

# Ring-opening polymerization of $\gamma$ -butyrolactone and its derivatives: A review

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*Dedicated to the memory of our colleague and good friend Prof. Andrzej Duda*

**Abstract:**  $\gamma$ -Butyrolactone ( $\gamma$ -BL) derivatives are reviewed from the point of view of their ability to form polymers by ring-opening polymerization. The thermodynamic limitations for polymerization of  $\gamma$ -BL are discussed. Polymerizability of naturally available unsaturated and synthetic functional  $\gamma$ -BL derivatives enabling postfunctionalization of final polyesters is presented. Homopolymerization of  $\gamma$ -BL derivatives with significant effect of the substituent on the  $\gamma$ -BL ring strain is shown.

**Keywords:** ring-opening polymerization,  $\gamma$ -butyrolactone,  $\gamma$ -butyrolactone derivatives, thermodynamic limitations, homopolymerization of  $\gamma$ -butyrolactone.

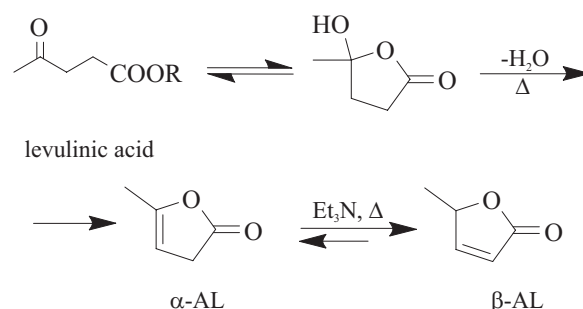
## Polimeryzacja z otwarciem pierścienia $\gamma$ -butyrolaktonu i jego pochodnych

**Streszczenie:** W artykule o charakterze przeglądu literatury przedstawiono możliwości syntezy polimerów  $\gamma$ -butyrolaktonu ( $\gamma$ -BL) i jego pochodnych w reakcjach polimeryzacji z otwarciem pierścienia. Omówiono ograniczenia termodynamiczne dla polimeryzacji  $\gamma$ -BL. Scharakteryzowano zdolność do polimeryzacji naturalnych nienasyconych oraz syntetycznych pochodnych  $\gamma$ -BL zawierających grupy funkcyjne umożliwiające post-funkcjonalizację zsyntetyzowanych poliestrów. Omówiono homopolimeryzację pochodnych  $\gamma$ -BL z istotnym wpływem podstawnika na naprężenie pierścienia.

**Słowa kluczowe:** polimeryzacja z otwarciem pierścienia,  $\gamma$ -butyrolakton, pochodne  $\gamma$ -butyrolaktonu, ograniczenia termodynamiczne, homopolimeryzacja  $\gamma$ -butyrolaktonu.

The great interest in the application of aliphatic polyesters comes from their biocompatibility and biodegradability [1]. Ring-opening polymerization (ROP) of cyclic lactones is well known reaction for production of such polyesters [2]. In addition, copolymerization with functional monomers enables these polymers to be fine-tuned towards a specific applications. The five-membered  $\gamma$ -butyrolactone ( $\gamma$ -BL) and some of its derivatives would also be a desirable bio-derived monomers for the chemical synthesis of biopolyesters. Nakayama *et al.* [3] and Xi *et al.* [4] showed that incorporation of  $\gamma$ -BL units into polyesters resulted in both enhanced biodegradability and flexibility. The reason can be ascribed to the lower crystalline degree of copolymers after incorporation of non-crystallizable  $\gamma$ -BL monomer into polymer chain and faster infiltration of water molecules into the internal structure of copolymers [5]. The renaissance of employing monomers with  $\gamma$ -butyrolactone ring in their structure for production of polyesters allow using the monomers from renewable resources such as:  $\alpha$ -methylene- $\gamma$ -butyro-

lactone (MBL),  $\beta$ -hydroxy- $\alpha$ -methylene- $\gamma$ -butyrolactone,  $\beta$ - and  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone ( $\beta$ -MMBL,  $\gamma$ -MMBL) and angelica lactones ( $\alpha$ - and  $\beta$ -AL). While MBL can be isolated from the tulips, MMBL and angelica lactones can be derived from itaconic or levulinic acids available from biomass feed stock. Synthesis of angelica lactones from levulinic acid is shown on Scheme A [6–9]. The advantage of these monomers is in enhanced functionality of the final polyesters bearing double bond or other substituents allowing for various functionalizations or employing combination with other polymerization technique for production of desired materials.



Scheme A

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In this paper we summarize some recent attempts toward ring-opening polymerization of five-membered  $\gamma$ -BL monomer. Additionally, its functional derivatives bearing double bond in- or outside the lactone ring or bromo-substituent is iterative functionality enhancing their application as building blocks for polymers with various topology or carriers for active biomolecules. Some of these  $\gamma$ -BLs were recently used for preparation of copolyesters by ROP approach what is reviewed in more details in this article.

## RING-OPENING COPOLYMERIZATION OF $\gamma$ -BUTYROLACTONE

### Kinetics and thermodynamic aspects $\gamma$ -butyrolactone polymerization

$\gamma$ -Butyrolactone monomer is known as non- (better said hardly) polymerizable monomer to produce polyester PBL. The problem is explained by high stability (low ring strain energy) giving positive enthalpy of polymerization ( $\Delta H_p$ ) (Table 1). Together with negative entropic factor coming from the fact, that polymerization of most of the monomers is accompanied by an entropy decrease ( $\Delta S_p$ ), the free Gibb's energy ( $\Delta G_p$ ) of the reaction in equation (1) is positive for  $\gamma$ -BL, thus the polymerization is thermodynamically forbidden.

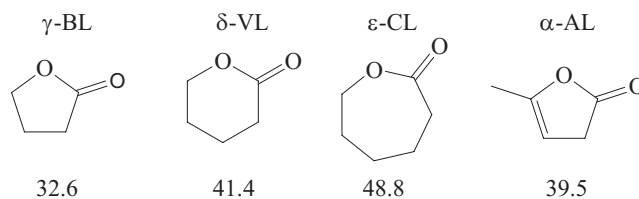
$$\Delta G_p = \Delta H_p - T\Delta S_p \quad (1)$$

where  $T$  – temperature (in K).

Indeed, for  $\gamma$ -BL the equilibrium concentration  $[BL]_{eq}$  is equal to  $\sim 3 \cdot 10^2$  mol/dm<sup>3</sup>, whereas the monomer concentration in bulk is 13 mol/dm<sup>3</sup>. This explanation is actually repeated in all works related to copolymerization of  $\gamma$ -BL monomer and its derivatives and was nicely summarized in Duda and Penczek [2] review. Very recently Olsen *et al.* [10] applied thermodynamically defined “ceiling” temperature  $T_c$ , which is independent of the catalytic system employed, but dependent on concentration. Hence, a pre-selected  $T_c$  value will act as an independent way to describe each monomer's relation (Table 1).

