

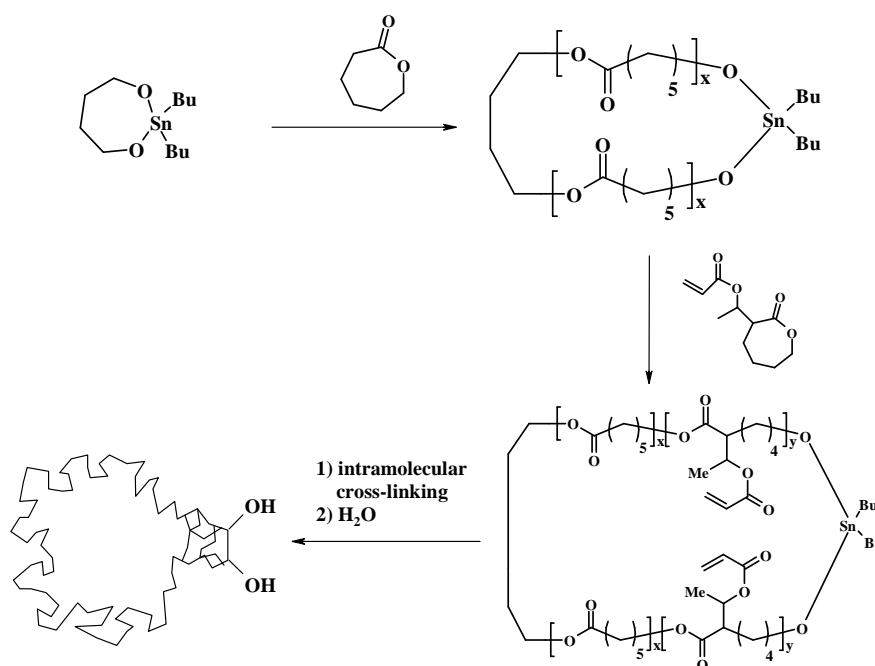
Macromolecular engineering of aliphatic polyesters based on cyclic units

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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, eight-shaped and symmetrical four-tail eight-shaped copolyesters.

References

- 1) H. R. Kricheldorf, S.-R. Lee, N. Schittenhelm, *Macromol. Rapid Commun.* **2003**, *24*, 359-381.
- 2) H. Li, A. Debuigne, R. Jérôme, Ph. Lecomte, *Ang. Chem. Int. Ed.* **2006**, *45*, 2264-2267.