Supporting Information

Properties of Cyclic Olefin-Based Photo-ROMP Resins Suitable for DLP 3D Printing Applications

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1 Materials and General Methods

Monomers were obtained from Promerus and have been disclosed previously.[1-4] The Ru precatalyst were obtained from Apeiron Synthesis, S.A.[5,6] 1-chloro-4-propoxy-9H-thioxanthen-9-one (CPTX), 4-dimethylaminopyridine (DMAP), 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (bTBBT), and Irgafos® 168 were purchased from Sigma-Aldrich. Irganox® 1076 was purchased from BASF.

1.1 Photo-DSC measurements.

Photo-differential scanning calorimetry (Photo-DSC) was carried out using a NETZCH DSC 204 F1 Phoenix® differential scanning calorimeter in conjunction with an OmniCure LX500 UV LED Spot Curing System Controller using 395 nm light. Each test was done isothermal at 30 or 60 °C with 1 J/cm^2 UV exposure (4 s at 0.25 W/cm^2 power) beginning ~10 seconds after starting the run. The exotherms were determined using the NETZSCH Proteus® software by integration of the curves.

1.2 GPC measurements

GPC data were obtained using a Tosoh EcoSEC HLC-8320GPC with a RI detector. The data were collected at 40 °C using 1 PLgel 5 µm Guard and 2 PLgel 5 µm Mixed-C columns with stabilized THF as the solvent. Polystyrene standards of known molecular weights were run using the same conditions to create a calibration curve.

1.3 Dynamic Mechanical Analysis measurements

DMA measurements were carried out in tension using a TA Instruments-Waters LLC Model Q-800 DMA with polymer film specimen sizes of approximately 0.75mm x 8mm x 12mm at a temperature ramp of 5 ºC/min using the following conditions: 15 µm amplitude stress at 1 Hz; preload force 0.01 N; force track 125%; soak time 1 min; temperature range 25 ºC-250 ºC; nitrogen purge.

Tan δ was determined as the peak appearing in the trace of the ratio of storage modulus to loss modulus. Tan δ (commonly accepted as the T_g) typically closely follows the peak appearing in the loss modulus trace.

Heat deflection temperature (HDT) was measured using a TA Instruments-Waters LLC Model Q-800 DMA fitted with a three-point sample mount capable of accepting samples of either 50 mm or 25 mm in length. The measurement follows the ASTM International D 648 “Deflection Temperature Under Load” procedure outlined by TA Instruments. Sample dimensions are used

to calculate the force and desired deflection. Force is calculated to be the strain induced in a sample at a load of 0.455 MPa. The HDT point is the temperature where the total deflection above a minimum reading reaches the calculated value.

1.4 Tensile measurements

Tensile measurements were done on a universal testing machine (Instron, Mdl. 68TM-R, Norwood, MA) equipped with 250N pneumatic sample holders with serrated faced clamps. A 1 kN load cell was used. Specimen were punched with an ASTM/ISO conforming D-638 Type 5 steel punch yielding a dog bone measuring 3.18 mm x 9.53 mm in the center parallel section for flood-cured samples and 5.6 mm x 16.8 mm in the center parallel section for 3D printed specimens. A non-contact extensometer (Instron, Mdl AVE-2, Norwood, MA) was used in the measurement of both modulus and extension to break (ETB). The crossbeam speed was 50mm/min with a preload force of 1N.

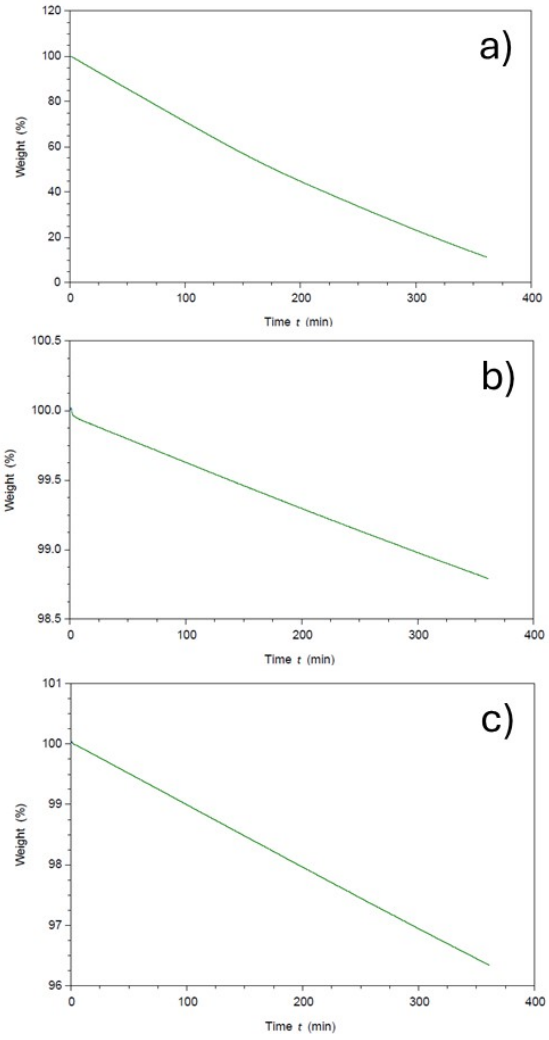
1.5 Impact measurements

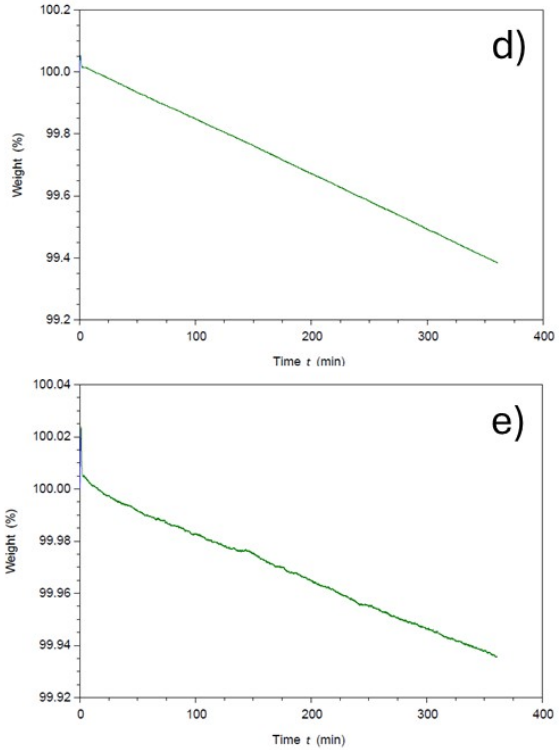
Impact measurements were done using an Advanced Pendulum Impact System (Test Machines Inc., New Castle, DE). The requisite 0.25 mm radius notch was cut with the Dual Tooth Cutting Wheel Autocycle Notching Cutter (Testing Machines, Inc., New Castle, DE). Specimen size typically measured 8 cm x 1 cm x 0.3 cm (l x w x d) for flood-cured samples and 9 cm x 1 cm x 0.3 cm (l x w x d) for 3D printed specimens. Impact strength in ftlbf/in were reported directly by the instrument and converted to J/m.

