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Ring-opening polymerization of *γ*-lactones and copolymerization with other cyclic monomers

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Abstract: Triggered by raised environmental awareness and the rising requirements for sustainable polymers such as degradable or recyclable polymers, studies on ring-opening (co)polymerization (ROP/ROCP) of (bio-based) cyclic monomers (*e.g.*, cyclic esters, lactides, epoxides *etc.*) have been booming in recent years. Renewable five-membered *γ*-butyrolactone (*γ*BL) and derivatives would thus be a desirable feedstock to produce poly(*γ*-butyrolactone) (P*γ*BL) and different (bio-based) functional polyesters. Their copolymerization with other cyclic monomers could also afford an alternative to tune the properties of the resulting materials. Although *γ*BL was traditionally regarded "non-polymerizable", some progresses were made recently concerning the ROP/ROCP of *γ*BL and derivatives. More importantly, some polyesters could be totally depolymerized back to their monomers by thermal or chemical treatment. This review is specially focused on ROP of *γ*-lactones and their copolymerization with other cyclic monomers by different catalytic/initiating systems, including Lewis/Brønsted acids, organic bases and alkali metal compounds, organometallic compounds, and cooperative bicomponent catalytic systems. The depolymerization process of some obtained polyesters is also discussed.

Keywords: *γ*-lactones, polyester, ring-opening (co)polymerization, sustainable polymer

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Contents

Abbreviations

γ-Lactones

αAcγBL	α-Acetyl-γ-butyrolactone
αAL	α-Angelica lactone (or 5-methyl-2(3*H*)-furanone)
βAL	β-Angelica lactone (or 5-methylfuran-2(5*H*)-one)
γAMMBL	γ-Allyl-γ-methyl-α-methylene-γ-butyrolactone
αBrγBL	α-Bromo-γ-butyrolactone
γBL	γ-Butyrolactone
BBL	Bicyclic bis(γ-butyrolactone)
BBL8	2,8-Dioxa-1-isopropenylbicyclo[3.3.0]octane-3,7-dione
γCL	γ-Caprolactone
4,5-C6L	4,5-*cis* Cyclohexyl-ring-fused γ-butyrolactone
rac-CBL	*racemic* 3,4-Cyclohexyl-ring-fused γ-butyrolactone
DAMBL	γ-Diallyl-α-methylene-γ-butyrolactone
FO	2(5*H*)-Furanone
βHMBL	Tulipalin B or β-hydroxy-α-methylene-γ-butyrolactone
3-HMFO	3-(Hydroxymethyl) furan-2(5*H*)-one
3-MFO	3-Methylfuran-2(5*H*)-one
αMBL	Tulipalin A or α-methylene-γ-butyrolactone
βMMBL	β-Methyl-α-methylene-γ-butyrolactone
γMBL	α-Methyl-γ-butyrolactone
γMMBL	γ-Methyl-α-methylene-γ-butyrolactone
γMe$_2$MBL	α-Methylene-γ,γ-dimethyl-γ-butyrolactone
αOHγBL	α-Hydroxy-γ-butyrolactone
αOHβMe$_2$γBL	α-Hydroxy-β,β-dimethyl-γ-butyrolactone
(R)-γVL	(R)-γ-Valerolactone
S-BBL	Bicyclic bis(γ-butyrolactone) derivatives bearing sulfide moieties
SBL	Spirocyclic (γ-butyrolactone)
SBBL	Spirocyclic bis(γ-butyrolactone)
3,4-T6L	3,4-*trans* Cyclohexyl-ring-fused γ-butyrolactone
4,5-T6L	4,5-*trans* Cyclohexyl-ring-fused γ-butyrolactone (or *trans*-hexahydro-2(3*H*)-benzofuranone)
γVL	γ-Valerolactone
VMBL	γ-Vinyl-α-methylene-γ-butyrolactone
γVMMBL	γ-Vinyl-γ-methyl-α-methylene-γ-butyrolactone
VMMBL	γ-Vinyl-β-methyl-α-methylene-γ-butyrolactone

Comonomers

AOMEC	2-Allyloxymethyl-2-ethyltrimethylene carbonate
βBL	β-Butyrolactone
t-BuGE	*tert*-Butyl glycidyl ether
BCMO	3,3-Bis(chloromethyl)oxetane
DGEBA	Diglycidyl ether bisphenol A
DGEBS	Diglycidyl ether bisphenol S
εCL	ε-Caprolactone
CHO	Cyclohexene oxide
CO$_2$	Carbon dioxide
EC	Ethylene carbonate
GP	Glycidyl pivalate
GPE	Glycidyl phenyl ether
GME	Glycidyl methyl ether
HO	1-Hexene oxide
LLA	L-Lactide
MMA	Methyl methacrylate
PO	Propylene oxide
PC	Propylene carbonate
βPL	β-Propiolactone
ωPDL	ω-Pentadecalactone
SO	Styrene oxide
TMC	Trimethylene carbonate
TeU	Tetramethylene urea
δVL	δ-Valerolactone

Polymers

PαAL	Poly(α-angelica lactone)
P(αAcγBL)	Poly(α-acetyl-γ-butyrolactone)
PγBL	Poly(γ-butyrolactone)
PγBL$_{L1}$	Linear poly(γ-butyrolactone) with acylated lactone/H chain ends
PγBL$_{L2}$	Linear poly(γ-butyrolactone) with BnO/H chain ends
PγBL$_{L3}$	Linear poly(γ-butyrolactone) with MeO/H chain ends
PγBL$_{C}$	Cyclic poly(γ-butyrolactone)
PCL	Poly(ε-caprolactone)
ht-PCBL	*heterotactic* Poly(3,4-cyclohexyl-ring-fused γ-butyrolactone)
it-PCBL	*isotactic* Poly(3,4-cyclohexyl-ring-fused γ-butyrolactone)
PFO	Poly(2(5*H*)-furanone)
PGA	Poly(glycolic acid)
PGM	Poly(glycidyl methacrylate)
PGMS	Poly(4-(glycidyl methyl)styrene)
P4HB	Poly(4-hydroxybutyrate)
P(αMBL)$_{VAP}$	Poly(α-methylene-γ-butyrolactone) produced by vinyl-addition polymerization
P(αMBL)$_{CLP}$	Poly(α-methylene-γ-butyrolactone) produced by cross-linked polymerization
P(αMBL)$_{ROP}$	Poly(α-methylene-γ-butyrolactone) produced by ring-opening polymerization
P(3,4-T6L)	Poly(3,4-*trans* cyclohexyl-ring-fused γ-butyrolactone)
P(4,5-T6L)	Poly(4,5-*trans* cyclohexyl-ring-fused γ-butyrolactone)
PVL	Poly(δ-valerolactone)

Catalysts/Initiators

$AlEt_3$-H_2O	Triethylaluminium-water
$Al(O^iPr)_3$	Aluminium isopropoxide
BDM	1,4-Benzenedimethanol
BEMP	2-*tert*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
BF_3•Et_2O	Trifluoride diethyl etherate
BF_3•$EtNH_2$	Boron trifluoride ethylamine complex
BF_3•4MA	Boron trifluoride *p*-methoxyaniline complex
$Bi(OTf)_3$	Bismuth(III) trifluoro methanesulfonate
$^nBu_4NBr$	Tetrabutylammonium bromide
t-BuOK	Potassium *tert*-butoxide
n-BuLi	*n*-Butyl lithium
n-Bu_2Mg	Di-*n*-butylmagnesium
n-BuEtMg	*n*-Butylethylmagnesium
n-BuONa	Sodium *n*-butoxide
t-BuP_1	*tert*-Butylimino-tris(dimethylamino)phosphorane
t-BuP_2	1-*tert*-Butyl-2,2,4,4,4-pentakis(dimethylamino)-$2\lambda^5,4\lambda^5$-catenadi(phosphazene)
t-BuP_4	1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis-[tris(dimethylamino)phosphoranylidenamino]-$2\lambda^5,4\lambda^5$-catenadi(phosphazene)
n-$Bu_2Sn(OMe)_2$	Dibutyldimethoxytin
Cyclic tin alkoxide	1,1,6,6-Tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclo-decane
CTPB	Cyclic trimeric phosphazene base
DABCO	1,4-Diazabicyclo[2.2.2] octane
DBU	1,8-Diazabicyclo[5.4.0] undec-7-ene
DMAP	*N,N*-Dimethyl-4-aminopyridine
DPP	Diphenyl phosphate
Et_2AlCl	Diethylaluminum chloride
$Et_3Al_2Cl_3$	Ethylaluminum sesquichloride
Et_3N	Triethylamine
$Et_3O(BF_4)$	Triethyloxonium tetrafluoroborate
$FeCl_3$	Iron(Ⅲ) chloride
FSO_3H	Fluorosulfonic acid
$HAPENAlO^iPr$	Aluminum Schiff's base complex
HBF_4•Et_2O	Tetrafluoroboric acid diethyl ether complex
HCl•Et_2O	Hydrochloric acid in diethyl ether
HO-PEG-OH	Dihydroxy-terminated poly(ethylene glycol)
H_3PO_4	Phosphoric acid

I^tBu	1,3-Di-*tert*-butylimidazol-2-ylidene
IMes	1,3-Bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene
I^iPr	1,3-Bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene
K_2CO_3	Potassium carbonate
KH	Potassium hydride
KOH	Potassium hydroxide
$LaCl_3$	Lanthanum(III) chloride
$La[N(SiMe_3)_2]_3$ (or La)	Tri[*N,N*-bis(trimethylsilyl)amide] lanthanum(Ш)
$[La(OBn)_3]_x$	Obtained by the stoichiometric reaction of La and BnOH
$La(OTf)_3$	Lanthanum(III) trifluoromethanesulfonate
LDA	Diisopropylamide
LiCl	Lithium chloride
LiX	Lithium halides
$Ln[N(SiMe_3)_2]_3$	Lanthanide analogues (Ln = Y, Sm)
MeLi	Methyllithium
Me_6TREN	Tris[2-(dimethylamino) ethyl]amine
$MgCl_2$	Magnesium chloride
1-MI	1-Methylimidazole
MSA	Methanesulfonic acid
MtOMe	Sodium or potassium methoxides
MtX	Metal halides
NaH	Sodium hydride
NaOH	Sodium hydroxide
NEMO	Non-eutectic mixture of organocatalysts (MSA/TBD = 3/1)
NHC	*N*-Heterocyclic carbene
NHO	*N*-Heterocyclic olefin
NHO3	1,3-Dimethyl-2-(1-methylethylidene)tetrahydropyrimidine
NHO4	2-Isopropylidene-1,3,4,5-tetramethylimidazoline
NHO6	1,3-Dimesityl-2-methylidene-tetrahydropyrimidine
NHO7	1,3,4,5-Tetramethyl-2-methyleneimidazoline
PBM	Polymer supported bimetallic complexes in the form of $P–Zn[Fe(CN)6]_aCl_{2-3a}(H_2O)_b$, where P is a polyether chelating agent, $a \approx 0.5$ and $b \approx 0.76$
P^nBu_3	Tri-*n*-butylphosphine
PCy_3	Tricyclohexylphosphine
PPh_3	Triphenylphosphine
PEG-OH	Monohydroxy-terminated poly(ethylene glycol)

Ph$_2$CHCH$_2$OH	2,2-Diphenylethanol
PhCH$_2$OH (or BnOH)	Benzyl alcohol
Ph$_2$CHOH	Diphenylmethanol
n-PrONa	Sodium *n*-propoxide
i-PrONa	Sodium isopropoxide
i-PrOH	Isopropanol
Ph$_4$Sn	Tetraphenyl tin
R$_3$N	*N,N*-Dimethylcyclohexylamine
SalenCo^{III}X	Salen = *N,N*-bis(3,5-di-tert-butylsalicylidene)-ethylenediimine, X = 2,4-dinitrophenoxide
SbF$_3$	Antimony(Ⅲ) fluoride
Sc(OTf)$_3$	Scandium(III) trifluoromethanesulfonate
SmI$_2$/Sm	Samarium(II) iodide-based complex
Sm(OAr)$_2$(THF)$_3$	Samarium(II) aryloxide complex
SnCl$_4$	Tin(Ⅳ) chloride
SnCl$_2$•2H$_2$O	Tin(II) chloride dihydrate
Sn(Oct)$_2$	Tin(Ⅱ) 2-ethylhexanoate
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TfOH	Trifluoromethanesulfonic acid
p-TfOH	*p*-Toluenesulfonic acid
TfOMe	Methyl trifluoromethanesulfonate
TPT	1,3,4-Triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene
TU	Thiourea
TU1	1,3-Diisopropyl-2-thiourea
TU2	1-[3,5-Bis(trifluoromethyl) phenyl]-3-cyclohexyl-thiourea
U1	1-Cyclohexyl-3-phenyl-urea
U2	1-Cyclohexyl-3-(4-methoxyphenyl)-urea
U3	1,3-Diphenylurea
U4	1-[3,5-Bis(trifluoromethyl) phenyl]-3-phenyl-urea
U5	1-Cyclohexyl-3-(4-(trifluoromethyl)phenyl)-urea
U6	1-(4-Chlorophenyl)-3-cyclohexyl-urea
U7	1,3-Bis(3,5-bis(trifluoromethyl)phenyl)-urea
Y	Discrete single-site yttrium complex
Y1a	Tetradentate amino-bisphenolate yttrium alkyl complex
Y1i	Bisphenolate yttrium amido complex with ∗–CMePh$_2$ substituents
Y1j	Bisphenolate yttrium amido complex with trityl substituents
Y2	Bisphenolate yttrium amido complex
Yb(OTf)$_3$	Ytterbium(III) trifluoromethanesulfonate
YCl$_3$	Yttrium(III) chloride
Y–O^{i}Pr	Obtained by the stoichiometric reaction of either Y1a or Y2 with 2-propanol
Zn1	2,6-Diisopropylphenylsubstituted *β*-diiminate zinc isopropoxide complex (or (BDI)ZnO^{i}Pr)
ZnCl$_2$	Zinc chloride
ZnEt$_2$-H$_2$O	Diethylzinc associated with water
ZnI$_2$	Zinc iodide

1. Introduction

Aliphatic (co)polyesters with biodegradability and biocompatibility, due to their widespread applications, have been the subject of increasing interest [1-3]. There are two pathways to produce such polymers. First, the polycondensation of diols with diacids or diesters or of hydroxyesters or hydroxyacids. This usually needs high energy-consumption and is also not atom-efficient as side-products are released (water, alcohols, *etc.*). Second, ring-opening polymerization (ROP) of the corresponding cyclic esters provides an interesting alternative. The latter was demonstrated to be a powerful strategy to synthesize (co)polyesters containing different macromolecular architectures in a controlled/living manner [4-7]. Among the manifold lactones used, the five-membered *γ*-butyrolactone (*γ*BL) is a renewable monomer derived from succinic acid, which was ranked as a top biomass-derived compound [8, 9]. The ROP of *γ*BL offers a feasible method to produce poly(*γ*-butyrolactone) (P*γ*BL), a structural equivalent of poly(4-hydroxybutyrate) (P4HB), which can be obtained from a bacterial fermentation process [10].

Different from the commonly employed lactones with high ring strain, *γ*BL was traditionally regarded as "non-polymerizable", resulting from the low strain energy of five-membered ring, so that the negative change of enthalpy (ΔH_p) on ring-opening is too small to overcome a large negative entropic change (ΔS_p) in a ROP [11-15]. Thus, the ceiling temperature and concentration of each γ-lactone should be considered to obtain a thermodynamically-favored polymerization. Tracing back to the 1930s–1950s, the first attempts to polymerize *γ*BL were unsuccessful [16, 17]. Later (1960s), only oligomers of PγBL were synthesized under extreme reaction conditions (*e.g.*, 20,000 atm, 160 °C) [18]. Therefore, synthesis of PγBL with high molar mass under mild conditions remained a challenge in polymer synthesis for several decades. In comparison, the ROP of γBL derivatives such as α-methylene-γ-butyrolactones (or tulipalin A, αMBL), α-angelica lactone (αAL) and β-angelica lactone (βAL) affords the formation of unsaturated polyesters, which could undergo post-functionalization [19]. However, the investigation of such process was limited due to the presence of additional functional groups (*i.e.*, endocyclic or exocyclic C=C) that may also be polymerized by vinyl-addition route [20]. Ring-opening copolymerization (ROCP) of γ-lactones or its derivatives with other cyclic monomers provides a bypass to circumvent the difficulties in their homopolymerization. The comonomers may be lactones, cyclic carbonates, and epoxides as well as some polymers. Examples of successful applications of this process will be discussed in this review.

Noticeably, a breakthrough was made in the ROP of γBL in recent years. The polymerization was carried out at low temperatures (below the ceiling temperature, T_c) and high monomer concentrations, yielding linear/cyclic PγBLs with high molar masses [21-26]. The recent development of powerful catalytic/initiating systems also allowed the ROP of γBL derivatives as well as their copolymerization. The thermal or chemical depolymerization of some resultant polyesters back to the corresponding monomer was also achieved, which not only highlights the advantage of these materials, but also satisfies the rising demand of sustainable/recyclable polymers [27-36].

Up until now, several reviews were published focusing on the ROP of γBL or its derivatives [10, 37-40]. In this review, we intend to summarize and comment on the previous and recent studies on ROP/ROCP of γBL and derivatives by different polymerization mechanisms including cationic, anionic, coordination-insertion mechanisms and related ones. The various catalytic systems described in the literatures will be presented, and the recent progresses will be emphasized. Noticeably, only the polymerization of γBL and derivatives via ring-opening is involved here, and other polymerization methods such as group-transfer polymerization (GTP), ring-opening olefin metathesis polymerization (ROMP), radical polymerization, vinyl-addition polymerization (VAP) or frustrated Lewis pair polymerization (FLP) through the C=C of γBL derivatives are not discussed [41-43]. In addition, only the derivatives containing γBL ring will be discussed. Other five-membered lactone derivatives such as γ-thiobutyrolactone [44, 45], γ-thionobutyrolactone [46], and γ-selenobutyrolactone [47, 48] are also excluded herein because of their different polymerizability, due to the variant hetero atoms contained in the ring.

2. General aspects of ROP of γ-lactones

2.1 γ-lactones and comonomers

Figure 1 lists γBL and representative derivatives that were studied for ROP/ROCP (except for the blue ones which are still unsuccessful in this chemistry). Functional γBL derivatives such as αMBL, αAL and βAL can be produced from renewable resources. For instance, αMBL can be isolated from the tulips, while αAL, βAL can be derived from levulinic acid [49]. The ROP/ROCP of these exocyclic/endocyclic C=C contained *γ*BL derivatives can afford the formation of unsaturated (co)polyesters. On the other hand, the polymerizability of *γ*BL could be highly improved by the presence of proper substitutes at suitable positions. Therefore, the polymerization of spirocyclic (*γ*-butyrolactone) or cyclohexyl-ring-fused *γ*BL was achieved under mild conditions.

In addition, copolymerization of *γ*BL or its derivatives with other cyclic monomers enriches the diversity of obtained polymer structures. Figure 2 lists the comonomers used in copolymerization with *γ*BL/its derivatives.

