# Photocurable Itaconic Acid-Functionalized Star Polycaprolactone in Bio-Based Formulations for Vat Photopolymerization

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## SUPPORTING INFORMATION

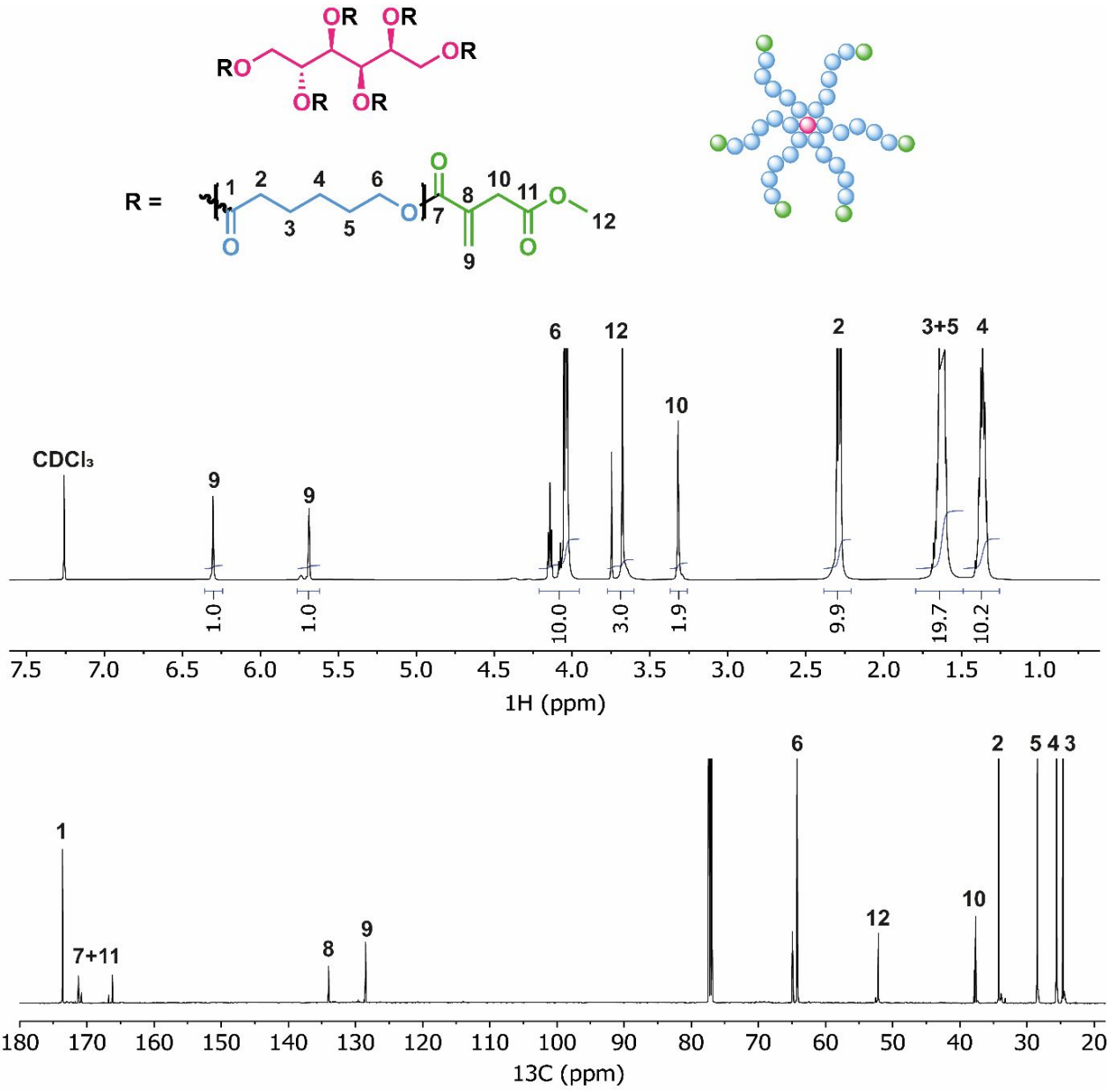


**Figure S1**. $^{1}$H- (600 MHz, $CDCl_3$, top) and $^{13}$C- (150 MHz, $CDCl_3$, bottom) NMR analysis and spectral assignments for SH(PCI).

