

Novel sustainable synthesis of resorcinol-terephthalaldehyde thermosetting phenolic resin through solvent-free reactive extrusion

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1. Sustainable synthesis routes for bio-based monomers

TPA can be produced from oxidation of bio-sourced para-xylene (which is used in large-scale production of bio-based PET). **Figure S1** shows a pathway for obtaining bio-based para-xylene for the production bio-terephthalic acid.¹

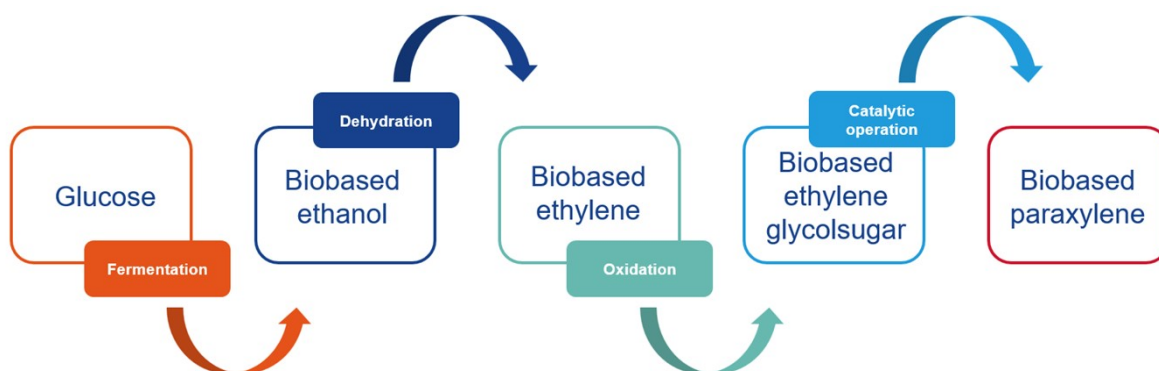


Figure S1 : General scheme for biobased paraxylene for bio-PET production

Other sustainable pathways for p-xylene production include cycloaddition of biomass-derived furans, direct conversion of lignocellulose via catalytic fast pyrolysis or synthesis from isobutanol.²

Resorcinol is a promising monomer as it can be produced from the biomass following different pathways. In fact, resorcinol can be synthesized from catechin or glucose by fermentation.³ Glucose is first converted into inositol via fermentation, which is then chemically transformed into 1,3,5-benzenetriol (phloroglucinol). This intermediate can subsequently be reduced to resorcinol (**Figure S2**).

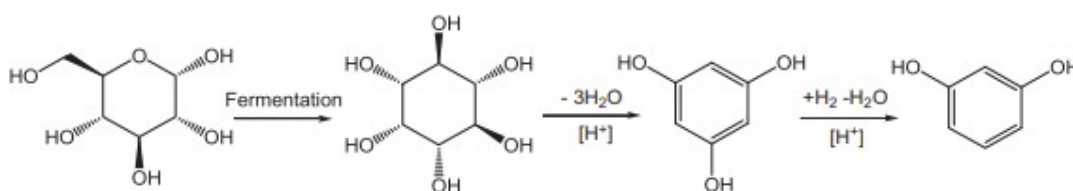


Figure S2 : Resorcinol synthesis from glucose via inositol

Glucose can also undergo fermentation to produce triacetic acid lactone. This compound is further converted to 1,3,5-benzenetriol methyl ether, which can be reduced to resorcinol either directly or via intermediate steps. (**Figure S3**)

