New photocatalytic systems for obtaining polymer nanocomposites in 3D VAT printing technologies

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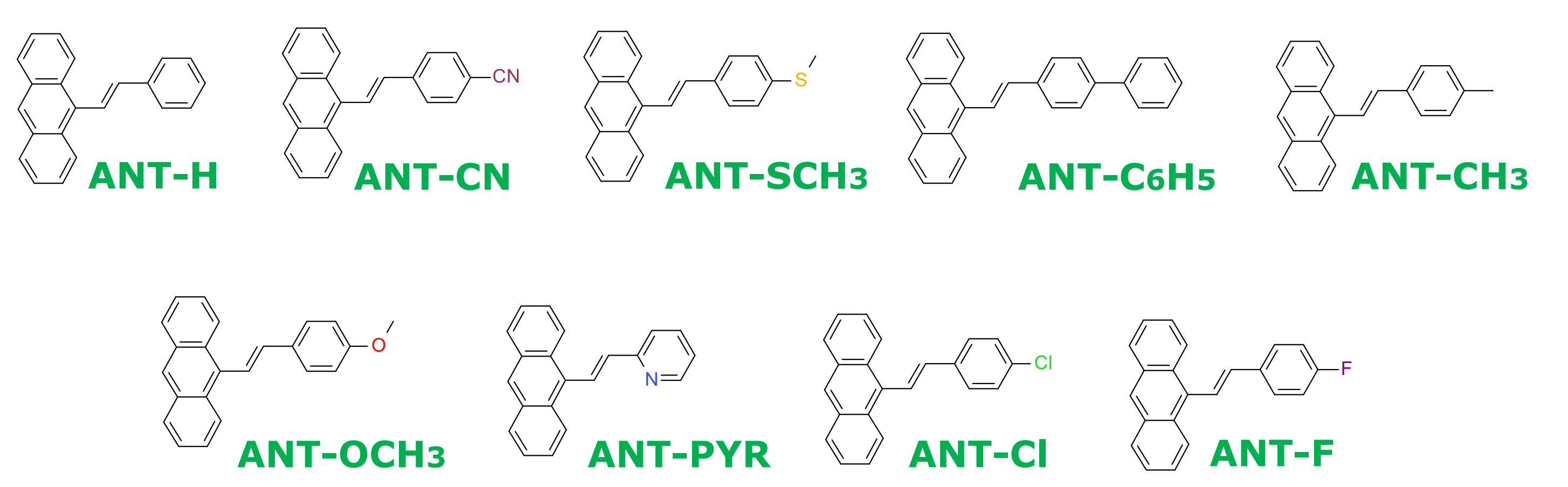
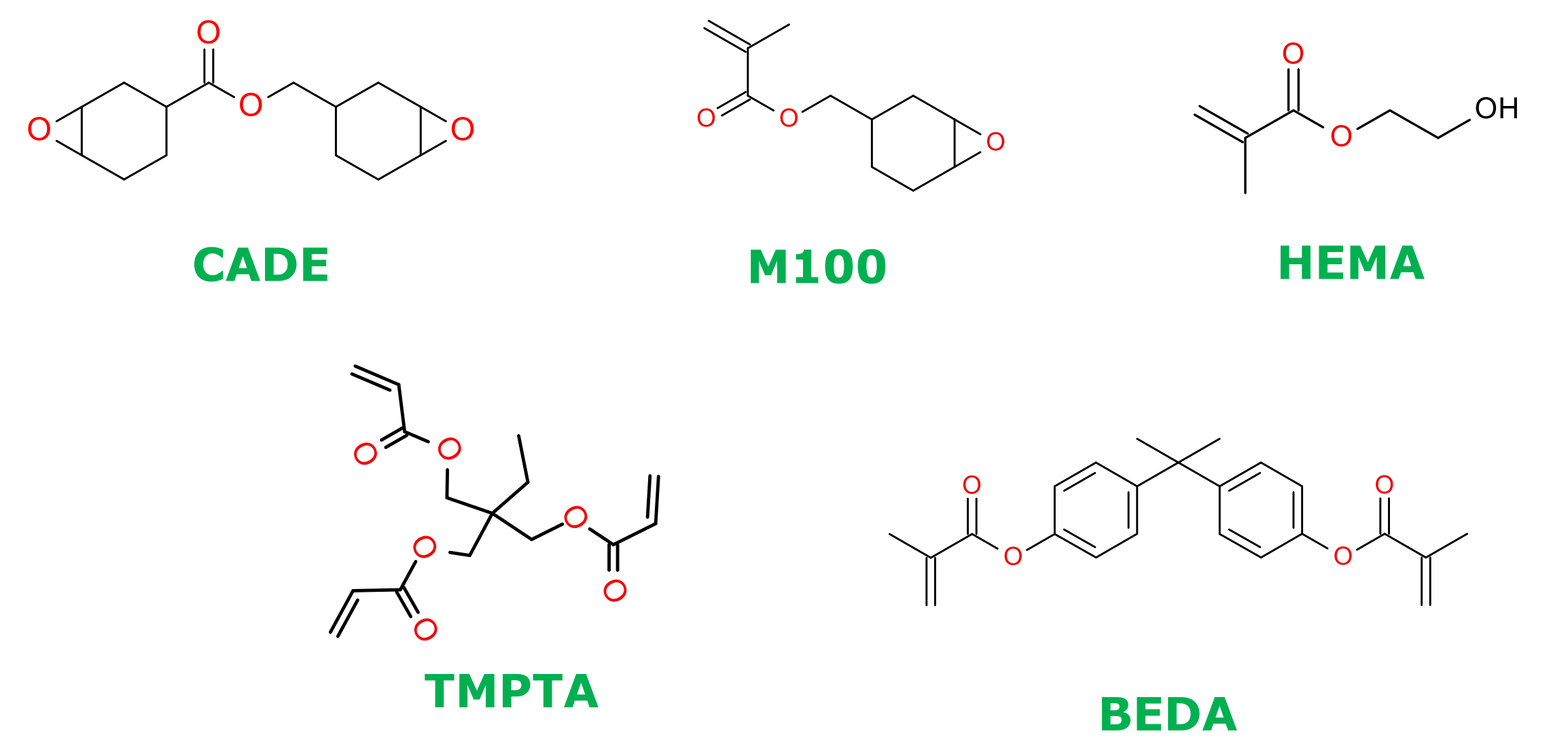
Photochemistry and consequently radiation-initiated polymerization processes play an extremely important role in materials engineering. Photopolymerization processes are widely used in many industries including biomedical engineering, automotive and dentistry. These processes are currently rapidly expanding with technologies related to forming 3D models using light-initiated 3D printing. Photopolymerization is also frequently used in the polygraphic industry to obtain photo-cure UV varnishes and inks. The wide range of applications of this process is mainly due to its speed and the fact that the process is not harmful to the environment.

