SYNTHESIS OF NEW SUBSTITUTED POLYCAPROLACTONES BY RING-OPENING POLYMERIZATION

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During the last few years, a great research effort has been devoted to the synthesis of aliphatic polyesters, e.g. poly(ε-caprolactone) and polylactides. Indeed, their remarkable properties of biodegradability and biocompatibility pave the way to many new applications not only in the biomedical field but also as substitutes for nondegradable polymers, e.g. packaging.. So aliphatic, polyesters with improved and/or original properties are highly desirable. In order to tailor the polyester properties, the grafting of functional groups along the polymer backbone is highly desirable. Up to now have been reported the synthesis and the (co)polymerization of a few γ-substituted-ε-caprolactones (R= ketal, protected alcohol, protected carboxylic acid, bromo…).

Unfortunately, the versatility of this strategy is poor because the preparation of original polyesters grafted with new functional groups requires too many times the preparation of new γ-substituted-ε-lactones. Furthermore, it is worth pointing out that the number of steps required for the synthesis of these lactones is too high and thus limits drastically the global yield and increase the cost of these materials.

Thus, we have decided to undertake the one-step synthesis of α-chloro-ε-caprolactone by a Baeyer-Villiger Oxydation of α-chlorocyclohexanone. The conditions found for its (co)polymerization with control of the molecular weight and with rather low polydispersity index (PDI around 1.2) will be reported. The presence of the α-chloro group is the key allowing to prepare a wide range of new materials in conditions mild enough to prevent detrimental transesterification reactions from occurring. Firstly, these polyesters have been used as macroinitiator for Atom Transfer Radical Polymerization (ATRP) in order to prepare graft copolymers. Secondly, Atom Transfer Radical Addition (ATRA) of a suitable is route to polyesters grafted with a wide range of functional groups. Finally, unsaturated crosslinkable polyesters have been prepared by elimination reactions.