

†Electronic Supplementary Information (ESI)

One-pot blue-light triggered tough interpenetrating polymeric network (IPN) using CuAAC and methacrylate reactions

Abhishek U. Shete^a and Christopher J. Kloxin^{*ab}

^a Department of Materials Science and Engineering, University of Delaware, 201 Du Pont Hall, Newark, DE 19716, USA

^b Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, DE 19716, USA

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Experimental Methods

Monomer Synthesis:

The azide (monomer **1**, **Figure 1C**) and alkyne (monomer **2**, **Figure 1C**) monomers are synthesized as per previous procedures from reference no. 39.

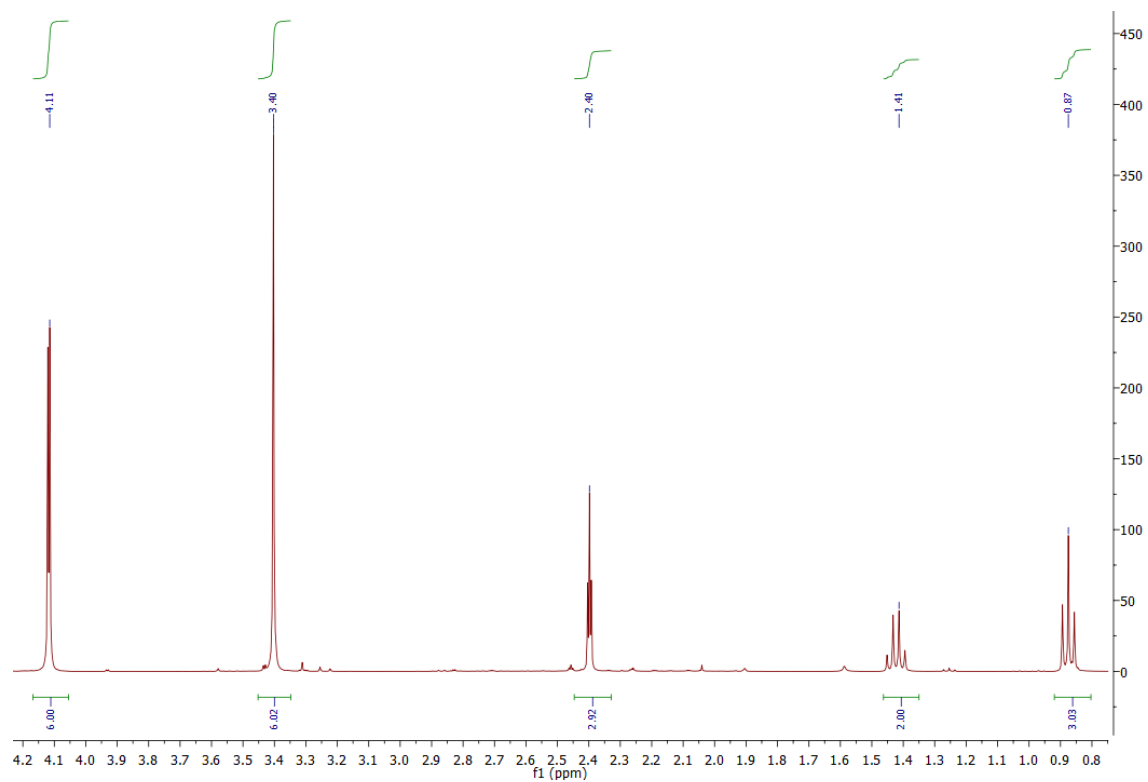
1-(prop-2-yn-1-yloxy)-2,2-bis((prop-2-yn-1-yloxy)methyl)butane (i.e., alkyne; monomer **2**): In a argon purged round bottom flask, a suspension of KOH (26.72 gm, 0.475 mol) in 150 mL DMSO was prepared and then 1,1,1-tris(hydroxymethyl)propane (7.49 gm, 0.66 mol) was added and the reaction mixture was cooled to 0 °C by placing it in an ice bath. Propargyl bromide (26 gm, 0.175 mol) was dropwise added to the cooled flask and the mixture was allowed to warm to the ambient temperature. It was then heated at 45 °C and the reaction was continued for 2-3 days. The resulting solution was diluted with water and extracted with diethyl ether followed by water washes, dried with Na₂SO₄, and purified by flash column chromatography (hexane/ethyl acetate) to produce a clear oil after evaporation of solvent (65% yield). The product was confirmed using ¹H NMR (Spectrum 1 below).