New photoredox catalysts



Monomers



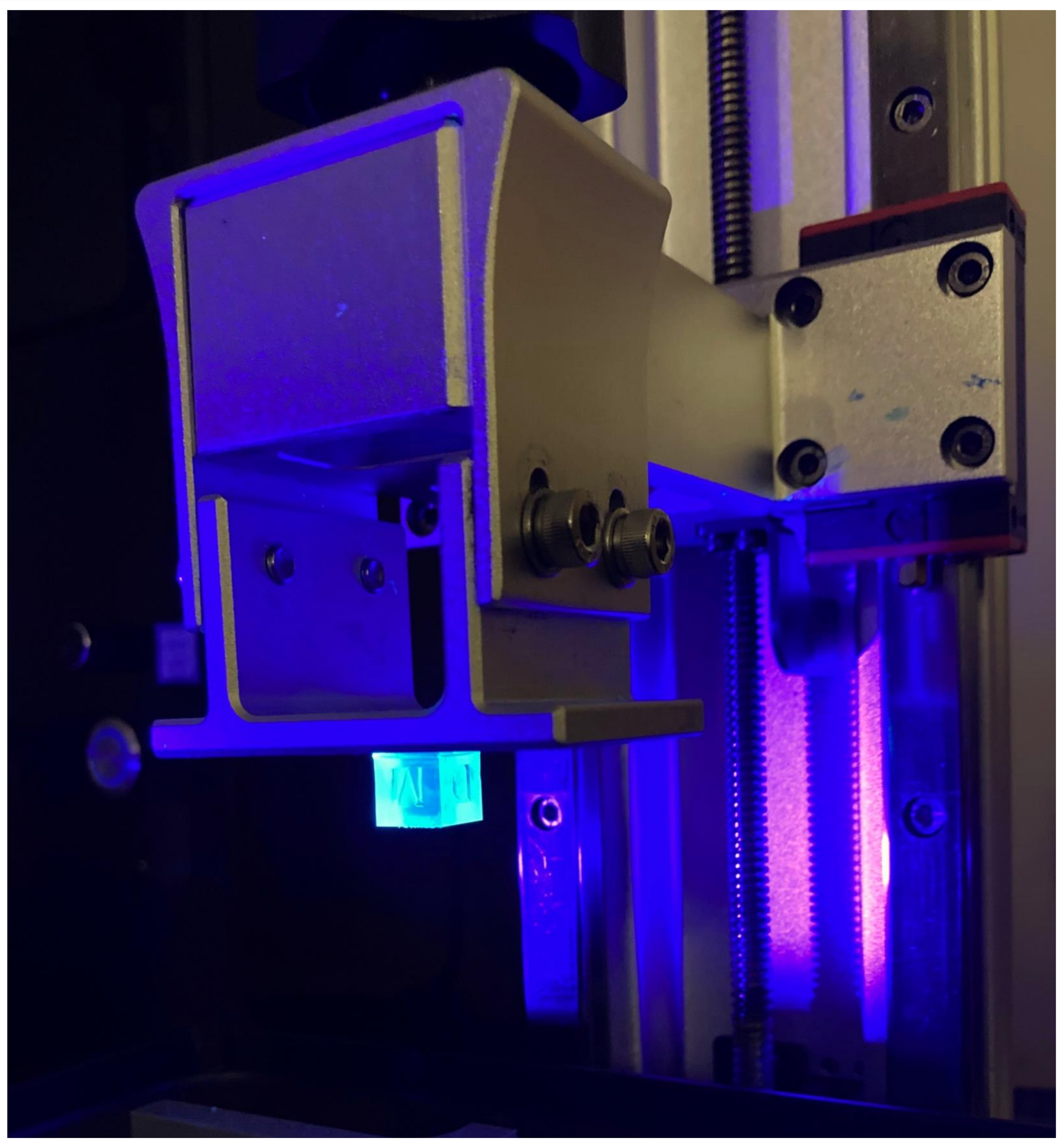


Photo 1. Printout obtained from a photo-cured resin: ANT-CH_3, IOD (0.1/1 w/w), 3% MDEA, HEMA/BEDA (3/7)

