

Synthesis of Photobase LED Sensitive Photoinitiators

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In recent decades, photopolymerization has undergone substantial progress, evolving into a prominent process across academic and industrial sectors. Its versatile applications span various fields, such as coatings, medical applications, additive manufacturing etc, establishing its widespread utilization. Extensively studied photochemical methods generating free radicals and acids are widely utilized for long time in photopolymerization [1]. Investigations into new polymerization pathways utilizing photobase generators aim to broaden the scope of materials in the field. Though it contends with various issues like oxygen inhibition, migration, and yellowing, the advantages of photobase generators (PBG) make them an appealing substitute. PBG systems offer a novel approach to catalyze a range of reactions, including thiol-Michael, thiol-isocyanate, epoxy polymerization, thiol-thiol, and ring-opening polymerization reactions [2]. The desirable features offered by visible-light activated PBGs include reduced scattering, increased penetration depth, greater functional group tolerance, biocompatibility, high pKa for the released base and potential for wavelength selective multimaterial fabrication. These aspects have inspired the design and utility of novel PBGs in polymer synthesis [3], [4], [5].

This work aims to devise LED-sensitive photobase (PBG) generators, this involves a synthesis process and subsequent characterization to evaluate their potential for application in additive manufacturing. Expected outcomes encompass well-established protocols detailing the synthesis of PBG, along with comprehensive investigations into its photochemical properties under LED irradiation. Sustainability metrics will be established to assess the environmental impact of the synthesized photoinitiators, concurrently fostering expertise in the synthesis and characterization of innovative ionic photoinitiators. This research not only contributes to the advancement of LED-sensitive photoinitiators but also cultivates a deeper understanding of their applicability in additive manufacturing processes, envisaging a pathway towards more sustainable and efficient photopolymerization techniques.

References

- [1] K. Suyama and M. Shirai, "Photobase generators: Recent progress and application trend in polymer systems," *Prog. Polym. Sci.*, vol. 34, no. 2, pp. 194–209, Feb. 2009, doi: 10.1016/j.progpolymsci.2008.08.005.
- [2] C. Ley, A. Siedel, T. Bertaux, C. Croutxé-Barghorn, and X. Allonas, "Photochemical Processes of Superbase Generation in Xanthone Carboxylic Salts," *Angew. Chem. Int. Ed.*, vol. 62, no. 11, p. e202214784, Mar. 2023, doi: 10.1002/anie.202214784.
- [3] M. T. Kiker, A. Uddin, L. M. Stevens, K.-Y. Chung, P. Lu, and Z. A. Page, "Visible light activated coumarin photocages: an interplay between radical and organobase generation to govern thiol-ene polymerizations," *Polym. Chem.*, vol. 14, no. 33, pp. 3843–3850, 2023, doi: 10.1039/D3PY00771E.
- [4] A. Chemtob et al., "A highly reactive photobase catalytic system for sol-gel polymerization," *Thin Solid Films*, vol. 550, pp. 177–183, Jan. 2014, doi: 10.1016/j.tsf.2013.10.146.
- [5] H. Salmi, X. Allonas, C. Ley, A. Defoin, and A. Ak, "Quaternary ammonium salts of phenylglyoxylic acid as photobase generators for thiol-promoted epoxide photopolymerization," *Polym Chem*, vol. 5, no. 22, pp. 6577–6583, 2014, doi: 10.1039/C4PY00927D.