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Ring-opening (co)polymerization of γ -butyrolactone: a review

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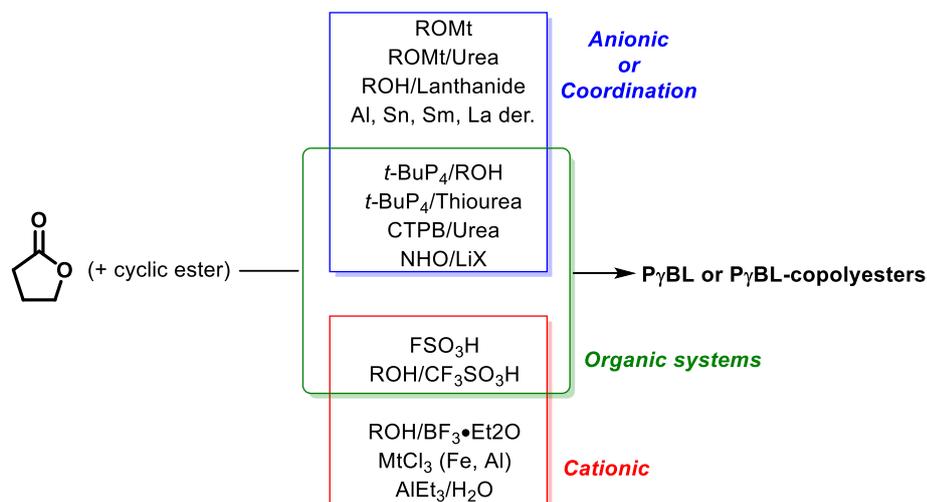
ABSTRACT

With increased environment concerns and the rising demands for sustainable polymers, *e.g.* degradable polymers and chemically recyclable polymers, studies on ring-opening polymerization (ROP) of cyclic esters have been developed during last decades. Biorenewable five-membered γ -butyrolactone (γ BL) could be a desirable feedstock for the chemical synthesis of poly(γ -butyrolactone) (P γ BL) or for the incorporation of γ BL units into polyester chains in order to modify their properties. Although γ BL is traditionally considered to be “non-polymerizable”, some progresses were recently made in ROP of γ BL. This mini-review is thus specially focused on the ROP of γ BL and its copolymerization with other cyclic esters.

KEYWORDS

γ -butyrolactone; polyester; ring-opening polymerization

GRAPHICAL ABSTRACT



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1 INTRODUCTION

2
3 Aliphatic polyesters are a compelling class of polymers considering their widespread
4 applications in different areas, thanks to their biodegradability and biocompatibility.¹⁻⁴ They
5 can be obtained either by polycondensation of diols with diacids or diesters, of hydroxyesters
6 or hydroxyacids, or by ring-opening polymerization (ROP) of cyclic esters. The latter has been
7 demonstrated to be a powerful strategy to synthesize polyesters with various macromolecular
8 architectures and properties in a controlled manner.⁵⁻⁸ Among the diversity of lactones, the five-
9 membered γ -butyrolactone (γ BL), a renewable monomer derived from succinic acid, ranked as
10 a top biomass-derived chemical, could be an alternative for the chemical synthesis of
11 biopolyester, poly(γ -butyrolactone) (P γ BL), a structural equivalent of poly(4-hydroxybutyrate)
12 (P4HB), which is obtained from a bacterial fermentation process.⁹ Moreover, it was
13 demonstrated that the incorporation of γ BL into polyesters resulted in an enhanced
14 biodegradability and flexibility.¹⁰