1.6 NMR measurements

The NMR spectrum was recorded at 298 K on a Bruker Avance III HD spectrometer operating at 500.15 MHz (^{1}H) in toluene-d_8. Chemical shifts are reported relative to $SiMe_4$ (0 ppm).

2 Isothermal TGA (30 °C) under N_2 of a) monomer 1, b) monomer 2, c) monomer 3, d) monomer 4, e) monomer 5.



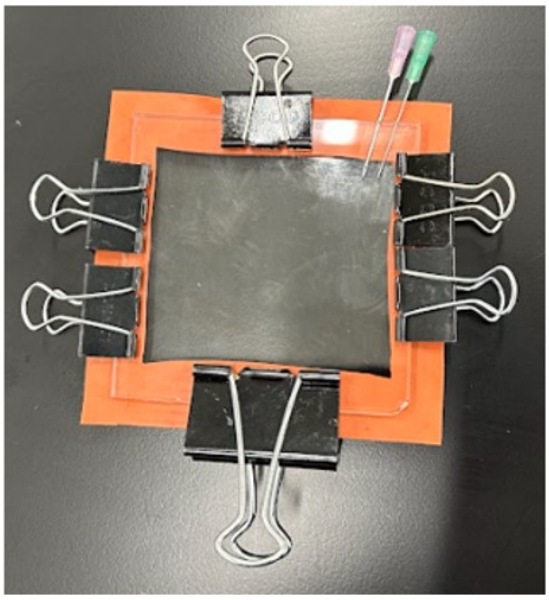


3 Flood exposed photo-curing of formulations to make test specimens

Procedure for Curing Films

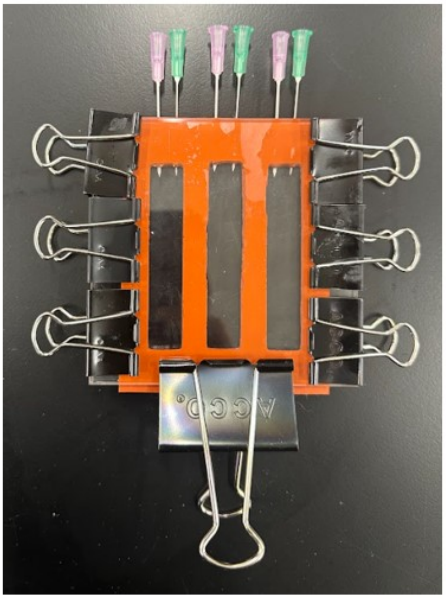
The procedure for curing films and bars is the same as described below and the following are the molds used for each.

Film Mold for Measuring Modulus, ETB, and T_g



Film Dimensions: 80 mm x 80 mm x 0.8 mm

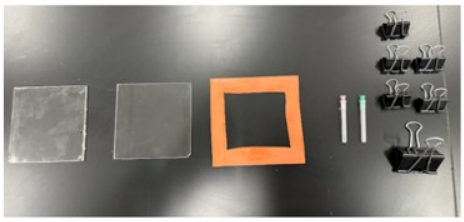
Bar Mold for Measuring Notched Izod Impact Resistance and Heat Deflection Temperature



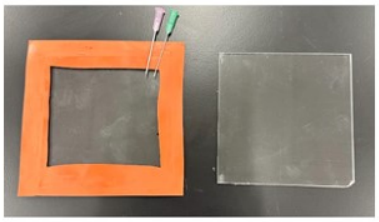
Bar Dimensions: 70 mm x 13 mm x 3 mm

The equipment used for curing was a Doctor UV 395 nm Linear UV LED curing system. Wearing UV-protective glasses, the formulation was exposed to UV light with the lamp one foot away from the mold for two seconds. The lamp was then brought to one inch from the mold for eight seconds. This process was immediately repeated on the other side of the mold giving a uniform film. The total exposure dose at 395 nm for each side was 10 J/cm^2.

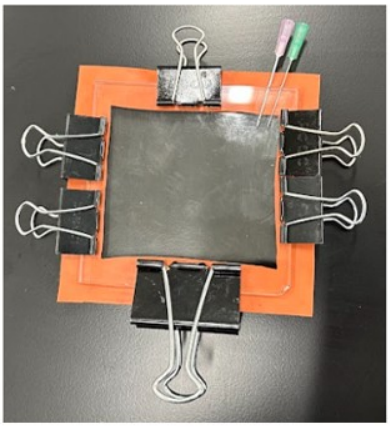
Materials for Mold to Cure Film
Two 4x4” Glass Pieces, 0.8 mm Silicone Piece
18G Injection Needle, 21G Vent Needle, Binder Clips



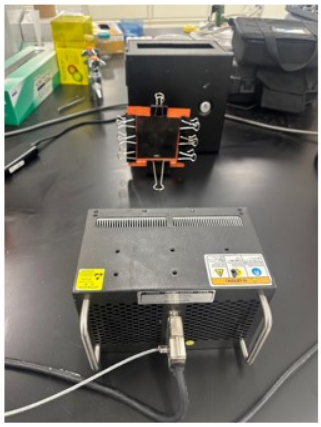
Put Injection Needle and Vent Needle on Silicone