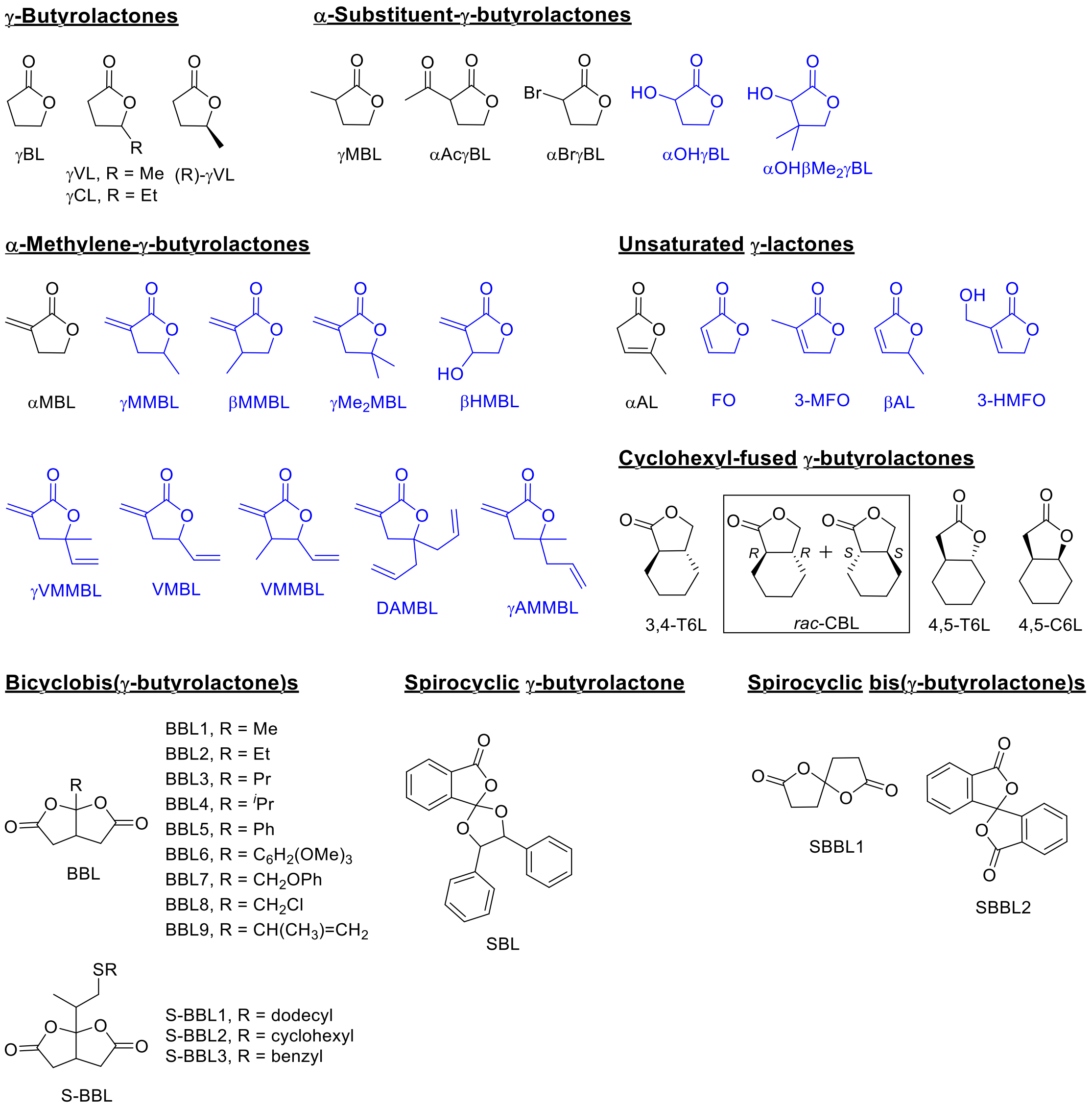


Fig. 1. γ-lactones (those in blue were not polymerized in ring-opening pathway).

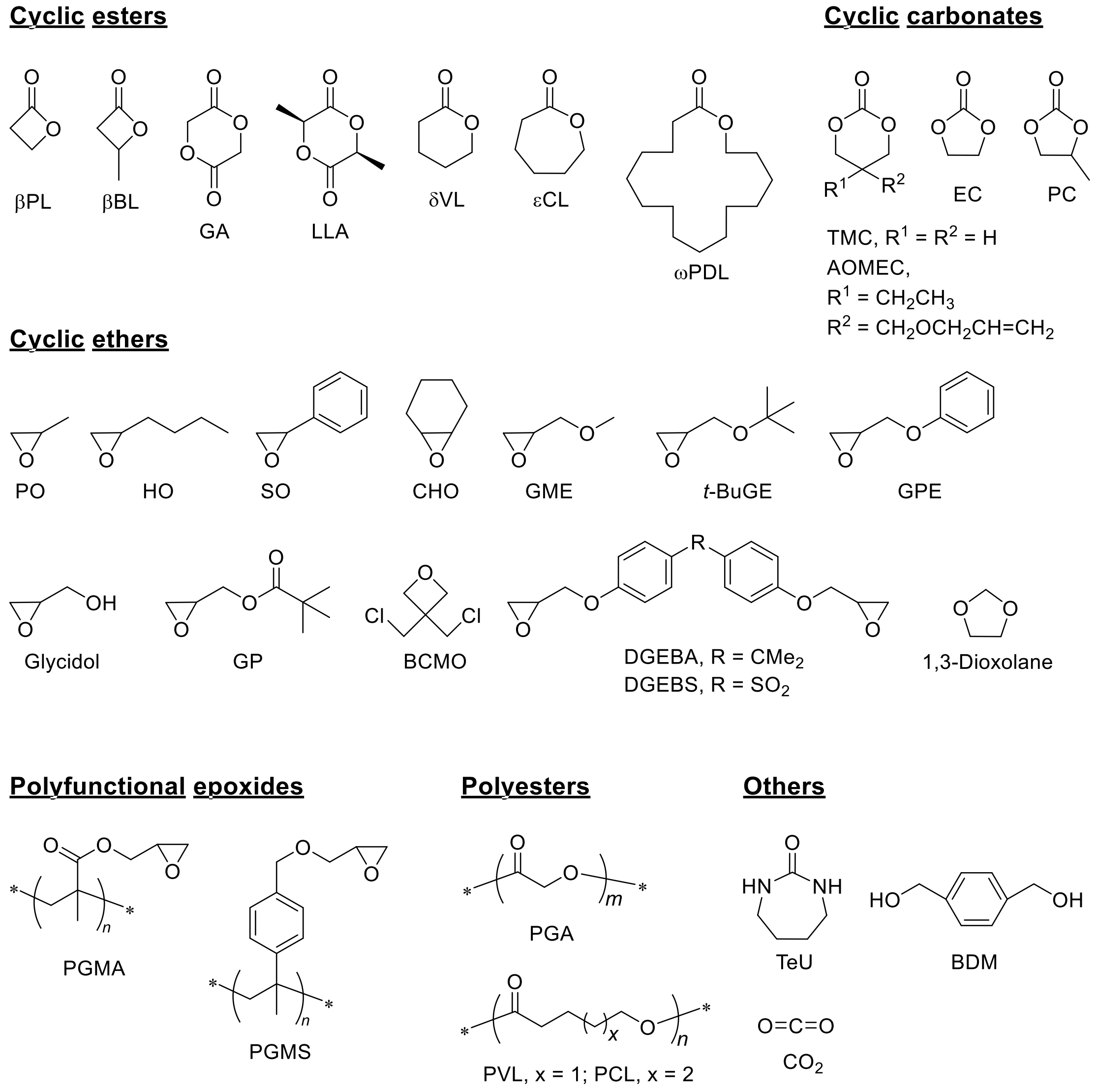


Fig. 2. Representative comonomers used in copolymerization with γ-lactones.

2.2 Catalytic systems

A variety of Lewis/Brønsted acids, metal-based complexes, and organic compounds were employed as catalysts/initiators for ROP/ROCP of γBL and derivatives. These catalytic systems induce mainly ionic and coordination-insertion mechanisms. Bicomponent catalytic systems, which usually consist of an acid (or hydrogen-bond donator) and a basic component (hydrogen-bond acceptor), were also employed. Figure 3 shows the representative catalysts/initiators which were used for the ROP/ROCP of γ-lactones. The chemistries discussed in detail in the following.

1. Acids

Lewis Acids

$AlEt_3$

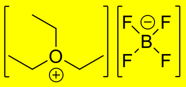
$ZnEt_2$

$ZnCl_2$

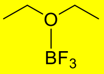
$AlCl_3$

$FeCl_3$

$SnCl_4$



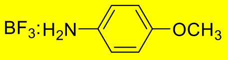
$Et_3O(BF_4)$



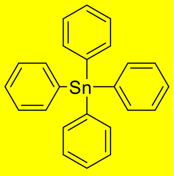
$BF_3•Et_2O$

$BF_3•EtNH_2$

$HBF_4•Et_2O$

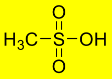


$BF_3•4MA$

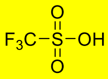


Ph_4Sn

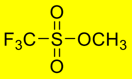
Brønsted Acids



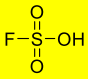
MSA



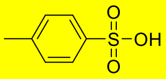
TfOH



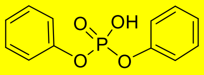
TfOMe



FSO_3H



p-TsOH



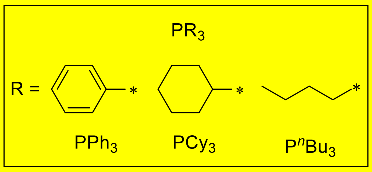
DPP

H_3PO_4

$HCl•Et_2O$

2. Bases

Organic bases



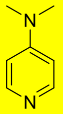
PR_3

R =

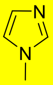
PPh_3

PCy_3

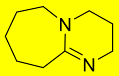
$\mathrm{P}^n\mathrm{Bu}_3$



DMAP



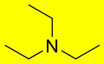
1-MI



DBU

TBD

DABCO



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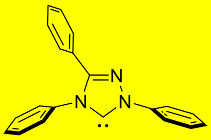

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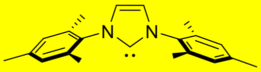

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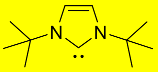
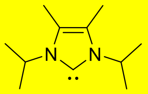
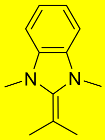


$\mathrm{I}^t\mathrm{Bu}$



$\mathrm{I}^i\mathrm{Pr}$



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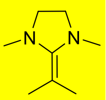

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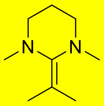

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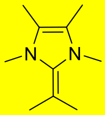

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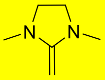
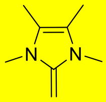


NHO5

NHO6



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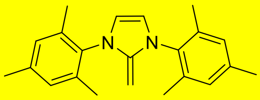

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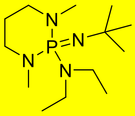
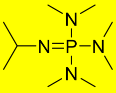
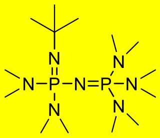


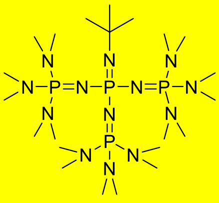
BEMP



t-BuP_1



t-BuP_2



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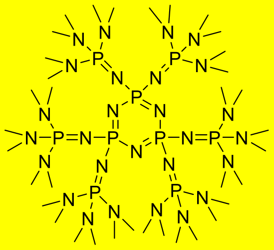


CTPB

Alkali metal compounds

NaH

KH

MeLi

n-BuLi

NaOH

KOH

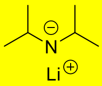
i-PrONa

n-PrONa

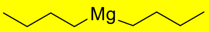
n-BuONa

t-BuOK

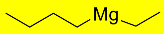
K_2CO_3



LDA

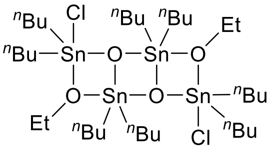


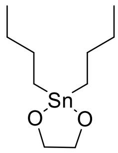
n-Bu_2Mg

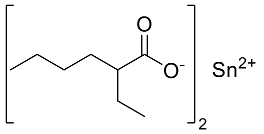


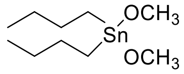
n-BuEtMg

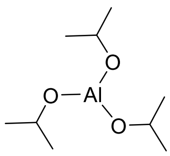
3. Organometallic compounds

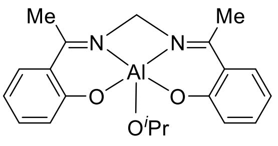

1-Ethoxy-3-chlorotetrabutyldistannoxane

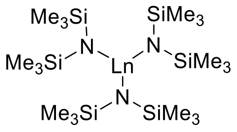

Cyclic tin alkoxide

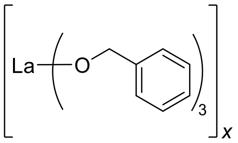

$Sn(Oct)_2$

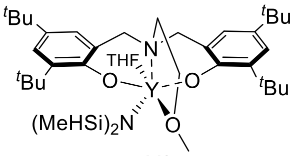

n-$Bu_2Sn(OMe)_2$

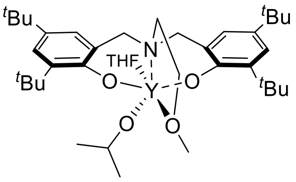

$Al(O^iPr)_3$

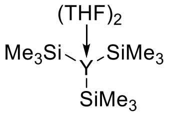

$HAPENAlO^iPr$


$Ln[N(SiMe_3)_2]_3$
Ln = La, Y, Sm

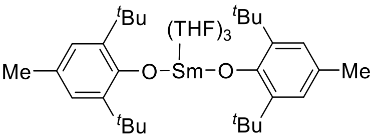

$[La(OBn)_3]_x$

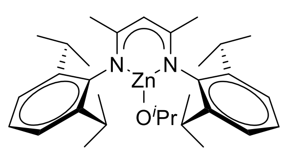

Y2

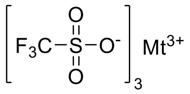

Y-O^iPr


Y-$(CH_2SiMe_3)_3(THF)_2$

SmI_2/Sm

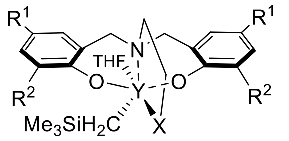

$Sm(OAr)_2(THF)_3$


Zn1

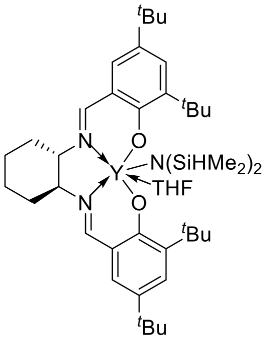

$[F_3C{-}SO_2{-}O^-]_3\,Mt^{3+}$

$Bi(OTf)_3$ $Sc(OTf)_3$

$La(OTf)_3$ $Yb(OTf)_3$



	X = OMe	X = NMe_2	X = NEt_2
$R^1 = R^2 = {}^tBu$	Y1a	Y1b	Y1k
$R^1 = R^2 = Me$	Y1c	—	—
$R^1 = R^2 = Cl$	Y1d	Y1e	—
$R^1 = R^2 =$ -Cumyl	Y1f	Y1g	Y1h
$R^1 = Me$, $R^2 = -CMePh_2$	—	Y1i	—
$R^1 = Me$, $R^2 = -CPh_3$	—	Y1j	—


Y3

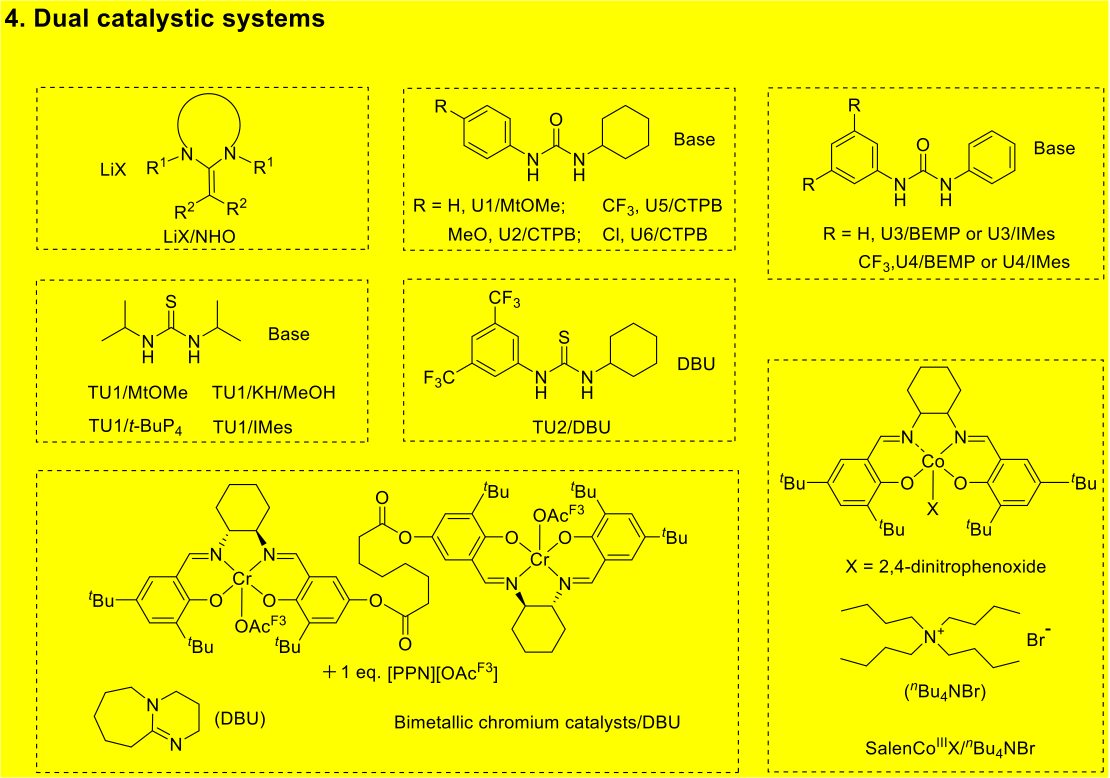


Fig. 3. Representative catalysts/initiators for ROP/ROCP of *γ*-lactones.

3. Lewis acid-catalyzed ROP/ROCP of *γ*-lactones

First attempts to polymerize *γ*BL by ROP started in the thirties, however, without success. Large sample volumes, high temperature, high pressure, using $ZnCl_2$ or $Et_3O(BF_4)$ yielded no polymer or oligomer [16, 18, 50]. The ROP of *α*AL, *β*AL, *α*OH*γ*BL and *α*Ac*γ*BL were also studied with very limited success, despite the use of Lewis acids based on Sn, B or Al [51-57].

