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# Ring-opening copolymerization of $\alpha$ -hydroxy- $\gamma$ -butyrolactone and $\epsilon$ -caprolactone. Towards the metal-free synthesis of functional polyesters

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## Abstract

Organocatalysis has been widely developed over the last decades as an alternative to metal-based catalysis. The actual concerns have also promoted the development of sustainable and degradable polymers. In this context,  $\gamma$ -lactones are an interesting class of monomers which counts many bio-based monomers yielding polyesters that can be readily depolymerized. Also, the use of functional substituted lactones such as the  $\alpha$ -hydroxy- $\gamma$ -butyrolactone (HBL) afford polyesters with pendant groups offering possible post-modification reactions. This article focuses on the ring-opening copolymerization (ROCP) of  $\alpha$ -hydroxy- $\gamma$ -butyrolactone (HBL) and  $\epsilon$ -caprolactone ( $\epsilon$ -CL) in the presence of phosphazene  $P_4$  base (*tert*-BuP<sub>4</sub>) as catalyst. The bulk copolymerization at high temperature (80°C) yielded fast kinetics (5 min) and high monomer conversions (98% for  $\epsilon$ -CL; 88% for HBL) and molar masses (14 900g/mol with  $D=3.8$ ). Kinetics study at 80°C revealed a partial HBL depolymerisation over time. This phenomenon induced changes in the microstructure of the copolymers. Similar high conversions and molar masses could be also achieved at room temperature in 6h without any depolymerization. Various monomer feed ratios were also evaluated affording copolyesters with up to 31% of incorporated HBL. In addition, DFT calculations with respect to the HBL homopolymerization, revealed similar activation energies between different possible reactions, which include ring-opening polymerization, branching and backbiting reactions.

## Keywords

Anionic ring-opening (co)polymerization, organocatalysis,  $\alpha$ -hydroxy- $\gamma$ -butyrolactone, functional polyesters, sustainable polymers.

## Introduction

In the last decades, the current issues have prompted the scientific community to look for more sustainable polymer syntheses. With this objective, various catalysts were developed for polymerization purposes, especially for the ring-opening polymerization (ROP) of cyclic esters and ethers.<sup>1,2</sup> However, the presence of metal residues in synthetic polymers can limit their use in several areas such as food packaging, biomedicine or microelectronic. As an alternative route to metal-based catalysts, the development of organocatalysis appeared as a promising way for ROP.<sup>3-5</sup> Indeed, organocatalysts revealed competitive in regard to metallic ones, offering high reactivities and a good polymerization control for some monomers.

Aliphatic polyesters such as polylactide (PLA) or poly( $\epsilon$ -caprolactone) (PCL) appeared as serious candidates to address the environmental challenges thanks to their degradability.<sup>6-8</sup> A particular class of monomers, the  $\gamma$ -lactones, stands out from other lactones by the ability of the poly( $\gamma$ -butyrolactone) to perform close-loop recycling with the complete depolymerization back to the monomer.<sup>9,10</sup> However, the polymerization of  $\gamma$ -lactones is known to be challenging due to the thermodynamic constraints of these low strain energy monomers.<sup>11-15</sup> For the ROP of  $\gamma$ -lactones, the free energy of polymerization ( $\Delta G_p$ ) is positive under ambient pressure and temperature due to the large negative entropic ( $\Delta S_p$ ) change that cannot be compensated by the too small negative enthalpy of polymerization  $\Delta H_p$ . Working below the ceiling temperature, at low temperature and high monomer concentration with an efficient catalyst (La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>) allowed Chen *et al.* to carry out the homopolymerization of  $\gamma$ -butyrolactone.<sup>16</sup> Following this work, other catalysts have been used for the ROP and ROCP of  $\gamma$ -butyrolactone and its derivatives.<sup>17-20</sup> With the goal to promote metal-free polyesters, a large palette of organocatalysts for the ROP of  $\gamma$ -lactones were

used. Organic bases such as guanidines, phosphazene bases and others, proceeding by a nucleophilic/anionic mechanism, were particularly used for  $\gamma$ -lactones ROP and ROCP.<sup>21–31</sup> More recently, dual-catalytic systems composed of a base and an electrophile (as hydrogen-bond donor, e.g. (thio)urea<sup>32–36</sup>) for both activated chain-end and activated monomer mechanisms were developed for ROP.<sup>37–39</sup> These cooperative systems were also applied in the  $\gamma$ -lactone ROP and ROCP<sup>30,40–45</sup> thanks to their high efficiency in converting monomers and reducing side reactions.

Considering the need to promote sustainable monomers<sup>46–49</sup> to preserve the fossil resources,  $\gamma$ -lactones have the advantage to count various biobased monomers.<sup>50,51</sup> As an example,  $\alpha$ -hydroxy- $\gamma$ -butyrolactone (HBL) is a sugar-based monomer that can be obtained by a biological synthetic route from glucose.<sup>52,53</sup> The peculiarity of this  $\gamma$ -lactone derivative is the presence of a hydroxyl group in  $\alpha$  position of the carbonyl group. Such functional monomers are an interesting class of molecules as the functions they bear can offer post-modification reactions.<sup>54–56</sup> In this way, the properties of the final material can be improved or tailored to the intended application. For the time being, only few studies were conducted on the HBL polymerization,<sup>57–59</sup> which therefore remains to be investigated.

In this study, the use of *tert*-BuP<sub>4</sub> as organocatalyst is investigated for the synthesis of metal-free and functional polyesters by ring-opening copolymerization of HBL and  $\epsilon$ -CL monomers. The characterization of the copolymers and kinetics investigations allowed us to identify the different structural patterns and to elucidate the polymerization mechanism. In parallel, a modelling study was conducted to have a better understanding of the HBL polymerization.

