



**HAL**  
open science

## Ring-opening (co)polymerization of $\gamma$ -butyrolactone: a review

Qilei Song, Junpeng Zhao, Guangzhao Zhang, Frédéric Peruch, Stéphane Carlotti

► **To cite this version:**

Qilei Song, Junpeng Zhao, Guangzhao Zhang, Frédéric Peruch, Stéphane Carlotti. Ring-opening (co)polymerization of  $\gamma$ -butyrolactone: a review. *Polymer Journal*, 2020, 52 (1), pp.3-11. 10.1038/s41428-019-0265-5 . hal-02431117

**HAL Id: hal-02431117**

**<https://hal.science/hal-02431117>**

Submitted on 9 Sep 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Ring-opening (co)polymerization of $\gamma$ -butyrolactone: a review

Qilei Song,<sup>†</sup> Junpeng Zhao,<sup>†</sup> Guangzhao Zhang,<sup>†</sup> Frédéric Peruch,<sup>\*‡</sup> Stéphane Carlotti,<sup>\*‡</sup>

<sup>†</sup>Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

<sup>‡</sup>Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France

\* Corresponding author E-mail: peruch@enscbp.fr, carlotti@enscbp.fr

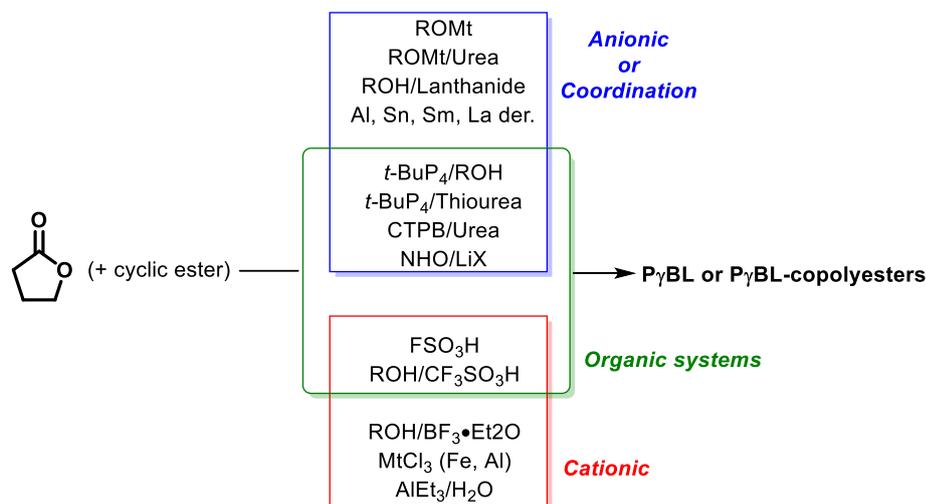
## ABSTRACT

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  $\gamma$ -butyrolactone ( $\gamma$ BL) could be a desirable feedstock for the chemical synthesis of poly( $\gamma$ -butyrolactone) (P $\gamma$ BL) or for the incorporation of  $\gamma$ BL units into polyester chains in order to modify their properties. Although  $\gamma$ BL is traditionally considered to be “non-polymerizable”, some progresses were recently made in ROP of  $\gamma$ BL. This mini-review is thus specially focused on the ROP of  $\gamma$ BL and its copolymerization with other cyclic esters.

## KEYWORDS

$\gamma$ -butyrolactone; polyester; ring-opening polymerization

## GRAPHICAL ABSTRACT



## 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.<sup>1-4</sup> 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.<sup>5-8</sup> Among the diversity of lactones, the five-  
9 membered  $\gamma$ -butyrolactone ( $\gamma$ 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( $\gamma$ -butyrolactone) (P $\gamma$ BL), a structural equivalent of poly(4-hydroxybutyrate)  
12 (P4HB), which is obtained from a bacterial fermentation process.<sup>9</sup> Moreover, it was  
13 demonstrated that the incorporation of  $\gamma$ BL into polyesters resulted in an enhanced  
14 biodegradability and flexibility.<sup>10</sup>

15 Compared to the commonly utilized lactones having high strain energy,  $\gamma$ 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 ( $\Delta H_p$ ) to overcome a large negative entropic  
18 change ( $\Delta S_p$ ) of its ROP.<sup>11-14</sup> It is then difficult to obtain high molar mass P $\gamma$ BL via a simple  
19 chemical synthesis process. As early as the 30s to the 50s, attempts to polymerize  $\gamma$ BL revealed  
20 unsuccessful.<sup>15,16</sup> In the 60s, oligomers of P $\gamma$ 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.<sup>17</sup> Thus, ROP of  $\gamma$ 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  $\gamma$ 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 $\gamma$ BL with linear or cyclic structures.<sup>18-24</sup> Ring-opening  
26 copolymerization (ROCP) of  $\gamma$ 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  $\gamma$ 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  $\gamma$ 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 $\gamma$ 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  $\gamma$ BL, all of them are performed at low  
38 temperature and high monomer concentration.