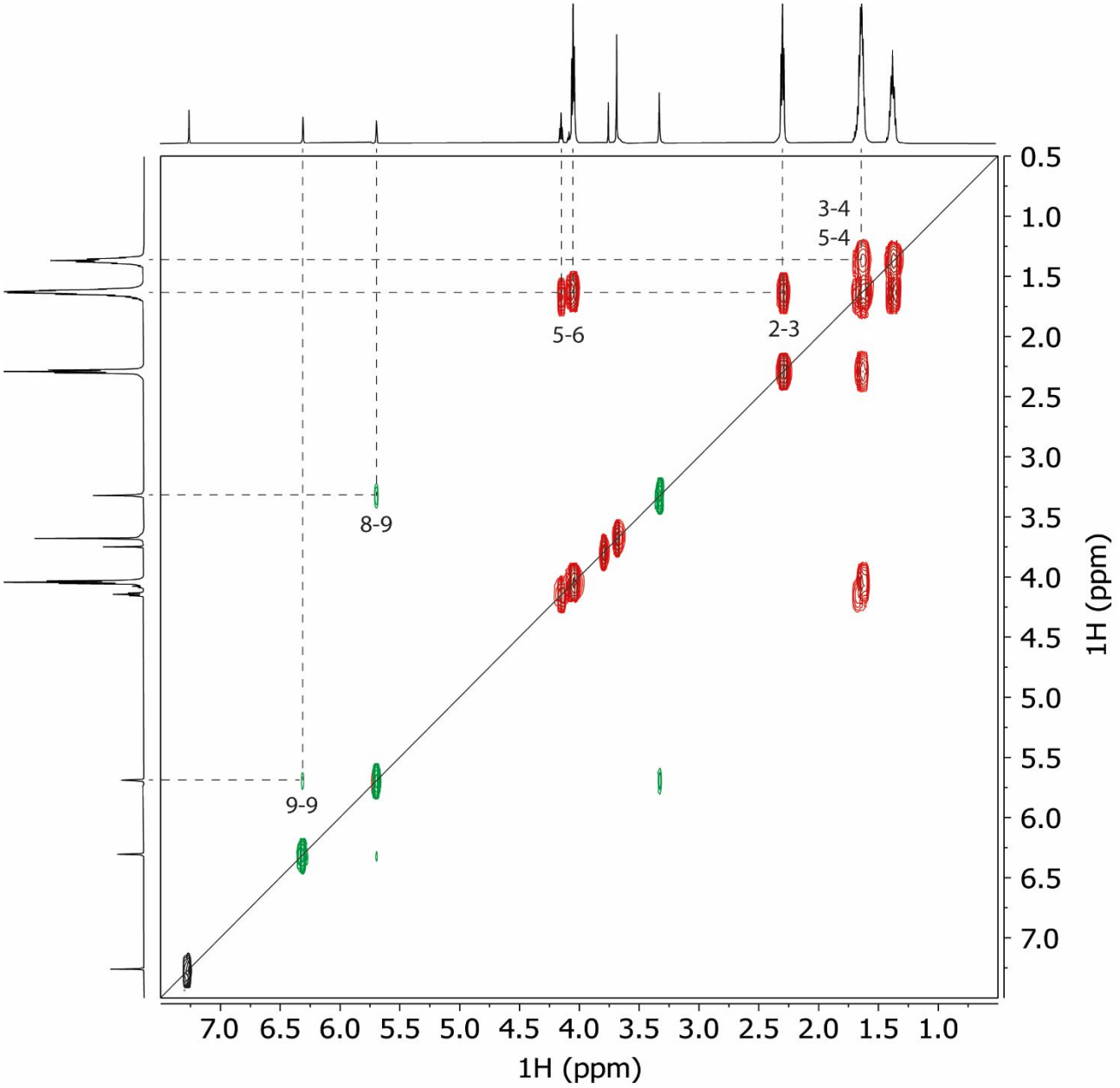


**Figure S2.** $^{1}$H-$^{1}$H COSY (600 MHz, $CDCl_3$) NMR analysis of sorbitol hexa(pentacaprolactone methylitaconate) SH(PCI) and attribution of the crosspeaks according to the numbering reported in Figure S1. Peaks related to PCL protons are colored in red, peaks related to itaconate groups are colored in green, and the residual solvent peak is colored in black. Effective functionalization of PCL with itaconic acid moieties is proved by the splitting of the $^{1}$H signal corresponding to position 6, caused by the presence of itaconic acid methyl ester in both orientations at the end of PCL chains.

