

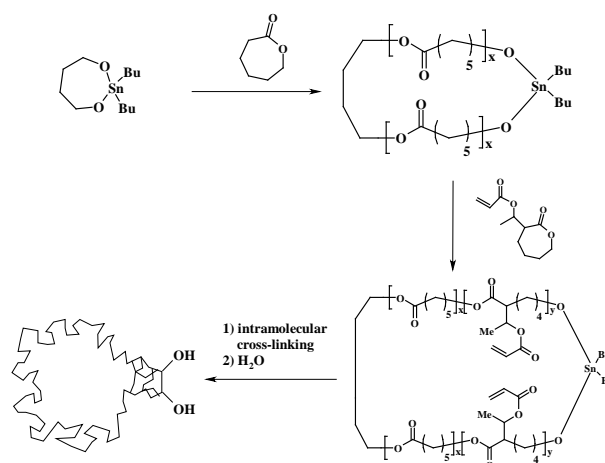
Macromolecular engineering of cyclic aliphatic polyesters by ring-opening polymerization and « click » chemistry

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The last decades have witnessed a steadily increasing progress in the macromolecular engineering of the main families of synthetic polymers. Ring-shaped copolymers show a unique topology due to the absence of any chain-end and exhibit distinct properties from their linear counterparts, such as glass transition temperature, order-disorder transition, reduced viscosity, lower hydrodynamic volumes.

This communication aims at reporting on a novel route to biodegradable cyclic polyesters. Our strategy is based on the work of Prof. Kricheldorf who initiated the ring-opening polymerization of ϵ -caprolactone by cyclic tin dialkoxides, e.g., 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) in order to obtain “living” macrocyclic PCL, still containing two endocyclic tin-oxygen bonds.¹ In this work, the resumption of polymerization by a few units of ϵ -caprolactone substituted by an acrylic unit, e.g., 1-(2-oxooxepan-3-yl)ethyl prop-2-enoate, followed by intramolecular photo-cross-linking of pendant unsaturations and finally by hydrolysis gave rise to macrocyclic PCL.² As a rule, this strategy is very well-suited for the synthesis of high molecular weight PCL. Moreover, tin alkoxides were kept untouched after the cross-linking step and remained thus available for further macromolecular engineering.



The process was extended to the synthesis of other architectures such as sun-shaped, two-tail tadpole-shaped, and eight-shaped copolyesters.

The second part of the lecture, it will be shown that the copper(I)-catalyzed Huisgen's [3+2] cycloaddition, which is the most popular “Click” reaction, is very efficient to graft alkynes, duly substituted by functional groups or chains, onto aliphatic copolyesters bearing pendant azides.^{3,4} Interestingly enough, mild conditions were found and no degradation was observed during the “click” derivatization of copolyesters of PCL. The “click” reactions of alkynes onto pendant azides of copolyesters of PLA, by far more sensitive than PCL, was also successfully carried out without any detectable degradation. “Click” chemistry is very versatile because this reaction was successfully implemented to graft functional groups or chains directly onto ω -azido- ϵ -caprolactone, without any ring-opening of the lactone, in order to make available a new range of functional caprolactones.⁵ Finally, the “click” grafting of PEO onto the tails of tadpole-shaped copolymers will be shown to be a route to amphiphilic copolymers with an original architecture.⁶

References

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