at 200 °C.

For both systems, obtained after 60 minutes curing at 200 °C, a second DMTA heating run was performed at 2 °C/min to determine the  $T_g$  of the fully cross-linked polymers. Interestingly, the  $T_g$  of the IAox based polymer (155.1 °C) was comparable with the  $T_g$  of the 2,5-FDCAox based polymer (156.3 °C), indicating that the fully cross-linked materials have comparable glass transition temperatures. Although the thermal properties of the fully cured systems are comparable, the DMTA experiments indicate that the cross-linking in the 2,5-FDCAox polymerization with SeA in the presence of TPP proceeds significantly faster than for the IAox based system.

To see if we can correlate the normalized intensity and the concentration of tertiary amide groups to the glass transition temperature, DMTA experiments were performed on polymers with varying 2,5-FDCAox to SeA ratios. The polymers were cured for 60 minutes at 200 °C prior to the DMTA analysis to ensure that the samples were fully cross-linked. Furthermore, FTIR analysis was performed on different spots of the samples obtained after DMTA analysis and the normalized intensity of the vibration band at 1417 cm<sup>-1</sup> was calculated following the FTIR analysis procedure. Figure S7 shows the normalized intensity signal obtained from FTIR plotted against the glass transition temperatures found via DMTA analysis for the different polymer glasses.



**Figure S7.**  $T_g$  values (°C) calculated from the maximum in the tan( $\delta$ ) trace obtained from a DMTA heating run performed at 2 °C/min versus the normalized intensity of the vibration band at 1417 cm<sup>-1</sup> obtained from FTIR analysis of cured systems having varying 2,5-FDCA to SeA ratio's.

It can be seen that the normalized intensity varied slightly over the surface of the cured samples, indicating that the obtained thermosets are probably not homogeneously cured. Nonetheless, it is clear that the normalized intensities obtained from FTIR analysis increase linearly with the increasing  $T_g$  of the polymers. These data suggest that the increase of the glass transition temperature is directly correlated to the increase of the bulk concentration of tertiary amides and thus to the concentration of branches and cross-links.

<sup>[</sup>i] Lustoň, J., Kronek, J., Markus, O., Janigová, I., Böhme, F., Polym.Advan. Technol., 2007, 18, 165-172