

Coumarin Derivatives as Versatile Photoinitiators/Photoredox Catalysts for 3D Printing, Polymerization in Water and Photocomposites Synthesis

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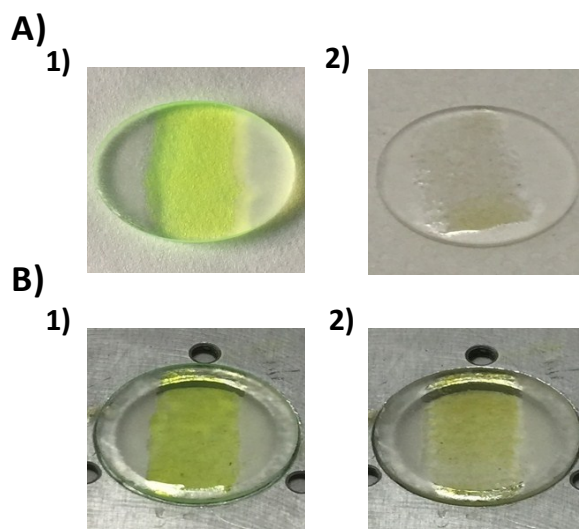


Figure S1. Photos of EPOX thin film (25 μm) upon irradiation with the LED @405 nm for 800s in the presence of the two-component photoinitiating systems: **(A)**: (1): CoumA/Iod (0.2%/1% w/w) before polymerization; and (2): CoumA/Iod (0.2%/1% w/w) after polymerization; respectively, under air. **(B)**: (1): CoumA/Iod (0.5%/1% w/w) before polymerization; and (2): CoumA/Iod (0.5%/1% w/w) after polymerization; respectively, under air.

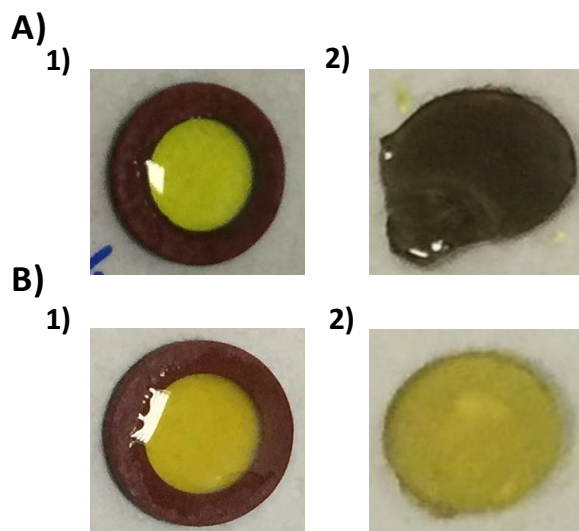


Figure S2. Photos of TMPTA thick film (1.4 mm) upon irradiation with the LED @405 nm for 100 s in the presence of the two-component photoinitiating systems: **(A)**: (1): CoumA/Iod (0.2%/1% w/w) before polymerization; and (2): CoumA/Iod (0.2%/1% w/w) after polymerization; respectively, under air. **(B)**: (1): CoumB/Iod (0.2%/1% w/w) before polymerization; and (2): CoumB/Iod (0.2%/1% w/w) after polymerization; respectively, under air.

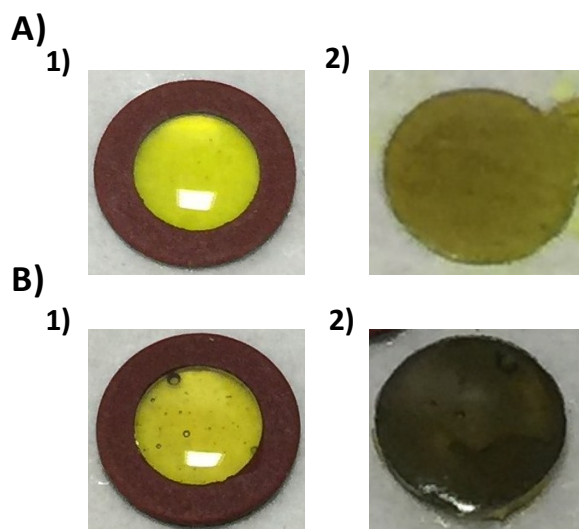


Figure S3. Photos of BisGMA/TEGDMA thick film (1.4 mm) upon irradiation with the LED @405 nm for 150 s in the presence of the two-component photoinitiating systems: **(A)**: (1): CoumA/Iod (0.2%/1% w/w) before polymerization; and (2): CoumA/Iod (0.2%/1% w/w) after polymerization; respectively, under air. **(B)**: (1): CoumB/Iod (0.2%/1% w/w) before polymerization; and (2): CoumB/Iod (0.2%/1% w/w) after polymerization; respectively, under air.

