

# **Synthesis of bio-sourced liquid resins and their photopolymerization with poly(ethylene glycol) diacrylate in the roadmap to more sustainable digital light processing technologies**

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## 2. Experimental procedures

### 2.2. Synthesis of photocurable bio-based liquid resins

To obtain diallyl malate (DAM), a solution of NaOH (80 mL, 10 wt. %) was added dropwise to a solution of L-malic acid (13.4 g, 0.10 mol) and allyl bromide (26.6 g, 0.22 mol) in 100 mL of acetone (pure grade), in a round 500 mL bottom flask, after reaching the adequate temperature (65 °C). The mixture was stirred at 65 °C for 8 h before sequentially washing with water (500 ml) and three times with dichloromethane (DCM, 100 ml). Then the excess of solvent was evaporated under an air flow, under vigorous stirring to eliminate the excess of allyl bromide and to avoid that the final product should be dragged with the solvent when rotary evaporators are employed. The final product, diallyl malate monomer (DAM), was isolated as a colourless liquid, with yields of about 60 %.

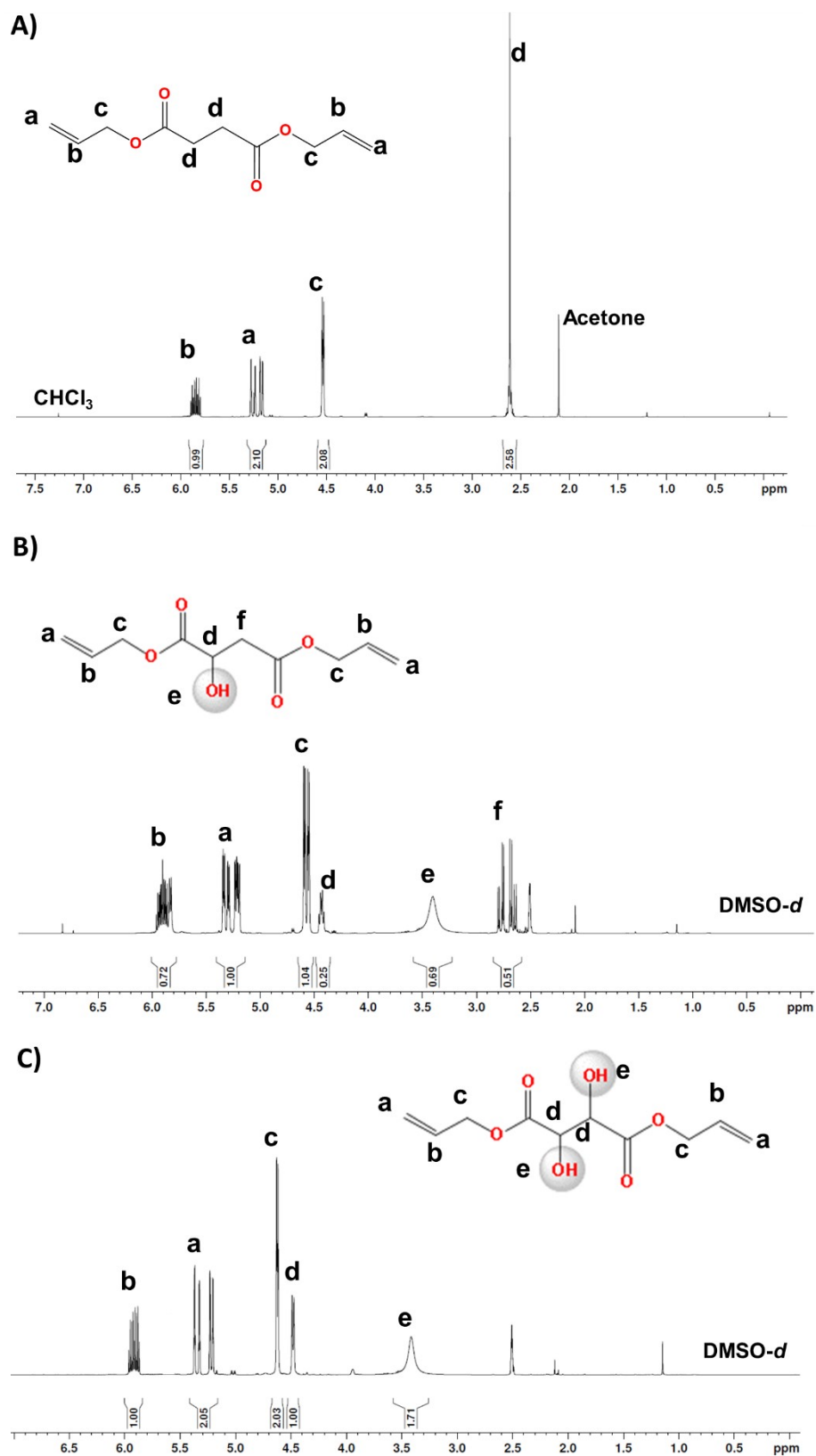
FTIR-ATR ( $\text{cm}^{-1}$ ): 3490 (OH, stretching); 3083 (=C-H, stretching); 2871-2994 (C-H, stretching); 1730 (C=O ester, stretching); 1647 (C=C, stretching); 1376, 1413, 1446 (=CH<sub>2</sub>, -CH<sub>2</sub>, in-plane bending); 1080-1270 (C-O-C ester, stretching); 786 (=C-H, out-of-plane bending). - Figure 2B (main text).