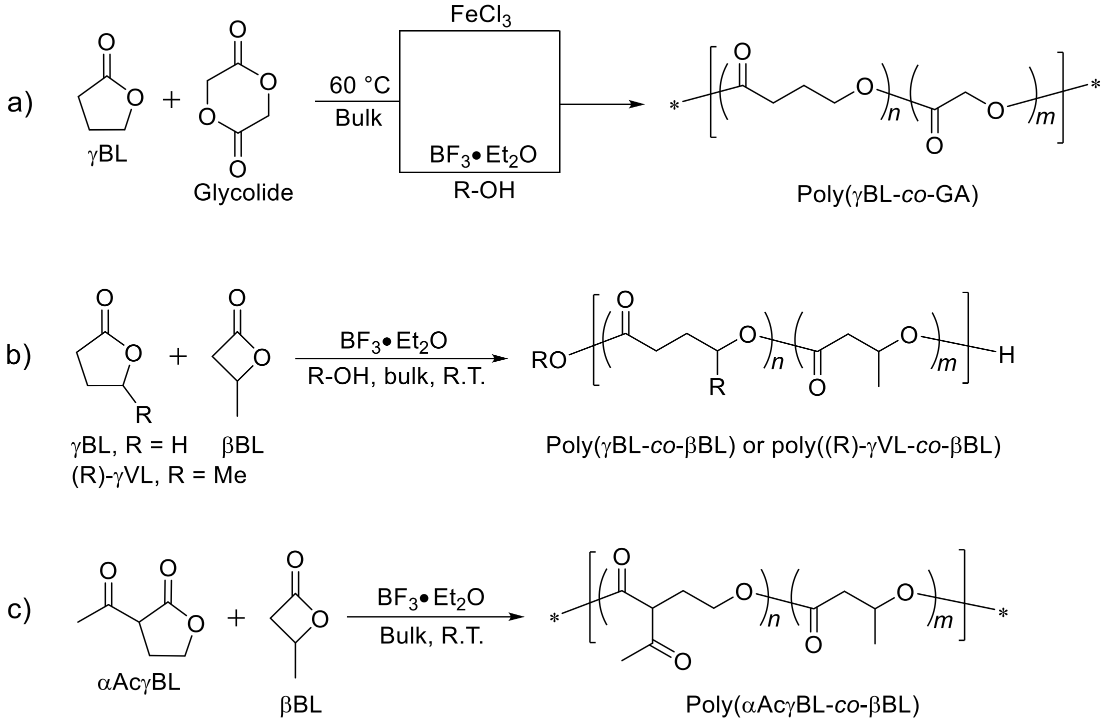
Considering those difficulties, copolymerization of *γ*BL with other cyclic monomers (*e.g.*, lactones, epoxides) provides an alternative and is the route to follow with Lewis acids. For instance, $AlEt_3/H_2O$ was shown to copolymerize *γ*BL with *β*-propiolactone (*β*PL) [58]. The polymerization was performed at 0 °C in dichloromethane (DCM) for 3 days, which yielded copolymers with up to 29% incorporation of γBL. The reactivity ratios were determined to be $r_{\gamma\mathrm{BL}} = 0.36$ and $r_{\beta\mathrm{PL}} = 18$, revealing the low copolymerizability of γBL. Those conditions and results revealed the tricky character of this monomer.

Following that study, copolymerization of γBL and 3,3-bis(chloromethyl)oxetane (BCMO) was investigated in toluene at RT with tin(IV) chloride ($SnCl_4$) and trifluoride diethyl etherate (BF_3•Et_2O) [59]. Alternating copolymers were produced in low yields. The γBL was believed to be coordinated to the Lewis acids, which contributed to its enhanced activity and led to the copolymerization in an alternating way. Glycidyl phenyl ether (GPE) was also used as a comonomer with BF_3-based systems, yielding spiroorthoesters and oligomers with low γBL content [60, 61].

In the 1980s, several Lewis acids such as iron(III) chloride ($FeCl_3$), aluminium (III) chloride ($AlCl_3$) and BF_3•Et_2O were utilized for the random copolymerization of γBL and glycolide at 60 °C in bulk (Scheme 1a) [62]. $FeCl_3$ showed the best performances, providing copolymers with the highest γBL incorporation (25%) at a feed ratio of [γBL]/[glycolide] = 4/1. In addition, BF_3•Et_2O was employed for this copolymerization under the same conditions with an alcohol (*e.g.*, benzyl alcohol, BnOH) as the initiator (Scheme 1a) [63]. The presence of alcohols improved both the polymer yield and γBL incorporation (up to 34%). Random poly(γBL-*co*-GA)s with $\overline{M_n}$ in the range 5.4–7.3 kg.mol^{-1} and relative low dispersity ($Đ = 1.17–1.30$) were obtained, exhibiting slightly lower degradation temperatures (T_d = 241 °C) than poly(glycolic acid).

ROCP of γBL or (R)-γ-valerolactone ((R)-γVL) with β-butyrolactone (βBL) was performed in bulk at RT for 7 days (Scheme 1b). $AlEt_3$ and $ZnEt_2$ were able to homopolymerize βBL, whereas BF_3•Et_2O was able to trigger the copolymerization to yield poly(γBL-*co*-βBL)s ($\overline{M_n}$ = 1.8–4.4 kg.mol^{-1}, $Đ$ = 1.3–1.8), which were identical to poly(hydroxy alkanoate)s produced by microorganisms [64, 65]. The γBL incorporation in the copolymer was enhanced with the increased feed ratio of [γBL]/[βBL], to reach 56% at a molar ratio of 90/10. It was inferred that the polymerization was initiated by residual water contained in the reaction medium through the attack of BF_3-activated monomer. This suggested the possibility of using alcohols as initiators, and such dihydroxy-telechelic copolymers were prepared as an example.

The copolymerization of αAcγBL and βBL was also performed using BF_3•Et_2O in bulk at RT for 4 weeks (Scheme 1c) [55]. Yields up to 78% were observed with 9–74% of αAcγBL in the copolymer as feed ratios of [αAcγBL]/[βBL] were varied from 20/80 to 80/20 ($\overline{M_n}$ = 1.6–2.0 kg.mol^{-1}, $Đ$ = 1.2–1.4). Pendant ketone functions were confirmed, opening a way to obtain hydroxyl ones for further functionalization.



Scheme 1. Examples of Lewis acid-catalyzed ROCP of *γ*-lactones with cyclic esters: (a) *γ*BL/glycolide [62, 63], (b) *γ*BL/(R)-*γ*VL and *β*BL [64, 65], (c) *α*Ac*γ*BL and *β*BL [55].

The copolymerization of *γ*BL and L-lactide (LLA) was achieved in bulk at 120 °C for 4 days using tetraphenyl tin (Ph_4Sn) [66]. Statistical copolyesters poly(*γ*BL-*co*-LLA) were obtained with molar mass as high as 70 kg.mol^{-1} (*Đ* = 1.3). The maximum *γ*BL incorporation obtained was *ca.* 17%. The use of *γ*BL derivatives bearing an alkyl substitute in the *γ*-position (*i.e.*, *γ*-valerolactone (*γ*VL), *γ*-caprolactone (*γ*CL)) only produced copolymers with low *γ*VL or *γ*CL incorporation (2%). The proposed copolymerization mechanism was based on the transesterification between the fast-produced PLLA and *γ*BL. This assumption was supported by the incorporation of *γ*BL units into PLLA, starting from PLLA in the presence of *γ*BL under similar conditions

($\overline{M_n}$ = 10.1 kg.mol^{-1}, $Đ$ = 1.5). The degradability of the resulting poly(γBL-*co*-LLA) was confirmed in H_2O (70 °C, 5 days) or in the presence of lipases from *Rhizopus arrhizus* and *R. delemar* (37 °C, 24 h), which both showed enhanced degradability with the increase of γBL content in the copolymer.

The Ph_4Sn catalyst was further used for the ROCP of γBL with other cyclic esters such as βPL, ε-caprolactone (εCL), δ-valerolactone (δVL) and glycolide [67]. Random copolymers were prepared with various γBL content (3–16% for poly(γBL-*co*-εCL) with $\overline{M_n}$ = 29.5–145 kg.mol^{-1} ; 3–15% for poly(γBL-*co*-δVL) with $\overline{M_n}$ = 18.6–52.2 kg.mol^{-1}). However, only low-molar-mass copolymers with slightly higher γBL content (4–23%, $\overline{M_n}$ = 1.3–2.2 kg.mol^{-1}) were produced during the copolymerization of γBL with βPL. The copolymerization of γBL and glycolide generated a mixture of insoluble parts which were glycolide-rich copolymers and soluble parts which were poly(γBL-*co*-glycolide) containing 3–26% of γBL content. The degradation of the obtained copolymers was investigated in water at 70 °C. The degradation rate of poly(γBL-*co*-glycolide) was higher than that of the others, whereas the reverse was observed in the presence of lipases (37 °C).

In summary, the use of Lewis acids as catalysts for the homopolymerization of γ-lactones has been shown to be inefficient. Copolymerization with other cyclic monomers using boron derivatives appears to be a way to produce biodegradable materials with enhanced degradability. In general, molar masses and γ-BL incorporation remain low for long polymerization times.

4. Brønsted acid-catalyzed ROP/ROCP of γ-lactones

Brønsted acids such as methanesulfonic acid (MSA), diphenyl phosphate (DPP) and trifluoromethanesulfonic acid (TfOH) were utilized for ROP/ROCP of lactones and/or cyclic carbonates through activated monomer mechanism (AMM) pathway following a cationic mechanism [4, 5, 7, 68-70]. Well-defined polymers (*i.e.*, controlled molar mass, narrow distribution, and targeted macromolecular architecture) could be obtained under mild conditions. Such Brønsted acids were employed for the ROP/ROCP of γBL or its functional derivatives as well.

High pressure (800–1000 MPa) was shown to achieve the ROP of γBL in bulk at 40 °C, initiated by methanol with TfOH as an example [71]. The $\overline{M_n}$ of the resulting PγBLs were in the range 6.4–7.9 kg.mol^{-1} with relatively high dispersities ($Đ$ = 1.49–1.57). It was proposed that the polymerization proceeded by the AMM pathway, which was based on the coordination of lactones to the acids to afford the activated cationic complex, followed by the attack of an initiator.

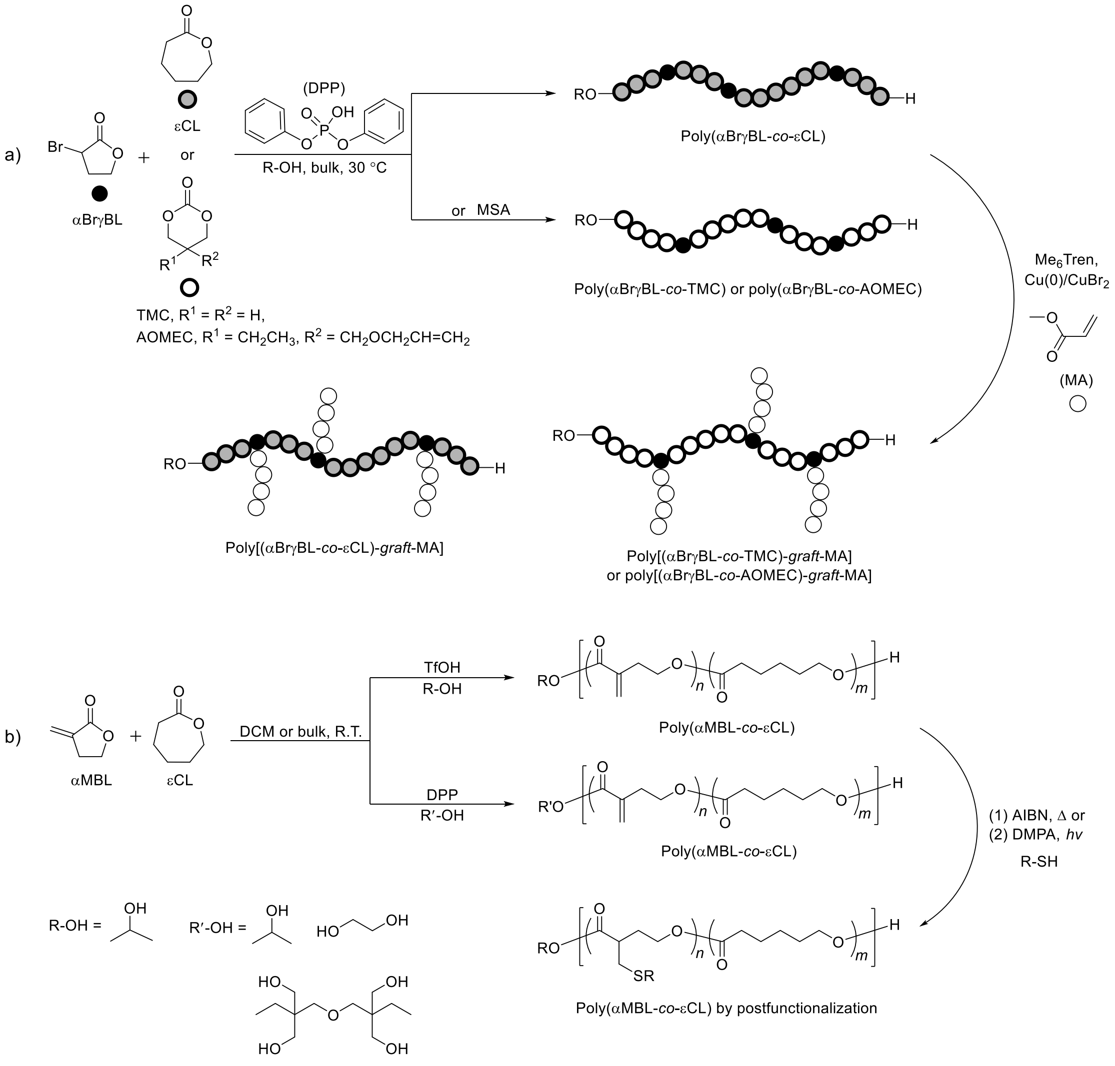
There is a possibility to polymerize γBL above its ceiling temperature. The polymer stability should be then studied for any polymers obtained.

TfOH or DPP was also used for the polymerization of a γBL derivative, *trans*-hexahydro-2(3*H*)-benzofuranone [*i.e.*, 4,5-*trans* cyclohexyl-ring-fused γBL (4,5-T6L)]. Only oligomers were produced with a maximum value of 20% of monomer conversion [72, 73]. The polymerization of αOHγBL was carried out at 90 °C using TfOH, producing oligomers with dehydration [56].

The more open copolymerization strategy was also developed with Brønsted acids. Fluorosulfonic acid (FSO_3H), TfOMe and TfOH were quite helpful to copolymerize *γ*BL (or (R)-*γ*VL) with different comonomers such as glycolide, 3,4-*trans* cyclohexyl-ring-fused *γ*BL (3,4-T6L) or *β*BL, allowing up to 30% of *γ*BL incorporation into low molar mass copolyester chains [62-65, 73]. Phosphoric acid (H_3PO_4) could also achieve the copolymerization of *γ*BL, *γ*VL or *γ*CL with *ε*CL in bulk at 200 °C [74]. Interestingly, semi-crystalline copolymers were synthesized ($\overline{M_n}$ = 17.8–41.2 kg.mol^{-1}) with melting temperature (T_m) ranging from 48 °C to 56 °C. The resulting products showed different degradation rates in acidic medium, *i.e.*, poly(*γ*BL-*co*-*ε*CL) > poly(*γ*VL-*co*-*ε*CL) > poly(*γ*CL-*co*-*ε*CL), which may be due to the varying hydrophobicity of the copolymers bearing side chains of different lengths. Either DPP or hydrochloric acid in diethyl ether (HCl•Et_2O) were used in bulk or solution, yielding poly(*γ*BL-*co*-*ε*CL) with limited *γ*BL incorporation [75].

α-Bromo-*γ*-butyrolactone (*α*Br*γ*BL), a commercial functional *γ*BL derivative, was copolymerized with other heterocyclic monomers including *ε*CL, trimethylene carbonate (TMC), and 2-allyloxymethyl-2-ethyltrimethylene carbonate (AOMEC) [76, 77]. The ROCP proceeded in bulk at RT with DPP or MSA (Scheme 2a) [77]. Copolymers with 4–12% of *α*Br*γ*BL were obtained ($\overline{M_n}$ = 17.0–31.2 kg.mol^{-1}, $Đ$ = 1.08–1.12). Separated *α*Br*γ*BL units along the copolymer backbone were confirmed by ^{13}C NMR analysis (*i.e.*, no homosequence of *α*Br*γ*BL). The narrow distribution may originate from the mild reaction temperature and the intrinsic merits of organic acids, which greatly suppressed the transesterification reactions. Therefore, a triblock copolymer, poly[(αBrγBL-*co*-εCL)-*b*-AOMEC-*b*-(αBrγBL-*co*-εCL)] ($\overline{M_n}$ = 40.8 kg.mol^{-1}, $Đ$ = 1.12) was synthesized in one-pot two-steps procedure, through the DPP-catalyzed sequential ROP of AOMEC and εCL/αBrγBL with 1,6-hexanediol as the initiator. The selective incorporation of separated αBrγBL site into the αBrγBL/εCL block was again demonstrated. Both poly(TMC-*co*-αBrγBL) and triblock copolymer were used as macroinitiators for single electron transfer living radical polymerization (SET-LRP) of methyl acrylates, the dispersed αBrγBL site along the polymer chain being the initiating sites. The "graft from" polymerization proceeded with good control and nearly complete initiation, resulting in well-defined poly(methyl acrylate) grafted-copolymers with degradable polymers based on αBrγBL and εCL [76]. In the same vein, amphiphilic triblock copolymers were synthesized starting from HO-PEG-OH.

Functional copolymers of αMBL and εCL were synthesized in DCM or bulk at RT using TfOH or DPP as a catalyst (Scheme 2b) [78]. Poly(αMBL-*co*-εCL)s with 4–11% αMBL incorporation ($\overline{M_n}$ = 3.3–17.9 kg.mol^{-1}) were obtained by TfOH-catalyzed copolymerization in DCM ([αMBL]/[εCL] < 1), while P(αMBL)$_{\text{VAP}}$ *via* vinyl-addition polymerization of αMBL or cross-linked polymers P(αMBL)$_{\text{CLP}}$ were observed in other cases (*e.g.* bulk, [αMBL]/[εCL] > 1). The desired linear structure of copolyesters containing unsaturated pendant side groups with ^{i}PrO/H chain ends was confirmed by ^{1}H NMR and MALDI-TOF MS analyses. A random distribution of the two monomers was expected by the authors. However, the less reactive DPP allowed a better control of the copolymerization, resulting in the formation of copolymers with 4–11% αMBL content ($\overline{M_n}$ = 2.9–7.9 kg.mol^{-1}). Due to the lower acidity of DPP, the copolymerization proceeded in bulk without the appearance of P(*α*MBL)$_{\text{VAP}}$. The copolymers obtained showed a reduced T_m due to the presence of non-crystallizable *α*MBL component and high thermal stability. The post-polymerization of unsaturated copolyesters poly(*α*MBL-*co*-*ε*CL) was verified by thiol-ene chemistry under thermal initiation (2,2′-azobis(2-methylpropionitrile), AIBN) or photoinitiation (2,2-dimethoxy-2-phenylacetophenone, DMPA). In addition, multihydroxyl copolymers with similar *α*MBL content (4–8%) were synthesized in bulk by employing multifunctional alcohols such as 1,2-ethanediol or di(trimethylolpropane) as the initiator.