bis(6-azidohexyl)(1,3-phenylenebis(propane-2,2-diyl))dicarbamate (i.e., azide monomer **1**): To a argon purged round bottom flask, a solution of 1,3-bis(2-isocyanatopropan-2-yl)benzene (9.99 gm, 0.0409 mol) and dibutyltin dilaurate (15 drops) in THF (50 ml) was prepared and cooled to 0 °C by placing it in an ice bath. The 6-chloro-1-hexanol (11.7 g; 0.0860 mol) was added dropwise to the solution and the reaction was allowed to warm to room temperature and then heated to 45 °C for 5 hours. The solution was then diluted with excess THF and passed through silica plug. The product was dried and verified using NMR and further transferred to a round bottom containing a solution of sodium azide (11 gm, 0.169 mol) in DMF (350 ml). The reaction flask was connected to a reflux condenser and the reaction was stirred at 80 °C overnight. The product was extracted with ethyl acetate and water, dried with Na₂SO₄, purified by flash column chromatography (hexane/ethyl acetate), and dried to obtain a colorless oil (80% yield). The product was confirmed using ¹H NMR (Spectrum 2 below).

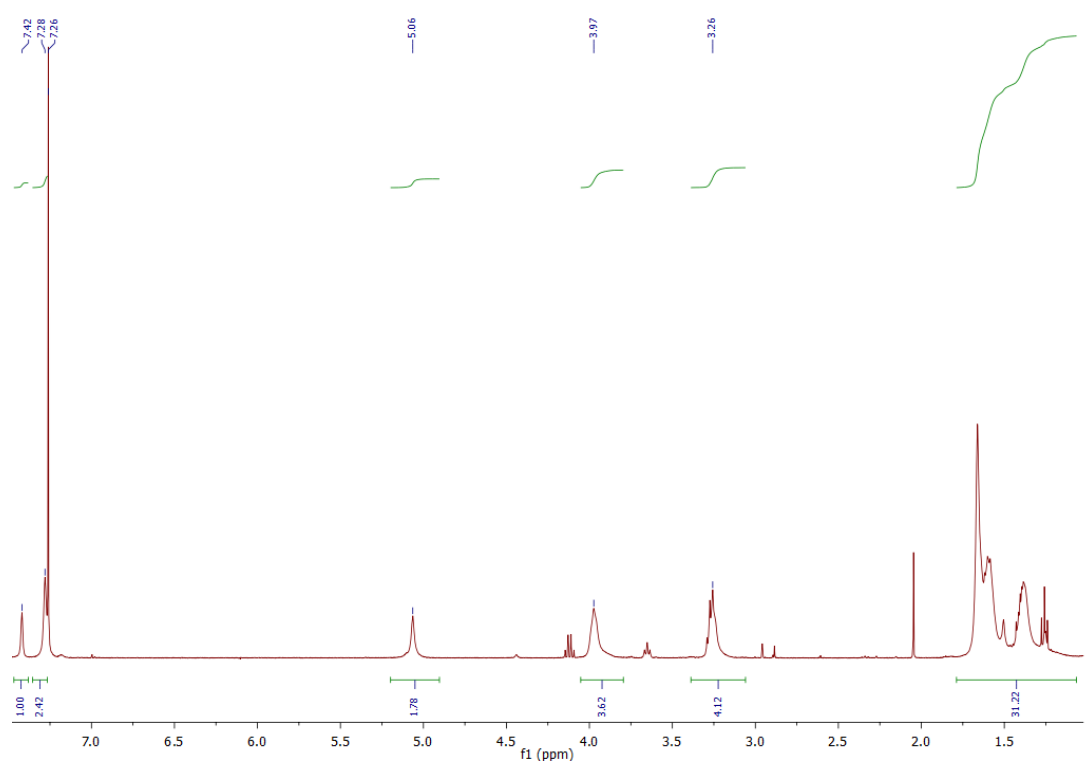
IPN Formulation:

Monomers **1** and **2** were added to a 20 mL vial such that the stoichiometric ratio of the azide:alkyne functional group were 1:1. The 1.5 wt% Cu complex (i.e., **3**) of total weight of CuAAC monomers is added to the same vial. 4-5 wt% methanol is used to solubilize the Cu complex, and is subsequently removed under vacuum (confirmed gravimetrically and by NMR analysis Spectrum 3). The methacrylate monomer (**4**) is added to the CuAAC monomer mixture in a 1:1 wt ratio for a 50-50 IPN. The photoinitiator, CQ (**5**) and tertiary amine (**6**), are added to the formulation (0.7 wt% CQ and 1.4 wt% tertiary amine of total monomer formulation), and the formulation is thoroughly mixed using DAC 150.1 FVZ-K Flacktek Speed Mixer for 5 minutes at 2000 rpm.

