Supporting Information

PET-RAFT Facilitated 3D Printable Resins with Multifunctional RAFT Agents

Xiaobing Shi,[a] *Jin Zhang,*[b*] *Nathaniel Corrigan,*[a,c *] *and Cyrille Boyer*[a,c*]

[a]Cluster for Advanced Macromolecular Design, [b]School of Mechanical and Manufacturing Engineering, and
[c]Australian Centre for NanoMedicine, School of Chemical Engineering, University of New South Wales,
Sydney, NSW 2052 (Australia)

*E-mail: cboyer@unsw.edu.au, n.corrigan@unsw.edu.au, jin.zhang6@unsw.edu.au

Materials

Triethanolamine (TEtOHA, Sigma-Aldrich, 99%), erythrosin B (EB, dye content 90%, Sigma-Aldrich), 2-(dodecylthiocarbonothioylthio) propionic acid (DTPA, Boron Molecular), 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid (2DTBA, Sigma-Aldrich, 98%), 1,1,1-tris[(dodecylthiocarbonothioylthio)-2-methylpropionate]ethane (3DDMAT, Sigma-Aldrich, 98%), pentaerythritol tetrakis[2-(dodecylthiocarbonothioylthio)-2-methylpropionate] (4DDMAT, Sigma-Aldrich, 97%), basic aluminum oxide (Al_2O_3, Sigma-Aldrich, 99.9%) were used as received. poly (ethylene glycol) diacrylate (PEGDA, average $M_n = 250$, Sigma-Aldrich, > 92%) and ethyl acrylate (EA, Sigma-Aldrich, 99%) were deinhibited by percolation through basic alumina column before use.

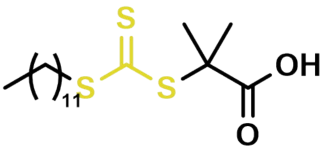

Figure S1. Structure of 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT).

Methods

Sample preparation for kinetics study

For kinetics study, 1.59 mg DTPA was weighed in a 4 mL glass vial, followed by addition of 85 μL EA and 155 μL PEGDA , followed by adding 180 μL stock solution of TEtOHA in PEGDA (30 mg/mL) and 80 μL stock solution of EB in PEGDA (1 mg/mL) to prepare a 500 μL resin in which molar ratio of [DTPA]:[EA]:[PEGDA]:[EB]:[TEtOHA] was 5:860:2004:0.1:40. The reaction mixture was then vortexed for 20 s prior to irradiation. Resins with different formulas were prepared in the same method while the amounts of reagents were varied to obtain desired ratios.

3D printing setup and procedures

A modified Anycubic Photon S 3D printer with green light source (530 nm, 0.32 $mWcm^{-2}$), custom printing platform (60 mm × 60 mm) and custom vat (65 mm × 65 mm × 20 mm) was utilized. The target printing objects were designed in Autodesk Fusion 360 and exported as .stl files. Printing parameters like layer thickness and exposure time were defined in Photon workshop and exported as .pws files for 3D printing. In all cases, layer thickness was 20 µm, off time was 2 s, bottom exposure time was 120 s, bottom layer was 2, Z lift distance was 2 mm, Z lift speed was 3 mm/s, Z retract speed was 3 mm For 3D printing, proper amount of resin was prepared in a 21 mL glass vial with the same method used for kinetics study.

Characterization

Attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy for monitoring polymerization kinetics.

A Bruker Alpha FT-IR was used for measurement in this study. In a typical experiment, 20 µL resin was dropped onto the ATR crystal plate followed by 16 scans with a resolution of 4 cm^{-1} in the range of 4000-500 cm^{-1} to obtain the spectrum for initial sample. Additional scans were conducted every 30 s of irradiation under green light ($\lambda_{\max}$ = 530 nm, I = 4.7 mW/cm^2) with a household lamp to obtain spectra at different time points. Vinyl bond conversions were calculated from the disappearance of the C=C bending peak at 812 cm^{-1} normalized to the C=O stretching peak at 1760 cm^{-1} as an internal standard. The conversion at different reaction times is given by **Equation 1**, where α_t is vinyl bond conversion after irradiation of t min, int_0 and std_0 refer to integration of peak in the range of 788-822 cm^{-1} and 1670-1800 cm^{-1} for unreacted sample, int_t and std_t refer these two values after irradiation of t min. For 3D printed samples, the samples were ground into fine powder for FTIR measurement. Double bond conversions were calculated in the same way above. All measurements were performed in duplicate.

$$\alpha_t = 1 - (int_t/std_t)/(int_0/std_0) \qquad \text{(Eq. 1)}$$

UV-Vis spectroscopy for comparing residual of EB in printed objects

UV−Vis spectroscopy spectra were recorded using a CARY series spectrophotometer. All measurements were obtained by placing the printed rectangular prism (40 mm × 8 mm × 2 mm) in a 1 cm × 1 cm plastic cuvette. The spectra were baseline corrected against the empty cuvette.