15 Compared to the commonly utilized lactones having high strain energy, γ BL is traditionally
16 considered as “non-polymerizable”, due to the low strain energy of the five-membered ring that
17 brings a too small negative change of enthalpy (ΔH_p) to overcome a large negative entropic
18 change (ΔS_p) of its ROP.¹¹⁻¹⁴ It is then difficult to obtain high molar mass P γ BL via a simple
19 chemical synthesis process. As early as the 30s to the 50s, attempts to polymerize γ BL revealed
20 unsuccessful.^{15,16} In the 60s, oligomers of P γ BL were synthesized under extreme reaction
21 conditions (*e.g.* 20,000 atm, 160 °C) or through catalysis with Lewis acid for long reaction
22 time.¹⁷ Thus, ROP of γ BL under mild conditions remained a challenge in polymer synthesis for
23 decades. Since a couple of years, there is a breakthrough in ROP of γ BL, which can now be
24 performed at low temperature (below the ceiling temperature (T_c)) and high monomer
25 concentration, to yield high molar mass P γ BL with linear or cyclic structures.¹⁸⁻²⁴ Ring-opening
26 copolymerization (ROCP) of γ BL and other lactones with high ring strain energy (or cyclic
27 ether) is another pathway to avoid its “non-polymerizability” (Fig. 1). Several examples have
28 been described with different catalysts under varied conditions.

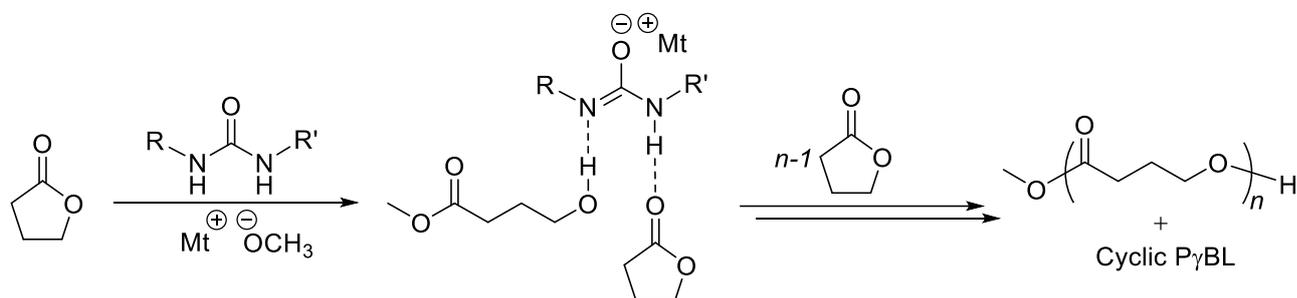
29 In this mini-review, we thus intend to summarize the studies and results on ROP and ROCP of
30 γ BL. The different catalysts described in the literature will be presented and the recent progress
31 will be emphasized. A variety of metal-based systems and organic compounds are employed as
32 catalysts/initiators in ROP/ROCP of γ BL (Fig.2), which can be classified as alkali metal bases,
33 other organometallics, organic bases, Lewis acids and Brønsted acids. Bimolecular catalytic
34 systems which consist of both an acid (or hydrogen donating) and a basic (hydrogen accepting)
35 component have also been utilized for the synthesis of P γ BL. Up to now, for the systems
36 mentioned above, lanthanides, organic bases and different acid-base pairs are proved to be most
37 efficient initiator/catalyst systems for ROP/ROCP of γ BL, all of them are performed at low
38 temperature and high monomer concentration.

1 RESULTS AND DISCUSSION

1 Alkali metal derivatives as initiators

Low reaction temperature and high monomer concentration are favorable for the ROP of γ BL due to the low ceiling temperature (T_c) of such a monomer. The bulk polymerization of γ BL was shown to proceed at $-40\text{ }^\circ\text{C}$ using potassium or sodium methoxide (MtOMe) with low monomer conversions up to 25% after a few hours.²³ Working in tetrahydrofuran (THF) at $-50\text{ }^\circ\text{C}$ was even worse as only 4% conversion was reached.²⁵ PEG-*b*-P γ BL block copolymers could be also prepared in low yields starting from poly(ethylene glycol) macroinitiator deprotonated by NaH followed by polymerization of γ BL in dichloromethane/THF (DCM/THF) mixture. This copolymerization was actually working at room temperature due to the presence of the second cyclic ester which is mandatory to stop any backbiting reaction.²⁶ Lithium diisopropylamide in dioxane was also shown to copolymerize at $25\text{ }^\circ\text{C}$ ϵ -caprolactone (ϵ CL) and γ BL with up to 26% incorporation of the second monomer into the copolymer after ring-opening.²⁷

