Supporting Information

Glycerol-based Sustainably Sourced Resin for Volumetric Printing

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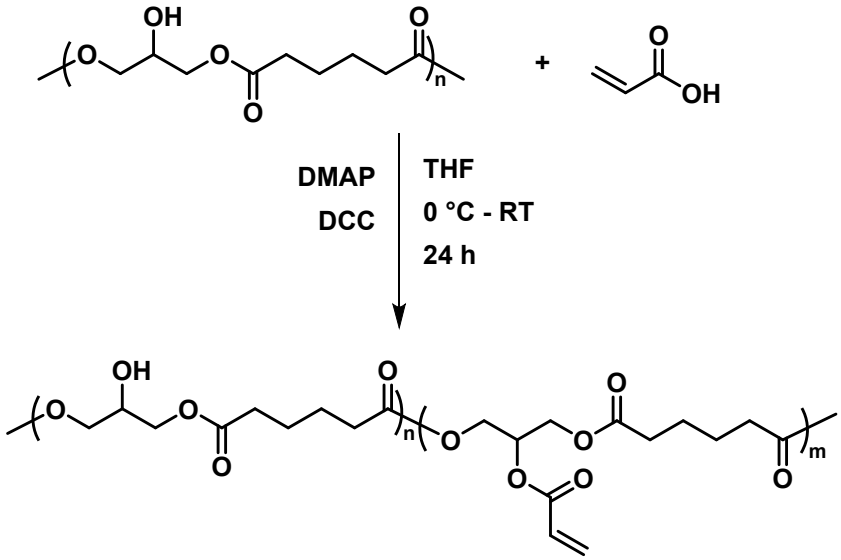
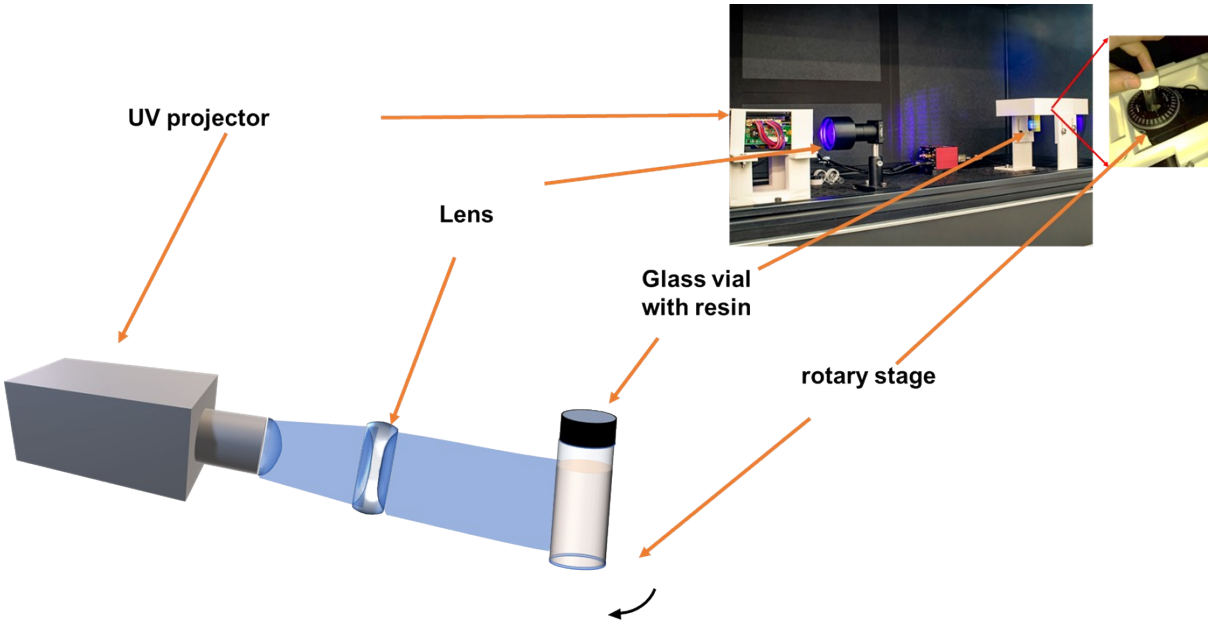
Schemes, Figures and Tables