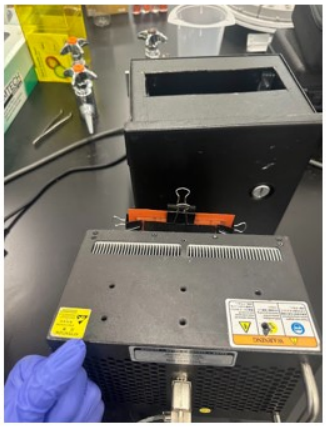
Mold Ready for Injection of Formulation



Wearing UV-protective glasses
begin UV exposure



Bring UV lamp close to mold



4 3D DLP Printing

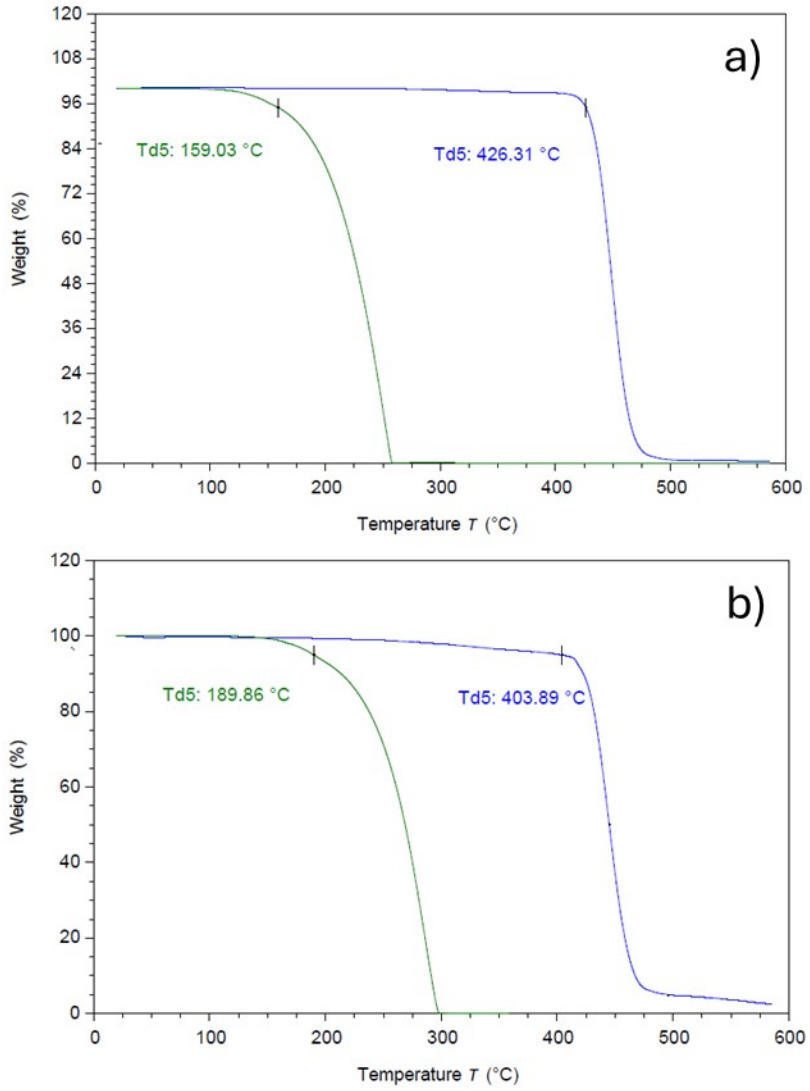
The 3D printer used was a FlashForge Hunter DLP Resin 3D printer.

The septum cap was removed from the amber serum bottle, and the formulation was poured into the printer vat up to the maximum line marked inside the vat. The following are the settings used in the FlashDLPrint software:

Layer Height	50 µm
Base Time (Exposure Time per Layer)	60 s
Attach Time	60 s
Light Intensity	200% (9 mW/cm^2)
Raft	Disabled
Exposure Wavelength	405 nm

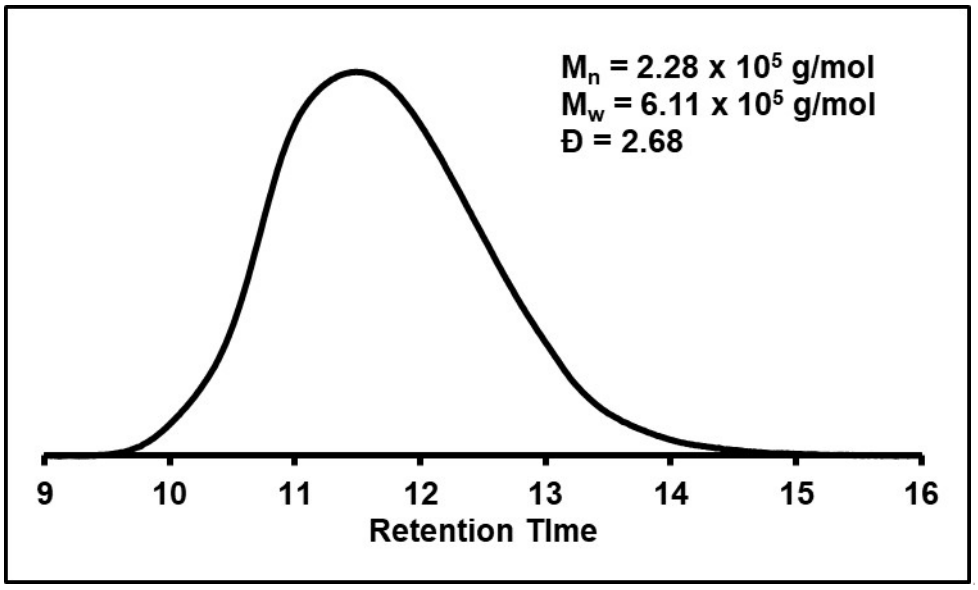
The print was then initiated and took 1 h and 19 min to complete. The base plate with the printed object attached was removed from the printer and excess formulation was removed using Kimwipes.

5 Dynamic TGA (10 °C/min under N) of a) monomer 4 (green) and poly(4) (blue) and b) monomer 5 (green) and poly(5) (blue) showing temperature at which 5% weight loss is observed, Td5.