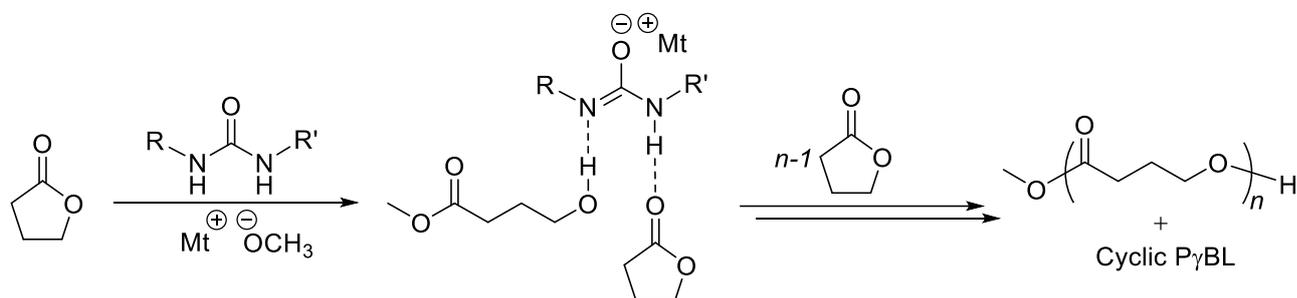


## 1 RESULTS AND DISCUSSION

### 1 Alkali metal derivatives as initiators

Low reaction temperature and high monomer concentration are favorable for the ROP of  $\gamma$ BL due to the low ceiling temperature ( $T_c$ ) of such a monomer. The bulk polymerization of  $\gamma$ BL was shown to proceed at  $-40$  °C using potassium or sodium methoxide (MtOMe) with low monomer conversions up to 25% after a few hours.<sup>23</sup> Working in tetrahydrofuran (THF) at  $-50$  °C was even worse as only 4% conversion was reached.<sup>25</sup> PEG-*b*-P $\gamma$ BL block copolymers could be also prepared in low yields starting from poly(ethylene glycol) macroinitiator deprotonated by NaH followed by polymerization of  $\gamma$ 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.<sup>26</sup> Lithium diisopropylamide in dioxane was also shown to copolymerize at  $25$  °C  $\epsilon$ -caprolactone ( $\epsilon$ CL) and  $\gamma$ BL with up to 26% incorporation of the second monomer into the copolymer after ring-opening.<sup>27</sup>

Adding ureas to NaOMe enhanced the reactivity of the active species making the polymerization feasible in bulk at  $-20$  °C with up to 70% monomer conversion in 2 hours.<sup>23</sup> Using KOMe with various ureas in THF at  $-50$  °C was less efficient in terms of monomer conversion.<sup>25</sup> In any case, urea anion is believed to both activate the alcohol initiator and  $\gamma$ 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.<sup>23</sup>

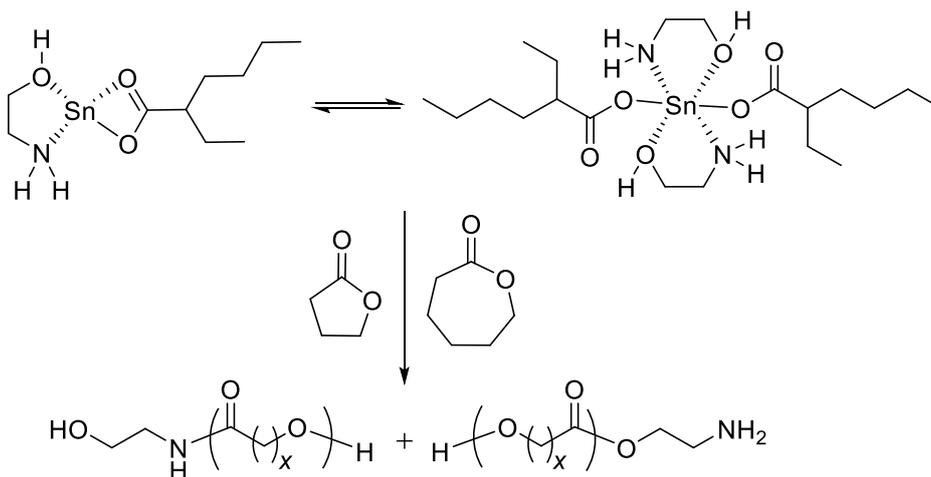


Scheme 1: ROP of  $\gamma$ BL by a metal alkoxide/urea system<sup>23</sup>

### 2 Stannous or lanthanide compounds associated to alcohols

Tin(II) octanoate (Sn(Oct)<sub>2</sub>) in the presence of ethanolamine was used to synthesize poly( $\epsilon$ -caprolactone) including randomly distributed  $\gamma$ BL units (16 mol%). It was shown that both the  $-OH$  and  $-NH_2$  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).<sup>27</sup> This result is

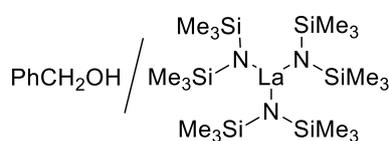
1 suggesting an anionic ring-opening polymerization process comparable with the nucleophilic  
 2 mechanism observed with alkali metal alkoxides used as initiators.  
 3



4  
 5  
 6  
 7  
 8  
 9  
 10  
 11  
 12  
 13  
 14  
 15  
 16  
 17  
 18

Scheme 2: Ethanolamine-initiated ROCP of  $\epsilon$ CL and  $\gamma$ BL catalyzed by  $\text{Sn}(\text{Oct})_2$ <sup>27</sup>

In the same vein, ROP of  $\gamma$ BL, that employed benzyl alcohol ( $\text{PhCH}_2\text{OH}$ ,  $\text{BnOH}$ ) 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  $\gamma$ BL, was achieved in THF at  $-40^\circ\text{C}$  with a yield up to 43% in half a day (Scheme 3).<sup>18</sup> 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  $\gamma$ BL with  $\epsilon$ CL and  $\delta$ -valerolactone ( $\delta$ VL) at low temperatures yielded a series of relatively high molar mass copolyesters with high levels of  $\gamma$ BL incorporation (8 to 84%).<sup>28</sup> The copolyesters exhibited random structure with a high content of  $\gamma$ BL.