Radical photopolymerization

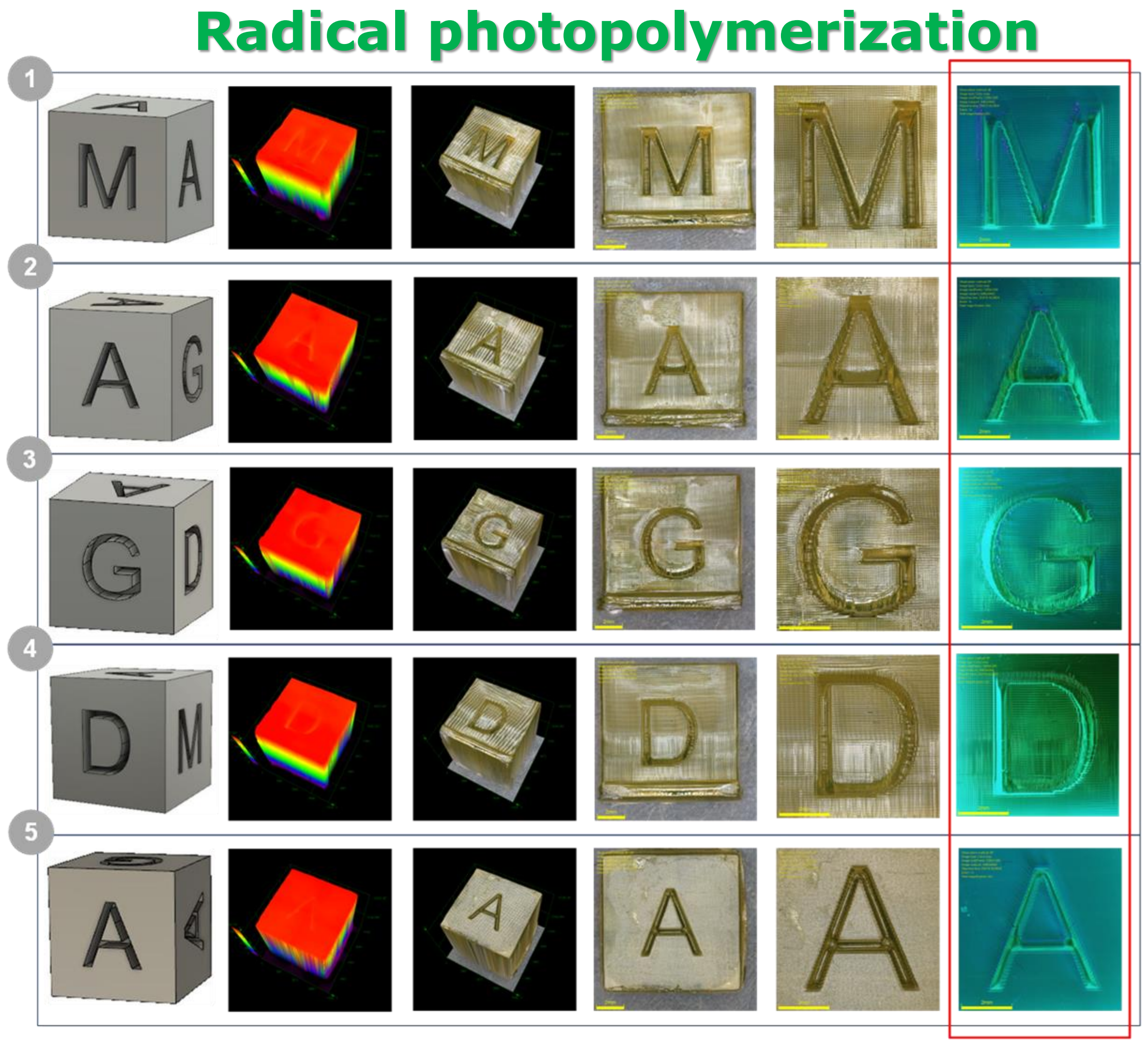


Figure 1. Photographs of a printout obtained from a photo-cured resin: ANT-CH_3, IOD (0.1/1 w/w), 3% MDEA, HEMA/BEDA (3/7) (1-5 individual faces of a cube with different letters); last column – photographs were taken under the UV flashlight.