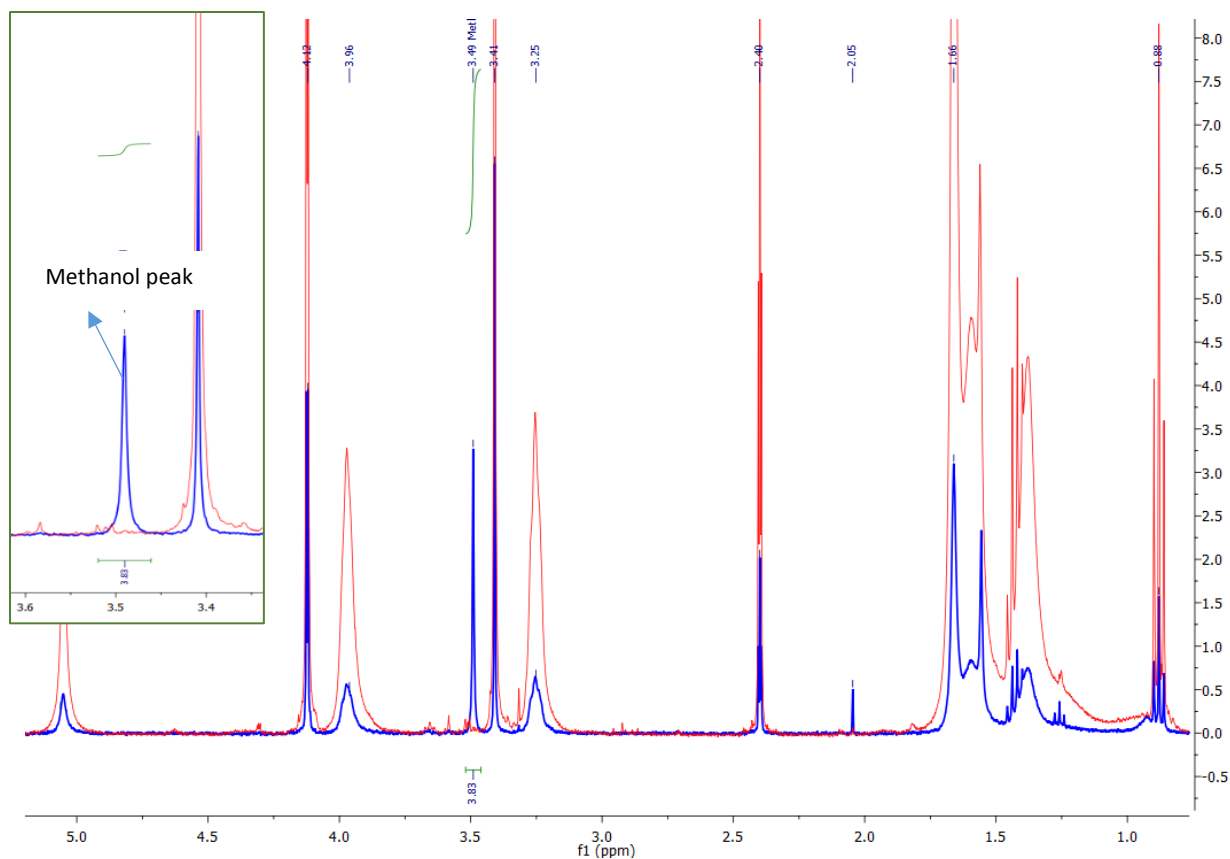
For the 100% Methacrylate formulation, monomer **4** is speed mixed with 0.7 wt% CQ and 1.4 wt% tertiary amine. For the 100% CuAAC formulation, monomers **1** and **2** are added in a 20 mL vial such that the stoichiometric ratio of the azide:alkyne functional group is 1:1. The 1.5 wt% Cu complex (i.e., **3**) of total weight of CuAAC monomers is added to the same vial and 4-5 wt% methanol is used to solubilize the Cu complex, which is subsequently removed under vacuum (confirmed gravimetrically). This monomer and the Cu mixture is then speed mixed with 0.7 wt% CQ and 1.4 wt% tertiary amine.