Changing the substituents on the  $\gamma$ -BL ring can give a chance to obtain negative  $\Delta H_p$  in the case of polymerization of  $\gamma$ -BL derivatives. The example can be higher strain ring energy of  $\alpha$ -angelica lactone ( $\alpha$ -AL), which has this value closer to polymerizable  $\delta$ -valerolactone ( $\delta$ -VL) as to

parent  $\gamma$ -BL. Strain energies (CBS-Q, kJ/mol) calculated for different lactones are presented in Scheme B [11].



Scheme B

### Homopolymerization of $\gamma$ -butyrolactone

Whereas  $\gamma$ -BL is not able to give high molar mass homopolymer under normal condition, it is incorrectly identified with an inability to undergo the ring-opening at all. There are ring-opening reactions that are not driven exclusively by ring strain as for example basic hydrolysis, which has comparable rate constant with  $\epsilon$ -CL [12]. Duda *et al.* [13, 14] showed, that concentration term contribution may outweigh a sum of enthalpic and entropic contributions and gives negative  $\Delta G_p$ , and published formation of poly(butyrolactone) (PBL) oligomers up to 10 units using aluminium *tris-isopropoxide* trimer catalyst  $[Al(OiPr)_3-A_3]$ . Continuing research led to successful polymerization of  $\gamma$ -BL using very active catalyst and performing the polymerization at lower temperature ( $-40$  °C) presented recently by Hong and Chen [15, 16]. Employing of lanthanide or yttrium complexes or metal free phosphazene base organo-catalyst they reported ROP of  $\gamma$ -BL proceeding smoothly to high conversions (90 %) under ambient pressure producing PBL with number average molecular weight  $\bar{M}_n$  up to 30 kg/mol and with controlled linear and/or cyclic topologies. From industrial point of view an interesting catalyst could be mesoporous zeolites or montmorillonite clays possessing various metal atoms in its structure which could act as coordinating centers and exhibit high surface area. Relatively high catalytic conversion of the monomer (*e.g.* 56 % yield) of PBL with  $\bar{M}_n \sim 1000$  g/mol [17] was presented. To circumvent thermodynamic rules valid for  $\gamma$ -BL polymerization, high molecular weight PBL were prepared by using ultra-high pressure [18] or extremely low reaction temperature [15]. It is also worth to note that high molecular weight PBL has been made using microbes achieving polymer with  $\bar{M}_n \sim 10^6$  g/mol [19].

**Table 1.** Thermodynamic parameters of polymerization at 20 °C for selected lactones [2]

Name of lactone	L,L-LA	$\epsilon$ -CL	GL	$\delta$ -VL	$\gamma$ -BL	$\beta$ -BL
Ring size	6	7	6	6	5	4
$\Delta H_p$ , kJ/mol	-22.9	-28.8	-34.0	-27.4	5.1	-74.4
$\Delta S_p^0$ , J/mol·K	-25.0	-53.9	-6.3	-65.0	-29.9	-51.0
$[M]_{eq}$	$1 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$2.3 \cdot 10^{-6}$	$3.9 \cdot 10^{-2}$	$2.9 \cdot 10^2$	$1 \cdot 10^{-3}$

L,L-LA – L,L-dilactide,  $\epsilon$ -CL –  $\epsilon$ -caprolactone, GL – glycolide,  $\delta$ -VL –  $\delta$ -valerolactone,  $\gamma$ -BL –  $\gamma$ -butyrolactone,  $\beta$ -BL –  $\beta$ -butyrolactone,  $\Delta H_p$  – enthalpy of polymerization,  $\Delta S_p^0$  – entropy of polymerization,  $[M]_{eq}$  – monomer concentration at equilibrium.

## Copolymerization of $\gamma$ -butyrolactone

Naturally, to force the  $\gamma$ -butyrolactone ring accessible for ROP, researchers adopt the strategy to copolymerize it with other lactones with high ring strain energy. The system of mixture of  $\gamma$ -BL with four-membered  $\beta$ -propiolactone ( $\beta$ -PL), seven-membered  $\epsilon$ -caprolactone ( $\epsilon$ -CL) or six-membered dilactide (L,L-LA) decreases the overall enthalpy  $\Delta H_p$  enough to overcome the positive contribution of  $T\Delta S_p$  to obtain negative total free Gibbs energy of polymerization ( $\Delta G_p < 0$ ). Although the literature presents number of examples, in this short review we will summarize only several of them from the point of view of total amount of  $\gamma$ -BL incorporated in polyester chain and molar masses obtained for various comonomers and catalytic systems (Table 2).

Relatively less successful were attempts employing lactide [20] and glycolide [21] as comonomers. More successful were those employed coordination-insertion mechanism of ROP using metal alkoxides or alkyls and strong acid as catalyst and monomers such as  $\epsilon$ -CL [13, 22, 23],  $\beta$ -PL [24] and  $\beta$ -BL [25, 26]. The most studied was copolymerization with  $\epsilon$ -CL, where authors precisely described kinetics for particular catalytic systems and mechanisms. For such reasons shorter polymers with control over molecular weight rather than higher molecular weight copolyesters were prepared. On the other hand, various

composition ratio of comonomers can be established in dependence on feed ratio. An application of most active catalyst led to the tailoring of composition ratio as well as to high molecular weight polyesters, what is interesting also from application point of view.