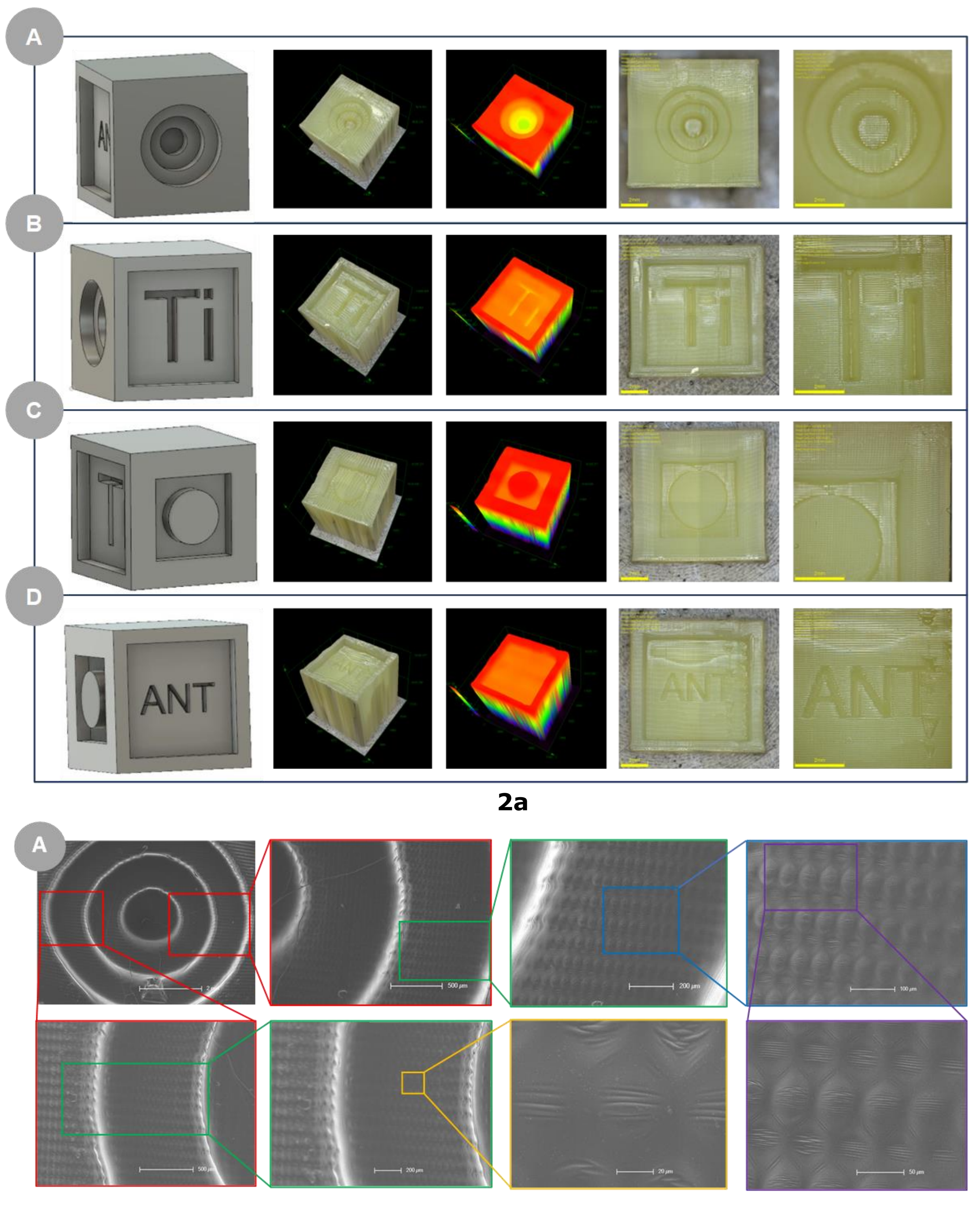


Figure 2a, 2b. Photographs of a printout obtained from a photo-cured resin: ANT-CH_3, IOD (0.1/1 w/w), 3% MDEA, HEMA/BEDA (3/7), 0.1 % TiO_2 (A-D individual faces of a cube with different letters): (a) under an optical microscope, (b) under a scanning electron microscope.

Table 1. The values of acrylate monomer conversion were obtained during hybrid radical photopolymerization using Vis LED @405 nm.

Light source: LED @405 nm									
					Functional group conversion				
Composition	Experimental conditions	Thickness	Monitoring wavelengths	Light intensity [mW/cm²]	ANT-CH_3 (without nanofiller)	ANT-CH_3, 1% w/w AlZnO	ANT-CH_3, 1% w/w ZnO	ANT-CH_3, 3% w/w Halloysite nanoclay	ANT-CH_3, 0.1 % w/w TiO_2
HEMA/BEDA (3/7 w/w), 3 % MDEA, 1% IOD	Thick layer	1.16 mm	ACRYLATE at 6165 cm^{-1}	26.50	96	95	86	94	94
				2.65	29	33	21	42	28
HEMA/BEDA (3/7 w/w), 1% IOD				26.50	68	56	63	71	88
				2.65	26	26	12	15	12