<sup>1</sup>H-NMR (400 MHz, *d*-DMSO,  $\delta$  ppm): 5.80-5.95 (m, 2H, CH<sub>2</sub>=CH-), 5.15-5.25 (m, 4H; CH<sub>2</sub>=CH-), 4.58 (dd, 4H, -CH<sub>2</sub>-O), 4.43 (t, 1H, -CH-OH), 3.39 (broad, s, 1H, OH), 2.70 (dq, 2H, -CH<sub>2</sub>-C=O). - Figure S1.B.

The same procedure was used to prepare diallyl tartrate (DAT), starting with L-(+)-tartaric acid (15.0 g, 0.10 mol) and little excess of allyl bromide (26.6 g, 0.22 mol). In this case, the mixture was left to react at 65 °C for 12 h, controlling that the solvent (acetone) volume is maintained. The purification step was similar to the previously described. The final product is a yellowish liquid resin (yield: 48-50%).

FTIR-ATR ( $\text{cm}^{-1}$ ): 3492 (OH, stretching); 3084 (=C-H, stretching); 2880-2940 (C-H, stretching); 1735 (C=O ester, stretching); 1647 (C=C, stretching); 1377, 1415, 1450 (=CH<sub>2</sub>, -CH<sub>2</sub>, in-plane bending); 1100-1200 (C-O-C ester, stretching); 823 (=C-H, out-of-plane bending) - Figure 2C (main text).

<sup>1</sup>H-NMR (400 MHz, *d*-DMSO,  $\delta$  ppm): 5.85-5.95 (m, 2H, CH<sub>2</sub>=CH-), 5.25 (d, 2H; CH<sub>2</sub>=CH-), 5.35 (d, 2H; CH<sub>2</sub>=CH-), 4.60 (d, 4H, -CH<sub>2</sub>-O), 4.48 (d, 2H, -CH-OH), 3.40 (broad, s, 2H, OH). - Figure S1.C



**Figure S1.**  $^1\text{H-NMR}$  spectra of: A) diallyl succinate (DAS) monomer, in  $\text{CDCl}_3$  solvent; B) diallyl malate (DAM) monomer, in  $d_6\text{-DMSO}$  solvent; and C) diallyl tartrate (DAT) monomer, in  $d_6\text{-DMSO}$  solvent.

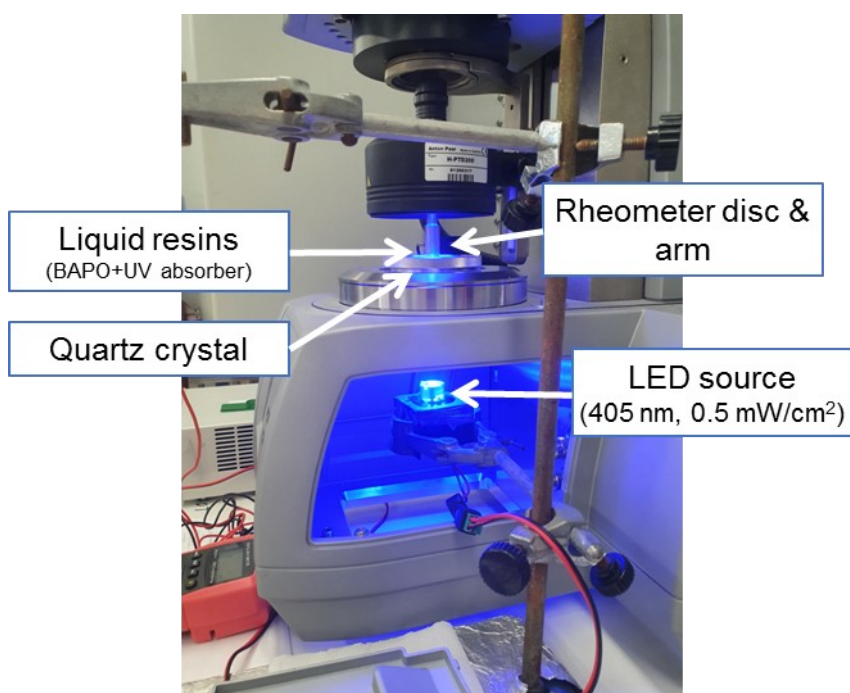
## 2.5. Techniques used for the characterization of the bio-based copolymers