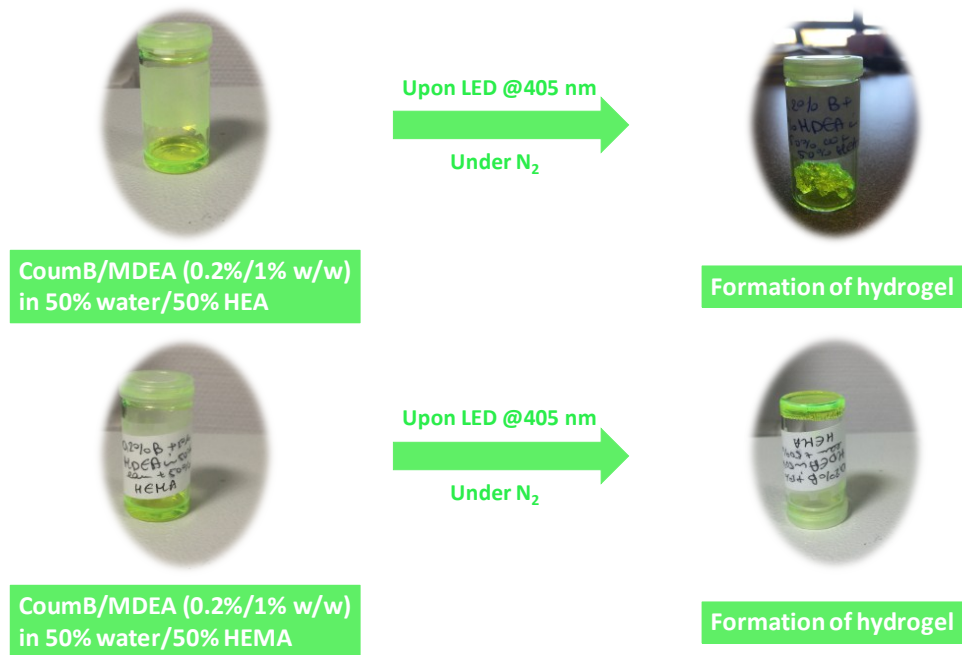


Figure S4. Hydrogels formation using CoumB/MDEA system under N₂, upon irradiation with LED @405 nm.

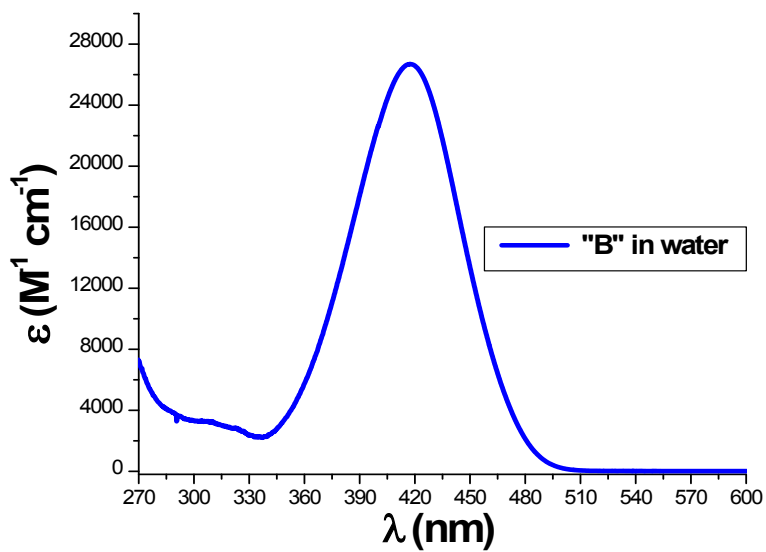


Figure S5. Absorption spectra of CoumB in water.



Figure S6. Composite produced upon Near-UV light (LED@395 nm), Belt Speed = 2m/min, using the free radical polymerization (FRP) in the presence of glass fibers/acrylate resin (0.2% CoumB + 1% Iod + 1% NPG in TMPTA). Glass fibers: ~ 2mm of thickness for one layer; 50% glass fibers/50% organic resin.