Cationic - radical photopolymerization

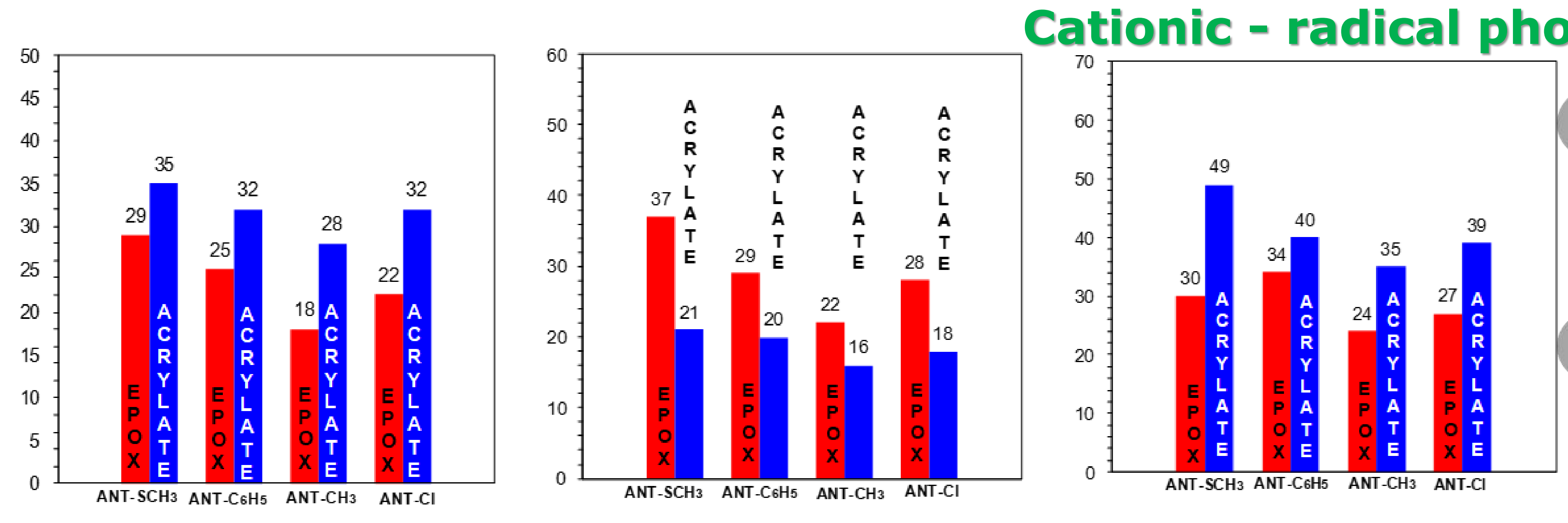


Figure 3. Acrylate and epoxy monomer conversions obtained during hybrid photopolymerization of CADE/TMPTA/M100 monomers: (a) laminate condition, thin layer; (b) air thin layer; (c) laminate condition, thick layer.

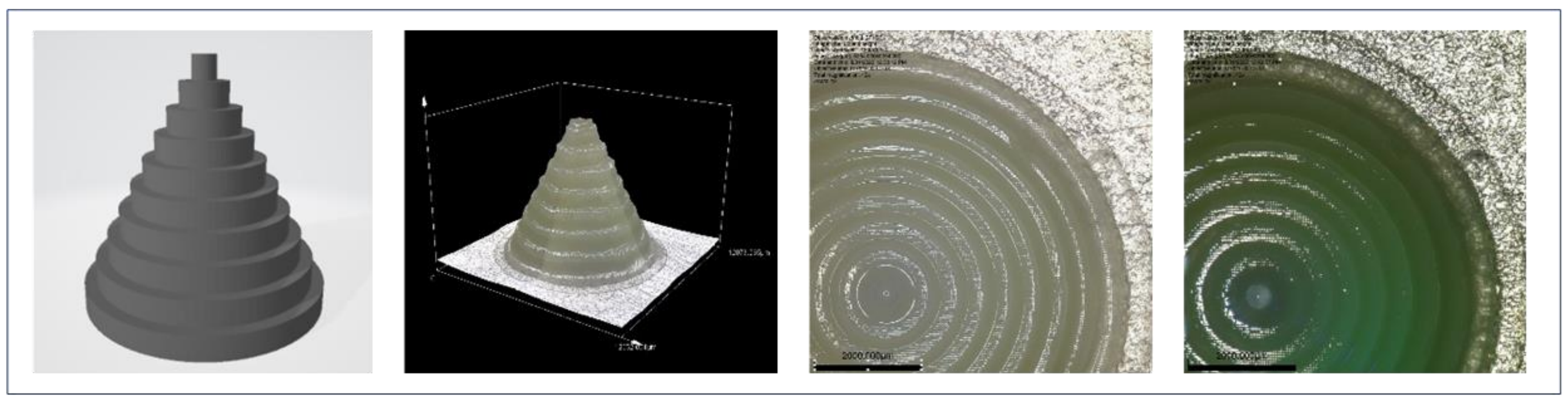


Figure 4. Photographs of a printout obtained from a photo-cured resin: ANT-SCH_3, IOD (0.1/1 w/w), CADE/TMPTA/M100 (2/2/1), 0.1% TiO_2.