## Experimental section

### Materials

ADISSEO supplied  $\alpha$ -hydroxy- $\gamma$ -butyrolactone (HBL). The monomer was left under dynamic vacuum at 40°C for an entire night and purified through cryo-distillation. For the experiments, only the second fraction was utilized. 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2 $\lambda$ 5,4 $\lambda$ 5-catenadi(phosphazene) (*tert*-BuP<sub>4</sub>, ~0.8

M in hexane) and 1,3-diisopropyl-2-thiourea (TU) were acquired from Sigma-Aldrich. *tert*-BuP<sub>4</sub> was kept into a glovebox and utilized without purification, the solvent was removed prior to use. TU was dried by azeotropic distillation under dry THF 2 times, kept under dynamic vacuum overnight and stored into a glovebox.  $\epsilon$ -Caprolactone ( $\epsilon$ -CL) and benzyl alcohol (BnOH) were acquired from Alfa Aesar. The compounds were vacuum distilled after being dried over CaH<sub>2</sub> overnight. For the solvent, the dehydration of tetrahydrofuran (THF) was carried out first using an alumina column, followed by the distillation of the solvent over Na/benzophenone.

### **General polymerization method(s)**

Polymerizations were conducted in dried glassware and under argon atmosphere. Here is an example for a typical copolymerization with *tert*-BuP<sub>4</sub> as catalyst. Inside a glovebox filled with argon, the catalyst (1 equivalent; 0.021 mmol; 26  $\mu$ L of a 0.8 M in hexane solution) was introduced into a Schlenk tube and closed with a rotaflow stopcock. After being removed from the glovebox, the Schlenk tube was connected to a dual-manifold Schlenk line. Then, the THF (0.15 mL) and BnOH (1 equivalent; 0.021 mmol; 26  $\mu$ L of a 0.8 M in THF solution) were mixed with the catalyst under argon atmosphere and stirred for about 10 min. The monomers (400 equivalents) were added to the reactor containing the blend. HBL (1.92 mmol, 0.15 mL) and  $\epsilon$ -CL (6.39 mmol, 0.71 mL) were mixed prior to addition. The Schlenk tube was closed and immersed in an oil bath heated to a chosen temperature. Finally, the reaction was quenched after a desired period of time by addition of an acetic acid solution (1 mL of a solution at 0.105 mol/L in chloroform). Aliquots of the crude product were taken to determine the conversions and molar masses. The conversion of monomers, copolymer compositions, HBL type units and degree of branching (DB) were determined according to a previous paper.<sup>59</sup> The crude products were precipitated in cold methanol and finally dried under vacuum overnight.

### **Polymerization kinetic studies**

Kinetics of reaction were carried out inside an argon-filled glovebox using flame-dried glassware. The catalyst, initiator and solvent were introduced in a reactor as a first step, and stirred for about 10 min. Then, the monomers were added to the previous blend and the resulting mixture was divided into multiple Schlenk tubes. Finally, the reactors were closed, removed from the glovebox and immersed in oil baths set at 25°C or 80°C. The reactions were quenched after a desired period of time and aliquots or the crude product were taken for analyses.

### **Characterization of the polymers**

Liquid-state  $^1\text{H}$  NMR of the samples were performed to assess the monomer conversions, HBL type units, copolymer compositions, and degree of branching (DB). The measurements were conducted at 298 K in  $\text{CDCl}_3$  on a Bruker Avance 400 spectrometer operating at 400 MHz. The structural characterization was carried out at 298 K in  $\text{CDCl}_3$  using a Bruker Prodigy spectrometer operating at 400 MHz. The samples were analyzed by  $^1\text{H}$  NMR,  $^1\text{H}$ - $^1\text{H}$  COSY NMR,  $^1\text{H}$ - $^1\text{H}$  TOCSY NMR,  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR, and DOSY NMR.

Size exclusion chromatography (SEC) was used to determine the polymer number-average molar masses ( $\overline{Mn}$ ) and dispersities ( $D = \overline{Mw}/\overline{Mn}$ ) of the polymers. The eluent used for the SEC analysis was THF. The measurements were conducted using an Ultimate 3000 system from ThermoScientific which was equipped with diode array detector DAD. A multi-angle laser light scattering detector (MALLS) and a differential refractive index detector dRI from Wyatt technology were also included in the system. At a flowrate of 1 mL/min, the polymers were separated using three G2000, G3000 and G4000 TOSOH HXL gel columns measuring 300 x 7.8 mm, with exclusion limits ranging from 1000 Da to 400 000 Da. The temperature of the columns was set at 40°C and polystyrene served as the reference standard.

To investigate the thermal properties of the copolyesters, differential scanning calorimetry (DSC) measurements were conducted. A DSC Q100 RCS apparatus from TA Instruments was used for the analysis. As a first step, the samples (approximately 5 mg) were heated from -80°C to 100°C at a

rate of 10°C/min. To eliminate any residual solvent, the samples were maintained 2 min at this temperature. Subsequently, a cooling ramp from 100°C to -80°C at a rate of 5°C/min was applied. The samples were equilibrated for 2 minutes, and then reheated to 100°C at a rate of 10°C/min. For the thermograms, the third cycle was kept and used.

### **Computational details**

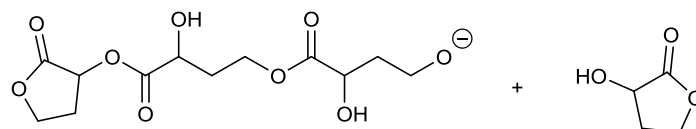
DFT calculations of geometries, energies, and vibrational frequencies reported in this paper were carried out with the M06-2X functional using the 6-311G(d,p) basis set, implemented in the Gaussian 16 package. All frequencies of each structure have also been calculated to verify the presence of a single imaginary frequency for transition states and the absence of imaginary frequency for ground states. To consider entropic effects, the energies mentioned in this study correspond to the Gibbs free energy (G) at 298K.