Dynamic mechanical analysis (DMA)

A TA Q800 dynamic mechanical analyzer equipped with liquid nitrogen gas cooling accessory (GCA) was used to conduct DMA experiments. The samples were measured with digital calipers to obtain their dimensions, placed in the calibrated single cantilever clamp, and fixed with a torque wrench operated at a force of 3 in lb. All experiments were conducted using the fowling method: equilibration at -20 °C, isothermal for 3 min, temperature ramped to 100 °C at rate of 2 °C/min, constant frequency of 1Hz and displacement of 30 µm. Storage modulus at 20 °C was used as standard for comparison. Glass transition temperature was determined using the temperature at the peak of the *Tan δ* curve.

Single-edge-notch bending (SENB) test for toughness study

ASTM D5045-14 was applied as the standard method for the plane-strain fracture toughness study. The SENB specimen was designed to have thickness (B) = 4 mm, width (W) = 2B = 8 mm and length (L) = 4.4 W = 35.2 mm. All samples were 3D printed with layers perpendicular to the direction of thickness, with a layer thickness of 20 µm and layer cure time (t_c) of 60 s. For each resin, three notch samples were printed at once to provide triplicate samples. Afterwards, printed samples were intentionally cut with a razor to create a weak point and the dimension as well as crack length (a) were measured with digital calipers. An Instron 3369 Bluehill universal testing machine was used to perform the 3-point bending test with support span of 20 mm. All tests were conducted using a crosshead rate of 10 mm/min under room temperature (20 °C). The critical-stress-intensity factor (K_{Ic}) was calculated using **Equation 2** and **Equation 3**, Where P_Q is maximum load in force-displacement curve, B is measured specimen thickness, W is measured specimen width, a is measured crack length and x is a/W.

$$K_{Ic} = (P_Q/BW^{\frac{1}{2}})f(x) \tag{Eq. 2}$$

$$f(x) = \frac{(2+x)\left(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4\right)}{(1-x)^{\frac{3}{2}}} \tag{Eq. 3}$$

Scanning electron microscopy (SEM)

The morphology of the fracture surface of selected SENB samples were studied via scanning electron microscopy (SEM). Samples were set on a double 90° angled stub using conductive type and coated with 15 nm golden nanoparticles utilizing Quorum Q3000T sputter coater. Hitachi TM4000Plus was used to capture the image of fracture surface. An accelerating voltage of 15 kV, standard vacuum and BSE detector were applied to capture 300× images of fracture surface for different samples.