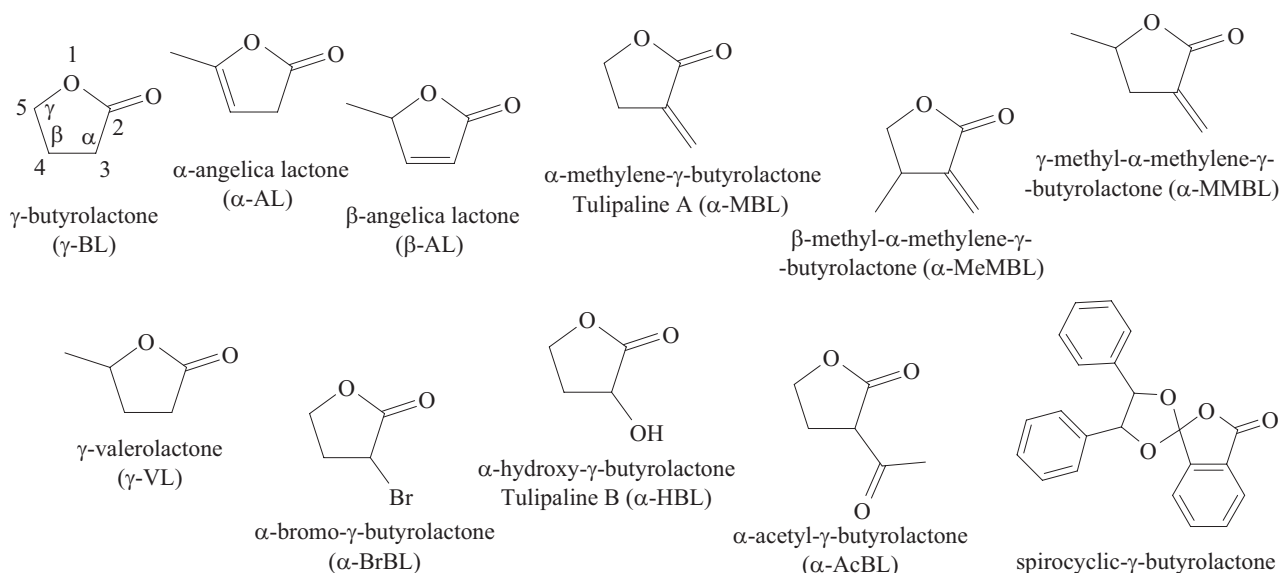
## RING-OPENING COPOLYMERIZATION OF $\gamma$ -BUTYROLACTONE DERIVATIVES

Due to increased interest in polymers from renewable resources, in recent years increased also the amount of articles studied polymerizations of  $\gamma$ -butyrolactone derivatives. Angelica lactones ( $\alpha$ - and  $\beta$ -) were distinguished by the location of the endocyclic double bond and chemical properties. On the other hand, MBL,  $\alpha$ -MMBL, and  $\alpha$ -MeMBL monomers have an exocyclic double bond in  $\alpha$ - position, but unlike MBL, the MMBLs have also a methyl group. Due to structure similarity of either MBL or MMBL with acrylates and ALs with vinyl acetates, these monomers offer also possibility of radical polymerization. While number of publications describe free or controlled radical, cationic and anionic polymerizations *via* double bond [selected examples: 27–31], these approaches are not the aim of this review. List of  $\gamma$ -butyrolactone monomers copolymerized using ROP ( $\gamma$ -BL,  $\alpha$ -AL,  $\alpha$ -MBL,  $\gamma$ -VL,  $\alpha$ -BrBL,  $\alpha$ -AcBL, spirocyclic  $\gamma$ -butyrolactone) and potential functional monomers for

**Table 2.** Examples of  $\gamma$ -BL copolymers obtained by ROP with various comonomers

Comonomer	Catalytic system	Reaction conditions	mol % of $\gamma$ -BL in copolymer	$\bar{M}_n$ or $\bar{M}_w \cdot 10^3$ g/mol (D)	Reference
L,L-LA	–	200 °C	19	2	[20]
GL	AlEt <sub>3</sub> /H <sub>2</sub> O	DCM, 0 °C	30	yield 3 % low $\bar{M}_w$	[21]
$\epsilon$ -CL	La[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	toluene, 25 °C	42	20.6 (1.55)	[46]
		bulk, 25 °C	51	21.0 (1.62)	
		toluene, -20 °C	53.8	75.7 (1.92)	
	Al(OiPr) <sub>3</sub> -A <sub>3</sub>	toluene, 20 °C	11	9 (1.18)	[13], [21]
		bulk, 60 °C	43	10 (1.22)	
		HAPEN-Al-OiPr	DCM, r.t.	26	NA
	Li [diisopropyl amide]	dioxane, r.t.	26	NA	
	Sn(Oct) <sub>2</sub> /ethanolamine	toluene, 110 °C	16	NA	
$\beta$ -PL	FeCl <sub>3</sub> · BF <sub>3</sub>	NA	25	yield 42 % no $\bar{M}_w$	[24]
$\beta$ -BL	BF <sub>3</sub> · OEt <sub>2</sub>	r.t., 4 weeks	56	3–5 (1.3–1.8)	[25]
	1-ethoxy-3-chlorotetrabutylidistannoxane	100 °C, 4 h	6–24	60–100	[26]

L,L-LA – L,L-dilactide, GL – glycolide,  $\epsilon$ -CL –  $\epsilon$ -caprolactone,  $\beta$ -PL –  $\beta$ -propiolactone,  $\beta$ -BL –  $\beta$ -butyrolactone, r.t. – room temperature, NA – not analyzed, DCM – dichloromethane, HAPEN-Al-OiPr – aluminium Schiff's base complex.



Scheme C

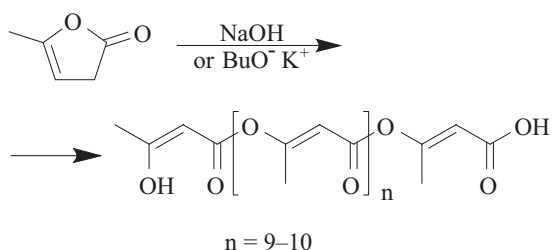
ROP ( $\beta$ -AL,  $\alpha$ -MeMBL,  $\alpha$ -MMBL,  $\alpha$ -HBL) are presented in Scheme C.

From derivatives studied recently by various polymerization techniques and/or possessing interesting functional groups (Scheme C), only seven were investigated for preparation of functional polyesters using ROP approach.

### Polymers from angelica lactones

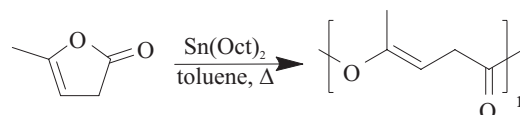
Anionic ROP of  $\alpha$ -angelica lactone [5-methyl-2(3H)-furan-1-one] (Scheme D) was conducted by Tabarko *et al.* [32] in the presence of sodium hydroxide at  $T \sim 290$  K for 210 hours. Oligomers with molecular weight of 893 g/mol and dispersity of 1.05 were obtained under described conditions. The same authors studied also the polymerization of  $\alpha$ -angelica lactone using solution of 5 mol % sodium butyrate as an initiator (Scheme D) at  $T \sim 395$  K. After 238 hours the molecular weight of the polymer reached value 1072 g/mol and dispersity 1.8. Moreover an increase of molecular weight with decrease of initiator concentration from 5 mol % of BuOH down to 3 mol % was observed. Even though polyesters of  $\alpha$ -angelica lactone were obtained by using these catalytic systems, only polymers with low polymerization degrees up to 20 monomer units were prepared under described reaction conditions.

Recently Chen *et al.* [11] described ROP with coordination-insertion mechanism of  $\alpha$ -angelica lactone using tin



Scheme D

octoate [ $\text{Sn}(\text{Oct})_2$ , tin(II) 2-ethyl-hexanoate] as an catalyst (Scheme E). Most probably the initiating species in this system were traces of water. Unexpectedly polymer with molecular weight up to 30 kg/mol were obtained using this initiator at  $T = 130$  °C. Conversion 85.6 % of  $\alpha$ -AL was reached after 50 hours and no further increase of conversion was observed after prolonged time. The polymerization probably achieved an equilibrium state, as typically observed also for ROP of other lactones [33].



Scheme E

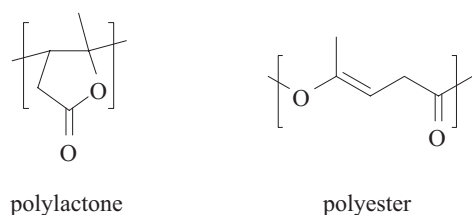
Values of  $\bar{M}_n$  and dispersity  $D$  of polyester were independent on monomer/initiator ratio ( $[\text{M}]_0/[\text{Sn}]_0$ ). The polymerization rate decreased with decrease of temperature and the polymerization did not take place below 80 °C. The values of  $\bar{M}_n$  and  $D$  of final polymer were dependent on the reaction time. At the beginning a growth of molecular weight with reaction time was observed and after 30 hours, the molecular weight reached a maximum and then decreased with prolonged polymerization, while the  $D$  increased from 1.09 up to 1.57 with the polymerization time. Here, the reduction of molecular weight and expansion of  $D$  with the reaction time could be explained by transesterification reactions [34, 35].