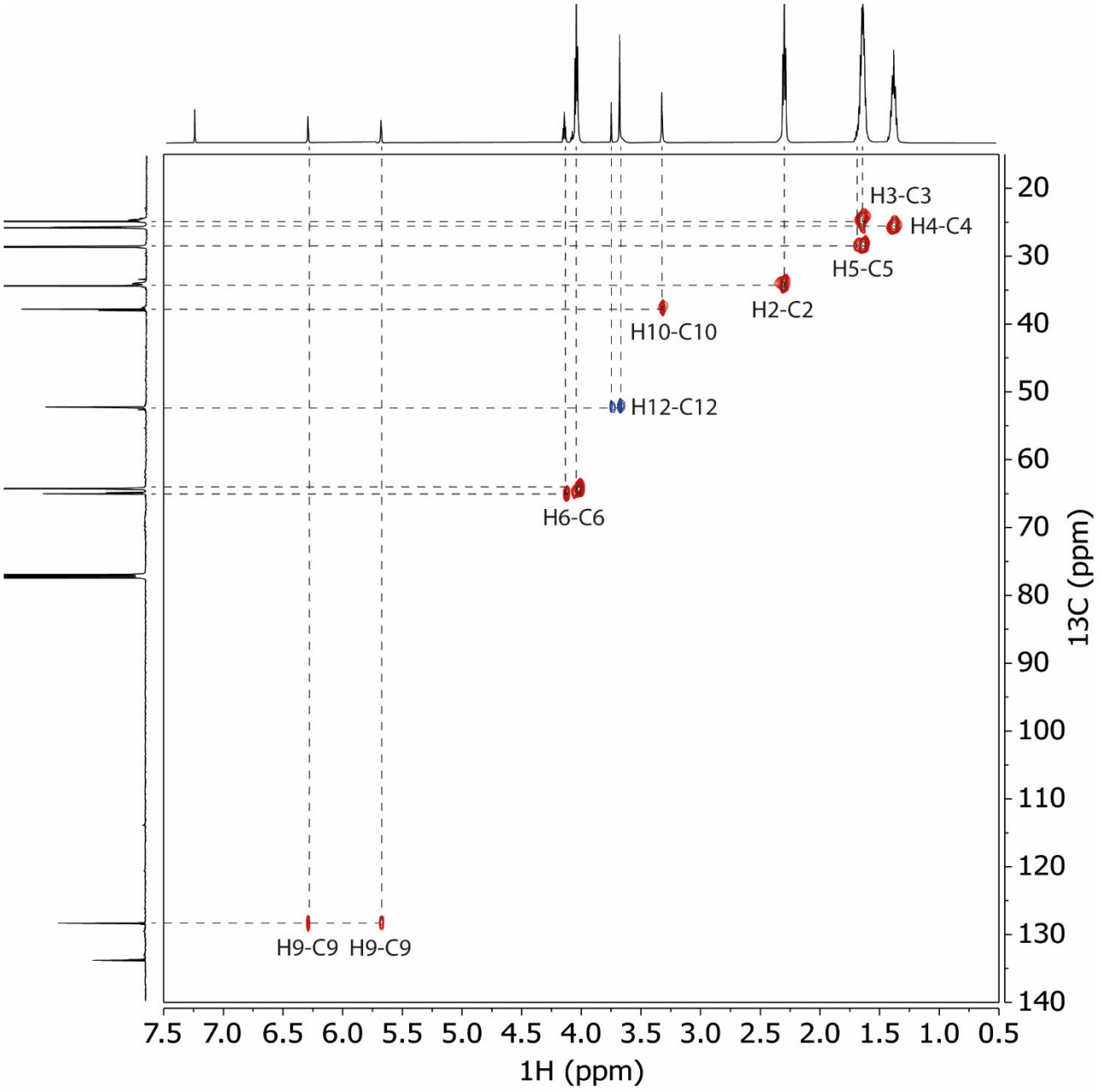


**Figure S3.** $^{1}H$-$^{13}C$-HSQC (600 MHz, $CDCl_3$) NMR analysis of sorbitol hexa(pentacaprolactone methylitaconate) SH(PCI) and attribution of the crosspeaks according to the numbering reported in Figure S1. Positive peaks are coloured in red and are related to CH and $CH_3$ groups, while negative peaks are coloured in blue and are related to $CH_2$ groups. As well as for COSY, this spectrum demonstrates the effective functionalization of the termini of PCL chains with itaconic acid, supported by the splitting of crosspeaks corresponding to position 6 (alcoholic $CH_2$ of PCL) and 12 (methyl ester) caused by the presence of itaconic acid in both orientations.

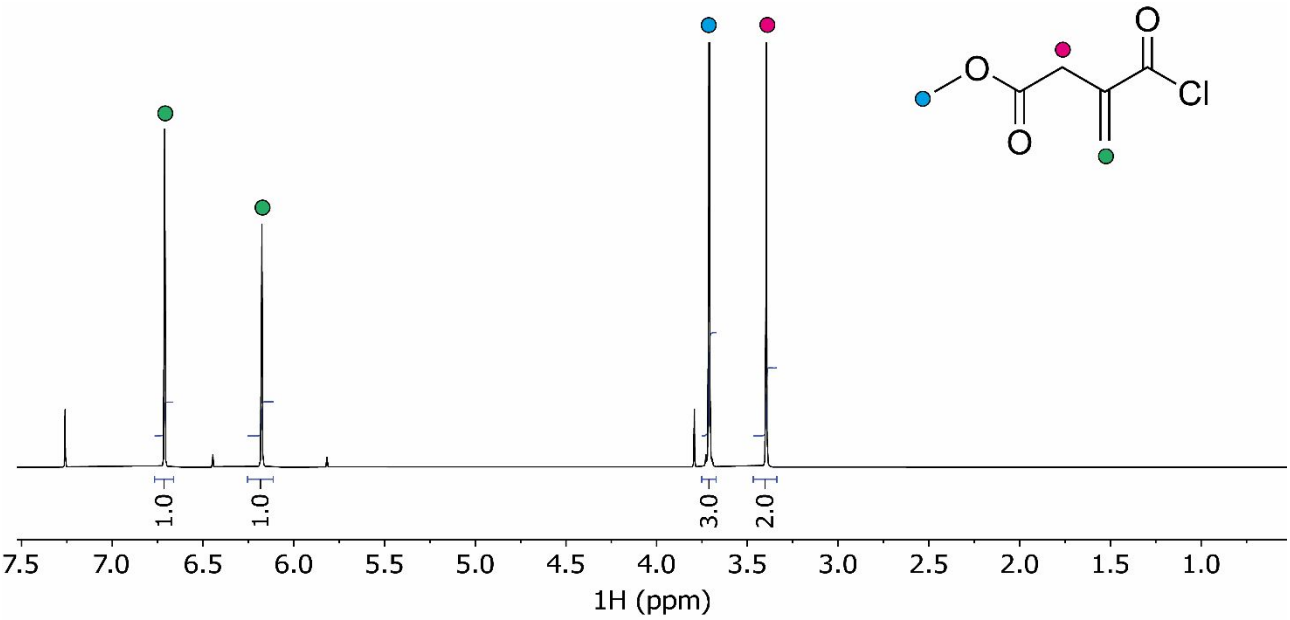


**Figure S4.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of monomethyl itaconoyl chloride, with the corresponding spectral assignments. Smaller amounts of the inverse compound, the α,β-unsaturated methyl ester, was also formed but could not be separated by distillation due to their similar boiling points.

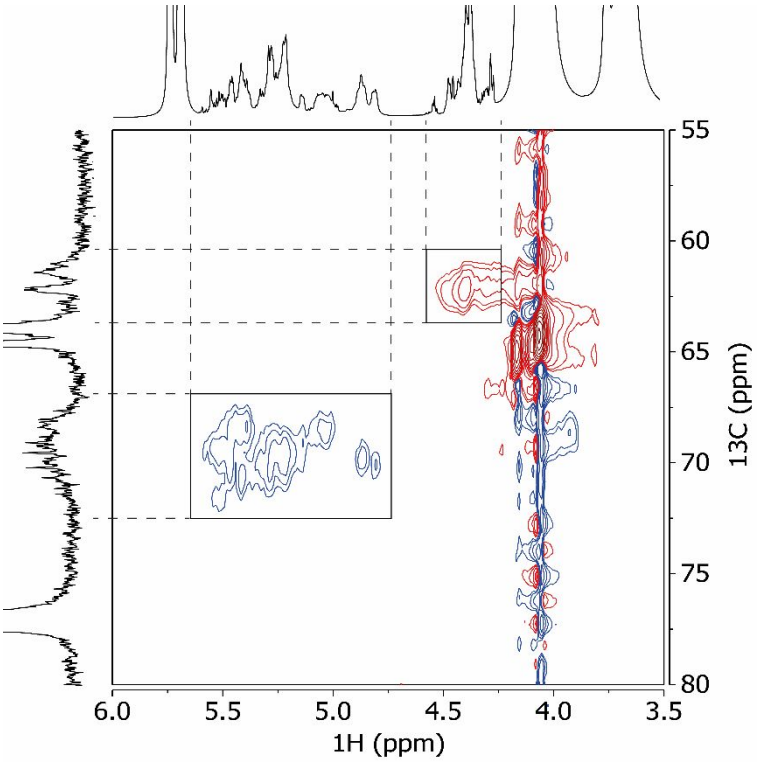


**Figure S5**. Detail of the $^{1}H$-$^{13}C$-HSQC (600 MHz, $CDCl_3$) NMR spectrum of sorbitol hexa(pentacaprolactone methylitaconate) SH(PCI), highlighting the cross-peaks related to the sorbitol core. In particular, terminal $CH_2$ groups correspond to the blue spot, while central CH groups are related to the red spot, due to the phase-sensitivity of the HSQC analysis that allows to distinguish them.

