

Doctoral Dissertation  
Doctoral Program in Material Science and Technology (34<sup>th</sup> Cycle)

# **Multifunctional cyclodextrin derivatives for digital light processing 3D-printing**

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## **Abstract**

By virtue of an almost unlimited freedom of design and customization, a near-zero material waste and the possibility to fabricate in one-single stage complex parts, additive manufacturing (alias 3D-printing) has opened in the last twenty years new horizons in many different fields, from automotive to medicine. In particular, photopolymerization based 3D-printing technologies (i.e. vat polymerization) are attracting growing interest due to the high versatility given by photochemistry, that is the possibility to exploit light to tune the structure-property relationships of polymers via fast and spatiotemporal controlled reactions. However, the need of polymers having suitable photopolymerizable functionalities limits the choice of printable materials and thus also the large-scale adoption of these techniques. To deal with this issue and the new stringent request of a more sustainable manufacturing, the research community is endeavoring to enlarge the photopolymers palette with “greener” alternatives prepared from natural molecules or their derivatives. In this framework, the experimental investigations presented throughout this dissertation focus on the synthesis of multifunctional cyclodextrin derivatives suitable for vat polymerization. Indeed, cyclodextrins are very versatile molecules and can be used as building blocks for the development of molecularly well-defined derivatives because their hydroxyl groups can be rather easily converted into the desired functionalities.

After a brief overview of additive manufacturing (chapter 1) and an in-depth investigation of vat polymerization (from the photochemical reactions involved to the photoresins typically used, chapter 2), the first experimental contribution (chapter 3) is focused on the synthesis of a multi-acrylated cyclodextrin and its use as photocurable macromer in bio-based formulations for digital light processing 3D-printing. Specifically, combining this multifunctional cyclodextrin derivative with a monofunctional monomer is presented as the most promising strategy, since this allows to get thermosetting polymers whose mechanical properties can be tuned

by balancing the high crosslinking efficiency of the former and the plasticizing effect of the latter.

However, the use of photocurable formulations containing multiunsaturated monomers as the multi-acrylated cyclodextrin presented in this study inherently entails anomalous behaviors, above all the incomplete conversion of the photopolymerizable functionalities during the printing step. In this sense, different strategies of post-printing functionalization are presented in the second experimental contribution (chapter 4) as a powerful tool to turn the unreacted acrylate functions into a potential advantage, since these can provide active sites for surface modifications. To support this, Michael-addition reactions are exploited to tune the surface-wettability of 3D-printed structures via the grafting of hydrophobic/hydrophilic polymeric brushes. Moreover, the modification of the surface with a thiolated active interface is used for a subsequent surface-anchoring of photoreduced silver nanoparticles.

In the third experimental contribution (chapter 5), cyclodextrins are used as building blocks to prepare a molecularly well-defined multifunctional photoinitiator via the grafting of multiple bis(acyl)phosphane oxide photoactive units. The high photoinitiating efficiency of this multi-photoactive cyclodextrin derivative is demonstrated, even when using it at low molar concentrations. But mostly, this multifunctional photoinitiator stands out by its ability to serve simultaneously as photo-crosslinking agent to convert monofunctional monomers into mechanically stable thermosets without the need of additional crosslinkers.

This unique feature is finally exploited in the last experimental contribution (chapter 6) to enable the printability of crosslinkers-free formulations. Indeed, a novel photopolymerizable system based only on monofunctional methacrylates bearing hydrogen-bonding groups is used to fabricate thermoresponsive shape memory polymers by means of digital light processing 3D-printing. In this context, the multi-photoactive cyclodextrin derivative is used as a *two-in-one* photoinitiator and crosslinking agent ensuring the printability of the monomethacrylates-based system. Moreover, it provides covalently crosslinked net-points which serve to impart dimensional stability and prevent chain slippage when heating the printed structures to above their glass transition temperature in the deforming and recovery stages of the shape memory cycle. The properties of the fabricated shape memory polymers are investigated in details and their potential integration in the fabrication of a smart thermoresponsive device is proved by the successful development of a prototype.