Supporting Information

N-Aryl Glycines as Versatile Initiators for Various Polymerizations

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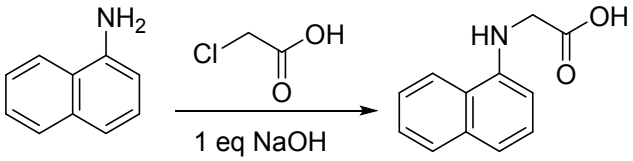
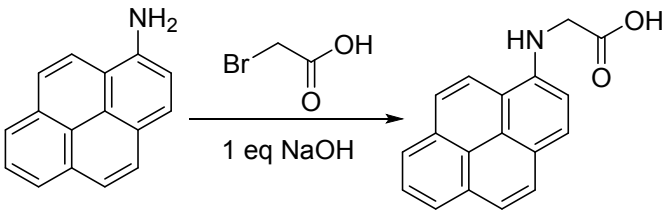
Synthesis and characterization of NNG and NPYG.



Naphthalen-1-amine (2.38 g, 16.6 mmol) was dissolved in 100 mL of ethanol, and chloroacetic acid (1.57 g, 16.6 mmol) was dissolved in 15 ml of ethanol followed by dropwise addition of aqueous NaOH solution (0.66 g dissolved in 3 ml of water). Then the solutions were combined and refluxed for 24 h. The solvent was evaporated out and the residue was purified by column chromatography using DCM/methanol (10/1, v/v) as eluent affording a grey solid (1.5 g, yield 45%). All characterization experiments were utilized Ascend^{TM} 300 MHz or 400 MHz NMR from Bruker. Chemical shifts are standardized by tetramethylsilane (TMS), δ = 0 ppm.

^{1}H NMR (300 MHz, d6-DMSO): δ = 8.14 (d, 1H), 7.78 (d, 1H), 7.44 (m, 2H), 7.28 (t, 1H), 7.13 (d, 1H), 6.47 (d, 1H), 3.98 (s, 2H). ^{13}C NMR (75 MHz, d6-DMSO): δ = 173.2, 143.9, 134.4, 128.5, 127.3, 125.9, 124.8, 123.4, 121.9, 116.2, 103.4, 45.3.



Pyrene-1-amine (0.90 g, 4.15 mmol) was dissolved in 20 mL of ethanol, and bromoacetic acid (0.86 g, 6.19 mmol) was dissolved in 5 ml of ethanol followed by dropwise addition of aqueous NaOH solution (0.25 g dissolved in 1 ml of water). Then the solutions were combined and refluxed for 24 h. The solvent was evaporated out and the residue was purified by column chromatography using DCM/methanol (10/1, v/v) as eluent affording a brown powder (350 mg, yield 31%). ^{1}H NMR (300 MHz, d6-DMSO): δ = 8.35 (d, 1H), 8.05 (m, 4H), 7.93 (m, 2H), 7.77 (d, 1H), 7.18 (d, 1H), 4.19 (s, 2H). ^{13}C NMR (75 MHz, d6-DMSO): δ = 173.1, 143.2, 132.3, 131.8, 128.1, 127.0, 126.7, 125.6, 125.2, 123.5, 123.1, 122.9, 122.8, 122.0, 121.8, 115.8, 108.7, 45.3.

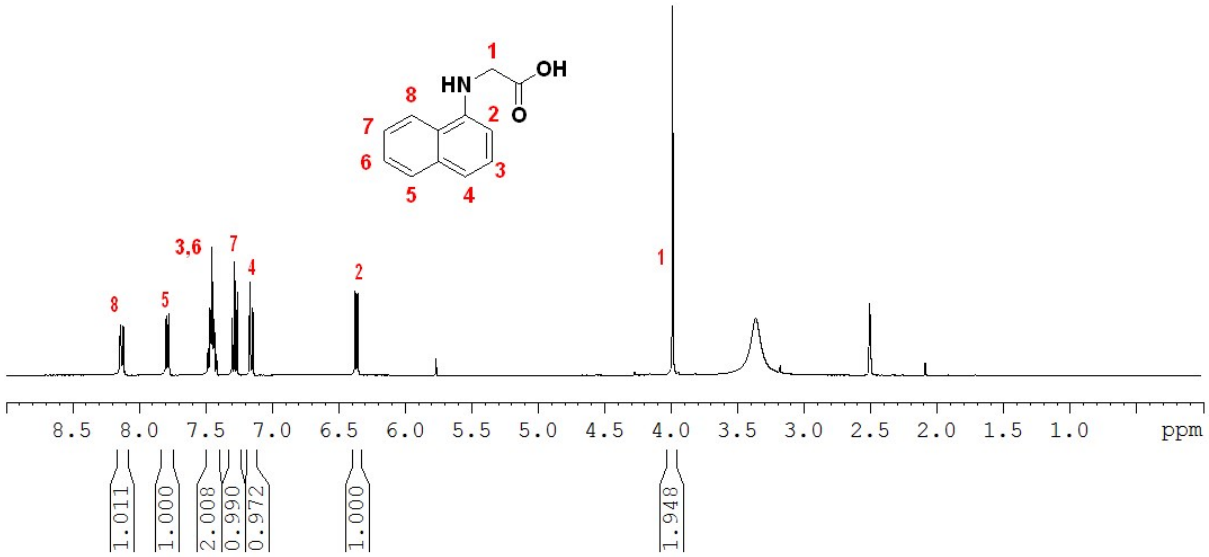


Figure S1. ^{1}H NMR of *N*-(1-naphthyl)glycine (NNG) in d_6-DMSO (300 MHz).