The chemical structure of the raw materials and bio-based PEGDA copolymers were characterized by Fourier-Transform Infrared Spectroscopy (FTIR), by using a Jasco 4700 spectrophotometer, coupled with an attenuated total reflection accessory (Specac model MKII Golden Gate Heated Single Reflection Diamond ATR). The resolution used was 4 cm<sup>-1</sup>, the number of scans was 64 for each sample and the spectral range was from 600 to 4000 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) at temperatures from -60 °C to 200 °C was performed using a Perkin Elmer model Pyris I instrument equipped with a refrigerated cooling system operating under a nitrogen atmosphere (50 mL/min). Samples were heated from -60 to 200 °C, at a constant heating rate of 10 °C/min, working with 5 mg of samples placed in sealed aluminium pans. Second-order transitions ( $T_g$ ) were determined by the StepScan DSC technique that yields enhanced characterization information by separating out the reversible and irreversible thermal events. The glass transition temperature ( $T_g$ ) of each cured sample was determined by the second heating scan (20 °C/min). Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA2 equipment from 30 °C to 600 °C at a heating rate of 10 °C/min, under a nitrogen atmosphere, and by placing 10 mg of cured sample in the holder.

In order to monitor the photopolymerization reaction and to determine a proper irradiation time per layer in the 3D printer, an indirect method was used, the shrinkage of the pieces by rheology study. Shrinkage was determined as the reduction of the gap sample from the beginning ( $gap_0$ ) to the end ( $gap_E$ ) of the experiment, following Eq. S1:

$$Shrinkage (\%) = \left(1 - \frac{gap_E}{gap_0}\right) \times 100 \quad (\text{Eq. S1})$$

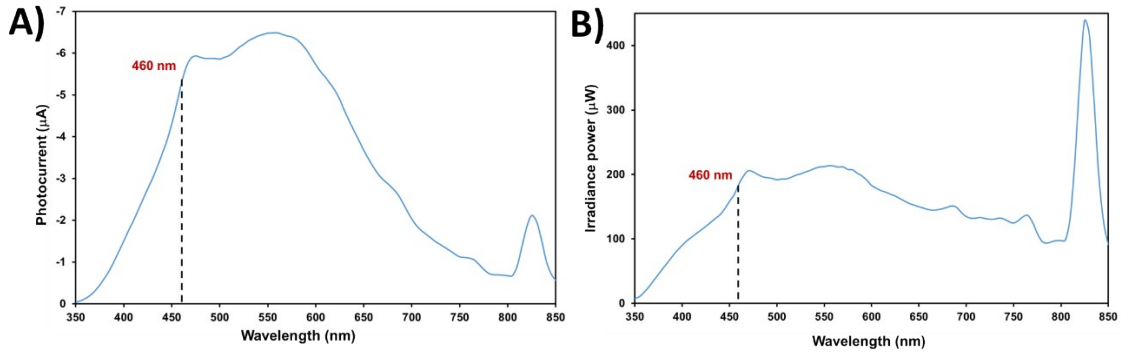
For this, the liquid composition of bio-based monomer:PEGDA, prepared as described in the main text, was placed between the quartz glass holder at the base and the aluminium plate at the top (Figure S2). The rheometer records the gap of the layer in real-time as it shrinks in the curing process, triggered by the activation of the LED lamp (405 nm, 0.5 mW/cm<sup>2</sup>), switched on 10 s after starting the experiment. This experiment helps to determine the time that will be needed to print 50 μm layers by DLP printer. The results were plotted as a reduction of the gap layer (in μm) versus time (in seconds), in the main text.



