

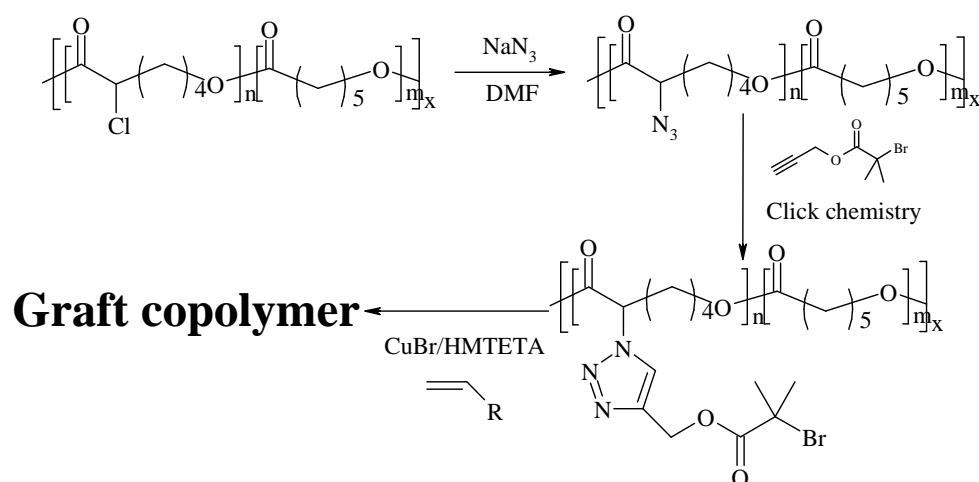
# $\alpha$ -chloro- $\epsilon$ -caprolactone, a versatile precursor for grafting of aliphatic polyesters

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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- $\epsilon$ -caprolactone (PCL) which is based on the use of a dual monomer / initiator compound,  $\alpha$ -chloro- $\epsilon$ -caprolactone ( $\alpha$ Cl $\epsilon$ CL). Indeed,  $\alpha$ Cl $\epsilon$ CL is not only polymerizable by ring opening initiated by metal alkoxides, but it is also an initiator for the atom transfer radical polymerization (ATRP) of vinyl monomers, so leading easily to the synthesis of macromonomers. Polystyrene macromonomer has been prepared by this method and successfully copolymerized with  $\epsilon$ -caprolactone ( $\epsilon$ CL) with formation of the corresponding grafted PCL.  $\alpha$ Cl $\epsilon$ CL is also a precursor of copolyesters with  $\epsilon$ CL that bear pendant chlorides. These (co)polyesters have been used as macroinitiators for the ATRP of methyl methacrylate in order to synthesise the corresponding graft copolymer<sup>1</sup>.

On the other hand, the pendant chlorides of poly( $\alpha$ Cl $\epsilon$ CL-co- $\epsilon$ CL) copolyesters were easily converted into azide with formation of the corresponding azide bearing copolyester. This copolyester was then reacted with an alkyne bearing an ATRP initiator by "Click chemistry". The conversion of chlorides into more efficient ATRP initiators led to the improvement of the initiation efficiency of the macroinitiator<sup>2</sup>.



## References

1. S. Lenoir, R. Riva, X. Lou, Ch. Detrembleur, R. Jérôme, Ph. Lecomte *Macromolecules* **2004**, 37, 4055-1061
2. R. Riva, S. Schmeits, Ch. Jérôme, R. Jérôme, Ph. Lecomte *Macromolecules* **2007**, 40, 796-803.