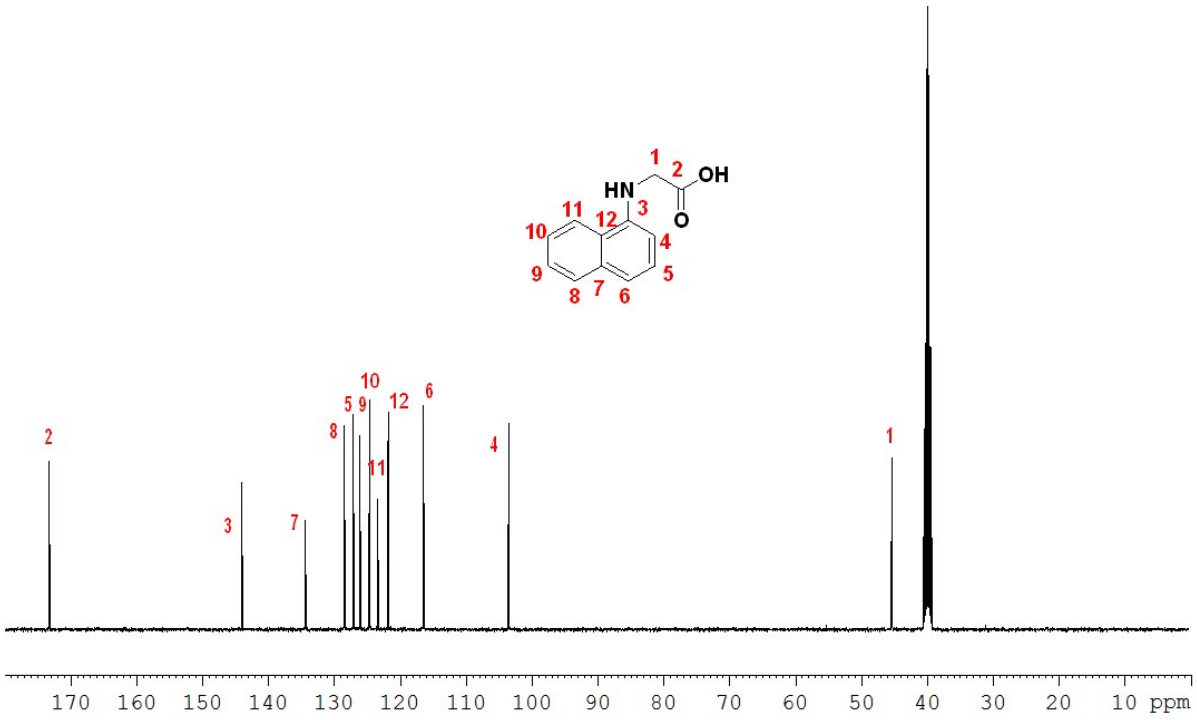


Figure S2. ^{13}C NMR of *N*-(1-naphthyl)glycine (NNG) in d_6-DMSO (300 MHz).

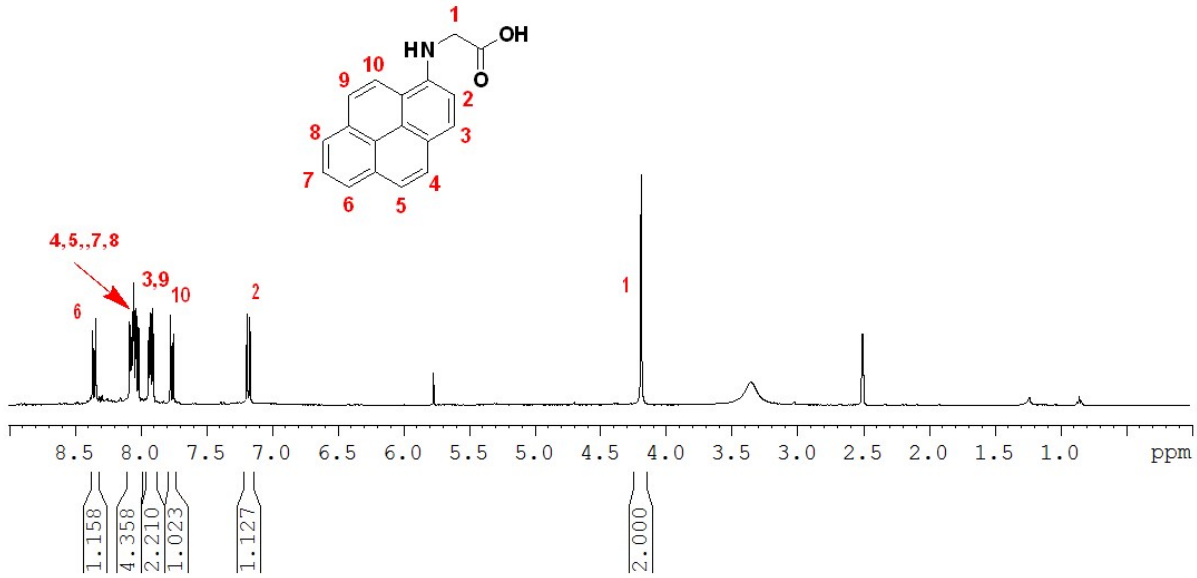


Figure S3. ^{1}H NMR of *N*-(1-pyrenyl)glycine (NPYG) in d_6-DMSO (300 MHz).