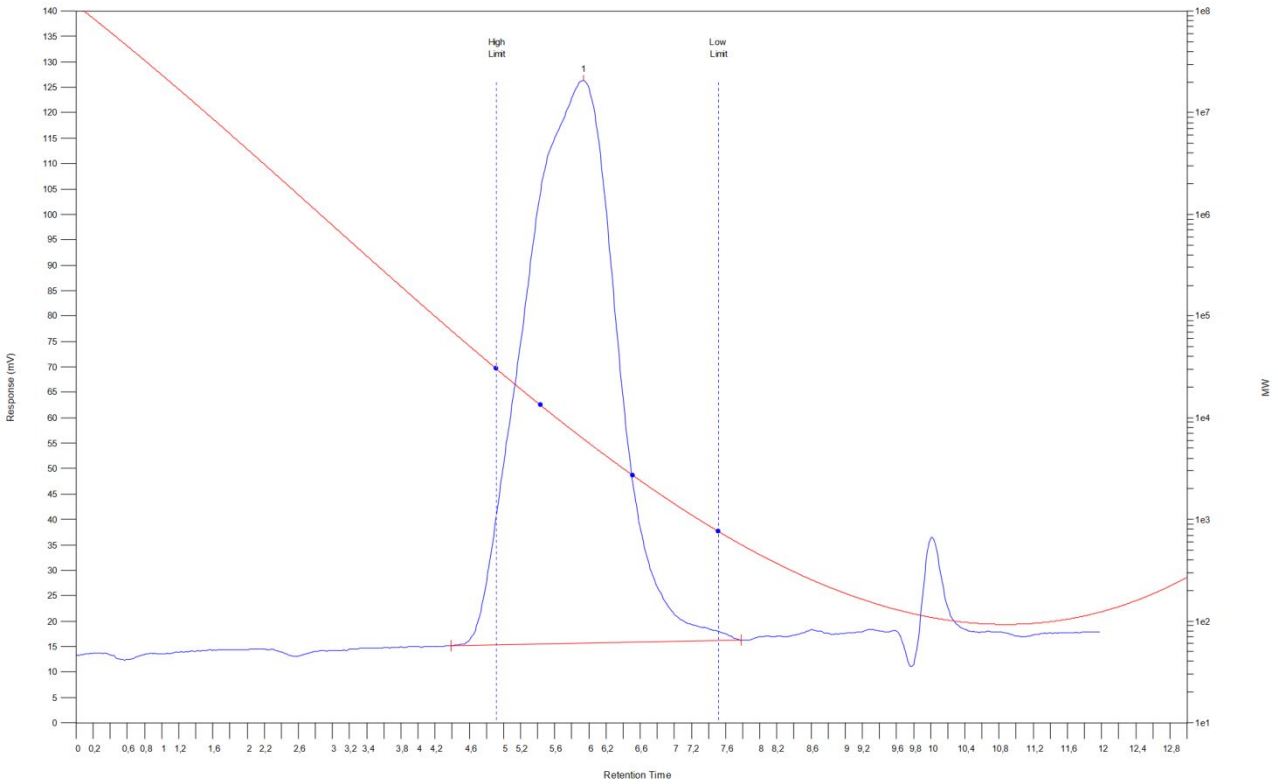


**Figure S6.** GPC-SEC trace of SH(PCI). The blue line corresponds to the chromatogram (amplitude of refraction index change), while the red curve corresponds to the calibration curve built using polystyrene standards with known molecular weight.

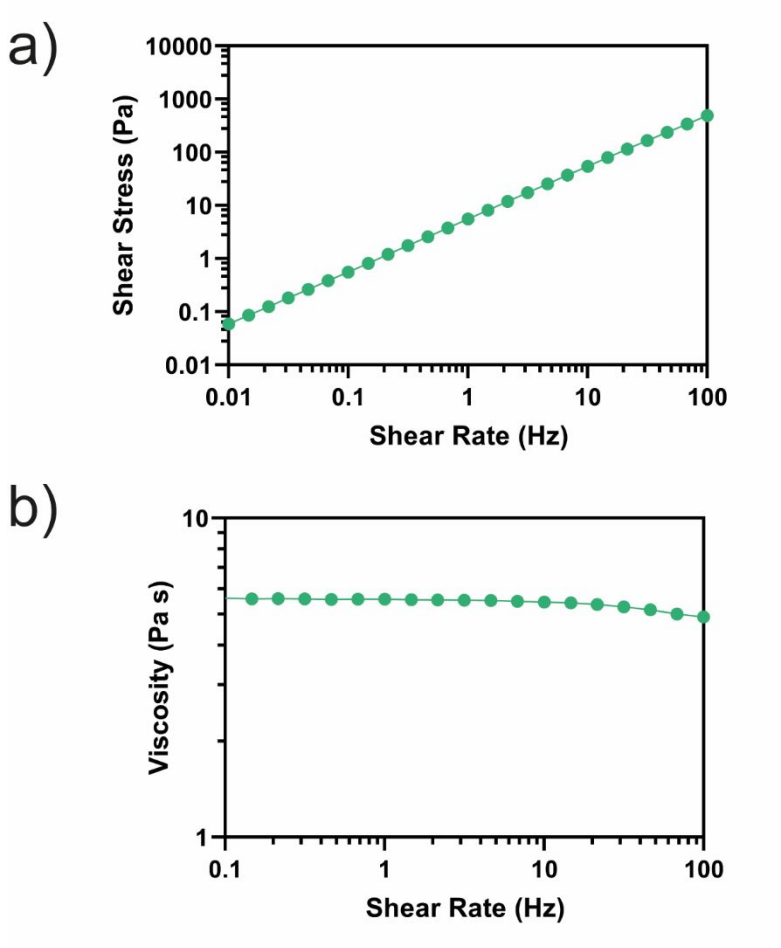


**Figure S7.** Rheological analysis of SH(PCI). a) Shear stress as a function of shear rate at 25°C. b) Viscosity as a function of shear rate at 25°C. SH(PCI) display viscosity values compatible with the formulation of photocurable resins for stereolithography throughout the entire range of temperatures, especially above 20°C.