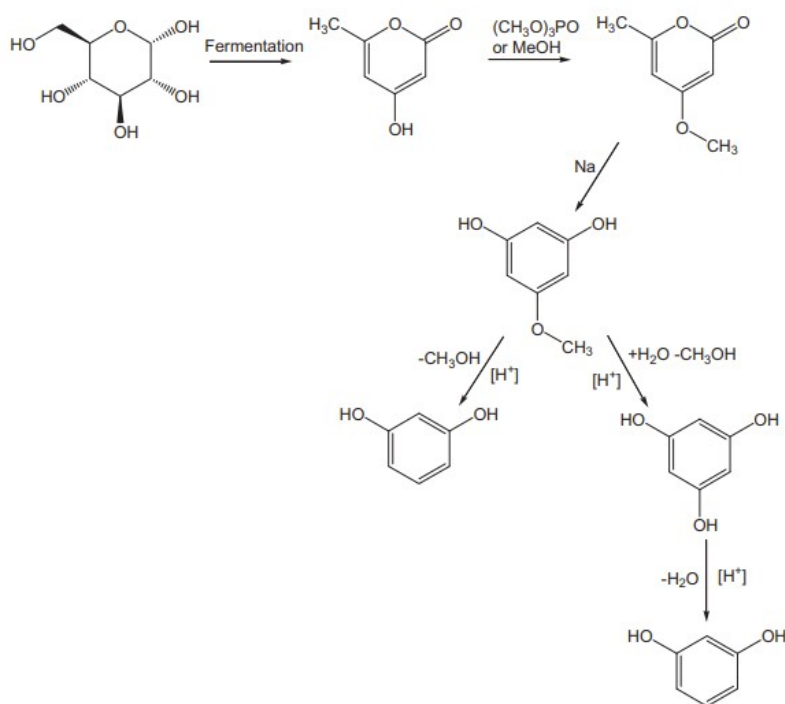


Figure S3 : Resorcinol synthesis from glucose via triacetic acid lactone

2. Structural characterization of the resin synthesized by reactive extrusion

a. 2D $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum

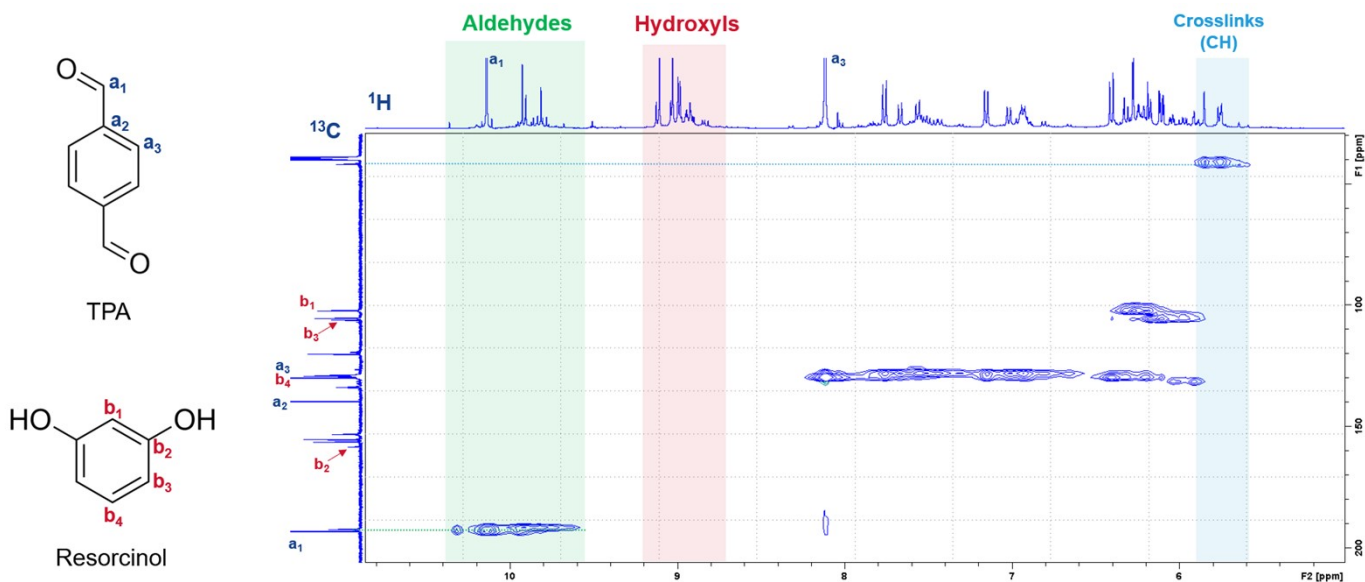


Figure S4 : 2D $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in DMSO-d_6 (298K) of the resin for a TPA-to-resorcinol molar ratio of 1.6. The extrusion temperature was set to 150 °C with a flow rate of 1 $\text{kg}\cdot\text{h}^{-1}$ and a screw speed of 100 rpm (RT1.6_T150[3'10]). The signal attributions of the residual monomers is shown on the spectra.