19  
 20  
 21

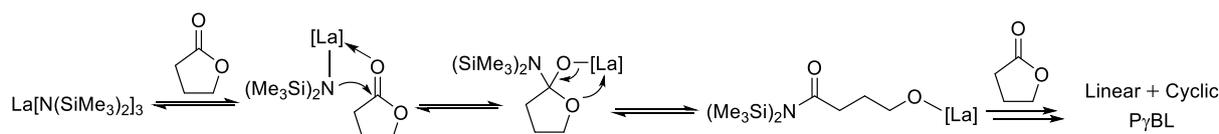
Scheme 3:  $\text{BnOH}/\text{La}[\text{N}(\text{SiMe}_3)_2]_3$  system used for ROP/ROCP of  $\gamma$ BL<sup>18,28</sup>

22  
 23  
 24  
 25

### 3 Organometallic compounds and lanthanides as catalysts

26 Organometallic compounds and lanthanides were also proposed without any addition of protic  
 27 species. A coordination-insertion mechanism is thus expected. Tentative copolymerization of  
 28  $\gamma$ BL with glycolide or  $\beta$ -propiolactone ( $\beta$ PPL) were performed using zinc chloride ( $\text{ZnCl}_2$ ) or  
 29 aluminum isopropoxide ( $\text{Al}(\text{O}^i\text{Pr})_3$ ) without real success.<sup>29,30</sup> Using aluminum isopropoxide  
 30 trimer at room temperature, in the 90s Penczek and Duda could prepare poly( $\epsilon$ -caprolactone-  
 31 *co*- $\gamma$ -butyrolactone) copolymers with molar masses up to 30 000 g/mol and containing up to 43

1 mol% of  $\gamma$ 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.<sup>31-33</sup>  
 4 Tetraphenyl tin catalyst revealed its efficiency at 140 °C for preparing statistical poly( $\gamma$ -  
 5 butyrolactone-*co*-L-lactide) copolyesters with molar masses as high as 70 000 g/mol. The  
 6 maximum  $\gamma$ BL content obtained was around 17%.<sup>10,34</sup> Cyclic tin alkoxide was also showing  
 7 some activities to synthesize  $\gamma$ BL-based copolymers with the same limitations.<sup>35</sup>  
 8 1-Ethoxy-3-chlorotetrabutyl-distannoxane was able to copolymerize  $\gamma$ BL with  $\beta$ -butyrolactone  
 9 ( $\beta$ BL) at 100°C in bulk.<sup>36</sup> The amount of  $\gamma$ BL in the copolymer is highly dependent on the  
 10 monomer feed ratio going from 6% to 35% for a molar ratio of  $\beta$ BL/ $\gamma$ 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  $\gamma$ BL in  
 13 the monomer feed (mol%) from 10% to 90%.  
 14 The samarium(II) aryloxide complex  $\text{Sm}(\text{OAr})_2(\text{THF})_3$ <sup>37</sup> or a samarium iodide based complex<sup>38</sup>  
 15 showed some activity for the ROCP of  $\gamma$ BL and  $\epsilon$ CL at 20 °C. The formation of  $\epsilon$ CL- $\gamma$ BL  
 16 copolymers without  $\gamma$ BL blocks and limited  $\gamma$ BL conversion were observed with this system.  
 17 Similar conclusions were drawn when using an aluminum Schiff's base complex  
 18 HAPENAIO<sup>*i*</sup>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  $\epsilon$ CL units in the copolymer.<sup>27</sup>  
 20 The ROP of  $\gamma$ BL using  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$  alone was also shown to synthesize P $\gamma$ 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.<sup>18,28</sup>

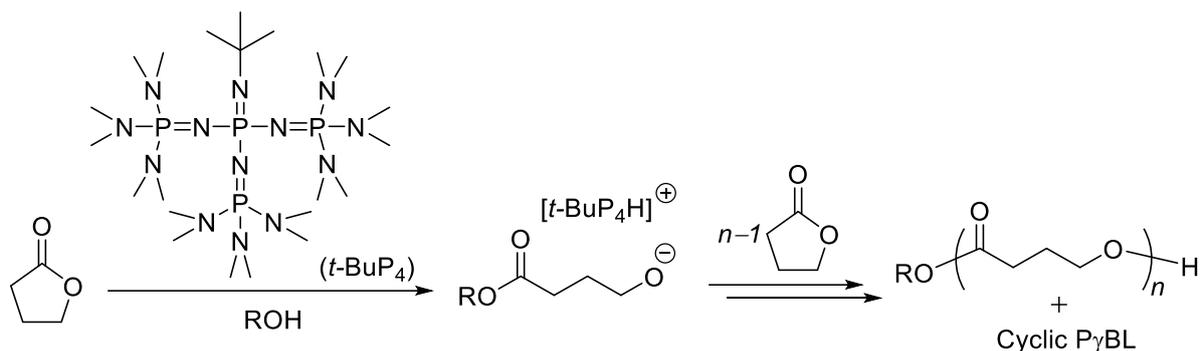


Scheme 4: Proposed mechanism for ROP of  $\gamma$ BL using  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ <sup>18</sup>