Additional data

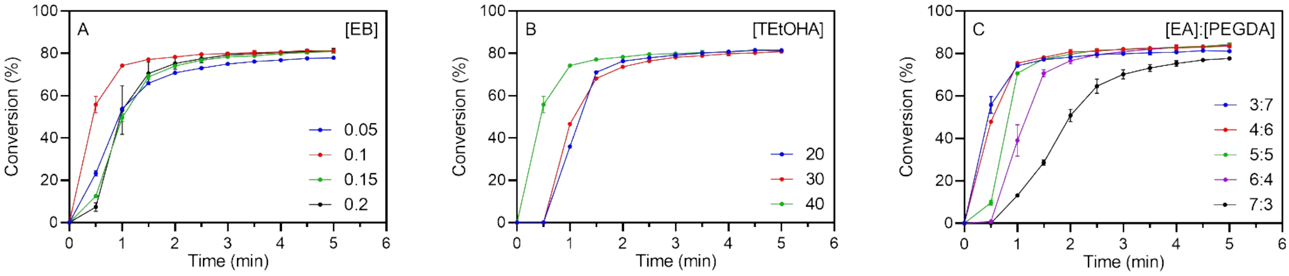

Figure S2. Optimization of resin formulations. A) Effect of ratio of EB on kinetics using [F1]:[EA]:[PEGDA]:[TEtOHA] = 5:860:2004:40 and [EB] = 0.05, 0.1, 0.15, 0.2. B) Effect of ratio of TEtOHA on kinetics using [F1]:[EA]:[PEGDA]:[EB] = 5:860:2004:0.1 and [TEtOHA] = 20, 30, 40. C) Effect of ratio of EA:PEGDA on kinetics using [F1]:[EB]:[TEtOHA] = 5:0.1:40 and [EA]:[PEGDA] = 3:7, 4:6, 5:5, 6:4, 7:3. *Note: Vinyl conversion at a time was determined using ATR-FTIR under 4.7 mWcm*$^{-2}$*green light (*λ_{max} *=530 nm).*

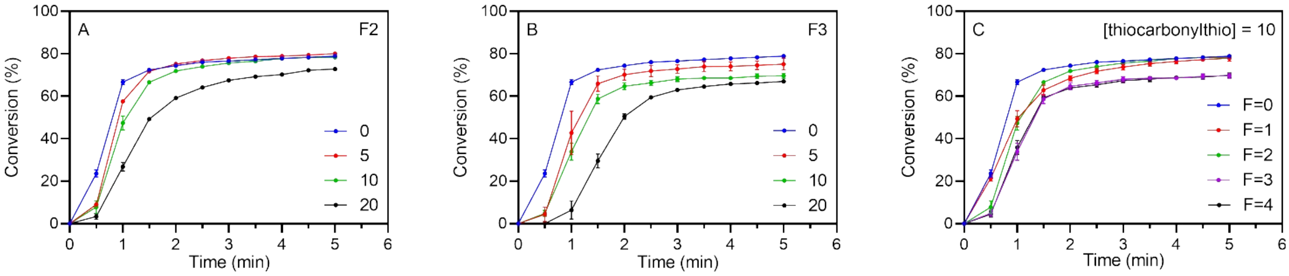

Figure S3. Effects of multi-arm RAFT agents on polymerization rate. A) Effect of ratio of F2. [EA]:[PEGDA]:[EB][TEtOHA] = 860:2004:0.1:40 using [thiocarbonylthio] = 0, 5, 10, 20. B) Effect of ratio of F3 using [EA]:[PEGDA]:[EB][TEtOHA] = 860:2004:0.1:40 and [thiocarbonylthio] = 0, 5, 10, 20. C) Comparison between different RAFT agents using [thiocarbonylthio]:[EA]:[PEGDA]:[EB]:[TEtOHA] = 5:860:2004:0.1:40. *Note: Vinyl conversion at a time was determined using ATR-FTIR under 4.7 mWcm*$^{-2}$ *green light (*λ_{max} *= 530 nm).*

