Radical Polymerization of Methylene Heterocyclic Compounds Towards Novel Functional and Responsive Polymers

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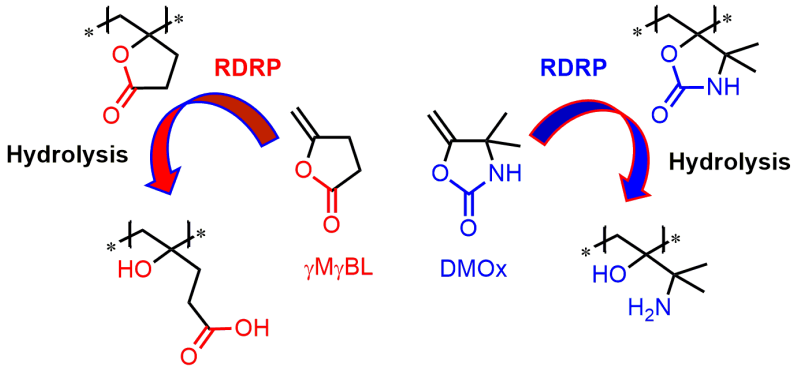
Methylene heterocyclic compounds (MHCs) are an attractive class of monomers for radical polymerization allowing the introduction of heteroatoms and functionalities in the side groups or in the main chain of polymers.[1] Until recently, the vast majority of the MHCs considered in polymer synthesis were conjugated derivatives, so well adapted to the modification of polymers derived from conjugated monomers. However, these MHCs are not suited to copolymerize with some industrially important non-conjugated less activated monomers (LAMs) such as vinyl acetate, ethylene, vinyl amides, etc. The present work aims to address this gap by developing the radical polymerization of non-conjugated MHCs and their copolymerization with LAMs in order to produce a new range of functional copolymers including stimuli-responsive ones. For example, we explored the potential of γ-methylene-γ-butyrolactone (γMγBL)[2,3] and of the CO_2-sourced 4,4-dimethyl-5-methyleneoxazolidin-2-one (DMOx)[4,5] as building blocks for the preparation of functional copolymers. In particular, their reversible deactivation radical copolymerization with VAc, *N*-vinyl caprolactam (*N*VCL) and ethylene, was studied leading to a series of γMγBL or DMOx containing copolymers with controlled molar mass and compositions.[2-5] Post-polymerization modifications of these MHC-based copolymers notably gave access to unique pH-, thermo- and dual-responsive acid- or amine-functional (co)polymers.



References: [1] *Polym. Rev.* **2023**, https://doi.org/10.1080/15583724.2023.2181819. [2] *Macromolecules* **2019**, 52, 8976. [3] *Polym. Chem.* **2022**, 13, 5212. [4] *Polym. Chem.* **2020**, 11, 7207. [5] *Macromolecules* **2021**, 54, 10415.

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