Homo- and copolymerization of  $\alpha$ -AL with  $\epsilon$ -CL under the same coordination-insertion mechanism using tin octoate was described recently by Xi *et al.* [4]. Polymerization at 130 °C for 30 hours give homo-polyangelica lactone (PAL) and copolymers P(AL-co-CL) with  $\bar{M}_n \sim 5000$ –7000 g/mol and  $D$  of 1.2–1.33. These  $\bar{M}_n$  were almost 4–5 times lower as that obtained for pure  $\epsilon$ -CL polymerization at relatively high yields (55–75 %) suggesting lower reactivity of  $\alpha$ -AL and chain transfer to the poly-



mer by transesterification, which results in some oligomers. However, the ratio of monomer units PAL/PCL in copolymer (1/1.1 and 1/2.3) were only slightly lower as in feed ratio (1/1 and 1/2, respectively). Prepared polyesters were characterized by thermal analyses as DSC and TGA and degradation (hydrolysis) in model environments with various pH. Its overall thermal stability was decreased with increased AL content in copolymer and 5 to 6 times higher degradation rate were observed in comparison with pure PCL.

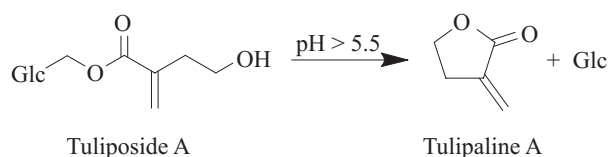
It is worth to mention that also cationic polymerization of  $\alpha$ -AL was carried out by triethyloxonium tetrafluoroborate, boron trifluoride etherate, and stannous tetrachloride at 0 °C [36]. All studied catalysts led to dark semi-solids with low value of molecular weight as determined by pressure osmometry. However, it was found from FTIR spectra, that the polymers prepared by cationic polymerization of  $\alpha$ -angelica lactone contained almost exclusively polylactone structural units produced by polymerization through the vinyl group. Polymers with ring-opened polyester structure were only minor products (Scheme F).



Scheme F

### Polymers from $\alpha$ -methylene- $\gamma$ -butyrolactone

The  $\alpha$ -methylene- $\gamma$ -butyrolactone moiety is a typical component of large number of natural products with wide-range of biological activities such as antitumor, bactericidal, fungicidal, and antibiotic properties [37–39]. The structural moiety  $O=C-C=CH_2$  of MBL derivatives was explained to be responsible for their cytotoxicity by acting as an alkylating agent through a Michael type reaction with bionucleophiles or sulfhydryl-containing enzymes [40]. The substituent in  $\gamma$ - position of lactone ring plays a significant role in pharmaceutical applications. The simplest member of this class,  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL) was first isolated in 1946 from *Erythronium americanum*. Because of its occurrence in various tulips in quite large amount [41], it is known also as a Tulipaline A. In the plants it is mostly present in the form of glycoside – Tuliposide A. This glycoside is hydrolyzed at pH > 5.5 and Tulipaline A is formed after spontaneous lactonization as shown in Scheme G [42].