b. ^{13}C -NMR and DEPT135 NMR spectra

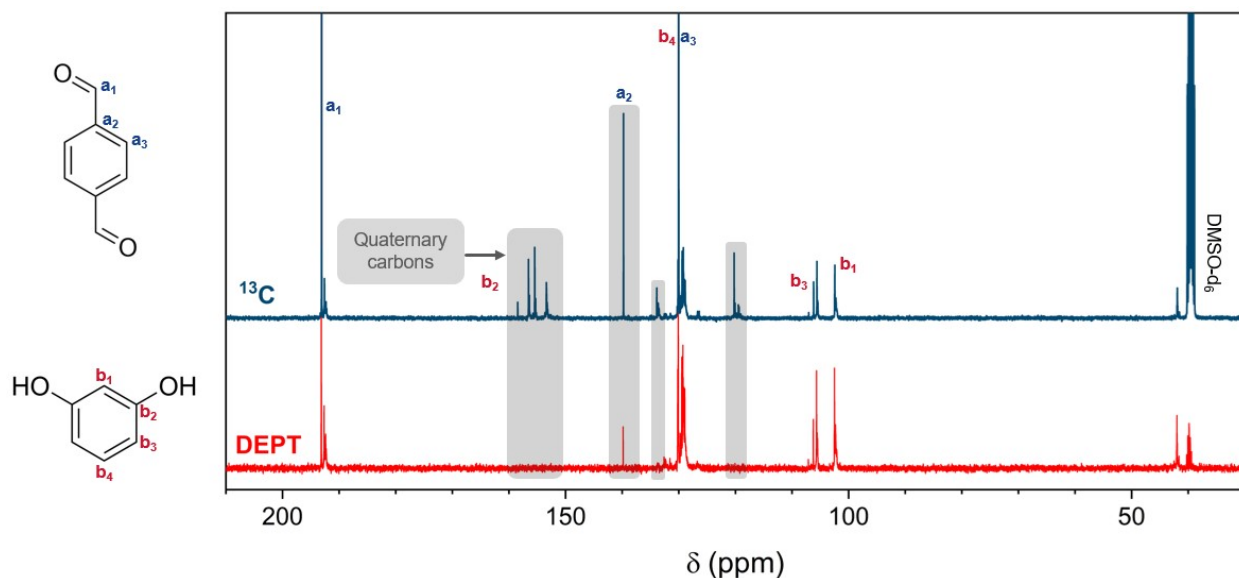


Figure S5: ^{13}C -NMR and DEPT135 NMR spectra in DMSO- d_6 (298K) of the resin for a TPA-to-resorcinol molar ratio of 1.6. The extrusion temperature was set to 150 °C with a flow rate of 1 kg·h $^{-1}$ and a screw speed of 100 rpm (RT1.6_T150[3'10]). The signal attributions of the residual monomers are shown on the spectra. The a_2 signal corresponds to a quaternary carbon but has not been but fully suppressed on the DEPT 135 NMR spectrum.