Scheme 2. Brønsted acid-catalyzed ROCP of *γ*-lactones with cyclic ester/carbonate: (a)

*α*Br*γ*BL and *ε*CL, TMC, AOMEC [77], (b) *α*MBL and *ε*CL [78].

Again, the copolymerization strategy is preferred to ring-open *γ*-lactones by Brønsted acids and take benefit of specific molecular structures. Indeed, TfOH or DPP are the most efficient acids to synthesize (co)polyesters bearing reactive functions introduced by the *γ*-lactones. Adjusting the acidity of the catalyst seems to be key to minimizing side reactions. Nevertheless, molar masses and γ-lactones incorporation are still limited, and a controlled copolymerization cannot be achieved by this route.

5. Organic base-catalyzed ROP/ROCP of *γ*-lactones

Organocatalytic polymerization following a nucleophilic/anionic mechanism is a powerful pathway for the synthesis of metal-free polymers with different macromolecular architectures. Since the first report of nucleophilic organocatalyzed ROP of lactide [79] or cyclic monomers [80], several reviews focusing on this subject have been published [4, 7, 69, 81-88], including on initiating/catalytic systems for the polymerization of γBL and derivatives.

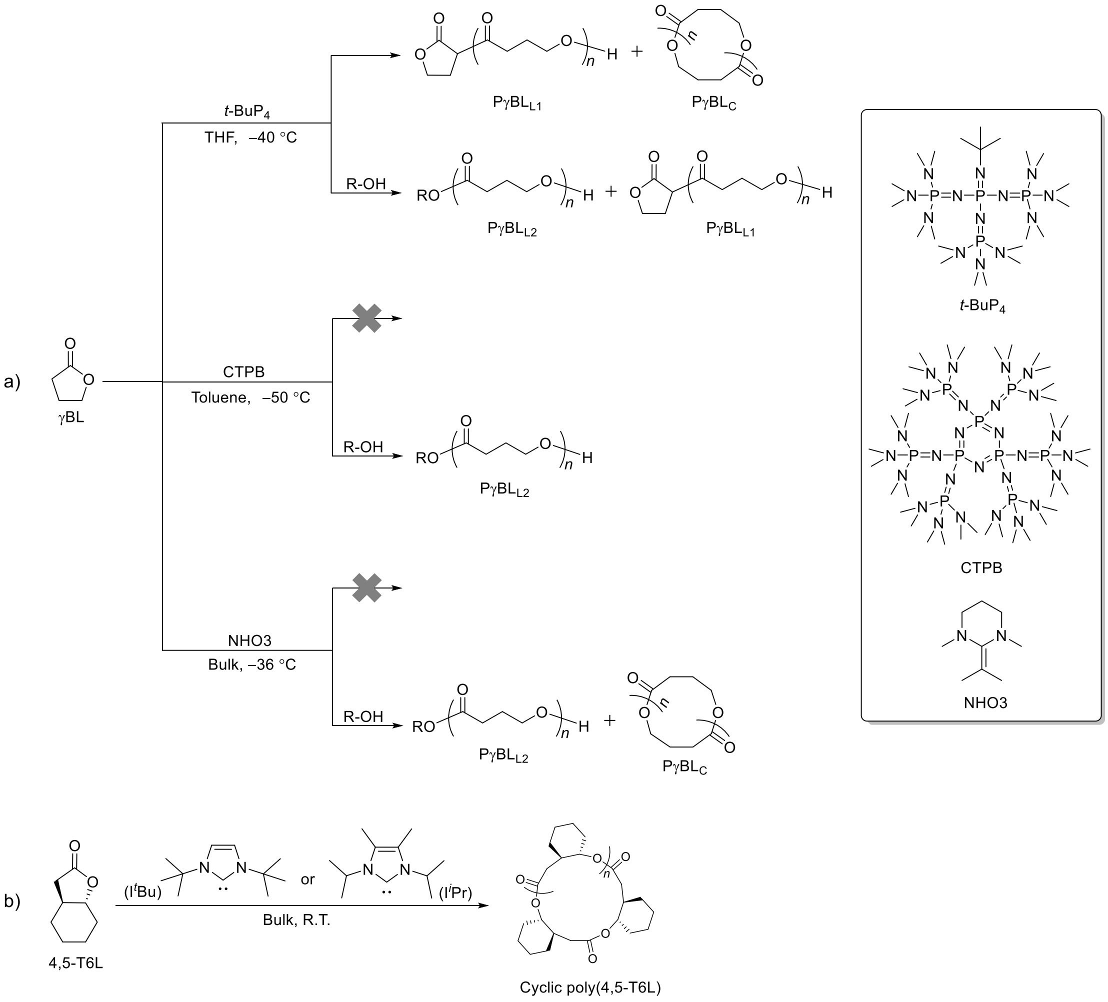
Different organic bases such as NHCs (*e.g.* IMes), guanidines (*e.g.* TBD), and phosphazene bases including *t*-BuP$_2$ and *t*-BuP$_4$ were used for the ROP of *γ*BL. The superbase *t*-BuP$_4$ was revealed to be the most efficient catalyst (Scheme 3a) [21, 22]. The polymerization was carried out in tetrahydrofuran (THF) at a high monomer concentration ($[\gamma BL]_0$ = 10 M) and a low reaction temperature (-40 °C) below T_c, which is 22 °C for *γ*BL in bulk [15]. Two different polymerization mechanisms were proposed, depending on the presence of an alcohol as the initiator or not. In absence of an alcohol, γBL can be directly deprotonated by the superbase to produce a reactive enolate species.This results in a mixture of linear PγBL with acylated lactone/H chain ends (PγBL$_{L1}$) and cyclic PγBL (PγBL$_C$), the latter was believed to be achieved by a back-biting reaction of the polymer chain ($\overline{M_n}$ = 9.2–26.4 kg.mol^{-1}, $Đ$ = 1.16–1.79). The addition of an alcohol (*e.g.*, benzyl alcohol, BnOH; [*t*-BuP$_4$]/[BnOH] = 1/0.5–1/1.5) was a more rapid and efficient pathway for the formation of relatively high molar mass polymers in high conversion (up to 90% in 4 h, $\overline{M_n}$ up to 27.1 kg.mol^{-1}, $Đ$ = 2.11). In this case, a mixture of PγBL$_{L1}$ and linear PγBL with BnO/H chain ends (PγBL$_{L2}$) was obtained. It was considered that the presence of alcohols led to more stabilized propagating alkoxide chain ends ([BnO$^-$/*t*-BuP$_4$H$^+$]), which also accounted for the more controlled polymerization behaviour. The absence of PγBL$_C$ under this condition was not explained. Moreover, the weaker phosphazene base *t*-BuP$_2$ showed lower activity under the same conditions, whereas the weakest *t*-BuP$_1$ was inactive.

The ROP of γBL was also performed in the presence of a cyclic trimeric phosphazene base (CTPB) as the catalyst [23]. The polymerization was conducted in toluene at -50 °C with a slightly lower monomer concentration ([γBL]$_0$ = 6 M) (Scheme 3a). Compared to the superbase *t*-BuP$_4$, CTPB was proved to be inactive in absence of an alcohol. The use of CTPB with BnOH as the initiator selectively afforded well-defined linear PγBL$_{L2}$ with a high monomer conversion (up to 98% in 4 h, $\overline{M_n}$ = 10.5–22.9 kg.mol^{-1}, $Đ$ = 1.27–1.72). The polymerization mechanism was similar to that proposed in *t*-BuP$_4$/BnOH catalytic system, *i.e.*, the loose ion pair [BnO$^-$/CTPBH$^+$]

could polymerize γBL. The relative lower basicity of CTPB (pK_a^{MeCN} = 33.3) compared to t-BuP$_4$ (pK_a^{MeCN} = 42.6) may account for the selective production of linear polymer with BnO/H chain ends (PγBL$_{L2}$) in this case.

Recently, *N*-heterocyclic olefins (NHOs) were utilized for the polymerization of γBL in bulk at -36 °C [24]. A mixture of linear and cyclic polyesters (PγBL$_{L2}$ + PγBL$_C$) ($\overline{M_n}$ = 3.3–7.2 kg.mol^{-1}, $Đ$ = 1.5–2.1) was obtained only when an initiator (BnOH) was initially added. The zwitterionic ROP of γBL with NHOs alone was completely supressed (Scheme 3a).

Organic bases were also used for the ROP of γBL derivatives such as αBrγBL and 4,5-T6L. DBU, TBD or t-BuP$_2$ were ineffective for the ROP of αBrγBL in bulk at RT, due to the elimination of the bromine atom under such conditions [77]. Several organic bases were also tested for the polymerization of 4,5-T6L performed in bulk with different temperatures [72, 73]. For instance, the attempts to utilize DBU or BEMP in presence of alcohols at RT were unsuccessful. Only 5% of monomer conversion was observed with t-BuP$_4$ after 24 h under such conditions, while IMes led to 20% monomer conversion after 96 h. TBD/BnOH could mediate well-controlled polymerization of 4,5-T6L ($\overline{M_n}$ = 9.1 kg.mol^{-1}, $Đ$ = 1.11). The monomer conversion was limited to 64% due to the polymerization-depolymerization equilibrium. However, cyclic P(4,5-T6L)s with $\overline{M_n}$ = 40.6–72.1 kg.mol^{-1} and $Đ$ = 1.21–1.30 were synthesized in bulk at RT in the presence of less sterically hindered NHCs alone (*e.g.* I^{t}Bu and I^{i}Pr) (Scheme 3b) [73]. DBU, Et$_3$N or DMAP were inactive for the ROP of 4,5-T6L in bulk at 40 °C [72].



Scheme 3. (a) ROP of γ-lactones by different organic bases: *t*-BuP$_4$ [22], CTPB [23] and NHO3 [24] (up to down, respectively), (b) ROP of 4,5-T6L by NHCs [73].

Recently, organic bases such as I^{t}Bu and I^{i}Pr, *t*-BuP$_4$ and DABCO were tested for the polymerization of βAL, 3-methylfuran-2(5*H*)-one (3-MFO), and their parent monomer 2(5*H*)-furanone (FO) [89]. Only vinyl-addition poly(2(5*H*)-furanone)s ($\overline{M_n}$ = 1.57–2.06 kg.mol^{-1}) and compounds with dimer or trimer structures (corresponding to βAL, 3-MFO, respectively) were obtained, no matter the catalyst and the reaction conditions (*e.g.*, solvent, temperature, initiator). Noteworthy, tri-functional monomers such as *β*-hydroxy-*α*-methylene-*γ*-butyrolactone (*β*HMBL or Tulipalin B) and 3-(hydroxymethyl) furan-2(5*H*)-one (3-HMFO) were also polymerized in solution using organocatalysts such as TPT, I^{t}Bu and *t*-BuP$_4$. The resultant products were considered as branched copolymers with various structures, originating from the multiple types of reactions and the relevant mechanistic crossovers [89, 90].

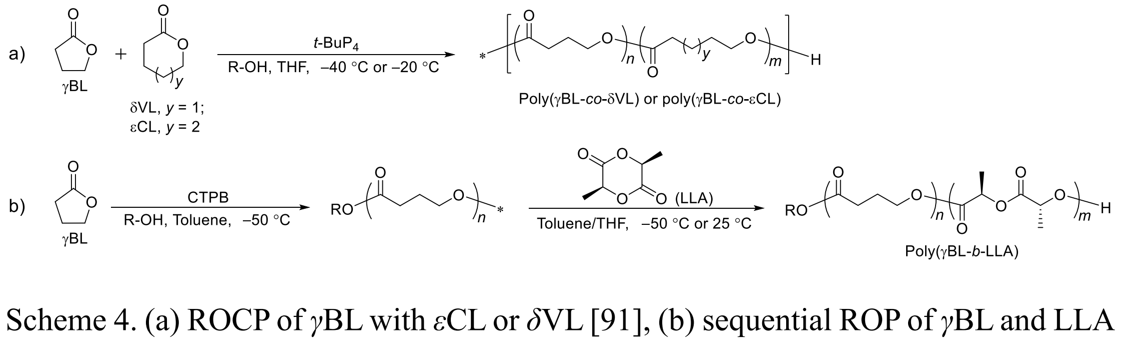
Eventually, some organic bases appear to be efficient catalysts for the homopolymerization of *γ*BL and derivatives using the ring-opening mechanism, preferably with an alcohol as the initiator. High monomer conversion can be reached in short time with phosphazene bases.

To go further with this approach, the ROCP of *γ*BL with *ε*CL or *δ*VL was studied in the presence of *t*-BuP$_4$/BnOH (1/1) (Scheme 4a) [91]. The copolymerization was carried out in THF at 25 °C or low reaction temperatures (-40 or -20 °C) with a relatively low molar ratio of [*γ*BL]/[*ε*CL] (3 or 4/1) or [*γ*BL]/[*δ*VL] (1, 3 or 10/1). The resultant random copolymers showed high *γ*BL incorporation, 42–80% for poly(*γ*BL-*co*-*ε*CL) ($\overline{M_n}$ = 5.2–26.0 kg.mol^{-1}, *Đ* = 1.35–1.91) and 19–75% for poly(*γ*BL-*co*-*δ*VL) ($\overline{M_n}$ = 5.3–20.7 kg.mol^{-1}, *Đ* = 1.49–1.88).

The use of a comonomer facilitates an increase of the polymerization temperature above the ceiling tempratufe.

The introduction of *γ*BL influenced the thermal properties and co-crystallization behaviour of the copolyesters. For example, poly(*γ*BL-*co*-*ε*CL)s showed unique eutectic phase behaviour, with an eutectic temperature of 11 °C at 66% *γ*BL incorporation. Such poly(*γ*BL-*co*-*ε*CL) copolyesters (with *γ*BL content up to 28%) were also produced with TBD as catalyst in bulk or solution [75]. With the same catalyst, using PEG-OH as a macroinitiator, amphiphilic diblock copolymers with random comonomer distribution of *γ*BL and *ε*CL in the polyester block were also synthesized.

Furthermore, diblock copolymers of *γ*BL and LLA were achieved using CTPB *via* one-pot two-steps sequential ROP of *γ*BL and LLA (Scheme 4b) [92]. The formation of poly(*γ*BL-*b*-LLA)s with high *γ*BL amount (up to 52%) was obtained ($\overline{M_n}$ = 6.5–20.5 kg.mol^{-1}, $Đ$ = 1.45–2.09). All block copolymers displayed two T_m, the lower temperature (*ca.* 56 °C) was attributed to the T_m of P*γ*BL block and the higher one (*ca.* 165 °C) was attributed to the T_m of PLLA block. The block copolymers also showed enhanced thermal stability compared to P*γ*BL ($T_d \geq 284$ °C *vs* 240 °C), which could be further improved with the increase of PLLA block length. Using *ε*CL or *δ*VL as the second monomer only led to the formation of random copolymers, which was also observed in the sequential ROP of *ω*PDL and LLA/*ε*CL/*δ*VL [93]. Amphiphilic block copolymers PEG-*b*-P*γ*BL could also be obtained starting from monohydroxy-terminated poly(ethylene glycol) (PEG-OH) and self-assemble to micelles and vesicles in water, indicating their potential for drug delivery carriers [94].



Scheme 4. (a) ROCP of *γ*BL with *ε*CL or *δ*VL [91], (b) sequential ROP of *γ*BL and LLA

[92].

Organic phosphines, including PPh_3, P^nBu_3 and PCy_3, were employed as initiator/catalysts in the zwitterionic copolymerization of bicyclic bis(γ-butyrolactone)s (BBLs) and glycidyl phenyl ether (GPE) performed in THF at 120 °C, generating polyesters with alternating sequence structures due to suppression of back-biting reactions. [95-97]. These monomer structures will be discussed further in section 6.

Looking at the possibility to prepare copolymers based on γ-lactones with mainly other lactones, lactides or epoxides, organic bases and in particular phosphazene bases are efficient systems permitting high molar masses and γ-BL incorporation under mild conditions. Properties of such copolymers only start to be investigated and will be developed in a near future, in particular, because of the possibility to introduce reactive functions via the γ-lactones.

6. Alkali metal compound-catalyzed ROP/ROCP of γ-lactones

The early investigation of ROP of γBL was conducted in bulk at 80 °C for 12 months in the absence/presence of potassium carbonate (K_2CO_3). No polymer was produced [16]. When the polymerization of γBL was performed with *t*-BuOK in bulk at 40 °C under high pressure (800 MPa), once again no PγBL was obtained[71]. However, the bulk ROP of γBL was shown to proceed at -40 °C with sodium or potassium methoxides (MtOMe) following an anionic mechanism to yield PγBLs ($\overline{M_n}$ = 9.2–14.0 kg.mol^{-1} and $Đ$ = 1.65–2.17) with low monomer conversion (≤ 25%) after 4

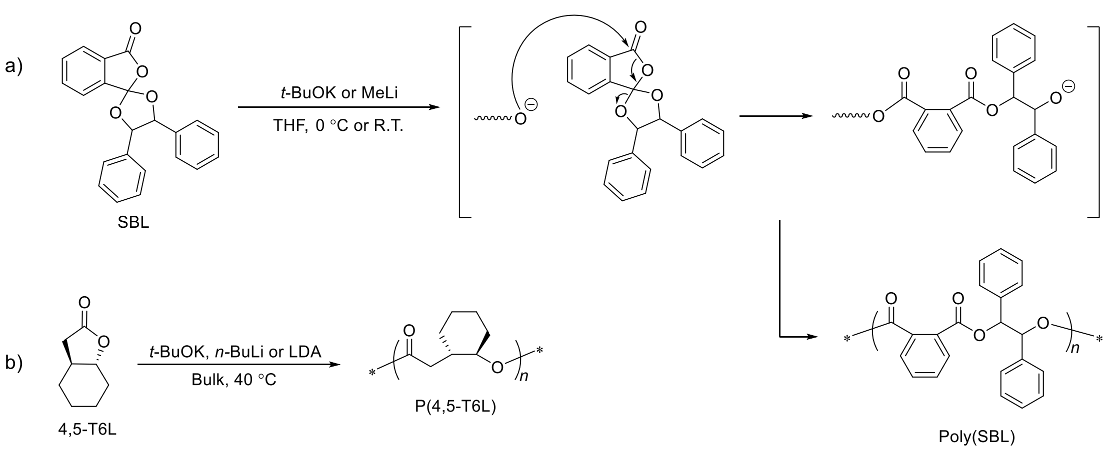
h. Block copolymers containing γBL were also synthesized. For example, with potassium methoxide (KOMe) or sodium hydride (NaH) in DCM/THF at -50 °C ($[\gamma\text{BL}]_0$ = 6 M), PEG-OH was used as a macroinitiator to yield amphiphilic block copolymers PEG-*b*-PγBL with $\overline{M_n}$ = 5.8–12.8 kg.mol^{-1} [94].

Sodium hydroxide (NaOH) or sodium n-butoxide (n-BuONa) were used for the ROP of αAL, and only oligomers were produced at RT, despite a T_c estimated at 152 °C [98-100].