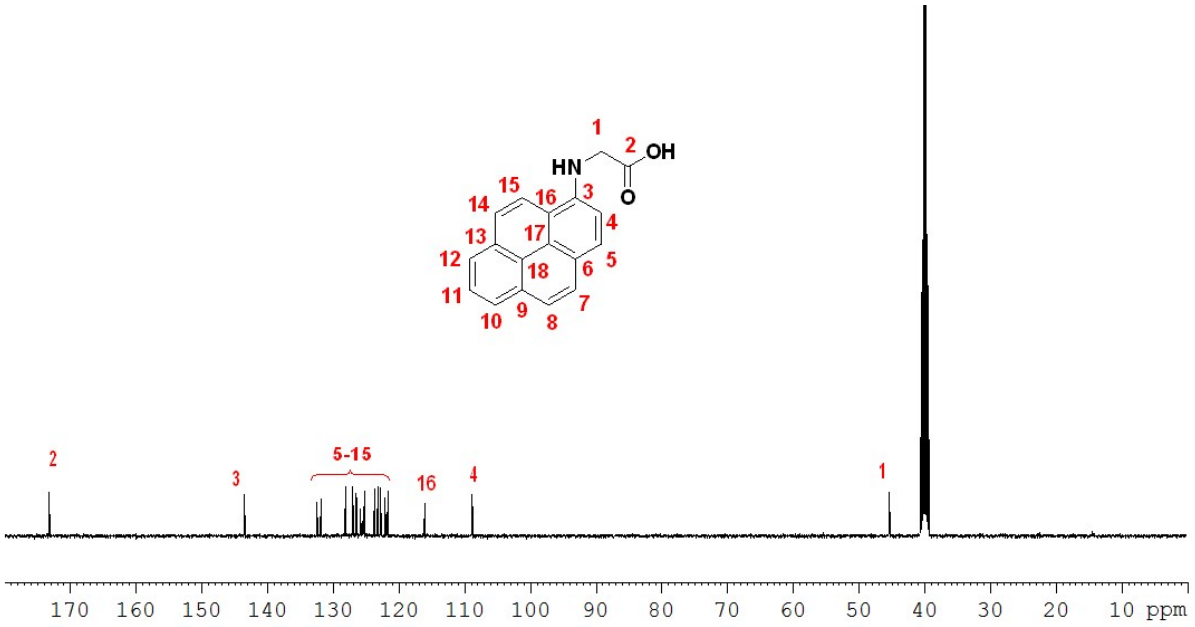
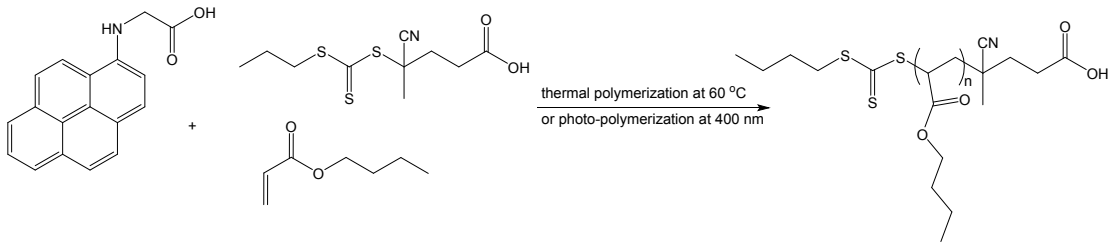


Figure S4. ^{1}H NMR of *N*-(1-pyrenyl)glycine (NPYG) in d_6-DMSO (300 MHz).



Scheme S1. NPYG as thermal- or photo-initiator for the RAFT polymerization of butyl acrylate.

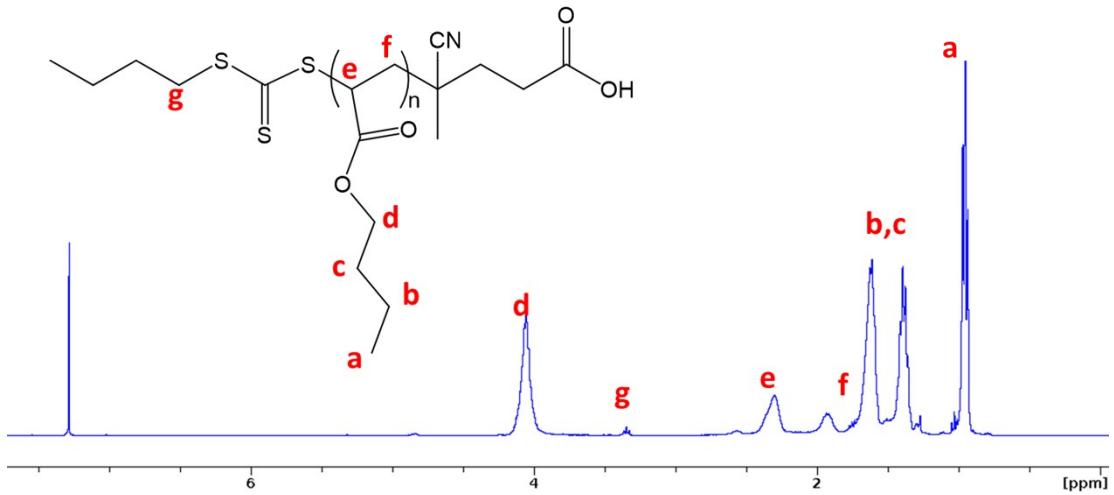


Figure S5. ^{1}H NMR of PBA_{25} synthesized by thermal polymerization of butyl acrylate using NPYG as thermal initiator in $CDCl_3$.