c. 2D $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum

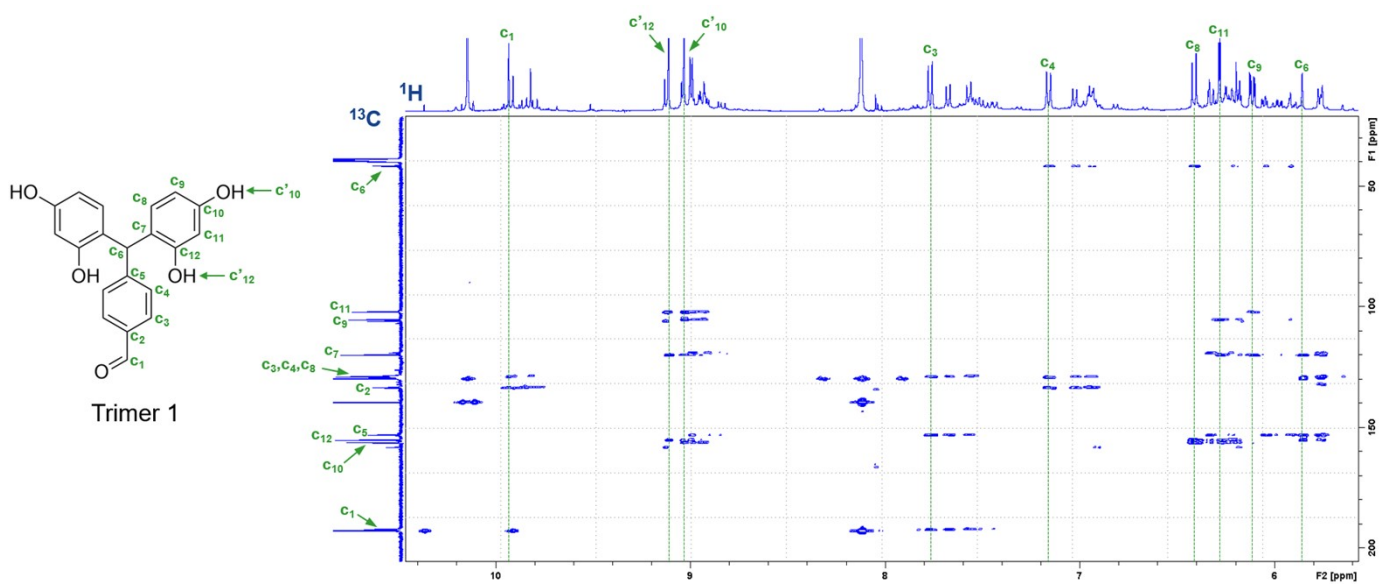


Figure S6: 2D $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in DMSO- d_6 (298K) of the resin for a TPA-to-resorcinol molar ratio of 1.6. The extrusion temperature was set to 150 °C with a flow rate of 1 kg·h $^{-1}$ and a screw speed of 100 rpm (RT1.6_T150[3'10]). The signal attributions of the trimer 1 synthesized is shown on the spectra.

d. Flash chromatography

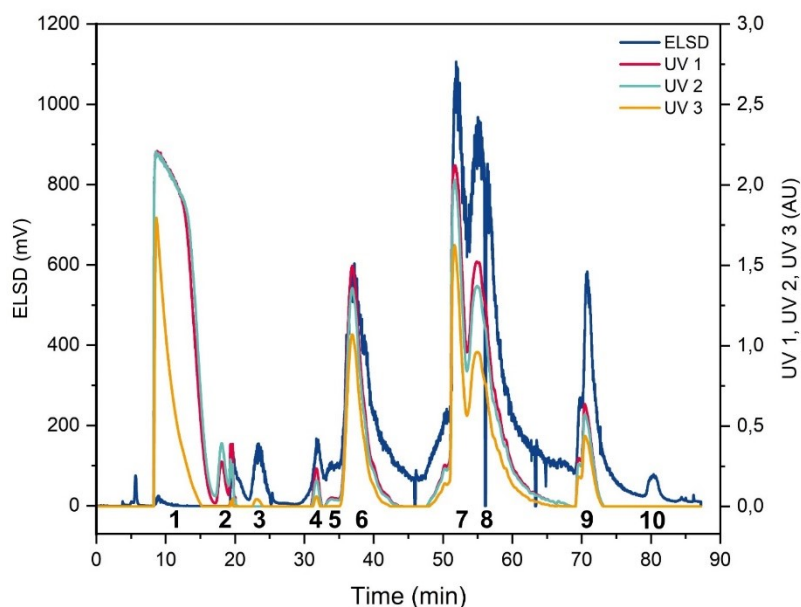


Figure S7: Chromatogram obtained from the flash chromatography of the resin for a TPA-to-resorcinol molar ratio of 1.6. The extrusion temperature was set to 150 °C with a flow rate of 1 kg·h⁻¹ and a screw speed of 100 rpm (RT1.6_T150[3'10]). The oligomers were separated with a gradient program of solvent A (dichloromethane) and solvent B (methanol). Initially, the separation started with a low percentage of solvent B (95% A, 5% B), which was gradually increased to reach 100% of solvent B as eluent.

