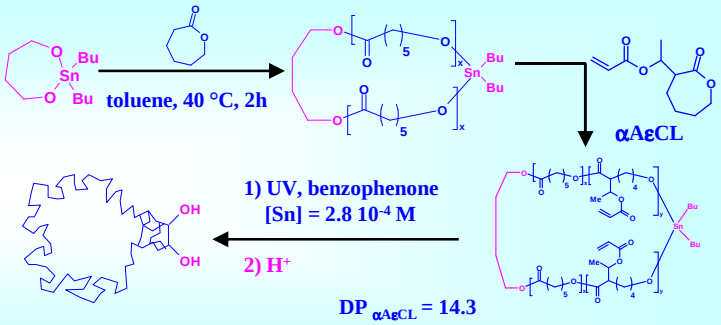
Macromolecular Engineering of Aliphatic Polyesters Based on Macrocyclic Units

H. Li, Ph. Lecomte, R. Riva, R. Jérôme

Center for Education and Research on Macromolecules (CERM), University of Liège, B6a Sart-Tilman, B-4000 Liège, Belgium: http://www.ulg.ac.be/cerm, E-mail: philippe.lecomte@ulg.ac.be

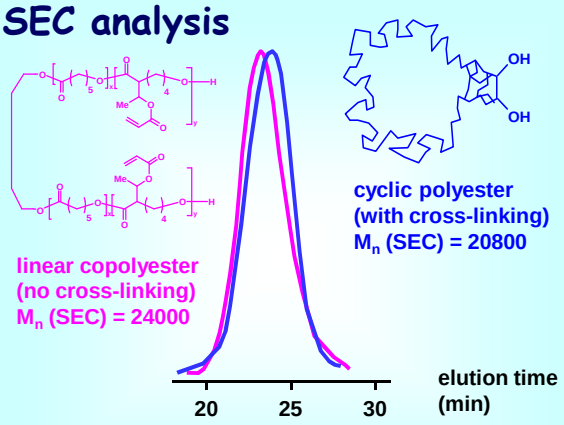
Synthesis of ring-shaped PCL

The ***usual process*** towards well-defined macrocycles is based on the coupling of the two chain-ends of a linear precursor under very high dilution (C <10^{-5} M). ***High molecular weight*** macrocylces are very ***difficult to synthesize*** by this route Herein, we report on a ***novel strategy*** based on the sequential ring-opening polymerization of ε-caprolactone followed by a few units (15-20) of an ε-caprolactone α-substituted by an acrylate, by using a cyclic tin dialkoxide as an initiator. The key step relies on the intramolecular photo-cross-linking of pendant acrylates. Interestingly enough, after hydrolysis, ***high molecular weight PCL*** is obtained. Moreover, the two ***Sn-O bonds are kept untouched*** after cross-linking and are ***still available for further macromolecular engineering***.



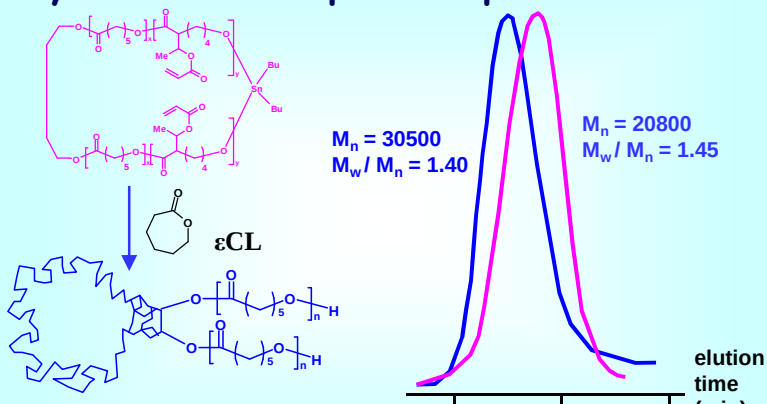
Li H. *Angew. Chem. Int. Ed.* **2006**, *45*, 2264

SEC analysis



M_p (cyclic) / M_p (linear) = 0.69

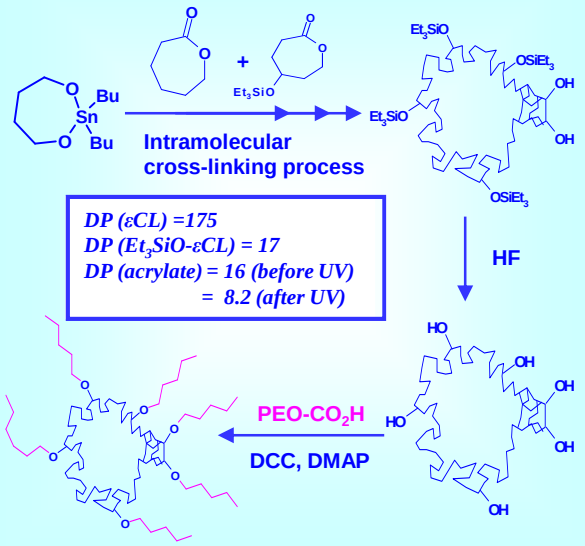
Synthesis of tadpole-shaped PCL



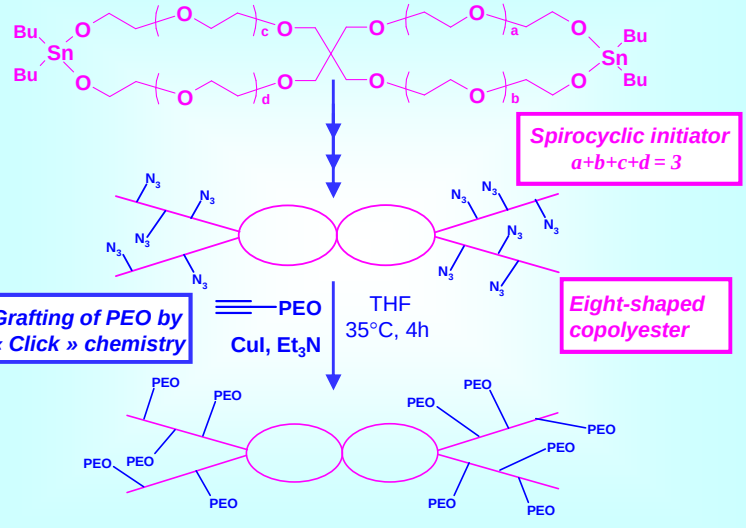
PCL still living after photo-cross-linking
Efficient resumption of polymerization with εCL, lactide or a mixture of εCL and αClεCL

Li H. *Polymer* **2006**, *47*, 8406
Li H. *Macromolecules* **2007**, *40*, 824

Synthesis of sun-shaped PCL



Synthesis of eight-shaped PCL



In collaboration with H. R. Kricheldorf

PhL is assiociate researchers by the belgian « FNRS ». RR thanks the «Fonds pour la Formation à la Recherche dans l'Industrie et L'Agriculture » (FRIA) for financial support. The authors are indebted to the «Belgian Science Policy » for financial support in the frame of «Interuniversity Attraction Poles Programme (PAI VI/27)».