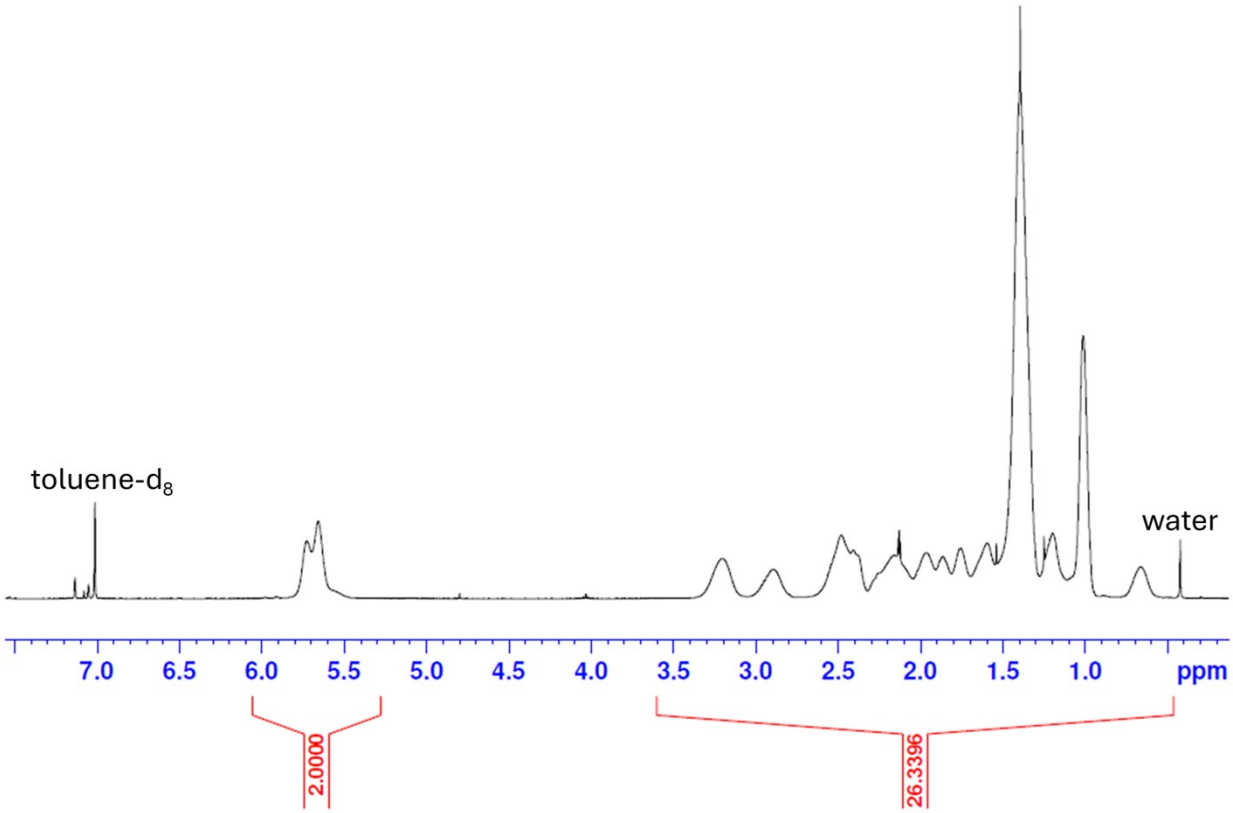


Thermogravimetric measurements from room temperature to 600 ºC were done on a TA Instruments-Waters LLC Model Q-550 TGA with specimen sizes typically 0.5-2 mg at a ramp rate of 20 ºC/min in a flowing nitrogen purge.

6 GPC of poly(4).



7 ^{1}H NMR of poly(4).



8 Thermomechanical Testing of Flood Exposed Formulations

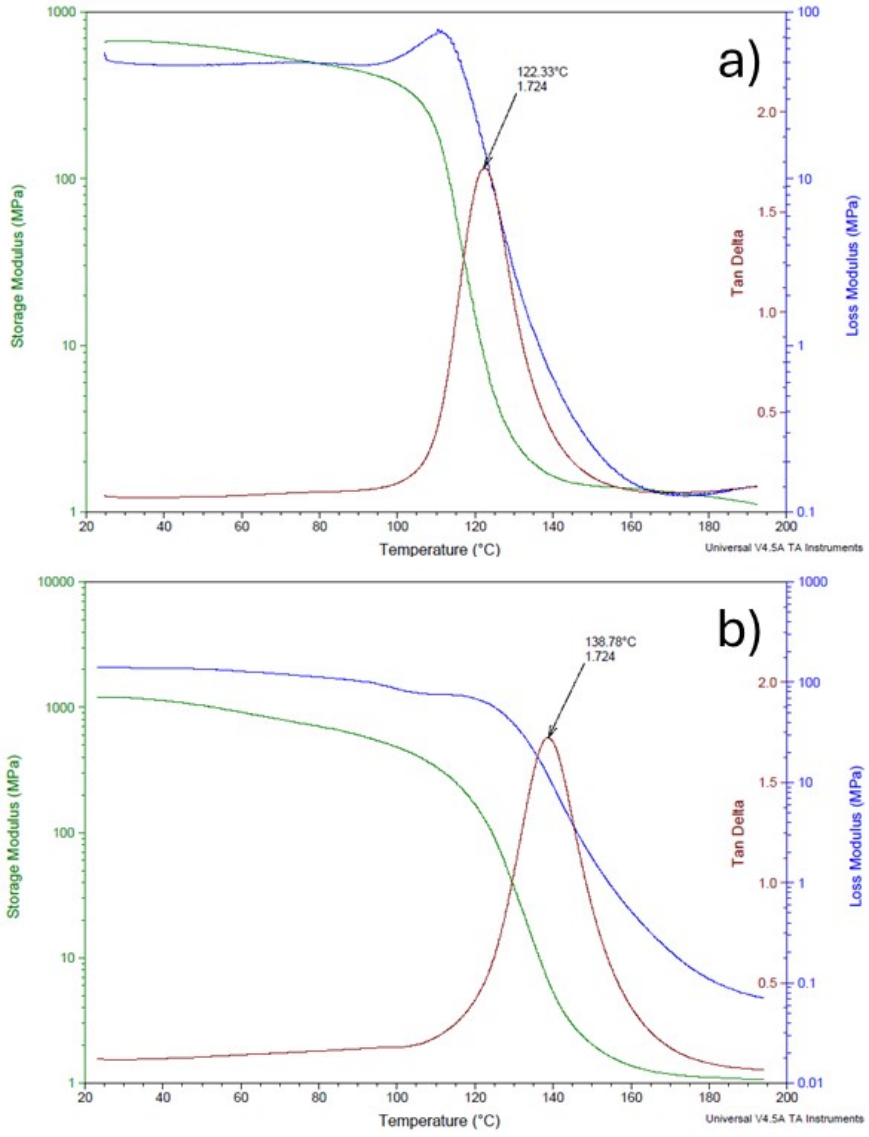
Protocol to make formulation with **Ru-2** and monomer **4**
Solid Irganox 1076 (400.0 mg, 0.4851 equiv, 0.7534 mmol) and Irgafos 168 (100.0 mg, 0.09955 equiv, 0.1546 mmol) were weighed on benchtop balances and then added into a 50 mL amber bottle. Then monomer **4** (40.00 g, 100 equiv, 163.7 mmol) was transferred into the amber bottle on a balance in the hood to the appropriate weight. The bottle was then capped and placed in an oven at 80 °C for 1 hour for complete dissolution of the solid contents in monomer **5**. The solution was then sparged with nitrogen overnight.

The amber bottle was then moved into a UV and blue light-protected glovebox and the cap was removed. **Ru-2** (13.7 mg, 0.01 equiv, 16.4 μmol) and CPTX (49.8 mg, 0.1 equiv, 0.164 mmol) were then added to the solution and then re-capped with a new cap. The bottle was then removed from the glovebox, placed in the sonicator at room temperature for 1 hour, and then heated at 80 °C for 1 hour to dissolve the catalyst and CPTX, completing the formulation.

