SUPPORTING INFORMATION

Volumetric photopolymerization confinement through dual-wavelength photoinitiation and photoinhibition

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Experimental Section

Materials: (±)-Camphorquinone (CQ; Esstech Inc., Essington, PA) was used as a visible light-active photoinitiator in conjunction with ethyl 4-(dimethylamino)benzoate (EDAB; Esstech) as a coinitiator. Butyl nitrite (BN; Sigma-Aldrich, St. Louis, MO) was employed as a UV-active photoinhibitor. Triethylene glycol dimethacrylate (TEGDMA; Esstech) and bisphenol A glycidyl methacrylate (bisGMA; Esstech) were formulated in a mixture as a 50/50 ratio by mass. Trimethylolpropane trimethacrylate (TMPTMA; Esstech), trimethylolpropane triacrylate (TMPTA; Alfa Aesar, Haverhill, MA), and bisphenol A ethoxylate diacrylate, EO/phenol 4.0 (BPAEDA, Sigma-Aldrich) were all used without comonomers. All chemicals were used as received without further purification.

Light sources and intensity measurement: Blue light was provided by a collimated, LED-based illumination source (Thorlabs M470L3-C1) with an emittance centered at 470 nm (FWHM 25 nm), used in combination with a current-adjustable LED driver (Thorlabs LEDD1B) for intensity control. Near-UV light was provided by a UV spot curing system (Omnicure LX500) equipped with an Omnicure LED MAX head with an emittance centered at 365 nm. Irradiation intensities were measured with an International Light IL1400A radiometer equipped with a UV-visible GaAsP detector (model SEL005), a 10× attenuation neutral density filter (model QNDS1), and a quartz diffuser (model W).

UV-Vis spectrophotometry: UV-visible spectrophotometry was performed using an Agilent Technologies Cary 60 UV–Vis spectrophotometer. Spectra were collected from 200 to 800 nm with 1 nm spacing on solutions using a 1 mm path length quartz cuvette in the dark.

FTIR spectroscopy: Resin formulations were introduced between NaCl salt crystals (International Crystal Laboratories) separated by spacers (13 µm thick) to maintain constant sample thickness during polymerization. Each sample was placed in a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a horizontal transmission accessory, as described previously, and spectra were collected from 650 to 4000 cm^{-1} at a rate of 2 per second. The functional group conversion upon irradiation was determined by monitoring the disappearance of the peak area centered at 1635 cm^{-1} for the methacrylate stretch, and 1636 cm^{-1} for the acrylate stretch. The sample thicknesses for the formulations were chosen to ensure that the functional group peaks remained within the linear regime of the instrument detector while affording good signal to noise and maintaining optically thin and isothermal polymerization conditions. Resins were formulated containing 0.2 wt% CQ and 0.5 wt% EDAB as the photoinitiator. The BN photoinhibitor concentration and irradiation intensities are as indicated in the figure insets. All conversion samples were formulated and measured in triplicate, and the presented data represent the mean and standard error of three runs.

Photopatterning: The 2D photopatterning was carried out using a formulation of 1.0 wt% CQ, 0.5 wt% EDAB, and 1.0 wt% BN in TMPTA. The resin was introduced between 2 glass slides, spaced

1.0 mm apart. The bottom slide was acrylic coated to improve adhesion, while the top slide was treated with Rain-X water repellent as a release agent to prevent adhesion. The photomask was placed on top, and the formulation was irradiated concurrently with 470 nm light at 100 mW/cm^2 from the bottom, and with 365 nm at 30 mW/cm^2 from the top for 30 seconds. The top glass slide was then removed and the sample was rinsed thoroughly with methanol to remove excess monomer. Reducing the concentration of CQ and BN to 0.2% each, allowed for inhibition through up to 5 mm of resin, while maintaining adequate curing.

The 3D photopatterning was carried out using a formulation of 0.2 wt% CQ, 0.5 wt% EDAB, and 0.2 wt% BN in TMPTA. The resin was introduced to a quartz fluorescence cuvette with a path length of 2 mm, and a width of 10 mm, and the cuvette was treated with Rain-X. Triangular photomasks were placed on the 2 mm wide edge, while circular photomasks were placed on the perpendicular side. The resin was irradiated from 2 sides by blue light at 250 mW/cm^2, and perpendicular from 1 side by UV light at 120 mW/cm^2 for 20 seconds. The cured structure was removed from the cuvette and rinsed with methanol to remove any unreacted monomer.