When the five-membered lactone is fused to other cyclic substitutes, the ring strain of this compound changes and thus the monomer may become more polymerizable in some cases. Therefore, the polymerization of substituted γBL derivatives such as spirocyclic γ-butyrolactone (SBL), 4,5-T6L and its *cis* isomer (4,5-C6L) were investigated [72, 101].

The ROP of SBL was investigated with *t*-BuOK or methyllithium (MeLi) at RT in THF (Scheme 5a) [101]. Polyesters with moderate molar masses ($\overline{M_n}$ = 6.5–10.0 kg.mol^{-1}, $Đ$ = 1.13–1.59) were obtained, which may be due to the tandem double ring-opening reaction that involves an isomerization. The successful ROP of SBL also indicated that the increased ring strain of spirocyclic skeleton would reduce the degree of back-biting.

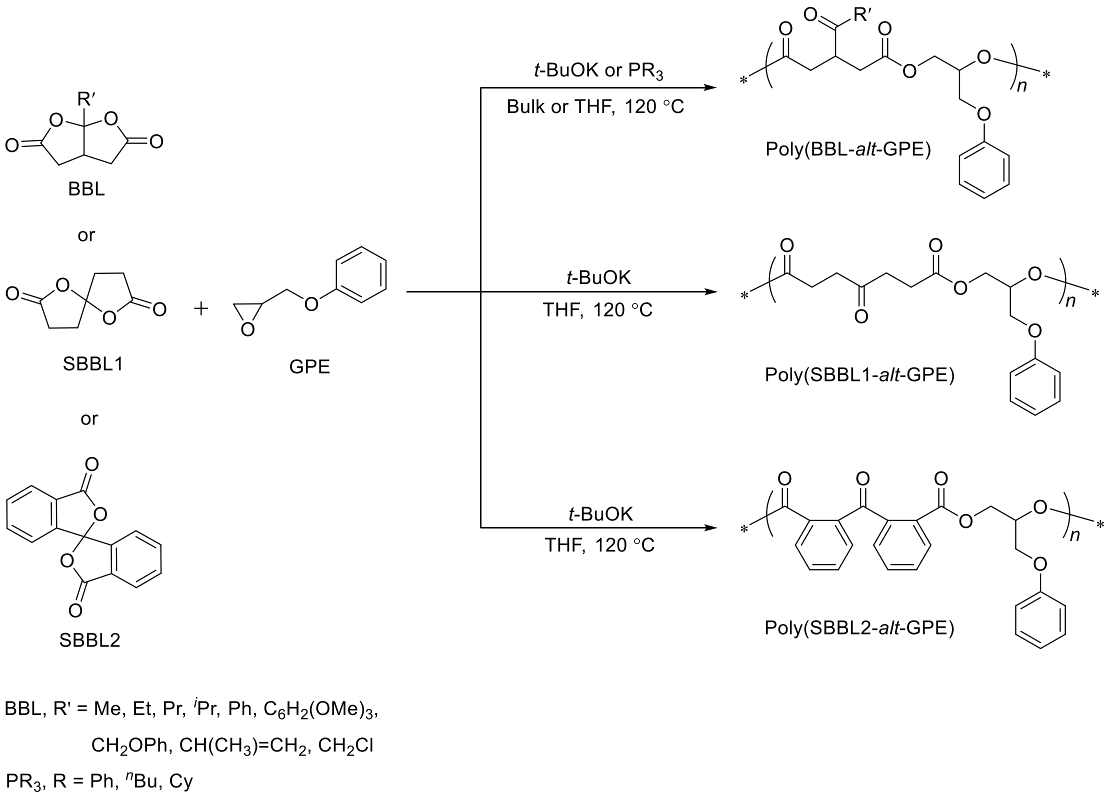
t-BuOK was also used for the homopolymerization of 4,5-T6L in bulk at 40 °C (Scheme 5b) [72]. The resultant product showed moderate molar mass and relatively broad distribution ($\overline{M_n}$ = 5.0 kg.mol^{-1}, $Đ$ = 1.62). Other anionic initiators with a stronger basicity such as *n*-butyllithium (*n*-BuLi) and lithium diisopropylamide (LDA) were also efficient under the same conditions, leading to the synthesis of the corresponding polyesters with similar molar masses as observed with *t*-BuOK [73]. Meanwhile, the polymerization of its *cis* isomer (4,5-C6L) with the same anionic systems was unsuccessful, highlighting the contribution of the *trans*-fused cyclohexane for the improved polymerizability of 4,5-T6L [73].



Scheme 5. Alkali metal-catalyzed/initiated polymerization of γBL derivatives: (a) ROP of SBL [101], (b) ROP of 4,5-T6L [72].

The copolymerization strategy was also employed here. The random copolymerization of γBL and εCL was conducted with LDA in dioxane at 25 °C, producing copolymers with 26% of γBL incorporation [102]. While the ROP of bicyclic γ-butyrolactones was yielding only oligomers [103, 104], the copolymerization of bicyclic or spirocyclic bis(γ-lactone)s (*e.g.*, BBL1–9, S-BBL1–3 and spirocyclic bis(γ-butyrolactone)s (SBBL) with GPE was investigated (Scheme 6) [95, 97, 105-109]. More particularly, the copolymerization of bicyclic bis(γ-lactone) bearing methyl group

(BBL1) and GPE was conducted in THF at 120 °C with *t*-BuOK as an initiator/catalyst [105, 106, 108]. The copolymerization was facilitated by the double ring-opening reaction of BBL1 that formed a ketone moiety in the polymer side chain, thus preventing the depolymerization reaction which would induce the reformation of stable five-membered lactones. The resultant copolymers show moderate molar masses ($\overline{M_n}$ = 4.6–8.2 kg.mol^{-1}) and relatively low dispersities ($Đ$ = 1.20–1.30). Linear alternating copolymers with α,ω-alkoxide/H chain ends, linear copolymers with α,ω-carboxyl chain terminals and cyclic alternating ones were obtained [109].



Scheme 6. Alkali metal compound-catalyzed/initiated ROCP of BBLs/SBBLs with GPE [105-110].

The scope of this alternating copolymerization system could be expanded to various BBL derivatives bearing different substitutes and diverse epoxides, including propylene oxide (PO), styrene oxide (SO) *etc.* (see cyclic ethers in Figure 3) [107, 108, 110, 111]. All the copolymers obtained showed a strictly alternating monomeric sequence distribution, with $\overline{M_n}$ = 1.3–7.6 kg.mol^{-1}, $Đ$ = 1.05–1.62. On the other hand, using SBBL as the comonomer also led to similar results, producing alternating polyesters [108]. In addition, polyfunctional epoxides such as poly(glycidyl methacrylate) (PGM) and poly(4-(glycidyl methyl)styrene) (PGMS) can also be copolymerized with BBLs or SBBLs under the same conditions, producing cross-linked copolymers [107, 111]. Moreover, it was shown that the volume shrinkage during cross-linking of epoxy groups containing polymers can be considerably suppressed by such alternating copolymerization. Furthermore, the alternating copolymerization of BBLs and bifunctional epoxides such as diglycidyl ether bisphenol A (DGEBA) and diglycidyl ether bisphenol S (DGEBS) showed similar volume shrinkage effect [110].

All research based on alkali metal compound-catalyzed ROP/ROCP of γ-lactones follow an anionic mechanism and are related to the ones carried out with organic bases. Results follow the same trend but appear less convincing, due to limited efficiencies for some monomers depending on the ring strain. Only monometallic catalysts were used, and a fine tuning of the reactivity of the active centers by using multi-metallic systems might be a way of improvement. Nevertheless, new copolymers were prepared showing the possibilities to copolymerized those γ-lactones to other cyclic monomers.

7. Organometallic compound-catalyzed ROP/ROCP of γ-lactones

Metal-based catalysts are employed for the ROP/ROCP or stereoselective ROP of cyclic esters to obtain corresponding (bio)degradable polyesters [112-116] following a coordination/insertion mechanism. Several metal-based compounds were also used for the ROP/ROCP of γBL and derivatives. For instance, PγBL with $\overline{M_n}$ of 3 kg.mol^{-1} and slightly high dispersity ($Đ$ = 1.36) was produced using scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$) with methanol as the initiator under harsh conditions (800 MPa, 40 °C) [71]. Oligomers with dehydration of αOHγBL was produced in presence of $Sc(OTf)_3$ at 40–80 °C [56].

More recently, $La[N(SiMe_3)_2]_3$ allowed the polymerization of γBL at high monomer concentration ($[\gamma BL]_0$ = 10 M) and -40 °C (Scheme 7a) [21]. In absence of protic species (*i.e.*, alcohols) as the initiator (sometimes also referred to chain transfer agent (CTA)), $Ln[N(SiMe_3)_2]_3$ alone could polymerize γBL with low yields (up to 3%) to produce both linear PγBL with MeO/H as the *α,ω*-chain ends (PγBL$_{L3}$) and cyclic PγBL (PγBL$_C$). The latter was presumably formed by the intramolecular back-biting reaction. Other Ln analogues gave similar results with a small decrease of the activity when the Ln ionic radius is varied (La > Sm > Y). However, the most efficient way was to generate metal alkoxides using the combination of alcohols and $La[N(SiMe_3)_2]_3$ by *in situ* alcoholysis to obtain PγBL with high molar mass in high yields. The initial molar ratio of La/$PhCH_2OH$ (BnOH) had an obvious effect on the polymer structures. When the feed ratio of La/BnOH = 1/1, linear PγBL with BnO/H chain ends (PγBL$_{L2}$) was the major product with the presence of minor PγBL$_{L3}$ and PγBL$_C$ ($\overline{M_n}$ = 10.2–11.8 kg.mol^{-1}, $Đ$ = 2.17–2.23). As the ratio of La/BnOH increased to 1/3, PγBL$_{L2}$ became predominant and P*γ*BL$_{L3}$/P*γ*BL$_C$ were negligible ($\overline{M_n}$ = 5.4–6.5 kg.mol^{-1}, $Đ$ = 1.26–1.38), indicating that most of the polymeric chains were obtained through the insertion of monomer into BnO–La bond. In general, P*γ*BLs displayed two T_m, in which the lower one (*ca.* 52 °C) was attributed to the T_m of the P*γ*BL$_C$ and the higher one (*ca.* 63 °C) was attributed to the T_m of the linear polymer. Moreover, both the T_d and maximum degradation temperature (T_{max}) of the P*γ*BL$_C$ (273 °C, 334 °C, respectively) was about 70 °C higher than that of the linear ones (202 °C, 225 °C, respectively), which was consistent with the hypothesis that the thermal stability of the cyclic polymer without chain ends is generally higher than that of the linear analogue [117]. Linear telechelic P*γ*BLs with different termination chain ends were synthesized by the post-polymerization chain-end capping process [118]. Compared with the uncapped P*γ*BL, chain-end capped P*γ*BL–OR with similar molar masses significantly enhanced the T_d value by 55, 65, 78, and 112 °C for R = ∗–C(=O)Ph, ∗–C(=O)CH=CH$_2$, ∗–C(=O)Me, and ∗–SiMe$_2$CMe$_3$, respectively. The resultant P*γ*BL–OR also showed enhanced resistance toward hydrolytic degradation, especially in basic medium. On the other hand, the thermal transition temperatures, thermal recyclability, and dynamic mechanical behaviour of the resulting polyesters were hardly influenced by the chain-end capping.

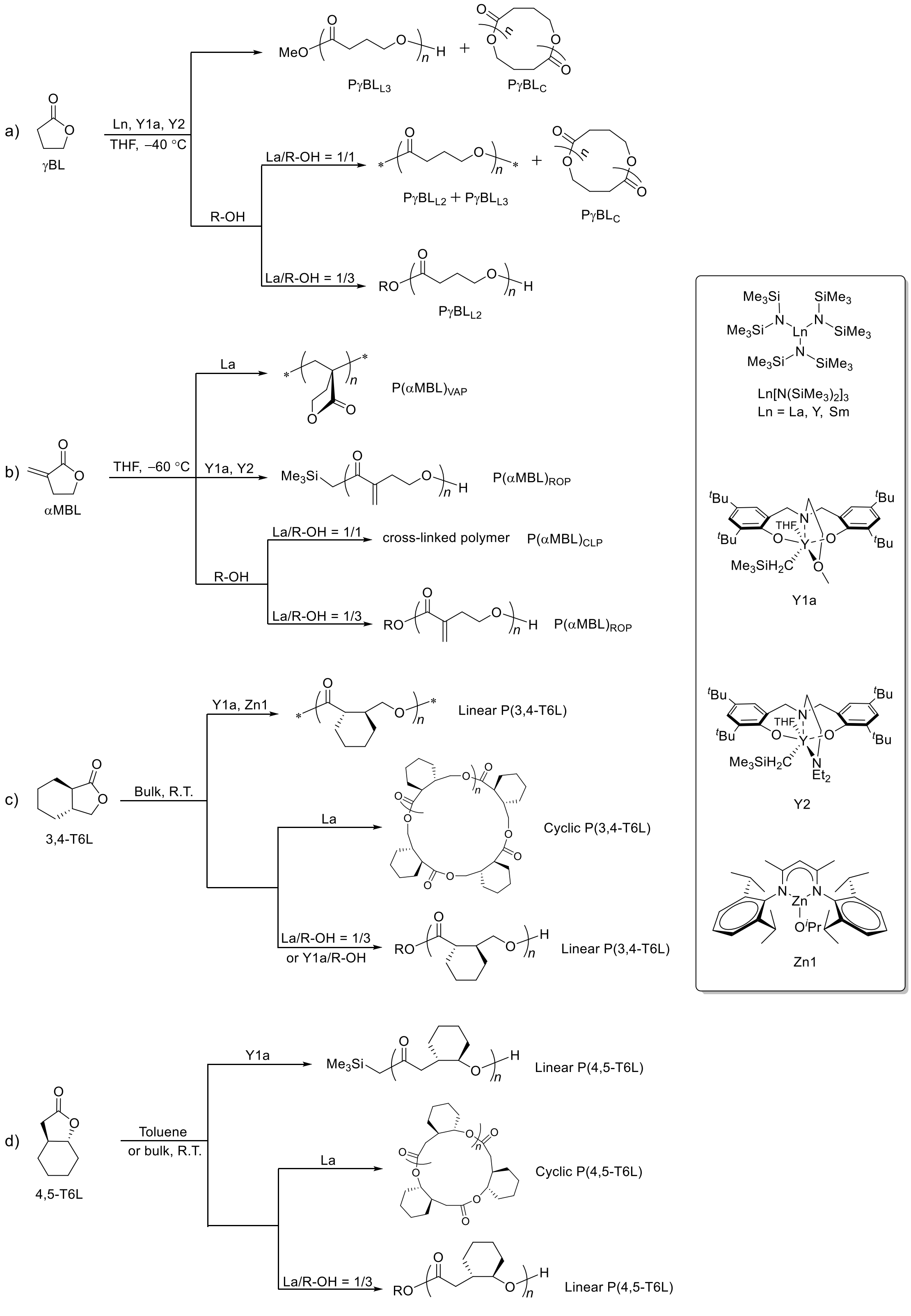
Functional *γ*BL derivatives such as tulipalin A (*α*MBL) which contains a highly reactive exocyclic C=C bond, was also polymerized in a ring-opening pathway for the synthesis of unsaturated and degradable polyesters (Scheme 7b) [119]. The combination of La[N(SiMe$_3$)$_2$]$_3$ and alcohols (La/ROH = 1/3) or Y1a, Y1k alone proved to be the best catalytic systems for the ROP of αMBL performed in THF at -60 °C ($[\alpha\text{MBL}]_0$ = 5 M). La alone led to the formation of vinyl-addition polymerization product $\text{P}(\alpha\text{MBL})_{\text{VAP}}$, while lower amount of alcohols (*e.g.*, La/ROH = 1/1) produced cross-linked polymers $\text{P}(\alpha\text{MBL})_{\text{CLP}}$. Interestingly, it was shown by density functional theory (DFT) calculation that the observed chemoselectivity was due to the steric bulkiness of the $*$–$\text{N(SiMe}_3)_2$ groups that would lead to the VAP process, while the La–OR group favoured the ROP one. Unsaturated $\text{P}(\alpha\text{MBL})_{\text{ROP}}$ with $\overline{M_n}$ = 4.6–10.4 kg.mol^{-1} and $Đ$ = 1.15–1.45 were obtained with a ratio La/ROH = 1/3 for various alcohols.

$\text{La[N(SiMe}_3)_2]_3$, Y1a or (BDI)ZnO^{i}Pr (Zn1) complexes were employed for the polymerization of 3,4-T6L in bulk at RT [120]. Different macromolecular structures with various and high molar masses were obtained depending on the conditions used (Scheme 7c). One can note that a zinc catalyst (i.e. Zn1) showed good performances in terms of polymerization activity and polymer dispersity ($\overline{M_n}$ = 27.1–588 kg.mol^{-1}, $Đ$ = 1.01–1.02). The T_{d} and T_{max} of the resulting linear polyesters (316 °C, 390 °C, respectively) obtained by La/ROH catalytic system were much higher than that of PγBL (202 °C, 225 °C, respectively), which demonstrated the positive effect of substitutes on the thermal properties of the corresponding polymer. In addition, the formation of nano-crystalline stereocomplexes of the two enantiomeric isotactic polymers (1:1) was observed and showed increased crystallinity, crystallization rate and solvent resistance as compared to the parent enantiomers.

Recently, commercial and simple organomagnesium compounds such as dialkylmagnesium (n-Bu_2Mg, n-BuEtMg *etc.*) were used as catalysts for the polymerization of 3,4-T6L and its enantiomers, forming linear polyesters with well-defined moderate molar masses in bulk at RT [121].

Similarly, and taking benefit of this coordination-insertion mechanism, stereoselective ROP of *racemic*-3,4-cyclohexyl-ring fused γ-butyrolactone (*rac*-CBL) [122] using achiral yttrium complexes bearing *N,O* tetradentate ligands (Y1a, Y1i, Y1j, Y3 *etc.*) could be achieved. The tethered donor sidearm of Y catalysts induced a switch from heteroselectivity to isoselectivity *via* a chain-end control mechanism. The ROP of *rac*-CBL by Y1a with the β-OMe side group alone or combined with alcohols produced heterotactic PCBL (*ht*-PCBL) ($\overline{M_n}$ = 18.6–102 kg.mol^{-1}, $Đ$ = 1.02–1.34). The coordination-insertion polymerization by more sterically hindered Y1i and Y1j with the β-NMe$_2$ side group afforded crystalline isotactic *it*-PCBL ($\overline{M_n}$ = 2.83 kg.mol^{-1}, $Đ$ = 1.04, probability of *meso* enchainment (P_m) = 0.95), with a T_m up to 171 °C. Meanwhile, the ROP of 4,5-T6L, a constitutional isomer of 3,4-T6L, was also investigated (Scheme 7d) [123]. Similar results were observed and poly(4,5-T6L-*b*-εCL) block copolymers were prepared.

This approach confirmed the expected possible stereoregulation for such γ-lactones, permitting control of the polymer tacticity and therefore the related properties.



Scheme 7. Examples of ROP of γ-lactones by coordination-insertion mechanism: (a) γBL [21], (b) αMBL [119], (c) 3,4-T6L [120], (d) 4,5-T6L [123].

