Supplementary Information (SI) for Faraday Discussions.
This journal is © The Royal Society of Chemistry 2025

Supporting Information

Polyglycerol Resin Towards Sustainable 3D-Printing

Polyglycerol Resin Towards Sustainable 3D-Printing

Katherine George,[¥a] Eduards Krumins,[¥a] Eileen Tan,[b] Yinfeng He,[a,c] Ricky Wildman,[a] Robert Owen,[b] Joel Segal, [d*] Valentina Cuzzucoli Crucitti,[e*] Vincenzo Taresco[f*]

[a] Centre for Additive Manufacturing and Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, United Kingdom

[b] School of Pharmacy, University of Nottingham Biodiscovery Institute, University of Nottingham, Nottingham, NG7 2RD UK

[c] Nottingham Ningbo China Beacons of Excellence Research and Innovation Institute, University of Nottingham Ningbo China, Ningbo 315100, China

[d] Advanced Manufacturing Technology Research Group, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK, UK

[e] Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

[f] School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, United Kingdom

¥ authors contributed equally

*corresponding authors emails: joel.segal@nottingham.ac.uk; valentina.cuzzucolicrucitti1@nottingham.ac.uk; vincenzo.taresco@nottingham.ac.uk

Materials:

Polyglycerols 4 and 6 (PG4, PG6 and PG10) used in this study were generously donated by Spiga Nord (https://www.spiganord.com/) and are fully biobased. Acrylic acid, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (IRG819), methacrylic Acid, 4-methoxyphenol, and sulfuric Acid were purchased from Sigma Aldrich UK. Carbic anhydride was purchased from Acros Organics. Maleic anhydride, phosphoric acid, cyrene and trimethylolpropane tris(3-mercaptopropionate) were purchased from Sigma Aldrich UK. Formlabs BioMed Amber was purchased Additive-X, UK, and ELEGOO 8K Standard Space Grey was purchased from Amazon, UK. Chemicals used as received. Minimum Essential Medium Eagle, foetal bovine serum (FBS) were purchased from Merck UK, L929 fibroblasts were purchased from ECACC, UK. LIVE/DEAD Viability/Cytotoxicity Kit was purchased from ThermoFisher, UK.

Methods:

Resins characterisations: ^{1}H-NMR analysis of the resins was performed on a Bruker DPX 400 MHz spectrometer assigning chemical shift in parts per million (ppm). Spectra were analysed using MestreNova 15.0.0 (MestreLab Research S.L.). Samples were analysed in deuterated DMSO (SI). Thermogravimetric analysis (TGA) was carried out using a TGA Q500

thermogravimetric analyser (TA Instruments). Analyses were performed from 40 to 800 °C, at a heating rate of 10 °C min^{-1} under a flow of air. Dynamic mechanical analysis (DMA) was used to determine the T_g of the 3D printed polymeric networks. Measurements were performed on a Triton Technologies DMA using the powder pocket accessory. The sample (40 mg ± 5 mg) was weighed into a powder pocket. Samples were measured at 1 Hz in single cantilever bending geometry between −50–100 °C depending on the region of interest. The value of the T_g was taken as the peak of the tan delta (tan δ) curve. Rheological measurements were carried out using an Anton Paar MCR102X Rheometer, equipped with a 25 mm parallel plate diameter. Measurements were carried out with a 1 mm gap at 25 °C. Microscope images were taken using the Nikon Eclipse LV100ND at a magnification of 20x with horizontal and vertical image stitching.

Synthesis of PG4 – A:

Acrylic acid was added to PG4 (3 : 1 ratio of acrylic acid to polyglycerol 4) and the mixture allowed to stir. The acrylic acid to PG4 ratio was the molar amount based on the glycerol units in the chain. 4-Methoxyphenol (1 wt%) was added (to prevent unwanted crosslinking of acrylic acid during the esterification process acting as an inhibitor) and dissolved, before subsequent addition of sulphuric acid (2.5 wt%). Finally, the reaction mixture was heated to 60 °C and stirred at 200 rpm for 3 h (scheme 1). Analogous reactions were performed with polyglycerol 6. The produced acrylated PGs were used for printing purposes without any purification steps

Synthesis of PG4 – MA:

Methacrylic acid was added to PG4 (3 : 1 ratio of acrylic acid to polyglycerol 4) and the mixture allowed to stir. The acrylic acid to PG4 ratio was the molar amount based on the glycerol units in the chain. 4-Methoxyphenol (1 wt%) was added (to prevent unwanted crosslinking of acrylic acid during the esterification process acting as an inhibitor) and dissolved, before subsequent addition of sulphuric acid (2.5 wt%). Finally, the reaction mixture was heated to 60 °C and stirred at 200 rpm for 3 h (scheme 1). Analogous reactions were performed with polyglycerol 6. The produced acrylated PGs were used for printing purposes without any purification steps

Synthesis of PG4 – Maleate

Maleic anhydride was added to PG4 (3 : 1 ratio of acrylic acid to polyglycerol 4) and the mixture allowed to stir. The maleic anhydride to PG4 ratio was the molar amount based on the glycerol units in the chain. Phosphoric acid (1 mol %) was added along with cyrene (10 wt % of PG4). Samples were prepared with and without phosphoric acid. Finally, the reaction mixture was heated to 80 °C and stirred at 100 rpm for 24 h (scheme 1, main text). Analogous reactions were performed with polyglycerol 6 and polyglycerol 10.

Synthesis of PG6 – Maleate

Maleic anhydride was added to PG6 (3 : 1 ratio of acrylic acid to polyglycerol 6) and the mixture allowed to stir. The maleic anhydride to PG6 ratio was the molar amount based on the glycerol units in the chain. Phosphoric acid (1 mol %) was added along with cyrene (10 wt % of PG6). Finally, the reaction mixture was heated to 80 °C and stirred at 100 rpm for 24 h (scheme 1, main text). Analogous reactions were performed with polyglycerol 10.

Synthesis of PG4 Norbornene

Carbic anhydride was added to PG4 (3 : 1 ratio of acrylic acid to polyglycerol 4) and the mixture allowed to stir. The maleic anhydride to PG4 ratio was the molar amount based on the glycerol units in the chain. Phosphoric acid (1 mol %) was added along with cyrene (10 wt % of PG4). Samples were prepared with and without phosphoric acid. Finally, the reaction mixture was heated to 80 °C and stirred at 100 rpm for 24 h (scheme 1, main text).

Synthesis of PG6 Norbornene

Carbic anhydride was added to PG6 (3 : 1 ratio of acrylic acid to polyglycerol 6) and the mixture allowed to stir. The maleic anhydride to PG6 ratio was the molar amount based on the glycerol units in the chain. Phosphoric acid (1 mol %) was added along with cyrene (10 wt % of PG6). Samples were prepared with and without phosphoric acid. Finally, the reaction mixture was heated to 80 °C and stirred at 100 rpm for 24 h (scheme 1, main text). Analogous reactions were performed with polyglycerol 10.