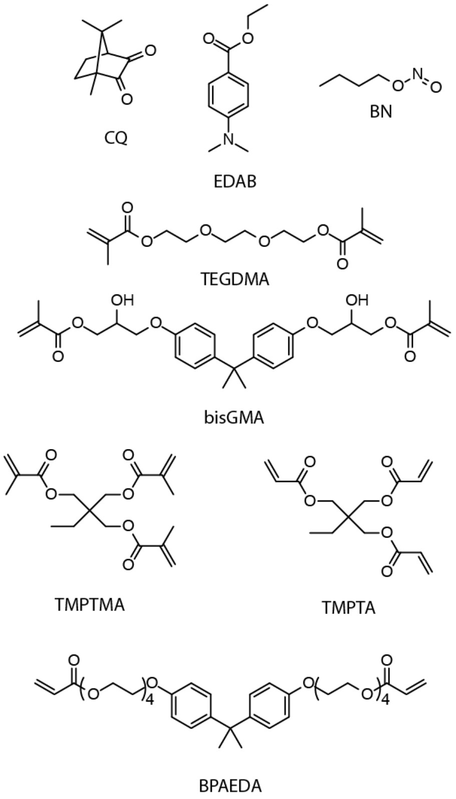

Figure S1. Structures and abbreviations of chemicals used in this study.

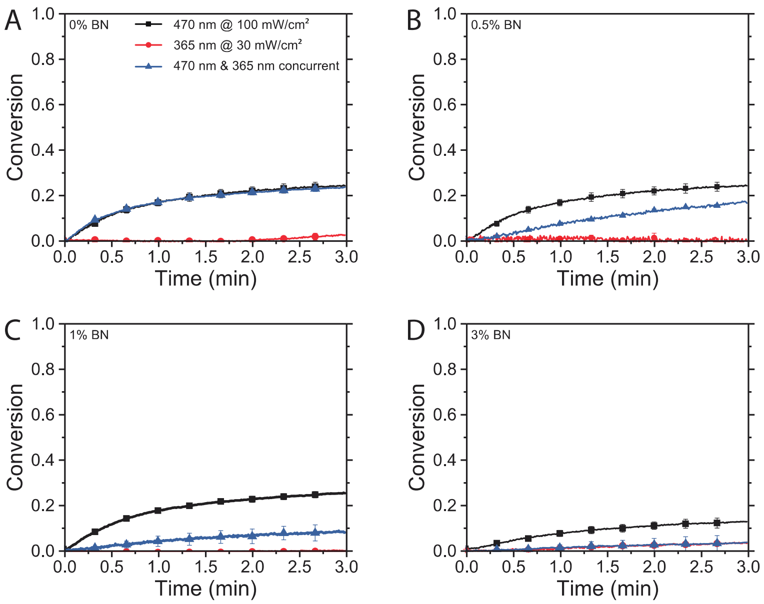

Figure S2. Methacrylate conversion versus time for the photopolymerization of TMPTMA resins formulated with 0.2 wt% CQ/0.5 wt% EDAB and (A) 0 wt% BN, (B) 0.5 wt% BN, (C) 1.0 wt% BN, and (D) 3.0 wt% BN. Formulations were irradiated with 470 nm light at an intensity of 100 mW/cm^2 (black, squares), 365 nm light at an intensity of 30 mW/cm^2 (red, circles), or concurrent 470 nm and 365 nm light at intensities of 100 and 30 mW/cm^2, respectively (blue, triangles).

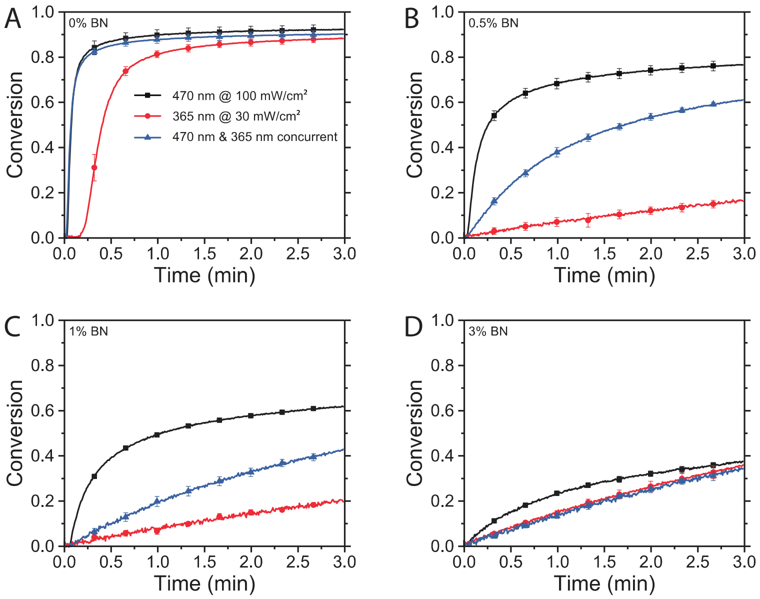

Figure S3. Acrylate conversion versus time for the photopolymerization of BPAEDA resins formulated with 0.2 wt% CQ/0.5 wt% EDAB and (A) 0 wt% BN, (B) 0.5 wt% BN, (C) 1.0 wt% BN, and (D) 3.0 wt% BN. Formulations were irradiated with 470 nm light at an intensity of 100 mW/cm^2 (black, squares), 365 nm light at an intensity of 30 mW/cm^2 (red, circles), or concurrent 470 nm and 365 nm light at intensities of 100 and 30 mW/cm^2, respectively (blue, triangles).

