

# From Free Radical to Radical-Free Lithographic 3D Printing

*Katharina Ehrmann,<sup>1,2</sup> Danijela Kojic,<sup>1</sup> Stephan Schandl,<sup>1</sup> Raffael Wolff,<sup>1</sup> Thomas Koch,<sup>3</sup> Jürgen Stampfl,<sup>3</sup> Steven Gauci,<sup>2</sup> Tugce Nur Eren Mert,<sup>4</sup> Christopher Barner-Kowollik,<sup>2,4</sup> Robert Liska<sup>1</sup>*

<sup>1</sup>Institute of Applied Synthetic Chemistry, Technische Universität Wien, Austria

<sup>2</sup>School of Chemistry and Physics, Queensland University of Technology, Australia

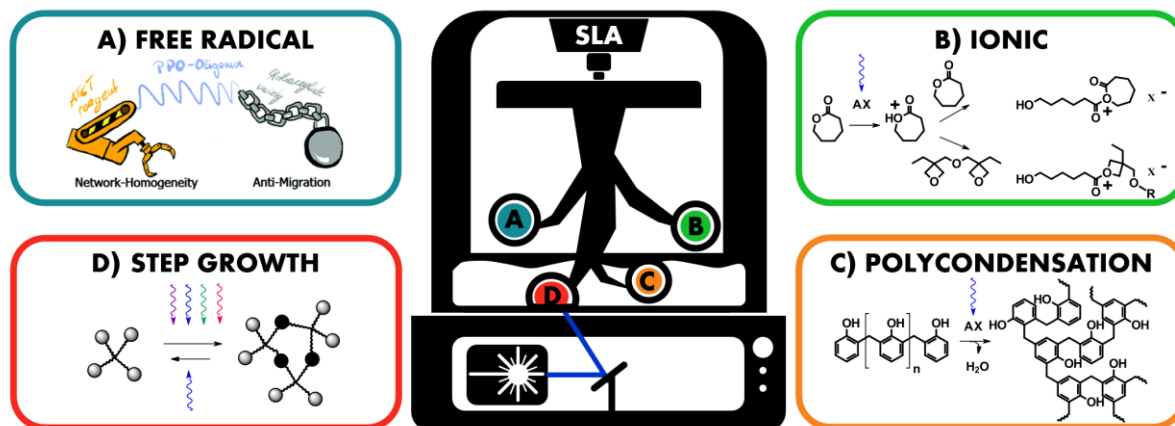
<sup>3</sup>Institute of Materials Science and Technology, Technische Universität Wien, Austria

<sup>4</sup>Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Germany

Stereolithographic 3D printing via free radical polymerization (**Fig.1 A**) is a versatile manufacturing method due to its high resolution, smooth surface finish and part size scalability compared to other printing techniques. While material formulation variability allows for some flexibility of material properties, most printing processes are restricted by the material properties of radically cured photopolymers. Overcoming major drawbacks such as brittle fracture and high volumetric shrinkage is the focus of ongoing research.

By enabling elevated printing temperatures up to 120 °C, slower and more controlled, non-radical polymerization mechanisms become available for stereolithographic 3D printing. For example, less reactive cyclic monomers as they are encountered in cationic and anionic ring-opening photopolymerization become accessible in light-based 3D printing at elevated temperatures. We have demonstrated printability of pure poly(ether)ester and poly(ether)carbonate networks (**Fig.1 B**), which exhibit highly desirable characteristics such as biocompatibility, degradability and low shrinkage. Moving from chain growth towards step growth polymerization mechanisms, judicious choice of the processing temperature even allows printing via polycondensation without bubble-formation from emerging small molecular byproducts. We have shown this for pure phenolic resins previously inaccessible to 3D printing (**Fig.1 C**). Furthermore, catalytic cyclotrimerization of cyanate ester resins gives polymers with  $T_g$ s well beyond 300 °C, which have not been reached for these materials so far.

An alternative approach to unlock new chemistries and properties for stereolithographic printing is to diversify the light source for light-induced polymerization during the printing process (**Figure 1 D**). For example, we have recently shown that a simple change in laser intensity during micro stereolithographic manufacturing enables us to produce stable and degradable structures from the same photoresist. Furthermore, wavelength-selective reactions are a promising avenue for stereolithographic 3D printing.



**Figure 1.** Diversification of polymerization mechanisms applicable in SLA printing