Adding ureas to NaOMe enhanced the reactivity of the active species making the polymerization feasible in bulk at $-20\text{ }^\circ\text{C}$ with up to 70% monomer conversion in 2 hours.²³ Using KOMe with various ureas in THF at $-50\text{ }^\circ\text{C}$ was less efficient in terms of monomer conversion.²⁵ In any case, urea anion is believed to both activate the alcohol initiator and γ BL before the polymerization following an anionic mechanism (Scheme 1). Such type of binary catalysts achieved better ROP control and monomer conversions than alkali metal alkoxides alone. Moreover, alkaline urea bearing electron-donating groups are exhibiting the lower activation barrier according to thermodynamic calculation, and should possess a higher reaction efficiency.²³

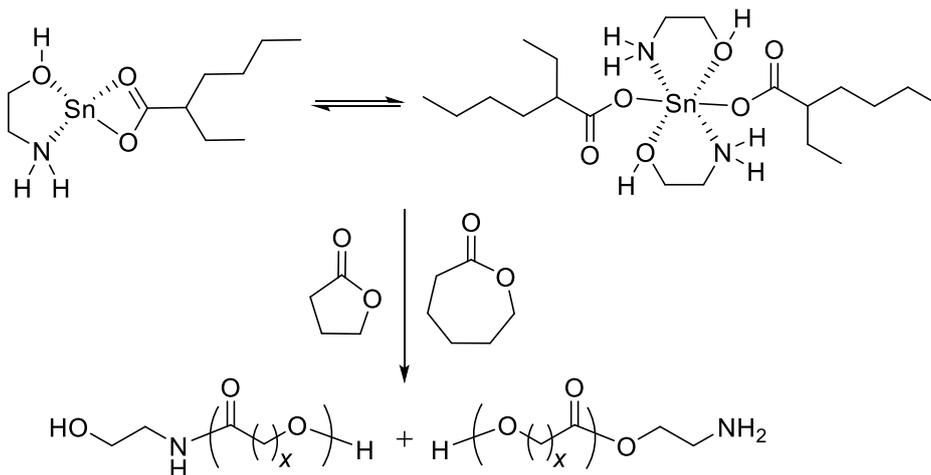


Scheme 1: ROP of γ BL by a metal alkoxide/urea system²³

2 Stannous or lanthanide compounds associated to alcohols

Tin(II) octanoate (Sn(Oct)₂) in the presence of ethanolamine was used to synthesize poly(ϵ -caprolactone) including randomly distributed γ BL units (16 mol%). It was shown that both the $-\text{OH}$ and $-\text{NH}_2$ groups of the ethanolamine were linked to the Sn center forming a new complex able to perform the copolymerization initiated by those 2 functions (Scheme 2).²⁷ This result is

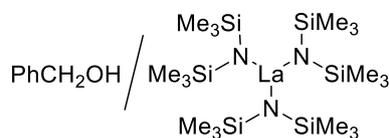
1 suggesting an anionic ring-opening polymerization process comparable with the nucleophilic
 2 mechanism observed with alkali metal alkoxides used as initiators.
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Scheme 2: Ethanolamine-initiated ROCP of ϵ CL and γ BL catalyzed by $\text{Sn}(\text{Oct})_2$ ²⁷

In the same vein, ROP of γ BL, that employed benzyl alcohol (PhCH_2OH , BnOH) as initiator, tri[*N,N*-bis(trimethylsilyl)amide] lanthanum(III) ($\text{La}[\text{N}(\text{SiMe}_3)_2]_3$) as catalyst, and high concentration of γ BL, was achieved in THF at -40°C with a yield up to 43% in half a day (Scheme 3).¹⁸ Linear and cyclic $\text{P}\gamma\text{BL}$ structures were shown to co-exist and to depend on the catalyst/initiator ratio. Intramolecular back-biting occurs in the $\text{La}-\text{OCH}_2\text{Ph}$ -initiated ROP, but in a much lesser extent than the ROP initiated by $\text{La}-\text{N}(\text{SiMe}_3)_2$ alone which will be discussed in the next section. Effective copolymerization of γ BL with ϵ CL and δ -valerolactone (δ VL) at low temperatures yielded a series of relatively high molar mass copolyesters with high levels of γ BL incorporation (8 to 84%).²⁸ The copolyesters exhibited random structure with a high content of γ BL.