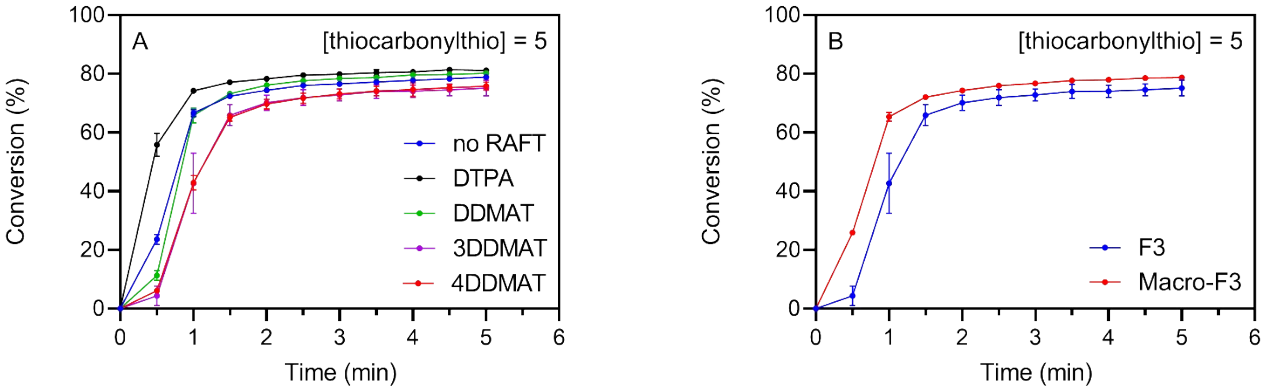

Figure S4. Effect of functionality (F) and leaving group (R) on polymerization rate. A) Comparison between DDMAT (F = 1, tertiary R group), DTPA (F = 1, secondary R group), 3DDMAT and 4DDMAT (F = 3 and 4, tertiary R group) using [thiocarbonylthio]:[EA]:[PEGDA]:[EB]:[TEtOHA] = 5:860:2004:0.1:40. B) Comparison between RAFT agent F3 (tertiary R group) and macro-F3 (secondary R group) using [thiocarbonylthio]:[EA]:[PEGDA]:[EB]:[TEtOHA] = 5:860:2004:0.1:40. *Note: Vinyl conversion at a time was determined using ATR-FTIR under 4.7 mWcm*$^{-2}$*green light* (λ_{max} = 530 nm)*.*

Table S1. Summary of kinetics study with different RAFT agents. [a]

RAFT agent	[thiocarbonylthio]	$\alpha_{0.5min}$ (%)	α_{1min} (%)	α_{5min} (%)
No RAFT	0	23	67	79
DTPA	5	55	74	81
DTPA	10	21	49	78
DTPA	15	7	22	72
DTPA	20	7	22	69
2DTBA	5	9	58	80
2DTBA	10	8	47	78
2DTBA	20	3	27	73
DDMAT	5	11	66	80
3DDMAT	5	5	43	75
3DDMAT	10	5	34	70
3DDMAT	20	0	6	67
Macro-3DDMAT	5	26	65	78
4DDMAT	5	6	43	76
4DDMAT	10	4	36	70
4DDMAT	20	0	8	70

[a] Conditions: [EA]:[PEGDA]:[EB]:[TEtOHA] = 5:860:2004:0.1:40 for all formulas. Vinyl conversion at a time was determined using ATR-FTIR under 4.7 mWcm^{-2} green light (λ_{max} = 530 nm).

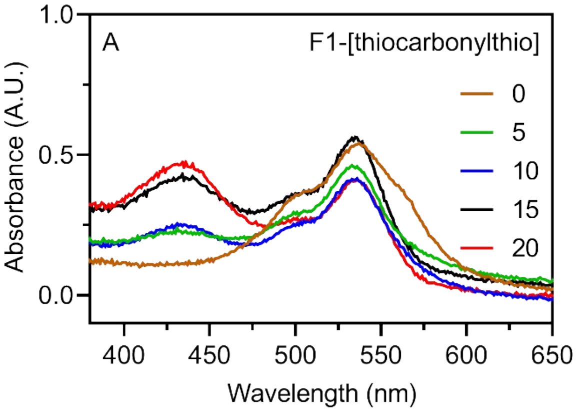

Figure S5. UV-Vis spectrum of printed rectangular prism (40 mm × 8 mm × 2 mm). A) Effect of ratio of F1 on Uv-Vis spectrum using [EA]:[PEGDA]:[EB]:[TEtOHA] = 860:2004:0.1:40 and [thiocarbonylthio] = 0, 5, 10 ,15, 20. B) Effect of functionality of RAFT agent on Uv-Vis spectrum using [thiocarbonylthio]:[EA]:[PEGDA]:[EB]:[TEtOHA] = 5 : 860 : 2004 : 0.1 : 40. *Note: All samples were printed under 0.32 mWcm^{-2} green light (λ_{max} = 530 nm) with t_c of 60s and layer thickness (T_{la}) of 20 µm.*

Figure S6. Resolution study of developed photocurable resin. A) Designed model for resolution test. B) Top view of printed resolution test model. C) Side view of printed resolution test model. *Note: The model was printed under 0.32 mWcm^{-2} green light (λ_{max} = 530 nm) with t_c of 30s and layer thickness (T_{la}) of 20 µm. using [F1]:[EA]:[PEGDA]:[EB]:[TEtOHA] = 5:860:2004:0.1:40.*