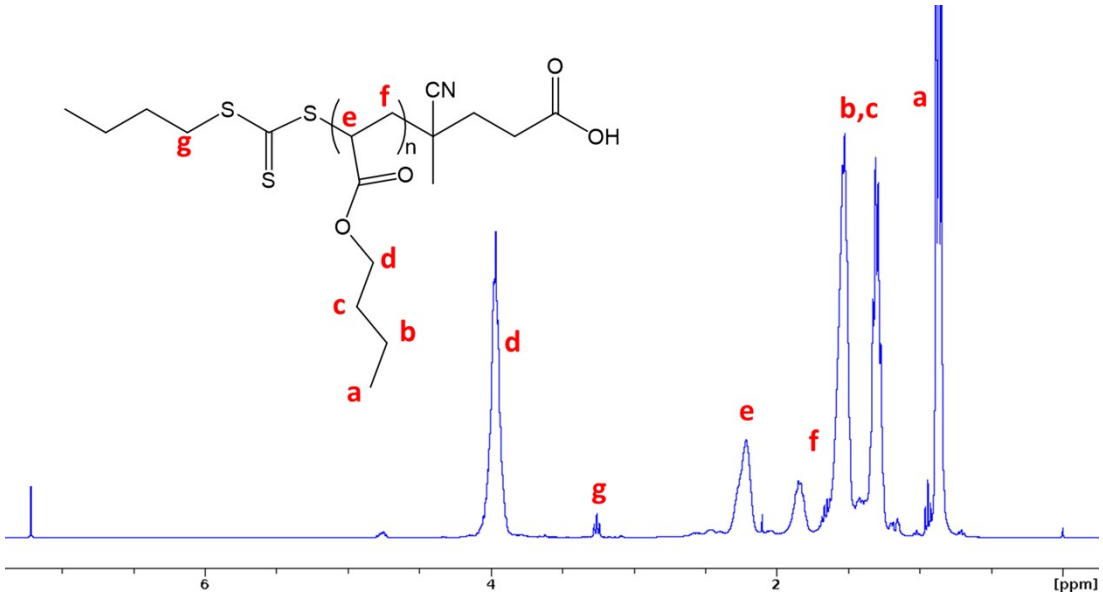


Figure S6. ^{1}H NMR of PBA_{37} synthesized by photopolymerization of butyl acrylate using NPYG as photoinitiator in $CDCl_3$.

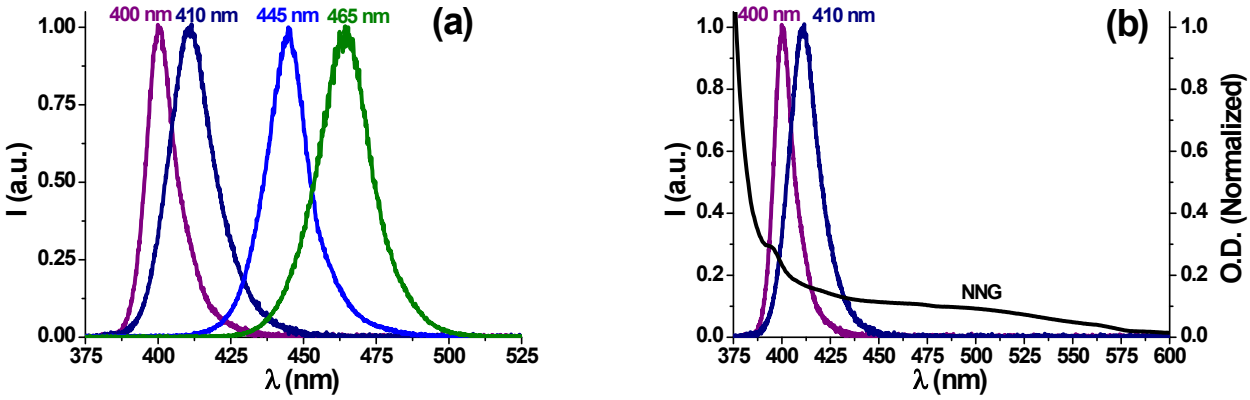


Figure S7. Emission spectra of LEDs centered at 400 nm, 410 nm, 445 nm, and 465 nm.