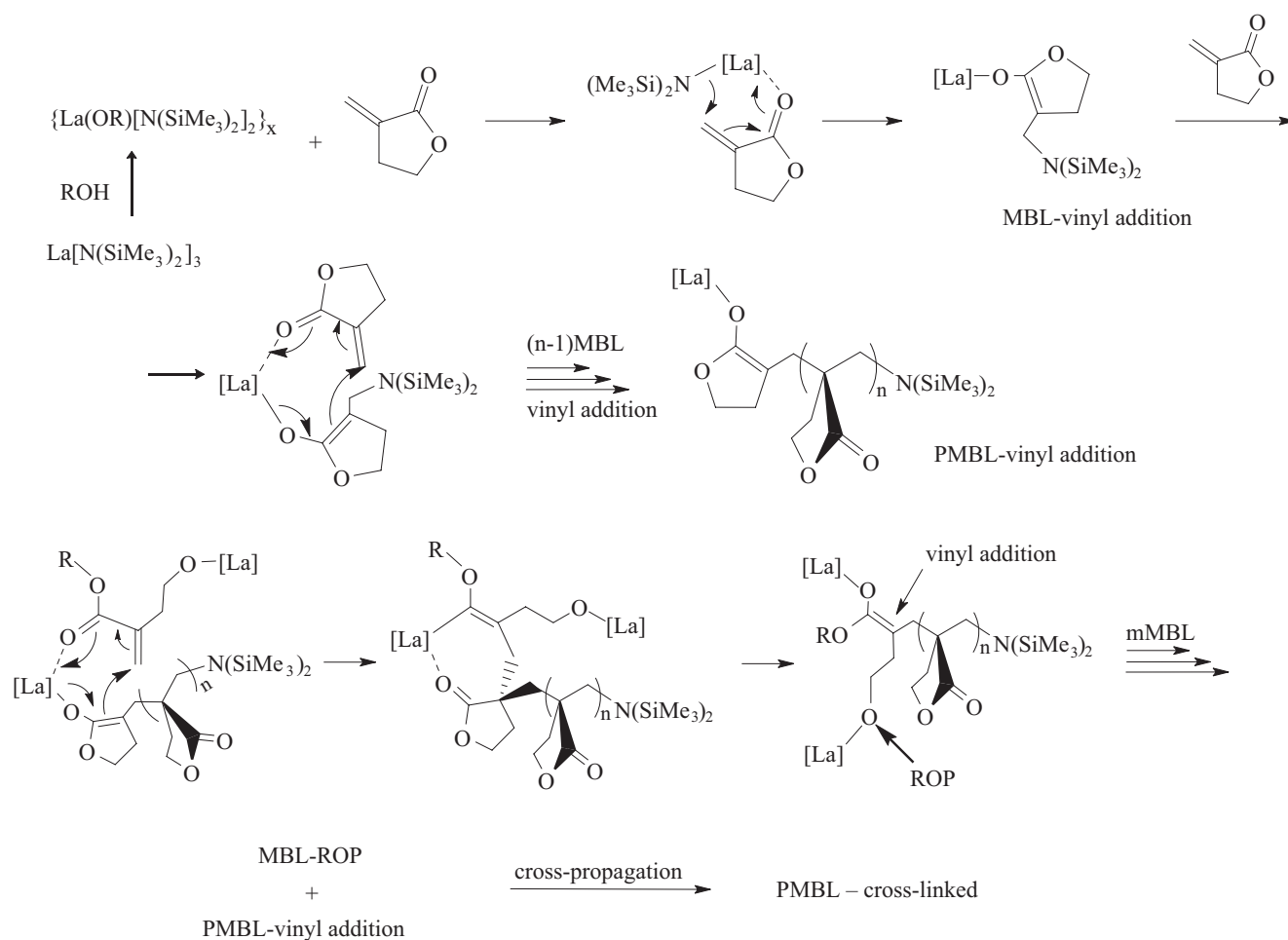


Scheme G

Very recently Tang *et al.* [43] reported the first ROP homopolymerization of MBL producing fully functional polyester. The authors were able to prepare polyester with  $\bar{M}_n$  up to 21 kg/mol and dispersity 1.42 by using of yttrium or lanthanum based catalyst. When the  $La[N(SiMe_3)_2]_3$  was applied in combination with alcohol in the ratio  $La[N(SiMe_3)_2]_3/ROH$  equal to 1/3 at temperature -60 °C, the polymerization proceeded as ROP under coordination-insertion mechanism while the real initiator in the MBL/La/ROH system was La-OR, as product of ligand-exchange reaction. Relatively high monomer concentration and low temperature of polymerization was needed to be used to overcome the thermodynamic requirements of the reaction. The ceiling temperature of MBL monomer  $T_c = -52$  °C for  $[MBL]_0 = 5$  M and  $T_c = -126$  °C for  $[MBL]_0 = 1$  M were determined based on experimentally achieved thermodynamic parameters  $\Delta H_p = -5.9$  kJ/mol and  $\Delta S_p^0 = -40.1$  J/mol·K and equation  $T_c = \Delta H_p / (\Delta S_p^0 + R \cdot \ln[MBL]_0)$ . Interestingly, at La/ROH ratio of 1/2, a cross-propagation through conjugated coordination of the La metal with monomer led to the cross-linked polymer. The cross-linked polymer was also obtained when slightly higher temperature (-40 °C) was used. Contrary that, exclusively PMBL polymer *via* addition of vinyl double bonds was obtain using La/ROH ratio below 1, or using pure  $La[N(SiMe_3)_2]_3$  without addition of any alcohol (Scheme H) [43]. The chemoselectivity of the system controlled by  $La[N(SiMe_3)_2]_3/ROH$  ratio, temperature or concentration may have wide practical applications. Moreover, PMBL polyester can be fully transformed back to its monomer MBL at elevated temperature in the presence of a simple catalyst, thus establishing its complete chemical recyclability.

Copolymerization of MBL with  $\epsilon$ -CL was described up to now in two articles. Zhou *et al.* described studies of copolymerization of MBL with  $\epsilon$ -CL using various catalysts [44]. He described, that ROP of MBL did not proceed when common catalysts such as  $Sn(Oct)_2$ , titanium(IV) *n*-butoxide or Novozym 425 were used. However MBL copolymerized with  $\epsilon$ -CL by using bismuth(III) trifluoromethanesulfonate like metal organic catalysts (Scheme I). Reaction was carried out without solvent at 130 °C and was suggested to proceed *via* coordination-insertion mechanism. However, at highest investigated MBL feed content (CL/MBL = 1) the reaction provided polyester in moderate yield with  $\bar{M}_n \sim 4000$  g/mol but with broad dispersity 2.3 (see Table 3) indicating low control over the molecular characteristics. Similarly for copolymers with higher MBL/CL ratios,  $\bar{M}_n$  values did not exceed 17 kg/mol and the dispersity values did not drop under 1.5. Conversion of  $\epsilon$ -CL was a markedly higher than less reactive MBL under the applied condition.

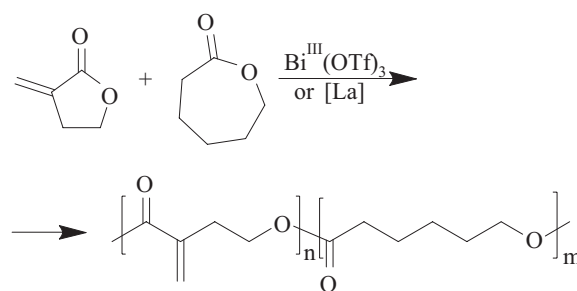
Homopolymer of  $\epsilon$ -CL is known to crystallize at about 55 °C. The crystallization process of prepared copolymer was found to be disturbed by the MBL sequences in the copolymer, because the increasing amount of MBL in result polymer caused shifting of the melting point of the



### Scheme H

copolyester toward lower temperature. Such copolymers are also expected to be subject of faster degradation in biological environment.

ROP copolymerization of MBL with  $\epsilon$ -CL enabled incorporation of double bonds into the polyester chain. Previously unsaturated polyesters were preferentially prepared *via* polycondensation reactions of different diols with either maleic anhydride or itaconic acid [45]. This type of polycondensation usually required exact stoichiometry to achieve high molecular mass polymers. Resultant unsaturated polyesters contained double bonds



### Scheme I

**Table 3. Characteristics of P(MBL-co-CL) copolymers [44]**

Entry	$[\epsilon\text{-CL}]/[\alpha\text{-MBL}]$	$\chi_{CL}^a$	$\bar{M}_n^b$ $10^3$ g/mol	$D$	$T_m^c$ $^{\circ}C$	Yield %
1	1	0.39	4.10	2.3	43.5	40
2	1.5	0.73	6.77	2.6	49.9	58
3	3	0.80	7.25	1.8	51.8	56
4	5	0.95	12.50	1.5	52.3	48
5	20	0.99	16.60	1.5	53.5	68
6	50	0.994	13.70	1.5	53.7	52

<sup>a)</sup> Molar fraction of CL units in the copolymer.

<sup>b)</sup> GPC with poly(styrene) calibration.