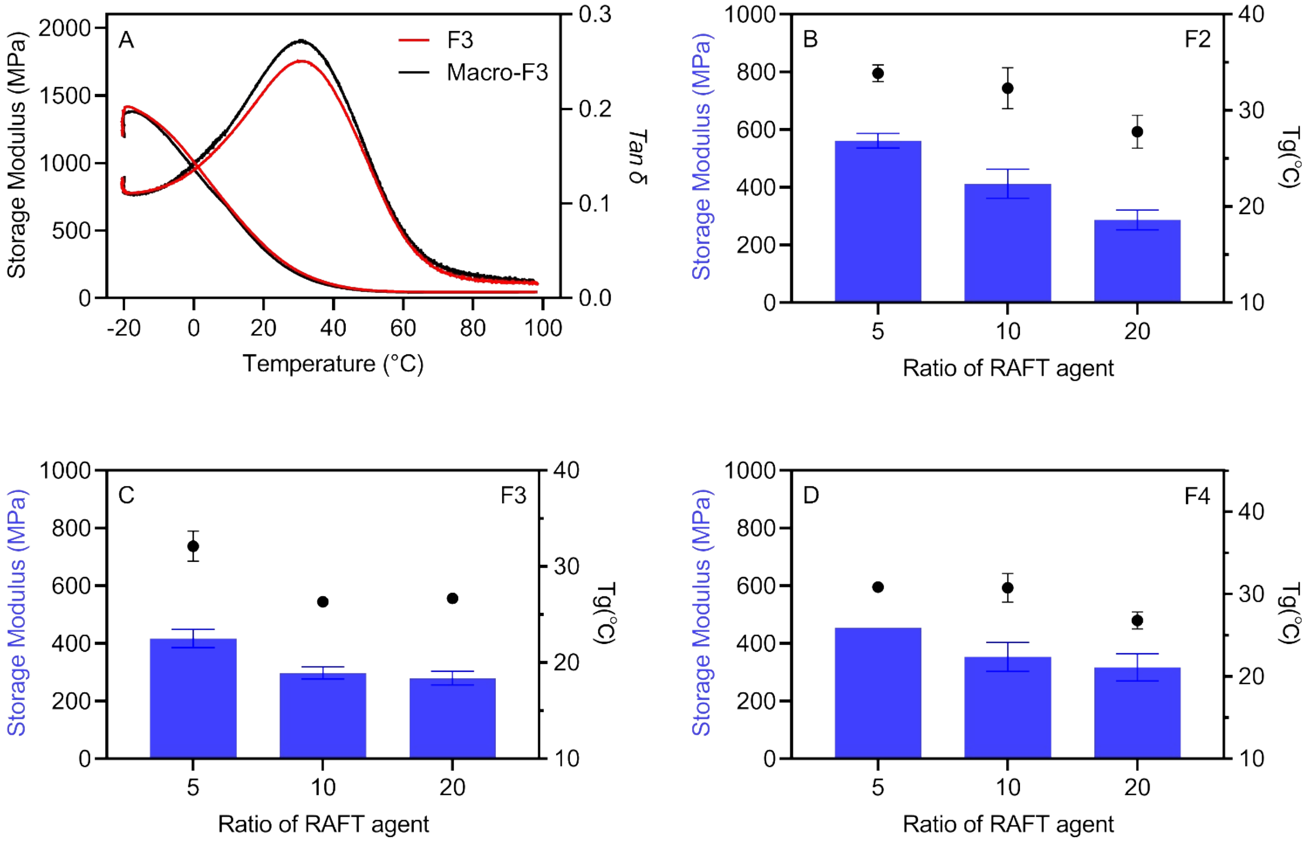

Figure S7. DMA study of 3D printed materials with multifunctional RAFT agents in varied concentrations. A) Comparison between F3 and macro-F3 in the range of -20 °C to 100 °C using [thiocarbonylthio]:[EB] = 5:0.1 and t_c = 60 s. B) $G'_{20°C}$ and T_g of 3D printed objects with F2 using [thiocarbonylthio]:[EB] = 5:0.1, 10:0.1, 20:0.1 and t_c = 60 s. C) $G'_{20°C}$ and T_g of 3D printed objects with F3 using [thiocarbonylthio]:[EB] = 5:0.1, 10:0.1, 20:0.1 and t_c = 80 s. D) $G'_{20°C}$ and T_g of 3D printed objects with F4 using [thiocarbonylthio]:[EB] = 5:0.1, 10:0.1, 20:0.1 and t_c = 80 s. *Note: Samples were printed under 0.32 mW/cm^2 green light (λ_{max} = 530 nm) with layer thickness (T_{la}) of 20 μm using [EA]:[PEGDA]:[EB]:[TEtOHA] = 860:2004:0.1:40.*