As already mentioned, ROCP of *γ*BL or its derivatives and other cyclic monomers with high ring-strain energy (*e.g.*, lactones, cyclic ether) is a different way to circumvent the "non-polymerizability" of *γ*BL and to tune the properties of polymers.

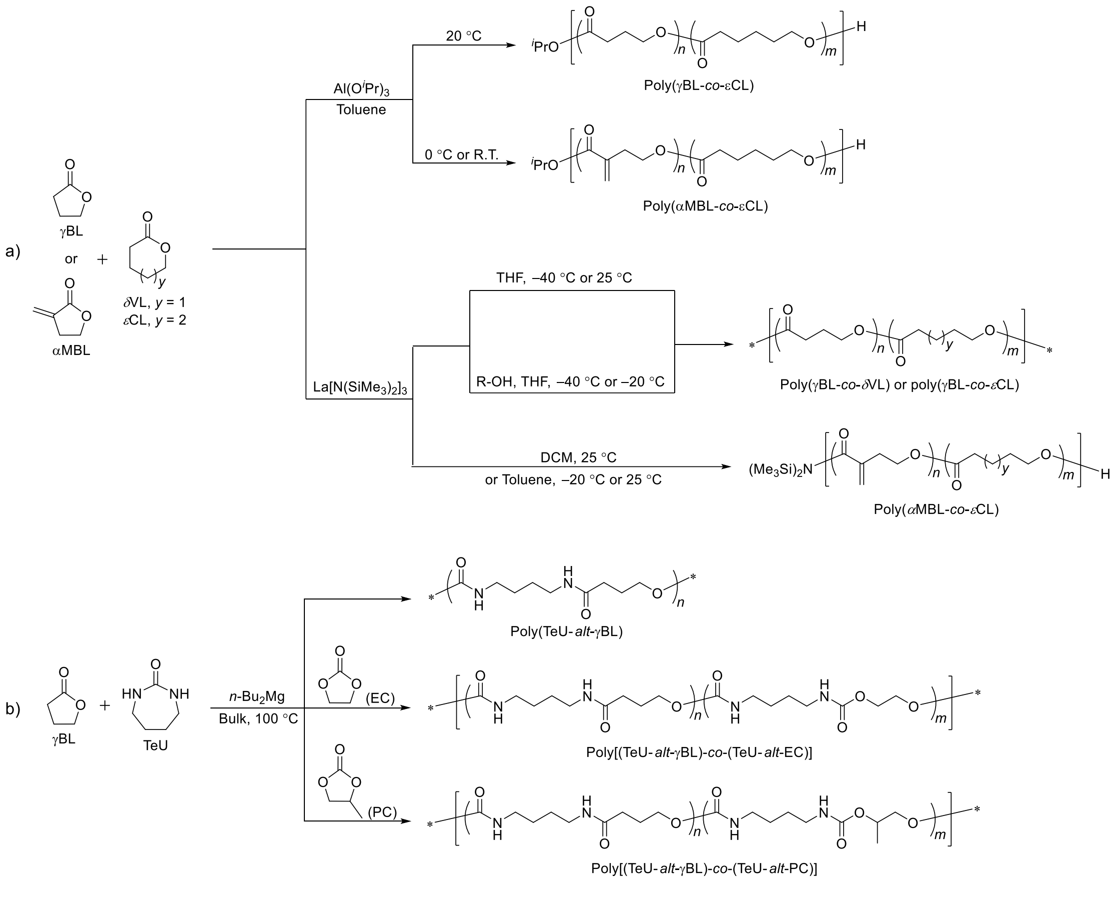
Many catalytic systems (*e.g.* $Sc(OTf)_3$, $Al(O^iPr)_3$, $La[N(SiMe_3)_2]_3$, Sn complexes, $Sm(OAr)_2(THF)_3$ or aluminum Schiff's bases) and comonomers (BCMO, *β*BL, *ε*CL) added to *γ*BL were investigated, enabling the synthesis of various polymer structures and *γ*BL fraction (Scheme 8a) [78, 91, 102, 124-130].

As an example, poly(*γ*BL-*co*-*ε*CL)s with 84% of *γ*BL content revealed a higher degradation rate than PCL, following the degradation order $[OH^-/H_2O] > [H^+/H_2O] > [H_2O]$. The incorporation of *γ*BL into PCL is a way to regulate its degradation rate.

Interestingly, alternated poly(amine urethane)s were synthesized by the copolymerization of tetramethylene urea (TeU) and *γ*BL [131]. Di-*n*-butylmagnesium (n-Bu_2Mg) was employed as the catalyst in bulk at 100 °C (Scheme 8b). Terpolymers of TeU, *γ*BL, and ethylene carbonate (EC) or propylene carbonate (PC) were also synthesized in the same reaction conditions.

CO_2 was also proposed to be part of the copolymerization of PO with *γ*BL in benzene at 60 °C with polymer supported bimetallic complexes (PBM, P–$Zn[Fe(CN)6]_aCl_{2-3a}(H_2O)_b$, where P is a polyether type chelating agent) [132, 133]. With the increased *γ*BL incorporation, the resultant copolymers exhibited varied $\overline{M_v}$ from 59.8 to 123 $kg.mol^{-1}$, as well as enhanced degradability.

Amphiphilic block copolymers of PEG-*b*-poly(*γ*VL-*co*-*ε*CL) were synthesized using PEG-OH as a macroinitiator with $Sn(Oct)_2$ at elevated temperatures (120–160 °C) [134, 135]. The lower temperature was beneficial to the copolymerization, providing more controlled copolymers with relatively narrow distribution ($\overline{M_n}$ = 8.6–10.6 kg.mol^{-1}, $Đ$ = 1.18–1.25). When the incorporation of *γ*VL was increased (9–16%), the copolymers showed higher surface hydrophilicity, decreased crystallization, and consequently higher biodegradation rates.



Scheme 8. Examples of ROCP of *γ*-lactones by coordination-insertion mechanism: (a) *γ*BL and *ε*CL/*δ*VL [91, 125], *α*MBL and *ε*CL [78, 136], (b) *γ*BL, TeU and/or EC, PC [131].

Following a similar approach, the copolymerization of αMBL and εCL was first carried out in bulk at 130 °C using bismuth(III) trifluoromethanesulfonate ($Bi(OTf)_3$) as the catalyst, which actually led to a mixture of ring-opening copolyester, poly(αMBL-*co*-εCL), and undesired homopolymer, P(αMBL)$_{VAP}$, originating from the vinyl-addition polymerization of αMBL [136, 137]. More recently, unsaturated copolyesters poly(αMBL-*co*-εCL) without contamination of P(αMBL)$_{VAP}$ were obtained with lanthanide compounds ($Ln[N(SiMe_3)_2]_3$) [136]. The T_m of the obtained poly(αMBL-*co*-εCL) decreased linearly with the increase of the amount of αMBL incorporated, as αMBL units prevented the crystallization of PCL segments.

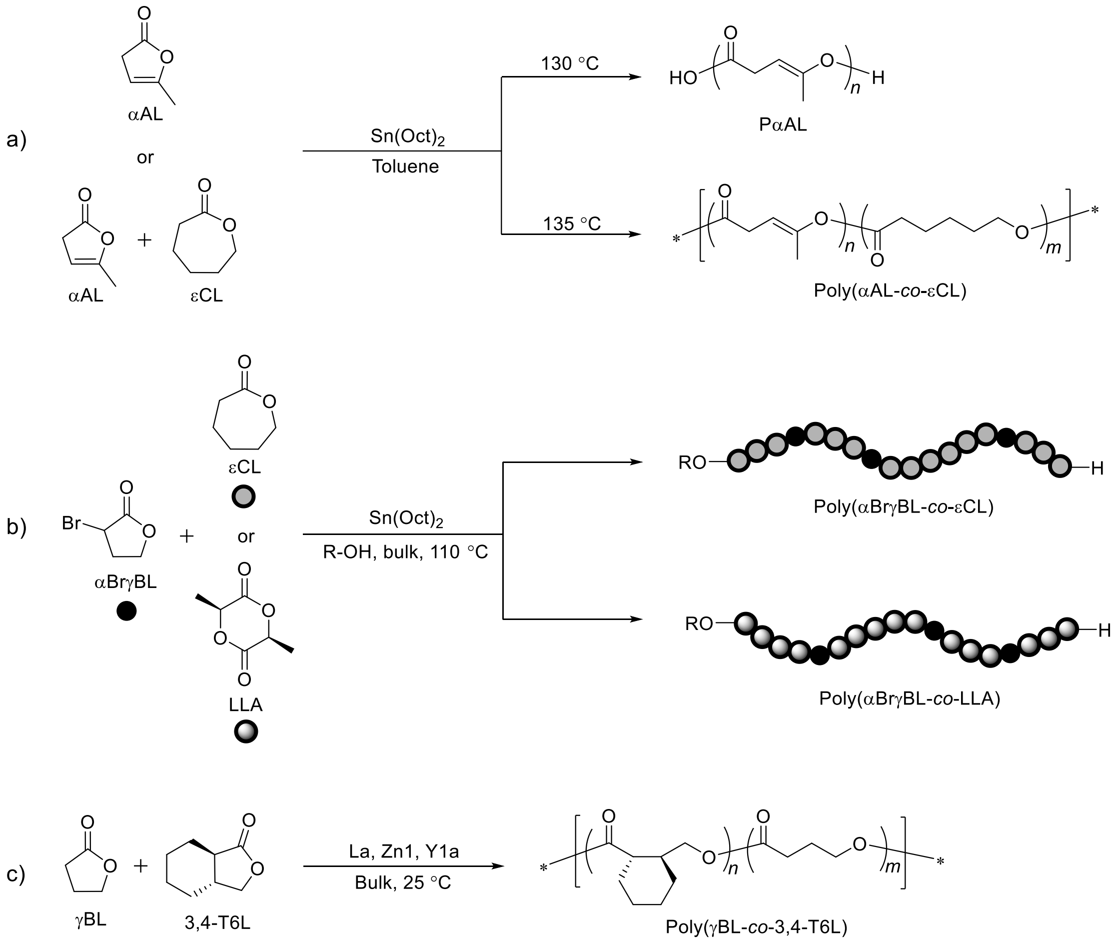
The ROP of αAL was successfully carried out in toluene at 110–130 °C using $Sn(Oct)_2$ as the catalyst/initiator (Scheme 9a) [138, 139]. Aliphatic unsaturated poly(α-angelica lactone)s (PαAL) with carboxylic and hydroxyl groups as the chain-ends were obtained ($\overline{M_n}$ = 8.9–29.4 kg.mol^{-1}, $Đ$ = 1.12–1.57), corresponding to a coordination-insertion mechanism. The degradability of these synthesized PαAL was tested in different conditions, and the degradation rate follows the order of basic (pH = 10.0) > acidic (pH = 2.5) > neutral (pH = 7.0). Through DFT analysis, it was inferred that the presence of endocyclic C=C significantly increased the strain energy of the corresponding five-membered ring, leading to the ROP of αAL under moderate conditions. This catalytic system was also applied for the copolymerization of αAL and εCL to produce poly(αAL-*co*-εCL)s with 30–47% of αAL incorporation ($\overline{M_n}$ = 5.8–7.4 kg.mol^{-1}, $Đ$ = 1.19–1.33) (Scheme 9a) [140]. The incorporation of αAL significantly decreased the crystallization of PCL and showed an enhanced degradability compared to PCL.

Graft copolymers with a degradable polyester backbone were obtained through the copolymerization of *α*-bromo-*γ*-butyrolactone (*α*Br*γ*BL) and *ε*CL or LLA. The ROCP was conducted in bulk at 110 °C using Sn(Oct)$_2$ as the catalyst (Scheme 9b) [141]. The non-homopolymerizability of *α*Br*γ*BL under such conditions was confirmed, and only separated *α*Br*γ*BL units were detected. The *α*Br*γ*BL incorporation was always below 12%. This was consistent with their reactivity ratios, *i.e.*, $r_{\mathrm{LLA}} = 18.48$, $r_{\varepsilon\mathrm{CL}} = 4.43$ and $r_{\alpha\mathrm{Br}\gamma\mathrm{BL}}$ close to 0 for both (0.32 and 0.01, respectively). These copolymers were used for SET-LRP, with separated *α*Br*γ*BL units as active grafting sites. Several acrylic monomers such as methyl methacrylate (MMA), 2-hydroxyethyl methacrylate, and butyl acrylate were successfully grafted onto the poly(*α*Br*γ*BL-*co*-*ε*CL) backbone in a controlled manner.

The ROCP of *γ*BL and 3,4-T6L was investigated in order to produce a new class of biorenewable and degradable materials (Scheme 9c) [142, 143]. La[N(SiMe$_3$)$_2$]$_3$, Zn1 and Y1a complexes proved to be suitable for the copolymerization. The obtained polymers showed ductility and barrier properties that are suitable for packaging applications and could be readily modified by adjusting the copolymer composition to obtain materials suitable for specific purposes.

The *α*OH*γ*BL was chosen as the inimer to be copolymerized with *ε*CL [144]. The copolymerization was performed in toluene or bulk at 110 °C using Sn(Oct)$_2$. Branched copolyesters with various degree of branching were synthesized. The higher amount of branching led to the decrease of T_m. Interestingly, *α*-hydroxy-*β,β*-dimethyl-*γ*-

butyrolactone (αOHβMe$_2\gamma$BL) could only serve as an initiator in such copolymerization due to the steric hindrance of the substitutes. Copolymerization of γBL and glycidol was also an alternative to produce such branched structures [145].

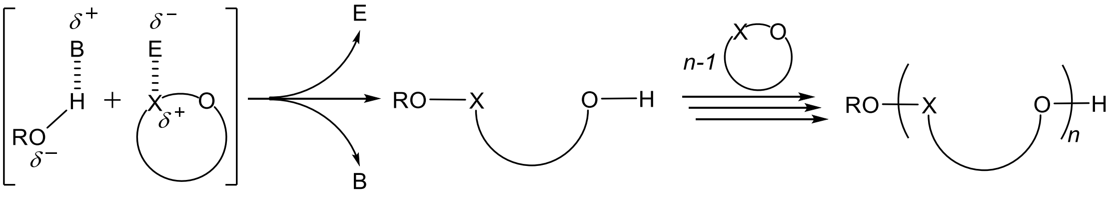


Scheme 9. Examples of ROCP of γ-lactones by coordination-insertion mechanism: (a) αAL and εCL [138, 140], (b) αBrγBL and εCL/LLA [141], (c) γBL and 3,4-T6L [143].

Organo-metallic systems permitting a coordination-insertion mechanism also appear to be efficient catalysts for the homopolymerization of γ-lactones and their copolymerization with other cyclic monomers, yielding polyesters with enhanced degradability. High molar masses can be reached by this route. A few works are dealing with stereoselectivity, which make this route unique to produce specific materials.

8. Dual catalytic system-catalyzed ROP/ROCP of γ-lactones

Bifunctional catalytic systems (also termed as cooperative catalysts) including bicomponent catalysts (Lewis acid-base pairs) and bifunctional unimolecular catalysts like the cyclic guanidine TBD were widely investigated and utilized for the polymerization of polar monomers (*e.g.*, polar vinyl monomers, cyclic esters and others). Several reviews focusing on this subject were already published [42, 43, 146-152]. The advantage of such systems originates from the cooperative dual activation of both the monomer and the initiator/chain end. Such bifunctional dual activation is the result of the combination of an electrophile (*e.g.*, weak Brønsted acids) activating the monomer (activated monomer mechanism, AMM) and a general base activating the initiator/chain end (activated chain-end mechanism, ACEM) (Scheme 10), which provides an effective means to trigger/promote the ROP and improves the selectivity of the polymerization over side reactions.



E = Electrophile; B = Base; X = CH_2, C=O, *etc.*

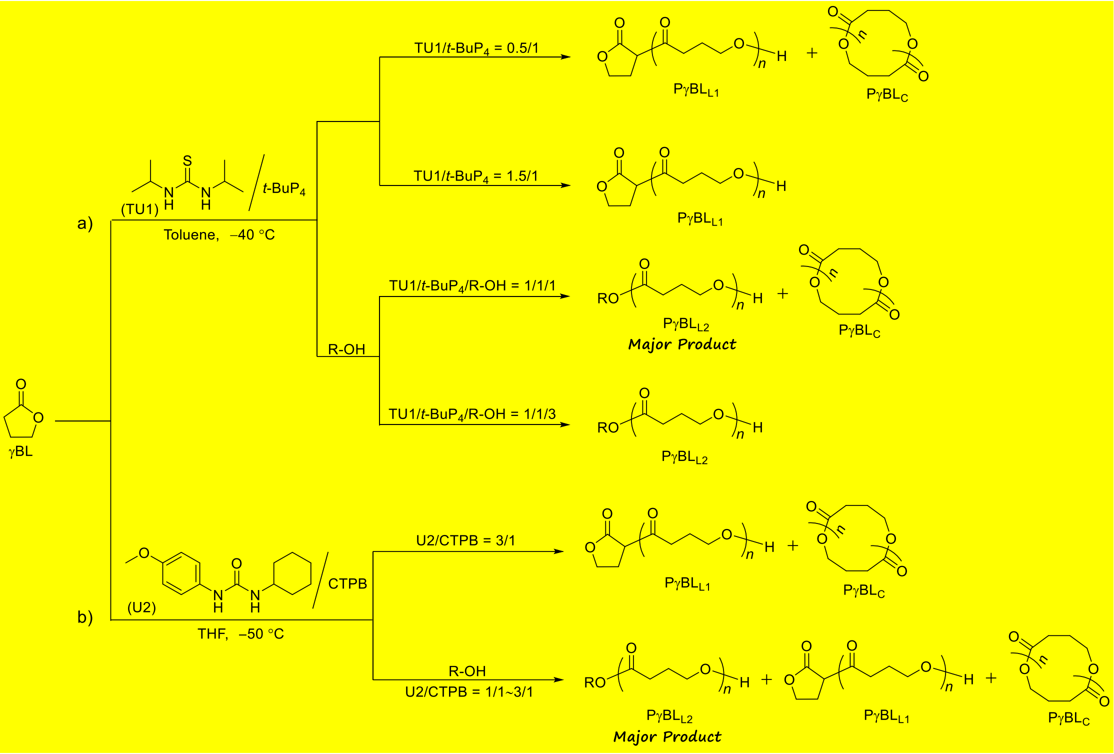
Scheme 10. Bifunctional activation mechanism for ROP of cyclic monomers.

Generally, (thio)ureas are a class of representative hydrogen-bonding donors which were widely utilized in organic base-catalyzed cyclic monomers (*e.g.*, lactones, lactides, cyclic carbonates *etc.*) [153-155]. The presence of (thio)ureas is usually considered to play dual roles during the polymerization, *i.e.*, activating the monomer as well as associating with the chain end. The latter character sometimes can also be regarded as modifying the basicity/nucleophilicity of the active species. This hypothesis was proven through the synthesis of polyether-based block copolymers *via* a "catalyst switch" strategy [156, 157]. The addition of thiourea (TU) was shown to attenuate the basicity of the active center. This allowed the controlled polymerization of the subsequently added monomers, and prevented side reactions that are usually caused by the strong basicity of alkoxides. Such retarded active species strategy was also applied to the ROP of γBL and derivatives.

