Supplementary Information for

Synthesis and characterization of new bio-based

poly(acylhydrazone) vanillin vitrimers

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1. Additional experimental procedures

Synthesis of epoxy compound from Vanillin (EPO-Van)

EPO-Van was prepared following a previously reported procedure.¹ Vanillin (7.6 g, 50.0 mmol), TEBAC (1.1 g, 5.0 mmol) and ECH (46.3 g, 500.0 mmol) were added to a 250 mL three-necked round bottom flask under magnetic stirring. The mixture was first stirred for 1.5 h at 80 °C and then cooled down to room temperature. A mixed solution of TEBAC (1.1 g, 5.0 mmol) and NaOH (8 g, 200.0 mmol, 5 M) was added and stirred for 30 min at room temperature. After the reaction was completed, ethyl acetate (EtOAc) and distilled water were poured and stirred, and the aqueous phase extracted three times with EtOAc. The organic phase was collected, dried over anhydrous MgSO₄ and concentrated in a vacuum rotary evaporator. The residual amount of ECH was eliminated by mixing the product with EtOAc and evaporating it under vacuum multiple times. The monoglycidyl compound was obtained as a yellowish-white solid with a 93 % of yield (9.7 g). M.p. 97.0 °C.

¹H NMR (CDCl₃, δ in ppm): 9.84 (s, 1H), 7.43 (d, 1H), 7.41 (s, 1H), 7.02 (d, 1H), 4.37 (dd, 1H), 4.08 (dd, 1H), 3.92 (s, 3H), 3.40 (m, 1H), 2.92 (dd, 1H) and 2.77 (dd, 1H). ¹³C NMR (CDCl₃, δ in ppm): 190.99, 153.51, 150.07, 130.78, 126.61, 112.37, 109.61, 70.05, 56.13, 50.00 and 44.86.

Synthesis of diesters of dicarboxylic acids

Diesters were synthesized following a previous procedure reported by Mills *et al.*² In a 250 mL three-necked round bottom flask equipped with a magnetic stirrer, 15 g of the corresponding diacid were dissolved in absolute EtOH (150 mL). Then, concentrated H_2SO_4 (80 µL, 1.3 mmol) was added and the mixture was heated up to 80 °C and kept it during 4 h under reflux. The mixture was cooled down to room temperature and concentrated. The concentrate was dissolved in EtOAc (150 mL) and the organic fraction was washed three times, once with a saturated solution of NaHCO₃, once with water and finally with brine, dried over anhydrous MgSO₄ and concentrated by rotary evaporator to yield the corresponding products as colorless oils.

Diethyl glutarate (DEG) was obtained in 85% yield. ¹H NMR (CDCl₃, δ in ppm): 4.11 (q, 4H), 2.34 (t, 4H), 1.93 (m, 2H) and 1.23 (t, 6H). ¹³C NMR (CDCl₃, δ in ppm): 173.06, 60.47, 33.45, 20.28 and 14.32.

Diethyl suberate (DES) was obtained in 89% yield. ¹H NMR (CDCl₃, δ in ppm): 4.10 (q, 4H), 2.26 (t, 4H), 1.60 (m, 4H), 1.32 (m, 4H) and 1.23 (t, 6H). ¹³C NMR (CDCl₃, δ in ppm): 173.83, 60.28, 34.36, 28.84, 24.86 and 14.34.

Diethyl dodecanoate (DEDD) was obtained in 90% yield. ¹H NMR (CDCl₃, δ in ppm): 4.10 (q, 4H), 2.26 (t, 4H), 1.59 (m, 4H), 1.26 (m, 12H) and 1.23 (t, 6H). ¹³C NMR (CDCl₃, δ in ppm): 174.05, 60.25, 34.47, 29.46, 29.32, 29.22, 25.06 and 14.35.