Preparation of PG4 and PG6 (meth)acrylates resins:

Preparation of PG4 – Acrylate and PG4 (meth)acrylate Blend resin:

TPO as the photoinitiator (PI) (1 wt %, 0.6 g) was added to PG4 – Acrylate (30 g) and PG4 – MA (30 g), the resin was mixed using a hotplate at 40 °C until the PI was dissolved and a fully homogenous mixture produced.

The methodology stated above was repeated for the remaining samples, PG6 – (meth)acrylates.

SLA printing of PG4-6 (methacrylate) resins:

All printing were performed on two different SLA:

- ELEGOO Mars 4 Ultra MSLA 3D Printer, Desktop Resin 3D Printer with 7 Inch 9K LCD, Wi-Fi Connectivity, Effortless Leveling System, ACF Release Liner Film, Printing Size of 153.36x77.76x165 mm^3

- ELEGOO Mars 5 Ultra 9K Resin 3D Printer, 150mm/h High Speed Printing, Smart Automatic Leveling, Intelligent Detection, WiFi-Transfer, Printing Size of 153.36 x 77.76 x 165 mm^3

Printing scaffolds:

The simple geometry CAD files were designed and converted to STL-type files using Fusion360 CAD software. The boat was downloaded from Thingiverse (https://www.thingiverse.com/thing:763622/files) designed by CreativeTools − Attribution license. The validation matrix was downloaded from Thingiverse (https://www.thingiverse.com/thing:4707289) designed by X3msnake - Attribution license. The rook was programmed on Elegoo Mars 4 Ultra USB when printed obtained.

Slicing the STL file for SLA printing:

To allow printing the 3D CAD models were sliced into individual 2D images for projecting onto the photocurable liquid. For the Elegoo Mars 4 Ultra 3D printer, the slicer software employed

was ChituBox enabling us to change the initial exposure time, exposure time, print orientation, support structures and layer heights.

PG4 – Acrylate resin (PG4 – A):

The curability and printability test using written in the paper was conducted to determine the optimal layer exposure settings. These were printed at 8s (normal layer), 12s (base layer). The samples were then washed in isopropyl alcohol (IPA) under sonication until any excess resin was removed.

PG4 – Methacrylate resin (PG4 – MA):

The same process described above was conducted to determine the optimal layer exposure settings. Once a homogeneous resin was achieved and the optimal conditions were established, simple and complex scaffolds were printed within the same print session. The normal layers were cured with an exposure time of 8s, while the base layer was cured for 10s.

PG6 – Acrylate resin (PG6 – A):

The same process described above was conducted to determine the optimal layer exposure settings. Once a homogeneous resin was achieved and the optimal conditions were established simple and complex scaffolds were printed within the same print session. The normal layers were cured with an exposure time of 8s, while the base layer was cured for 10s.

PG6 – Methacrylate resin (PG6 – MA):

The same process described above was conducted to determine the optimal layer exposure settings. Once a homogeneous resin was achieved and the optimal conditions were established, simple and complex scaffolds were printed within the same print session. The normal layers were cured with an exposure time of 10s, while the base layer was cured for 12s.

PG4 – Acrylate and PG4 – Methacrylate resin blend (PG4 – A + PG4 – MA):

The same process described above was conducted to determine the optimal layer exposure settings. Once a homogeneous resin was achieved and the optimal conditions were established, simple and complex scaffolds were printed within the same print session. The normal layers were cured with an exposure time of 8s, while the base layer was cured for 10s.

Biocompatibility testing

IRG819 as the photoinitiator (PI) (1 wt %) was added to all PG materials and stirred overnight at 30 °C in a water bath to ensure complete dissolution and homogeneity. Test coupons were designed in Autodesk Fusion 360 (Autodesk Inc., USA) and sliced using CHITUBOX Basic v2.3.1 (CBD-Tech) for SLA printing on the ELEGOO Mars 5 Ultra SLA 3D printer. Print parameters for the PG-based resins, BioMed Amber and Space Grey are given below in table 1.

Table 1. *Optimised print settings for each resin formulation.*

Material	Bottom Layer Count	Normal Exposure Time (s)	Bottom Exposure Time (s)	Rest Time After Lifting (s)
ELEGOO Space Grey	10	3	37	7.5
Formlabs BioMed Amber	10	3	25	7.5
PG4-MA	2	8	10	15
PG4-A	2	12	14	60
PG6-MA	2	8	10	40
PG6-A	2	20	22	40

After printing, models were detached from the build plate using a razor blade and transferred into 50 mL Falcon tubes containing isopropanol for washing. PG-based prints were washed for 30 minutes, air-dried for 30 minutes, and post-cured under 365–405 nm UV light for 30 minutes using a CureBox (Wicked Engineering, USA). ELEGOO prints were washed and post-cured for 5 minutes each. BioMed Amber prints were washed for 20 minutes, air-dried, and post-cured at 70 °C for 30 minutes, as per manufacturer guidelines. All post-processing was conducted under ambient laboratory conditions (21 °C).

Extract biocompatibility testing was performed in accordance with ISO 10993-5. Post-processed samples were disinfected by immersion in 70% ethanol for 2 minutes, followed by two rinses with sterile phosphate-buffered saline (PBS). Samples were then air-dried in a Class II microbiological safety cabinet and further sterilised using 254 nm ultraviolet light for 20 minutes in a UVClave unit. At this stage, alkali washed samples were immersed in sterile-filtered 1M sodium bicarbonate for 40 (PG4 – A, PG6 – A/MA) or 55 minutes (PG4 – MA), then rinsed in PBS before proceeding to extraction.