### **Results and discussion**

Considering the thermodynamic constraints, the polymerization of  $\alpha$ -hydroxy- $\gamma$ -butyrolactone (HBL) using *tert*-BuP<sub>4</sub> alone or with a thiourea (1,3-diisopropyl-2-thiourea, TU) and benzyl alcohol as initiator was performed at high monomer concentration (8M) and low temperature (-40°C). In these conditions, no polymers could be obtained. A higher temperature (80°C) was also checked without success as well.

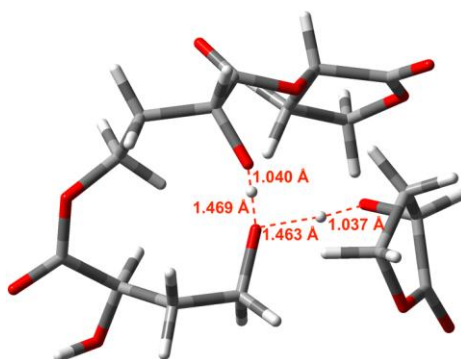
A modelling study was then performed to investigate the HBL reactivity and to identify sticking points in its homopolymerization. To alleviate the computational simulations and facilitate the structural elucidation of the transition states and products formed during the polymerization or depolymerization, all calculations were performed on a model fragment of HBL polymer, namely an oligomer of 3 HBL units in presence of a monomer unit of HBL (all in the R enantiomeric

configuration) (Scheme 1). The oligomer is negatively charged, and the cationic catalyst wasn't taken into account to save significant time of calculations.



*Scheme 1: HBL oligomer and monomer used as reaction model.*

First, a study of the most stable van der Waals complex was carried out and resulted in the structure shown in Figure 1 where the oxygen of the alkoxide undergoes two H-bonds with respectively the hydroxyl group of the HBL monomeric unit (1.463 Å) and with a hydroxyl group internal to the oligomer (1.469 Å). More interestingly, because of these strong H-bonds, the O-H bonds of these 2 hydroxyl groups are elongated, in comparison to an usual O-H bond (1.037 Å and 1.040 Å), suggesting that the primary alkoxide moieties, coexists with its secondary form as well as with the deprotonated HBL monomeric unit (which can initiate new polymerization with surrounding HBL for example).



*Figure 1: Structure of the van der Waals complex.*

From that point and as depicted in Figure 2, several reactions were considered: 'normal' propagation (blue arrows) or branching (green arrows) reactions where the terminal or secondary alkoxide (after hydrogen transfer) respectively attacks the HBL monomer unit, and backbiting



reactions with the formation of a monomer unit of HBL (yellow ochre arrows) or a 10 membered-ring unit, *i.e.* cyclic dimer (red arrows).

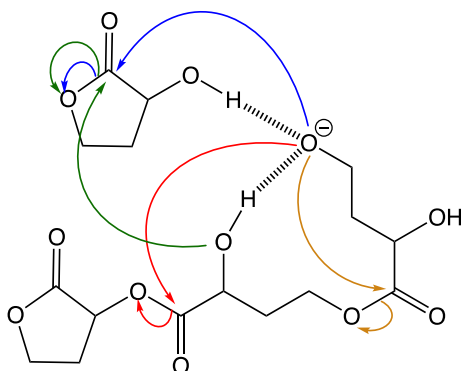


Figure 2: Schematic representation of the considered model reactions.

For all these reactions, the associated transition states are depicted Figure S1 and the barrier height for each pathway is calculated as the difference of the Gibbs free energies of the transition state and the van der Waals complex (Table 1).

Table 1: Activation energy (in  $\text{kJ}\cdot\text{mol}^{-1}$  at 298 K) obtained at the M06-2X/6-311G(d,p) level of calculation.

Model Reactions	$\Delta G^\ddagger$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
Linear polymerization ( $\rightarrow$ )	58.6
Branched polymerization ( $\rightarrow$ )	54.4
Backbiting to monomer ( $\rightarrow$ )	62.7
Backbiting to cyclic dimer ( $\rightarrow$ )	54.4

These DFT calculations show that all the considered reactions have very close and pretty low barrier heights (ranging from 54.4 to 62.7  $\text{kJ}\cdot\text{mol}^{-1}$ ). It should therefore be considered that, given the small difference between these activation energies, such reactions can occur in an almost equiprobable manner or at least that the side reactions strongly compete the polymerization step, explaining the non-ability to get linear poly(HBL).

Calculations on an (R,R,S) oligomer with an I-HBL monomer unit were carried out to ensure that the enantiomeric configuration does not impact the reactivity. It was only performed for the backbiting reaction leading to the formation of the cyclic dimer (*i.e.* the (R,S) cyclic dimer in this

case). The activation energy is calculated at  $62.8 \text{ kJ}\cdot\text{mol}^{-1}$ , slightly higher than the one of the cyclic dimer (R,R) formation ( $54.4 \text{ kJ}\cdot\text{mol}^{-1}$ ) but still within the same amplitude. Thus, the previous conclusions are valid regardless of the enantiomeric configuration of the oligomer and/or of the HBL monomeric units.

Also, the transition state energy for the formation of an 8-membered ring revealed the competitiveness of this pathway (Scheme S1).