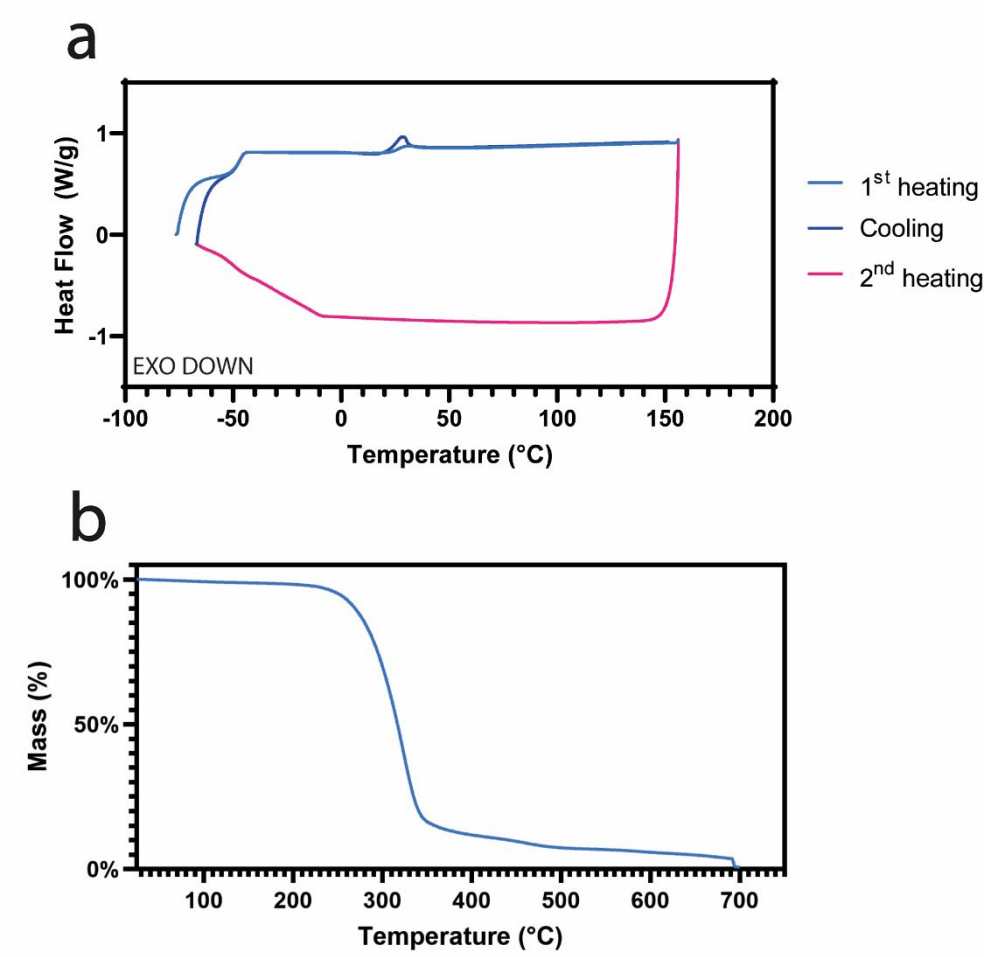


**Figure S8**. Thermal analysis of SH(PCI). A) Differential scanning calorimetry (DSC) and b) thermogravimetric analysis (TGA).

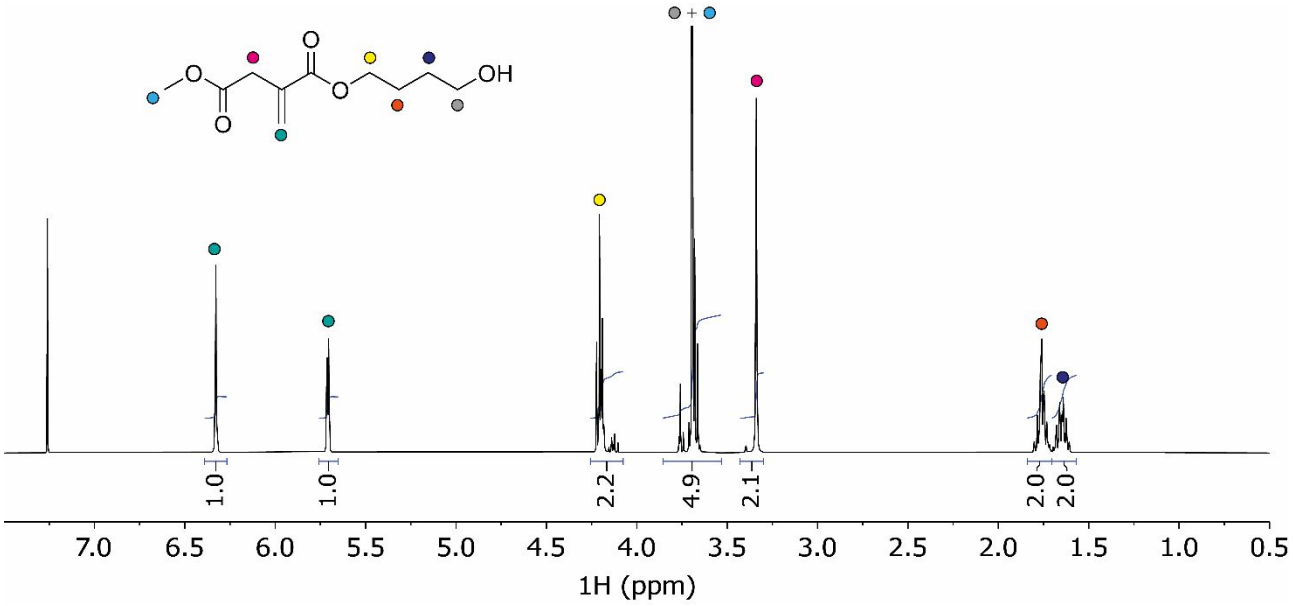


**Figure S9.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of butanediyl mono(methyl itaconate), Me-MONO, with the corresponding spectral assignments.