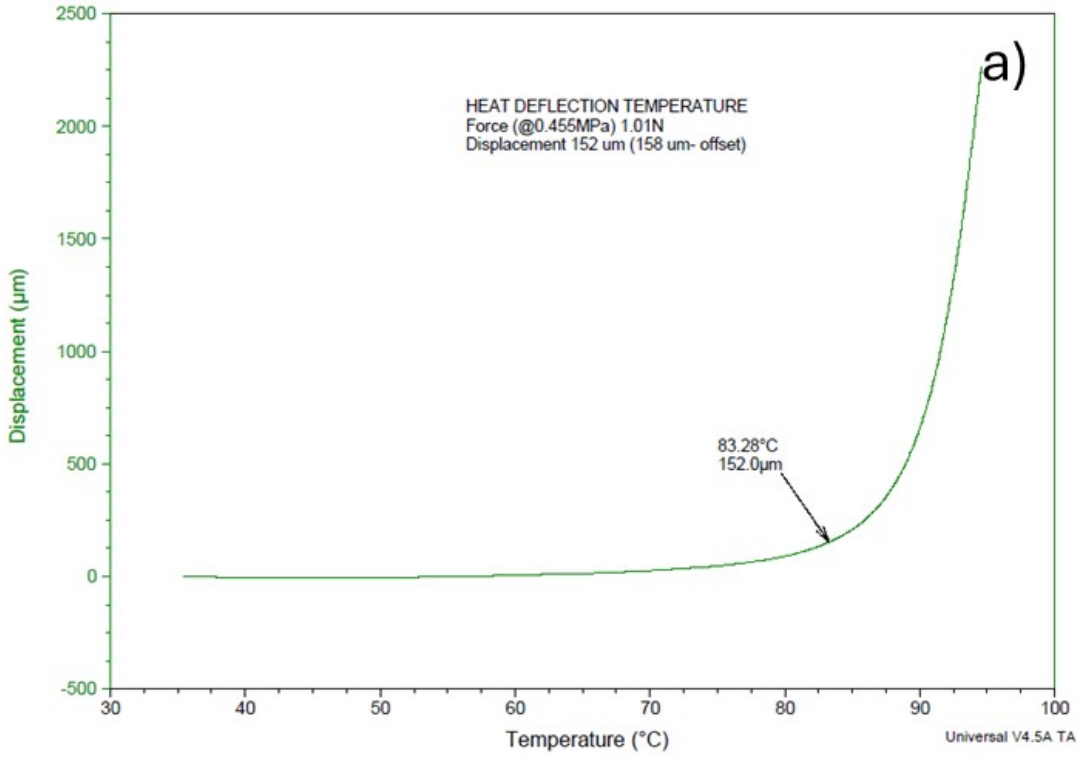
Protocol to make formulation with **Ru-2** and monomer **5**
Solid Irganox 1076 (400.0 mg, 0.4851 equiv, 0.7534 mmol) and Irgafos 168 (100.0 mg, 0.09955 Eq, 0.1546 mmol) were weighed on benchtop balances and then added into a 50 mL amber bottle. Then monomer **5** (40.00 g, 100 equiv, 151.4 mmol) was transferred into the amber bottle on a balance in the hood to the appropriate weight. The bottle was then capped and placed in an oven at 80 °C for 1 hour for complete dissolution of the solid contents in monomer **5**. The solution was then sparged with nitrogen overnight.

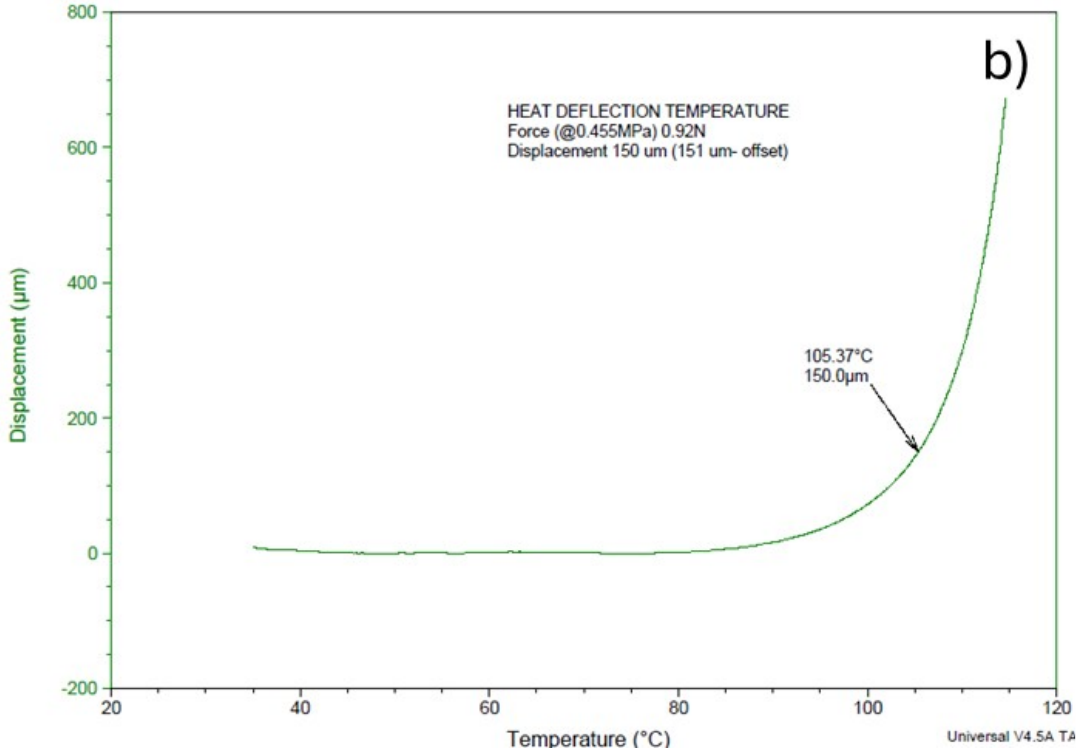
The amber bottle was then moved into a UV and blue light-protected glovebox and the cap was removed. **Ru-2** (12.7 mg, 0.01 equiv, 15.14 μmol) and CPTX (46.0 mg, 0.1 equiv, 0.154 mmol) were then added to the solution and then re-capped with a new cap. The bottle was then removed from the glovebox, placed in the sonicator at room temperature for 1 hour, and then heated at 80 °C for 1 hour to dissolve the catalyst and CPTX, completing the formulation.

8a Representative DMA of Flood Exposed Formulations for a) poly(4) and b) poly(5).