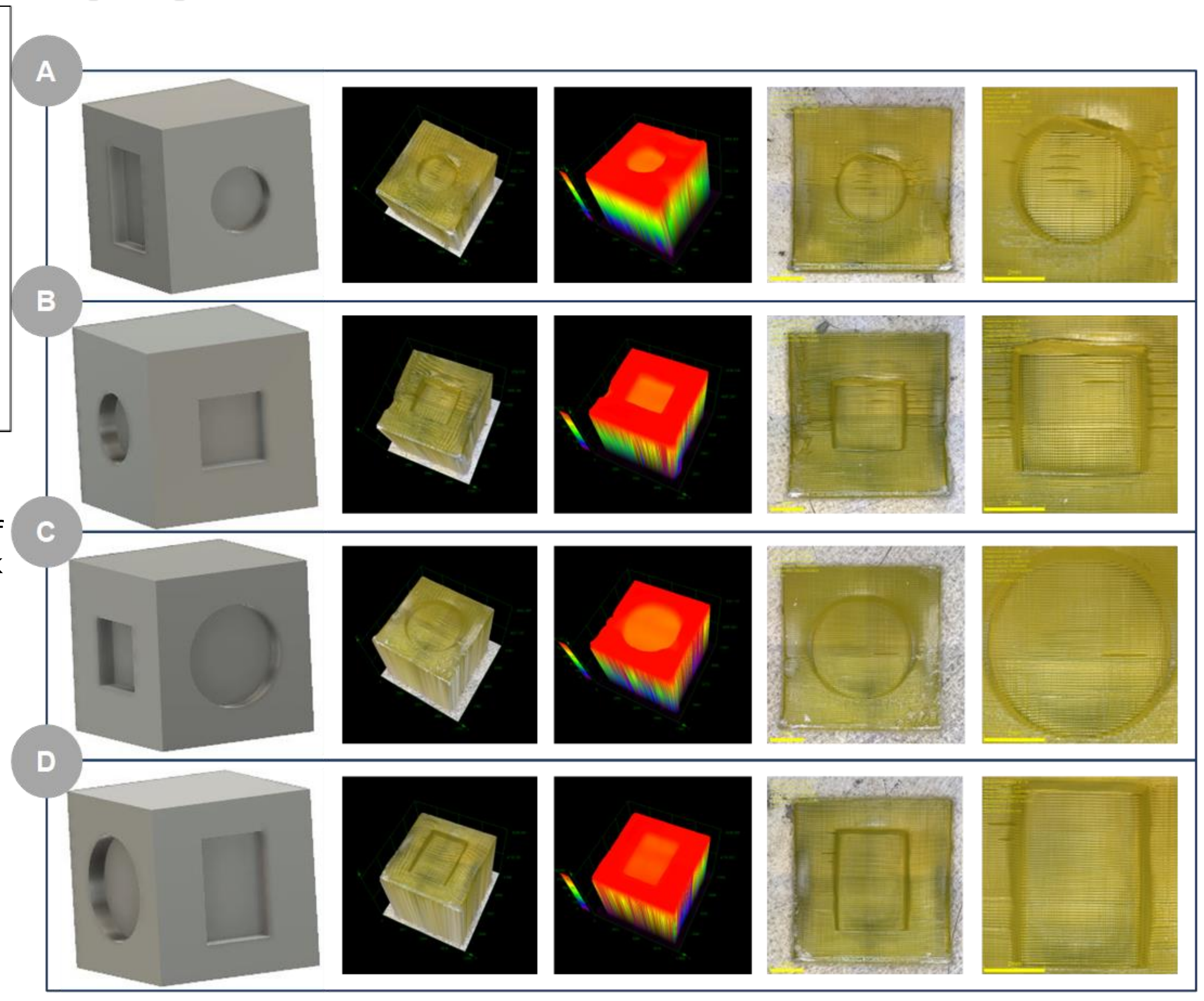
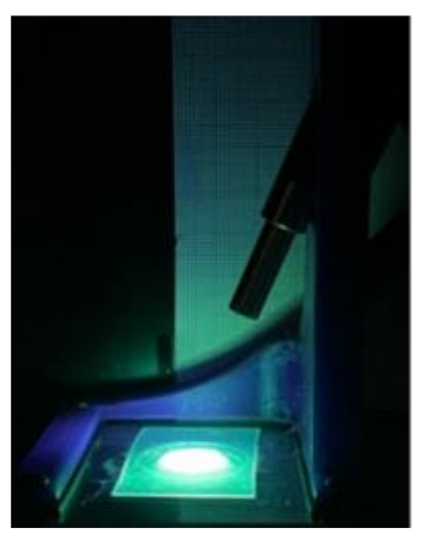
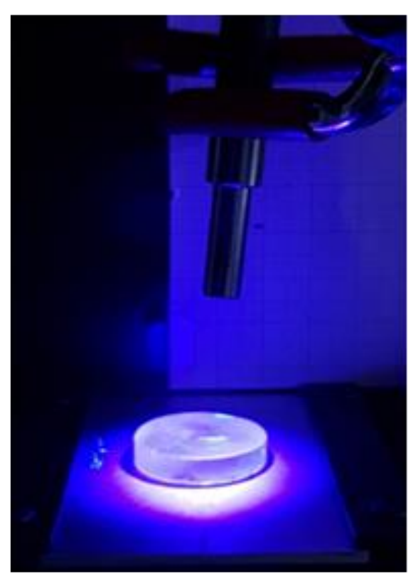