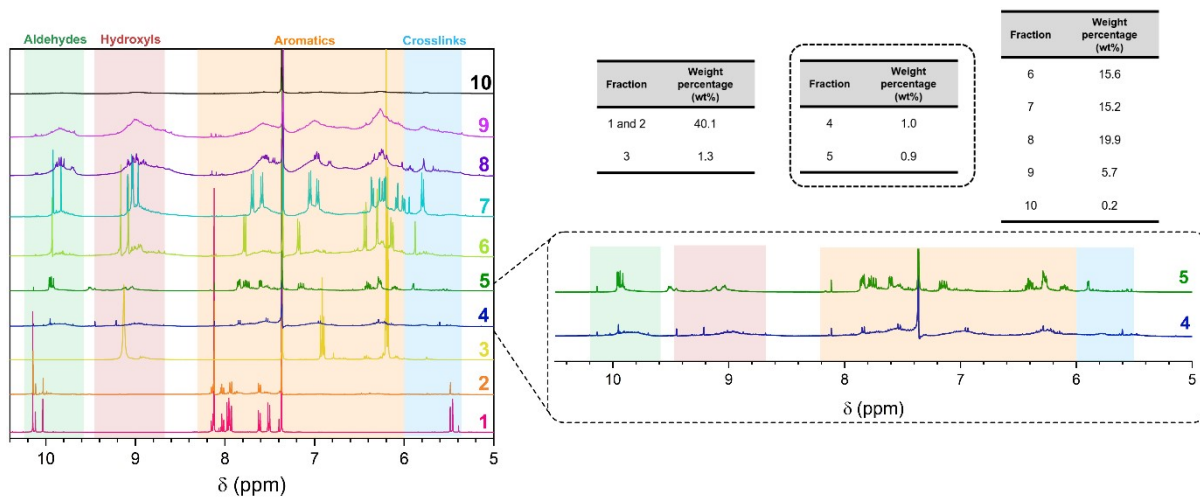


Figure S8: ¹H NMR spectra of the different fractions obtained from the separation by flash chromatography with a magnification on fractions 4 and 5. The weight percentage of each fraction is summarized in the tables.

e. Mass spectrometry

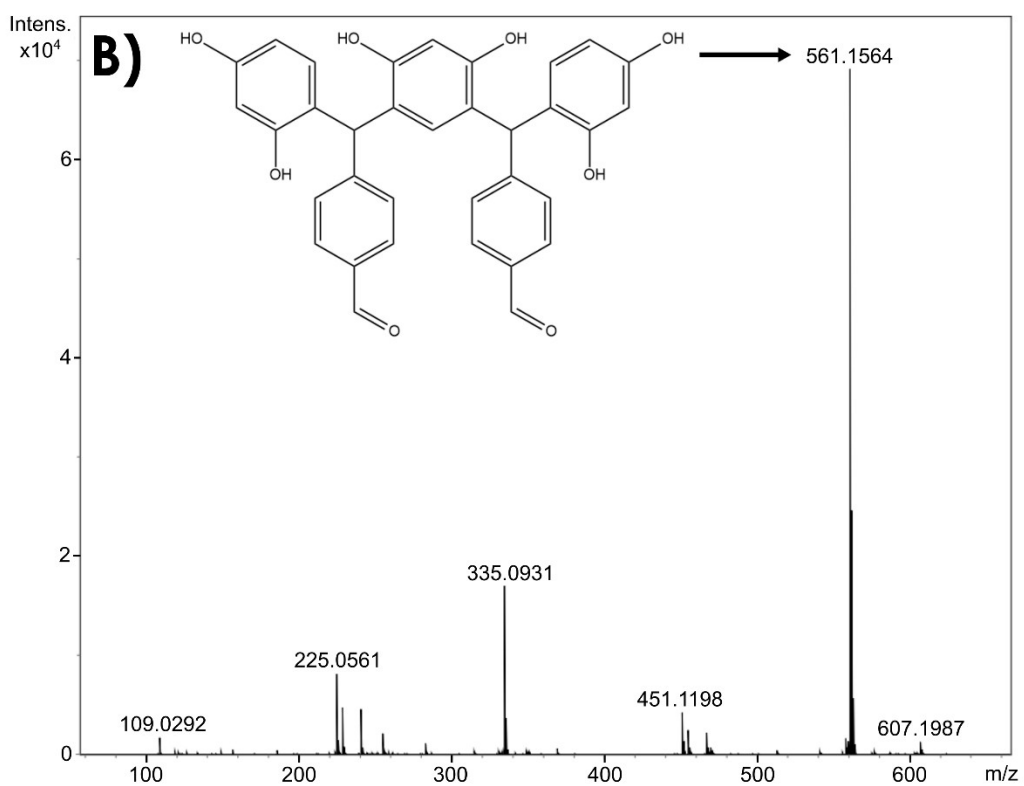
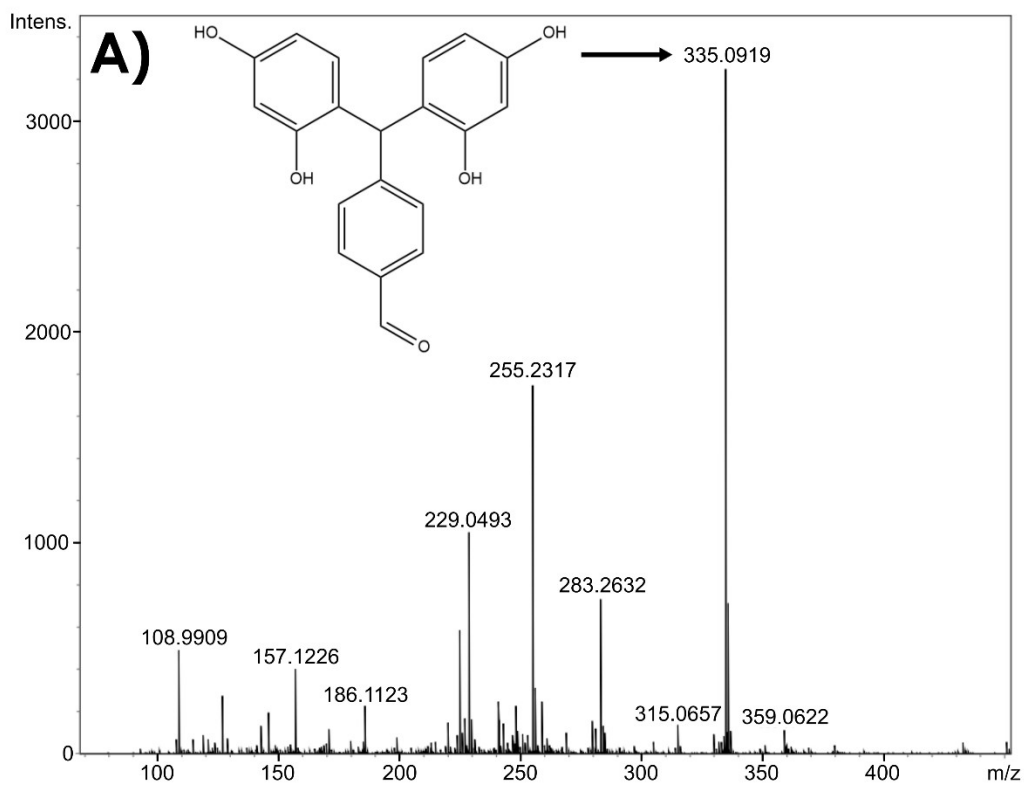