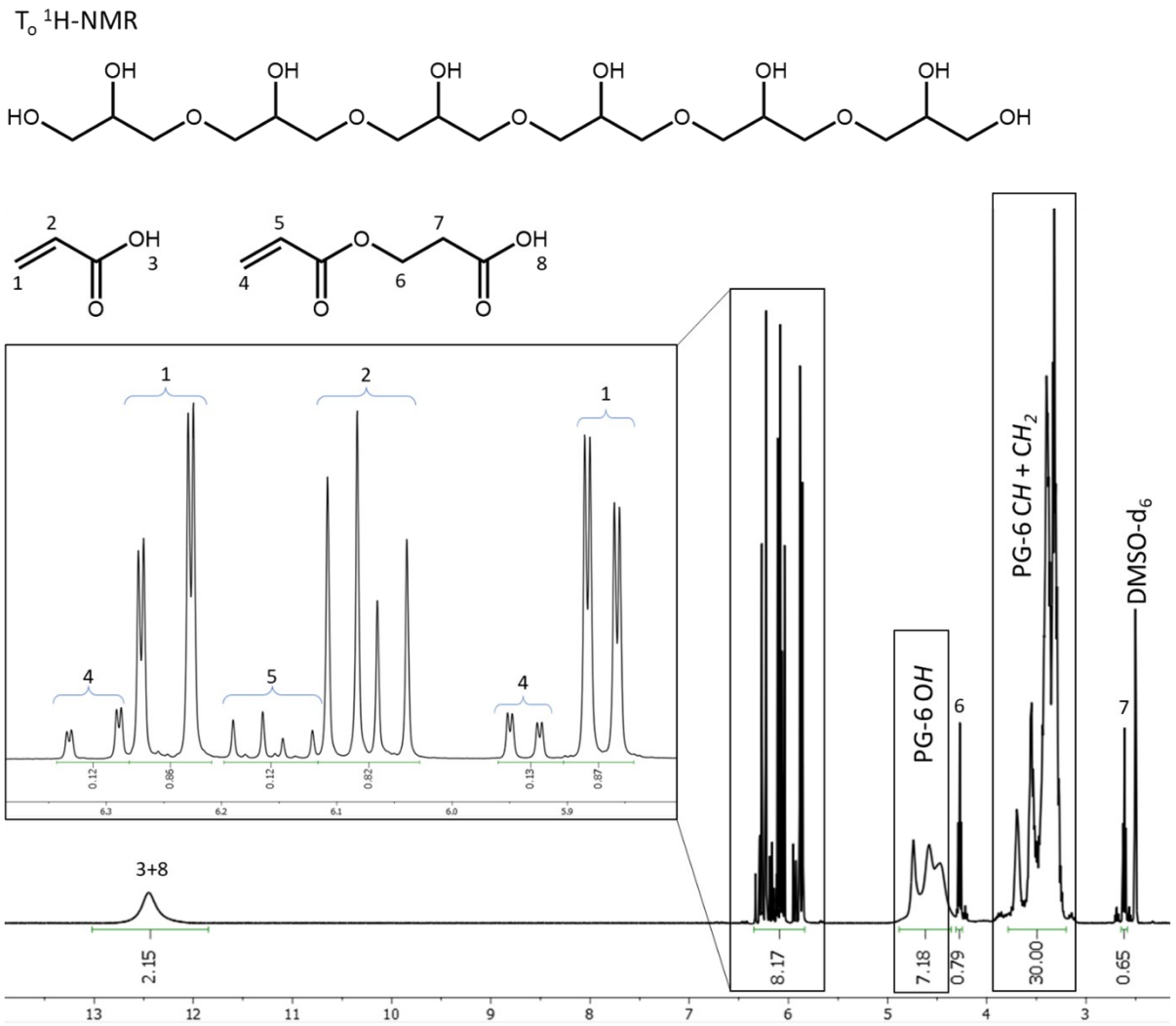


SI Scheme 1. *Synthesis of PGA-A via Steglich esterification.*

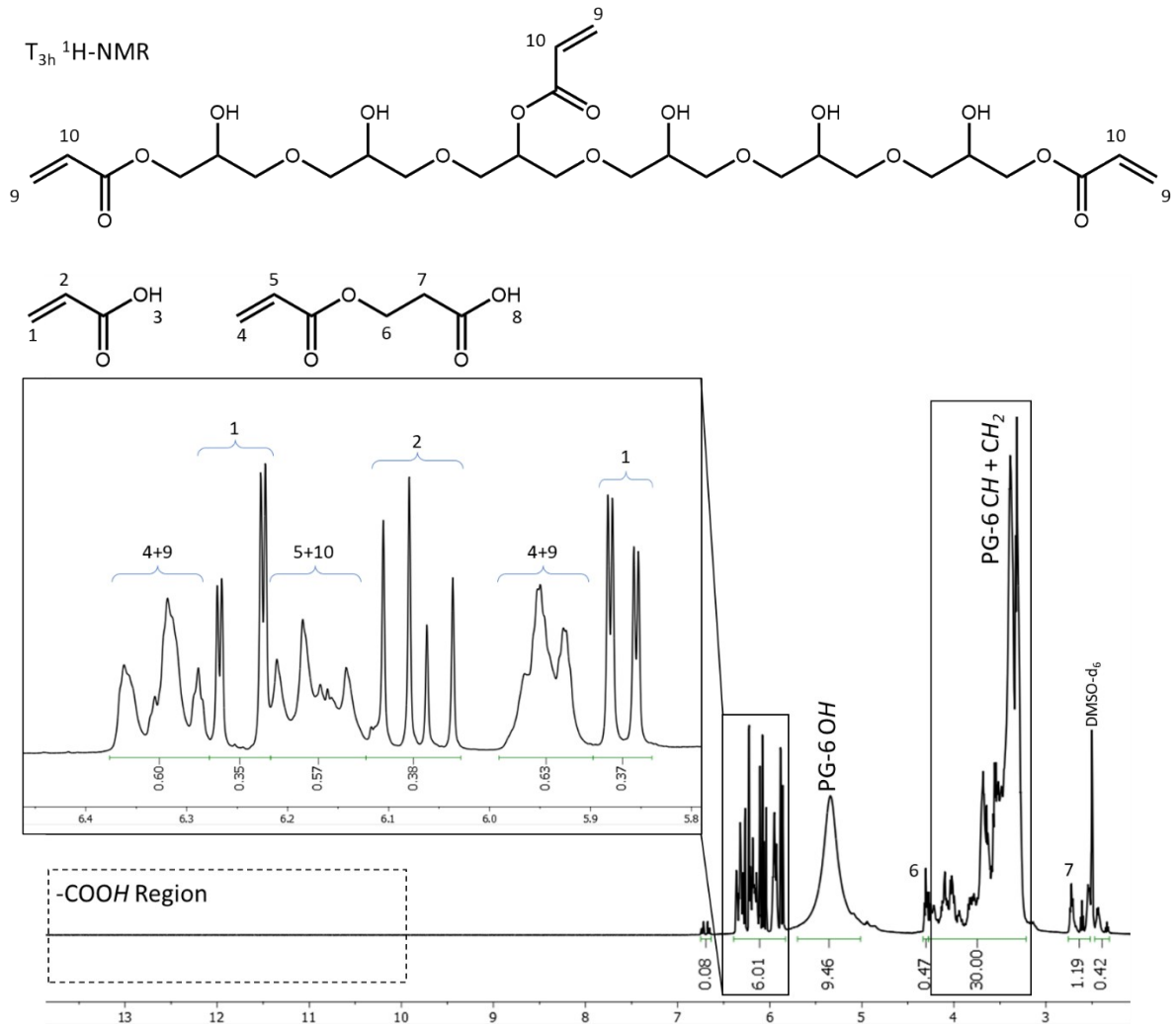


SI Figure 1 *Computed Axial Lithography (CAL) setup consisting of a projector, optics, and a rotary stage (based on hardware design files available from https://github.com/computed-axial-lithography).*

SI Figure 2. *Vial containing PG6-acrylate resin.*



SI Figure 3. *^{1}H-NMR at Time Zero of resin synthesis. Note the presence of a -COOH signal around 12.5 ppm, and the presence of Michael addition product in the acrylic acid starting material.*



SI Figure 4. *^{1}H-NMR at Time=3 h of resin synthesis. Inset showing the acrylate region of the spectrum. New signals corresponding to acrylate esters have formed. Conversion of acrylic acid is calculated to be approximately 63%, using the integrals of signals assigned 4+9 and 1. Some error in this estimation is a result of signal overlap between acrylic esters with the Michael addition product.*