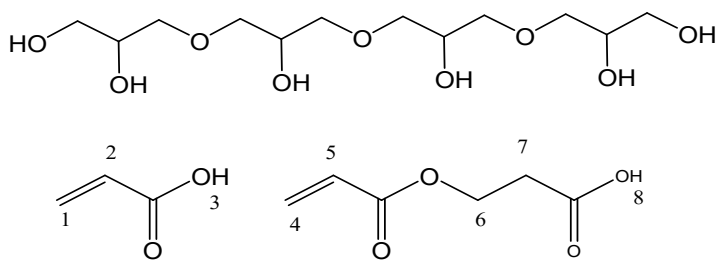
To extract, samples were incubated in Minimum Essential Medium Eagle (MEM) supplemented with 10% (v/v) foetal bovine serum (FBS) at 37 °C for 24 hours, using a mass-to-volume ratio of 0.1 g/mL to generate extract media containing any leachable substances. L929 fibroblasts were seeded in 96-well plates at 20,000 cells/cm² in 100 µL basal culture media (BM) and allowed to adhere for 24 hours. The medium was then replaced with either extract media or control BM (prepared identically but without specimens). Dead controls were killed with 100% isopropanol for 5 minutes prior to assaying. A LIVE/DEAD™ Viability/Cytotoxicity Kit was used to assess cell viability, with cells imaged using an EVOS

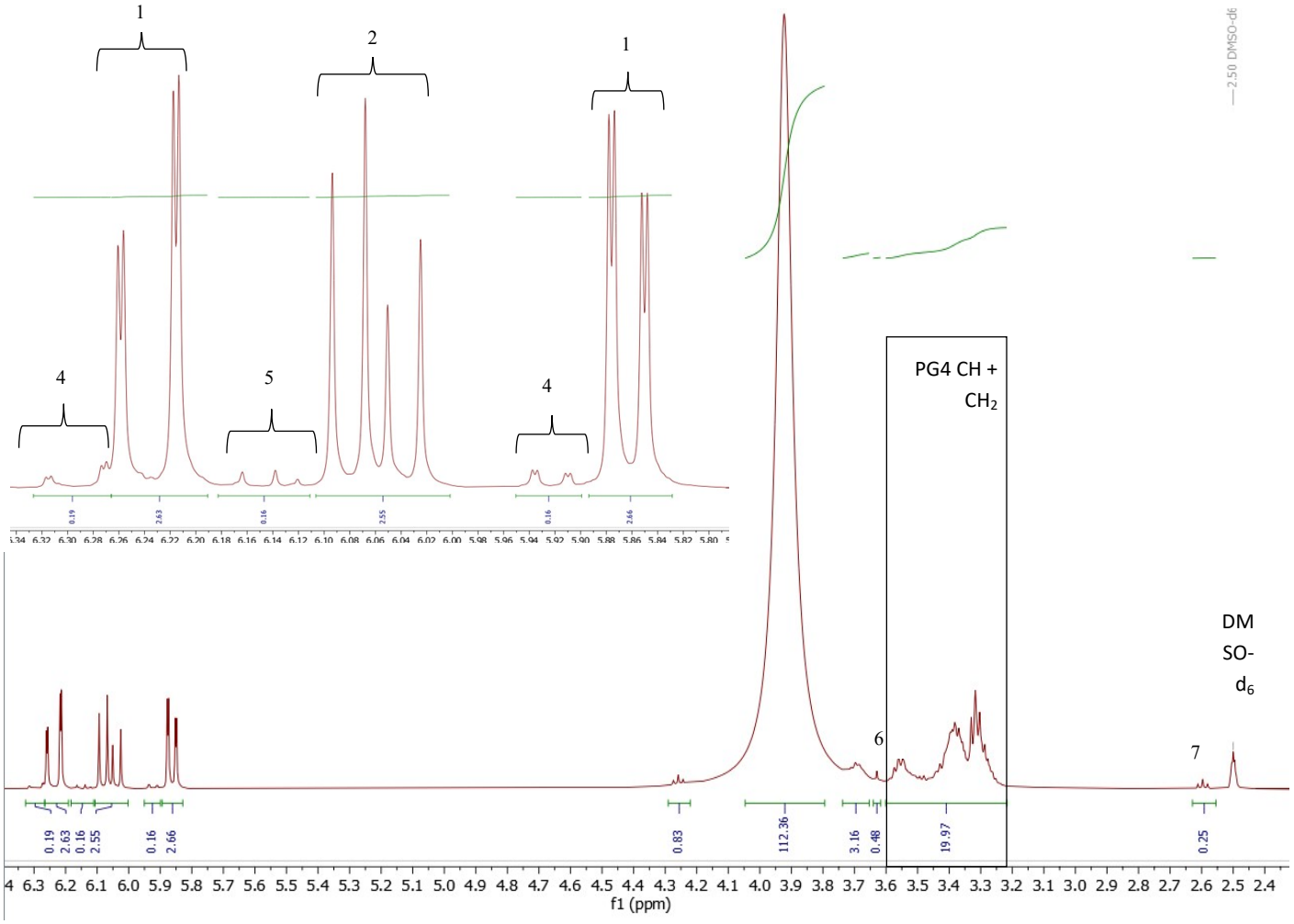
M7000 (Thermo Fisher, UK) and analysed using CellProfiler. All experiments were repeated three times in triplicate.

Preparation of PG4 and 6 malate and Norbornene resin:

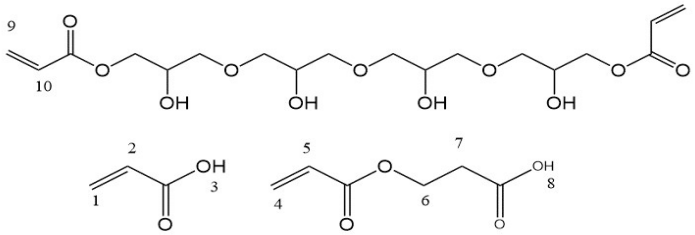
Photocurable resins were formulated by blending PGX malate and Norbornene resin with cyrene (10 wt% of PG) and Trimethylolpropane tris(3-mercaptopropionate) as the thiol cross-linker. The ratio of the thiol cross-linker was adjusted based on the molar ratio of double bonds (DB) to thiol groups (SH) at 1:1, 1:2, and 1:3. TPO was used as the photoinitiator (PI) at 5 wt %. PG4 and PG6 contain three reactive DB groups, while Trimethylolpropane tris(3-mercaptopropionate) has three reactive SH groups. PG10, on the other hand, has six reactive DB groups, requiring two thiol groups per acrylate for proper cross-linking. Once the homogeneous resin was produced, a drop was placed onto a microscope slide and cured under UV light in 10-second increments to determine the estimated cure time per layer (SI Table 2).