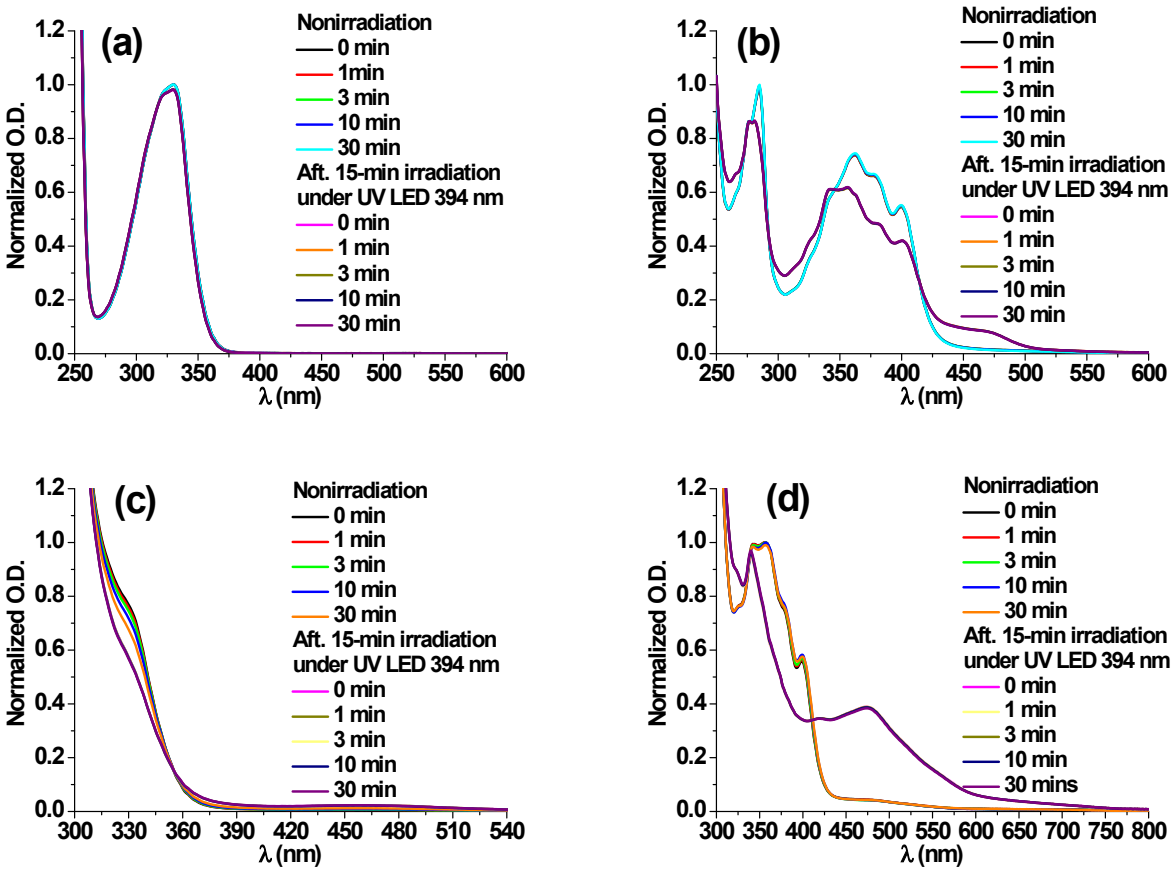


Figure S8. UV-vis absorption spectra of (a) NNG alone, (b) NPYG alone, (c) NNG/Iod and (d) NPYG/Iod in acetonitrile at different storage time before and after 15-min irradiation under UV LED@394 nm ([Iod] = 10 mM).

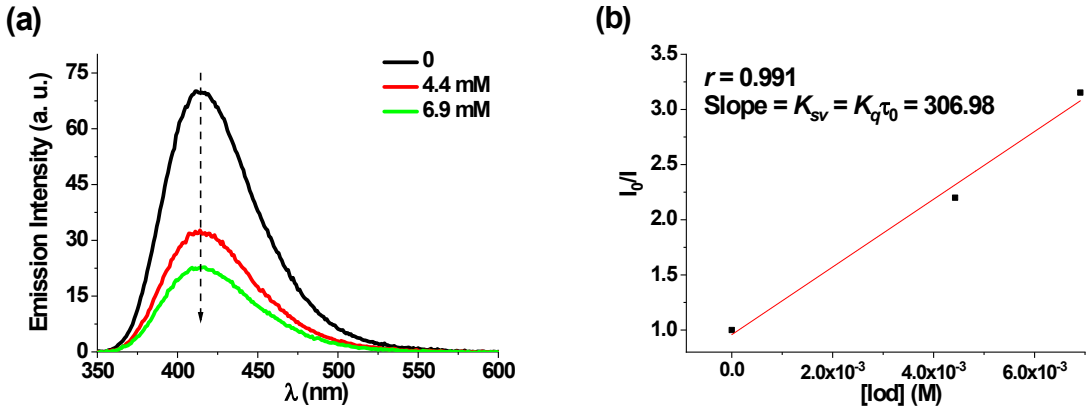


Figure S9. (a) Fluorescence spectra of NNG as the function of [Iod] in acetonitrile and (b) relevant stern-volmer plot (λ_{ex} = 330 nm).

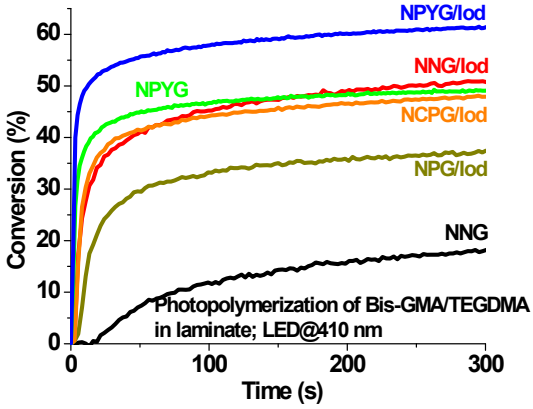


Figure S10. Photopolymerization profiles (double bond conversions vs time) of Bis-GMA/TEGDMA in laminate in the presence NPG, NCPG, NNG, and NPYG based photoinitiating systems (NPG, NCPG, NNG or NPYG: 18 μmol/g; Iod: 47 μmol/g) upon exposure to the LED@410 nm (110 mW cm-2).