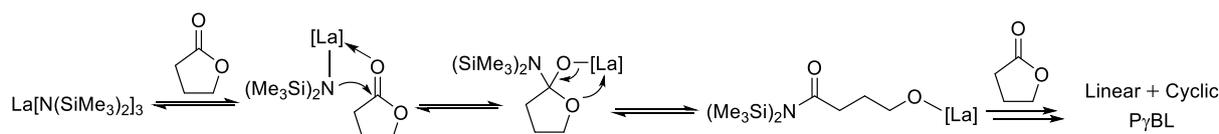
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Scheme 3: $\text{BnOH}/\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ system used for ROP/ROCP of γ BL^{18,28}

3 Organometallic compounds and lanthanides as catalysts

Organometallic compounds and lanthanides were also proposed without any addition of protic species. A coordination-insertion mechanism is thus expected. Tentative copolymerization of γ BL with glycolide or β -propiolactone (β PPL) were performed using zinc chloride (ZnCl_2) or aluminum isopropoxide ($\text{Al}(\text{O}^i\text{Pr})_3$) without real success.^{29,30} Using aluminum isopropoxide trimer at room temperature, in the 90s Penczek and Duda could prepare poly(ϵ -caprolactone-*co*- γ -butyrolactone) copolymers with molar masses up to 30 000 g/mol and containing up to 43

1 mol% of γ BL repeating units. Noteworthy, the molar masses were controlled by the
 2 concentrations of the consumed comonomers and the starting concentration of the aluminum
 3 initiator.³¹⁻³³
 4 Tetraphenyl tin catalyst revealed its efficiency at 140 °C for preparing statistical poly(γ -
 5 butyrolactone-*co*-L-lactide) copolyesters with molar masses as high as 70 000 g/mol. The
 6 maximum γ BL content obtained was around 17%.^{10,34} Cyclic tin alkoxide was also showing
 7 some activities to synthesize γ BL-based copolymers with the same limitations.³⁵
 8 1-Ethoxy-3-chlorotetrabutyl-distannoxane was able to copolymerize γ BL with β -butyrolactone
 9 (β BL) at 100°C in bulk.³⁶ The amount of γ BL in the copolymer is highly dependent on the
 10 monomer feed ratio going from 6% to 35% for a molar ratio of β BL/ γ BL going from 90/10 to
 11 10/90 respectively. Number-average molar mass (\overline{M}_n) and polymerization yields decreased
 12 from 96 000 g/mol and 96% to 2700 g/mol and 13% with the increase of the amount of γ BL in
 13 the monomer feed (mol%) from 10% to 90%.
 14 The samarium(II) aryloxide complex $\text{Sm}(\text{OAr})_2(\text{THF})_3$ ³⁷ or a samarium iodide based complex³⁸
 15 showed some activity for the ROCP of γ BL and ϵ CL at 20 °C. The formation of ϵ CL- γ BL
 16 copolymers without γ BL blocks and limited γ BL conversion were observed with this system.
 17 Similar conclusions were drawn when using an aluminum Schiff's base complex
 18 HAPENAlO^{*i*}Pr with calculated reactivity ratios equal to $r_{\epsilon\text{CL}}=19.4$ and $r_{\gamma\text{BL}}=0.11$, confirming
 19 the presence of long sequence of ϵ CL units in the copolymer.²⁷
 20 The ROP of γ BL using $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ alone was also shown to synthesize P γ BL in a few
 21 percent yield when working at high monomer concentration and -40 °C (Scheme 4). A typical
 22 coordination-insertion mechanism for chain initiation and propagation steps was proposed with
 23 the formation of linear and cyclic polymers due to intramolecular back-biting.^{18,28}