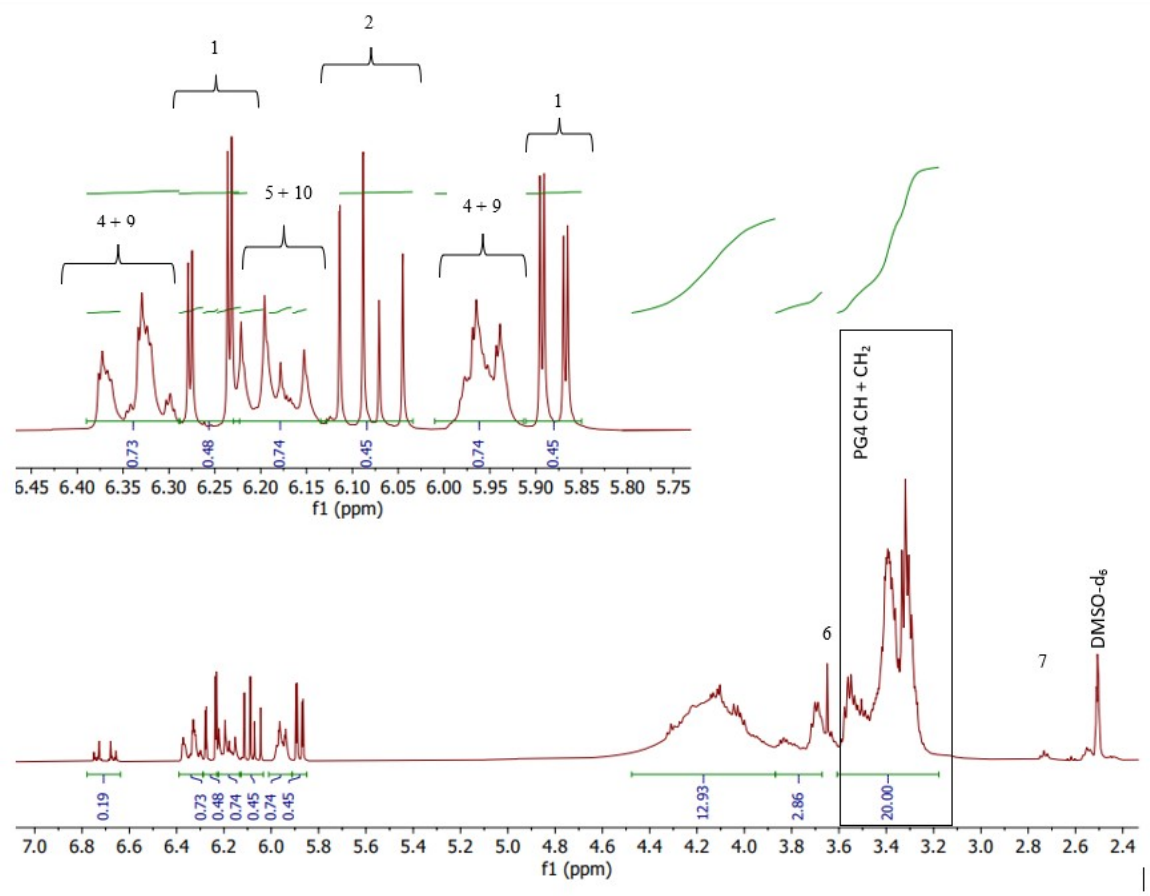
^{1}HNMR analysis



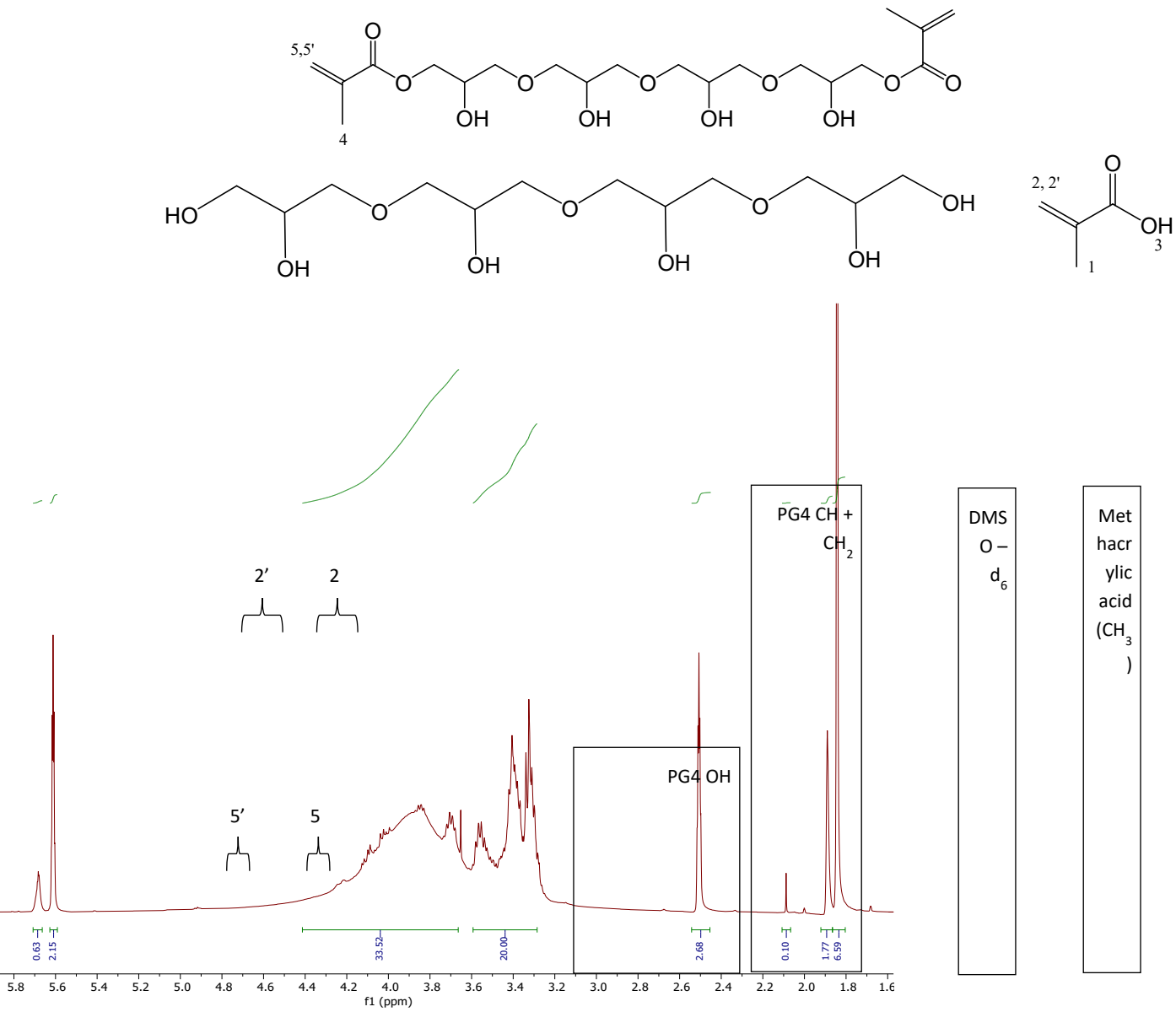


SI Figure 1: *^{1}H-NMR at Time Zero of resin synthesis for PG4 – Acrylate 3:1 molar ratio*



