

**Supplementary Information: Visible and Sunlight driven
RAFT Photopolymerization Accelerated by Amines: Kinetics
and Mechanism.**

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Supplementary Data

UV-Vis Data for CTAs

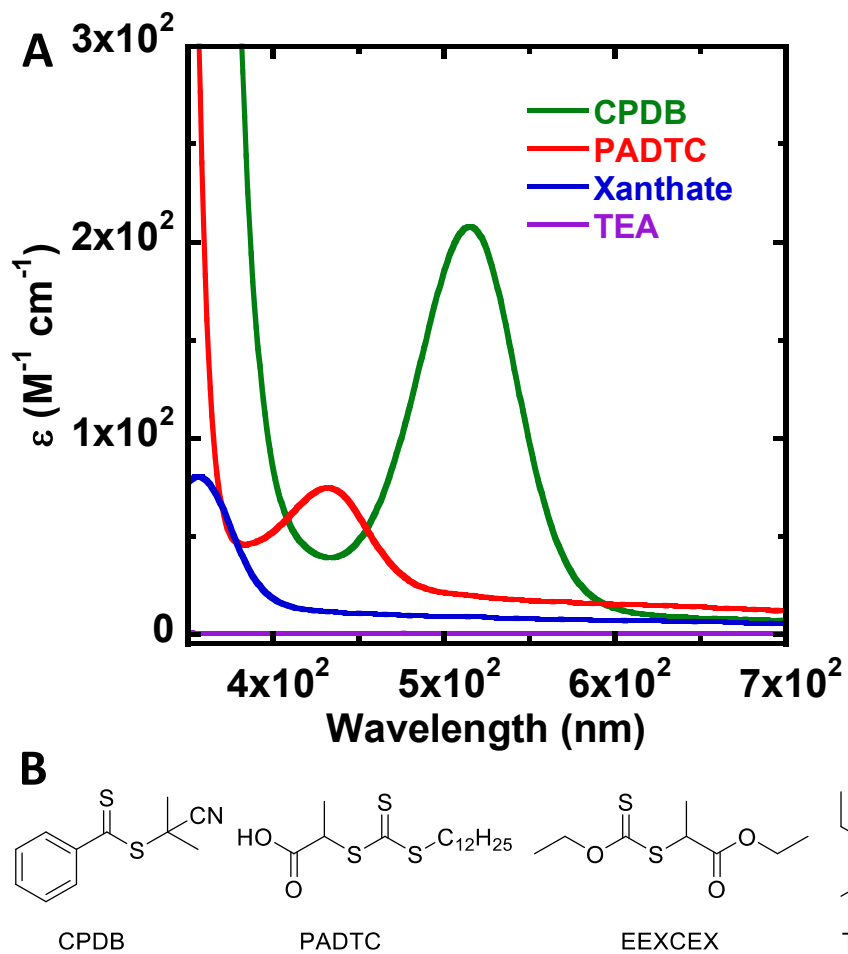


Figure S1: A UV-Vis spectra for CPDB, PADTC, EEXCEX and TEA in DMF. **B** Structures for CPDB, PADTC, EEXCEX, and TEA