SI Table 1 *Acid Values of the reaction mixture with correction applied to account for the presence of catalytic sulphuric acid (AV of batch used= 1112 mg KOH g^{-1}). Conversion was calculated following SI Equation 1.*

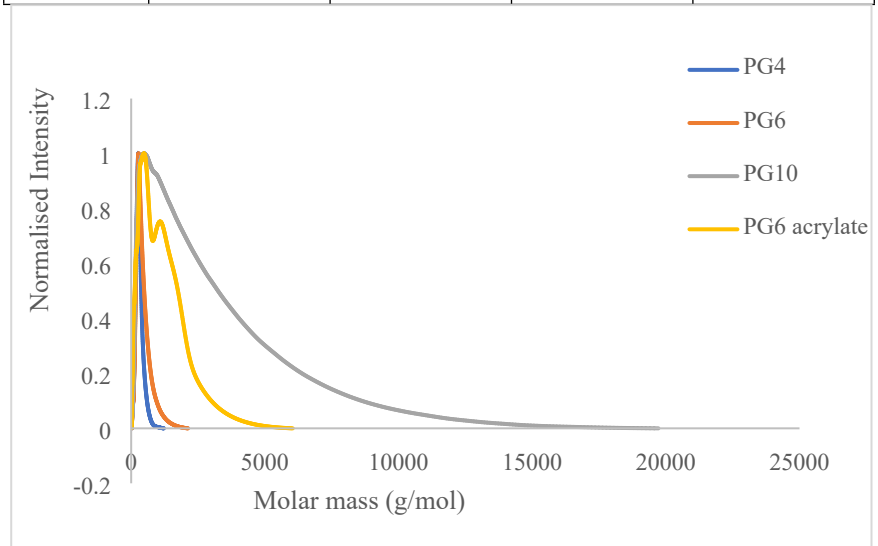
Time (h)	AV (mg KOH g^{-1} sample)	Conversion of Acrylic Acid (%)
0	220.4	0
3	55.0	75

$$Conversion\ (\%) = 100 \times (1 - \frac{AV\ Time\ zero}{AV\ Time\ X})$$

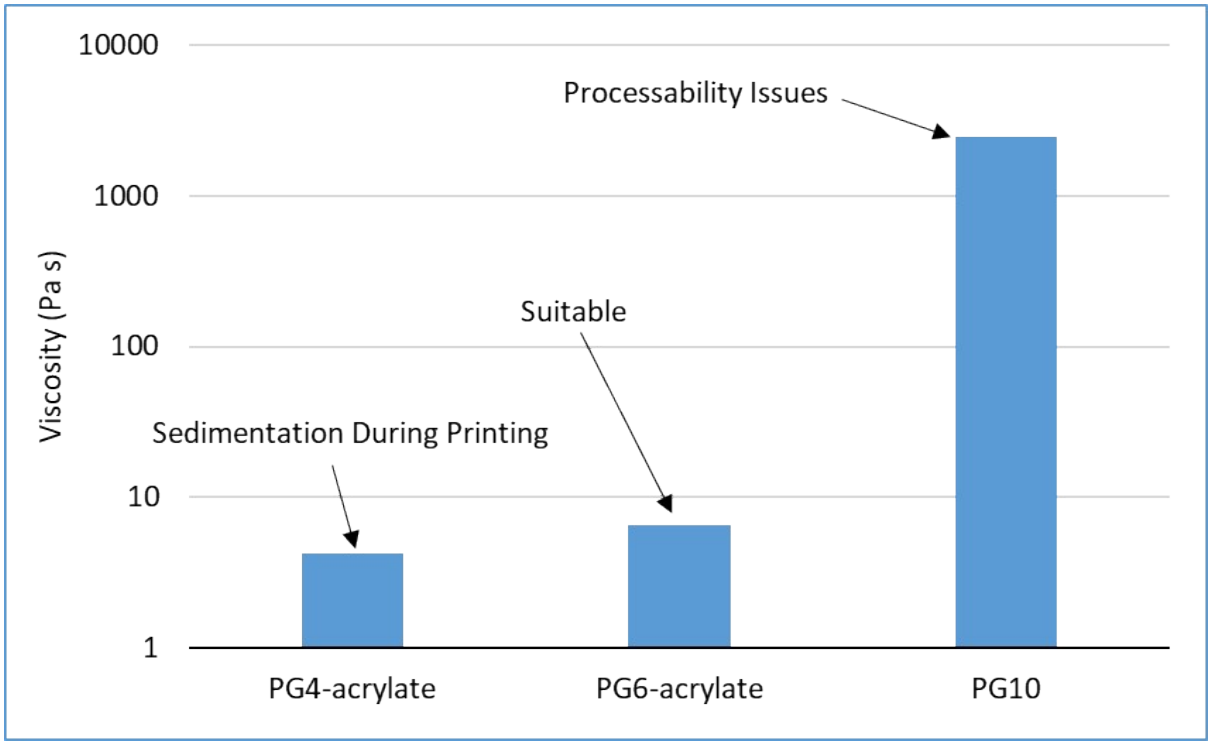
SI Equation 1 *Conversion of acrylic acid (%) from acid value obtained at time zero and at measured timepoint during PG6-acrylate synthesis.*