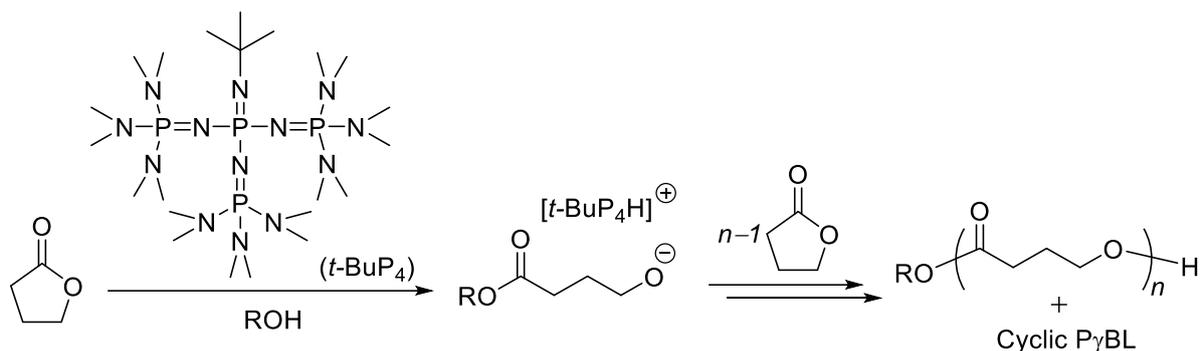


Scheme 4: Proposed mechanism for ROP of γ BL using $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ ¹⁸

4 Organic bases and acid-base pairs as initiators/catalysts

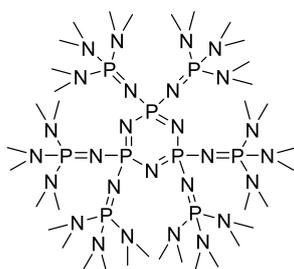
31 Since the description in 2001 of the first nucleophilic organocatalyzed ROP of lactide³⁹, lots of
 32 organocatalytic systems have been studied for the ROP of cyclic esters.⁴⁰ The phosphazene base,
 33 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis-[tris(dimethylamino)phosphoranylideneamino]-
 34 2 λ^5 ,4 λ^5 -catenadi(phosphazene) (*t*-BuP₄) is one of them and is shown to achieve the synthesis of
 35 metal-free P γ BL.¹⁹ The polymerization is performed at high monomer concentration and low
 36 temperature (-40 °C). Two different mechanisms are proposed by E. Chen and coworkers
 37 depending on the use of an alcohol as initiator or not. The superbases can directly initiate the
 38 polymerization by deprotonation of γ BL to generate a reactive enolate species. But the most
 39 efficient method is to deprotonate an alcohol such as BnOH by the organic base and get high
 40 molar mass polymers in high yields (Scheme 5). Linear and cyclic P γ BL were obtained in both
 41 cases. ROCP of γ BL with ϵ CL and δ VL following the same approach was also successful.²⁸

1 Noteworthy, the organic catalyst system based on *t*-BuP₄/BnOH afforded the copolyesters with
 2 high γ BL incorporation (42 to 80%) at a relatively low γ BL/ ϵ CL feed ratio (3 or 4/1).



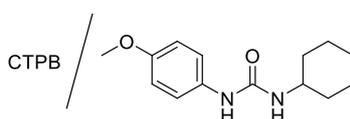
Scheme 5: *t*-BuP₄/alcohol system as initiating species for ROP of γ BL¹⁹

8 Cyclic trimeric phosphazene base (CTPB, Scheme 6) was also proposed as an organocatalyst
 9 for ROP of γ BL.²⁰ CTPB was said inactive in the absence of any alcohol whereas it serves as a
 10 highly efficient system in the presence of BnOH in toluene at -60 °C to offer well-defined P γ BL
 11 with high monomer conversion (up to 98% in 4 hours). The mechanism proposed is similar to
 12 the one involving *t*-BuP₄/BnOH initiating system (Scheme 5). The ion pair [BnO⁻⋯CTPBH⁺]
 13 can polymerize γ BL and the bulky counter-ion seems to prevent the back-biting reaction and
 14 therefore producing only P γ BL with linear structures. In comparison with alkali metal alkoxides
 15 discussed previously, this system showed a better efficiency probably due to its improved
 16 solubility in the reaction medium. Block copolymers of γ BL and L-lactide (LLA) were prepared
 17 with the same phosphazene base via sequential ROP of γ BL and LLA.⁴¹