Figure S9: APCI mass spectra of two fractions in negative mode. A) Fraction 6; B) Fraction 7.

3. Thermal analyses of the resin synthesized by reactive extrusion (TGA-IR)

a. TGA of TPA

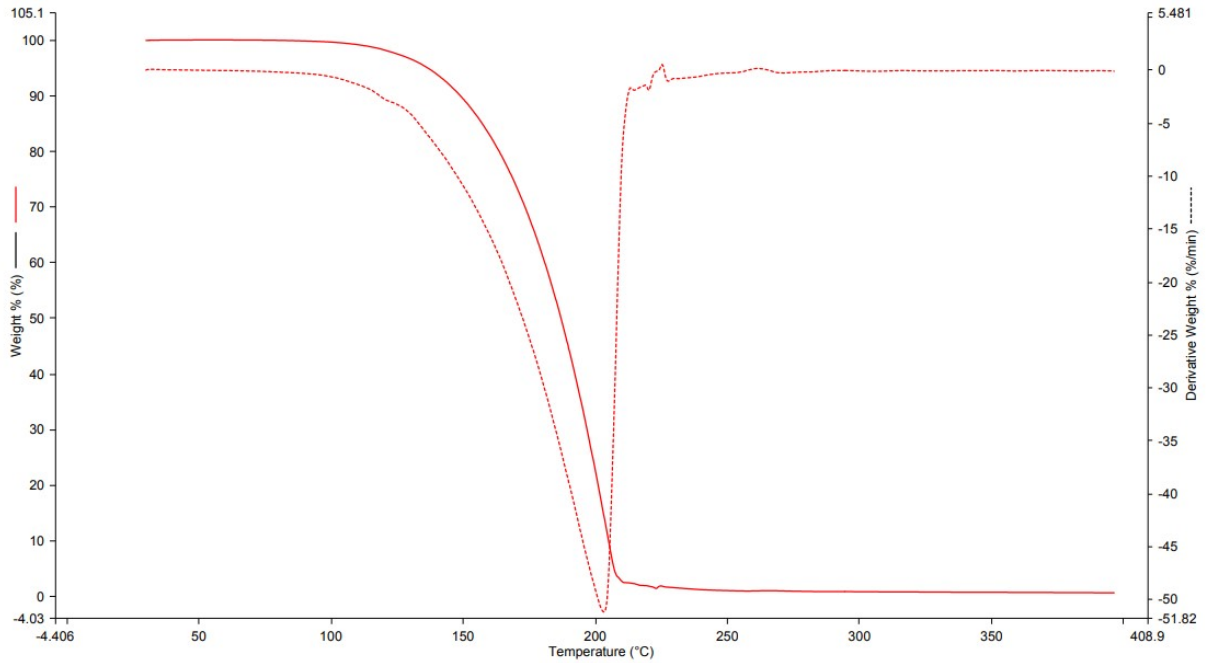


Figure S10: Thermogravimetric analysis of TPA at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under inert atmosphere.