SI Table SEC

	PG4	PG6	PG10	PG6 acrylate
M_n	250.0	330.0	1230.5	609.0
M_w	315.0	467.0	3270.0	1233.0
Đ	1.25	1.41	2.65	2.03



SI Table and Figure SEC – Molar masses (g/mol) and Đ for PG4, PG6, PG10, and PG6 acrylate. Measured via aqueous SEC.



SI Figure 5. *Viscosity of PG4-acrylate, PG6-acrylate, and PG10 at 25 °C, shear rate of 10 s^{-1}. Due to low viscosity, rapid sedimentation of the cured resin was observed with PG4-acrylate. PG10's viscosity made the resin synthesis impractical. PG6-acrylate's viscosity was found to be in the desired region.*

SI Table 2. *Volumetric Printing Optimisation of virgin Resin. Print result was assessed visually based on physical appearance of the print on a scale from 1 to 10, where 1 denotes a poor print and 10 an excellent print. Parts marked with an asterisk (*) were produced using two consecutive printing cycles.*

Part	Vial size (mL)	Exposure per frame (s)	Frames	Total Exposure Time (s)	Rotation per Frame (°)	Result
cylindrical structures	4	0.1	120	12	3	1
cylindrical structures	4	0.1	40	4	9	2
cylindrical structures	4	0.1	60	6	6	10
Chess piece	4	0.1	60	6	6	10
Ball in cage	20	0.1	60	6	6	1
Ball in cage	20	0.12	60	7.2	6	2
Ball in cage	20	0.12	120	14.4	3	3
Ball in cage	20	0.12	210	25.2	3	4
Ball in cage	20	0.12	160	19.2	3	6
Ball in cage	20	0.12	150	18	3	9
Rectangle	20	0.1	60	6	3	10
Thinker*	20	0.11 + 0.11	120 + 120	26.4	3	9
Rabbit*	20	0.12 + 0.15	120 + 30	18.9	3	9
Tensile bar	20	0.12	60	7.2	6	6
Tensile bar	20	0.12	120	14.4	3	9

SI Table 3. *Volumetric Printing Optimisation of Recycled Resin. Print result was assessed visually based on physical appearance of the print on a scale from 1 to 10, where 1 denotes a poor print and 10 an excellent print.*