Linear PγBLs with high molar masses were synthesized in toluene at low temperatures (< -40 °C) through the combination of t-BuP$_4$ and symmetrical thioureas bearing electron-donating groups (Scheme 11a) [25]. In absence of alcohol as the initiator, the ROP of PγBL could be directly initiated/catalyzed by the dual organocatalyst 1,3-diisopropyl-2-thiourea (TU1) TU1/t-BuP$_4$. Depending on the feed ratios of TU1/t-BuP$_4$, a mixture of PγBL$_{L1}$ and PγBL$_C$ or only PγBL$_{L1}$ (TU1/t-BuP$_4$ = 1 or 1.5) was obtained. Using the latter feed ratio, PγBL$_{L1}$ with higher molar mass ($\overline{M_n}$ = 64.3 kg.mol^{-1}, $Đ$ = 2.35) was produced when the polymerization was performed at -55 °C. On the other hand, the addition of an alcohol (BnOH) could greatly decrease the formation of PγBL$_{L1}$ and cyclic polymer. Fully BnO-initiated polyester (PγBL$_{L2}$) was obtained. The combination of DBU and TU2 (1-[3,5-bis(trifluoromethyl) phenyl]-3-cyclohexyl-thiourea) was also effective to polymerize γBL in bulk [75].

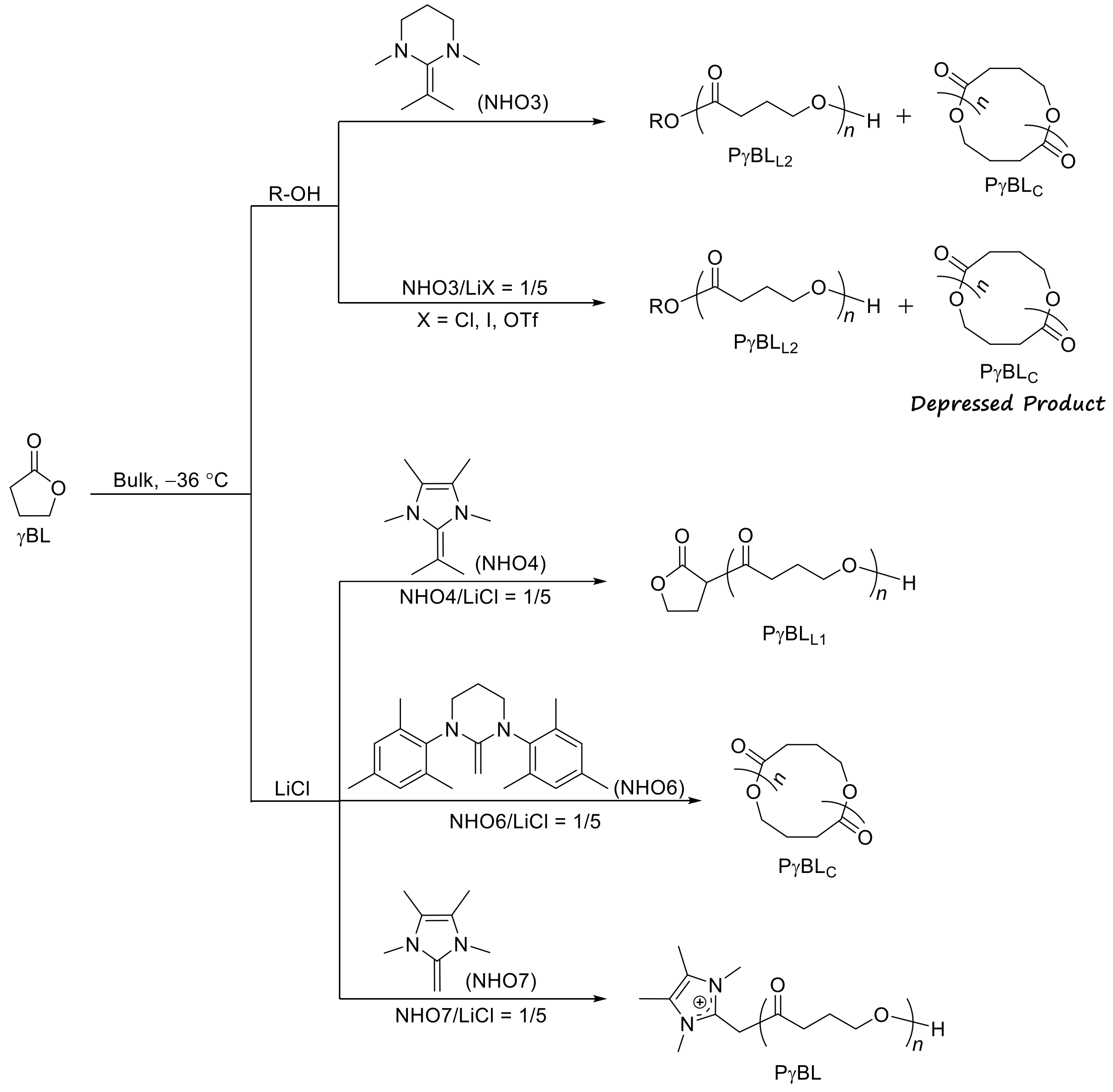
Similarly, a binary catalytic system composed of ureas and CTPB was also studied for the polymerization of γBL conducted in THF at -50 °C (Scheme 11b) [158]. In the absence of the initiator (BnOH), 1-cyclohexyl-3-(4-methoxyphenyl)-urea (U2; U2/CTPB = 3/1), a urea bearing unsymmetrical and electron-donating substituents, yielded a mixture of high molar mass PγBL$_{L1}$ and PγBL$_{C}$ with *ca.* 50% monomer conversion ($\overline{M_n}$ = 28–35 kg.mol^{-1}, $Đ$ = 1.90–2.06). However, keeping U2/CTPB at 3/1 and adding BnOH as the initiator favoured the formation of mainly PγBL$_{L2}$ ($\overline{M_n}$ = 9.1–23.3 kg.mol^{-1}, $Đ$ = 1.38–2.13). Noticeably, the thermal stability and mechanical properties of the resultant PγBLs were improved with increasing molar mass.

Adding (thio)ureas to phosphazene bases for the polymerization of γBL appeared to be efficient. Initiation was more selective, and defined (linear) structures were produced.



Scheme 11. ROP of *γ*BL by different dual catalytic systems: (a) TU1/*t*-BuP4 [25], (b) U2/CTPB [158].

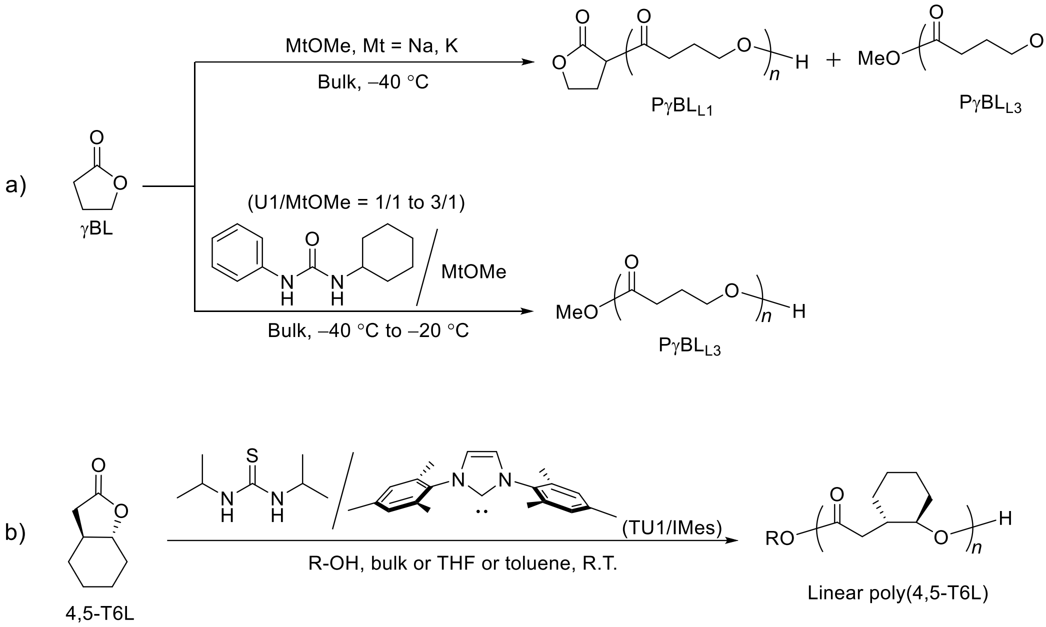
Bicomponent catalysts composed of NHOs and lithium halides (LiX) were used for the ROP of *γ*BL in bulk at -36 °C (Scheme 12) [24]. With BnOH as the initiator, NHO3 and LiX (NHO3/LiX = 1/5) provided a mixture of P*γ*BL$_{L2}$ and P*γ*BL$_C$ with a monomer conversion similar to the one obtained with NHOs alone ($\overline{M_n}$ = 4.7–7.8 kg.mol^{-1}, $Đ$ = 1.4–1.8). Interestingly, NHOs/LiX could also trigger the polymerization without any alcohol. The topological structures of the obtained P*γ*BLs depended on the nucleophilicity and steric hindrance of involved NHOs. For example, the combination of LiCl and NHO4, which is highly basic and sterically hindered, led to the formation of linear P*γ*BL$_{L1}$ ($\overline{M_n}$ = 5.8 kg.mol^{-1}, $Đ$ = 1.6) based on an anionic ROP mechanism. On the contrary, the association of LiCl and NHO7, which is highly nucleophilic and sterically non-hindered, provided NHO-terminated PγBL based on a zwitterionic ROP mechanism ($\overline{M_n}$ = 3 kg.mol^{-1}, $Đ$ = 1.9). The association of LiX and NHO6, which is mildly polarized and sterically hindered, delivered exclusively the macrocyclic PγBL$_C$ in short reaction time, whereas increasing amounts of enolate-terminated PγBL$_{L1}$ appear with time ($\overline{M_n}$ = 1.6–9 kg.mol^{-1}, $Đ$ = 1.4–2.4). In addition, and irrespective of the pathway, low monomer conversion was observed (< 20%).



Scheme 12. ROP of γBL by LiX/NHOs dual catalytic system [24].

Commercial alkoxides such as sodium or potassium methoxides (MtOMe) were also combined with ureas to polymerize γBL (Scheme 13a) [26]. Its bulk polymerization was shown to procced at -40 °C using MtOMe alone with limited monomer conversion ($\leq$ 25%). Combination of 1-cyclohexyl-3-phenyl-urea (U1) and MtOMe (U1/MtOMe = 1/1 to 3/1) enhanced the reactivity of the active species, allowing for the ROP of γBL in bulk at low temperatures (-40 to -20 °C), and a monomer conversion with up to 86% was achieved in a few hours. The obtained PγBLs showed two different chain ends, *i.e.*, MeO/H and acylated lactone/H ($\overline{M_n}$ = 7.0–68.2 kg.mol^{-1}, $Đ$ = 1.33–2.08) [158].

The ROP of substituted γBL, 4,5-T6L, was also investigated with binary catalytic system (Scheme 13b) [73]. Initially, various bicomponent catalysts with balanced acidity of (thio)ureas and basicity of co-catalysts ((thio)ureas/base = 1/1) were studied. Among them, the combination of 1,3-diphenylurea (U3) and BEMP or IMes (U3/BEMP or IMes), 1-[3,5-bis(trifluoromethyl) phenyl]-3-cyclohexyl-urea (U4) and BEMP or IMes (U4/BEMP or IMes), and TU1/IMes afforded the best results. The monomer conversion was higher than 50% in a few minutes with the polymerization performed at RT in bulk. Linear P(4,5-T6L)s with various molar masses were obtained using TU1/IMes under the same conditions ($\overline{M_n}$ = 21.1–106 kg.mol^{-1}, $Đ$ = 1.02–1.04). Block copolymers poly(4,5-T6L-*b*-LLA) were obtained, verifying the living character of the polymerization. Linear P(4,5-T6L) produced by this binary organocatalyst showed a higher T_d (by 13 °C) than that of the polymer synthesized with a metal catalyst, which highlights the advantages of organocatalysis c due to better selectivity of the active centers.



Scheme 13. ROP of γBL or 4,5-T6L by different dual catalytic systems: (a) U1/MtOMe [26], (b) TU1/IMes [73].

Recently, the chemoselective ROP of biorenewable αMBL was achieved in THF at -50 °C through the cooperative catalysis of 1-cyclohexyl-3-(4-(trifluoromethyl)phenyl)-urea (U5) and CTPB (U5/CTPB = 3/1) [159]. Low reaction temperature and the choice of urea were critical to produce these unsaturated polyesters ($\overline{M_n}$ up to 6.7 kg.mol^{-1}). Moreover, high monomer concentration ([αMBL]$_0$ = 8 M) improved yields. DFT calculation results also indicated that the ROP pathway was more kinetically favored, whereas the competing VAP pathway was thermodynamically favored. The resultant polyesters could be recycled back to αMBL with the dual catalysis of CTPB and a urea with more electron-withdrawing substituents (1,3-bis(3,5-

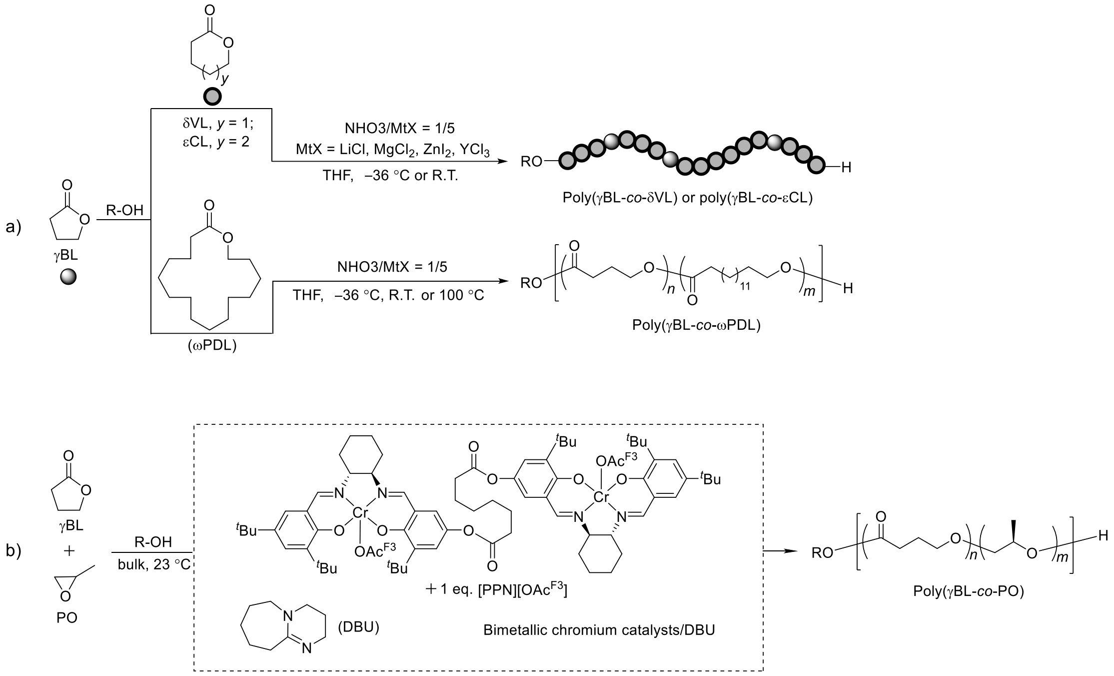
bis(trifluoromethyl)phenyl)-urea, U7).

Selective ring-opening copolymerization of αMBL and εCL or δVL was also achieved at low temperatures with similar bicomponent catalyst based on CTPB [160].

The ROCP of γBL and δVL, εCL or ω-pentadecalactone (ωPDL) was performed in the presence of NHO3/BnOH associated with several metal halides (MtX) such as LiCl, magnesium chloride ($MgCl_2$), yttrium(III) chloride (YCl_3), and zinc iodide (ZnI_2) (NHO3/MtX = 1/5) (Scheme 14a) [161]. Copolymers with moderate γBL content (up to 22%) were generally obtained.

Another dual catalytic system based on the combination of bimetallic chromium catalyst which could mediate enantioselective polymerization of *racemic* propylene oxide (*rac*PO) and DBU (1/5) was used to copolymerize γBL and *rac*PO. The copolymerization was performed in bulk at 23 °C with 1,6-hexanediol as the CTA (Scheme 14b) [162]. Both the monomer conversion of γBL and PO were limited ($\leq$ 13%,), generating statistical poly(γBL-*co*-PO)s with isotactic polyether sequences ($\overline{M_n}$ = 2.7–10.5 kg.mol^{-1}, $Đ$ = 1.07–1.14). The poly(ether-ester) copolymers obtained showed adjustable ester content and crystallinity, the latter decreasing with increasing γBL and CTA loadings.

The terpolymerization of PO, CO_2 and γBL was also investigated in bulk at 50 °C using the combination of salen Co^{III}X (X = 2,4-dinitrophenoxide) and a bulky ionic salt tetrabutylammonium bromide (^{n}Bu$_4$NBr) [163]. The $\overline{M_n}$ of terpolymers obtained was affected by several reaction parameters, such as the feed ratio of monomer, temperature, and reaction time (74–102.1 kg.mol^{-1}). Compared with the copolymers of PO and CO_2, these terpolymers revealed improved thermal properties with the introduction of *γ*BL.



Scheme 14. ROCP of *γ*BL with cyclic monomers by dual catalysts in the presence of an alcohol: (a) *γ*BL and *δ*VL, *ε*CL or *ω*PDL [161], (b) *γ*BL and *racemic* PO [162].

Comparing this dual catalysis approach to the mono-component organic one discussed previously (section 5), a better control seems to be achieved and can be attributed to a finely tuned reactivity of the active centers and monomers. Combining a urea to a metal alkoxide allows, for example, the ROP of *γ*BL with a monomer conversion higher than 80% in short times. Thus, the utilizzation of bicomponent catalysts, such as Lewis acids and bases, or bifunctional unimolecular catalysts, permits the modulation of the basic and nucleophilic character as well as steric hindrance of the chain ends. This enables control of reactivities and selectivities and, is definitely a route to follow in order to progress in the polymerization control of such lactones.

9. Other polymerization methodologies for *γ*-lactones

In this section, several approaches used for polymerization of *γ*BL and its derivatives are summarized. The related mechanism depends on the specific catalytic system used, such as polycondensation, enzymatic catalysis, transesterification, or ring-opening..