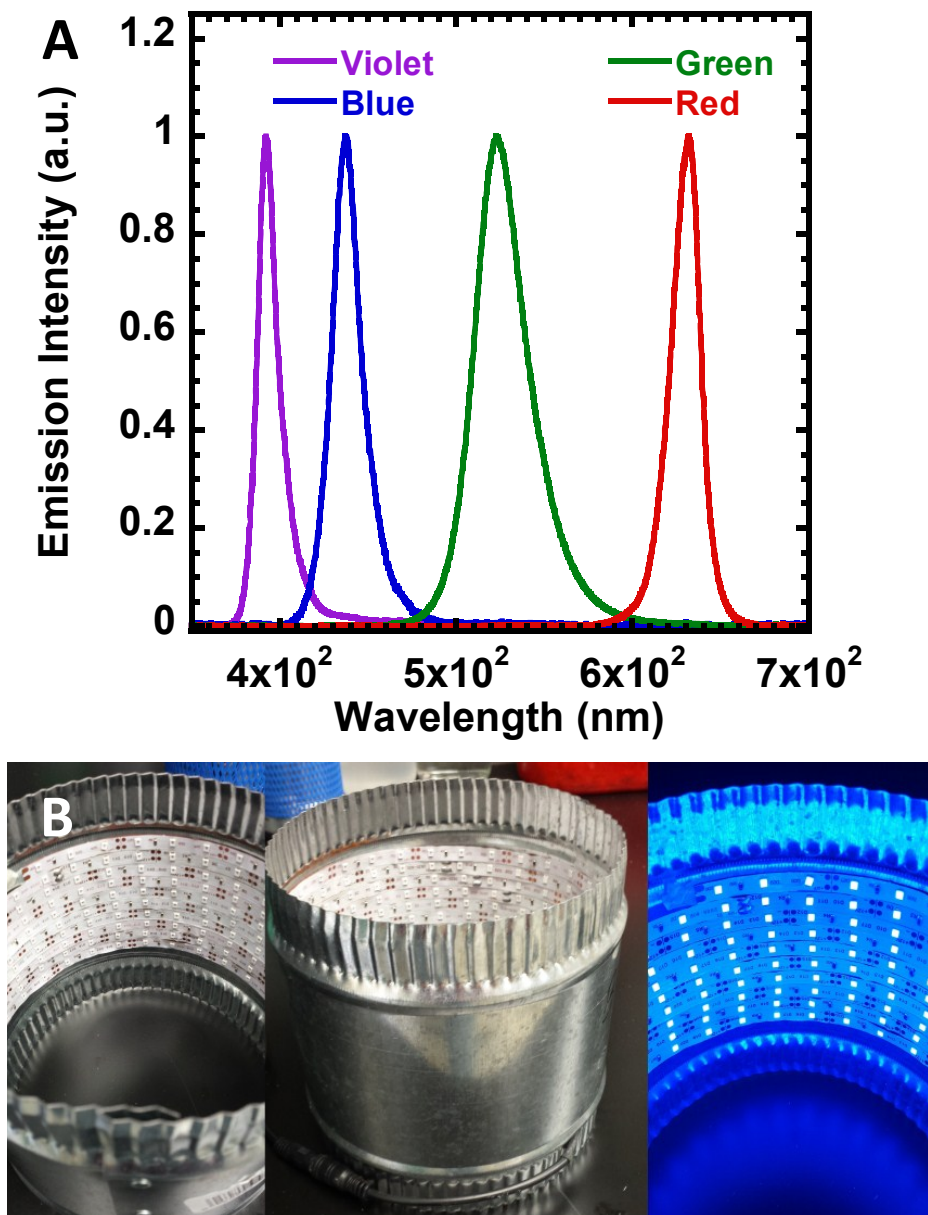


Figure S2: **A** Emission spectra with peak height normalization (to a value of 1) of the violet, blue, green and red photoreactors. **B** Blue light LED photoreactor

The photoreactors were constructed using adhesive 5 m LED strips wrapped inside cylindrical metal casing (Figure S2B). A reaction flask was suspended inside the cylinder during reactions. The cylinder was covered with aluminum foil during reactions. The

blue, red, and green LED strips were purchased from Lighting Ever. The violet LED strip was purchased from Wit-Lighting

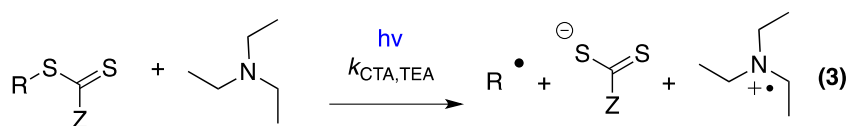
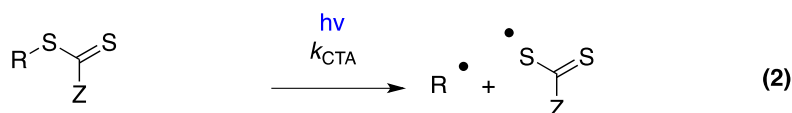
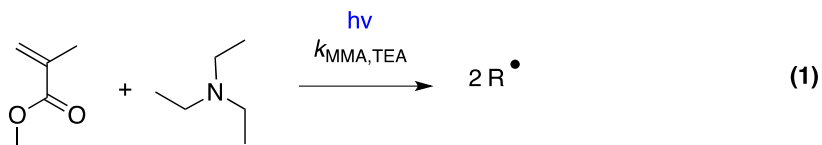
Table S1: Characterization data for the Violet, Blue, Green and Red photoreactors. The wavelength of peak emission (λ_{\max}), Full width at half maximum (FWHM), and power output intensity are given

Reactor	λ_{\max} (nm)	FWHM (nm)	Intensity (mW/cm ²)
Violet	390	10	3.7±0.3
Blue	440	20	11.6±0.3
Green	520	30	5.9±0.3
Red	630	20	4.7±0.3

