THIOL-YNE PHOTO-CLICK CHEMISTRY: TOWARDS HIGHLY HOMOGENEOUS POLYMERIC NETWORKS WITH UNIQUE PROPERTIES

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The last decade has seen a remarkable increase in the development of lithography based additive manufacturing techniques for polymeric materials. Compared to other 3D printing methods these light-based techniques offer several advantages including higher writing speed and better resolutions.[1] However, state-of-the art UV curable resins are limited to (meth)acrylate based monomers and their resulting polymeric networks.[2] One considerable drawback of (meth)acrylate building blocks is their comparably low polymer toughness in their cured state, which drastically limits their applicability. This behavior can be attributed to the evolution of shrinkage stress during the fast radical chain growth polymerization and the formation of an inhomogeneous polymeric network structure.

In this contribution, the versatility of the thiol-yne photo-click reaction [3] for the fabrication of photopolymers with unique thermo-mechanical properties is shown. The obtained polymers yield highly homogenious network structures that exhibit a sharp and defined thermal glass transition greatly above room temperature together with outstanding polymer toughness.[4,5] Additionally, it turned out that the synthesized monomers provide high reactivities comparable to those of acrylates, an almost quantitative conversion and low cytotoxicity,[6] which makes these polymers interesting for challenging applications such as medical implants.

The herein described monomer system paves the way towards the fabrication of ultra tough photopolymers for demanding applications by means of stereolithography.

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[2] Basics and applications of photopolymerization reactions: New highly reactive acrylate monomers: The importance of the hydrogen abstraction reaction; Fouassier, J. P.; Allonas, X., Eds. 2; Research Signpost: Kerala, India, 2010.

[3] Lowe, A. B.; Hoyle, C. E.; Bowman, C. N. Thiol-yne click chemistry: A powerful and versatile methodology for materials synthesis. J. Mater. Chem 2010, 20, 4745, DOI: 10.1039/b917102a.

[4] Oesterreicher, A.; Gorsche, C.; Ayalur-Karunakaran, S.; Moser, A.; Edler, M.; Pinter, G.; Schlögl, S.; Liska, R.; Griesser, T. Exploring Network Formation of Tough and Biocompatible Thiol-yne Based Photopolymers. Macromolecular Rapid Communications 2016, 37, 1701–1706, DOI: 10.1002/marc.201600369.

[5] Oesterreicher, A.; Wiener, J.; Roth, M.; Moser, A.; Gmeiner, R.; Edler, M.; Pinter, G.; Griesser, T. Tough and degradable photopolymers derived from alkyne monomers for 3D printing of biomedical materials. Polym. Chem. 2016, 7, 5169–5180, DOI: 10.1039/C6PY01132B.

[6] Oesterreicher, A.; Ayalur-Karunakaran, S.; Moser, A.; Mostegel, F. H.; Edler, M.; Kaschnitz, P.; Pinter, G.; Trimmel, G.; Schlögl, S.; Griesser, T. Exploring thiol-yne based monomers as low cytotoxic building blocks for radical photopolymerization. Journal of Polymer Science Part A: Polymer Chemistry 2016, 54, 3484–3494, DOI: 10.1002/pola.28239.