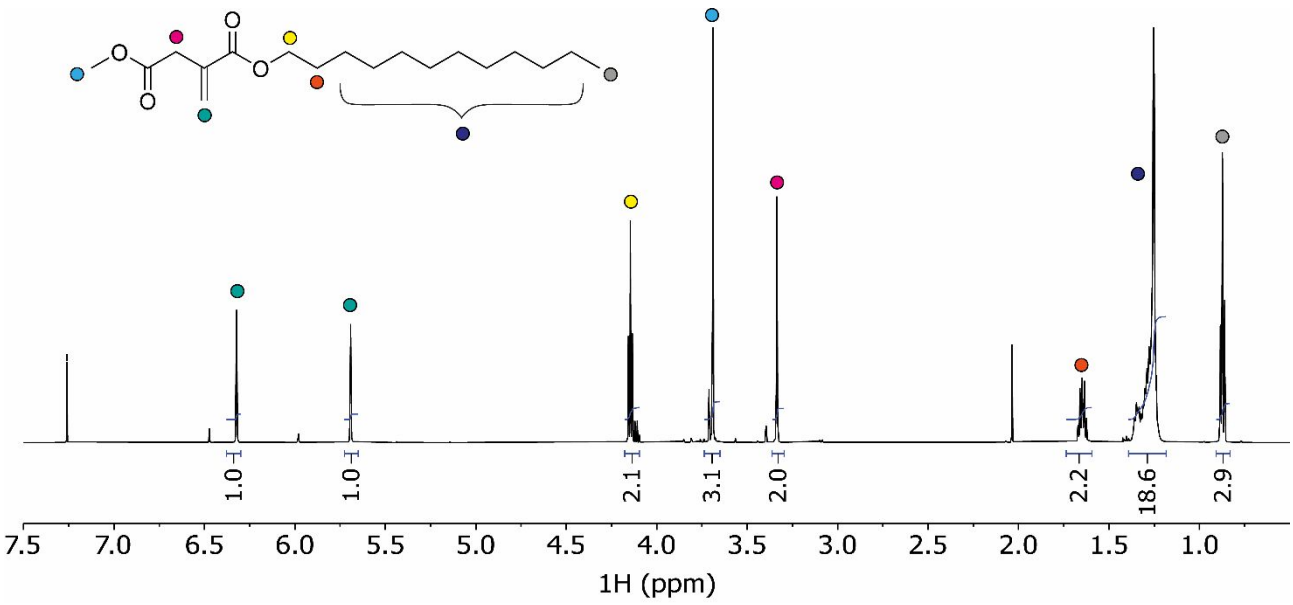


**Figure S10.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of dodecyl methyl itaconate, with the corresponding spectral assignments.

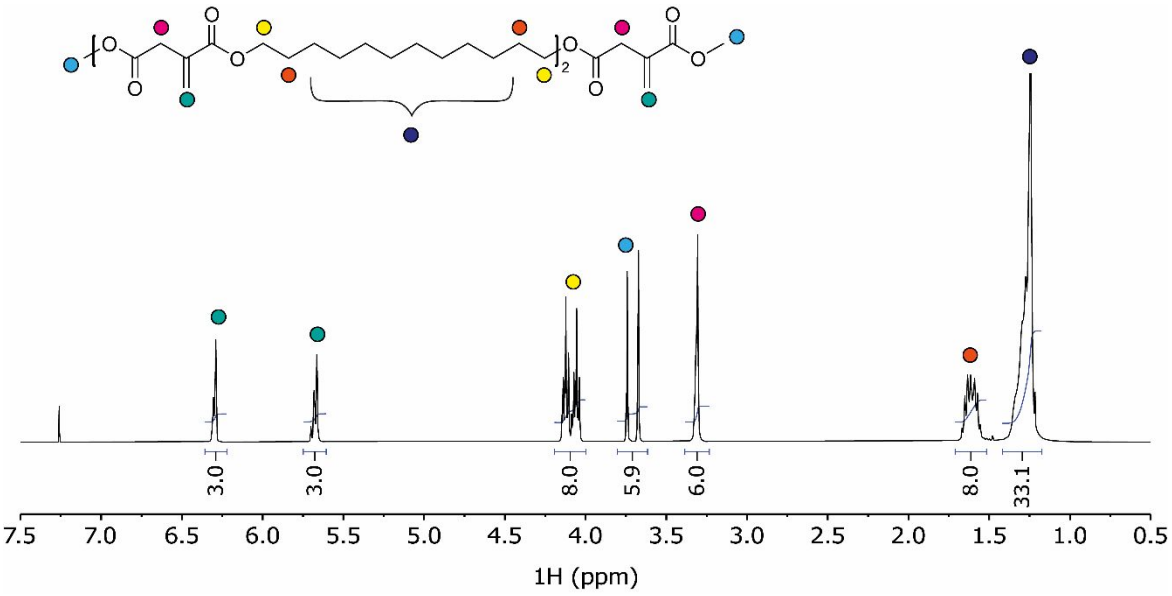


**Figure S11.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of poly(dodecanediyl itaconate) oligomer (oligoPDI), with the corresponding spectral assignments.

**Evaluation of the biobased content of the formulations**

The total biobased content of the prepared formulations reported in **Table 1** was evaluated in terms of their overall biobased mass content. For the single components, the biobased mass content was determined by considering the fraction of the product's molecular weight that is composed of biobased or bioderived building blocks. For the photoinitiating system, the biobased content was 0%.