b. Absorption spectra of TPA

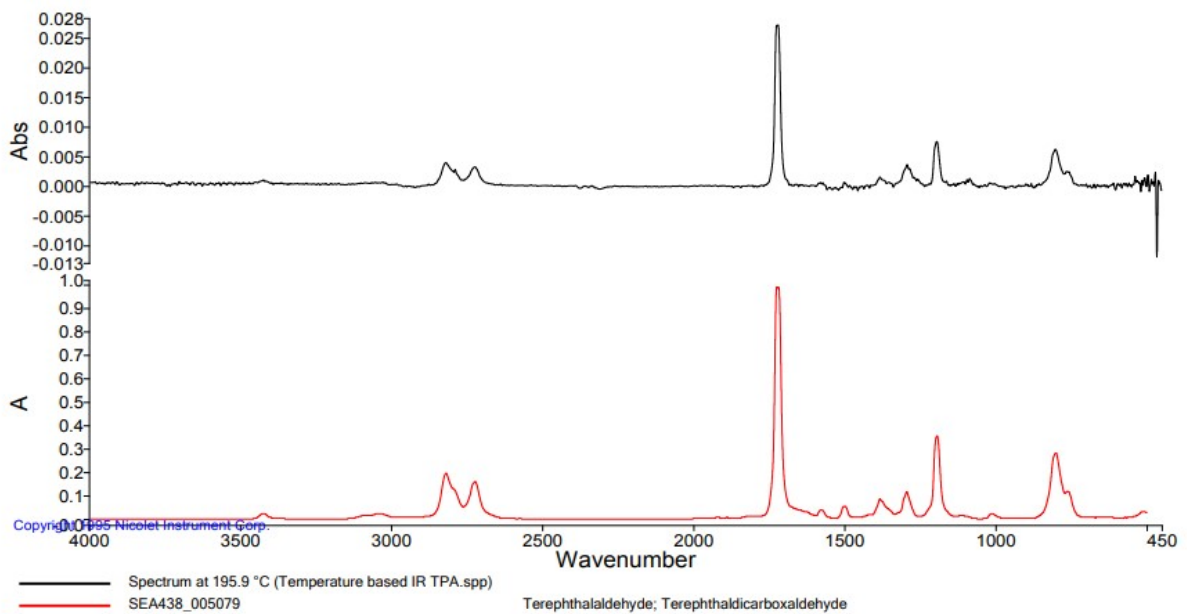


Figure S11 : Absorption spectra of the TPA obtained with the TGA-IR analysis at 196 °C (black) vs. the absorption spectra of TPA from the database (red)