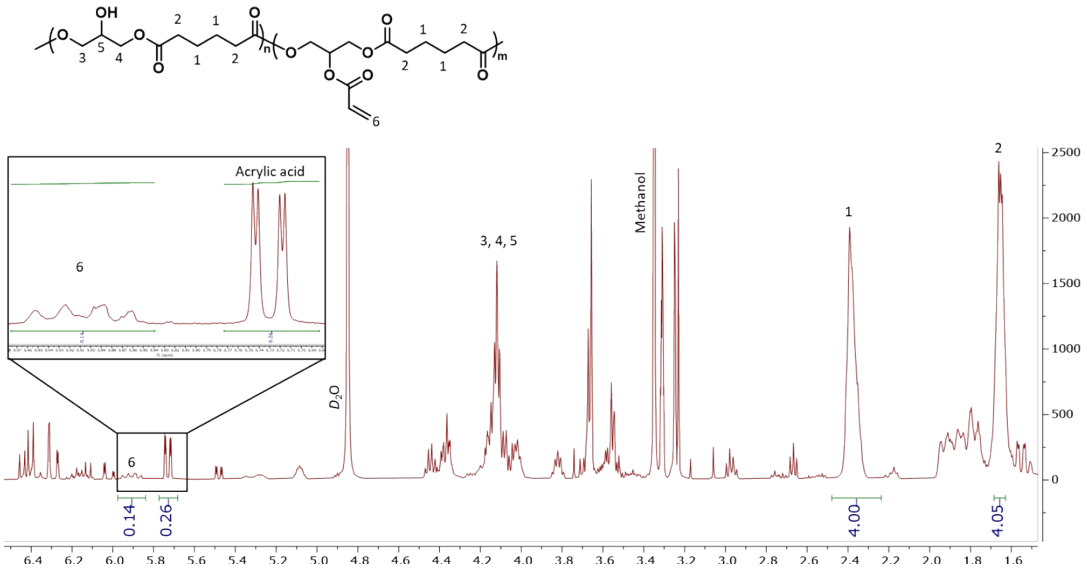
Part	Vial size (mL)	Exposure per frame (s)	Frames	Total Exposure Time (s)	Rotation per Frame (°)	Result
cylindrical structures	20	0.12	120	14.4	3	10
cylindrical structures	20	0.12	140	16.8	3	7
cylindrical structures	20	0.12	120	12	3	10

SI Table 4. *Volumetric Printing Optimisation of PGA-AA Doped Resin. Print result was assessed visually based on physical appearance of the print on a scale from 1 to 10, where 1 denotes a poor print and 10 an excellent print.*

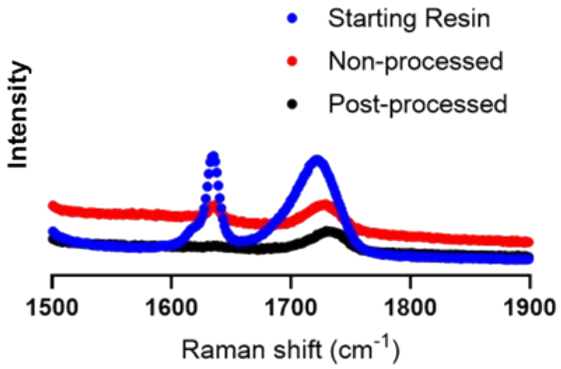
Part	PGA Content (wt.%)	Vial size (mL)	Exposure per frame (s)	Frames	Total Exposure Time (sec)	Rotation per Frame (°)	Result
cylindrical structures	5	20	0.1	120	12	3	8
cylindrical structures	10	20	0.125	120	15	3	7
cylindrical structures	20	20	0.1	100	10	3	10

SI Table 5. *Volumetric Printing Optimisation of 10,12-Pentacosadyinoic Acid (PCDA) Doped Resin. Print result was assessed visually based on physical appearance of the print on a scale from 1 to 10, where 1 denotes a poor print and 10 an excellent print.*

Part	PCDA Content (wt.%)	Vial size (mL)	Exposure per frame (s)	Frames	Total Exposure Time (s)	Rotation per Frame (°)	Result
cylindrical structures	10	4	0.12	60	7.2	6	5
cylindrical structures	10	4	0.12	80	9.6	3	5
cylindrical structures	10	4	0.12	40	4.8	6	8
cylindrical structures	20	4	0.12	40	4.8	6	8
cylindrical structures	30	4	0.12	40	4.8	6	3



SI Figure 6. *^{1}H-NMR spectrum of PGA-A in D_2O demonstrating ~14% functionalisation of pendant OH bonds along polymer backbone of PGA.*



$$DC = \left[1 - \frac{(A_{c=c}/A_{C=O})\text{monomer}}{(A_{c=c}/A_{C=O})\text{polymer}}\right] \times 100$$