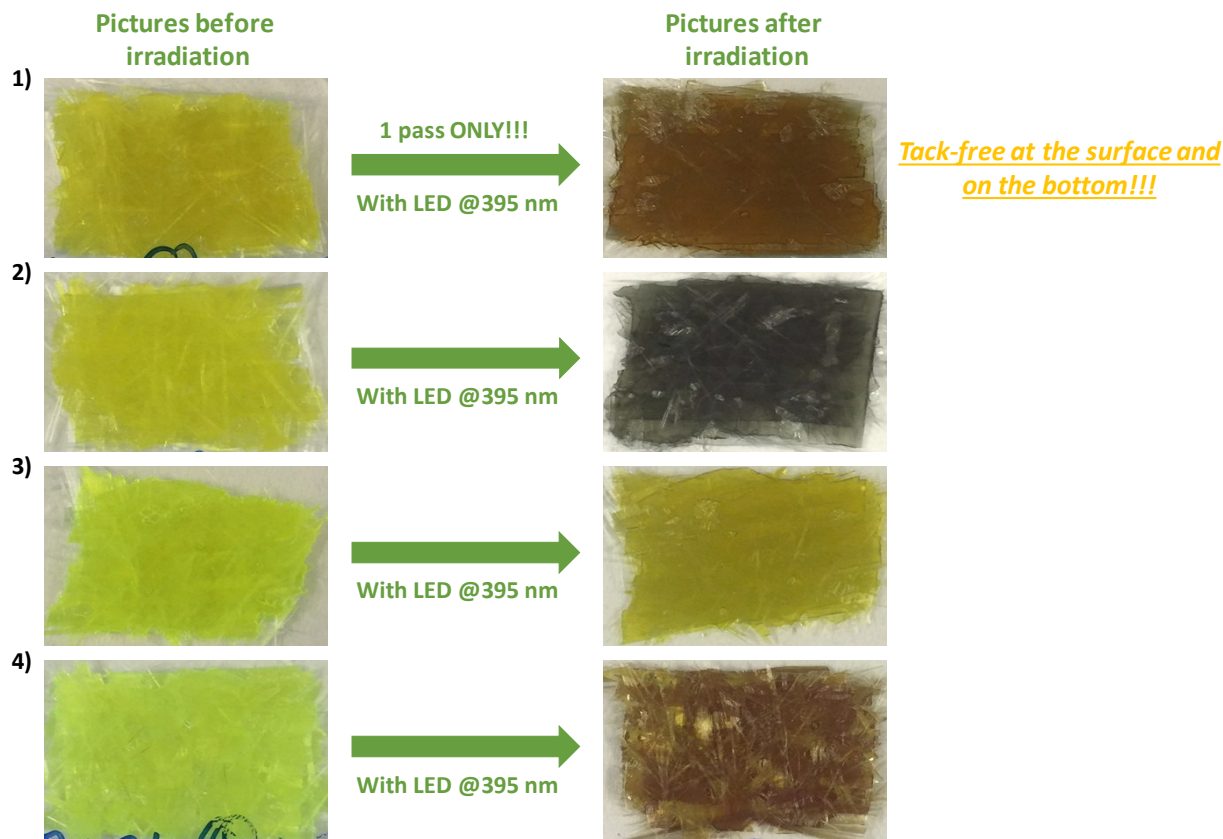


Figure S7. Composites produced upon Near-UV light (LED @395 nm), Belt Speed = 2m/min, using the free radical polymerisation (FRP) in the presence of glass fibers/(meth)acrylate resin for different systems : **(1)**: 0.2% CoumB + 1% Iod + 1% NPG in BisGMA/TEGDMA; **(2)**: 0.2% CoumB + 1% Iod in BisGMA/TEGDMA; **(3)**: 0.2% CoumA + 1% Iod + 1% NPG in BisGMA/TEGDMA; and **(4)**: 0.2% CoumA + 1% Iod + 1% NPG in TMPTA. Glass fibers: ~ 2mm of thickness for one layer; 50% glass fibers/50% organic resin.

Table S1. Number of passes to be tack-free for impregnated glass fibers with (meth)acrylate resins using Near-UV conveyor (LED @395 nm), belt speed used = 2 m.min⁻¹

Composites (50% glass fibers/50% (meth)acrylate resin)	At the surface	On the bottom
0.2% CoumB + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1 pass
0.2% CoumB + 1% Iod + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 1 pass
0.2% CoumB + 1% Iod in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 7 passes
0.2% CoumA + 1% Iod + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 2 passes
0.2% CoumA + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 8 passes

T.F.: Tack-free