

General Conclusions

In the recent past, the effort devoted to the design and synthesis of cyclic (co)polymers with different compositions and architectures has been steadily increasing. Among other incentives, the quest for new structure-properties relationships and the discovery of DNA molecular ring have stimulated the exploration of cyclic polymers.

This work is a search for a novel and efficient strategy for the synthesis of well-defined macrocyclic aliphatic polyesters, to which steadily more complex topologies can be imparted. In this respect, combination of controlled ring-opening polymerization initiated by cyclic tin(IV) dialkoxides and intramolecular photo cross-linking of unsaturations close to the propagating site proved to be successful. Compared to the traditional techniques of cyclization of linear precursors by the end-to-end coupling at very high dilution, the herein reported process has the substantial advantage that linear species are never involved while pre-cyclized species are concerned. Accordingly, this new strategy is very well-suited to the synthesis of high molecular weight macrocycles (20000) under moderate dilution, which is a sizeable improvement.

Very importantly, the macrocyclic polyesters prepared in this work, can be accommodated into more complex architectures as part of a macromolecular engineering effort of the basic macrocycles. Indeed, the propagating tin alkoxides remain active after cyclization and remain

available to further derivatization. As a first example, polymerization of either ϵ CL or LLA was resumed after cyclization, so leading to tadpole-shaped architectures, thus two adjacent tails grafted onto the macrocycles. In another version, copolymerization of ϵ CL and α Cl ϵ CL was resumed, with formation of a functional tadpole-shaped copolyester with two activated chloride containing tails. The chloride groups were then converted into azides, that were added with alkyne end-capped PEO by a copper mediated “click” reaction. New amphiphilic PEO/PCL copolymers with a tadpole-shaped architecture were accordingly made available.

So, this work paved the way to the synthesis of a variety of novel tadpole-shaped copolyesters, whose both the size and composition can be extensively tuned.

A third engineering route was pioneered to novel functional star- and eight-shaped copolyesters based on the initiation of the ring-opening polymerization by spirocyclic tin(IV) alkoxides. Remarkably, an amphiphilic eight-shaped copolyester, whose the constitutive macrocycles were grafted by two PCL-g-PEO tails was synthesized. The grafting of the PCL tails was carried out again by the Huisgen’s [3+2] cycloaddition of alkyne end-capped PEO onto azide containing comonomers. To the best of our knowledge, this is the first example ever reported of a twin tadpole architecture with tails consisting of an amphiphilic graft copolymer.

Finally, the herein reported strategy was successfully extended to the synthesis of a functional macrocyclic copolyester, i.e., poly(γ -Et₃SiO ϵ CL-co- ϵ CL). The triethylsilanolate

groups were deprotected, followed by the esterification of the hydroxyl groups by carboxylic acid end-capped PEO, so resulting in sun-shaped amphiphilic copolymers.

The properties of the new macrocyclic aliphatic polyesters prepared in this work, have not been studied in detail. A very preliminary study showed that the cyclic polyesters are less crystalline than their linear counterparts. Moreover, micellization in water of all the new amphiphilic copolymers was observed by transmission electron microscopy (TEM). The impact of the macromolecular architecture on the macroscopic properties and the self-assembly in solution and in bulk will be explored in the future.