

# YOUNG MACROMOLECULAR RESEARCHER WEBINAR

Tue 12-March 2024 15:00-15:45 (UK)

Helen Tunstall-Garcia, University of Cambridge

## *Interplay of Luminores and Photoinitiators During Synthesis of Bulk and Patterned Luminescent Photopolymer Blends*

Four-dimensional printing with embedded photoluminescence is emerging as an exciting area in additive manufacturing. Slim polymer films patterned with three-dimensional lattices of multimode, cylindrical waveguides (waveguide-encoded lattices, WELs) with enhanced fields of view can be fabricated by localizing light as self-trapped beams within a photopolymerizable formulation. Luminescent WELs have potential applications as solar cell coatings and smart, planar optical components. However, the presence of luminophores can result in changes in the refractive index or cure depth of the final photopolymer, and as luminophore-photoinitiator interactions are expected to alter the photopolymerization kinetics for the self-trapping process, the design of robust luminescent photopolymer sols is non-trivial.

Here, we investigate the influence of the highly efficient luminophore Lumogen® Violet (LV) on the photolysis kinetics of the free-radical photoinitiator Omnirad™ 784 through UV/Vis absorption spectroscopy in methacrylate-siloxane and epoxide homopolymers, and their blends.

Initial rate analysis with different bulk polymers reveals differences in the zero-order rate constants in the absence and presence of LV, with a notable increase (~ 40%) in the photolysis rate for the blend. Fluorescence quenching studies, coupled with density functional theory calculations, establish that these differences arise due to electron transfer from photoexcited LV to the ground state photoinitiator molecules. We also demonstrate an in-situ UV/Vis absorbance technique that enables real-time monitoring of both waveguide formation and photoinitiator consumption during the fabrication of WELs. The in-situ photolysis kinetics confirm that LV-photoinitiator interactions also influence the photopolymerization process during WEL formation. Our findings show that luminophores play a non-innocent role in photopolymerization and highlight the necessity for both careful consideration of the photopolymer formulation and a real-time monitoring approach to enable the fabrication of high-quality micropatterned luminescent polymeric films.

Dr. Jussi Isokuortti, University of Texas at Austin

## *Digital light processing 3D-printing in ambient conditions using triplet photon upconversion*

We present a photopolymerization system utilizing triplet-triplet annihilation upconversion (TTA-UC) to drive a Type I photocuring process using green light at a low power density (<10 mW/cm<sup>2</sup>) and in the presence of ambient oxygen. Notably, this system displays a superlinear dependence between cure depth and light exposure intensity, thereby enhancing spatial resolution. This allows for the integration of TTA-UC into digital light processing (DLP) 3D printing, offering an economical, rapid, and high-resolution manufacturing process. Additionally, compared to conventional Type I and Type II (photoredox) approaches, our TTA-UC photoinitiation method demonstrates improved confinement of cure depth and resin shelf life. This study introduces a user-friendly approach to employing TTA-UC in ambient photochemical processes, laying the foundation for the production of next-generation plastics with superior geometric precision and functionality.

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