Sample	DC (%)
Non-processed	58±4.0
Post-processed	99±0.4

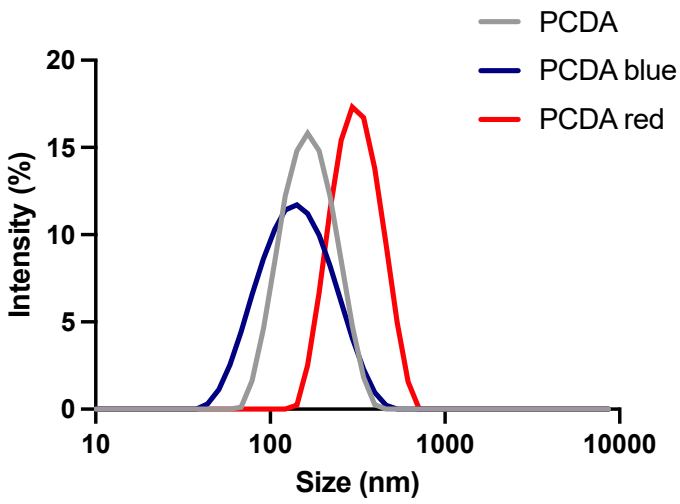
SI Figure 7. *Raman Spectroscopy to assess degree of curing (DC). Left, Stacked Raman spectra of an example of starting resin, printed resin (non-processed) and resin post curing (post-processed) in the Raman shift range between 1500-1900 cm^{-1}. Right, DC was determined by measuring the change in the ratio of peak areas associated with the C=C (≈1634 cm^{-1}) and C=O (≈1720 cm^{-1}) bonds before and after polymerisation.*

SI Table 6. *Storage modulus of printed cylindrical samples with increasing PGA-A loading.*

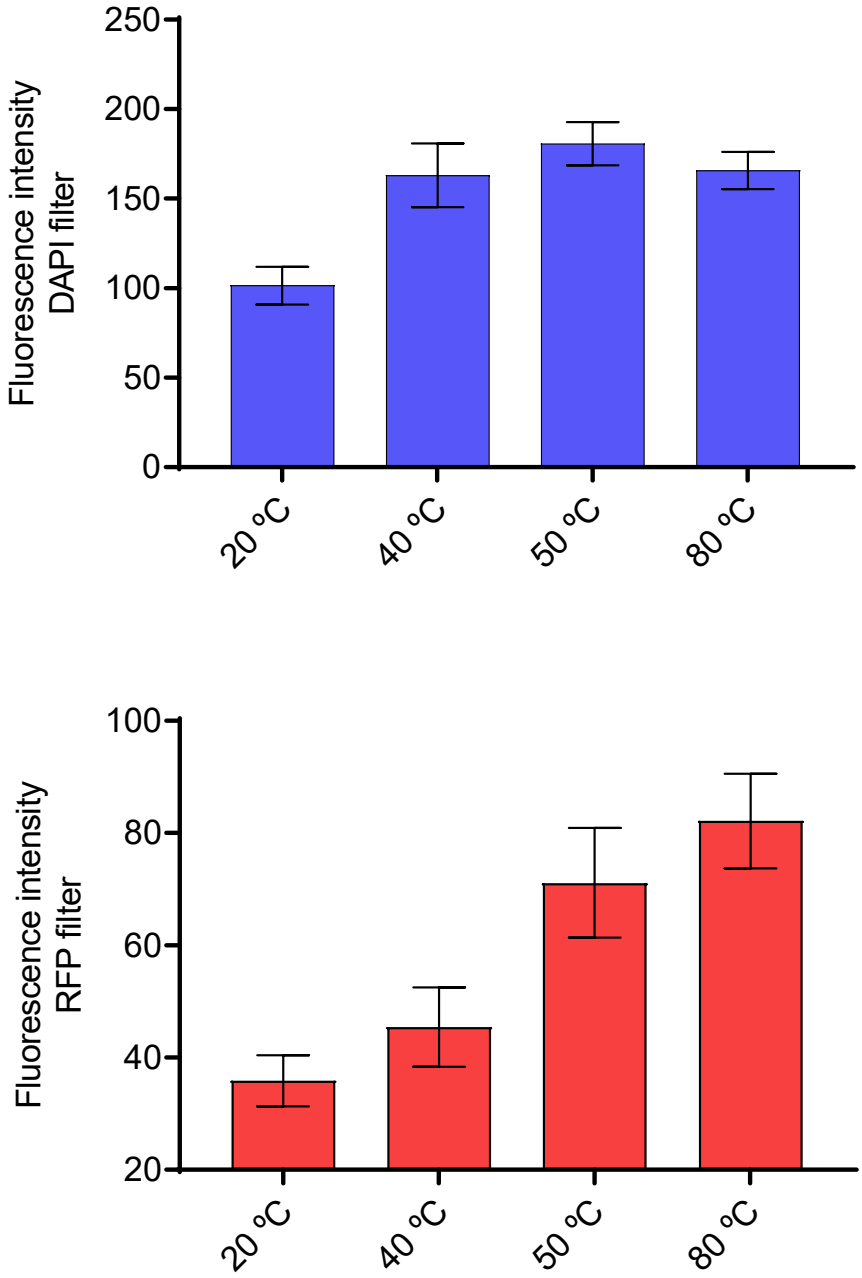
PGA-A Loading (wt%)	Storage Modulus (kPa)
0	2221
5	450
20	522

