EXPANDING SPIROCYCLIC MONOMERS FOR HOT LITHOGRAPHY TECHNOLOGY

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Additive manufacturing is raising great interest as a polymer manufacturing technique since it enables rapid production of complex geometries. Stereolithography, a widely used light-based 3D-printing method combines high resolution and excellent surface quality with short printing times. Layers of the desired object are cured sequentially by a UV-laser, which is focused on a liquid photopolymer resin. Hot Lithography is a stereolithography-based process that enables the application of solid and highly viscous resins at room temperature through high operating temperatures. Methacrylates and epoxides are conventional monomers in 3D-printing processes but their shrinkage upon polymerization results in crack formation and lowers surface quality. Expanding monomers like spiro-orthoesters and spiro-orthocarbonates polymerize *via* a cationic (double) ring-opening process, thereby exhibiting low shrinkage. [1]

Herein, the applicability of spiro-orthoesters and spiro-orthocarbonates for Hot Lithography systems is investigated. Hence, spirocyclic compounds were synthesized and investigated with regard to their photopolymerization efficiency at different temperatures.

Photo-DSC analysis gave information about the reactivity of the spirocyclic compounds and monomer conversions were calculated from NMR-spectra. GPC-analysis provided the molecular weight of the obtained polymers. The impact of the ring size on the polymerization modes was examined. Seven-membered spiro-orthoester proved to be the most feasible monomer in terms of reactivity and polymerization mode. Difunctional spiro-orthoester derivatives were synthesized and investigated in analogy to the monofunctional compounds. Furthermore, the resulting polymers were tested with thermomechanical methods.

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[1] Takata, T.; Endo, T., Recent advances in the development of expanding monomers: Synthesis, polymerization and volume change. *Progress in Polymer Science* **1993,** *18* (5), 839-870.