Kinetics analysis of Photopolymerization

Apparent rate coefficients for the photopolymerization can be extracted from the kinetic data. It is important to note that the rate coefficients extracted are only apparent rate coefficients based on the specific system studied and the concentration of all amine and CTA, rather than the concentration of the excited state species that are responsible for the reaction. True rate coefficients would require the determination of the quantum yield for each process, and the excited state lifetimes. Nevertheless, mechanistic information and comparison of reaction rates and contributions of various processes to the overall reaction can be determined from apparent rate coefficients.¹ Throughout this analysis the steady state approximation is applied to extract rate coefficients. Conventional radical termination is assumed to be the major pathway for radical loss in this system, which is justified since methacrylic monomers display minimal RAFT rate retardation.^{2, 3}

Photoinduced radical generation is assumed to occur by one of three processes. These are outlined in Scheme S1. Pathway 1 in Scheme S1 is the photoinduced electron transfer between MMA monomer and TEA, with apparent rate coefficient $k_{\text{TEA,MMA}}$.¹ The pathway 2 in Scheme S1 is the photoinduced fragmentation of the chain transfer agent with apparent rate coefficient k_{CTA} .^{4, 5} The thiocarbonyl-thio radical could dimerize, removing it from the system. Finally, the bimolecular reaction between the CTA and the amine is given as pathway 3 in Scheme S1, which occurs with apparent rate coefficient $k_{\text{CTA,TEA}}$.⁶ Note that the radical cation generated from the amine can undergo hydrogen transfer giving a carbon centered radical that will initiate polymerization.¹ Note that apparent rate coefficients are used, since the exact population of excited state molecules is not known.



Scheme S1: Proposed pathways for photochemical radical generation.

This Scheme gives the following equation for rate of change of radical concentration, assuming the thiocarbonyl-thio radical does not reinitiate polymerization.

$$\frac{d[\text{R}^\bullet]}{dt} = 2k_{\text{MMA,TEA}}[\text{MMA}][\text{TEA}] + k_{\text{CTA}}[\text{CTA}] + 2k_{\text{CTA,TEA}}[\text{CTA}][\text{TEA}] - 2k_t[\text{R}^\bullet]^2 \quad (\text{S1})$$

Table 1 Entry 6 indicates that in the absence of CTA the polymerization is very slow. This implies that the reaction between TEA and MMA is very slow under the polymerization conditions, and allows the first gain term to be neglected. This creates the simplified rate equation given in Eq. S2.

$$\frac{d[\text{R}']}{dt} = k_{\text{CTA}}[\text{CTA}] + 2k_{\text{CTA,TEA}}[\text{CTA}][\text{TEA}] - 2k_t[\text{R}']^2 \quad (\text{S2})$$

Applying the steady state approximation gives Eq. S3.

$$2k_t[\text{R}']^2 = k_{\text{CTA}}[\text{CTA}] + 2k_{\text{CTA,TEA}}[\text{CTA}][\text{TEA}] \quad (\text{S3})$$

This implies that the kinetic studies can be used to extract the apparent rate coefficients k_{CTA} and $k_{\text{CTA,TEA}}$ by studying how the square of the radical concentration is affected by the [CTA] or [TEA] present in the reaction medium. Using the known propagation rate coefficient of MMA at 25 °C of $323 \text{ M}^{-1} \text{ s}^{-1}$,⁷ gives the radical concentrations present in Table S2 and S3. Table S2 is for variations in the [CTA] with fixed [TEA], while Table S3 is for variations in [TEA] with fixed [CTA]. Note that the highest [CTA] and highest [TEA] were excluded from this analysis due to the plateau in the rate observed. Chain length dependence in the termination rate coefficient k_t is not considered at this level of calculation, and the average value for MMA termination of $k_t = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ is used for conditions near ambient temperature.⁸