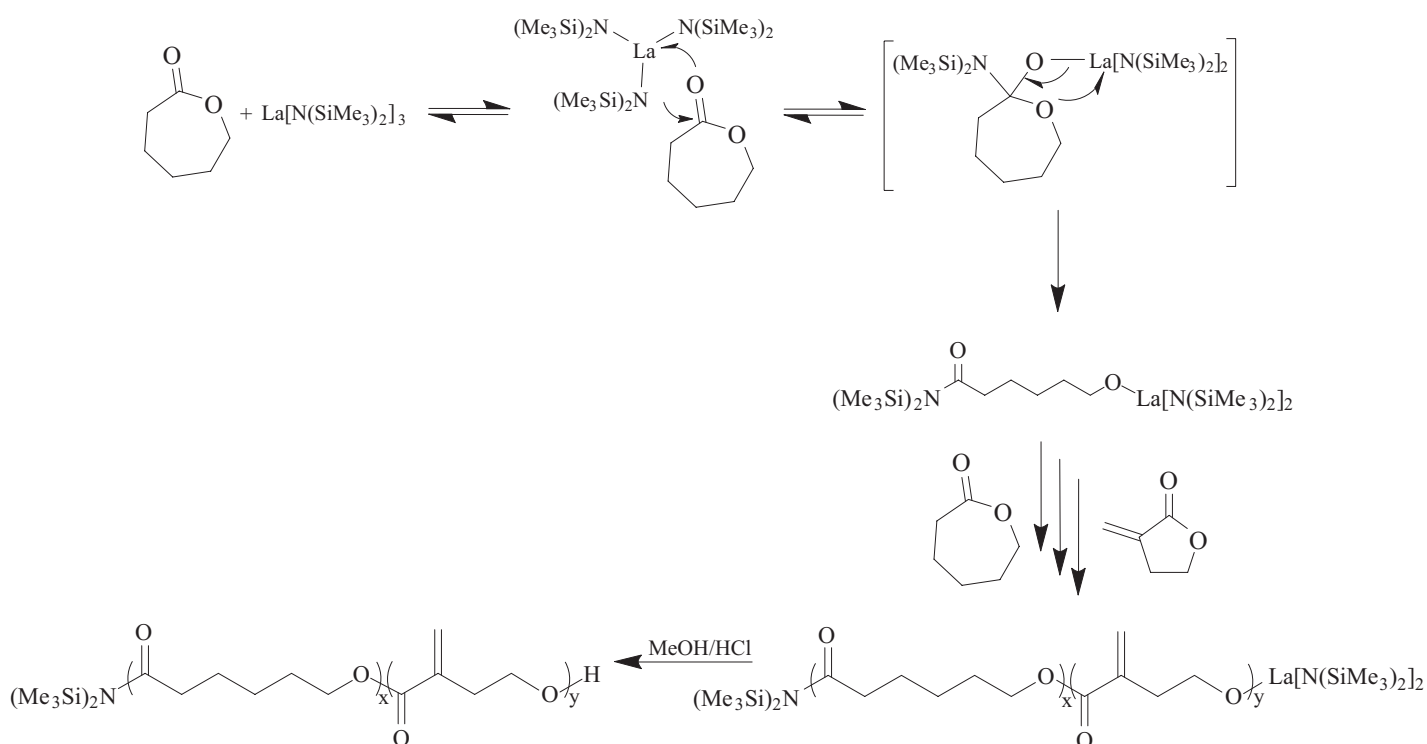
<sup>c)</sup>  $T_m$  – melting temperature, DSC, average of the second and third heating cycle.

that allowed to subsequent copolymerization with vinyl monomers, such as styrene or vinyl ethers. In the work of Zhou *et al.* [44] the *exo*-vinylidene group of incorporated MBL in the P(MBL-*co*-CL) copolyester was subsequently used for cross-linking reactions with methacrylates to yield bicomponent networks with shape memory effect.

Second work describing copolymerization of MBL with  $\epsilon$ -CL used more active lanthanum based catalysts ([La]) suggested as suitable to achieve desired coordination-insertion mechanism and thus controlled ROP [46]. Authors showed that polymerization reaction conditions in the previous work led to the mixture of P(MBL-*co*-CL) copolyester and vinyl-addition (lactone ring-retention) homopolymer PMBL. MBL bifunctionality promotes competing ring-opening and vinyl-addition pathway in the copolymerization. Authors had chosen Ln coordination catalysts – La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (1), Sm[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (2), Nd[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (3), and Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (4) for the study of copolymerization of MBL and  $\epsilon$ -CL, due to the combination of the high Lewis acidity and coordination number of the Ln center (desirable for monomer coordination and activation) and the high nucleophilicity of the ligand (desirable for chain initiation). Suggested mechanism of ROP using [La] catalysts is shown in Scheme J. They obtained exclusively PMBL homopolymer through polymerization of vinyl bonds when pure MBL and [La(1)] catalyst was mixed at 25 °C. Oppositely, in copolymerization approach using the same catalyst and MBL/ $\epsilon$ -CL mixture only ring-opening polyester as product was obtained free of any PMBL homopolymer. Polymerizations were carried out in dichloromethane or toluene in

temperature range -20–130 °C with various MBL/CL ratio. Obtained polyesters had  $\bar{M}_w$  in range 20–90 kg/mol with dispersity not lower than 1.5 showing that system is more active and less selective. Generally, the formation of PMBL through polymerization of vinyl bonds was more pronounced in mixtures with higher MBL/CL feed ratio and at higher temperatures (> 50 °C). However, at MBL/CL molar feed ratio below 5/1, no PMBL was obtained at 25 °C. Additionally, no PMBL was formed at -20 °C even for 10/1 MBL/CL ratio. Interesting was MBL mol % incorporated in copolyester P(MBL-*co*-CL). Lower reactivity of MBL was proved in 1/1 feed ratio where 7.7 mol % of MBL in P(MBL-*co*-CL) was obtained at 25 °C. For 3/1 feed ratio it was 20 mol % while at -20 °C it was 26 mol % showing positive incorporation of MBL with decreasing temperature. In this work the authors discussed and experimentally proved two strategies for decreasing free Gibb's energy of polymerization thus enabling ring-opening of the  $\gamma$ -BL ring in MBL: (a) – copolymerization of MBL with  $\epsilon$ -CL in order to make the overall negative change in  $\Delta H_p$  sufficiently large to offset the positive  $-T\Delta S$  term and (b) – decreasing reaction temperature in order to reduce the positive contribution of the  $-T\Delta S$  term. Achieving higher content of MBL in P(MBL-*co*-CL) at lower polymerization temperature agrees also with proposition of Olsen *et al.* [10] considering the theory of ceiling temperature  $T_c$ .

To summarize this work, authors showed comprehensive set of ROP with MBL and  $\epsilon$ -CL and preparation of functional polyesters with incorporated double bond functionalities along the polymer chain up to 40 mol % what is in average approximately 10 double bonds per



Scheme J

polymer chain. Although copolyesters were characterized by DSC and TGA thermal analysis, further functionalization or chain extension was not performed. Moreover, employment of relatively expensive catalyst and preparation of polyesters in low amount (overall yields were not provided and total amount of polyester did not exceed 0.5 g) more practical applications of this attempt is questionable.

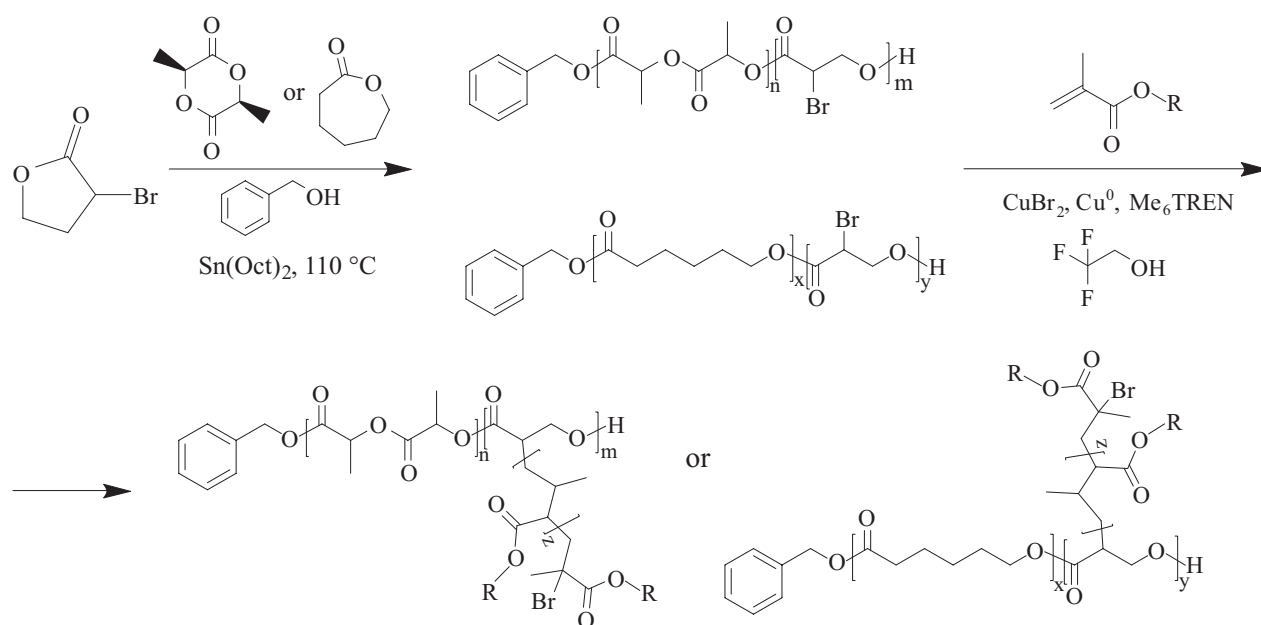
### Polymers from other $\gamma$ -butyrolactone derivatives