**Figure S2.** Assembly diagram for monitoring the photopolymerization with a rheometer.

The mechanical properties of the cured 3D-printed dumbbell format samples (Figure 6B, main text) were evaluated through stress-strain assays with a Shimadzu AGS-X (Kyoto, Japan) testing machine equipped with a 10 kN load cell at a crosshead speed of 5 mm/min. The test samples have dimensions of 50 mm in length, 35 mm in the narrow area and thicknesses of about 3 mm. They were printed according to the procedure described in the section 2.4 (main text) and were post-cured under 460 nm of visible light for 12 hours. The UV-visible irradiation spectra from 350 nm to 850 nm, in current and power intensity, are depicted in Figure S3. The power of the visible light was determined at 460 nm, being 35  $\mu\text{W}/\text{cm}^2$ . The deformation rate used in the stress-strain experiments was 10  $\text{mm}\cdot\text{min}^{-1}$ . All the mechanical parameters reported in this work were obtained by averaging the results obtained from at least 7 independent curves. The maximum tensile stress ( $\sigma_{\text{max}}$ ) is given by the equipment and deformation at break ( $\varepsilon_b$ ) is determined from the failure point. The elastic modulus  $E$  is calculated from the slope of the curve in the initial linear part of the curve (taken between 10 and 20 N of the device force). The average values of the elastic modulus, maximum tensile stress

and elongation at break of DAS:PEGDA polyester copolymer are discussed in the main text.



**Figure S3.** UV–vis irradiation spectra in the wavelength from 350 nm to 850 nm: A) photocurrent versus wavelength, and B) irradiance power versus wavelength.

Dynamic mechanical thermal analysis (DMA) was performed with a TA Instruments DMA Q800 analyzer. Prismatic rectangular samples were photocured in a Teflon mold ( $25 \times 5 \times 3 \text{ mm}^3$ ), with a glass sheet in the surface to avoid oxygen inhibition and were post-cured under visible light (460 nm) for 12 hours (6h per side). Three specimens were analyzed by a 3-point bending clamp at a heating rate of 3 K/min from -70 to 85 °C, the temperature at which rubbery state was observed, using a frequency of 1 Hz and oscillation of 0.1 % of sample strain. The elastic modulus ( $E$ ) in flexion mode was determined at 20 °C by means of a force ramp at a constant rate of 0.1 N/min, without exceeding 0.15% of deformation to make sure the material does not go in the plastic behavior. The slope between 0.05 and 0.10% was taken to calculate  $E$  using the following equation:

$$E = \frac{L^3 m}{4bt^3} \quad (\text{Eq. S2})$$

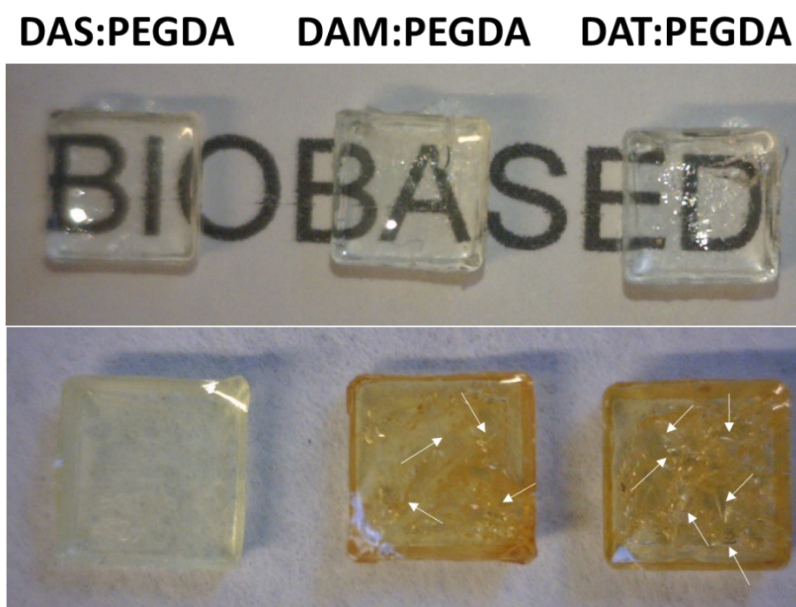
where  $E$  is the elastic modulus of the copolymer sample (MPa),  $L$  is the support span (mm),  $b$  and  $t$  are the width and the thickness of test samples (mm) and  $m$  is the gradient of the slope (N/mm).

