Diversifying Processing Parameters and Polymerization Mechanisms for SLAPrinting

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Stereolithographic (SLA) printing utilizing free radical polymerization as curing mechanism has become a versatile manufacturing method due to its high resolution, smooth surface finish and part size scalability compared to other printing techniques.[1] While material formulation variability allows for some flexibility of material properties, this flexibility is considerably restricted by a narrow process window.[1] Formulation viscosities must remain low, curing times until the gel point is reached should be fast, and initiation systems largely rely on UV light with the initiation system being responsive to a broad wavelength range.

On the one hand these shortcomings can be overcome within free radical polymerization-based SLA printing through parallel adjustment of processing parameters and formulation components. In particular, elevated printing temperatures are a promising route to make highly viscous monomers accessible: We show examples for successful SLA printing of oligomeric monomers[2] and monomers with strong intramolecular interactions, which were utilized in Hot Lithography, an SLA process with temperatures up to 120 °C (**Fig.1 A**). Resulting materials have been shown to exhibit higher toughness compared to conventional highly crosslinked (meth)acrylic resins.

On the other hand, the introduction of more controlled, non-radical polymerization mechanisms to SLA printing promises diversification of accessible SLA printable materials. For example, less reactive cyclic monomers as they are encountered in cationic and anionic photopolymerization become accessible in Hot Lithography (**Fig.1 B**). Resulting pure poly(2-oxazolines),[3] poly(ether)esters[4] and poly(ether)carbonates exhibit highly desirable characteristics such as biocompatibility, degradability and shapememory. Moving from chain growth towards step growth polymerization mechanisms, clever choice of processing parameters even allows printing via polycondensation without bubble-formation from emerging small molecular byproducts. We have shown this for pure phenolic resins, previously inaccessible for SLA printing (**Fig.1 C**).[5]

Figure 1. Diversification of polymerization mechanisms applicable in SLA printing

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