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

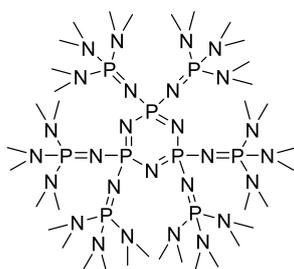
31 Since the description in 2001 of the first nucleophilic organocatalyzed ROP of lactide<sup>39</sup>, lots of  
 32 organocatalytic systems have been studied for the ROP of cyclic esters.<sup>40</sup> The phosphazene base,  
 33 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis-[tris(dimethylamino)phosphoranylideneamino]-  
 34  $2\lambda^5,4\lambda^5$ -catenadi(phosphazene) (*t*-BuP<sub>4</sub>) is one of them and is shown to achieve the synthesis of  
 35 metal-free P $\gamma$ BL.<sup>19</sup> 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  $\gamma$ 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 $\gamma$ BL were obtained in both  
 41 cases. ROCP of  $\gamma$ BL with  $\epsilon$ CL and  $\delta$ VL following the same approach was also successful.<sup>28</sup>

1 Noteworthy, the organic catalyst system based on *t*-BuP<sub>4</sub>/BnOH afforded the copolyesters with  
 2 high  $\gamma$ BL incorporation (42 to 80%) at a relatively low  $\gamma$ BL/ $\epsilon$ CL feed ratio (3 or 4/1).



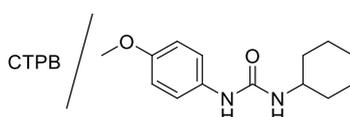
8 Scheme 5: *t*-BuP<sub>4</sub>/alcohol system as initiating species for ROP of  $\gamma$ BL<sup>19</sup>

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



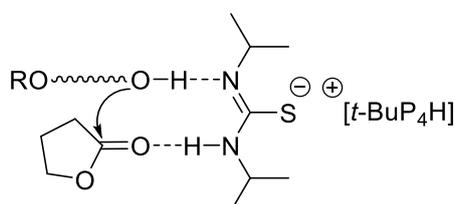
21 Scheme 6: Cyclic trimeric phosphazene base (CTPB) for ROP/ROCP of  $\gamma$ BL<sup>20,25,26</sup>

22  
23 CTPB/ureas binary organocatalysts were also studied for the ROP of  $\gamma$ BL<sup>25</sup>. Using 1-  
 24 cyclohexyl-3-(4-methoxyphenyl) urea, a urea bearing unsymmetrical and electron-donating  
 25 substituents (Scheme 7), P $\gamma$ 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  $\gamma$ BL<sup>25</sup>

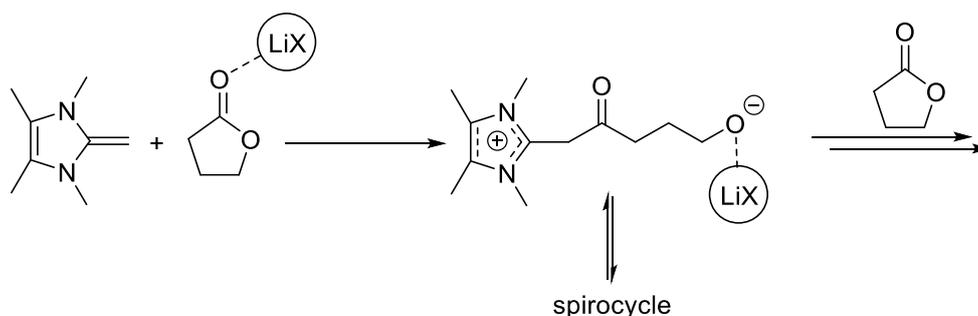
A dual organocatalysts based on the combination of *t*-BuP<sub>4</sub> and symmetrical thioureas bearing electron-donating groups was also demonstrated as an efficient organocatalytic system to synthesize linear P $\gamma$ BL with high polymerization rates (up to 80% monomer conversion in 4 hours) at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



Scheme 8: *t*-BuP<sub>4</sub>/thiourea system for the ROP of  $\gamma$ BL<sup>22</sup>

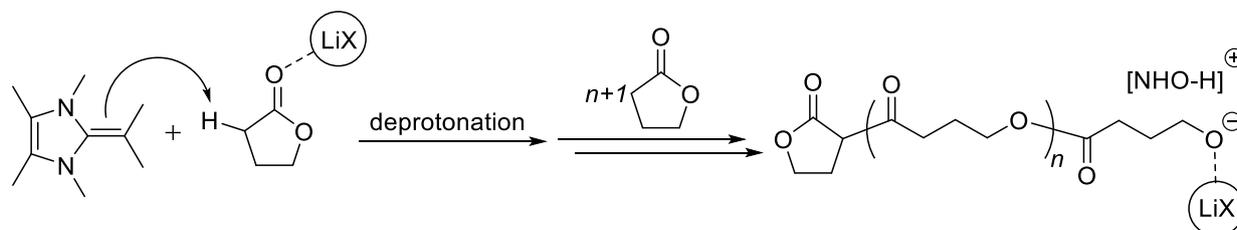
*N*-heterocyclic olefins (NHOs) were also recently used for the polymerization of  $\gamma$ BL in bulk at -36 °C. Polyesters with a mixture of cyclic and linear structures were obtained only when an initiator (BnOH) was initially added, meaning that a zwitterionic polymerization cannot occur.<sup>21</sup> 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  $\omega$ -pentadecalactone,  $\epsilon$ CL and  $\delta$ VL as comonomer) could also be prepared at low polymerization temperature in the presence of an alcohol as initiator with a  $\gamma$ BL content in copolymers reaching 22%.<sup>42</sup>