Synthesis of dihydrazides

Dihydrazides were synthesized following a previous procedure reported by Tomuta *et al.*³ In a 100 mL three-necked round bottom flask provided with a magnetic stirrer, 5.6 g of the corresponding diester were added and dissolved in 25 mL of absolute EtOH. Then, hydrazine hydrate (80%, 6.7 g, 107.6 mmol) was added drop by drop. When the addition was complete, the mixture was kept 6 h under reflux. The precipitate formed was filtered through a Büchner funnel, washed twice with cold EtOH and dried in the vacuum oven at 60 °C during 4 h. All products were obtained as white powders with yields higher than 90%. Glutaric dihydrazide (GDh): ¹H NMR (DMSO-d₆, δ in ppm): 8.91 (s, 2H), 4.13 (s, 4H), 1.99 (t, 4H) and 1.69 (m, 2H). ¹³C NMR (DMSO-d₆, δ in ppm): 171.17, 32.87 and 21.48. M.p. 181.8 °C.

Suberic dihydrazide (SDh): ¹H NMR (DMSO-d₆, δ in ppm): 8.89 (s, 2H), 4.13 (s, 4H), 1.98 (t, 4H), 1.46 (m, 4H) and 1.20 (m, 4H). ¹³C NMR (DMSO-d₆, δ in ppm): 171.58, 33.37, 28.39 and 25.10. M.p. 188.1 °C.

Dodecandioic dihydrazide (DDh): ¹H NMR (DMSO-d₆, δ in ppm): 8.91 (s, 2H), 4.13 (s, 4H), 1.98 (t, 4H), 1.46 (m, 4H) and 1.22 (m, 12H). ¹³C NMR (DMSO-d₆, δ in ppm): 171.64, 33.42, 28.92, 28.77, 28.67 and 25.24. M.p. 192.0 °C.

Synthesis of model compounds

Ethyl octanoate was synthesized following the same procedure previously described.²

¹H NMR (CDCl₃, δ in ppm): 4.11 (q, 2H), 2.27 (t, 2H), 1.60 (m, 2H), 1.27 (m, 8H), 1.24 (t, 3H) and 0.87 (t, 3H). ¹³C NMR (CDCl₃, δ in ppm): 173.83, 60.13, 34.39, 31.66, 29.10, 28.93, 24.99, 22.59, 14.25 and 14.05.

Hydrazides were synthesized following the same procedure previously described for the synthesis of dihydrazide compounds.³

Acetyl hydrazide (Ah): ¹H NMR (DMSO-d₆, δ in ppm): 8.94 (s, 1H), 4.13 (s, 2H) and 1.74 (s, 3H). ¹³C NMR (DMSO-d₆, δ in ppm): 168.75 and 20.55. M.p. 60.1 °C.

Octanoyl hydrazide (Oh): ¹H NMR (DMSO-d₆, δ in ppm): 8.91 (s, 1H), 4.14 (s, 2H), 1.98 (t, 2H), 1.46 (m, 2H), 1.23 (m, 8H) and 0.85 (t, 3H). ¹³C NMR (DMSO-d₆, δ in ppm): 171. 65, 33.44, 31.22, 28.65, 28.48, 25.27, 22.11 and 14.00. M.p. 88.3 °C.

Acylhydrazones were synthesized by the following procedure. In a 50 mL threenecked round bottom flask provided with a magnetic stirrer 10 mmol of aldehyde (vanillin or benzaldehyde) were added. After that, 10 mL of EtOH were poured followed by the addition of 10 mmol of the corresponding hydrazide (acetyl hydrazide or octanoyl hydrazide). When the addition was completed, the mixture was kept under reflux during 12 h. The precipitate formed was filtered through a Büchner funnel, washed twice with cold EtOH and dried in the vacuum oven at 60 °C during 4 h. All products were obtained as white powders with yields higher than 90%.

Benzylideneacetohydrazide (B-Ah) mixture of *cis/trans* isomers 1:2: ¹H NMR (DMSO-d₆, δ in ppm): 11.37 (s, 1H), 11.25 (s, 1H_a), 8.14 (s, 1H), 7.98 (s, 1H_a), 7.66 (m, 2H, 2H_a), 7.41 (m, 3H, 3H_a), 2.20 (s, 3H_a) and 1.95 (s, 3H). ¹³C NMR (DMSO-d₆, δ in ppm): 171.99, 165.61, 145.57, 142.51, 134.38, 134.31, 129.88, 129.67, 128.81, 128.79, 126.97, 126.64, 21.66 and 20.27.