SI Table 7. *Size of PCDA nanosystems non-polymerised, polymerised (blue) and after thermal stimulus (red)*

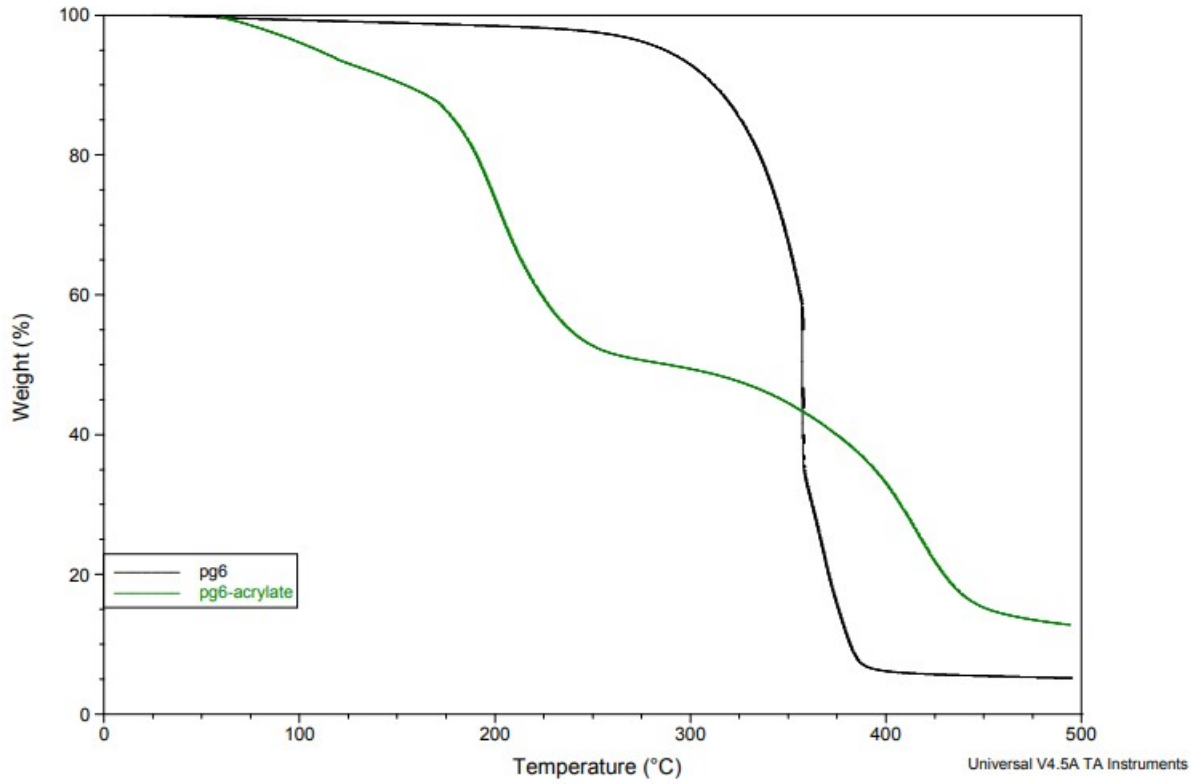
Sample	Hydrodynamic diameter (nm)	PDI
PCDA	152.1 ± 0.1	0.12 ± 0.10
PCDA blue	120.3 ± 0.5	0.21 ± 0.01
PCDA red	293.2 ± 0.8	0.10 ± 0.01



SI Figure 8. *DLS traces of PCDA nanosystems non-polymerised (grey), polymerised (blue) and after thermal stimulus (red).*



SI Figure 9. *Fluorescence Intensities during microscopy, blue (top) and red (bottom) of the samples seen in Figure 4 of the main text. Data presented as mean ± S.D; n=3.*



SI Figure TGA. TGA of PG6 and PG6 acrylate