



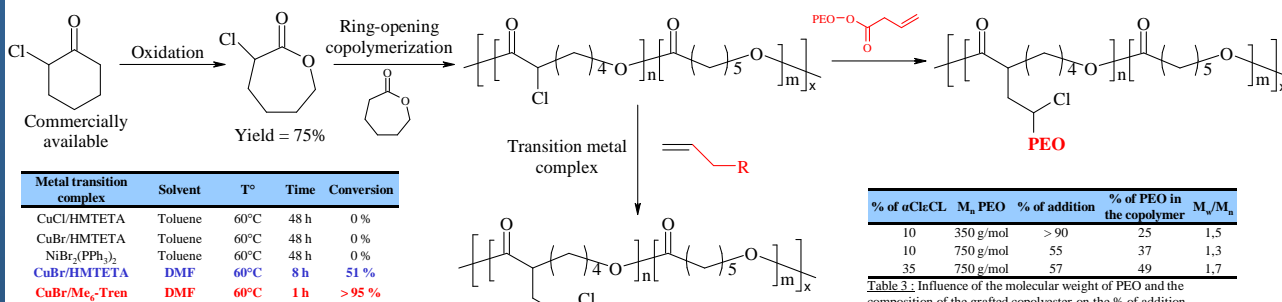
α -chloro- ϵ -caprolactone, a versatile precursor for grafting of aliphatic polyesters

Raphaël Riva, Sandrine Lenoir, Philippe Lecomte, Christine Jérôme

raphael.riva@ulg.ac.be, University of Liège, Sart-Tilman, B6a, B-4000 Liège

Abstract: Macromolecular engineering is one of the most powerful tool to synthesise many polymers of various architectures and with tailored properties. This contribution aims at reporting on a novel strategy for the macromolecular engineering of poly- ϵ -caprolactone (PCL) which is based on the use of a dual monomer / initiator compound, α -chloro- ϵ -caprolactone (α Cl ϵ CL).

Atom Transfer Radical Addition (ATRA)

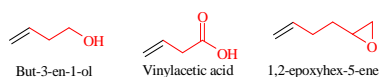


Conversion measured by ¹H NMR analysis

Table 1: Influence of the solvent and the transition metal complex on the addition of but-3-enyl benzoate.

Olefin	Time	Conversion
But-3-enyl benzoate	24 h	51%
But-3-en-1-ol	8 h	37%
Vinylacetic acid	24 h	32%
1,2-epoxyhex-5-ene	8 h	42%

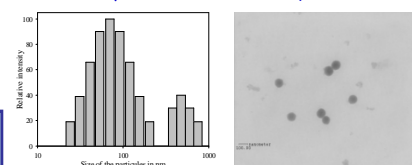
Table 2: ATRA for the different olefins by using CuBr/HMTETA in DMF.



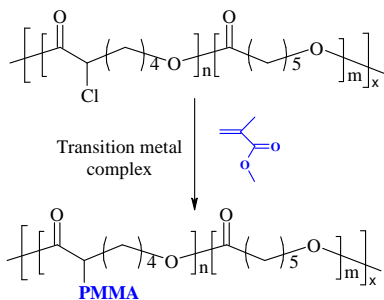
% of α Cl ϵ CL	M _n PEO	% of addition	% of PEO in the copolymer	M _w /M _n
10	350 g/mol	> 90	25	1,5
10	750 g/mol	55	37	1,3
35	750 g/mol	57	49	1,7

Table 3: Influence of the molecular weight of PEO and the composition of the grafted copolymer on the % of addition.

Formation of spherical micelles in aqueous solution



Atom Transfer Radical Polymerisation (ATRP)

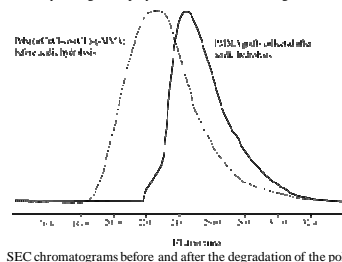


The PMMA grafts have been collected after the degradation of poly(ϵ CL) by a mixture of 1,4-dioxane / HCl 37% (95/5) at 85°C for 32 hours.

Theor. M _n ^a PMMA grafts	M _n ^b SEC	M _n ^c SEC	M _w /M _n ^d SEC	M _w /M _n ^e SEC	f
10500	72000	19000	2,0	2,3	0,6
8500	80000	28000	1,5	1,4	0,3
16000	94000	39100	1,8	1,4	0,4

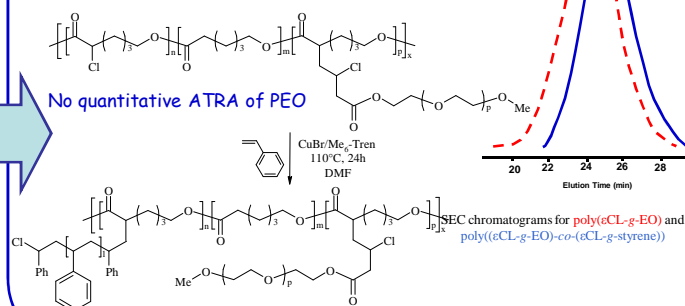
a: Theor. M_n = [n MMA] / n poly(α Cl ϵ CL) · % conversion.
b, d: for the graft copolymer (PMMA calibration).
c, e: for the PMMA grafts PMMA (PMMA calibration).
f: initiation efficiency.

Table 4: SEC analysis of graft copolymers before and after degradation of poly(ϵ CL).



SEC chromatograms before and after the degradation of the poly(ϵ CL)

Combination of ATRA and ATRP



Synthesis of an heterografted PCL

Click chemistry

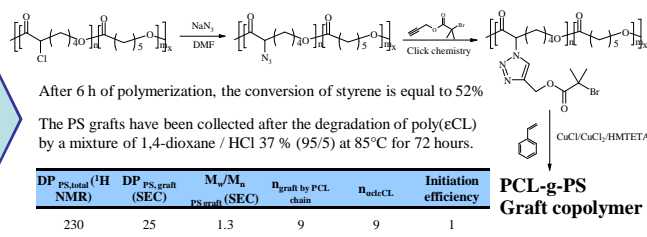


Table 5: Results of the synthesis of PCL-g-PS graft copolymer

Improvement of the initiation efficiency by the grafting of an activated bromide

Conclusion: Various functionalized and graft copolyesters can be easily prepared from one functionalized lactone, the α Cl ϵ CL. Several functions can be grafted by ATRA onto α Cl ϵ CL containing chains without significant degradation. Grafted PCL are also rapidly prepared by the initiation of the polymerization of vinyl monomers either from the pendant chloro atoms of the copolyester, either from pendant bromide introduced onto the copolyester by "click chemistry". ATRA of PEO chains on a poly(ϵ -caprolactone-co- α Cl ϵ CL) is a convenient way to access to amphiphilic and biocompatible copolymers.