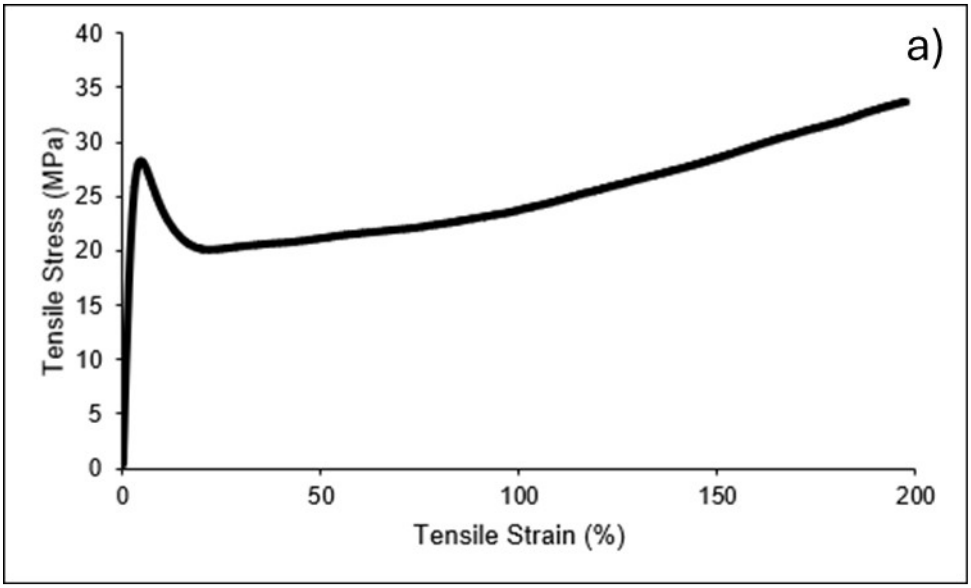


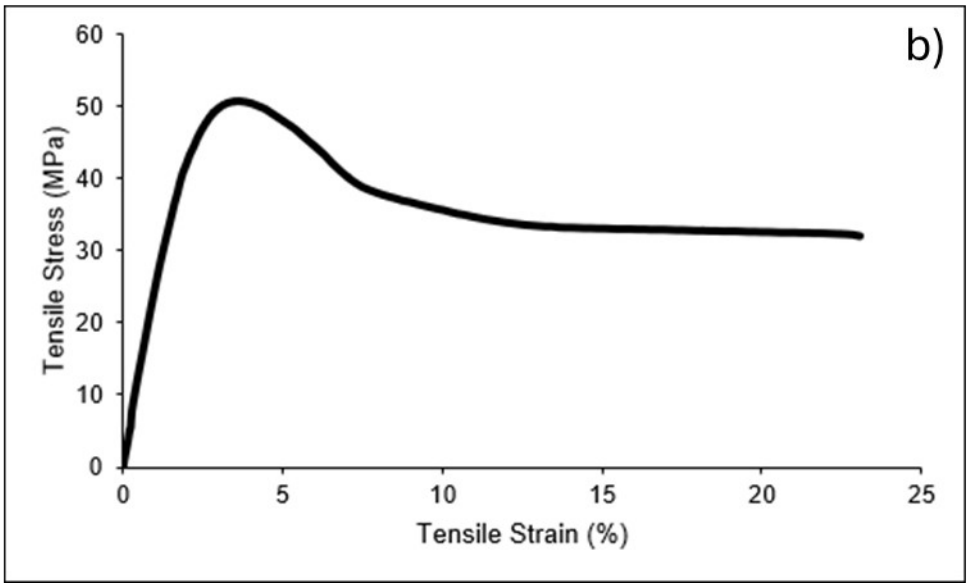
8b Representative HDT of Flood Exposed Formulations for a) poly(4) and b poly(5).





8c Representative Tensile Stress/Strain Behavior of Flood Exposed Formulations for a) poly(4) and b) poly(5).





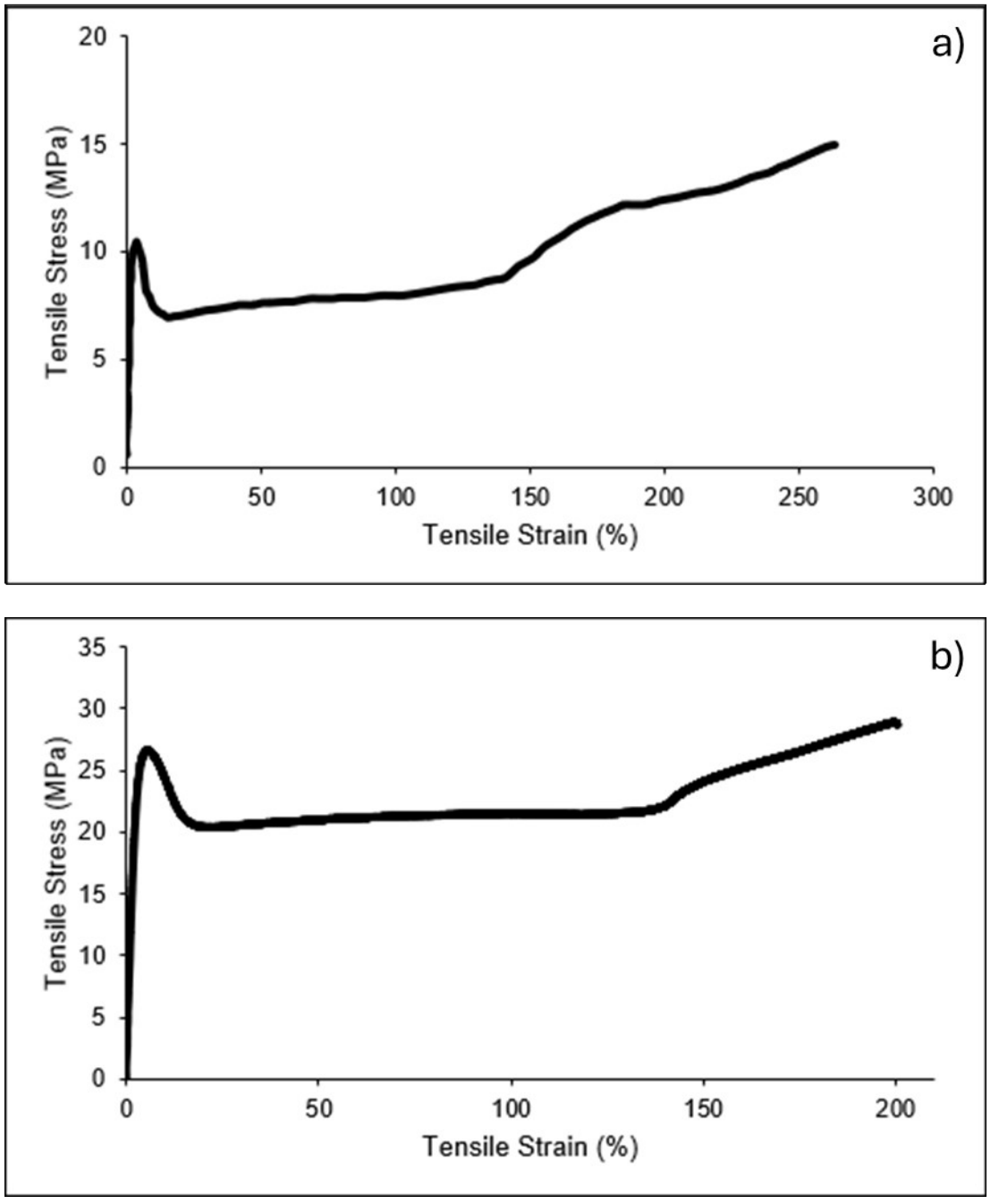
9 Thermomechanical Testing of 3D Printed Formulations