Spectrum 1. ^1H NMR using Bruker 400 MHz NMR machine (alkyne; monomer 2).



Spectrum 2. ^1H NMR using Bruker 400 MHz NMR machine (azide; monomer 1).



Spectrum 3. ^1H NMR using Bruker 400 MHz NMR machine for IPN monomer formulation with 4 wt% methanol (blue line) and after removal of methanol from IPN formulation under vacuum (red line). Inset shows the magnified version of methanol peak at 3.49 ppm completely disappearing.

IPN Preparation:

The solvent-free IPN formulation, as described before, is placed between glass slides separated by plastic spacers to control the thickness of the samples. The samples are irradiated using an OmniCure Series 2000 lamp which is equipped with a 200 Watt mercury arc bulb (Lumen Dynamics) and a waveguide to direct the output light that was filtered using a 470 nm (blue-light) band pass interference filter onto the sample. The time under irradiation depends on what type of test is being performed.

Near Infrared Spectroscopy (NIR):

A Nicolet iS50 FT-IR Spectrometer (ThermoFisher Scientific) is used to monitor the polymerization kinetics of IPN formation in real-time (under 470 nm blue-light irradiation). The spectrometer is equipped with a nitrogen cooled MCT detector. The spectra was collected over 16 scans s^{-1} with a 16 cm^{-1} resolution. The decrease in peak area of functional groups (alkyne groups ($6540\text{-}6460\text{ cm}^{-1}$) and vinyl groups ($6200\text{-}6140\text{ cm}^{-1}$)) provides the real-time conversion data for the two independent interwoven networks forming the 50-50 IPN.

Dynamic Mechanical Analysis (DMA): The thermo-mechanical data shown in **Fig. 3A** and **Fig. 3B** was collected using a Q800 DMA (TA Instruments) while heating the specimen from 20 °C to 150 °C at a heating rate of 3 °C min⁻¹. The samples were of 0.5 mm thickness. The DMA was run in dynamic (oscillatory) tension mode with a strain frequency of 1 Hz and a strain amplitude of 0.1%. The tan (δ) in **Fig. 3A** is ratio of the loss and storage modulus, the peak value of which we assign as the glass transition temperature (T_g). The elongation experiments in **Fig. 4A** are performed on a 0.07 mm thick films polymerized for 20 minutes under 470 nm blue-light. The test was performed in tension mode with a preload force of 0.1 N and initial strain of 0.5% and at the strain rate of 0.1% strain min⁻¹ until the sample breaks. The numerical integration of area under the stress-strain curve in **Fig. 4A** gives the tensile toughness of each material and is shown in **Fig. 4B**.¹

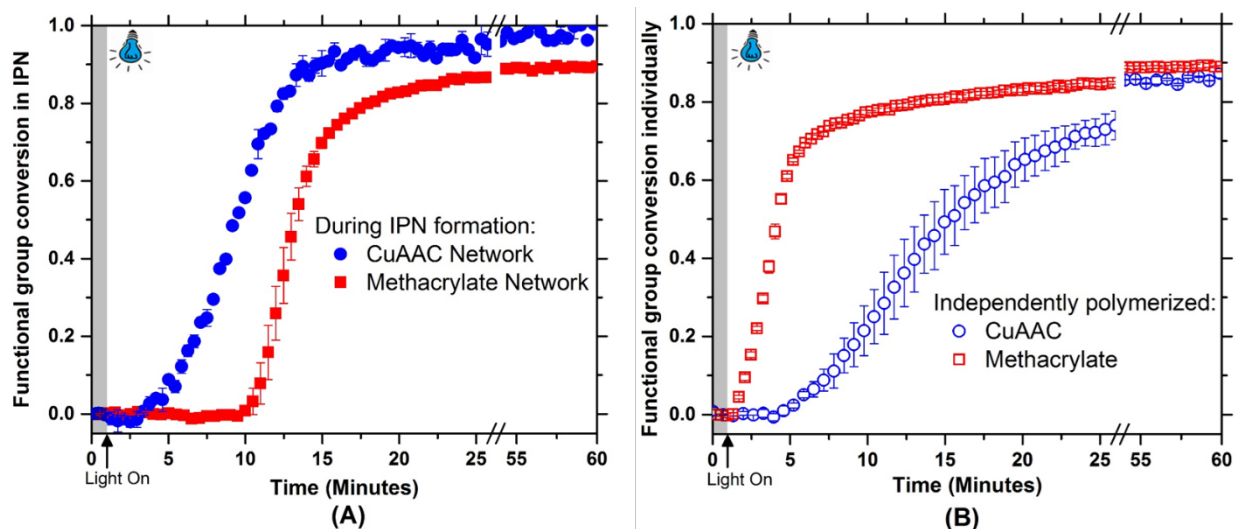


Fig. S1. Kinetics and sequence of polymerization in (A) one-pot IPN, and (B) separate polymerizations under 470 nm blue-light at 10 mW cm⁻¹ intensity.

