

Aims of the Thesis

Synthetic methods of macrocyclic (co)polymers with different architectures was reviewed in the introduction of the thesis. The main approaches to macrocycles are based on the end-to-end ring-closure (coupling) of homo- or hetero-difunctional linear precursors under high dilution. Although the linear precursors prepared by living/controlled polymerization are well-defined, the unavoidable competition between intramolecular cyclization and intermolecular extension is the major problem to be solved. In order to increase the cyclization yield at the expense of the detrimental intermolecular polycondensation, the intramolecular cyclization must be performed at very high dilution. Nevertheless, even under optimized conditions, the efficiency of cyclization is inversely proportional to the molecular weight of the precursor. Anytime, the cyclization is not very effective, contamination by undesired polycondensates is a concern and requires an additional and tedious step of purification by fractionation. Therefore, the quest for more efficient cyclization methods remains a challenging priority, even though alternative synthetic strategies have been explored as reported in the introduction.

This work aims at reporting a novel strategy that combines controlled ring-opening polymerization of lactones initiated by a cyclic tin(IV) dialkoxide and intramolecular cyclization by photo-cross-linking of pendant unsaturations next to the propagating sites. No linear species is ever involved in the polymerization and permanent cyclization steps, which allows higher molecular weight macrocycles to be prepared with high efficiency. Moreover,

this synthetic route is very flexible to the point where macrocyclic polyesters with more complex although well-defined architectures, such as tadpole-shaped and sun-shaped copolyesters, can be tailored. Synthesis of well-defined star- and eight-shaped polyesters and twin tadpole-shaped amphiphilic copolymers has also been explored by using a spirocyclic tin(IV) alkoxides as an initiator.

The main targets of the thesis are as follows:

- 1) Synthesis of macrocyclic poly(ϵ -caprolactone) (PCL).
- 2) Synthesis of tadpole-shaped copolyesters.
- 3) Synthesis of amphiphilic sun-shaped copolymers.
- 4) Synthesis of amphiphilic tadpole-shaped copolymers.
- 5) Synthesis of star- and eight-shaped polyesters and amphiphilic twin tadpole-shaped copolymers.

The research program is discussed hereafter in greater detail.

Content of the thesis chapters

Let us remind that the first chapter is a review of the methods used to prepare monocyclic polymers and diblock copolymers, tadpole-shaped (co)polymers, sun-shaped copolymers and pluri-cyclic polymers. The advantages and drawbacks of these synthetic methods are discussed.

The chapter 3 reports on a novel strategy for the synthesis of macrocyclic PCL of high molecular weight ($M_n = 24 \times 10^3 \text{ g mol}^{-1}$). It relies on the intramolecular cyclization by photo cross-linking of a few acrylic unsaturations in the very close vicinity of the propagating sites of chains synthesized by ring-opening polymerization initiated by a cyclic tin(IV) dialkoxide. Remarkably, the propagating tin(IV) dialkoxide remains active after cyclization and paves the way to further derivatization and macromolecular engineering. As a very representative example, the ϵ -caprolactone (ϵ CL) polymerization has been resumed after cyclization, so leading to tadpole-shaped chains, thus two adjacent PCL tails grafted onto the macrocycles.

Chapter 4 deals with the synthesis of an asymmetric tadpole-shaped aliphatic copolyester consisting of a poly(ϵ -caprolactone) ring and two poly(L-lactide) tails. First, a high molecular weight cyclic PCL macroinitiator ($M_n=31000$) was prepared by intramolecular photo-crosslinking of "living" chains. Polymerization of L-lactide was resumed by the tin dialkoxide containing macrocycles, so making the targeted tadpole-shaped copolyester available. A preliminary investigation of the crystallization of these copolyesters was carried out by differential scanning calorimetry and polarized optical microscopy.

In the chapter 5, a macrocyclic random copolyester of ϵ -caprolactone and the same monomer substituted by a triethylsilanolate group in γ -position poly(γ -Et₃SiO ϵ CL-co- ϵ CL) was prepared. Selective hydrolysis of the triethylsilanolate groups released hydroxyl groups that were esterified by carboxylic acid end-capped PEO, with formation of an amphiphilic sun-shaped copolymer, whose the micellization in water was confirmed by TEM.

A tadpole-shaped copolyester was prepared in the chapter 6, that was made amphiphilic by grafting the two PCL tails with PEO. In a first step, a macrocyclic PCL ($M_n = 24.5 \times 10^3 \text{ g mol}^{-1}$) was synthesized by ring-opening polymerization of ϵ CL initiated by a cyclic tin(IV) dialkoxide and stabilized by local intramolecular photo-cross-linking. In a second step, copolymerization of ϵ CL and α -chloro- ϵ -caprolactone ($\alpha\text{Cl}\epsilon\text{CL}$) was resumed with formation of two activated chloride containing PCL tails. In the third step, the chlorides were converted into azides onto which alkynyl end-capped PEO was grafted by the copper-mediated Huisgen's cycloaddition [3+2], thus a "click" reaction. The thermal properties of the final copolymer and the precursors were analyzed by differential scanning calorimetry. The amphiphilicity of the final copolymer was also confirmed by micellization in water.

Chapter 7 is a report on the synthesis of star- and eight-shaped (co)polyester and amphiphilic derivatives. Spirocyclic tin dialkoxides are unique initiators for the ring-opening polymerization of lactones leading to complex although well-defined macromolecular architectures. In a first example, ϵ CL was copolymerized with ϵ CL α -substituted by an azide ($\alpha\text{N}_3\epsilon\text{CL}$) with formation of "living" eight-shaped chains. Upon hydrolysis of the tin alkoxides, a four-arm star-shaped copolyester was formed, whose each arm was grafted by the Huisgen's [3+2] cycloaddition of alkyne end-capped PEO onto the azide substituents. The complexity of this novel amphiphilic architecture was increased further by substituting the 4-arm interconnecting carbon by an eight-shaped polyester (PCL). In a preliminary step, ϵ CL was polymerized followed by a few units of ϵ CL α -substituted by an acrylate. The

intramolecular photo-crosslinking of the acrylates adjacent to the tin dialkoxides was effective in stabilizing the 8-shaped polyester while preserving the chain growth sites. This quite unusual difunctional macroinitiator was used to copolymerize ϵ CL and $\alpha N_3\epsilon$ CL, followed by hydrolysis of the alkoxides and grafting of the arms by PEO (cfr supra). This architecture reported for the very first time may be viewed as twin tadpole-shaped macromolecules.