Protocol to make formulation

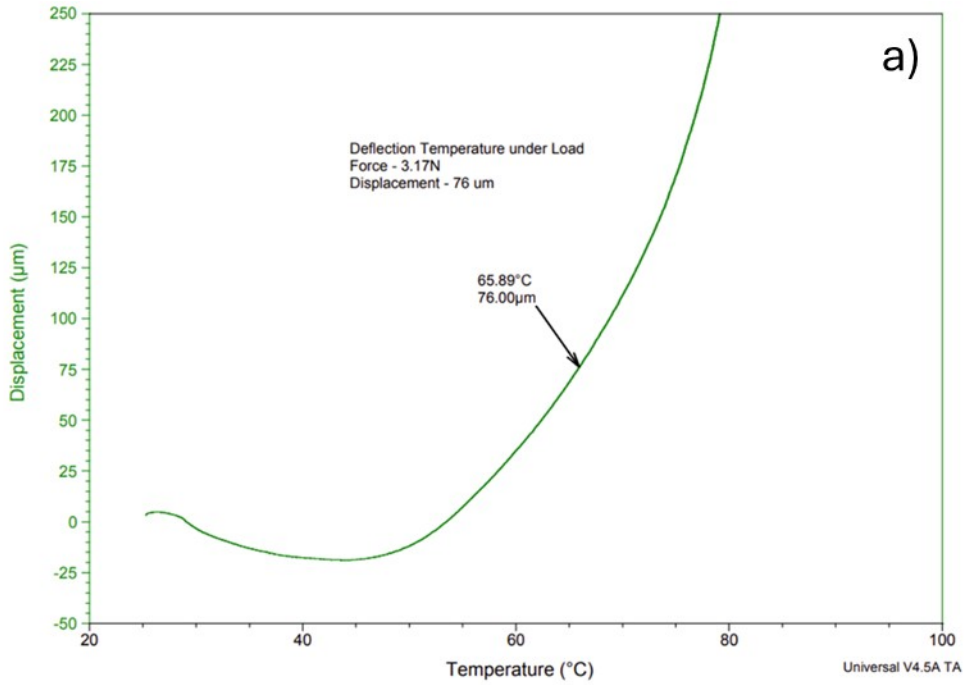
In a glass brown bottle, CPTX (0.5 phr), Irganox® 1076 (1 phr), Irgafos® 168 (0.25 phr), DMAP (0.1 molar part) and bTBBT (0.01 molar part) were dissolved in monomer **4** (10,000 molar 15 parts) via sonication at 40 °C for 1 hour to form a clear solution. The solution was purged with nitrogen for 8 hours. **Ru-2** catalyst (1 molar part) was added in a glove box to the purged solution and sonicated for 30 minutes to completely dissolve the catalyst.

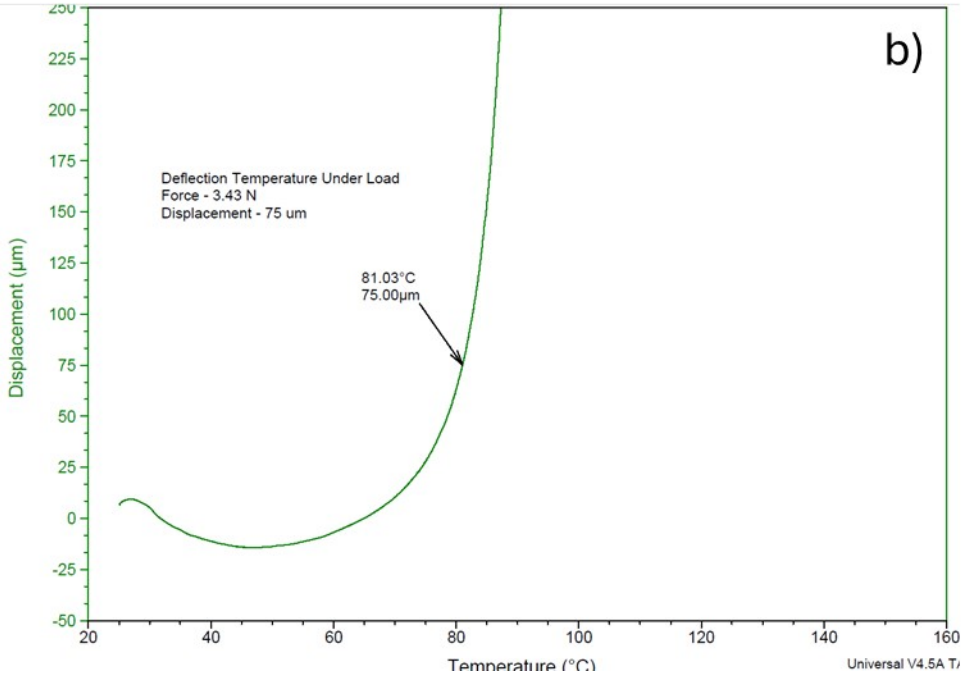
After the specimen was printed, thermomechanical tests were performed before and after post printing UV exposure curing (20 min with a 25 mW/cm^2 exposure dose using a Hg lamp, Dymax model 2000-EC flood system).

9a Representative Tensile Stress/Strain Behavior of 3D Printed Formulations Before (a) and After UV-Postcure (b) of poly(4).

