

## Nitro-Carbazole Based Oxime Esters as Dual Photo/Thermal Initiators for 3D Printing and Composite Preparation

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### Résumé

As efficient Type I photoinitiator (PI), oxime esters have attracted a wide attention due to their high photoreactivity. A series of oxime esters based on the nitrocarbazole scaffold have been developed and examined for visible light photopolymerization. The oxime esters varying by the terminal groups (acetyl, acryloyl and benzoyl) attached via the oxime ester group were originally prepared. Favorable molar absorption coefficients are found at 405 nm for these PIs due to the presence of the nitro group attached to the carbazole chromophore. As a result of this, the PIs exhibit excellent photoinitiation abilities in the presence of acrylate monomers upon LED@ 405 nm irradiation. Markedly, a better performance than the benchmark PI diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was observed. Chemical mechanisms supporting the polymerization process with these PIs were investigated by steady state photolysis, molecular orbital calculations and real-time Fourier transformed infrared spectroscopy. After the cleavage of N-O bond and decarboxylation, free radicals are generated to initiate the free radical polymerization efficiently. Free radical photopolymerization of the PI was applied in direct laser write and 3D printing. Interestingly, the most interesting structure exhibits thermal initiation behaviors in monomers and can be used as dual photo and thermal initiators. The highly opaque feature of carbon fibers makes it difficult for light penetration, so dual photo/thermal curing are used here to prepare carbon fiber composites.

### Références

- 1) Shaohui Liu, Bernadette Graff, Pu Xiao, Frédéric Dumur, Jacques Lalevée, *Macromolecular Rapid Communications* **2021**, <https://doi.org/10.1002/marc.202100207>.