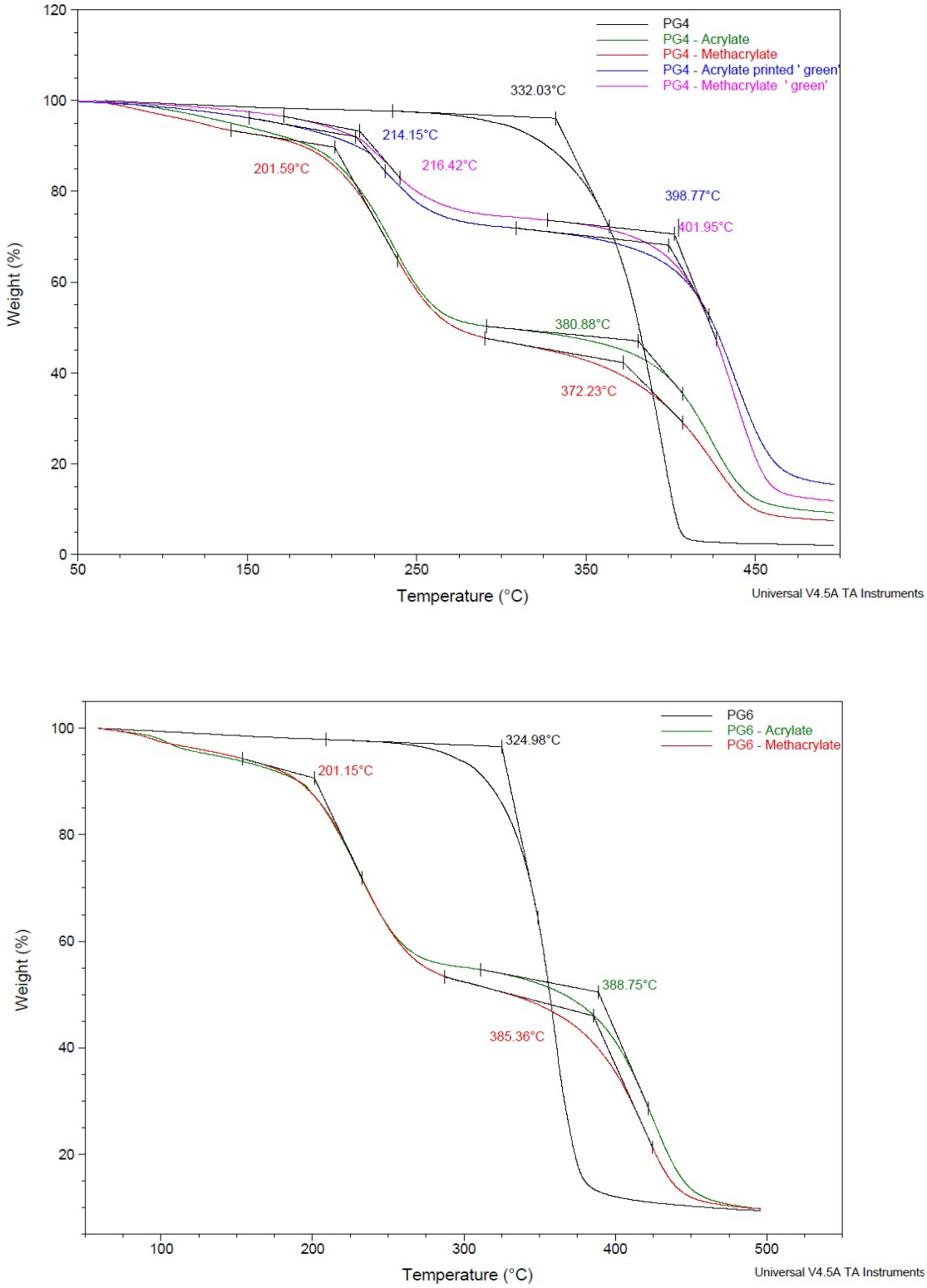


SI Figure 2: *^{1}H-NMR at Time = 3 hrs of resin synthesis for PG4 – Acrylate 3:1 molar ratio. New signals corresponding to acrylate esters have formed. Conversion of acrylic acid is calculated to be approximately 62 %, using the integrals of signals assigned 4+9 and 1. Some error in this estimation is a result of signal overlap between acrylic esters with the Michael addition product.*

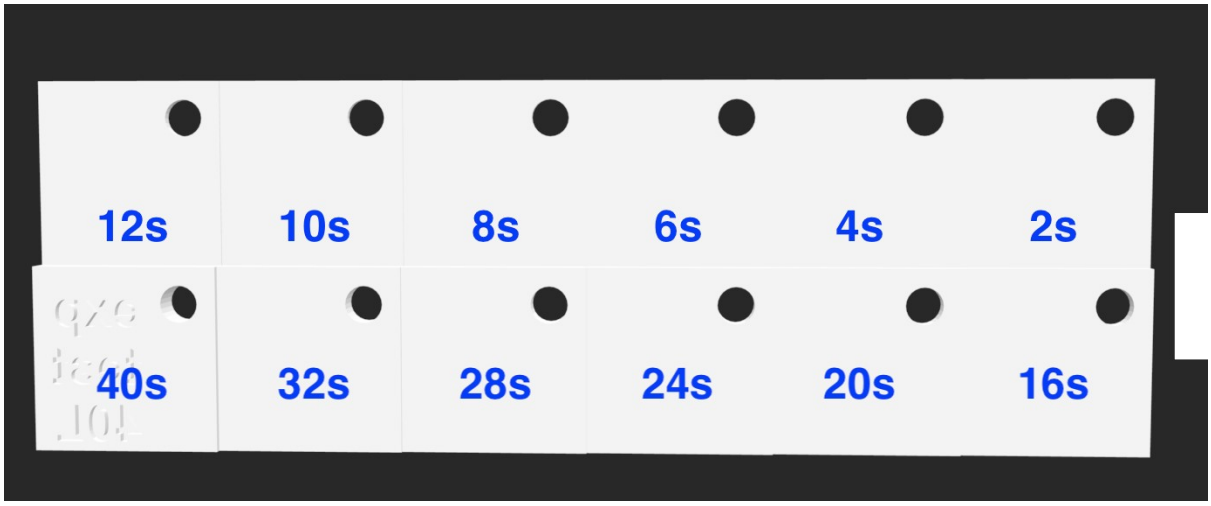


SI Figure 3: *^{1}H-NMR at Time = 3 hrs of resin synthesis for PG4 – Methacrylate 3:1 molar ratio. Conversion of methacrylic acid is calculated to be approximately 25 %, using the integrals of signals assigned 5 and 2.*