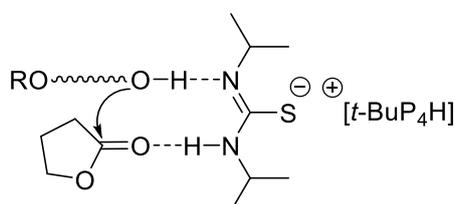
Scheme 6: Cyclic trimeric phosphazene base (CTPB) for ROP/ROCP of γ BL^{20,25,26}

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23 CTPB/ureas binary organocatalysts were also studied for the ROP of γ BL²⁵. Using 1-
 24 cyclohexyl-3-(4-methoxyphenyl) urea, a urea bearing unsymmetrical and electron-donating
 25 substituents (Scheme 7), P γ BL contained linear and cyclic structures with \overline{M}_n up to 35 000
 26 g/mol, four times higher than CTPB alone, was prepared. The mechanism involved is similar
 27 to the one described for alkali metal alkoxide / urea systems (Scheme 1).



Scheme 7: CTPB/urea system used for ROP of γ BL²⁵

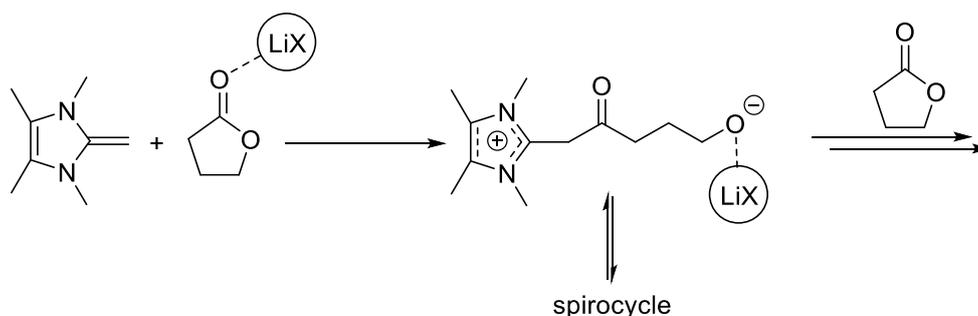
A dual organocatalysts based on the combination of *t*-BuP₄ and symmetrical thioureas bearing electron-donating groups was also demonstrated as an efficient organocatalytic system to synthesize linear P γ BL with high polymerization rates (up to 80% monomer conversion in 4 hours) at low temperature (Scheme 8).²²



Scheme 8: *t*-BuP₄/thiourea system for the ROP of γ BL²²

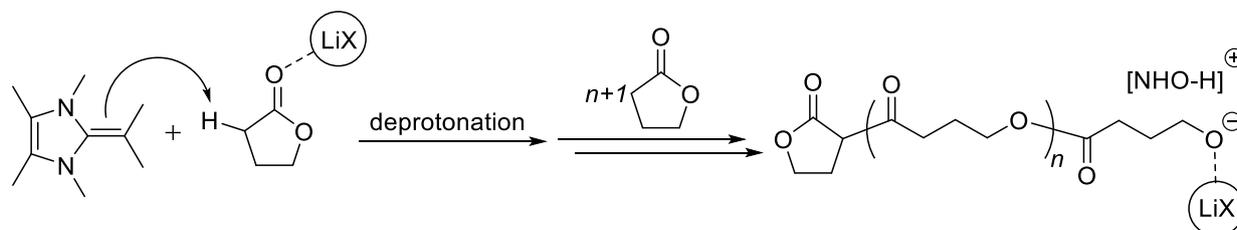
N-heterocyclic olefins (NHOs) were also recently used for the polymerization of γ BL in bulk at -36 °C. Polyesters with a mixture of cyclic and linear structures were obtained only when an initiator (BnOH) was initially added, meaning that a zwitterionic polymerization cannot occur.²¹ 70% monomer conversion could be reached after 2 days and polymers with \overline{M}_n up to 7 000 g/mol with a dispersity around 1.8 were observed. The addition of a Lewis acid such as lithium halides (LiX) was shown to retard/decrease the backbiting reaction by transesterification and therefore the formation of macrocycle polymers. Random copolyesters (with ω -pentadecalactone, ϵ CL and δ VL as comonomer) could also be prepared at low polymerization temperature in the presence of an alcohol as initiator with a γ BL content in copolymers reaching 22%.⁴²

