Radical Ring-Opening Polymerization as a Powerful Tool to Prepare Degradable Materials

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Polymers' light weight, low cost, and, importantly, stability under thermal, chemical, and mechanical stress make them valuable for a range of demanding applications. This stability, on the other hand cau*sed* environmental pollution. Since it is very difficult but also very expensive (REACH registration, etc.) to design brand-new materials that could both have the desired properties (mechanical, thermal, solvent resistance, etc.) and that are in the same time either recyclable and/or biodegradable, transforming already known materials to make them biodegradable/recyclable is more interesting. This approach relies on the introduction of labile bonds onto the polymer backbone. The degradation could thus occur from these weak bonds leading to oligomers that could be easily recyclable and/or bioassimilable. Degradation of commodity thermoplastics prepared by radical polymerization, like LDPE, PMMA and PS, is generally not possible due to the stability of their C–C backbone. A simple and useful method of incorporating weak bonds randomly onto the C–C polymer backbone is by radical copolymerization of vinyl monomers with cyclic monomers via radical ring-opening polymerization (rROP).

This method combines both the advantages of ring-opening polymerization and radical polymerization, that is the production of polymers having heteroatoms and/or functional groups in the main chain together with the robustness, the ease of use and the mild polymerization conditions of a radical process. The polymerization occurs via the addition of radicals onto cyclic monomers bearing an exo-methylene function or equivalent groups followed by a fragmentation of the intermediate cyclic radical to afford a new radical and the incorporation of heteroatoms into the C-C backbone (Figure 1a).

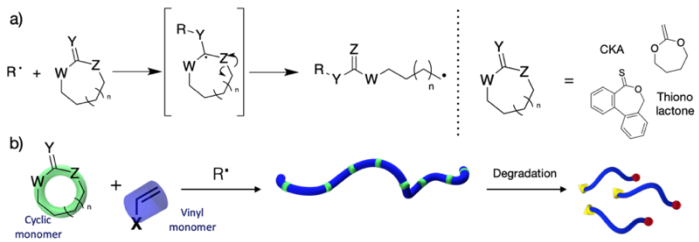
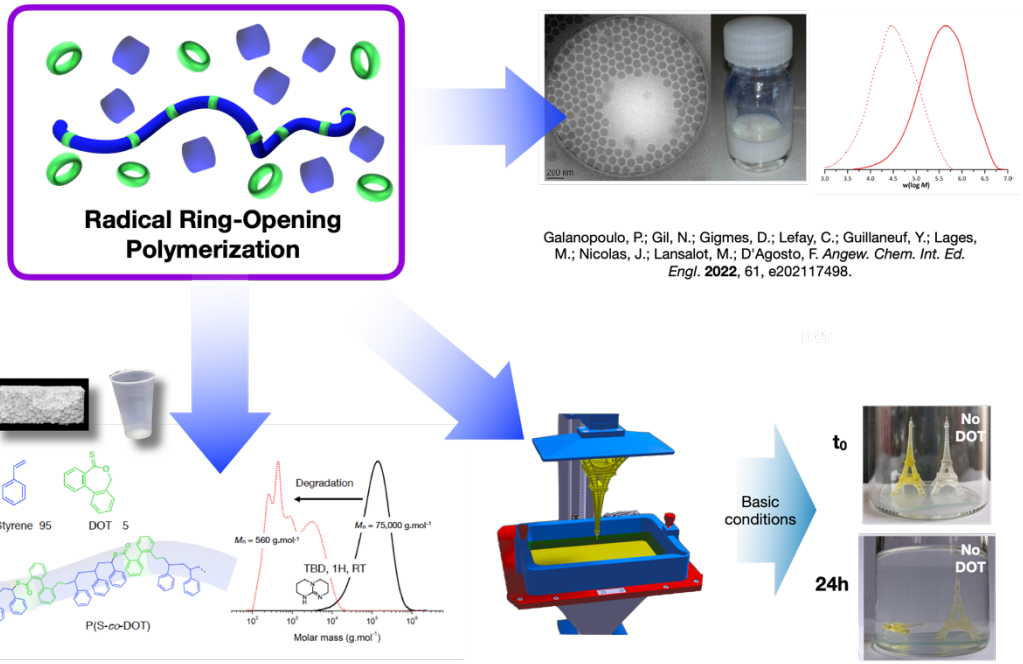


Figure 1. a) Mechanism of rROP. b) Preparation of degradable polymers

Our approach consists in understanding the impact of the structure of the cyclic monomer on the degradability of the copolymer obtained via a theoretical/experimental approach. These studies have made possible to highlight key parameters to obtain degradation products with low molar masses and thus to conclude on the impact of the structure of the cyclic monomer on the copolymerization. Some recent examples are presented in Figure 2.



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