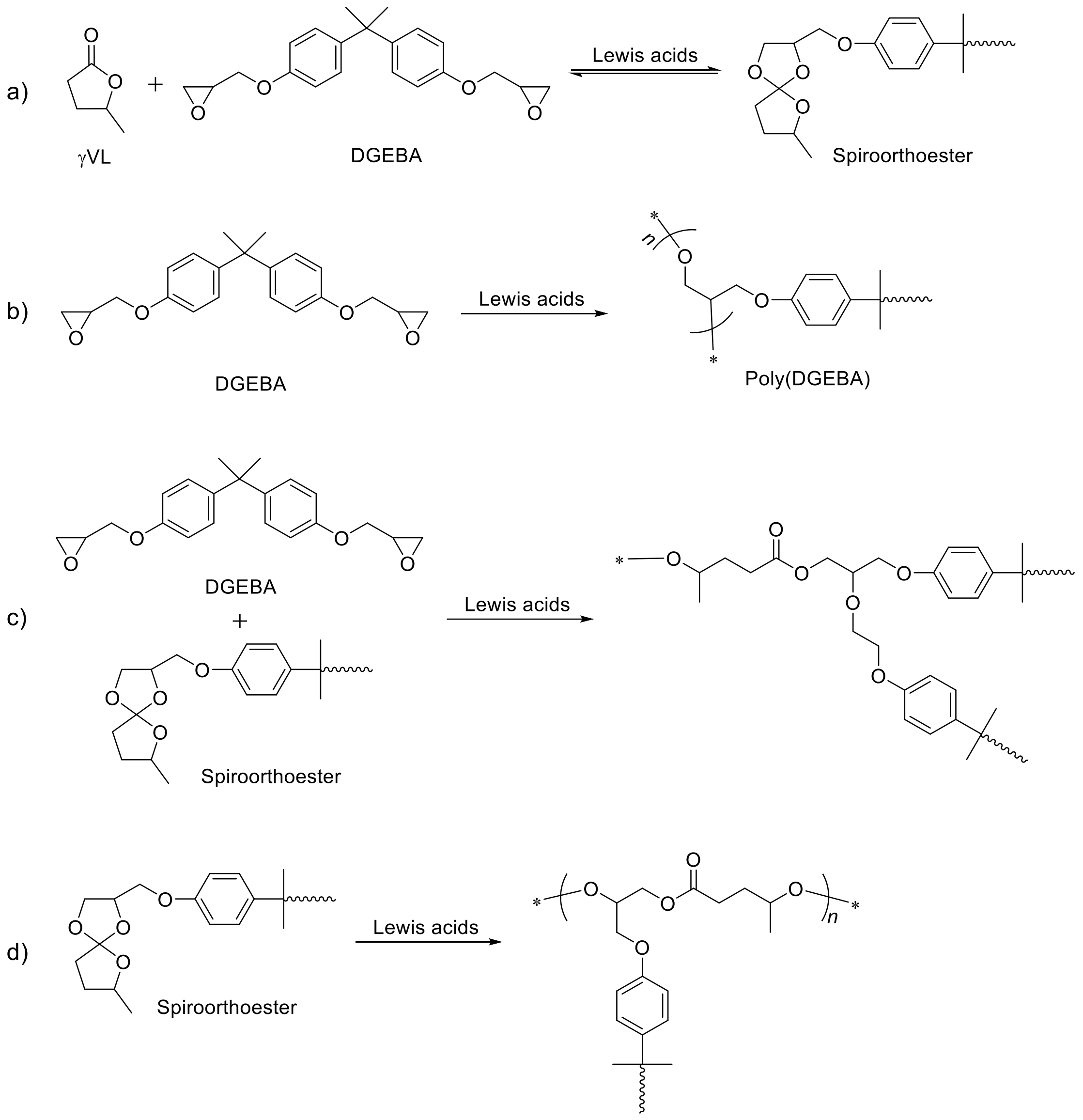
The copolymerization of *γ*BL and L-Lactic acid or glycolic acid was conducted without catalysts in bulk at 200 °C [164-166]. Copolymers with relatively low molar masses and *γ*BL content (1.1–5.2 kg.mol^{-1}, 10–20%) were synthesized, containing single *γ*BL units in the polymeric chain. The proposed mechanism was a direct polycondensation between the linear acids and the *ω*-hydroxy acid produced by the hydrolysis of *γ*BL in presence of water.

Enzymatic ROP (eROP) of lactones has been studied since 1993 [167-170]. A few studies described the use of lipases for the ROP/ROCP of *γ*BL. For instance, P*γ*BL with $\overline{DP}$ around 10 was produced by the use of lipases from Porcine Pancreatic or from *Pseudomonas cepacia* in *n*-hexane at 60 °C after 20 days [171]. A poly(*γ*BL-*co*-*ε*CL) copolymer was also synthesized under similar conditions with 3% of *γ*BL conversion ($\overline{M_n}$ = 2.9 kg.mol^{-1}, Đ = 2.16) [172]. Besides, the use of immobilized *Candida antarctica* lipase B in ionic liquids led to the oligomerization of *γ*BL ($\overline{DP}$ = 5) [173].

The ROP of *γ*BL was also studied at RT using tin(IV) ion-exchanged montmorillonite, mainly producing dimers and trimers, while its copolymerization with

δVL led to the formation of copolyester with a limited γBL incorporation ($\overline{DP}$ around 4–6) [174]. Activated clay could also promote the copolymerization of γBL and 1,2-ethanediol in xylene at reflux to produce oligomeric polyether-polyester with single γBL units in the polymeric chain. They were used as precursors for polyurethane synthesis [175].

The curing reaction of DGEBA and γVL or γMBL was performed in the presence of boron trifluoride ethylamine complex (BF_3•$EtNH_2$) or rare earth triflates such as $Sc(OTf)_3$ and lanthanum(III), ytterbium(III) trifluoromethanesulfonate ($La(OTf)_3$, and $Yb(OTf)_3$, respectively) (Scheme 15) [176-178]. Four different reactions were observed during the curing process, that is, (1) spiroorthoester intermediates formation by the reaction of DGEBA and γVL (or γMBL), (2) homopolymerization of DGEBA, (3) copolymerization of DGEBA with the spiroorthoester intermediate, and (4) homopolymerization of the spiroorthoester [179]. Compared with the conventional epoxy resin, the obtained thermosets were more thermally degradable, due to the introduction of ester group in the polymer chain [180]. In addition, DMAP, DBU, and 1-methylimidazole (1-MI) were applied for the copolymerization of DGEBA and BBLs (BBL1, BBL5). The stoichiometric proportion of DGEBA/BBL led to the desirable alternating poly(ether-ester-ketone) structure [181].



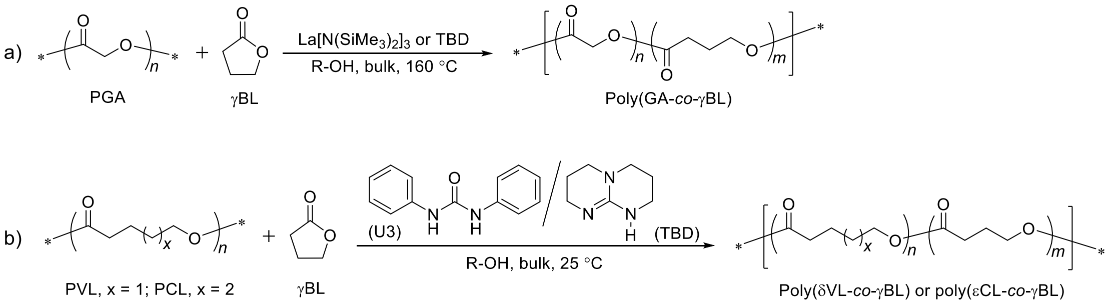
Scheme 15. Curing procedure between DGEBA and *γ*VL: (a) spiroorthoester intermediates formation, (b) homopolymerization of DGEBA, (c) copolymerization of DGEBA with the spiroorthoester, (d) homopolymerization of the spiroorthoester [179].

The polycondensation of BBLs (BBL1, 8, 9) and 1,4-benzenedimethanol (BDM) was promoted by *p*-toluenesulfonic acid (*p*-TsOH) under ambient or reduced pressure at 80–120 °C, generating corresponding polyesters with a ketone group in the side chain ($\overline{M_n}$ = 3.0–5.0 kg.mol^{-1}, Đ = 1.6–8.9) [182]. On the other hand, *γ*BL was shown able to end-functionalize oligoethylene glycol (HO-PEG-OH, $\overline{M_w}$ = 0.8 kg.mol^{-1}) [183]. The process was performed at 130 °C with non-eutectic mixture of organocatalysts (NEMO), composed of a non-stoichiometric complex of MSA and TBD (MSA/TBD = 3/1). 52% of the oligo-PEG hydroxyl end-groups were functionalized by about 1.5 units of γBL, and polyethers were subsequently produced by the thermal/vacuum polycondensation of these functionalized oligomers. The resulting polycondensate PEG ($\overline{M_p}$ = 17.0 kg.mol^{-1}, Đ = 1.7) was completely degradable in a 0.5 M NaOH solution.

Transesterification, which is normally regarded as a detrimental side reaction for the synthesis of polyester, could nevertheless be utilized to modify the polyesters. The original strategy was to employ an organic superbase that acted as the promoter for both ROP of epoxides and transesterification reactions with hydroxyl-terminated polyester, to provide a random poly(ester-ether) [184]. This approach was employed for the upcycling of polyesters with ROP of γBL (Scheme 16a). Poly(glycolic acid) (PGA) was chosen as the first candidate for the transesterification, combined with ROP of γBL, which served as both a solvent and a comonomer [63]. The reaction was performed in the presence of BnOH as the initiator at 160 °C using $La[N(SiMe_3)_2]_3$ or TBD. The γBL incorporation in the poly(GA-*co*-γBL)s varied from 12 to 20% and improved the solubility of the copolymer ($\overline{M_n}$ = 4.7–7.2 kg.mol^{-1}, Đ = 1.15–1.30). The resulting poly(GA-*co*-γBL)s also showed enhanced thermal properties compared to PGA.

The transesterification on poly(δ-valerolactone) (PVL) - or PCL in the process of ROP of γBL - was also investigated (Scheme 16b) [185]. Dual organocatalyst based on U3/TBD (1/1 to 10/1) was employed for the reaction of PVL and γBL performed at

25 °C. TBD alone could catalyze the transesterification of PVL and *γ*BL, whereas its association to U3 (U3/TBD = 1/1) improved the *γ*BL incorporation without deteriorating the $\overline{M_n}$ of obtained copolyesters. The enhanced *γ*BL incorporation in U3/TBD-mediated transesterification was proposed to be due to the preferential activation of *γ*BL monomer over the polymer chain. Poly(*δ*VL-*co*-*γ*BL) with higher *γ*BL incorporation (up to 38%) could be synthesized by increasing the feed ratio of U3/TBD from 1/1 to 10/1 ($\overline{M_n}$ = 10.5–20.5 kg.mol^{-1}, *Đ* = 1.56–1.63). The reaction could also be performed in the absence of alcohols, and high molar mass copolymers with various *γ*BL incorporation (7–28%; $\overline{M_n}$ = 21.0–40.6 kg.mol^{-1}, *Đ* = 1.72–1.89) were obtained. When switching to PCL, the reaction was more efficient if conducted at 80 °C, producing poly(*ε*CL-*co*-*γ*BL) with moderate *γ*BL incorporation (5–13%; $\overline{M_n}$ = 9.6–26.7 kg.mol^{-1}, *Đ* = 1.33–1.77). Noticeably, both reactions could be carried out under air to give similar copolymers, highlighting the air/moisture tolerance of such binary catalytic system.



Scheme 16. Copolyesters produced by transesterification and ring-opening of *γ*BL: (a) PGA with *γ*BL [63], (b) PVL or PCL with *γ*BL [185]

Polycondensation and enzymatic catalysis remain limited both in their use and efficiency. The transesterification route combined to ring-opening polymerization of γ-BL, which is following the organometallic or dual catalysis methodologies and results, offers another way to get copolyesters.

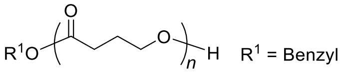
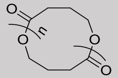
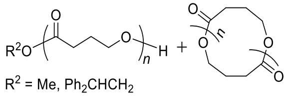
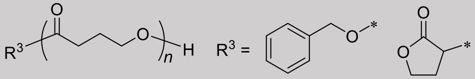
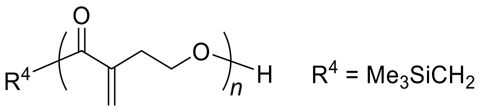
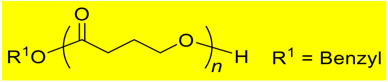
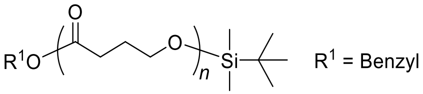
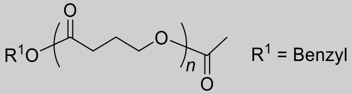
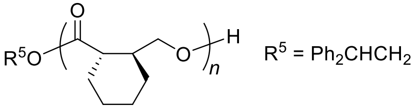
10. Thermal or chemical recycling of P*γ*BL and other derivatives

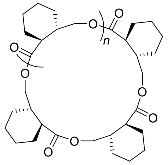
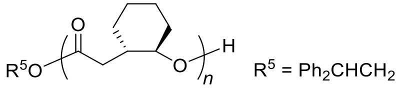
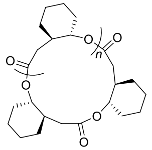
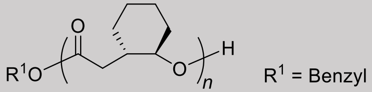
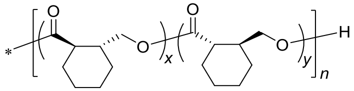
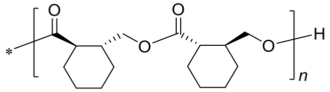
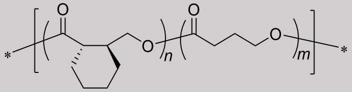
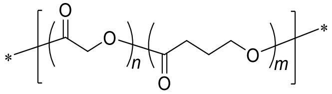
Table 1 summarizes the methods to recycle the P*γ*BL and other derivatives back to the corresponding monomer, based on thermal or chemical procedures. In most cases, the use of a catalyst allowed to depolymerize the product in a more energy-efficient way. For example, the depolymerization of P*γ*BL in the absence of a catalyst needed to be carried out at 220 °C or 300 °C in bulk (linear or cyclic product, respectively), while the employment of TBD or $La[N(SiMe_3)_2]_3$ allowed it to proceed at 25 °C in solution [21]. The linear P*γ*BL with different termination chain ends showed also similar depolymerization behaviours [118].

The recycling process of P(*α*MBL)$_{ROP}$ was slightly different from other derivatives [119]. Due to the appearance of unsaturated C=C in polyester, insoluble cross-linked products would be formed when the depolymerization was performed in bulk at high temperatures. In the presence of $La[N(SiMe_3)_2]_3$, P(*α*MBL)$_{ROP}$ could be recycled back to *α*MBL in a dilute dimethyl sulfoxide (DMSO) solution (H_2O is added to inhibit polymerization) at relatively low temperatures. Moreover, the depolymerization of P(*α*MBL)$_{ROP}$ could also be achieved in DMSO using simple metal halides such as lanthanum(III) chloride ($LaCl_3$), which was incapable to reinitiate the VAP of *α*MBL generated from depolymerization.

The depolymerization of other derivatives such as P(3,4-T6L), P(4,5-T6L) and *it*-PCBL, *ht*-PCBL also showed similar behaviours [73, 120, 122, 123]. Compared with thermal recycling of related polymers in bulk at high temperatures, the depolymerization process was more favourable using catalysts in toluene. In addition, the copolyester poly(*γ*BL-*co*-3,4-T6L) could also be chemically recycled back to its building monomers (*γ*BL, 3,4-T6L, respectively) [143], while the recycling of poly(GA-*co*-*γ*BL) was achieved in a hydrolysis pathway [63].

Table 1 Summary of methods used for depolymerizing PγBL and derivatives

Polymer		Catalyst	Conditions	Time (h)	Conv. (%)	Mon.	Refs.
PγBL		–	220 °C, bulk	1	100	γBL	[21]
		–	300 °C, bulk	1	100		
		TBD	25 °C, DCM	24	100		
		$La[N(SiMe_3)_2]_3$	25 °C, THF	10 mins	100		
		–	260 °C, bulk	1	100		[22]
P(αMBL)$_{ROP}$		$La[N(SiMe_3)_2]_3$	130 or 100 °C	1	100	αMBL	[119]
		$La[N(SiMe_3)_2]_3$	60 °C	24	100		
		$LaCl_3$	130 °C	24	97		
		$LaCl_3$	160 °C	6 or 24	100		
		U7/CTPB	50 °C, THF	48	100	αMBL	[159]
PγBL-OX$_1$		–	250 °C, bulk	5	100	γBL	[118]
PγBL-OX$_2$		–	250 °C, bulk	2	100		
P(3,4-T6L)		–	≥ 300 °C, bulk	1	100	3,4-T6L	[120]
		$ZnCl_2$	120 °C, toluene	12			

		–	≥ 300 °C, bulk	24			
		$ZnCl_2$	120 °C, toluene	12			
P(4,5-T6L)		–	230 °C, bulk	40	100	4,5-T6L/4,5-C6L (89/11)	[123]
		$La[N(SiMe_3)_2]_3$	120 °C, toluene	24	100	4,5-T6L	
		$La[N(SiMe_3)_2]_3$	120 °C, toluene	24			
		TBD	120 °C, toluene	24			[73]
it-PCBL		$ZnCl_2$	130 °C, toluene	24	100	*rac*-CBL	[122]
ht-PCBL							
Poly(*γ*BL-*co*-3,4-T6L)		$ZnCl_2$	120 °C, toluene	60	100	*γ*BL, 3,4-T6L	[143]
Poly(GA-*co*-*γ*BL)		1 M NaOH and subsequent chemical steps	–	–	98, 94	Glycolic acid, *γ*BL	[63]

11. Conclusion

The ROP of *γ*BL under mild conditions was regarded as impossible or rarely possible for several decades. This review summarizes and comments on the development in polymerization of *γ*BL, especially focusing on the recent advances, to synthesize P*γ*BL with a high molar mass under moderate reaction conditions. Dual catalytic systems made of ureas and bases, that can be commercially available and inexpensive, are quite efficient. Anionic and coordination-insertion polymerizations, which were investigated more than cationic ones, showed better results. Low reaction temperatures (to keep $\Delta G_p < 0$) and high initial monomer concentrations are required for the homopolymerization of *γ*BL. On the other hand, such success was also applied to the ROP of *γ*BL derivatives to deliver a broad diversity of polyesters. Through the prudent design of substitutes, some of them could even be polymerized at ambient temperature. Furthermore, the use of multifunctional *γ*BL derivatives provided an alternative to obtain functional polyesters. More significantly, several resultant polymers could be depolymerized to their corresponding monomer by thermal or chemical treatments.

The ROCP of *γ*BL or its derivatives with other cyclic monomers afforded an opportunity to circumvent the obstacles in their homopolymerization, which also enriched the variety of chain structures and properties of resultant polymers. In this case, the incorporation of *γ*BL or its derivatives could even be performed at mild temperatures. However, challenges still remain in this field, such as polymerization of *γ*BL at ambient temperature, enhancement of the selectivity of polymerization over side reactions (*e.g.*, back-biting), and more precise control of the molar masses and thermal/mechanical properties of the resulting materials. Again, the dual catalytic approach seems to be a method to develop further if the polymerization control is expected.

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