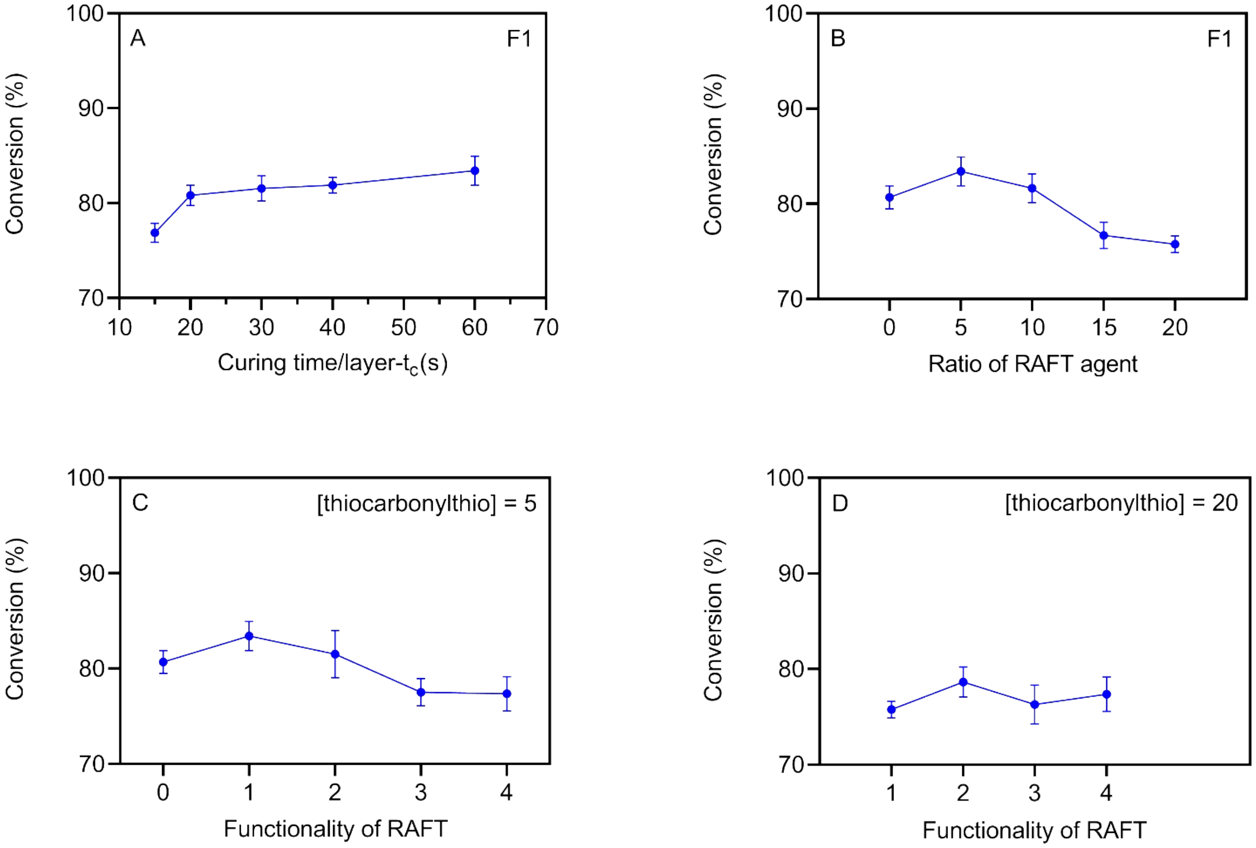

Figure S8. Conversion study of 3D printed objects. A) Effect of curing time/layer using t_c=10, 15, 20, 30, 40, 60 s and [F1]:[EB] = 5:0.1. B) Effect of concentration of F1 using [F1]:[EB] = 0:0.1, 5:0.1, 10:0.1, 15:0.1, 20:0.1 and t_c = 60 s. C) Effect of functionality of RAFT agents using [thiocarbonylthio]:[EB] = 5:0.1 for F1-F4, [thiocarbonylthio]:[EB] = 0:0.1 for F0 and t_c = 60 s.D) Effect of functionality of RAFT agents using [thiocarbonylthio]:[EB] = 20:0.1 for F1-F4, [thiocarbonylthio]:[EB] = 0:0.1 for F0 and t_c = 80 s. *Note: Samples were printed under 0.32 mW/cm^2 green light (λ_{max} = 530 nm) with layer thickness (T_{la}) of 20 µm using [EA]:[PEGDA]:[EB]:[TEtOHA] = 860:2004:0.1:40. Vinyl conversion was determined using ATR-FTIR.*