

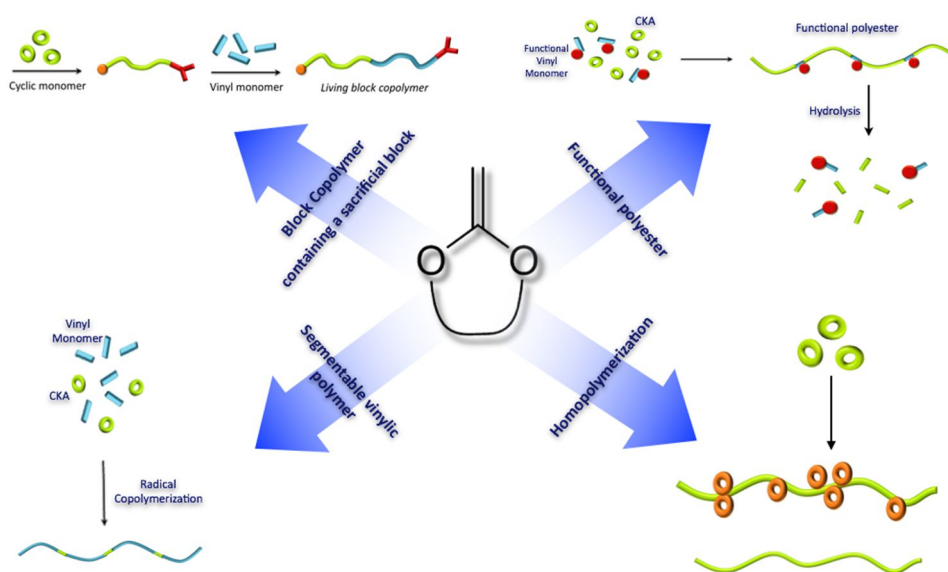
Degradable Materials by the radical polymerization of cyclic ketene acetals

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Among the various polymerization methods, ring-opening polymerization (ROP) is fascinating since it enables the incorporation of heteroatoms and also functional groups into the polymer backbone, thus giving access to a broad range of (bio)degradable materials, such as those deriving from the ROP of lactones and lactides. Although polymerization of traditional vinyl monomers proceeds by chain addition with the creation of carbon-carbon bonds, some cyclic monomers bearing vinyl or exomethylene groups can be polymerized by a radical pathway through a ring-opening mechanism. Radical ring-opening polymerization (rROP) thus combines the advantages of both ring-opening polymerization and radical polymerization, that is the production of polymers having heteroatom 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. Since the first report on rROP during the 60s, many structures from totally different chemical families (e.g., spiro-ortho-carbonates, etc.) were tested for their ring-opening ability. Among them, cyclic ketene acetals (CKA) were reported by Bailey and coworkers in the early eighties as suitable monomers for rROP. This monomer family was then extensively studied as a way to produce similar polymers to classic aliphatic polyesters, but through a radical pathway.¹

rROP was extensively studied in the 80s-90s but has been recently rejuvenated by the possibility to copolymerize cyclic vinyl monomers with classical vinyl monomers, leading to cleavable functions into the copolymer backbone. This led to a broad range of novel (bio)degradable materials suitable for a large scope of applications, particularly in the biomedical field where degradability and/or bioresorption are often required. It has to be noted that all these recent studies used well-known cyclic monomers (e.g., CKA, sulfide cyclic methacrylate, etc.) without newly developed compounds, since it is difficult to rationalize the reactivity of this kind of monomers. The interest towards rROP has also been renewed by the development of controlled/living radical polymerization (CLRP) techniques. These techniques enable the preparation of complex macromolecular architectures (e.g., block, star, grafted copolymers, etc.) that could self-assemble at the nanoscale to create materials with advanced properties. The combination of both RDRP and rROP makes now possible the preparation of block copolymers with different levels of degradability by a unique radical polymerization mechanism. In this talk I will present the recent advances we made in this field.²



¹ A. Tardy; J. Nicolas; D. Gigmes; C. Lefay; Y. Guillauneuf *Chem. Rev.* **2017**, 117, 1319-1406.

² A. Tardy; J.-C. Honoré; J. Tran; D. Siri; V. Delplace, I. Bataille; D. Letourneur; J. Perrier, C. Nicoletti; M. Maresca; C. Lefay; D. Gigmes; J. Nicolas; Y. Guillauneuf *Angew. Chem. Int. Ed.* **2017**, 129, 16742-16747.