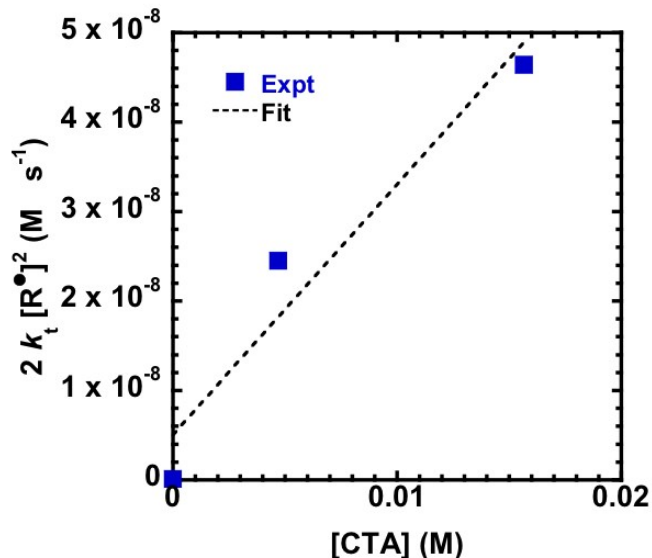


Figure S3: Dependence of rate of termination, and consequently rate of radical generation, on the concentration of CTA added to the reaction mixture. Polymerization of MMA at ambient temperature under blue light ($\lambda_{\text{max}} = 440 \text{ nm}$, $11.6 \pm 0.3 \text{ mW/cm}^2$). MMA in 50% DMF, $[\text{TEA}] = 0.094 \text{ M}$ in all experiments.

Table S2: Polymerization kinetic data for photopolymerization of MMA in the presence of dithiobenzoate and TEA. Polymerization of MMA performed with different $[\text{CTA}]$ at ambient temperature under blue light ($\lambda_{\text{max}} = 440 \text{ nm}$, $11.6 \pm 0.3 \text{ mW/cm}^2$). MMA in 50% DMF with $[\text{TEA}] = 0.094 \text{ M}$ in all experiments.

[CTA] (M)	[TEA] (M)	k_p^{app} (s ⁻¹)	$[\text{R}^\bullet]$ (M)	$2 k_t [\text{R}^\bullet]^2$
0	0.094	4.9×10^{-7}	1.5×10^{-9}	9.2×10^{-11}
0.0047	0.094	8.0×10^{-6}	2.5×10^{-8}	2.5×10^{-8}
0.0157	0.094	1.1×10^{-5}	3.4×10^{-8}	4.6×10^{-8}

Using the steady state approximation implies that the rate of radical generation equals to:

$$2 k_t [\text{R}^\bullet]^2 = (k_{\text{CTA}} + 2 k_{\text{CTA,TEA}} [\text{TEA}]) [\text{CTA}] \quad (\text{S4})$$

Therefore this should lead to a linear relationship between $2 k_t [\text{R}^\bullet]^2$ and $[\text{CTA}]$ with slope $k_{\text{CTA}} + 2 k_{\text{CTA,TEA}} [\text{TEA}]$ and intercept of 0. As seen in Figure S3, indeed this linear

relationship is observed. However, there are two unknowns, k_{CTA} and $k_{\text{CTA,TEA}}$. This can be resolved by creating an equivalent plot using the variation in [TEA]. Table S4 presents the kinetic data for this analysis.

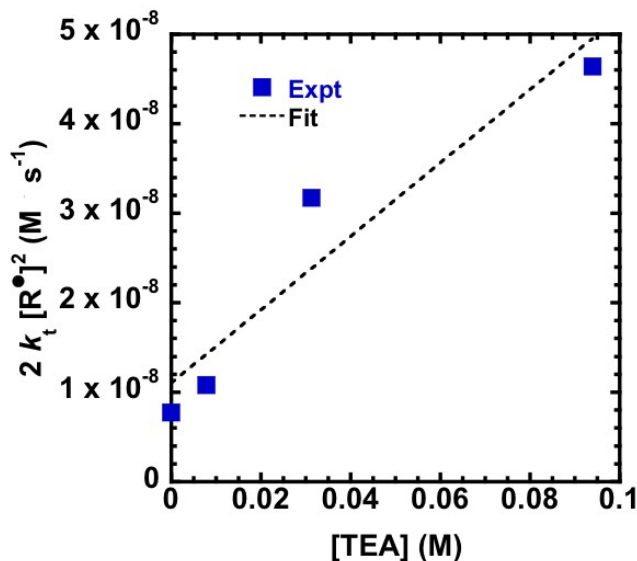


Figure S4: Dependence of rate of termination, and rate of radical generation, on the concentration of TEA added to the reaction mixture. Polymerization of MMA at ambient temperature under blue light ($\lambda_{\text{max}} = 440 \text{ nm}$, $11.6 \pm 0.3 \text{ mW/cm}^2$). MMA in 50% DMF, [TEA] = 0.016 M in all experiments.