*Sorbitol hexa(pentacaprolactone methylitaconate) – SH(PCI)*
Building blocks:

- Itaconic acid (biobased)
- 6-hydroxyhexanoic acid (biobased)
- Sorbitol (biobased)
- Methanol (biobased)

Biobased content = 100%

*Dodecyl methyl itaconate – DOIT*
Building blocks:

- Itaconic acid (biobased)
- Dodecanol (biobased)
- Methanol (biobased)

Biobased content = 100%

*Poly(dodecanediyl itaconate) oligomer – oligoPDI*
Building blocks:

- Itaconic acid (biobased)
- Dodecanediol (biobased)
- Methanol (biobased)

Biobased content = 100%

*1,4-butanediyl bis(methyl itaconate) – $I_2B_1$*
Building blocks:

- Itaconic acid (biobased)
- 1,4-butanediol (biobased)
- Methanol (biobased)

Biobased content = 100%

*Pentaerythritol tetraacrylate- PETA*
Building blocks:

- Acrylic acid (non-biobased)
- Pentaerythritol (non-biobased)

Biobased content = 0%

*Glycerol dimethacrylate- GDMA*
Building blocks:

- Methacrylic acid (non-biobased)

- Glycerol (biobased)

Biobased content = 32.4%

*Glycerol porpoxylate triacrylate - GPT*

Building blocks:

- Acrylic acid (non-biobased)
- Propylene glycol (from propylene oxide, non-biobased)
- Glycerol (biobased)

Biobased content = 17.3%

*Grinsted Sonft-N-Safe - SNS*

Building blocks:

- 9-hydroxystearic acid monoglyceride (biobased)
- Acetic acid (biobased)

Biobased content = 100%

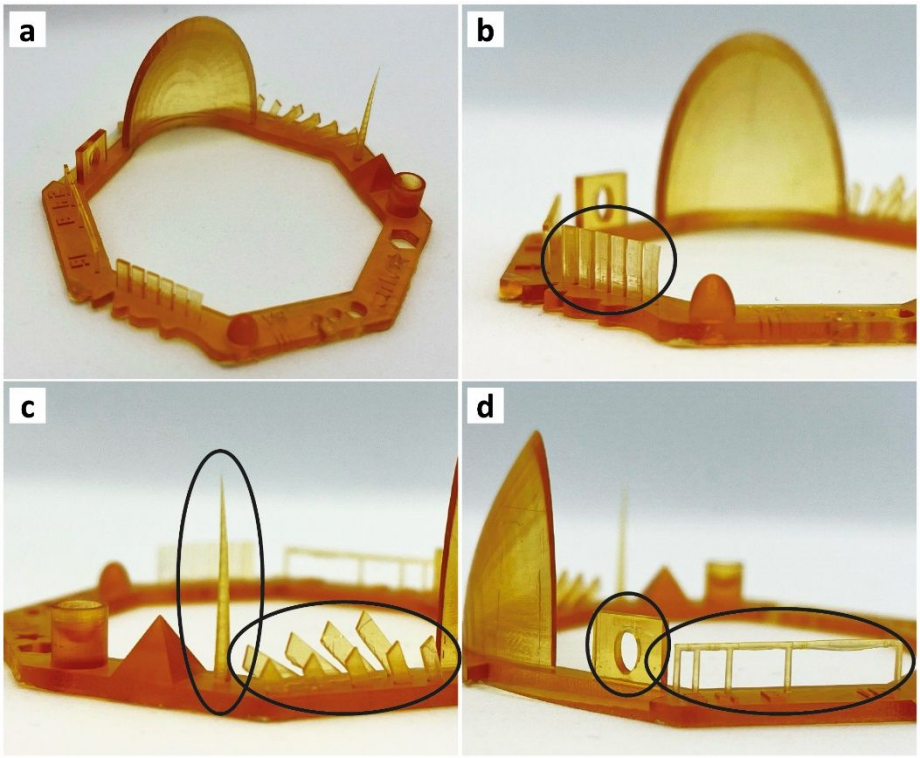


**Figure S12**. Evaluation of the printing performances of resin A3. Overview of the printed object (a) and details, showing the performances achieved with the resin for the printing of walls of decreasing thickness up to 0.1 mm (b), spike and overhanging walls up to 70° inclination (c), vertical hole in wall and bridge print with bridge length up to 16 mm (d). The diameter of the test print is xxx mm. The 3D object was downloaded free of charge from Makerworld.com (https://makerworld.com/en/models/54359#profileId-56081 )

