Recent Progress in the Macromolecular Engineering of Aliphatic Polyesters

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Over the past 20 years, increasing attention has been paid to the Ring-Opening Polymerization (ROP) of lactones and lactides initiated by alkoxides of a series of metals, including Al, Sn and rare-earth metals [1]. The major incentive has to be found in unique properties of biodegradability and biocompatibility exhibited by poly-ε-caprolactone (PCL) and polylactides (PLA).

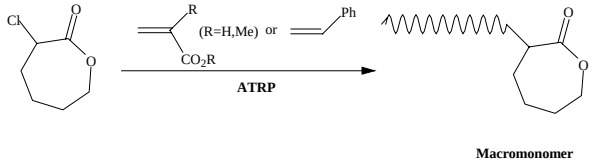
As result of well-controlled ROP, the macromolecular engineering of these aliphatic polyesters has been carried out extensively [2]. This paper aims at reporting on recent progress in the field.

Novel functional ε-caprolactones

α and γ-substituted ε-caprolactones, mainly 1,4,8-trioxaspiro[4.6]-9-undecanone [3-6], γ-bromo-ε-caprolactone [6–8], γ-$tBuMe_2Si_2OC$-ε-caprolactone [8], γ-Et_3SiO-ε-caprolactone [9], γ-(acryloyloxy)-ε-caprolactone [10], 6,7-dihydro-2(5H)-oxepinone [11], 6,7-dihydro-2(3H)-oxepinone [12], 2-oxepane-1.5-dione [13,14] have been synthesized and polymerized recently, which has contributed to the synthesis of novel macromolecules.

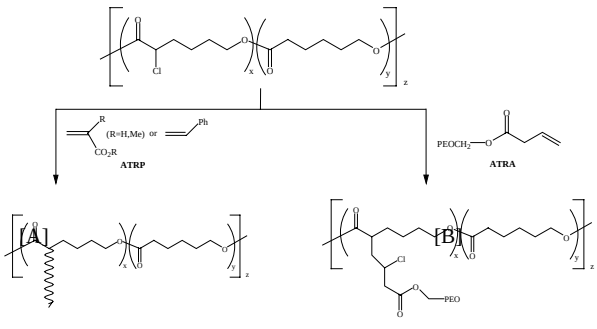
Contribution of α-chloro ε-caprolactone to the controlled synthesis of graft copolymers

α-chloro ε-caprolactone (CCL) is quite an interesting (co)monomer, because it opens the way to new strategies for the controlled synthesis of graft copolymers. Indeed, the activated chlorine substituent of CCL can initiate the Atom Transfer Radical Polymerization (ATRP) of (meth)acrylates and styrenic derivatives, so leading to the formation of macromonomers (Scheme 1)that can be copolymerized with, e.g., ε-CL.



Scheme 1

Similarly, the chlorine substituents of random copolymers of ε-CL and CCL can initiate the same ATRP processes with formation of graft copolymers (Scheme 2; route A).

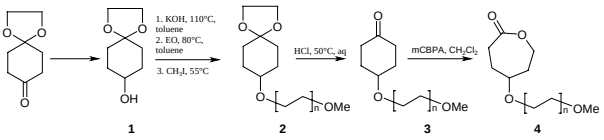


Scheme 2

As illustrated in the previous scheme, olefin end-capped polymers (e.g., poly(ethylene oxide)) can be added to the activated chlorine substituents of CCL or copolymers of it by Atom Transfer Radical Addition (ATRA) (Scheme 2; route B).

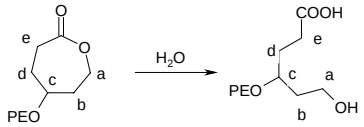
Poly(ethylene oxide) macromonomer polymerizable by ROP

A poly(ethylene oxide) (PEO) macromonomer consisting of PEO attached to ε-CL in γ-position has been successfully synthesized. The living anionic polymerization of ethylene oxide (EO) has been initiated by potassium alkoxide of 1,4-hydroxycyclohexanone monoacetal, followed by the acidic hydrolysis of the acetal and the Baeyer-Villiger oxidation of the cyclohexanone (Scheme 3).



Scheme 3

Copolymerization of this macromonomer with ε-CL has been carried out in solution and from aluminum alkoxide immobilized on a metal surface.



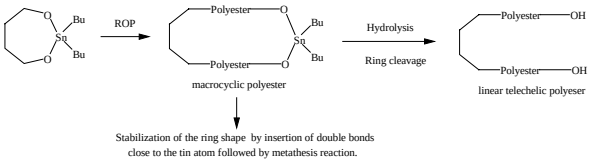
The hydrolysis of the lactone end-group into a hydroxy-acid makes the synthesis of three arm star shaped copolymers possible (Scheme 4).

Scheme 4

Indeed, the carboxylic acid and the hydroxyl groups are precursors of initiators for ROP of β-malolactonate and ε-CL (or lactide), respectively.

Macrocyclic polyesters

Finally, cyclic tin (IV) alkoxides have been used to initiate ROP of ε-CL with formation of macrocyclic polyesters that contain endocyclic Sn-O bonds (Scheme 5). A few units of γ-unsaturated ε-CL have been added to the living chains, followed by metathesis reaction. This cyclization strategy does not require high dilution.



Scheme 5

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