Advantage of the above presented functional butyrolactone monomers lay in the possibility to obtain them from renewable resources. On the other hand the synthetic strategies to prepare functional monomers appropriate for ring-opening polymerization are basically infinite. Admittedly, limiting factors for applicability of such synthetic monomers could be multistep synthetic route and low yield. Hence, inexpensive and straightforward synthesis of comonomer is a key item to produce desired functional polyesters. Such a monomer could be  $\alpha$ -bromo- $\gamma$ -butyrolactone ( $\alpha$ -BrBL) which was recently used by Olsén *et al.* [47] and Undin *et al.* [48], used directly for combination of ROP prepared polyesters grafted by vinyl polymer chains using single electron-transfer living radical polymerization (SET-LRP).

In the first attempt [47], the copolymerization of  $\alpha$ -BrBL was described with two of the most commonly used cyclic ester monomers,  $\epsilon$ -CL and L,L-LA, under coordination-insertion mechanism of ROP using tin octoate as the catalyst. Polymerizations were carried out at 110 °C in bulk using benzyl alcohol as initiating nucleophile. Maximum incorporated  $\alpha$ -BrBL into the polyester chains was confirmed by NMR and was 12 and 8 mol % for copolymerization with  $\epsilon$ -CL and L,L-LA, respectively. With higher feed ratio, more  $\alpha$ -BrBL was incorporated into the polymer chain, but with

lower overall  $\alpha$ -BrBL conversion. The copolymerization parameter  $r_1 = k_{11} / k_{12}$  (calculated using the Fineman and Ross method) was determined to be 18.5 and 4.4 for L,L-LA and  $\epsilon$ -CL, respectively, whereas the  $r_2 = k_{22} / k_{21}$  (for  $\alpha$ -BrBL) was close to zero in the case of both comonomers. Since the trial to homopolymerize  $\alpha$ -BrBL under the same condition was reported as unsuccessful, the low  $r_2$  parameter means very low probability of reaction of  $\alpha$ -BrBL\* active chain-end with  $\alpha$ -BrBL monomer. The topology of the copolymers was verified by  $^{13}\text{C}$  NMR showing isolated  $\alpha$ -BrBL units along the chain. Generally, the prepared P( $\alpha$ -BrBL-co-LA) copolyesters having  $\bar{D}$  in the range of 1.2–1.3 exhibited higher degree of control as those P( $\alpha$ -BrBL-co-CL) having  $\bar{D}$  in the range of 1.6–1.7. Prolongation of the reaction time led to the decreasing of  $\bar{M}_n$  due to the transesterification but also to the reduction of the incorporated  $\alpha$ -BrBL amount. This observation was explained as a consequence of  $\alpha$ -BrBL being more easily transesterified than CL or LA units, resulting in chain-ends of  $\alpha$ -BrBL unit that, for thermodynamic reasons, produce the monomeric  $\alpha$ -BrBL unit by ring-closure, thus reducing the amount of  $\alpha$ -BrBL units in the copolymer. In summary, isolated  $\alpha$ -BrBL along the degradable polyester chain was showed to provide an excellent sites for subsequent SET-LRP proved by successful preparation of set of grafted copolymers with vinyl monomers such as methyl methacrylate, *n*-butyl acrylate and 2-hydroxyethyl methacrylate. Ring-opening copolymerization of  $\alpha$ -bromo- $\gamma$ -butyrolactone with various lactones and subsequent reversible deactivation radical copolymerization with methacrylates is shown in Scheme K.

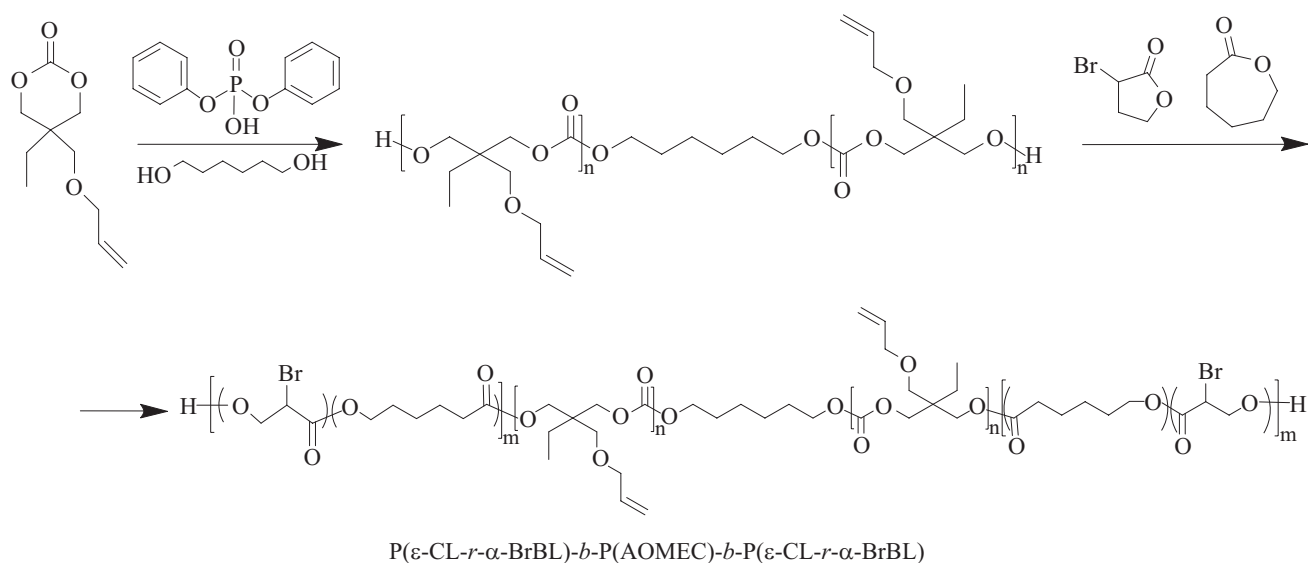
$\alpha$ -BrBL monomer was also copolymerized with  $\epsilon$ -CL and trimethylene carbonates (TMC) using various organocatalysts [48]. This attempt was employed to obtain polyester macroinitiators with better control on molecular weight and narrower dispersity. Frequently used organocatalyst



