Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information:

3D Printing and Growth Induced Bending based on PET-RAFT polymerization

Chris William Anderson Bainbridge[#], Kyle Edward Engel[#], and Jianyong Jin[*]

[a] *School of Chemical Sciences, The University of Auckland, Auckland 1010, New Zealand*

[b] *Dodd-Walls Centre for Quantum and Photonic Technologies, Auckland 1010, New Zealand*

[#] *Authors contributed equally to the work*

ORCID:

Chris Bainbridge: 0000-0002-6135-3382

Kyle Engel: 0000-0003-3749-6890

Jianyong Jin: 0000-0002-5521-6277

S1: Materials:

Poly (ethylene glycol) diacrylate (PEGDA) (average Mn ~250 g/mol), N, N-dimethylacrylamide (DMAm), butyl acrylate (BA) and methyl methacrylate (MMA) were purchased from Sigma Aldrich and deinhibited by passing through a column of basic alumina. 2-(butylthiocarbonothioylthio) propanoic acid (BTPA), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA), phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (TPO), Eosin Y disodium salt (EY), Erythrosin B (EB), and triethanolamine (TEtOHA) were purchased from Sigma Aldrich and used as received. All the other reagents were used as received unless otherwise specified.

S2: Characterization:

Photo-Differential Scanning Calorimetry was performed using a Netzsch DSC3500 Sirius and a Klerex Delolux 04 discharge lamp (filtered to 400-500nm). Samples were placed into an open top aluminium liquid pan and exposed to the discharge lamp guided by fibre optics. Samples were measured under isothermal conditions at 25˚C and a nitrogen purge flow of 249 ml/min. The data was recorded for 5mins.

Rectangular DMA sample strips with dimensions 40 × 12 × 1.6 mm (length × width × thickness) were 3D printed for use in a TA instruments Q800 dynamic mechanical analyser (DMA). For each batch, six DMA samples were printed simultaneously on one build platform using a layer thickness of 30 µm an attachment time of 60 seconds and a normal exposure time of 30 seconds per layer (53 layers total). For temperature control the Q800 was fitted with a TA instruments liquid nitrogen gas cooling accessory (GCA). The rectangular DMA samples were remeasured using a digital Vernier callipers prior to being fitted into a calibrated single cantilever clamp. Samples were fixed into place using a torque screwdriver with a force of 5 in lb. The DMA analysis was performed using the following temperature profile; samples were cooled to -50˚C at a rate of 2˚C/min and held there for 5 minutes to stabilise, samples were then heated to 100˚C at a rate of 2˚C/min. A constant frequency of 1 Hz was used with a displacement of 30µm. As mentioned, the storage modulus (E') was determined around room temperature. Glass transition temperature (T_g) was determined from the peak of the Tan δ curve. DMA results were determined after repeated measurements.

UV-Vis absorbance spectroscopy was performed using a Shimadzu UV-2700. Samples of EB and EY were prepared at concentrations of 0.01 mg/ml with DMSO as a solvent in quartz cuvettes. The initial absorbance spectrum was then measured between 200-900nm, after which the cuvette was removed and irradiated by an external 405nm lamp (397.45μW/cm^2) for 10 minutes. The absorbance was measured again, and this process was repeated until the total exposure time reached 40 minutes. Both EB and EY received the same intensity and length of exposure.

3D-RAFT printing was conducted using FlashForge Hunter Digital light process 3D printer. The physical specifications of the printer are:

Build volume: 120L × 150 W × 67.5 H mm (4.72” × 5.91” × 2.66”)
Layer Resolution: 0.001”/0.0020” (25/50μm)
Pixel Size: 0.0025”/ (62.5μm)
Light Source: 405nm light engine

S3: Experimental section:

S3.1 Optimisation of the resins

For use in the Photo-DSC studies, test resins were prepared as follows:

Sample 1: [PEGDA]: [BTPA]: [EY]: [TEtOHA] = 500:1:0.01:20 in molar ratio

A test resin containing PEGDA (524.35 mg, 2.10 mmol), Eosin Y (2.90x10^{-2} ml from a stock solution of EY in PEGDA 1mg/ml, 4.19x10^{-5} mmol), BTPA (1.00 mg, 4.19x10^{-3} mmol) and TEtOHA (12.52 mg, 8.38x10^{-2} mmol) was prepared. The test resin was vortexed and sonicated until BTPA had completely dissolved.

Sample 2: [PEGDA]: [DMAm]: [BTPA]: [EY]: [TEtOHA] = 350:150:1:0.01:20

A test resin containing PEGDA (367.05 mg, 1.47 mmol), DMAm (62.37 mg, 0.63 mmol), Eosin Y (2.90x10^{-2} ml from a stock solution of EY in PEGDA 1mg/ml, 4.19x10^{-5} mmol), BTPA (1.00 mg, 4.19x10^{-3} mmol) and TEtOHA (12.52 mg, 8.38x10^{-2} mmol) was prepared. The test resin was vortexed and sonicated until BTPA had completely dissolved.