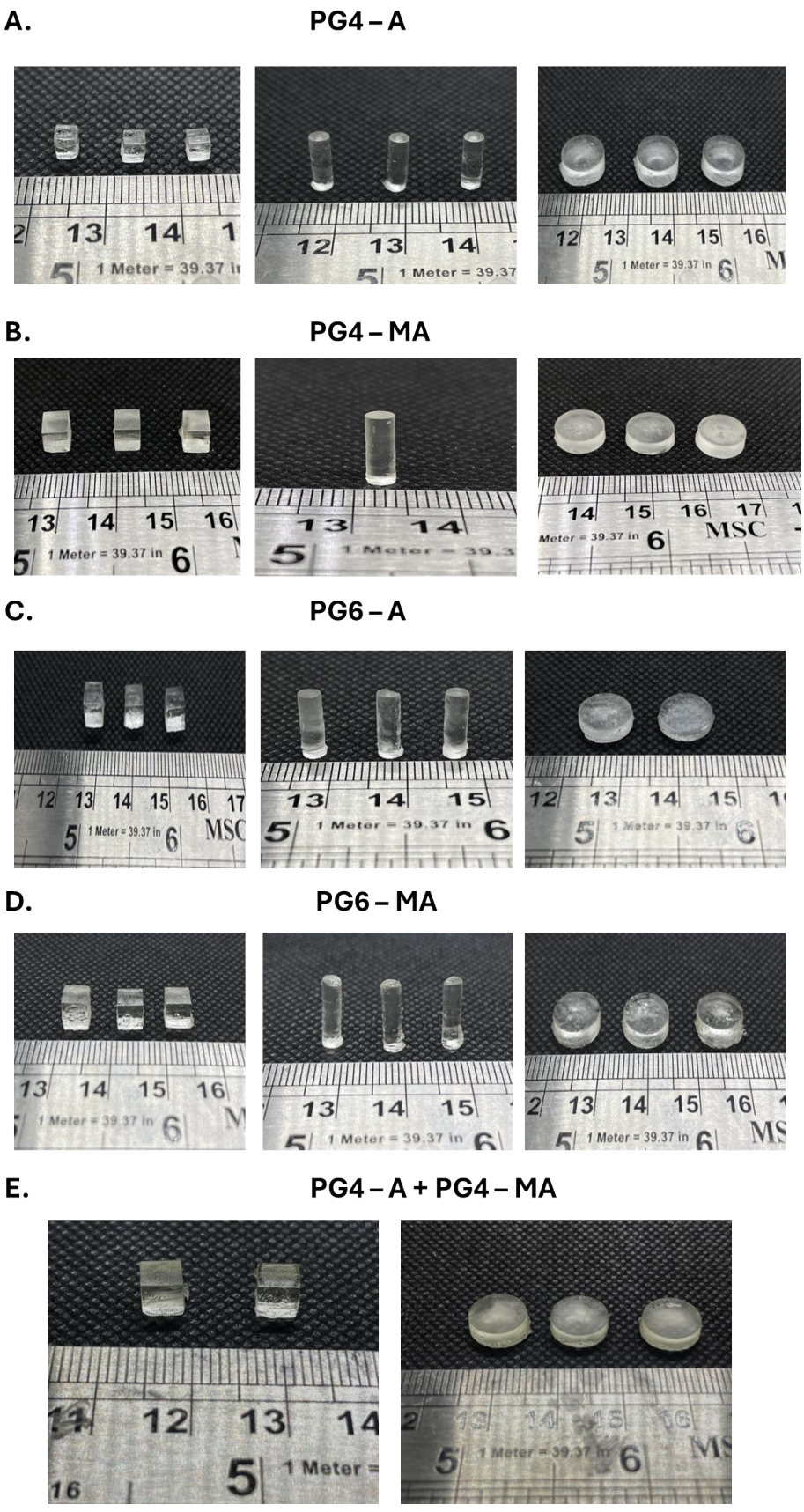
TGA analysis



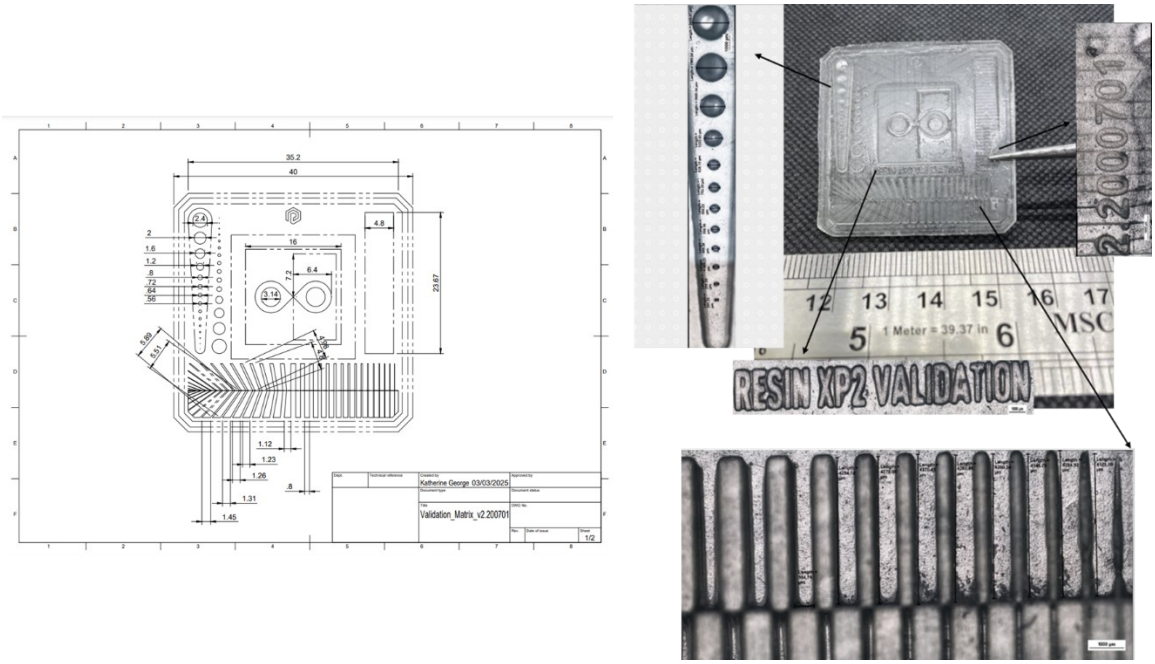
SI Figure 4: *TGA degradation profile of PG4 resins (top) and PG6 resins (below)*



SI Figure 5: *Design schematic used for SLA printing optimisation of resins.*



SI Figure 6: *SLA printing results of (A) PG4 – A (B) PG4 MA (C) PG6 – A (D) PG6 MA (E) PG4 A + PG4 MA*

