



# Macromolecular Engineering of Poly( $\epsilon$ -Caprolactone) Based on Macrocylic Units

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

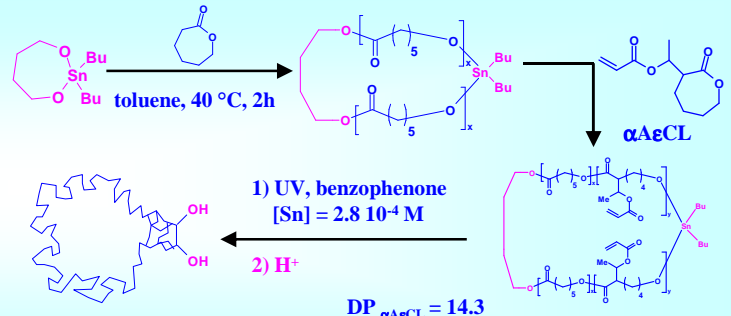
Center for Education and Research on Macromolecules (CERM),  
University of Liège, B6a Sart-Tilman, B-4000 Liège,

Belgium: <http://www.ulg.ac.be/cerm>, E-mail: philippe.lecomte@ulg.ac.be



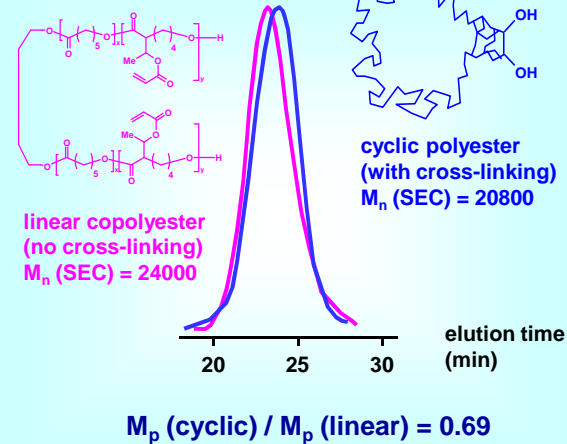
## Synthesis of ring-shaped PCL

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** macrocycles are very **difficult to synthesize** by this route. Herein, we report on a **novel strategy** based on the sequential ring-opening polymerization of  $\epsilon$ -caprolactone followed by a few units (15-20) of an  $\epsilon$ -caprolactone  $\alpha$ -substituted by an acrylate, by using a cyclic tin dialkoxide as 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**.

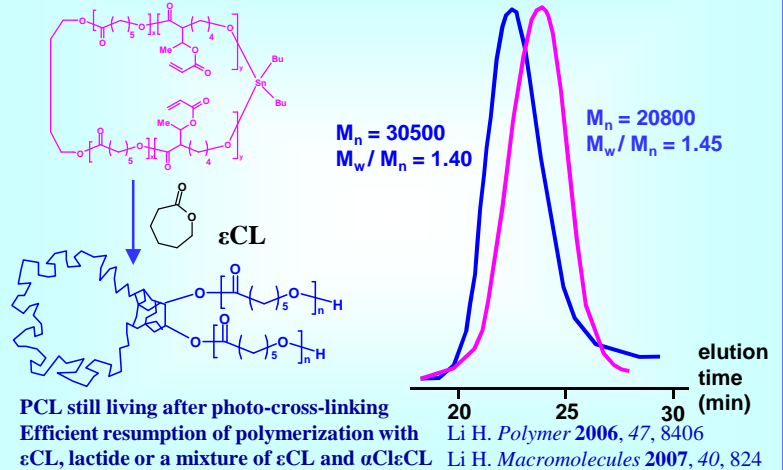


Li H. *Angew. Chem. Int. Ed.* 2006, 45, 2264

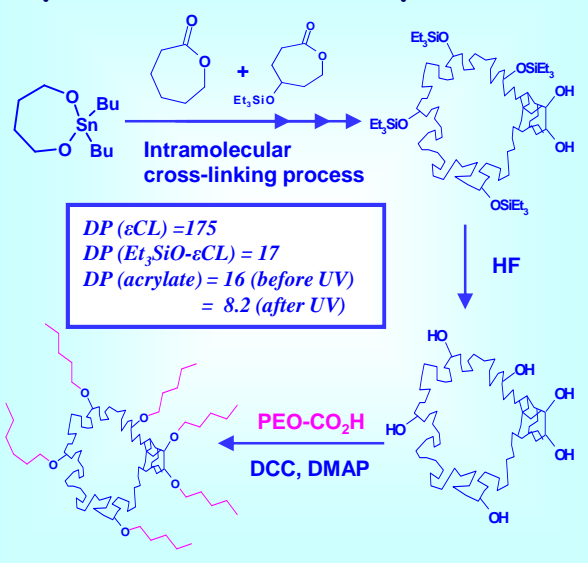
## SEC analysis



## Synthesis of tadpole-shaped PCL

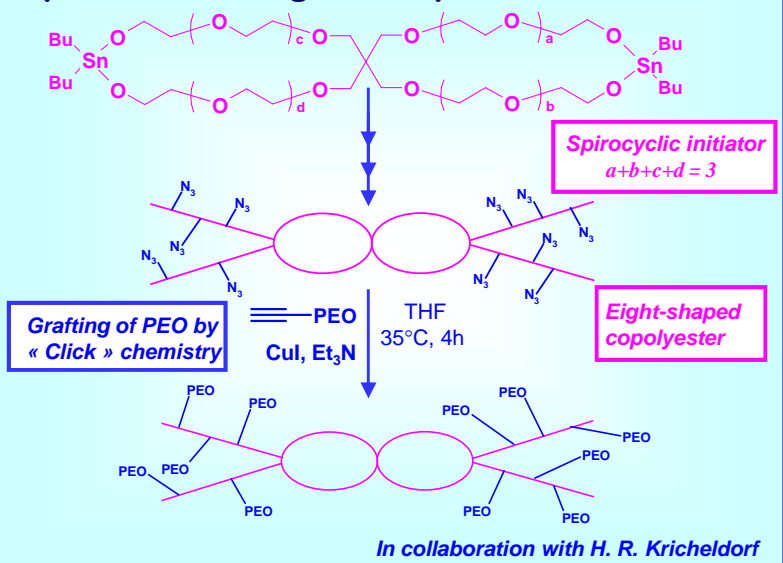


## Synthesis of sun-shaped PCL



$DP(\epsilon\text{CL}) = 175$   
 $DP(\text{Et}_3\text{SiO}-\epsilon\text{CL}) = 17$   
 $DP(\text{acrylate}) = 16$  (before UV)  
 $= 8.2$  (after UV)

## Synthesis of eight-shaped PCL



Grafting of PEO by « Click » chemistry

THF  
35°C, 4h  
CuI, Et<sub>3</sub>N

Spirocyclic initiator  
 $a+b+c+d = 3$

Eight-shaped copolyester

In collaboration with H. R. Kricheldorf