Sample 3: [PEGDA]: [DMAm]: [BTPA]: [EY]: [TEtOHA] = 150:350:1:0.01:20

A test resin containing PEGDA (157.31 mg, 0.63 mmol), DMAm (145.54 mg, 1.47 mmol), Eosin Y (2.90x10^{-2} ml from a stock solution of EY in PEGDA 1mg/ml, 4.19x10^{-5} mmol),

BTPA (1.00 mg, 4.19×10^{-3} mmol) and TEtOHA (12.52 mg, 8.38×10^{-2} mmol) was prepared. The test resin was vortexed and sonicated until BTPA had completely dissolved.

Sample 4: [PEGDA]: [CDTPA]: [EY]: [TEtOHA] = 500:1:0.01:20

A test resin containing PEGDA (309.66 mg, 1.24 mmol), Eosin Y (1.71×10^{-2} ml from a stock solution of EY in PEGDA 1mg/ml, 2.48×10^{-5} mmol), CDTPA (1.00 mg, 2.48×10^{-3} mmol) and TEtOHA (7.39 mg, 4.96×10^{-2} mmol) was prepared. The test resin was vortexed and sonicated until CDTPA had completely dissolved.

S3.2 Preparation of 3D -RAFT resin for 3D printing

3D-RAFT resin formula: [PEGDA]: [DMAm]: [BTPA]: [EY]: [TEtOHA] = 350: 150:1:0.01:20

A resin containing PEGDA (44.05 g, 176.18 mmol), DMAm (7.48 g, 75.51 mmol), Eosin Y (3.48 mg, 5.03×10^{-3} mmol), BTPA (120.00 mg, 0.503 mmol) and TEtOHA (1501.96 mg, 10.07 mmol) was prepared. The resin was vortexed and sonicated until BTPA had completely dissolved. This resin was then used for 3D-RAFT prints.

S3.3 Preparation of FRP resin for 3D printing

Conventional Free Radical (FRP) resins: [PEGDA]: [DMAm] = 350: 150, with 2wt% TPO

A resin containing PEGDA (44.05g, 176.18 mmol). DMAm (7.48 g, 75.51 mmol) and TPO (1.03 g, 2%wt) was prepared. The solution was vortexed and sonicated until TPO had completely dissolved.

S3.4 Flashforge Hunter 3D Printer Printing parameters and CAD modelling

All CAD models were designed and exported using the free online database TinkerCAD (https://www.tinkercad.com/). CAD models were then sliced for 3D printing using the Flashforge Hunter provided software (FlashDLPrint). Final printing parameters for the 3D-RAFT resin and FRP resin is as follows: a base time of 30 seconds with a 60 second attachment time, layer thickness of 30µm, gradual time layers were set to 15 and light intensity was 100%. All samples were washed using EtOH while still on the build platform prior to a 1.5 hour post-

cure using two green lights (532 nm, 117.45μW/cm^2 combined) for the 3D-RAFT resin printed objects and 405 nm light (397.45μW/cm^2) for the FRP resin printed objects, respectively.

S3.5 Non-3D printed DMA samples as control

The same resin for 3D-RAFT printed DMA samples in **S3.2** was used to prepare the rectangular DMA sample strip in casting petri dish.

Procedure: This resin was poured into the bottom of a petri dish to a thickness of about 2 mm. For consistency with 3D printed DMA samples, the resin in the petri dish was polymerised using 405 nm light (397.45μW/cm^2) for 40 minutes, the same total run time as the 3D printed DMA samples. After which the sample was washed with EtOH and cured further using green light (532 nm, 117.45μW/cm^2 combined) for 1.5 hours. The sample was then removed from the petri dish and cut into rectangular strip with dimensions 40 × 12 × 1.6 mm (length × width × thickness) for use in the DMA.

S3.6 Post-production modification of the 3D-RAFT printed DMA samples

Photo-growth of a 3D-RAFT printed DMA sample was carried out as follows: three rectangular DMA samples were soaked together in a 25mL vial using a growth medium of Eosin Y (0.19 ml, 2.80x10 $^{-4}$ mmol from a stock solution of EY in THF, 1mg/ml), TEtOHA (83.55 mg, 0.56 mmol) with MMA added to cover the samples (25 mL). The samples were covered with aluminium foil to limit light penetration and soaked for 18 hours in a refrigerator. The DMA samples were then removed from the growth medium, excess growth medium was wiped off with a paper towel. After drying the samples were placed into a petri dish and irradiated using green light (532nm, 58.72μW/cm^2) for 24 hours. Then the samples were ready for DMA testing.

S3.7 Procedure for the photo-growth induced Bending of the 3D-RAFT printed strip

The growth medium for growth induced bending was prepared by adding BA (2.96 g, 23.07 mmol), Eosin Y (0.32 ml, 4.61x10^{-4} mmol from a stock solution of Eosin Y in THF, 1 mg / ml) and TEtOHA (137.68 mg, 0.92 mmol) into DMSO (30 mL). A 3D-RAFT printed strip with a thickness of 0.6mm (120 × 20 × 0.6 mm (length × width × thickness)) was lowered into the growth medium until it covered half the length and was soaked for 30 minutes. The strip was

then irradiated with green light (532nm, 58.72μW/cm^2), directed at one face for a total period of 60 minutes. The strip was taken out for measurement at 15 minute intervals, while the bending was monitored by the naked eye. After 30 minutes no noticeable further bending of the strip was observed.