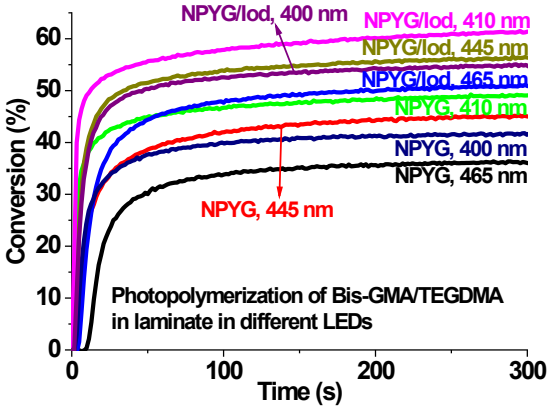


Figure S11. Photopolymerization profiles (double bond conversions vs time) of (a) Bis-GMA/TEGDMA in laminate in the presence of NPYG-based PI systems (NPYG: 0.5 wt%; Iod: 2 wt%) upon exposure to the LEDs at 400 nm (6.5 mW cm^{-2}), 410 nm (110 mW cm^{-2}), 445 nm(80 mW cm^{-2}) and 465 nm (55 mW cm^{-2}).

Table S1. Photopolymerization rates and double bond conversions of photopolymerization of Bis-GMA/TEGDMA blend (70%/30%, w/w) in the presence of NPYG-based PISs (NNG or NPYG: 0.5 wt%; Iod: 2 wt%) as PISs upon exposure to several LEDs for 300 s.

LEDs	NPYG		NPYG/Iod	
	$(R_p/[C=C])\times100$[a] (s^{-1})	C[b]	$(R_p/[C=C])\times100$[a] (s^{-1})	C[b]
400 nm[c]	4.28	42%	6.71	55%
410 nm[c]	8.40	49%	12.32	62%
445 nm[c]	4.16	45%	7.22	57%
465 nm[c]	2.40	36%	3.86	51%

[a]: maximum rates of photopolymerization, calculated from the maximum of the first derivative of the double bond conversions versus time curves during photopolymerization;

[b]: final double bond conversions after photopolymerization for 300 s;

[c]: LED@400 nm (6.5 mW cm^{-2}); LED@410 nm (110 mW cm^{-2}); LED@445 nm (80 mW cm^{-2}); LED@465 nm (55 mW cm^{-2}).

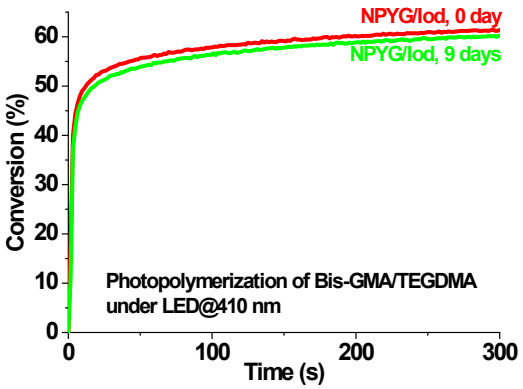


Figure S12. Photopolymerization profiles (double bond conversions vs time) of Bis-GMA/TEGDMA blend (70%/30%, w/w) along with storage time in laminate in the presence of NPYG/Iod (0.5%/2%, wt) upon exposure to the LED@410 nm (110 mW cm^{-2}).

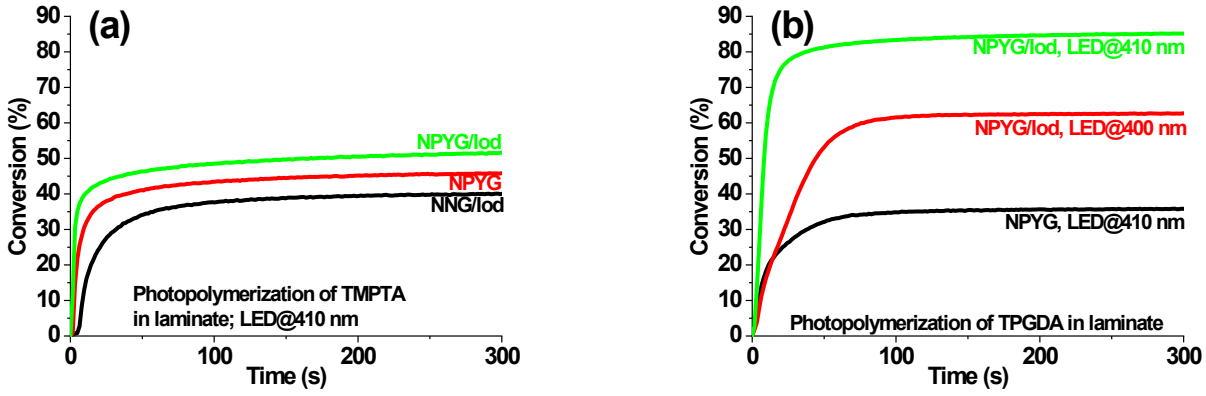


Figure S13. Photopolymerization profiles (double bond conversions vs time) of (a) TMPTA upon exposure to the LED@410 nm (110 mW cm^{-2}) and (b) TPGDA upon exposure to the LED@400 nm (6.5 mW cm^{-2}) and 410 nm (110 mW cm^{-2}) in laminate in the presence of NNG- or NPYG-based PI systems (NNG or NPYG: 0.5 wt%; Iod: 2 wt%).