The modelling study revealed the competition between the different steps of the HBL homopolymerization which can prevent the formation of polymer chains. Therefore, the random copolymerization with a cyclic monomer of higher strain ( $\epsilon$ -CL) appeared as the best compromise for the synthesis of HBL-based polyesters. Kinetics of the copolymerization between HBL and  $\epsilon$ -CL monomers were performed at  $80^\circ\text{C}$  and  $25^\circ\text{C}$  with benzyl alcohol as initiator and were catalyzed with *tert*-BuP<sub>4</sub>. The reactions were conducted keeping other parameters constant. First, kinetics was performed at  $80^\circ\text{C}$  as high temperatures appeared to be necessary for efficient monomer conversions with the  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$  catalyst published recently.<sup>59</sup>

The monomer conversions and variation of the different HBL structural patterns were followed over time. At  $80^\circ\text{C}$ , the  $\epsilon$ -CL conversion is almost complete after 5 min of reaction and remains constant at  $>98\%$  over 6h of reaction (Figure 3A, solid green lines). On the other hand, the conversion of HBL is also high in the first minutes (85%) and then gradually decreases, to reach a plateau after 3h of reaction (53%). This feature is in agreement with a depolymerization phenomenon with re-formation of the HBL monomer. A decrease of the molar masses (Figure S2 and Table S1) from  $6\,600 \text{ g/mol}$  to  $4\,900 \text{ g/mol}$  and of the dispersity from  $D=5.6$  to  $D=3.8$  is observed. Compared to previous results with a La-based catalyst<sup>59</sup> higher  $\epsilon$ -CL conversions (up to 98%) and molar masses were reached.

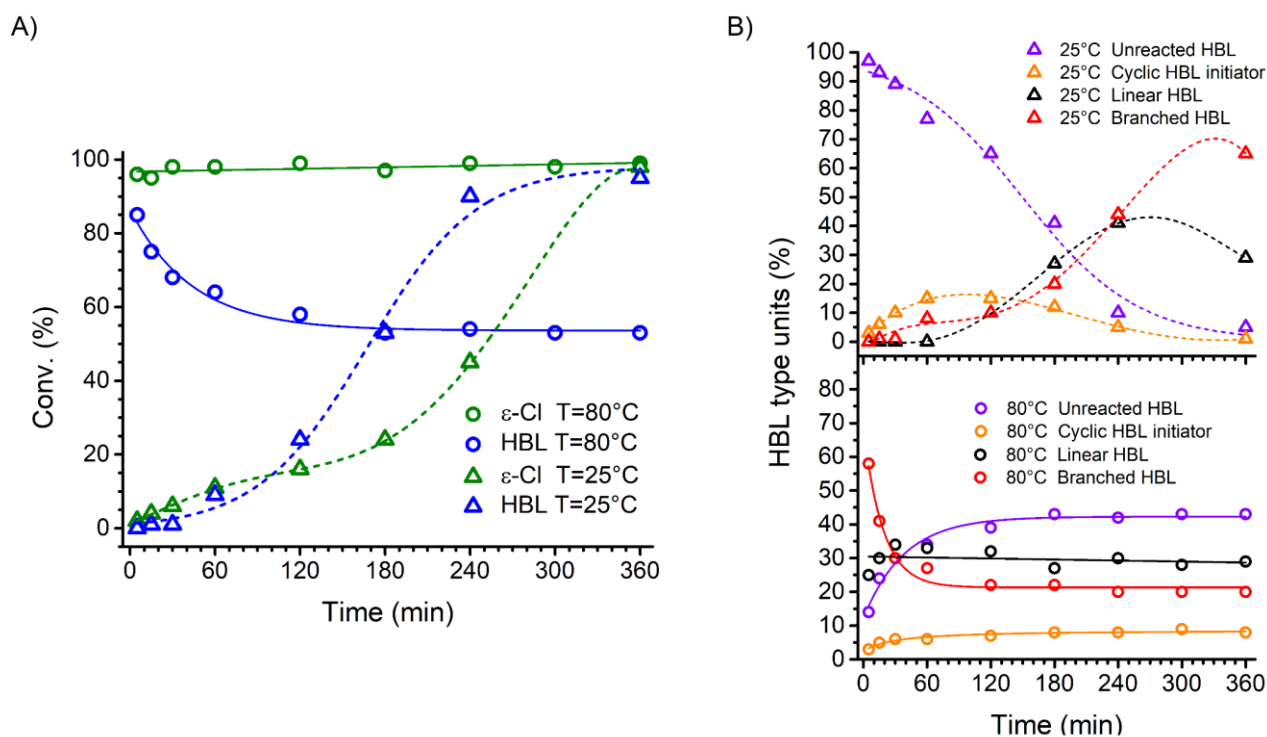


Figure 3: Copolymerization of HBL and  $\epsilon$ -CL (ratio M/C/I = 400/1/1;  $[M1+M2] = 8M$ ; THF;  $\epsilon$ -CL/HBL ratio = 77/23): kinetic studies at 25°C and 80°C. A) Monomer conversions as a function of time. B) Variation of the HBL type units over time.

The microstructure of the so-formed copolymers was analyzed by NMR (Figure 4 + Figure S3-S8). Formation of several HBL type units were revealed. First, as shown on the  $^1H$  NMR spectrum (Figure 4), BnOH and cyclic HBL (orange rectangle, BLO-) chain ends were identified. In both cases, their formation started by the deprotonation of the hydroxyl groups by the base (*tert*-BuP<sub>4</sub>) which generated alkoxides. The BnO- and BLO- termini are thus produced by the initiation step of the alkoxides on the monomers (Scheme 2A and B). Linear HBL units (Figure 4, black rectangle) with a free secondary hydroxyl group are also formed by the ring-opening of the monomer (Scheme 2A). Another linear motive (black rectangle, dash dots) was also considered due to the high reactivity of the secondary alcohol but couldn't be identified. It is assumed that after the ring-opening of HBL, the deprotonation of the secondary alcohol by the base could continue the propagation. Branching units (Figure 4, red rectangle) were also identified on the  $^1H$  NMR spectrum. As the pendant free hydroxyl groups along the backbone can be deprotonated by the base,

the growth of a side chain can be induced by the ring-opening of the monomers (Scheme 2C). Moreover, the macrocycle formation couldn't be evidenced but was still considered, as this phenomenon was well reported for the  $\gamma$ -BL polymerization (Scheme 2D). The single diffusion coefficient observed by the DOSY analysis (Figure S9) of the copolymer testified the effective HBL incorporation into the copolymer chains.

