## **3D** printing materials based on anionic photopolymerisation processes

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3D printing is an emerging technique in scientific, industrial and commercial areas, expected to revolutionise our day-to-day lives. Photo-induced polymerisation techniques are well recognised within 3D printing for their speed and precision in addition to their low energy and solvent consumption [1]. The traditionally used (meth)acrylate resins for radical photopolymerisation show drawbacks associated with shrinkage during polymerisation, toxicity in uncured state and inhibition by oxygen [2]. Therefore, there is plenty of room for the development of novel light-sensitive materials for 3D Printing [3]. Anionic photopolymerisation can help to achieve novel functional materials opening up the way to overcome the limitations of radical photopolymerisation. Upon exposure to UV or visible light photolatent base generators (PBG) are able to release reactive bases initiating anionic polymerisation reactions. Such reactions among others are ring-opening polymerisation (ROP) of epoxides, polyurethane catalysis and thiol click reactions involving thiolether and thiourethane systems as well as Michael addition reactions [1]. These reactions can open up opportunities for creating bio-based, biodegradable polymers along with materials with dynamic covalent bonds (DCB) capable of being repaired and reprocessed [4].

The aim of this work is to develop new polymeric materials and formulations for PBG-initiated anionic photopolymerization by LED light for 3D printing. Apart from the protocol of formulation, the development process involves the characterisation of the new photocured materials and 3D printed objects together with the optimisation of the 3D printing process. The overarching goal is to obtain a new system with better functionalities and sustainability than the current benchmark. To achieve this bio-based monomers would be used for the creation of biodegradable polymer chains by ROP and for the development of covalent adaptable networks (CANs). The research is aimed to provide indepth knowledge about the formulation, and properties of materials created by anionic photopolymerisation and their use in 3D printing. The anticipated new material is foreseen to help light-based 3D printing become a more environment and customer-friendly manufacturing method.

## References

<sup>[4]</sup> V. S. D. Voet, 'Closed-Loop Additive Manufacturing: Dynamic Covalent Networks in Vat Photopolymerization', *ACS Mater. Au*, vol. 3, no. 1, pp. 18–23, Jan. 2023, doi: 10.1021/acsmaterialsau.2c00058.





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<sup>[1]</sup> D. Perrot, C. Croutxé-Barghorn, and X. Allonas, 'UV-curable thio-ether-urethane network with tunable properties', *J. Polym. Sci. Part Polym. Chem.*, vol. 54, no. 19, pp. 3119–3126, Oct. 2016, doi: 10.1002/pola.28196.

 <sup>[2]</sup> A. Bagheri and J. Jin, 'Photopolymerization in 3D Printing', ACS Appl. Polym. Mater., vol. 1, no. 4, pp. 593–611, Apr. 2019, doi: 10.1021/acsapm.8b00165.

<sup>[3]</sup> I. Roppolo et al., '3D printable light-responsive polymers', Mater. Horiz., vol. 4, no. 3, pp. 396–401, 2017, doi: 10.1039/C7MH00072C.