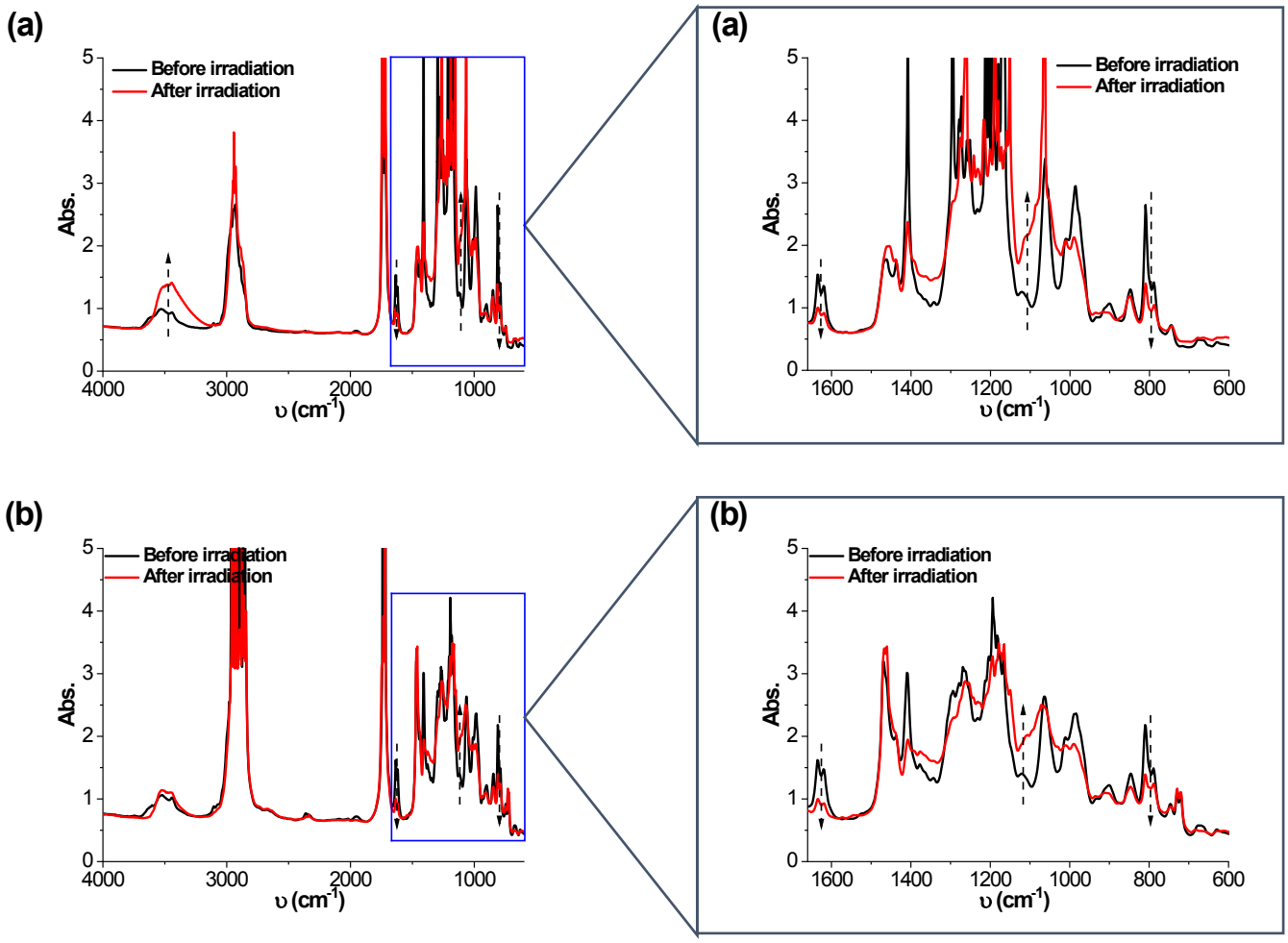


Figure S14. IR spectra of TMPTA/EPOX blend (50%/50%, wt) before and after photopolymerization (a) under air and (b) in laminate using NPYG/Iod as the photoinitiating system upon exposure to LED@410 nm (110 mW cm^{-2}).

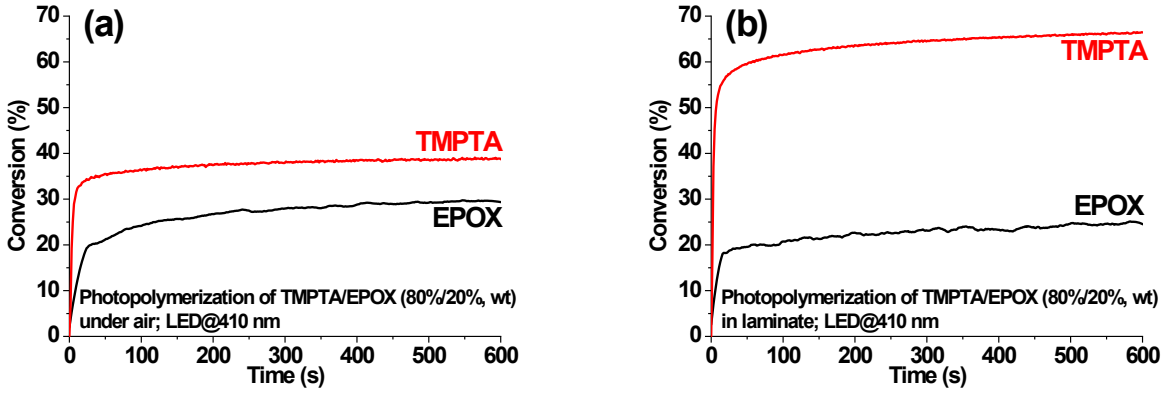


Figure S15. Photopolymerization profiles (double bond and epoxy bond conversions vs time) of TMPTA/EPOX blend (80%/20%, wt) (a) under air and (b) in laminate in the presence of NPYG/Iod (0.5 %/2%, wt) upon exposure to the LED@410 nm (110 mW cm^{-2}).