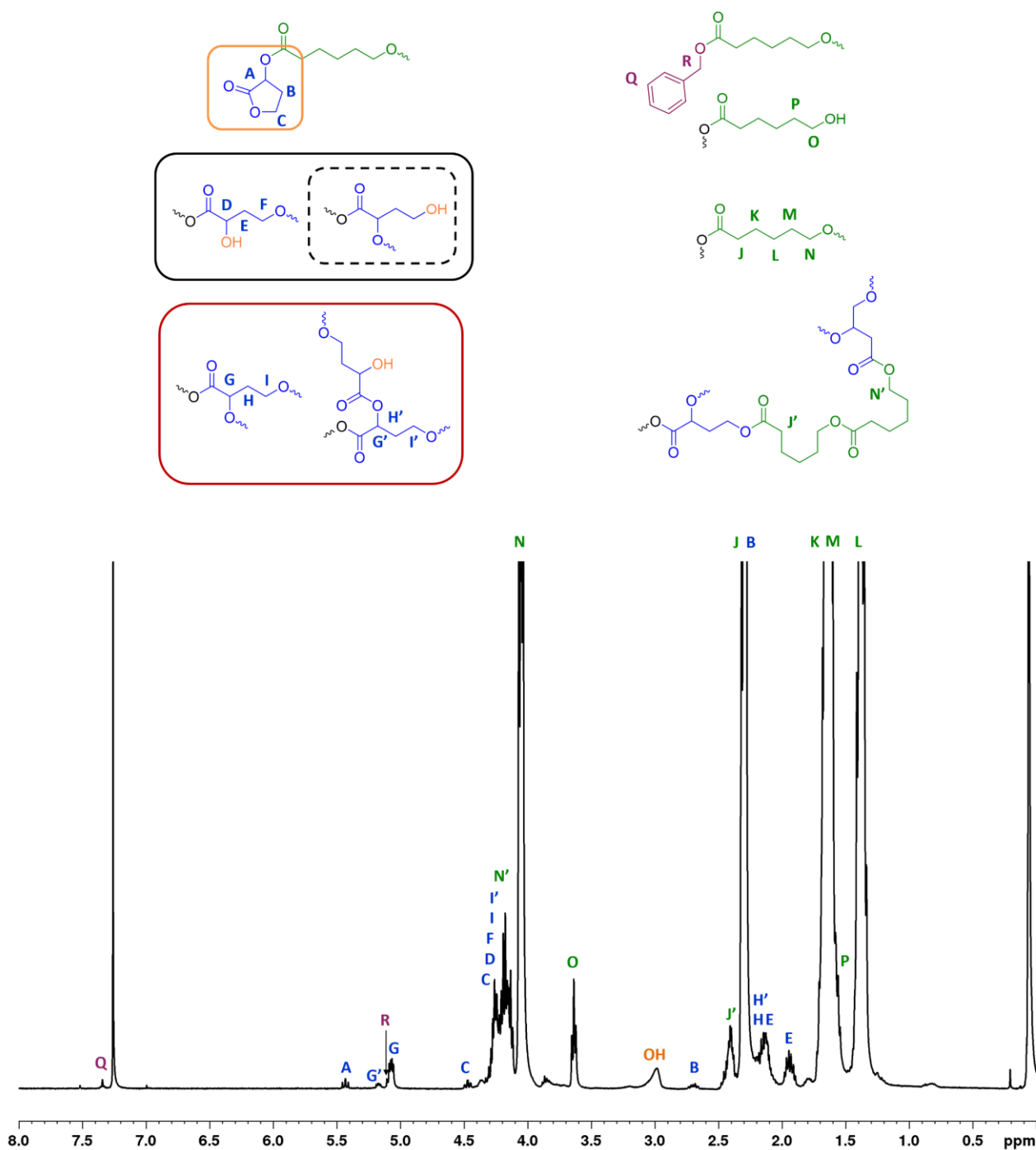
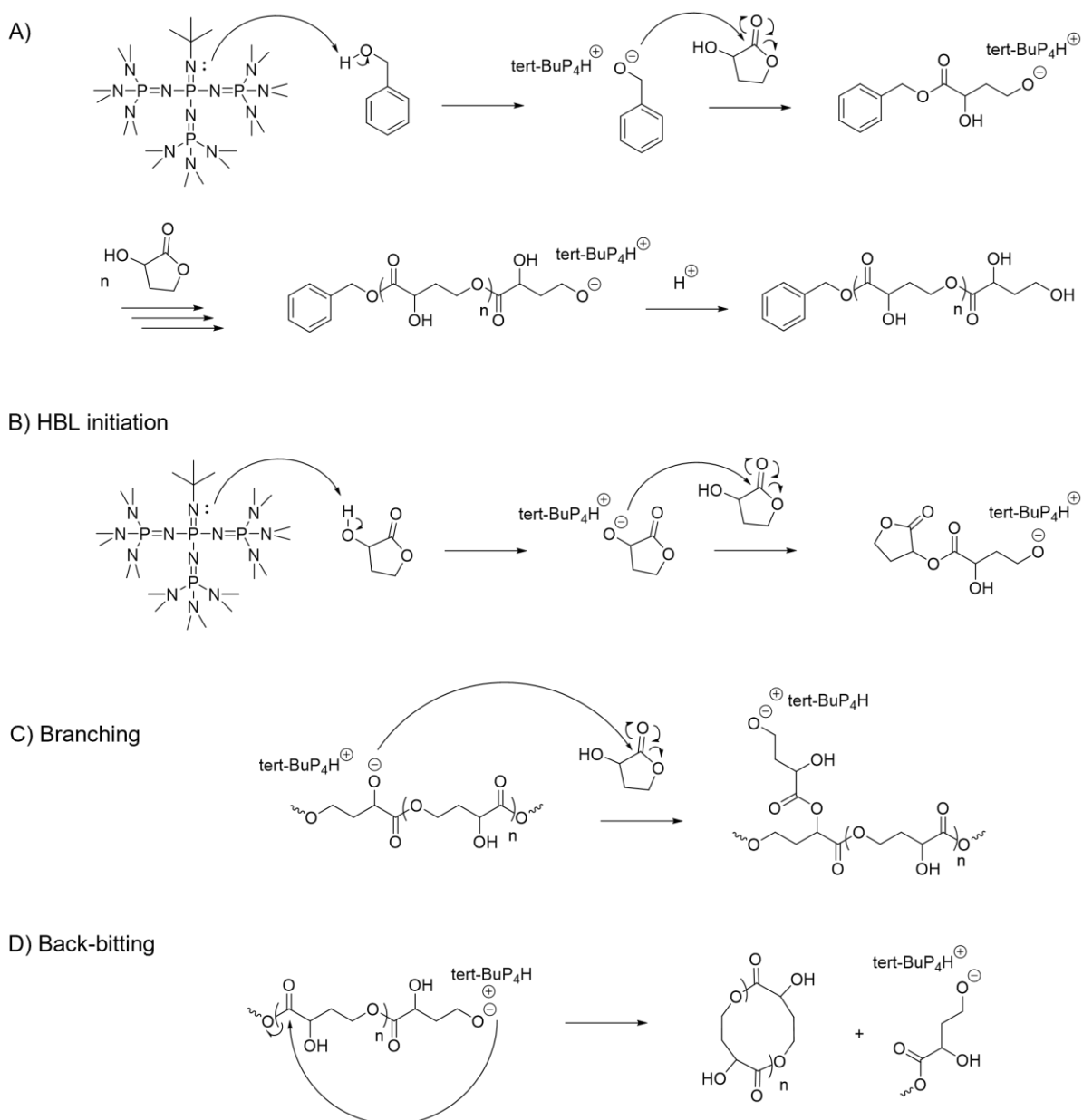