Table S3: Polymerization kinetic data for photopolymerization of MMA in the presence of dithiobenzoate and TEA. Polymerization performed with different [TEA] at ambient temperature under blue light ($\lambda_{\text{max}} = 440 \text{ nm}$, $11.6 \pm 0.3 \text{ mW/cm}^2$). MMA in 50% DMF with [CTA] = 0.016 M in all experiments.

[CTA] (M)	[TEA] (M)	k_p^{app} (s^{-1})	$[R^\bullet]$ (M)	$2 k_t [R^\bullet]^2$
0.0157	0	4.5×10^{-6}	1.4×10^{-8}	7.8×10^{-9}
0.0157	0.0078	5.3×10^{-6}	1.6×10^{-8}	1.1×10^{-8}
0.0157	0.031	9.1×10^{-6}	2.8×10^{-8}	3.2×10^{-8}
0.0157	0.094	1.1×10^{-5}	3.4×10^{-8}	4.6×10^{-8}

Using the steady state approximation implies that the rate of radical generation equals to:

$$2 k_t [\text{R}\cdot]^2 = k_{\text{CTA}} [\text{CTA}] + 2 k_{\text{CTA,TEA}} [\text{CTA}][\text{TEA}] \quad (\text{S5})$$

Therefore this should lead to a linear relationship between $2 k_t [\text{R}\cdot]^2$ and $[\text{CTA}]$ with slope $2 k_{\text{CTA,TEA}} [\text{CTA}]$ and intercept $k_{\text{CTA}} [\text{CTA}]$. As seen in Figure S4, indeed this linear relationship is observed. The intercept gives $k_{\text{CTA}} = 7 \times 10^{-7} \text{ s}^{-1}$. The slope of the $2 k_t [\text{R}\cdot]^2$ v.s. $[\text{TEA}]$ plot gives $k_{\text{CTA,TEA}} = 1.3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. Substituting the apparent rate coefficient $k_{\text{CTA}} = 7 \times 10^{-7} \text{ s}^{-1}$ into eq. S4 with the slope seen in Figure S3 gives $k_{\text{CTA,TEA}} = 1.1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. These two values of the apparent rate coefficient $k_{\text{CTA,TEA}}$ are in excellent agreement giving an average value of $k_{\text{CTA,TEA}} = (1.2 \pm 0.1) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

Polymerization of acrylates and vinyl acetate

Table S4: Summary Results of all homopolymerizations of MA and VA performed. All polymerizations performed in 50 wt% monomer+polymer using DMF as the solvent under blue light. All conversions were determined using $^1\text{H-NMR}$. ^a All molecular weight data determined using SEC with THF as the eluent. ^b $M_{n,\text{th}} = M_{\text{CTA}} + M_{\text{M}} \times \text{conv} \times \frac{[\text{M}]_0}{[\text{CTA}]_0}$.

Entry	Monomer	CTA	[M]:[CTA]:[TEA]	Time (h)	Conv. %	k_p^{app} (s^{-1}))	M_n^{a}	$M_{n,\text{th}}^{\text{b}}$	M_w/M_n^{a}
1	MA	PADTC	300:1:6	24	58.3	1.1×10^{-5}	23000	17850	1.59
2	VA	EECEX	300:1:6	30	7%	6.5×10^{-7}	2000	2028	1.28

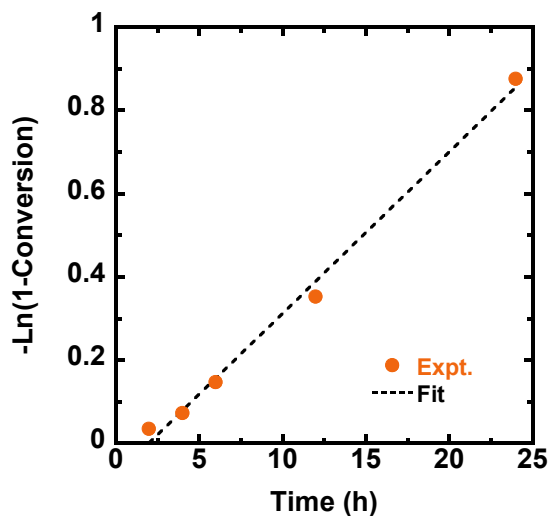


Figure S5: First order kinetic plot, for the polymerization of MA using PADTC as the CTA in the presence of TEA under blue light ($\lambda_{\text{max}} = 440 \text{ nm}$, $11.6 \pm 0.3 \text{ mW/cm}^2$). Conditions: [MA]:[PADTC]:[TEA] = 300:1:6, 50 wt% MA in DMF, at room temperature.

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