Interestingly, the polymerization could occur also without any alcohol but only in the presence of a highly nucleophilic NHO, in agreement with a zwitterionic mechanism (Scheme 9).<sup>21</sup> 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).<sup>21</sup>



Scheme 9: Zwitterionic ROP of  $\gamma$ BL by NHOs/LiX system<sup>21</sup>

1

2  
34 Scheme 10: Deprotonation and ROP of  $\gamma$ BL by strongly basic NHO/LiX<sup>21</sup>

5

6 **4 Lewis acids and Brønsted acids**

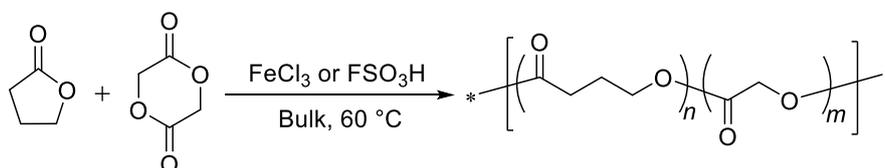
7 Cationic ROCP of  $\gamma$ BL was far less studied than anionic or coordination-insertion  
8 polymerization. Nevertheless, the first paper dealing with cationic ROP of  $\gamma$ BL was published  
9 in 1951.<sup>43</sup> Indeed, Meerwein used tertiary oxonium salts (based on boron Lewis acids) to  
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  $\gamma$ BL and  $\beta$ PL, whereas diethylzinc associated to water ( $\text{ZnEt}_2\text{-H}_2\text{O}$ )  
13 was only able to achieve the homopolymerization of  $\beta$ PL.<sup>29</sup> Up to 29.5% of  $\gamma$ 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  $\gamma$ BL were performed in  
16 toluene at room temperature with Tin(IV) chloride ( $\text{SnCl}_4$ ) and  $\text{BF}_3\cdot\text{Et}_2\text{O}$ .<sup>44</sup> Alternating  
17 copolymers with low yield were produced. This is the only paper about copolymerization of  
18  $\gamma$ BL and cyclic ether as cyclic lactones are usually used as comonomer.

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

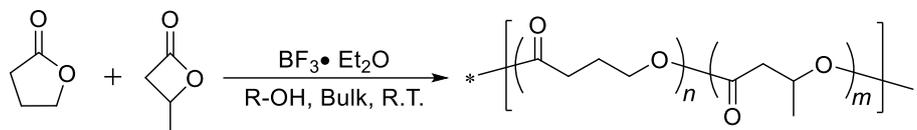
26

27  
2829 Scheme 11: Acid-catalyzed ROCP of  $\gamma$ BL and glycolide<sup>30</sup>

30

31 Copolymerization of  $\gamma$ BL and  $\beta$ 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  $\text{AlCl}_3$  and antimony(III) fluoride ( $\text{SbF}_3$ ) were  
34 shown to be ineffective (Scheme 12).<sup>45</sup> Combination of  $\gamma$ BL and  $\beta$ BL leads to the random  
35 poly( $\gamma$ BL-co- $\beta$ 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  $\gamma$ BL increases with the feed ratio ( $\gamma$ BL/ $\beta$ BL) and reaches 56% at a molar ratio of 90/10  
 2 ( $\gamma$ BL/ $\beta$ BL). Determined reactivity ratios were equal to  $r_{\gamma$ BL=0.48 and  $r_{\beta$ BL=0.58. It is proposed  
 3 that adventitious water contained in the reaction medium served as the initiator by reacting with  
 4  $\text{BF}_3$ -activated monomers. Lauryl alcohol was also used as an initiator.



6  
7  
8 Scheme 12: Lewis acid-catalyzed ROCP of  $\gamma$ BL and  $\beta$ BL<sup>45</sup>

9  
10  $\text{CF}_3\text{SO}_3\text{H}$  was also shown to catalyze the ROP of  $\gamma$ BL initiated by methanol under high pressure  
 11 (800-1000 MPa) at 40 °C.<sup>46</sup> The  $\overline{M}_n$  of obtained P $\gamma$ 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  $\gamma$ BL in similar conditions.

14 Copolymers of  $\gamma$ BL and  $\epsilon$ 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.<sup>47</sup>

17  
18 **5 enzymatic-catalyzed ROP of  $\gamma$ BL**

19  
20 More than 20 years ago, lipases have also been employed as catalysts for the ROP of  $\gamma$ BL. For  
 21 instance, P $\gamma$ 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.<sup>48</sup>  
 23 Copolymers with  $\epsilon$ CL were also prepared with nevertheless a low incorporation of  $\gamma$ BL.<sup>49</sup> More  
 24 recently, the use of immobilized lipase B from candida Antarctica in ionic liquids has led to the  
 25 oligomerization of  $\gamma$ BL ( $DP=5$ ).<sup>50</sup>

26  
27 **6 Miscellaneous catalytic systems**

28  
29 Tin(IV) ion-exchanged montmorillonite has been used for the polymerization of  $\gamma$ BL and its  
 30 copolymerization with  $\delta$ 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  $\gamma$ BL.<sup>51</sup>

33 The copolymerization of  $\gamma$ 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.<sup>52</sup>

36 It was also shown that even in the absence of any catalyst, it was possible to copolymerize  $\gamma$ BL  
 37 with L-lactic acid or glycolic acid at 200 °C in bulk.<sup>53,54</sup> 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  $\gamma$ BL incorporated  
 39 in the copolymer.