Figure 4: <sup>1</sup>H NMR spectrum of the copolymer (ratio M/C/I = 400/1/1; [M1+M2] = 8M; THF;  $\epsilon$ -CL/HBL ratio = 77/23; T=80°C; t=5h) and structural patterns.

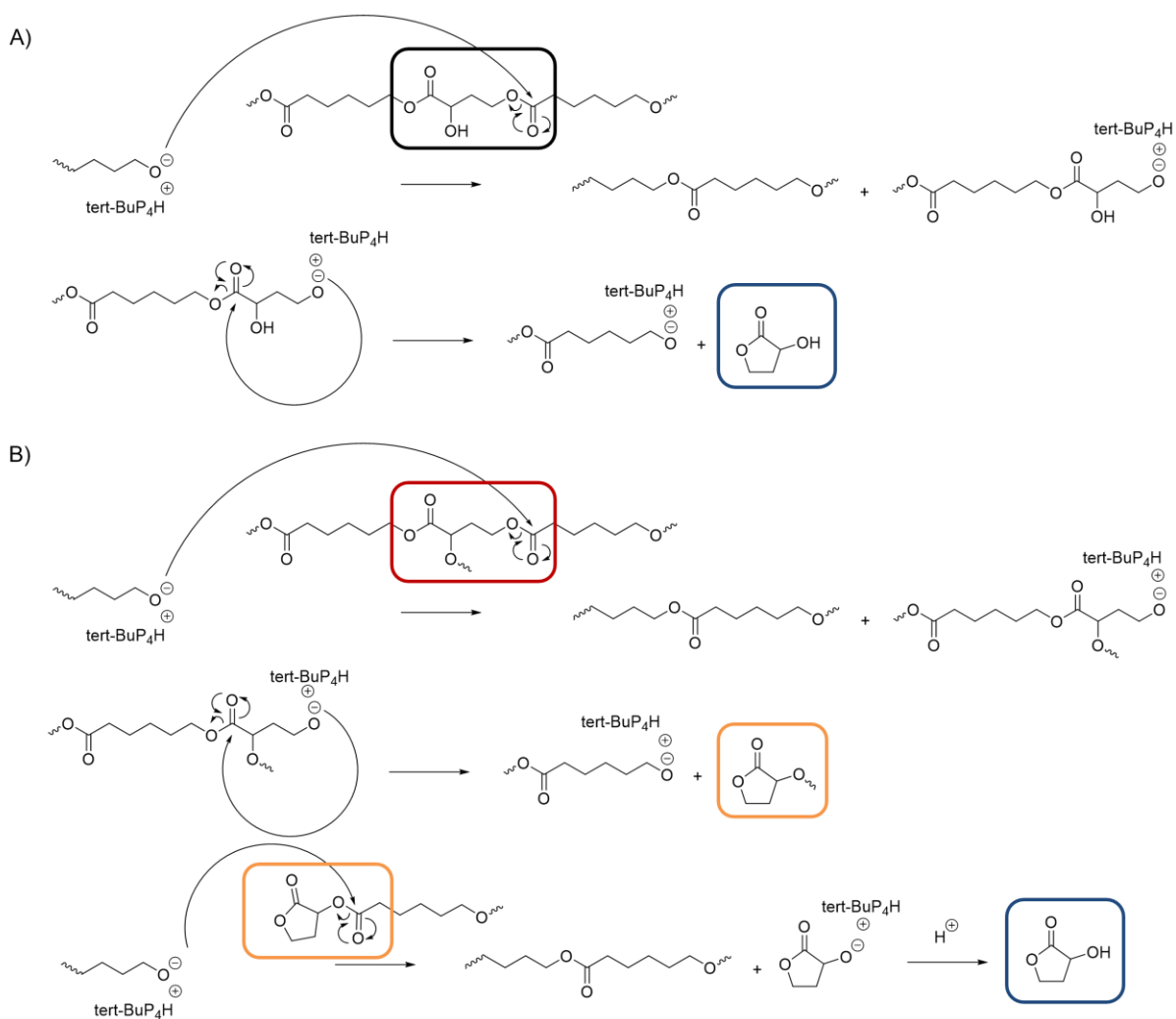


Scheme 2: Proposed polymerization mechanism for the HBL ROP with  $\text{tert-BuP}_4$  as catalyst. A) Standard mechanism with  $\text{BnOH}$  as initiator. B) HBL initiation step. C) Branching step. D) Back-biting reaction.

The scheme was simplified by showing only the HBL ROP and not the  $\epsilon\text{-CL}$  incorporation.

The variation of the HBL type units was also monitored in order to see the depolymerisation effects at  $80^\circ\text{C}$  on the copolymer composition (bottom Figure 3B). At short reaction times, the amount of cyclic HBL is very low (3%). Indeed, both monomers reacted fast and the HBL cycles at the chain-end were then opened leading to the formation of branching points. In addition, DFT calculations

revealed that secondary hydroxyl groups of the linear units were equireactive inducing more branched structures (58% at 5 min). With longer reaction times, the depolymerization reaction induced changes in the HBL-type units. The cyclic HBL increased slowly from 3% to 8% while the branched HBL drastically fell down from 58% to 20%. Several mechanisms are proposed to explain this variation in the monomer motives linked to the depolymerization. As active species are present in the medium, the attack of an alkoxide onto a carbonyl close to one HBL linear unit can be considered (Scheme 3A). The intermolecular reactions lead to chains redistribution and the intramolecular thermodynamically favourable reaction of ring-closure by the alkoxide will reform the monomer. The same mechanism can be also considered with HBL branched units (Scheme 3B). In this case, chains terminated by a cyclic HBL are reformed and the depolymerization reaction can be pursued until the formation of the monomer.



*Scheme 3: Proposed HBL depolymerization mechanism. A) Attack close to a linear unit. B) Attack close to a branched unit.*

In a second step, a kinetic study has been also performed at 25°C. The results showed that the monomer conversion proceeded in two distinct stages (Figure 3A, dash dots). First, from 5 min to 1h, both monomers were slowly converted, 11% for the  $\epsilon$ -CL and 9% for the HBL. In contrast, from 1h to 6h, the monomer conversions significantly increased with a faster rate for HBL. After 6h