R = Me, *n*-Bu,  $-\text{CH}_2\text{-CH}_2\text{-OH}$

Scheme K





Scheme L

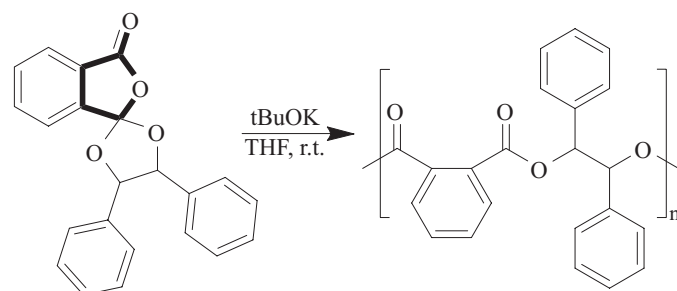
for ROP of lactones as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 4-(dimethylamino)pyridine (DMAP) exhibiting slightly basic character led to an elimination of the bromine moiety at the  $\alpha$ - position, hence removing the monomer's ability for acting as initiator in CRP. Among the used catalyst only diphenyl phosphate (DPP) and Brønsted acid methane sulfonic acid (MSA) provided copolymers of  $\alpha$ -BrBL with  $\epsilon$ -CL and TMC. Polymerizations were carried out at ambient temperature and benzyl alcohol or hexane diol were used as co-initiators. Prepared copolymers had  $\bar{M}_n$  in the range of 20–40 kg/mol and polymerization showed high degree of control expressed by  $\bar{D}$  in the range of 1.08–1.13. The amount of incorporated  $\alpha$ -BrBL in copolymers varied in the range of 5–12 mol % depending on used comonomer for 70/30 initial  $M_1/\alpha$ -BrBL feed ratio. Versatility of this procedure was shown in preparation of ABA triblock copolymer by sequential addition of monomers (Scheme L) still possessing good control over molecular characteristic of copolymer with  $\bar{M}_n \sim 40$  kg/mol and  $\bar{D} = 1.12$  and high control of the block purity. Results indicate the robustness of the copolymerization of  $\alpha$ -BrBL in conjunction with DPP enabling the synthesis of more complex macromolecular structures.

$\alpha$ -Acetyl- $\gamma$ -butyrolactone ( $\alpha$ -AcBL) [49] is an example, how can substitution on the butyrolactone ring affect the reactivity and accessibility of such a monomers for ROP.  $\alpha$ -AcBL was homopolymerized and copolymerized with  $\beta$ -BL in bulk at room temperature using various catalysts, such as boron trifluoride ethyl etherate ( $\text{BF}_3 \cdot \text{OEt}_2$ ),  $\text{Al}(\text{O}i\text{Pr})_3$  and tin chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ). While no polymer was observed employing  $\text{Al}(\text{O}i\text{Pr})_3$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , the polymerization was successful using  $\text{BF}_3 \cdot \text{OEt}_2$  as a catalyst. It is pertinent to note, that polymerization time was 4 weeks, but the yields of polymers were rather high 50–80 %. Formed polymers exhibited unimodal GPC traces and  $\bar{M}_w \sim 1\text{--}2 \cdot 10^3$  g/mol and  $\bar{D}$  in the range of 1.2–1.7. The reactivity of  $\alpha$ -AcBL was slightly lower as for  $\beta$ -BL, which was

confirmed by NMR analysis of copolymers. It was shown, that when the feed ratio of  $\alpha$ -AcBL/ $\beta$ -BL increased from 20 % to 80 %, the ratio of  $\alpha$ -AcBL/ $\beta$ -BL units in the copolymer increased from 9 % to 74 %.

Ability to ROP using the same catalyst for five-membered lactone was shown by Lee *et al.* [50]. In this case,  $\gamma$ -valerolactone ( $\gamma$ -VL) was the non-functional monomer copolymerized with  $\beta$ -BL. This work was extended for other strong acid catalyst namely triflic acid (trifluoromethanesulfonic acid,  $\text{CF}_3\text{SO}_3\text{H}$ ), methyl trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_3\text{CH}_3$ ) and trifluoromethanesulfonic anhydride [ $(\text{CF}_3\text{SO}_3)_2\text{O}$ ]. Obtained polyesters similarly as for  $\alpha$ -AcBL had  $\bar{M}_n$  in range 2–4 kg/mol with  $\bar{D}$  in range 1.5–1.7. The best result from the point of view of incorporated amount of  $\gamma$ -VL was obtained for  $\gamma$ -VL/ $\beta$ -BL ratio 1/3 and was 27 mol % using 2 mol % of catalyst with good yield 82 % of polyester. In the last two presented works, the cationic mechanism of ring-opening was considered.

Although ROP of simple  $\gamma$ -butyrolactone and above mentioned rather simple derivatives to the higher polymerization degree is still challenge, more complicated derivatives bearing  $\gamma$ -butyrolactone ring can be successfully homopolymerized to produce corresponding polyesters. This is most probably due to positive changes of thermodynamic parameters of lactone ring in designed butyrolactone derivatives. The example of first successful anionic ROP of spirocyclic butyrolactone (Scheme M) us-



Scheme M

ing *tert*-butoxide or methyl-lithium was described by Tadokoro *et al.* [51]. They prepared corresponding polyester with full conversion of monomer and high yield (76–91 %) with GPC/PS standards estimated  $\bar{M}_n \sim 10$  kg/mol and narrow  $D$  of 1.13–1.14. However, this monomer does not possess additional functionality for further derivatization as those presented in previous section.

## CONCLUSIONS

Regardless low ring strain energy of five-membered  $\gamma$ -BL and positive free Gibb's energy during its polymerization, there are still systems enabling its homopolymerization, involving extremely low polymerization temperature, ultra-high pressure and/or highly active catalysts. More accessible is copolymerization of  $\gamma$ -BL derivatives with other lactones. The ring strain of  $\gamma$ -BL can be also increased by substitution at the ring thus leading to easier incorporation of  $\gamma$ -BL units into the polymer chains. Therefore, homopolymers of angelica lactone and acetyl  $\gamma$ -BL were obtained under relatively mild conditions. On the other hand, precise investigation of the system and determination of the ceiling temperature for the particular monomer and condition is helping to offset the thermodynamic restrictions and to produce polyesters in a predicted way. Incorporation of  $\gamma$ -BL units into the polyester chain affects the properties of the polyesters. The polyesters have lower crystallinity and thus higher flexibility and show faster degradability. Moreover, incorporation of substituted  $\gamma$ -BL can provide polyesters with various functional groups available for post-functionalization reactions thus allowing preparations of materials with more complex structures and/or increasing potential of the applicability of the polyesters in biomedicine.

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