Table S1. Maximum C=C conversion rates for the photopolymerization of bisGMA/TEGDMA resins formulated with 0.2 wt% CQ/0.5 wt% EDAB and varying concentrations of BN as shown.

Irradiation conditions	C=C conversion rate @ 0 wt% BN (M.s^{-1})	C=C conversion rate @ 0.5 wt% BN (M.s^{-1})	C=C conversion rate @ 1.0 wt% BN (M.s^{-1})	C=C conversion rate @ 3.0 wt% BN (M.s^{-1})
Blue (470 nm, 100 mW/cm^2)	0.156±0.005	0.0620±0.0139	0.0033±0.0018	-0.0003±0.0012
Near UV (365 nm, 30 mW/cm^2)	0.0191±0.0004	0.0008±0.0002	0.0007±0.0002	0.0017±0.0005
Concurrent blue (470 nm, 100 mW/cm^2) & near UV (365 nm, 30 mW/cm^2)	0.145±0.003	0.0075±0.0008	0.0010±0.0002	0.0011±0.0013

Table S2. Maximum C=C conversion rates for the photopolymerization of TMPTA resins formulated with 0.2 wt% CQ/0.5 wt% EDAB and varying concentrations of BN as shown.

Irradiation conditions	C=C conversion rate @ 0 wt% BN (M.s^{-1})	C=C conversion rate @ 0.5 wt% BN (M.s^{-1})	C=C conversion rate @ 1.0 wt% BN (M.s^{-1})	C=C conversion rate @ 3.0 wt% BN (M.s^{-1})
Blue (470 nm, 100 mW/cm^2)	0.583±0.077	0.590±0.004	0.534±0.086	0.194±0.053
Near UV (365 nm, 30 mW/cm^2)	0.0546±0.0091	0.0147±0.0670	0.0024±0.0002	0.0057±0.0006
Concurrent blue (470 nm, 100 mW/cm^2) & near UV (365 nm, 30 mW/cm^2)	0.585±0.067	0.139±0.019	0.0274±0.0068	0.0060±0.0008

Table S3. Maximum C=C conversion rates for the photopolymerization of TMPTMA resins formulated with 0.2 wt% CQ/0.5 wt% EDAB and varying concentrations of BN as shown.

Irradiation conditions	C=C conversion rate @ 0 wt% BN (M.s^{-1})	C=C conversion rate @ 0.5 wt% BN (M.s^{-1})	C=C conversion rate @ 1.0 wt% BN (M.s^{-1})	C=C conversion rate @ 3.0 wt% BN (M.s^{-1})
Blue (470 nm, 100 mW/cm^2)	0.0224±0.0040	0.0278±0.0025	0.0285±0.0024	0.0128±0.0020
Near UV (365 nm, 30 mW/cm^2)	0.0010±0.0012	0.0001±0.0014	0.0001±0.0012	0.0022±0.0008
Concurrent blue (470 nm, 100 mW/cm^2) & near UV (365 nm, 30 mW/cm^2)	0.0155±0.0023	0.0093±0.0002	0.0047±0.0023	0.0028±0.0025

Table S4. Maximum C=C conversion rates for the photopolymerization of BPAEDA resins formulated with 0.2 wt% CQ/0.5 wt% EDAB and varying concentrations of BN as shown.

Irradiation conditions	C=C conversion rate @ 0 wt% BN (M.s^{-1})	C=C conversion rate @ 0.5 wt% BN (M.s^{-1})	C=C conversion rate @ 1.0 wt% BN (M.s^{-1})	C=C conversion rate @ 3.0 wt% BN (M.s^{-1})
Blue (470 nm, 100 mW/cm^2)	0.653±0.033	0.229±0.006	0.0951±0.0060	0.0167±0.0024
Near UV (365 nm, 30 mW/cm^2)	0.106±0.014	0.0051±0.0023	0.0042±0.0006	0.0073±0.0010
Concurrent blue (470 nm, 100 mW/cm^2) & near UV (365 nm, 30 mW/cm^2)	0.675±0.020	0.0287±0.0015	0.0106±0.0004	0.0072±0.0010

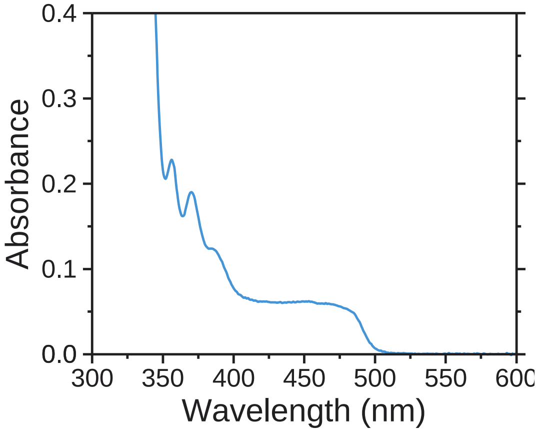

Figure S4. UV-visible absorbance spectrum of TMPTA formulated with 0.2 wt% CQ, 0.5 wt% EDAB, and 0.2 wt% BN.