Real-time NIR spectroscopy is utilized for monitoring conversion of CuAAC and methacrylate during photopolymerization in **(A)** bulk one-pot photo-IPN and **(B)** separate methacrylate and photo-CuAAC formulation. One-pot 50-50 IPN formulation in **(A)** is 50:50 (wt/wt) CuAAC: methacrylate component. The CuAAC component contains 1:1 azide: alkyne functional group ratio from monomers **(1)** and **(2)**, 1.5 wt% CuCl₂-PMDETA **(3)**, and the methacrylate component is tetraethylene glycol dimethacrylate **(4)**. The separate CuAAC network formulation in **(B)** contains 1.5 wt% Cu(II)-PMDETA **(3)**. All specimens contain constant photoinitiator concentration of 0.7 wt% CQ **(5)** and 1.4 wt% tertiary amine **(6)** of total formulation. The 0.5 mm thick samples are irradiated with blue-light of 470 nm wavelength under 10 mW cm⁻² intensity after 1 minute in dark marked by (■) shaded region, monitoring alkyne groups (6540-6460 cm⁻¹) for photo-CuAAC and vinyl groups (6200-6140 cm⁻¹) for methacrylate reaction.

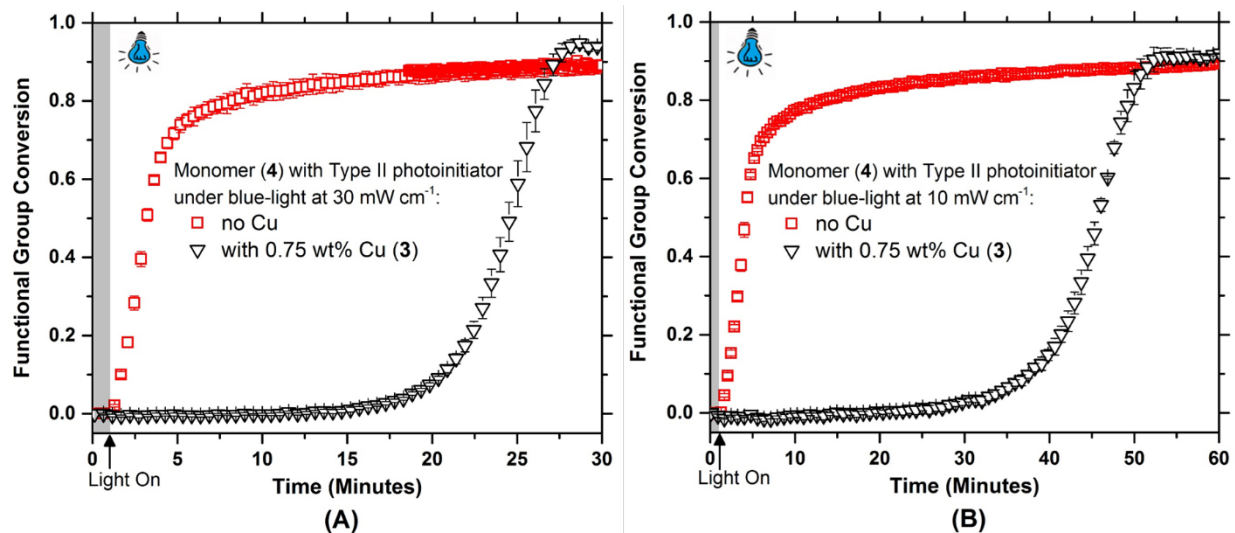


Fig. S2. Quenching in Norrish Type II initiated methacrylate polymerization in presence of Cu cation.