### 3. Results and discussion

**Table S1.** Data from gel fraction study of post-cured samples DAS:PEGDA, DAM:PEGDA and DAT:PEGDA.

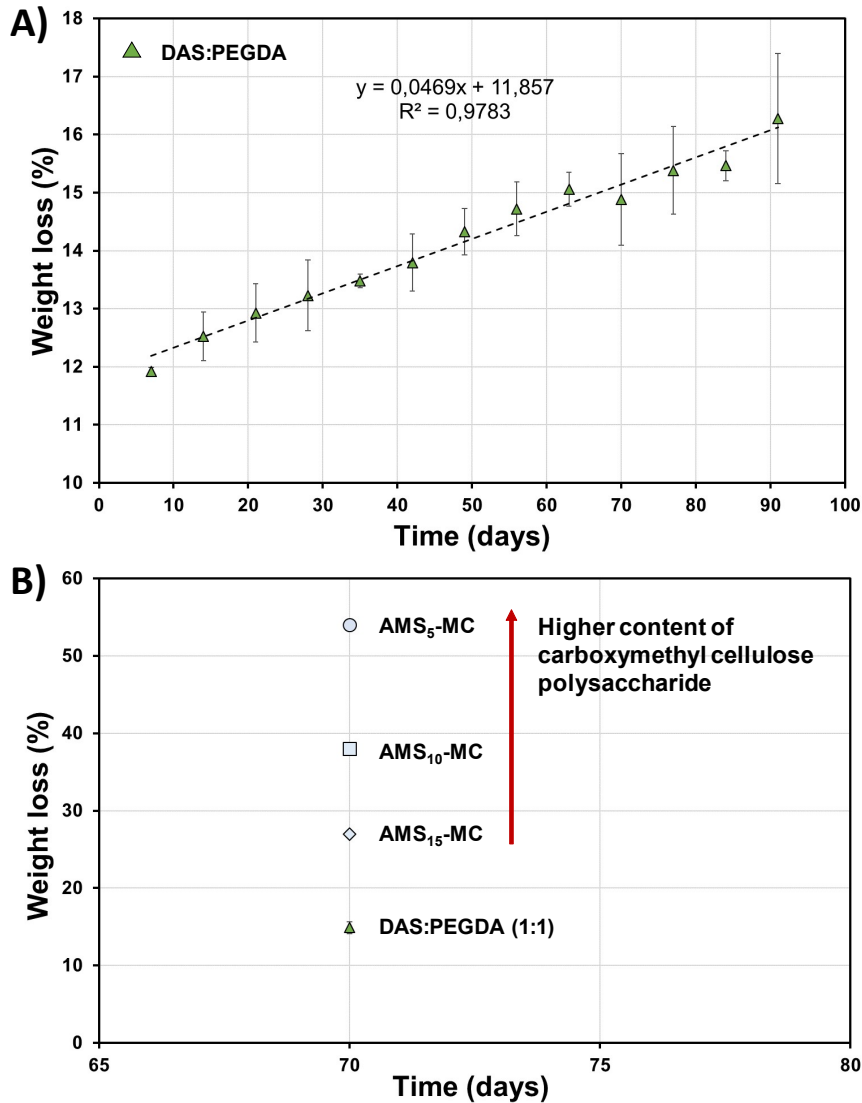
Composition	Specimen	Gel content	
		Swelling ratio <sup>a)</sup>	Percent extract (%) <sup>b)</sup>
DAS:PEGDA	1	1.0063	4.58
	2	1.0087	4.75
DAM:PEGDA	1	1.0428	6.32
	2	1.0038	6.39
DAT:PEGDA	1	1.1652	4.20
	2	1.1694	4.57

Notes: Tests performed in hot xylene, according to ASTM 2765-16: <sup>a)</sup> equation 1 and <sup>b)</sup> equation 2.



**Figure S4.** Photographs of the bio-based DAS:PEGDA, DAM:PEGDA and DAT:PEGDA copolymers, before and after thermal post-curing (170 °C, 12h). Arrows in the bottom image show some cracks the thermal process induced in DAM:PEGDA and DAT:PEGDA pieces after the thermal treatment, with the further appearance of yellowish colour, not observed in the light post-cured samples.





**Figure S5.** A) Weight loss versus time of DAS:PEGDA dual-cured 3D-printed pieces, in PBS buffer with *Rhizopus oryzae* lipase, at 37 °C. Symbols indicate the experimental data and the dashed curve is the linear regression. B) Comparison of the hydrolytic degradation of DAS:PEGDA, in lipase enzyme, with carboxymethyl cellulose-based bioactive hydrogels (AMS<sub>x</sub>-MC), in PBS/cellulase solutions at 37 °C. For AMS<sub>x</sub>-MC composition description, please, refer to Table 1 inside reference [4] from the main text. Both works use DLP additive manufacturing to prepare the samples.