Interestingly, the polymerization could occurred also without any alcohol but only in the presence of a highly nucleophilic NHO, in agreement with a zwitterionic mechanism (Scheme 9).²¹ In the absence of any initiator, one can note that the enolization of the lactone is favored over nucleophilic ring-opening when a sterically hindered but strongly basic NHOs is used. The typical anionic polymerization mechanism observed was proposed (Scheme 10).²¹



Scheme 9: Zwitterionic ROP of γ BL by NHOs/LiX system²¹

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34 Scheme 10: Deprotonation and ROP of γ BL by strongly basic NHO/LiX²¹

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6 **4 Lewis acids and Brønsted acids**

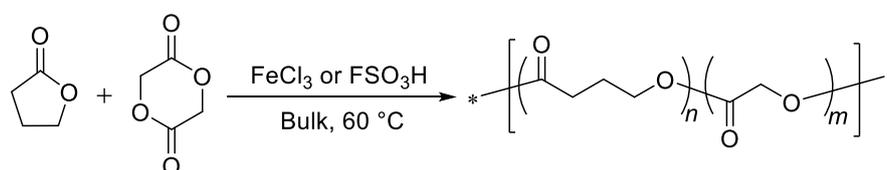
7 Cationic ROCP of γ BL was far less studied than anionic or coordination-insertion
8 polymerization. Nevertheless, the first paper dealing with cationic ROP of γ BL was published
9 in 1951.⁴³ Indeed, Meerwein used tertiary oxonium salts (based on boron Lewis acids) to
10 produce merely dimers and trimers.

11 Later, triethylaluminium associated to water ($\text{AlEt}_3\text{-H}_2\text{O}$) revealed an effective catalytic system
12 for the copolymerization of γ BL and β PL, whereas diethylzinc associated to water ($\text{ZnEt}_2\text{-H}_2\text{O}$)
13 was only able to achieve the homopolymerization of β PL.²⁹ Up to 29.5% of γ BL could be
14 incorporated and reactivity ratios were determined to be $r_{\gamma\text{BL}}=0.36$ and $r_{\beta\text{PL}}=18$.

15 Copolymerization of 3,3-Bis(chloromethyl)oxetane (BCMO) and γ BL were performed in
16 toluene at room temperature with Tin(IV) chloride (SnCl_4) and $\text{BF}_3\cdot\text{Et}_2\text{O}$.⁴⁴ Alternating
17 copolymers with low yield were produced. This is the only paper about copolymerization of
18 γ BL and cyclic ether as cyclic lactones are usually used as comonomer.

19 In the 80s, Kricheldorf showed that iron(III) chloride (FeCl_3), aluminium (III) chloride (AlCl_3)
20 $\text{BF}_3\cdot\text{Et}_2\text{O}$ and fluorosulfonic acid (FSO_3H) were able to catalyze the random copolymerization
21 of γ BL and glycolide at 60 °C in bulk with an incorporation of γ BL up to 30% with FeCl_3
22 (Scheme 11).³⁰ It was also shown that an increase of the amount of γ BL in the monomer feed
23 decreased significantly the polymerization yield. On the contrary, ZnCl_2 , $\text{Al}(\text{O}^i\text{Pr})_3$ and
24 dibutyldimethoxytin ($n\text{Bu}_2\text{Sn}(\text{OMe})_2$) were only able to achieve the homopolymerization of
25 glycolide.

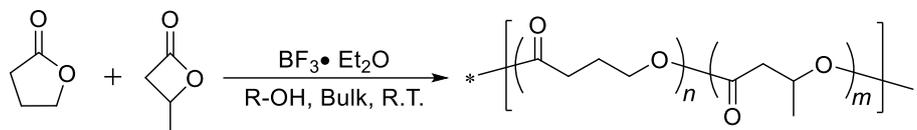
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2829 Scheme 11: Acid-catalyzed ROCP of γ BL and glycolide³⁰