(4-Hydroxy-3-methoxybenzylidene)octanehydrazide (V-Oh) mixture of *cis/trans* isomers 1:1: ¹H NMR (DMSO-d₆, δ in ppm): 11.15 (s, 1H), 11.04 (s, 1H_a), 9.49 (s, 1H, 1H_a), 8.02 (s, 1H), 7.85 (s, 1H_a), 7.24 (d, 1H), 7.20 (d, 1H_a), 7.03 (dd, 1H), 7.02 (dd, 1H_a), 6.81 (d, 1H), 6.80 (d, 1H_a), 3.80 (s, 3H), 3.79 (s, 3H_a), 2.58 (t, 2H_a), 2.15 (t, 2H), 1.56 (m, 2H, 2H_a), 1.26 (m, 8H, 8H_a), 0.86 (t, 3H_a) and 0.84 (t, 3H). ¹³C NMR (DMSO-d₆, δ in ppm): 174.16, 168.30, 148.79, 148.51, 148.00, 147.93, 146.25, 142.78, 125.83, 125.77, 121.89, 120.83, 115.56, 115.38, 109.31, 108.83, 55.52, 55.46, 34.23, 31.92, 31.22, 28.82, 28.66, 28.51, 28.50, 25.17, 24.41, 22.11 and 13.98.

(4-Hydroxy-3-methoxybenzylidene)acetohydrazide (V-Ah) mixture of *cis/trans*isomers 2:3: ¹H NMR (DMSO-d₆, δ in ppm): 11.17 (s, 1H), 11.07 (s, 1H_a), 8.01 (s, 1H),
7.86 (s, 1H_a), 7.24 (d, 1H), 7.21 (d, 1H_a), 7.04 (d, 1H), 7.02 (d, 1H_a), 6.81 (d, 1H_a), 6.79

(d, 1H), 3.81 (s, 3H), 3.80 (s, 3H_a), 2.17 (s, 3H_a) and 1.91 (s, 3H). ¹³C NMR (DMSO-d₆, δ in ppm): 171.68, 165.28, 148.79, 148.53, 148.01, 147.95, 146.14, 142.99, 125.77, 121.88, 120.97, 115.54, 115.40, 109.29, 108.93, 55.55, 55.53, 21.65 and 20.28.

Benzylideneoctanehydrazide (B-Oh) mixture of *cis/trans* isomers 2:3: ¹H NMR (DMSO-d₆, δ in ppm): 11.32 (s, 1H), 11.21 (s, 1H_a), 8.15 (s, 1H), 7.97 (s, 1H_a), 7.65 (m, 2H, 2H_a), 7.42 (m, 3H, 3H_a), 2.61 (t, 2H_a), 2.18 (t, 2H), 1.57 (m, 2H, 2H_a), 1.27 (m, 8H, 8H_a), 0.86 (t, 3H) and 0.85 (t, 3H_a). ¹³C NMR (DMSO-d₆, δ in ppm): 174.89, 169.11, 146.12, 142.78, 135.07, 134.83, 130.30, 130.08, 129.97, 129.64, 129.27, 129.24, 127.39, 127.03, 34.66, 32.32, 31.63, 29.18, 29.09, 28.93, 28.92, 25.48, 24.75, 22.54, 14.41.



Figure S1. ¹H NMR spectrum of glutaric dihydrazide (GDh) in DMSO-d₆.



Figure S2. ¹³C NMR spectrum of glutaric dihydrazide (GDh) in DMSO-d₆.



Figure S3. ¹H NMR spectrum of suberic dihydrazide (SDh) in DMSO-d₆.





Figure S5. ¹H NMR spectrum of dodecandioic dihydrazide (DDh) in DMSO-d₆.









Figure S8. ¹³C NMR spectrum of EPO-Van in DMSO-d₆.



3. Structural characterization of model compounds

Figure S9. ¹H NMR spectrum of V-Oh in DMSO-d₆.





Figure S10. ¹³C NMR spectrum of V-Oh in DMSO-d₆.

Figure S11. Mass spectrum of pure V-Oh.







Figure S14. Mass spectrum of pure B-Ah.





Figure S17. Mass spectrum of pure V-Ah.



Figure S18. ¹H NMR spectrum of B-Oh in DMSO-d₆.







Figure S20. Mass spectrum of pure B-Oh.

Supporting References

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