of reaction, both monomers reached almost complete conversions (97% for the  $\epsilon$ -Cl and 95% for the HBL) without depolymerization. In agreement with the monomer conversions, the SEC traces showed a gradual increase in the molar masses from 320 g/mol to 8 500 g/mol and dispersity from  $D=1.2$  to  $D=5.9$  (Figure S10 and Table S2). Regarding the HBL type units, a completely different behaviour was observed at 25°C as compared to 80°C (top Figure 3B). First, from 5 min to 1h, HBL

mainly reacted as an initiator with 15% of cyclic HBL at the chain end. After 6h of reaction, the trend was changed with a gradual drop in the cyclic HBL form till 1% due to its ring-opening. In contrast, the linear and branched units increased rapidly to reach 29% and 65% respectively at the end of the copolymerization. As the HBL conversion remained high after 6h of reaction, longer polymerization times were performed at 25°C (Table S3) in order to highlight possible HBL depolymerization. After 72h of reaction, the  $\epsilon$ -CL conversion remained constant (99%), while the HBL one progressively decreased from 95% to 80% in line with the expected depolymerization at room temperature.

In order to improve such copolymerization between HBL and  $\epsilon$ -CL and play further on the copolyester composition, the influence of the M/C/I ratio and the monomer concentration on the monomer conversions and copolymer compositions were investigated. However, as HBL depolymerization occurred with time at 80°C, short reaction times (5 min) were used to avoid the depolymerisation reaction.

The copolymerization was carried out with and without benzyl alcohol (Table 2, run 1 and 2 respectively). Similar monomer conversions (95% for the  $\epsilon$ -CL and 84% for the HBL) were obtained as HBL can also act as an initiator.

The combination of the *tert*-BuP<sub>4</sub> with several amounts of TU was tested for the copolymerization (Table 2, runs 3 and 4). Indeed, this combination is described in the literature to decrease the reactivity of the active centers, thus diminishing side reactions. In both cases, high monomer conversions (up to 99% for  $\epsilon$ -CL and 85% for HBL) were obtained. However, the molar masses control couldn't be improved with such bifunctional catalyst as lower molar masses and high dispersities were obtained ( $D=8-9$ ). This could be explained by the increase of the amount of the branched units as it can be seen in Table 2.