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31 Copolymerization of γ BL and β BL has been performed with boron trifluoride diethyl etherate
32 ($\text{BF}_3\cdot\text{Et}_2\text{O}$), trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$) or methyl trifluoromethanesulfonate in
33 bulk at room temperature for 7 days, whereas AlCl_3 and antimony(III) fluoride (SbF_3) were
34 shown to be ineffective (Scheme 12).⁴⁵ Combination of γ BL and β BL leads to the random
35 poly(γ BL-co- β BL) ($\overline{M}_n=1800\text{-}4400$ g/mol, $\overline{D}=1.3\text{-}1.8$) whose structure is identical to that of
36 poly(hydroxy alkanooate)s produced by micro-organisms. With $\text{BF}_3\cdot\text{Et}_2\text{O}$, the incorporation of

1 γ BL increases with the feed ratio (γ BL/ β BL) and reaches 56% at a molar ratio of 90/10
 2 (γ BL/ β BL). Determined reactivity ratios were equal to r_{γ BL=0.48 and r_{β BL=0.58. It is proposed
 3 that adventitious water contained in the reaction medium served as the initiator by reacting with
 4 BF_3 -activated monomers. Lauryl alcohol was also used as an initiator.



6
 7
 8 Scheme 12: Lewis acid-catalyzed ROCP of γ BL and β BL⁴⁵

9
 10 $\text{CF}_3\text{SO}_3\text{H}$ was also shown to catalyze the ROP of γ BL initiated by methanol under high pressure
 11 (800-1000 MPa) at 40 °C.⁴⁶ The \overline{M}_n of obtained P γ BL were in the range of 6000-8000 g/mol
 12 ($D \approx 1.5$). Scandium trifluoromethanesulfonate revealed also able to catalyze the
 13 homopolymerization of γ BL in similar conditions.

14 Copolymers of γ BL and ϵ CL have been synthesized with phosphoric acid at 200 °C after 3 days.
 15 Semi-crystalline copolymers ($\overline{M}_n=17\ 800$ g/mol) with a melting temperature of 48 °C was
 16 obtained.⁴⁷

17
 18 **5 enzymatic-catalyzed ROP of γ BL**

19
 20 More than 20 years ago, lipases have also been employed as catalysts for the ROP of γ BL. For
 21 instance, P γ BL has been obtained with Porcine Pancreatic lipase or lipase PS30 from
 22 *pseudomonas cepacia* after 18 days at 60 °C with a degree of polymerization (DP) around 10.⁴⁸
 23 Copolymers with ϵ CL were also prepared with nevertheless a low incorporation of γ BL.⁴⁹ More
 24 recently, the use of immobilized lipase B from candida Antarctica in ionic liquids has led to the
 25 oligomerization of γ BL ($DP=5$).⁵⁰

26
 27 **6 Miscellaneous catalytic systems**

28
 29 Tin(IV) ion-exchanged montmorillonite has been used for the polymerization of γ BL and its
 30 copolymerization with δ VL at room temperature. For the homopolymerization, dimers and
 31 trimers were mainly obtained. For the copolymerization, DP around 4-6 were obtained with a
 32 low incorporation of γ BL.⁵¹

33 The copolymerization of γ BL with (di)ethylene glycol catalyzed by activated clay in xylene at
 34 reflux was also studied. Oligomers were obtained and served as precursors for polyurethane
 35 synthesis.⁵²

36 It was also shown that even in the absence of any catalyst, it was possible to copolymerize γ BL
 37 with L-lactic acid or glycolic acid at 200 °C in bulk.^{53,54} Molar masses were below 2500 g/mol
 38 for L-lactic acid and below 5200 g/mol for glycolic acid with 10 to 20% of γ BL incorporated
 39 in the copolymer.

40
 41 **CONCLUSION**

1
2 The ROP of γ BL has been considered for a long time to be impossible or hardly possible.
3 Nevertheless, it is reported in this review the recent progress that allow to control its ROP
4 process to yield P γ BL with high molar mass especially with alkali metal alkoxide / urea systems
5 in relatively mild reaction conditions. Anionic and coordination-insertion polymerizations have
6 been more studied than cationic ones. Low reaction temperatures remain compulsory to perform
7 the homopolymerization of γ BL as well as high initial monomer concentration.
8 The ROCP of γ BL with other cyclic esters has been more studied than its homopolymerization.
9 In this case, it was shown that γ BL could be incorporated even if the polymerization was not
10 performed at low temperature.
11

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