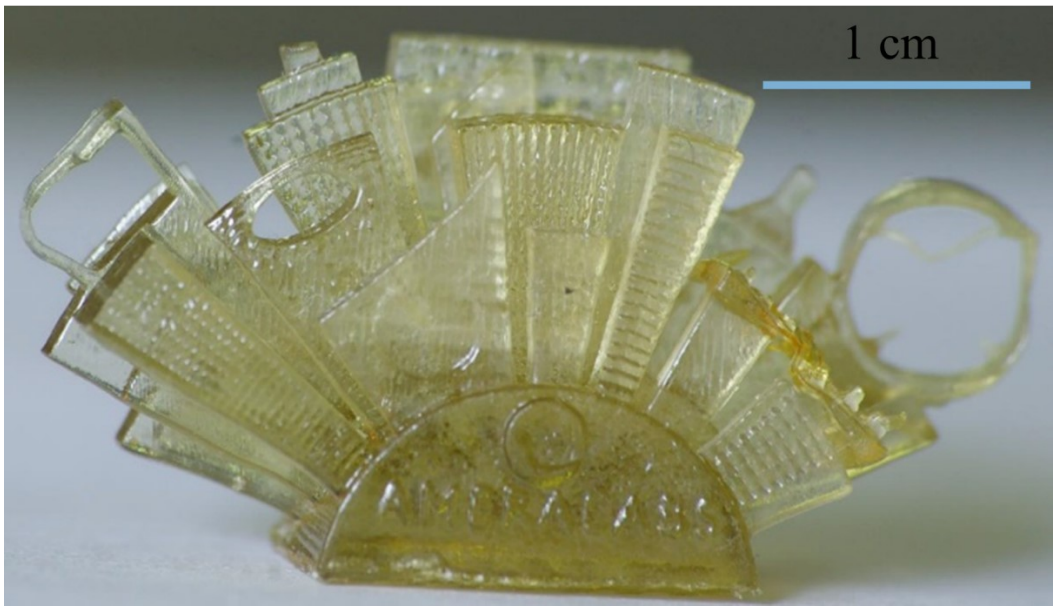


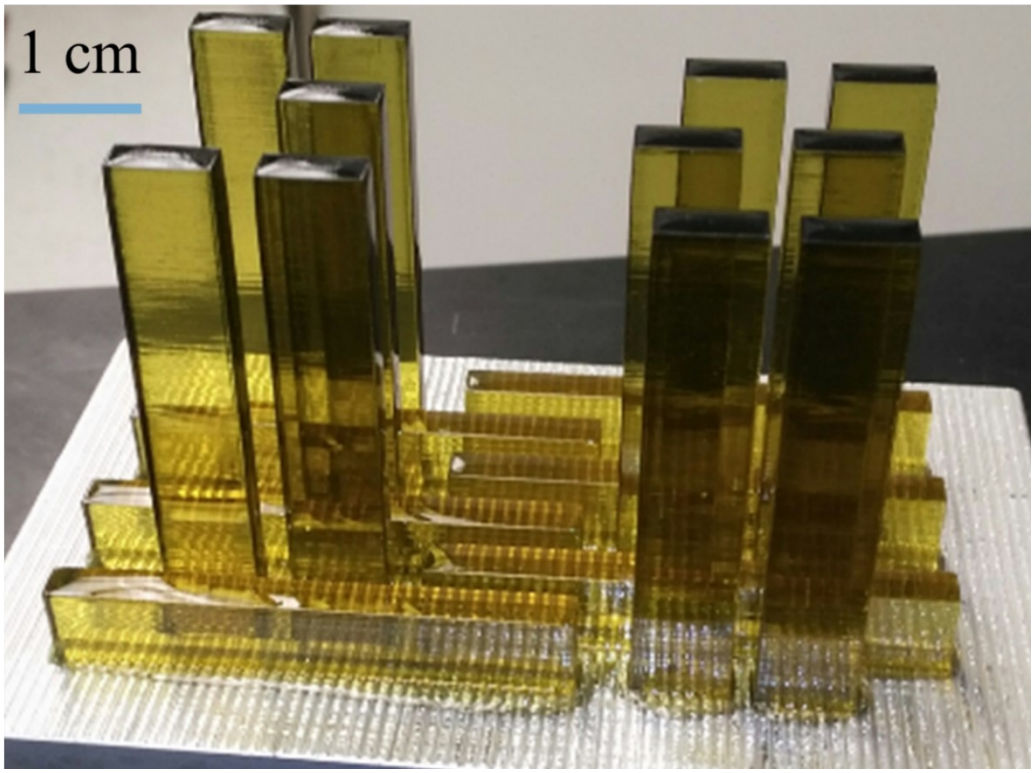
9b Representative HDT of 3D Printed Formulations Before (a) and After UV-Postcure (b) of poly(4).

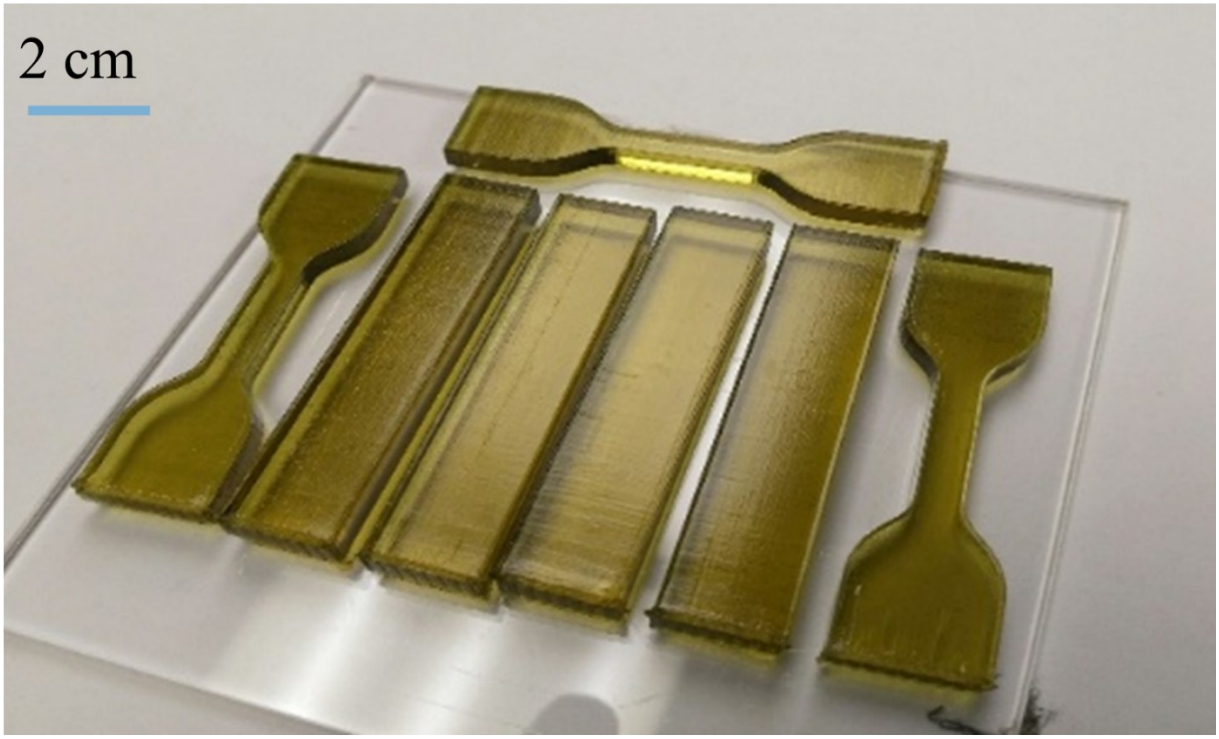




10 3D Printed Objects






2 cm

11 References

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