Figure 5. Photographs of a printout obtained from a photo-cured resin: ANT-SCH_3, IOD (0.1/1 w/w), CADE/TMPTA/M100 (2/2/1) (A-D individual faces of a cube).

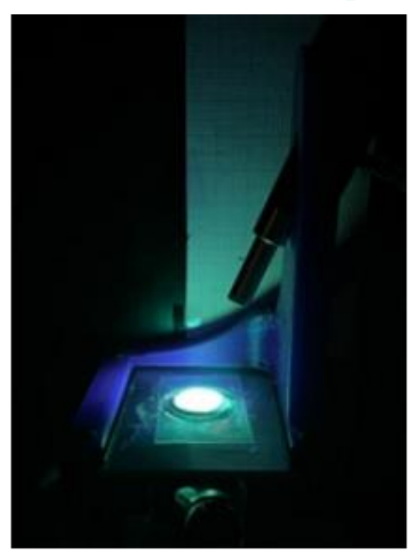
Process conditions



a – laminate condition; thin layer



b – air thin layer



c – thick layer

Table 2. The values of acrylate and epoxy monomer conversion were obtained during hybrid photopolymerization using Vis LED @405 nm.

Light source: LED @405 nm							
				Functional group conversion			
Composition	Experimental conditions	Thickness	Monitoring wavelengths	ANT-SCH_3	ANT-C_6H_5	ANT-CH_3	ANT-Cl
CADE/TMPTA/M100 (2/2/1 w/w/w)	Laminate	25 μm	EPOX at 790 cm^{-1}	29	25	18	22
			ACRYLATE at 1.635 cm^{-1}	35	32	28	32
	Air thin layer	25 μm	EPOX at 790 cm^{-1}	37	29	22	28
			ACRYLATE at 1.635 cm^{-1}	21	20	16	18
	Air thick layer	1.16 mm	EPOX at 3.700 cm^{-1}	30	34	24	27
			ACRYLATE at 6.165 cm^{-1}	49	40	35	39

The examined initiator systems showed versatile performance, and can be successfully applied as photoinitiators for radical, cationic and hybrid photopolymerization. The innovative application of the new high-performance initiator systems is their usage for obtaining photo-curable nanocomposites from radical resins, as well as hybrid resins, which has been confirmed by kinetic studies, as well as DLP 3D printing experiments using low-cost equipment. The research studied the effects of different nanoparticles on the kinetic parameters of photo-curable resins, as well as on 3D printing parameters (such as critical energy, for example). The selection of the right amount of nano-additive, resin composition, as well as 3D printing parameters is essential for the correct printing process of nanocomposites, as well as for obtaining a print with high quality and very good resolution.

Acknowledgment
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