Photoinduced Hydrogen Atom Transfer Mechanisms in Polymer Degradation, Functionalization and Depolymerization

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Résumé :

Polymers are indispensable to modern life, with global plastic production exceeding 400 million tons annually, a figure projected to reach 1.2 gigatons by 2060.[1] Despite their remarkable material properties, the growing demand for plastics has led to a critical accumulation of waste, raising serious environmental and health concerns. This has intensified research efforts into advanced recycling and upcycling strategies. Upcycling enhances material value by transforming end-of-life materials into products with improved properties or novel functionalities through functionalization or chemical decomposition.[2-4] However, most upcycling strategies are not broadly applicable across various polymer types and often lack versatility. In contrast, chemical recycling, particularly depolymerization, seeks to recover monomers by selectively cleaving polymer chains, enabling closed-loop reuse through repolymerization.[5, 6] Although significant progress has been made, many existing methods require pre-installed functional end-groups or low molecular weight polymer.

In this context, Hydrogen Atom Transfer (HAT) chemistry has emerged as a powerful and versatile tool for polymer upcycling/recycling, enabling C-H bond abstraction from polymer backbones to generate carbon-centered radicals along the polymer backbone.[2] Under aerobic conditions, this process promotes photo-oxidative degradation, while in an inert atmosphere, it enables functionalization or main-chain scission depolymerization, depending on the reaction condition, in the presence of radical acceptors such as disulfide-based RAFT agents.

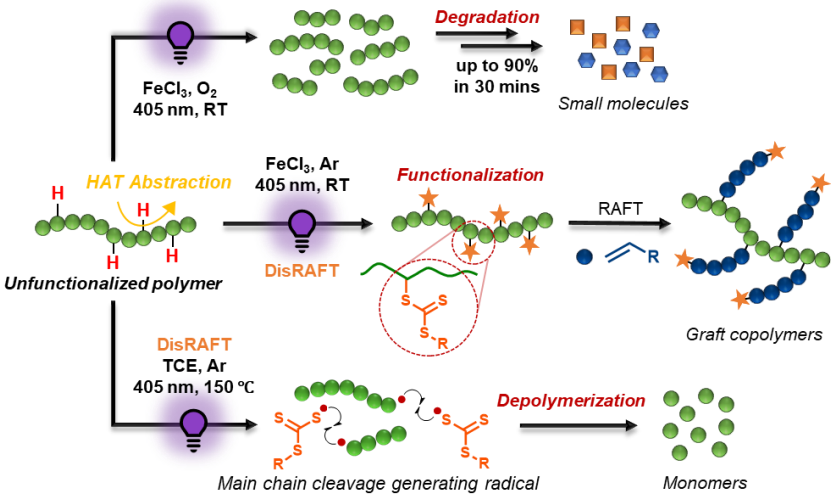

Figure. *Hydrogen atom abstraction from a non-functionalized polymer backbone enabling (top) photo-oxidative degradation, (middle) functionalization, and (bottom) main-chain initiated depolymerization.*

Références :

[1] Global plastics outlook: Policy scenarios to 2060. *OECD.* 2022.

[2] Wimberger, L.; Ng, G.; Boyer, C., Light-driven polymer recycling to monomers and small molecules. *Nat Commun.* 2024, **15** (1), 2510.

[3] Michelas, M.; Wimberger, L.; Boyer, C., A General Approach for Photo-Oxidative Degradation of Various Polymers. *Macromol. Rapid Commun.* 2024, **45** (20), e2400358.

[4] Kumar, M.; Michelas, M.; Boyer, C., Polymer Chain Modification via HAT Chemistry and Its Application in Graft Copolymer Synthesis. *ACS Macro Lett.* 2025, **14**, 4, 396–404.

[5] Michelas, M.; Kumar, M.; Lin, Z.; Boyer, C., In Situ Modification Assisted by HAT Chemistry for the Main Chain Initiated Depolymerization of Polymethacrylates, *ACS Macro Lett.* 2025, **14**(6), 822-829.

[6] Jones, G. R.; Whitfield, R.; Wang, H. S.; De Alwis Watuthanthrige, N.; Antonopoulou, M.-N.; Lohmann, V.; Anastasaki, A., Harnessing Non-Thermal External Stimuli for Polymer Recycling. *Macromolecules* 2025, **58**, 5, 2210–2223.