40  
41 **CONCLUSION**

1  
2 The ROP of  $\gamma$ 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 $\gamma$ 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  $\gamma$ BL as well as high initial monomer concentration.  
8 The ROCP of  $\gamma$ BL with other cyclic esters has been more studied than its homopolymerization.  
9 In this case, it was shown that  $\gamma$ BL could be incorporated even if the polymerization was not  
10 performed at low temperature.  
11

## 1 REFERENCES

- 2 1. Longo JM, Sanford MJ, Coates GW. Ring-Opening Copolymerization of Epoxides and Cyclic  
3 Anhydrides with Discrete Metal Complexes: Structure–Property Relationships. *Chem Rev.*  
4 2016.
- 5 2. Hillmyer MA, Tolman WB. Aliphatic polyester block polymers: renewable, degradable, and  
6 sustainable. *Acc Chem Res.* 2014;47(8):2390-2396.
- 7 3. Schneiderman DK, Hillmyer MA. Aliphatic Polyester Block Polymer Design. *Macromolecules.*  
8 2016;49(7):2419-2428.
- 9 4. Gonçalves FMM, Fonseca AC, Domingos M, Gloria A, Serra AC, Coelho JFJ. The potential of  
10 unsaturated polyesters in biomedicine and tissue engineering: Synthesis, structure-  
11 properties relationships and additive manufacturing. *Prog Polym Sci.* 2017;68:1-34.
- 12 5. Kamber NE, Jeong W, Waymouth RM, Pratt RC, Lohmeijer BG, Hedrick JL. Organocatalytic  
13 ring-opening polymerization. *Chem Rev.* 2007;107(12):5813-5840.
- 14 6. Penczek S, Cypryk M, Duda A, Kubisa P, Slomkowski S. Living ring-opening polymerizations of  
15 heterocyclic monomers. *Prog Polym Sci.* 2007;32(2):247-282.
- 16 7. Jerome C, Lecomte P. Recent advances in the synthesis of aliphatic polyesters by ring-  
17 opening polymerization. *Adv Drug Deliv Rev.* 2008;60(9):1056-1076.
- 18 8. Hu S, Zhao J, Zhang G, Schlaad H. Macromolecular architectures through organocatalysis.  
19 *Prog Polym Sci.* 2017;74:34-77.
- 20 9. Moore T, Adhikari R, Gunatillake P. Chemosynthesis of bioresorbable poly( $\gamma$ -  
21 butyrolactone) by ring-opening polymerisation: a review. *Biomaterials.* 2005;26(18):3771-  
22 3782.
- 23 10. Nakayama A, Kawasaki N, Aiba S, Maeda Y, Arvanitoyannis I, Yamamoto N. Synthesis and  
24 biodegradability of novel copolyesters containing  $\gamma$ -butyrolactone units. *Polymer.*  
25 1998;39(5):1213-1222.
- 26 11. Houk K, Jabbari A, Hall H, Alemán C. Why  $\delta$ -valerolactone polymerizes and  $\gamma$ -butyrolactone  
27 does not. *J Org Chem.* 2008;73(7):2674-2678.
- 28 12. Dubois P, Coulembier O, Raquez J-M. *Handbook of Ring-Opening Polymerization.* 2009.
- 29 13. Aleman C, Betran O, Casanovas J, Houk KN, Hall HK, Jr. Thermodynamic control of the  
30 polymerizability of five-, six-, and seven-membered lactones. *J Org Chem.* 2009;74(16):6237-  
31 6244.
- 32 14. Saiyasombat W, Molloy R, Nicholson TM, Johnson AF, Ward IM, Poshyachinda S. Ring strain  
33 and polymerizability of cyclic esters. *Polymer.* 1998;39(23):5581-5585.
- 34 15. Carothers WH, Dorough GL, Natta FJv. Studies of Polymerization and Ring Formation. X. The  
35 Reversible Polymerization of Six-Membered Cyclic Esters. *J Am Chem Soc.* 1932;54(2):761-  
36 772.
- 37 16. Hall HK, Schneider AK. Polymerization of Cyclic Esters, Urethans, Ureas and Imides. *J Am*  
38 *Chem Soc.* 1958;80(23):6409-6412.
- 39 17. Korte F, Glet W. Hochdruckreaktionen. II. Die polymerisation von  $\gamma$ -Butyrolacton und  $\delta$ -  
40 Valerolactam bei hohen drücken. *Journal of Polymer Science Part B: Polymer Letters.*  
41 1966;4(10):685-689.
- 42 18. Hong M, Chen EY. Completely recyclable biopolymers with linear and cyclic topologies via  
43 ring-opening polymerization of  $\gamma$ -butyrolactone. *Nat Chem.* 2016;8(1):42-49.
- 44 19. Hong M, Chen EY. Towards Truly Sustainable Polymers: A Metal-Free Recyclable Polyester  
45 from Biorenewable Non-Strained  $\gamma$ -Butyrolactone. *Angew Chem Int Ed Engl.*  
46 2016;55(13):4188-4193.
- 47 20. Zhao N, Ren C, Li H, Li Y, Liu S, Li Z. Selective Ring-Opening Polymerization of Non-Strained  
48  $\gamma$ -Butyrolactone Catalyzed by A Cyclic Trimeric Phosphazene Base. *Angew Chem Int Ed*  
49 *Engl.* 2017;56(42):12987-12990.
- 50 21. Walther P, Frey W, Naumann S. Polarized olefins as enabling (co)catalysts for the  
51 polymerization of  $\gamma$ -butyrolactone. *Polym Chem.* 2018;9(26):3674-3683.