Real-time NIR spectroscopy is used to monitor the inhibition effect of the Norrish Type II photoinitiator on individual bulk methacrylate network polymerization of monomer tetraethylene glycol dimethacrylate (**4**) in presence of copper. Specifically, both the formulations contain 0.7 wt% of CQ (**5**) & 1.4 wt% of the tertiary amine (**6**), but one of the formulations contains 0.75 wt% of Cu(II)-PMDETA (**3**) (i.e., consistent with effective copper concentration in a 50-50 IPN). The 0.5 mm thick samples were irradiated with 470 nm blue-light at intensity **(A)** 30 mW cm^{-2} and **(B)** 10 mW cm^{-2} after 1 minute in dark, marked by (■) shaded region. The conversion is tracked by following the decrease in vinyl peak area over the $6200\text{-}6140 \text{ cm}^{-1}$ region in NIR. The observed inhibition time of ≈ 16 minutes in **(A)** and ≈ 32 minutes in **(B)** (denoted by- ▽) owes to the presence of Cu(II) which has been shown to quench the triplet state of the Type II photoinitiators due to their longer lifetime and has a high reactivity towards radical species. Upon depletion of Cu(II), the radicals on $\alpha\text{-C}'$ atom on tertiary amine become available for reaction with the methacrylate. The formulation without the copper has negligible inhibition as seen in both **(A)** and **(B)** (denoted by- □).

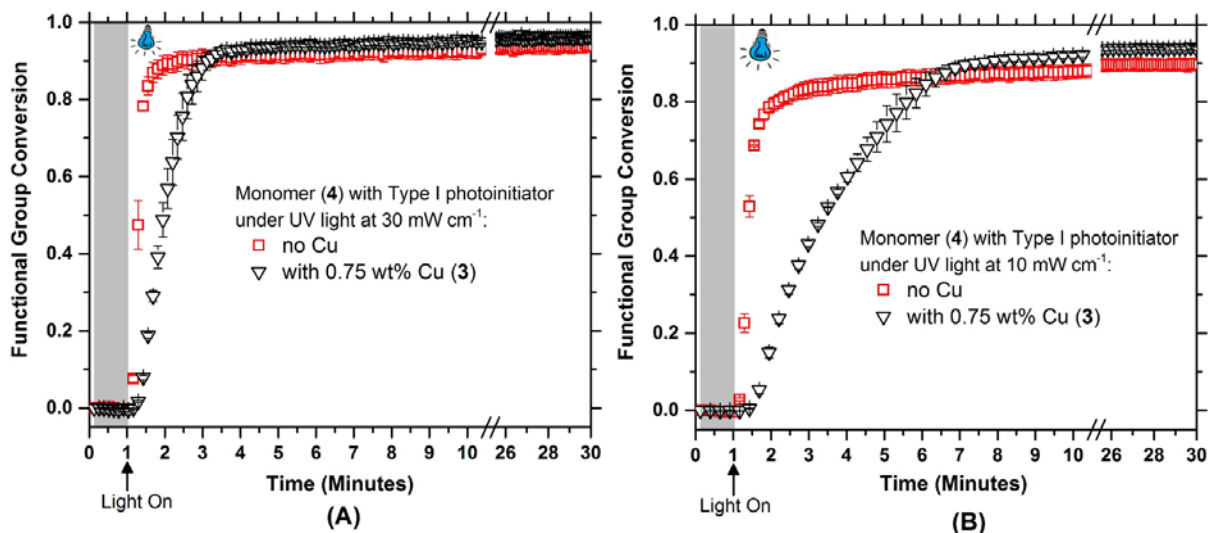


Fig. S3. Minimal inhibition in Norrish Type I initiated methacrylate polymerization in presence of Cu cation.

Real-time NIR spectroscopy is used to monitor the inhibition effect from Norrish Type I photoinitiator (Irgacure 819 in this case) on individual bulk methacrylate network polymerization from monomer tetraethylene glycol dimethacrylate (**4**) in presence of copper. Specifically, both formulations contain tetraethylene glycol dimethacrylate monomer (**4**), 1.0 wt% of **I-819** (commercially available Norrish Type I photoinitiator with high UV absorbance), but one of the formulation additionally contains 0.75 wt% of Cu(II)-PMDETA (**3**) (i.e., consistent with effective copper concentration in a 50-50 IPN). The 0.5 mm thick samples were irradiated with 365 nm UV-light of intensity **(A)** 30 mW cm^{-2} and **(B)** 10 mW cm^{-2} after 1 minute in dark, marked by (■) shaded region. The conversion is tracked by following the decrease in vinyl peak area over the $6200\text{-}6140 \text{ cm}^{-1}$ region in NIR. While retardation of the reaction is observed, there is negligible inhibition for the resin containing copper (denoted by-▽).