c. Absorption spectra of the resin synthesized by reactive extrusion

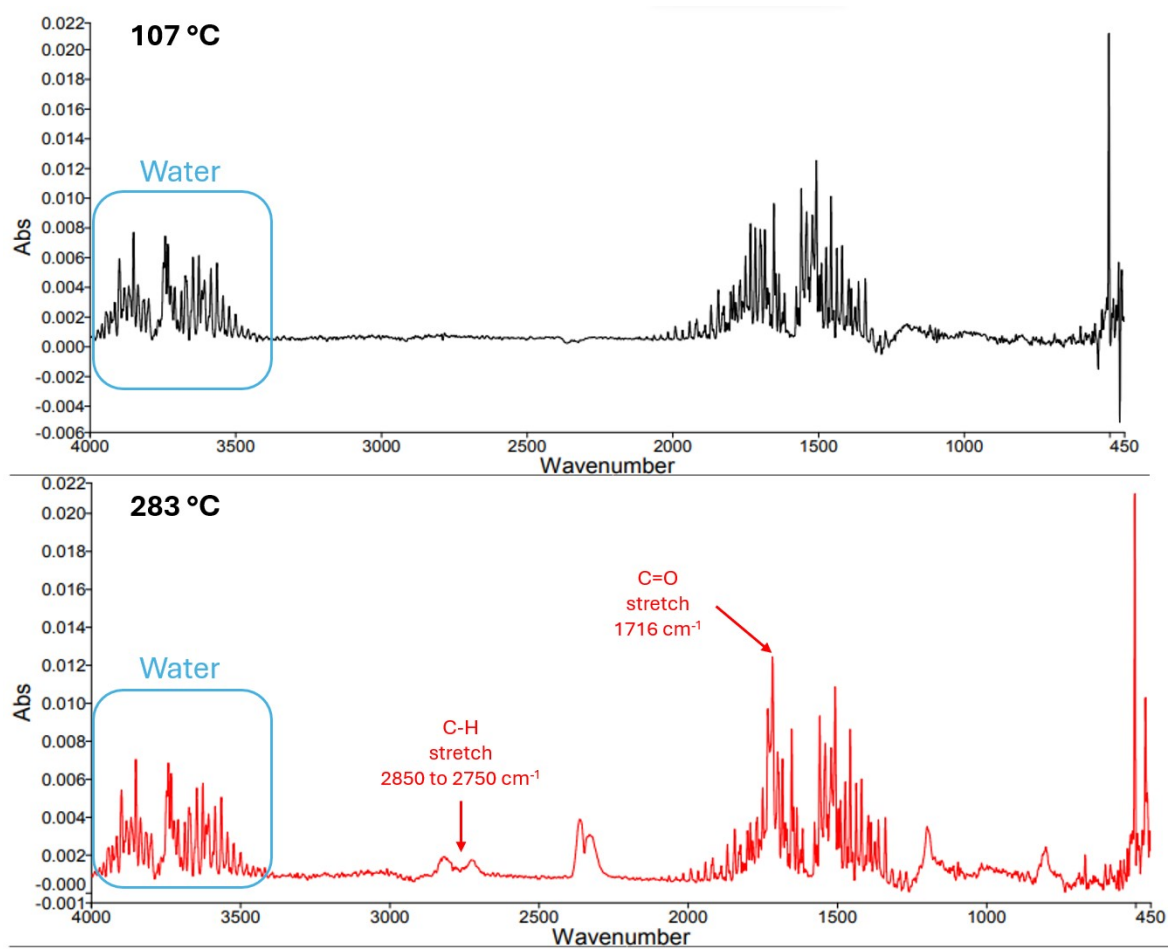


Figure S12 : Absorption spectra from TGA-IR analyses of the resin of molar ratio 1.6 at 107 °C (black) and at 283 °C (red).

d. TGA of the resin synthesized by reactive extrusion

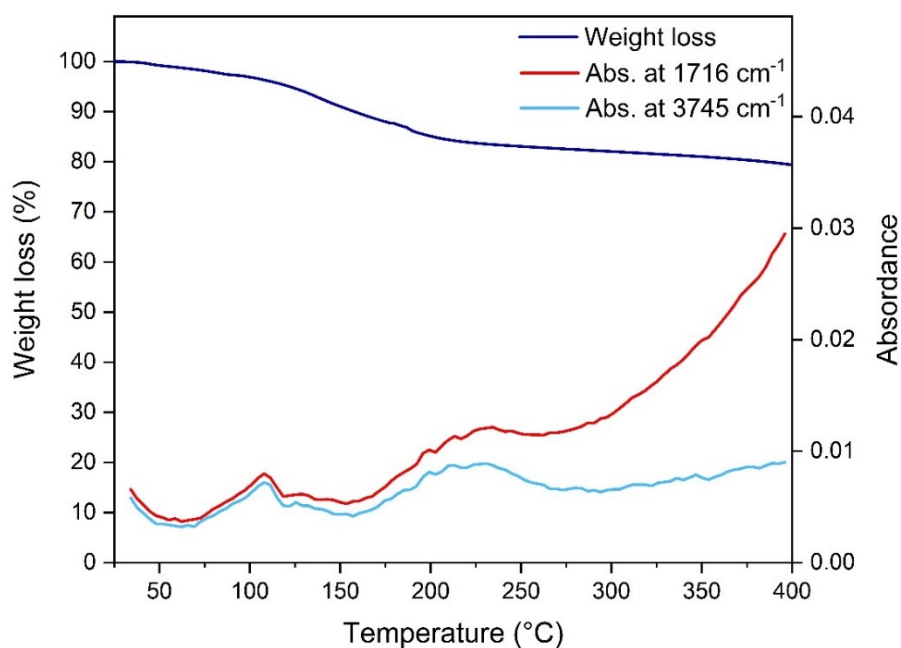


Figure S13 : TGA thermogram of the resin of molar ratio 1.6 correlated with the absorbance profiles at 1716 cm^{-1} (TPA) and 3745 cm^{-1} (water).

References

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- 3 C. Gioia, M. B. Banella, M. Vannini, A. Celli, M. Colonna and D. Caretti, *Eur. Polym. J.*, 2015, **73**, 38–49.