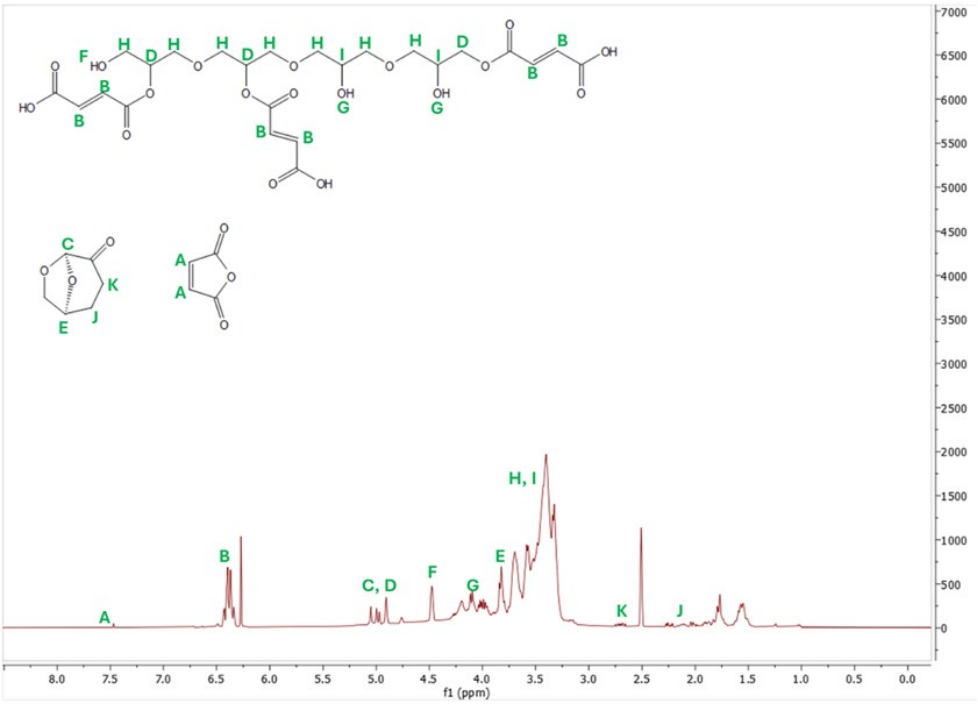


SI Figure 7: *(left) Design schematic for validation matrix used for printing resolution testing; (right) Microscope images of PG4 – A validation matrix*

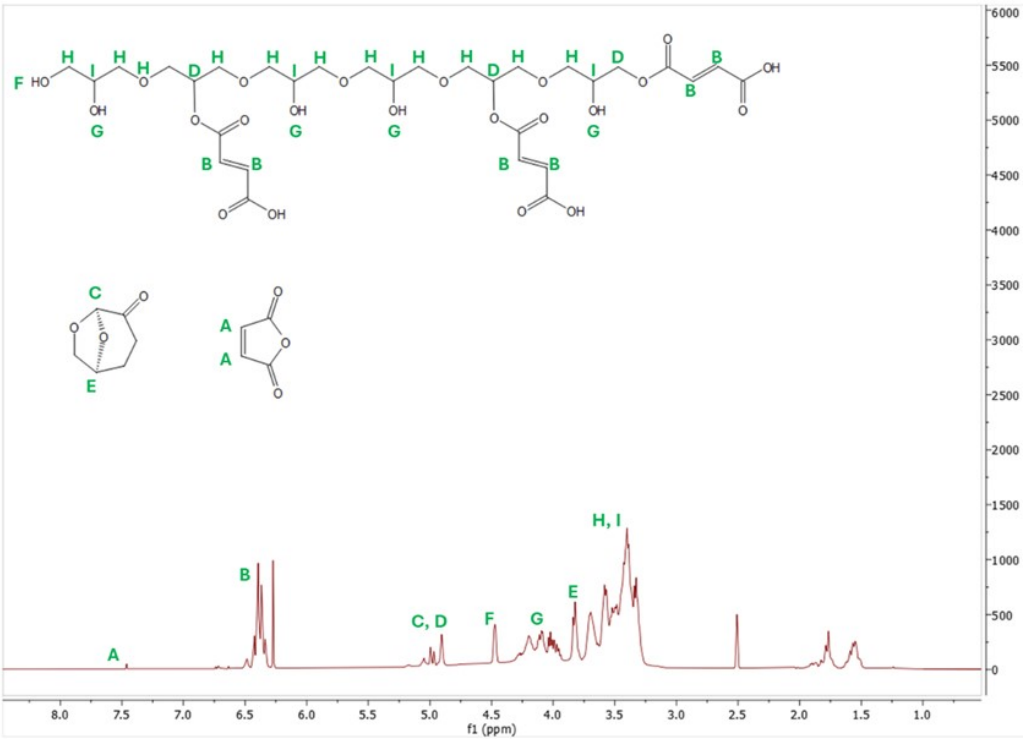
***SI Table 2**: Curability test for PG4 and 6 malate and Norbornene resins prepared with and without phosphoric acid and cured at various double bond (DB)/ thiol (SH) molar ratios*

Test Number	Sample	Thiol ([DB]: [SH] molar ratio)	Observations (minutes) 2	4	6
1	PG4 Mal (Acid)	1:1	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
2	PG4 Mal (Acid)	1:2	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
3	PG4 Mal (Acid)	1:3	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
4	PG4 Mal	1:1	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
5	PG4 Mal	1:2	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
6	PG4 Mal	1:3	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
7	PG4 Norb (Acid)	1:1	Hardened/gluey	Hardened	Hardened
8	PG4 Norb (Acid)	1:2	Uncured (gluey)	Gluey	Hardened/gluey
9	PG4 Norb (Acid)	1:3	Uncured (gluey)	Gluey	Hardened/gluey
10	PG4 Norb	1:1	Hardened/gluey	Hardened	Hardened
11	PG4 Norb	1:2	Uncured (gluey)	Gluey	Hardened/gluey
12	PG4 Norb	1:3	Uncured (gluey)	Gluey	Hardened/gluey
13	PG6 Mal (Acid)	1:1	Hardened/gluey	Hardened	Hardened
14	PG6 Mal (Acid)	1:2	Uncured (gluey)	Gluey	Hardened/gluey
15	PG6 Mal (Acid)	1:3	Uncured (gluey)	Gluey	Hardened/gluey
16	PG6 Mal	1:1	Gluey	Gluey	Gluey
17	PG6 Mal	1:2	Increased gluey from 1:1 ratio	Increased gluey from 1:1 ratio	Increased gluey from 1:1 ratio
18	PG6 Mal	1:3	Increased gluey from 1:2 ratio	Increased gluey from 1:2 ratio	Increased gluey from 1:2 ratio
19	PG6 Norb (Acid)	1:1	Hardened/gluey	Hardened	Hardened
20	PG6 Norb (Acid)	1:2	Uncured (gluey)	Gluey	Hardened/gluey
21	PG6 Norb (Acid)	1:3	Uncured (gluey)	Gluey	Hardened/gluey
22	PG6 Norb	1:1	Hardened/gluey	Hardened	Hardened
23	PG6 Norb	1:2	Uncured (gluey)	Gluey	Hardened/gluey
24	PG6 Norb	1:3	Uncured (gluey)	Gluey	Hardened/gluey
25	PG10 Mal (Acid)	1:1	Hardened/gluey	Hardened/gluey	Hardened/gluey
26	PG10 Mal (Acid)	1:2	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
27	PG10 Mal (Acid)	1:3	Uncured (Liquid)	Uncured (Liquid)	Uncured (Liquid)
28	PG10 Mal	1:1	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
29	PG10 Mal	1:2	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
30	PG10 Mal	1:3	Uncured (Liquid)	Uncured (Liquid)	Uncured (Liquid)
31	PG10 Norb (Acid)	1:1	Hardened/gluey	Hardened/gluey	Hardened/gluey
32	PG10 Norb (Acid)	1:2	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
33	PG10 Norb (Acid)	1:3	Uncured (Liquid)	Uncured (Liquid)	Uncured (Liquid)
34	PG10 Norb	1:1	Hardened/gluey	Hardened/gluey	Hardened/gluey
35	PG10 Norb	1:2	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)
36	PG10 Norb	1:3	Uncured (gluey)	Uncured (gluey)	Uncured (gluey)