- 1 22. Zhang C-J, Hu L-F, Wu H-L, Cao X-H, Zhang X-H. Dual Organocatalysts for Highly Active and  
2 Selective Synthesis of Linear Poly( $\gamma$ -butyrolactone)s with High Molecular Weights.  
3 *Macromolecules*. 2018;51(21):8705-8711.
- 4 23. Lin L, Han D, Qin J, et al. Nonstrained  $\gamma$ -Butyrolactone to High-Molecular-Weight Poly( $\gamma$ -  
5 butyrolactone): Facile Bulk Polymerization Using Economical Ureas/Alkoxides.  
6 *Macromolecules*. 2018;51(22):9317-9322.
- 7 24. Olsen P, Odelius K, Albertsson AC. Thermodynamic Presynthetic Considerations for Ring-  
8 Opening Polymerization. *Biomacromolecules*. 2016;17(3):699-709.
- 9 25. Shen Y, Zhao Z, Li Y, Liu S, Liu F, Li Z. A facile method to prepare high molecular weight bio-  
10 renewable poly( $\gamma$ -butyrolactone) using a strong base/urea binary synergistic catalytic system.  
11 *Polym Chem*. 2019;10(10):1231-1237.
- 12 26. Shen Y, Zhang J, Zhao Z, Zhao N, Liu F, Li Z. Preparation of Amphiphilic Poly(ethylene glycol)-  
13 b-poly( $\gamma$ -butyrolactone) Diblock Copolymer via Ring Opening Polymerization Catalyzed  
14 by a Cyclic Trimeric Phosphazene Base or Alkali Alkoxide. *Biomacromolecules*.  
15 2019;20(1):141-148.
- 16 27. Bhaw-Luximon A, Jhurry D, Motala-Timol S, Lochee Y. Polymerization of  $\epsilon$ -Caprolactone and  
17 its Copolymerization with  $\gamma$ -Butyrolactone using Metal Complexes. *Macromolecular*  
18 *Symposia*. 2005;231(1):60-68.
- 19 28. Hong M, Tang X, Newell BS, Chen EYX. "Nonstrained"  $\gamma$ -Butyrolactone-Based Copolyesters:  
20 Copolymerization Characteristics and Composition-Dependent (Thermal, Eutectic,  
21 Cocrystallization, and Degradation) Properties. *Macromolecules*. 2017;50(21):8469-8479.
- 22 29. Tada K, Numata Y, Saegusa T, Furukawa J. Copolymerization of  $\gamma$ -butyrolactone and  $\beta$ -  
23 propiolactone. *Makromol Chem*. 1964;77(1):220-228.
- 24 30. Kricheldorf HR, Mang T, Jonté JM. Polylactones, 2 Copolymerization of glycolide with  $\beta$ -  
25 propiolactone,  $\gamma$ -butyrolactone or  $\delta$ -valerolactone. *Makromol Chem*. 1985;186(5):955-976.
- 26 31. Duda A, Penczek S, Dubois P, Mecerreyes D, Jérôme R. Oligomerization and copolymerization  
27 of  $\gamma$ -butyrolactone — a monomer known as unable to homopolymerize, 1. Copolymerization  
28 with  $\epsilon$ -caprolactone. *Macromol Chem Phys*. 1996;197(4):1273-1283.
- 29 32. Duda A, Biela T, Libiszowski J, et al. Block and random copolymers of  $\epsilon$ -caprolactone. *Polym*  
30 *Degrad Stab*. 1998;59(1-3):215-222.
- 31 33. Duda A, Libiszowski J, Mosnáček J, Penczek S. Copolymerization of Cyclic Esters at the Living  
32 Polymer-Monomer Equilibrium. *Macromolecular Symposia*. 2005;226(1):109-120.
- 33 34. Nakayama A, Kawasaki N, Arvanitoyannis I, Aiba S, Yamamoto N. Synthesis and  
34 biodegradation of poly( $\gamma$ -butyrolactone-co-l-lactide). *Journal of Environmental Polymer*  
35 *Degradation*. 1996;4(3):205-211.
- 36 35. Wei Z, Liu L, Qi M. Synthesis and characterization of homo- and co-polymers of (R,S)- $\beta$ -  
37 butyrolactone and  $\gamma$ -butyrolactone or  $\beta$ -valerolactone initiated with cyclic tin alkoxide. *React*  
38 *Funct Polym*. 2006;66(12):1411-1419.
- 39 36. Hori Y, Yamaguchi A, Hagiwara T. Chemical synthesis of high molecular weight poly(3-  
40 hydroxybutyrate-co-4-hydroxybutyrate). *Polymer*. 1995;36(24):4703-4705.
- 41 37. Nishiura M, Hou Z, Koizumi T-a, Imamoto T, Wakatsuki Y. Ring-Opening Polymerization and  
42 Copolymerization of Lactones by Samarium(II) Aryloxide Complexes. *Macromolecules*.  
43 1999;32(25):8245-8251.
- 44 38. Agarwal S, Xie X. SmI<sub>2</sub>/Sm-Based  $\gamma$ -Buyrolactone- $\epsilon$ -Caprolactone Copolymers:  
45 Microstructural Characterization Using One- and Two-Dimensional NMR Spectroscopy.  
46 *Macromolecules*. 2003;36(10):3545-3549.
- 47 39. Nederberg F, Connor, EF., Möller, M., Glauser, T., Hedrick, JL. . New paradigms for organic  
48 catalysts: the first organocatalytic living polymerization. *Angew Chem Int Ed Engl*.  
49 2001;40:2712-2715.
- 50 40. Carlotti S, Peruch F. . Cyclic Monomers: Epoxides, Lactide, Lactones, Lactams, Cyclic Silicon-  
51 containing monomers, Cyclic Carbonates and others. In: Hadjichristidis N, Hirao, A. , ed.