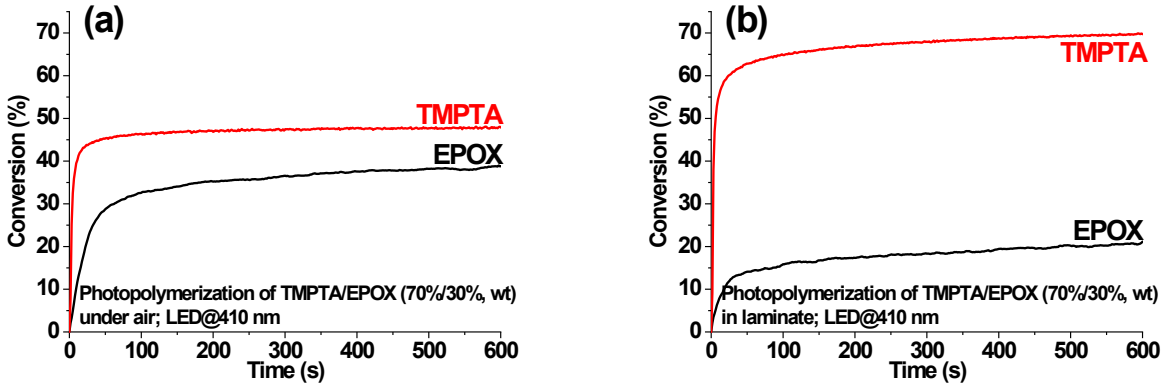


Figure S16. Photopolymerization profiles (double bond and epoxy bond conversions vs time) of TMPTA/EPOX blend (70%/30%, wt) (a) under air and (b) in laminate in the presence of NPYG/Iod (0.5 %/2%, wt) upon exposure to the LED@410 nm (110 mW cm^{-2}).

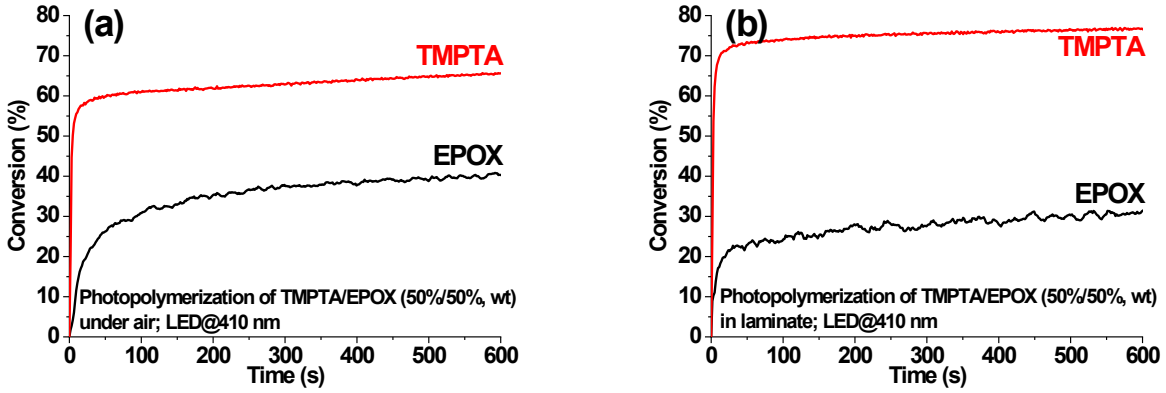


Figure S17. Photopolymerization profiles (double bond and epoxy bond conversions vs time) of TMPTA/EPOX blend (50%/50%, wt) (a) under air and (b) in laminate in the presence of NPYG/Iod (0.5 %/2%, wt) PIS upon exposure to the LED@410 nm (110 mW cm^{-2}).

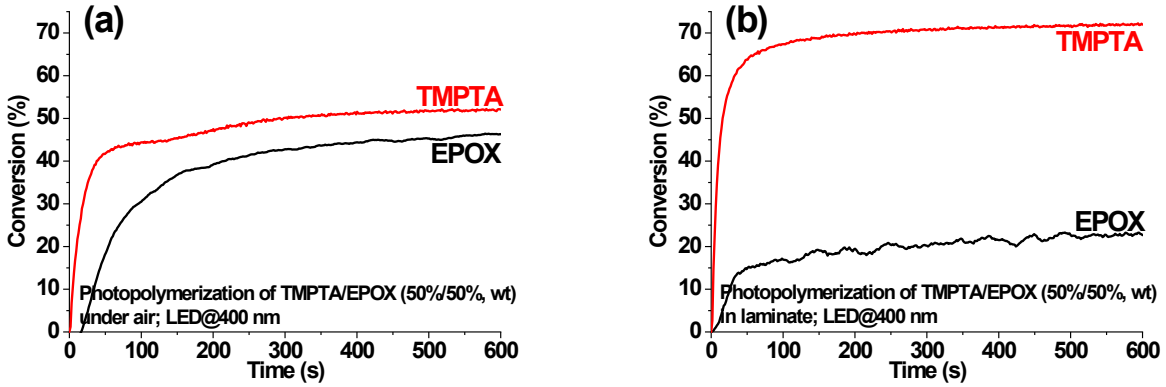


Figure S18. Photopolymerization profiles (double bond and epoxy bond conversions vs time) of TMPTA/EPOX blend (50%/50%, wt) (a) under air and (b) in laminate in the presence of NPYG/Iod (0.5 %/2%, wt) upon exposure to the LED@400 nm (6.5 mW cm^{-2}).