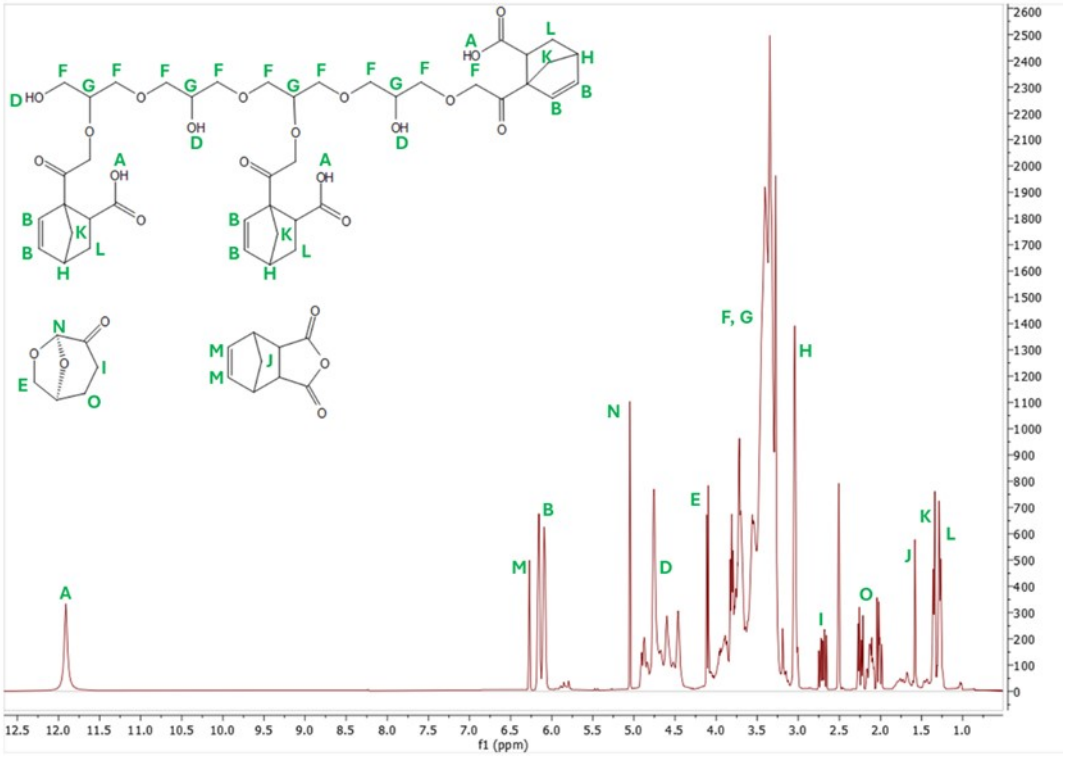
^{1}H NMR analysis of PG maleate and norbornene macromonomers



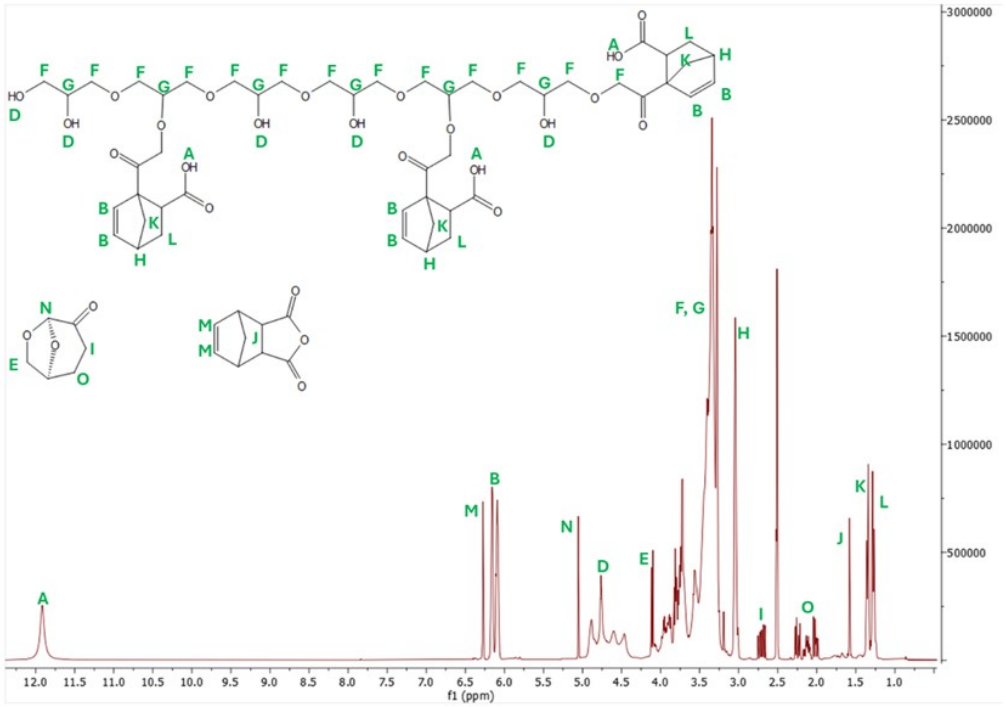
SI Figure 8 *- ^{1}H NMR in deuterated DMSO of PG4 – Mal. Conversion was calculated to be 98%.*



SI Figure 9 *- ^{1}H NMR in deuterated DMSO of PG6 – Mal. Conversion was calculated to be 98%.*



SI Figure 10 *- ^{1}H NMR in deuterated DMSO of PG4 – Norb. Conversion was calculated to be 86%.*



SI Figure 11 *- ^{1}H NMR in deuterated DMSO of PG6 – Norb. Conversion was calculated to be 88%.*