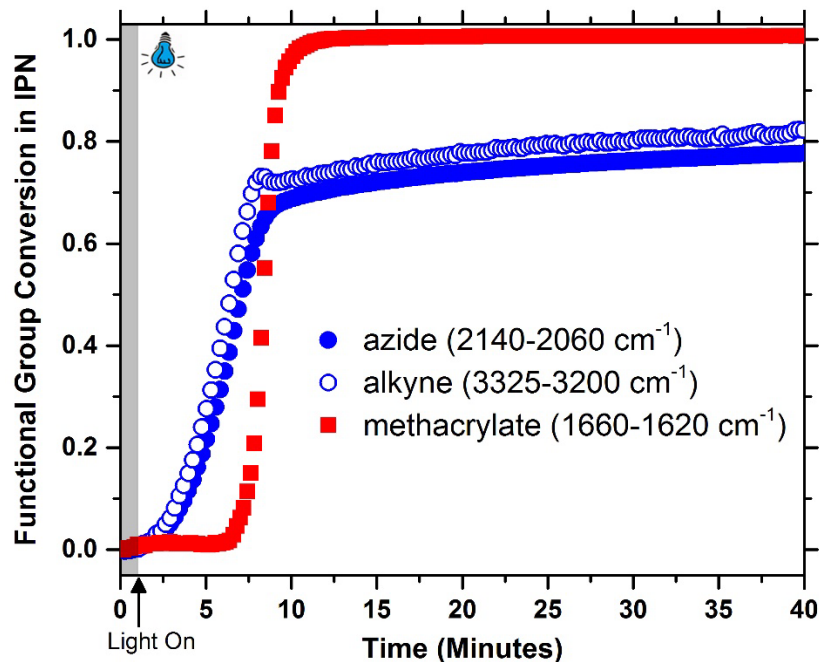


Fig. S4. Mid-IR spectroscopy showing the orthogonal nature of CuAAC and methacrylate polymerization in 50-50 IPN under ambient conditions.

Real-time mid-IR spectroscopy enables to monitor the conversion of all the functional groups involved in both polymerizations (i.e., azide, alkyne and methacrylates). The specimens contain 50:50 (wt/wt) CuAAC: Methacrylate monomers. The CuAAC component contains 1:1 azide: alkyne functional group ratio from monomers (1) and (2), 1.5 wt% Cu(II)-PMDETA (3), whereas the methacrylate component is tetraethylene glycol dimethacrylate (4). The specimen has 0.7 wt% of CQ (5) and 1.4 wt% tertiary amine (6) of total formulations. The 0.04 mm thick samples are irradiated with 470 nm blue-light at 30 mW cm⁻² intensity under ambient conditions after 1 minute in dark marked by (■) shaded region. The one-to-one conversion shows that the functional groups of azide and alkyne disappear at same rate, suggesting that the CuAAC and methacrylate polymerization are orthogonal under these reaction conditions.

