RECENT ADVANCES IN THE MACROMOLECULAR ENGINEERING OF ALIPHATIC POLYESTERS BY RING-OPENING POLYMERIZATION

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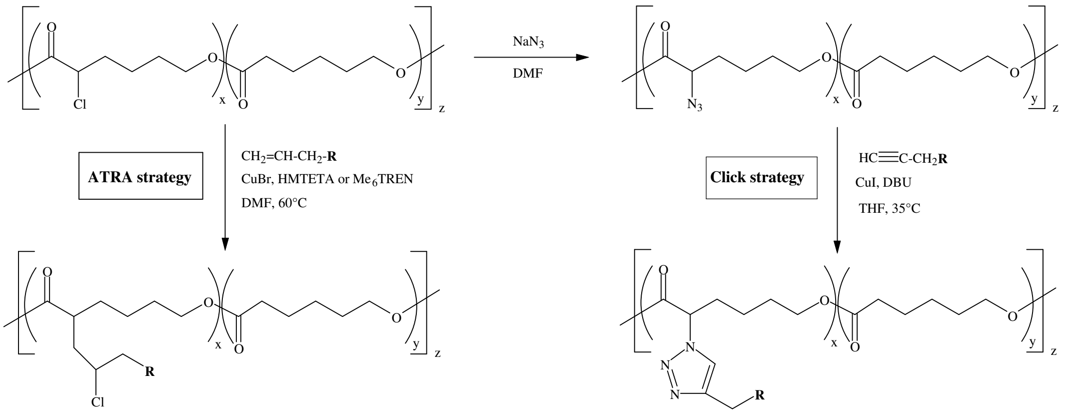
During the last few years, a great research effort has been devoted to the ring-opening polymerization of lactones and lactides initiated by alkoxides of different metals, such as tin, aluminum and rare earth metals. Indeed, the remarkable properties of biodegradability and biocompatibility of the parent polyesters pave the way to applications in the biomedical field and to substitutes for nondegradable polymers. This lecture aims at reporting on recent progress in the macromolecular engineering of aliphatic polyesters.

In order to tailor the polyester properties, it is highly desirable to attach pendent functional groups onto the polyester backbone. This target has been reached by the synthesis and the ring-opening polymerization of duly substituted ε-caprolactones (εCL), e.g., 1,4,8-trioxaspiro[4,6]-9-undecanone, 2-oxepane-1.5-dione, γ-bromo-εCL, γ-Et_3SiO-εCL, γ-$tBuPh_2SiOC(=O)$-εCL, γ-acryloxy-εCL, 6,7-dihydro-2(3H)-oxepinone, 6,7-dihydro-2(5H)-oxepinone. Moreover, a poly(ethylene oxide) (PEO) macromonomer consisting of εCL substituted in γ position by PEO has been prepared and copolymerized with εCL, with formation of poly(εCL-*g*-EO) graft copolymers. Amphiphilic poly(εCL-*g*-EO) have also been synthesized by the Michaël addition of ω-HS-PEO chains onto the pendent acrylic groups of PCL, prepared by copolymerization of γ-acryloxy-ε-caprolactone and εCL.

α-chloro-ε-caprolactone (αClεCL) is a very versatile monomer because a wide range of functional poly(caprolactone)s can be prepared from the parent homopolymer and copolymer with εCL. Indeed, non polymerizable olefins can be added to the α-chloro substituents by copper-mediated catalysis according to the well-known "Atom Transfer Radical Addition" (ATRA). Similarly, ATRP of terminal olefins can be initiated by the activated chlorides, as exemplified by the grafting of PCL by polystyrene and poly(methyl methacrylate). Alternatively, "Click" chemistry mediated by copper-based catalysts turned out to be very efficient. For this purpose, the α-chloro units have been reacted with sodium azide (NaN_3) and converted into α-azides (α-N_3), followed by reaction with terminal alkynes. Various functional groups including hydroxyl, carboxylic and epoxide have been grafted by either

"ATRA" or "Click" processes, just by choosing the appropriate structure of the vinylic and acetylenic derivatives. No cumbersome protection/deprotection reactions are needed. Grafting conditions are mild enough to prevent significant degradation of the polyester from occurring. Click and ATRA reactions are also well-suited to the synthesis of graft copolymers by the "grafting onto" technique. Indeed, poly(εCL-*g*-EO) have been prepared either by grafting ω-H_2C=CH-PEO and ω-HC≡C-PEO, respectively, onto poly(αClεCL-*co*-εCL) and poly(αN_3εCL -*co*-εCL).



R : polymeric or not, bears functional groups (epoxide, alcohol, ester, carboxylic acid)

Finally, cyclic tin(IV) alkoxides have been used to initiate ROP of εCL with formation of macrocyclic PCL containing endocyclic Sn-O bonds, which are however sensitive to hydrolysis. Strategies for stabilizing the macrocyclic structure by substituting non hydrolyzable C-C bonds for Sn-O bonds will be reported. This process has been extended to the preparation of macrocylic aliphatic poly(substituted caprolactone)s. With the macromolecular engineering in mind, new architectures based on macrocyclic units have been made available. For example, the grafting onto/from a macrocyclic precursor is a route to original sun-shaped copolymers.