- 1 *Anionic Polymerization: Principles, Practice, Strength, Consequences, and Applications.*  
2 Springer of Japan; 2015:191-305.
- 3 41. Shen Y, Zhang J, Zhao N, Liu F, Li Z. Preparation of biorenewable poly( $\gamma$ -butyrolactone)-b-  
4 poly(l-lactide) diblock copolyesters via one-pot sequential metal-free ring-opening  
5 polymerization. *Polym Chem.* 2018;9(21):2936-2941.
- 6 42. Walther P, Naumann S. N-Heterocyclic Olefin-Based (Co)polymerization of a Challenging  
7 Monomer: Homopolymerization of  $\omega$ -Pentadecalactone and Its Copolymers with  $\gamma$ -  
8 Butyrolactone,  $\delta$ -Valerolactone, and  $\epsilon$ -Caprolactone. *Macromolecules.* 2017;50(21):8406-  
9 8416.
- 10 43. Meerwein H. Über oxoniumverbindungen des Säure-ester und lactone. *Angew Chem.*  
11 1951;63(20):480-481.
- 12 44. Ito K, Inoue T, Yamashita Y. Copolymerizations of 3,3-bis(chloromethyl)oxacyclobutane with  
13  $\beta$ -propiolactone and  $\gamma$ -butyrolactone by lewis acids: "Two-state" polymerization mechanism.  
14 *Makromol Chem.* 1970;139(1):153-164.
- 15 45. Lee CW, Urakawa R, Kimura Y. Copolymerization of  $\gamma$ -butyrolactone and  $\beta$ -butyrolactone.  
16 *Makromol Chem Phys.* 1997;198(4):1109-1120.
- 17 46. Yamashita K, Yamamoto K, Kadokawa J-i. Acid-catalyzed Ring-opening Polymerization of  $\gamma$ -  
18 Butyrolactone under High-pressure Conditions. *Chem Lett.* 2014;43(2):213-215.
- 19 47. Lin WJ. Comparison of thermal characteristics and degradation properties of epsilon-  
20 caprolactone copolymers. *J Biomed Mater Res.* 1999;47(3):420-423.
- 21 48. Nobes GAR, Kazlauskas RJ, Marchessault RH. Lipase-Catalyzed Ring-Opening Polymerization  
22 of Lactones: A Novel Route to Poly(hydroxyalkanoate)s. *Macromolecules.* 1996;29(14):4829-  
23 4833.
- 24 49. Dong H, Wang H-d, Cao S-g, Shen J-c. Lipase-catalyzed polymerization of lactones and linear  
25 hydroxyesters. *Biotechnol Lett.* 1998;20(10):905-908.
- 26 50. Gorke JT, Okrasa K, Louwagie A, Kazlauskas RJ, Sreenc F. Enzymatic synthesis of  
27 poly(hydroxyalkanoates) in ionic liquids. *J Biotechnol.* 2007;132(3):306-313.
- 28 51. Kadokawa J, Iwasaki Y, Tagaya H. Ring-opening polymerization of lactones catalyzed by ion-  
29 exchanged clay montmorillonite. *Green Chem.* 2002;4(1):14-16.
- 30 52. Miura H, Tajima T, Nagata M, Royama T, Saito K, Hasegawa M. Synthesis of Poly(ester ether)s  
31 by the Reaction of  $\gamma$ -Butyrolactone with Diols and Their Application to Polyurthanes.  
32 *Kobunshi Ronbunshu.* 1999;56(5):291-297.
- 33 53. Fukuzaki H, Aiba Y, Yoshida M, Asano M, Kumakura M. Direct copolymerization of L-lactic  
34 acid with  $\gamma$ -butyrolactone in the absence of catalysts. *Die Makromolekulare Chemie.*  
35 1989;190(7):1553-1559.
- 36 54. Fukuzaki H, Yoshida M, Asano M, Aiba Y, Kumakura M. Direct copolymerization of glycolic  
37 acid with lactones in the absence of catalysts. *European Polymer Journal.* 1990;26(4):457-  
38 461.

39