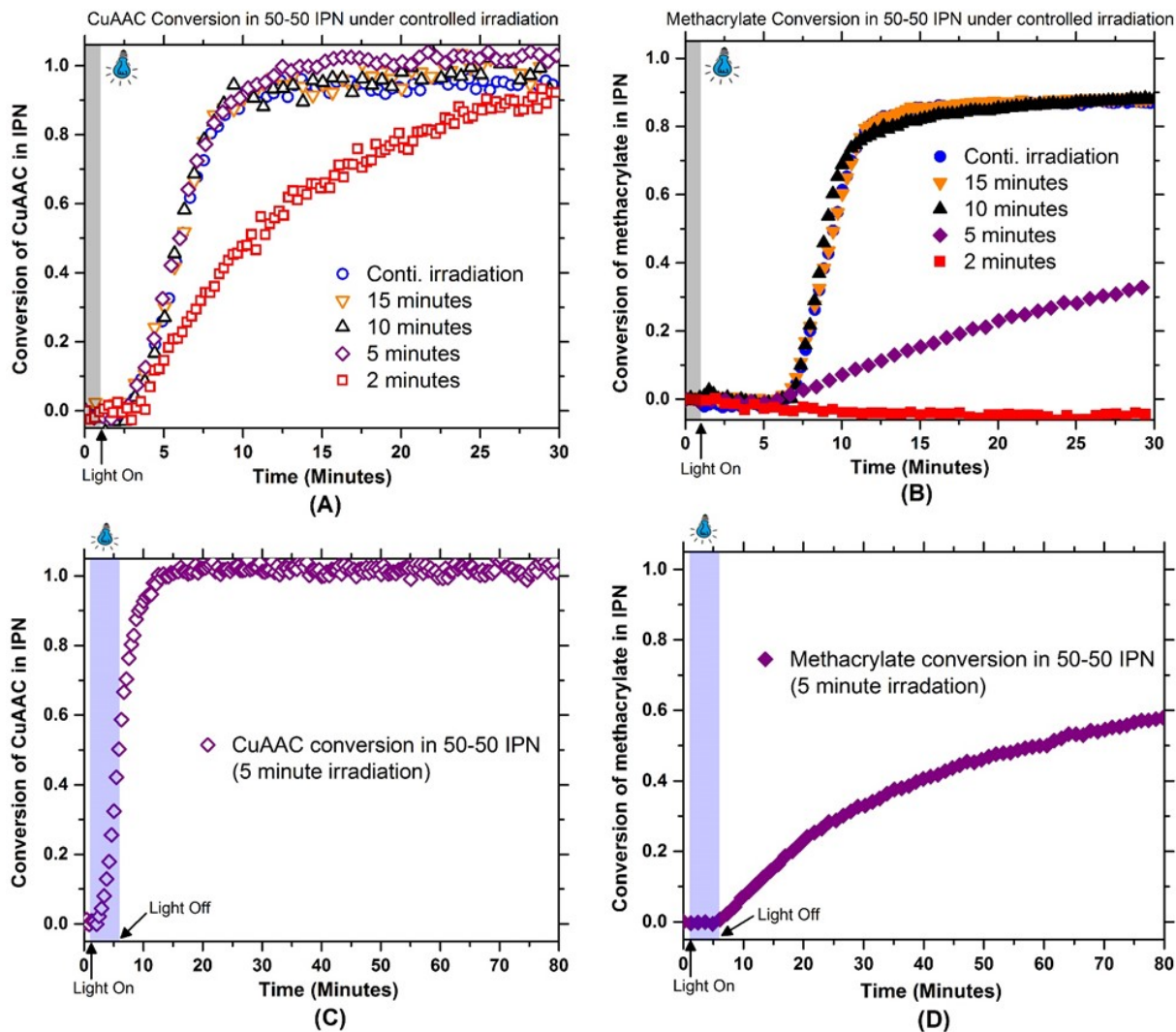


Fig. S5. Polymerization kinetics of 50-50 IPN under blue-light at 30 mW cm^{-1} intensity.

Real-time NIR spectroscopy is utilized for monitoring the conversion during IPN photopolymerization under 470 nm blue-light at 30 mW cm^{-1} intensity by monitoring alkyne groups ($6540\text{--}6460 \text{ cm}^{-1}$) for photo-CuAAC and vinyl groups ($6200\text{--}6140 \text{ cm}^{-1}$) for methacrylate reaction. One-pot 50-50 IPN formulation in all specimens is 50:50 (wt/wt) CuAAC: methacrylate component. The CuAAC component contains 1:1 azide: alkyne functional group ratio from monomers (1) and (2), 1.5 wt% $\text{CuCl}_2\text{-PMDETA}$ (3) and the methacrylate component is tetraethylene glycol dimethacrylate (4). The photoinitiator content is 0.7 wt% CQ (5) and 1.4 wt% tertiary amine (6) of total formulation. The conversion of CuAAC and the methacrylate are shown in (A) and (B) as a function of irradiation time. The irradiation of IPN samples for greater than 10 minutes exhibits comparable chemical kinetics. In the samples irradiated for only 5 minutes, marked by shaded region (■) in figures (C) and (D), the amount of Cu(II) reduced to Cu(I) is sufficient to catalyze the CuAAC reaction (C) and exhibits similar kinetic behavior as seen in (A). While the generated radicals are insufficient to initiate the methacrylate polymerization, the reduction of Cu(II) to Cu(I) presumably

facilitates the polymerization through a living radical polymerization mechanism. The steady increase in methacrylate conversion in **(D)** depicts the redox nature of copper oxidation states activated from Type II photoinitiation.^{2,3} Geng et.al.⁴ have seen a similar behavior in case of linear polymers, and Xu et.al.⁵ have observed similar behavior in the case of crosslinked networks.

References

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