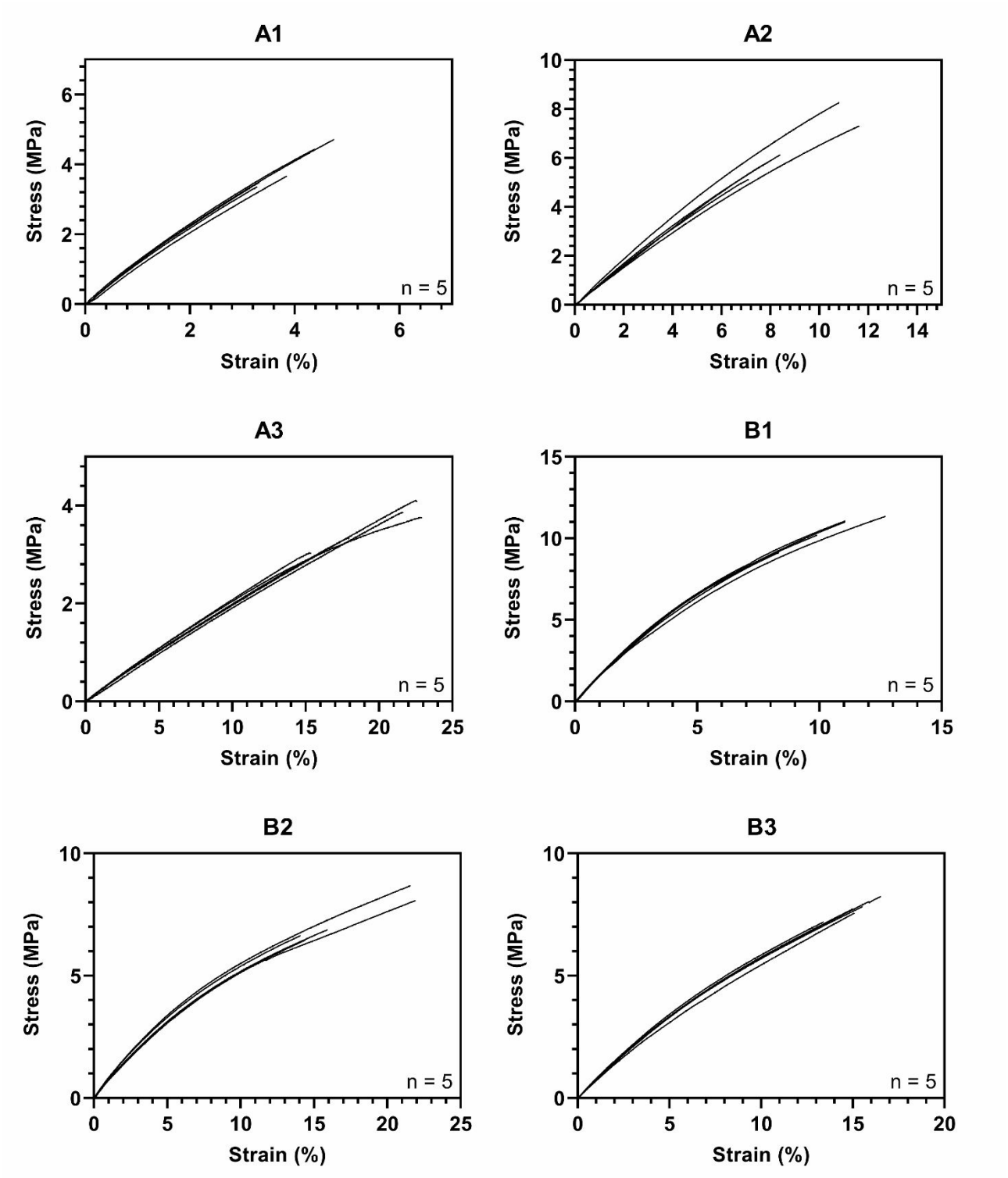


**Figure S13.** Tensile stress-strain curves of 3D printed A1-B3 formulations.

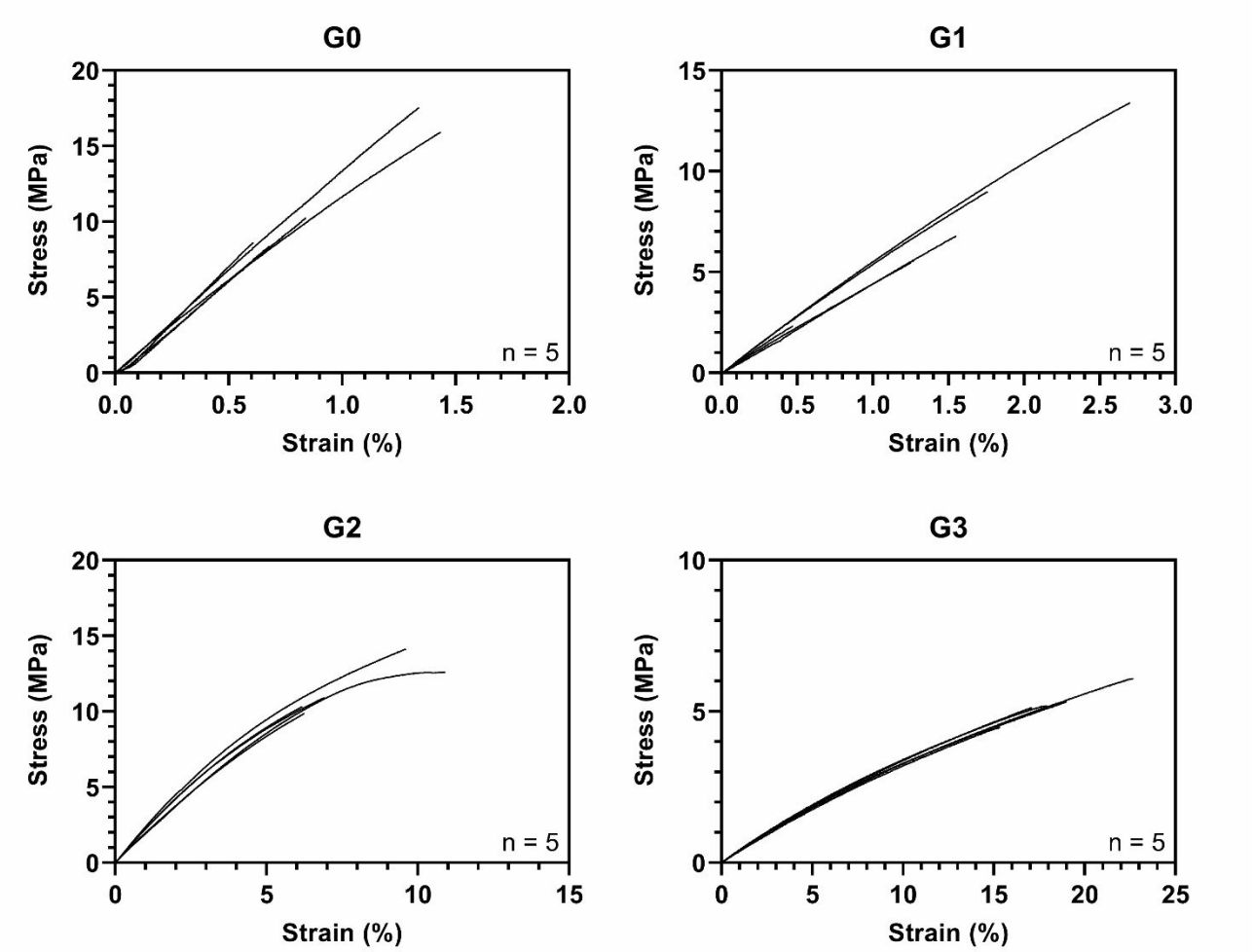


**Figure S14.** Tensile stress-strain curves of 3D printed G0-G3 formulations.