Performing the reaction in bulk (Table 2, run 5) did not really change the HBL conversion but increased the molar masses up to 15 000 g/mol within 5 min, permitting to carry out such reaction



without any solvent. Varying the temperature parameter demonstrates that 80°C or 100°C are required to get any polymer with high conversions and molar masses about 9 000 g/mol (Table 2 run 2 and 6-10) with short reaction times (5 min).

Table 2: ROCP of  $\epsilon$ -CL and HBL monomers with *tert*-BuP<sub>4</sub> as catalyst. Ratio M/C/I = 400/1/0; [M1+M2] = 8M; THF;  $\epsilon$ -CL/HBL ratio = 77/23; time = 5min.

Run	Temperature (°C)	Conv. $\epsilon$ -CL (mol.%) <sup>e</sup>	Conv. HBL (mol.%) <sup>e</sup>	HBL incorporation (mol.%) <sup>e</sup>	HBL type units <sup>e</sup>			$\overline{Mn}_{SEC}$ (g/mol) <sup>f</sup>	$\overline{D}$ <sup>f</sup>	DB <sup>e</sup>
					Cyclic HBL (mol.%)	Linear HBL (mol.%)	Branched HBL (mol.%)			
1 <sup>a</sup>	80	96	85	21	3	29	67	6 600	5.6	0.20
2	80	95	84	21	5	23	72	10 900	4.3	0.22
3 <sup>b</sup>	80	99	76	19	6	12	82	5 100	8.5	0.19
4 <sup>c</sup>	80	98	85	21	5	18	77	4 400	9.8	0.21
5 <sup>d</sup>	80	98	88	21	3	30	67	14 900	3.8	0.21
6	0	<1	0	0	0	0	0	-	-	0
7	25	<1	0	0	0	0	0	-	-	0
8	50	6	1	5	93	0	7	320	1.3	0.08
9	65	14	7	13	81	0	19	460	1.7	0.16
10	100	96	82	20	6	38	56	8 700	4.2	0.19

<sup>a</sup>Ratio M/C/I = 400/1/1. <sup>b</sup>Copolymerization with *tert*-BuP<sub>4</sub> and TU as catalysts, Ratio M/C/I = 400/1-1/0.

<sup>c</sup>Copolymerization with *tert*-BuP<sub>4</sub> and TU as catalysts, Ratio M/C/I = 400/1-3/0. <sup>d</sup>Bulk, [M1+M2]=9.68M.

<sup>e</sup>Calculated from <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>f</sup>Determined from SEC analysis in THF with polystyrene standards.

HBL incorporation could also be modulated by the  $\epsilon$ -CL/HBL initial ratio (Table S4). An increase of the HBL amount in the feed from 33% to 50% resulted first in no conversion of both monomers. It can be assumed that a high HBL amount mainly promotes HBL deprotonation by the base. Thus, a higher amount of catalyst was employed: M/C/I ratio: 200/1/0. Using 33% of HBL in the feed,  $\epsilon$ -CL and HBL were both almost fully converted, 92% and 82% respectively. The HBL incorporation in the so-formed copolymer was raised to 31% and the molar masses to 5 100 g/mol with a dispersity of 4.2. However, the increase of HBL content in the feed to 50% resulted in a drop of monomer conversions (18% for  $\epsilon$ -CL and 3% for HBL) and molar masses (Mn= 470 g/mol,  $\overline{D}$ = 1.6). It is supposed again that the main reaction is the deprotonation of HBL due to its large amount in the medium.

The use of *tert*-BuP<sub>4</sub> allowed to achieve relatively high molar masses but with a maximum HBL incorporation of 31% as compared to the La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> catalyst where high HBL incorporations (63%) were reached but with low molar masses (M<sub>n</sub>= 850 g/mol, *D*= 3.4).<sup>59</sup>

The amount of branching was also quantified by calculating the degree of branching (DB). As a general trend, copolyesters with about 20% of branched units are obtained. This value is shown as a bit lower as compared to the one obtained with the La-based system (26%).<sup>59</sup> This can be explained by the higher  $\epsilon$ -CL conversions with the present system which increase the amount of linear units.

Furthermore, the thermal properties of the so-formed copolyesters were studied by differential scanning calorimetry (DSC) analysis (Figure S11). The  $\epsilon$ -CL/HBL based copolyesters were compared to a PCL sample used as reference. The random copolymerization prevented any crystallization from 21% of incorporated HBL.

## Conclusion

The HBL homopolymerization using *tert*-BuP<sub>4</sub> as a catalyst couldn't be achieved at low or high temperatures. An investigation of the homopolymerization by DFT calculations revealed that the different possible stages of polymerization, *i.e.* ring-opening, branching and backbiting, have close free energy values preventing the polymer formation. Therefore, the random copolymerization with cyclic monomer of higher strain was performed to obtain HBL-based copolyesters. The metal-free copolyesters prepared by ring-opening copolymerization of HBL and  $\epsilon$ -CL monomers with *tert*-BuP<sub>4</sub> as catalyst exhibited several HBL structural patterns (cyclic, linear and branched). Achieving the reaction at 80°C in bulk allowed us to obtain high monomer conversions (98% for  $\epsilon$ -CL and 88% for HBL) and molar masses ( $\overline{M}_n$ = 14 900 g/mol with *D*= 3.8) after 5 min of reaction. As a general trend, broad dispersities were obtained due to the formation of branching points. HBL depolymerization was observed at 80°C after longer reaction times, thus decreasing the molar masses. Performing the polymerization at 25°C also enabled the synthesis of copolymers with high

monomer conversions and molar masses after reasonable reaction time (6h). HBL was shown to behave both as initiator and monomer with the formation of linear and branched motives. By tuning the HBL amount in the monomer feed ratio and the amount of catalyst, copolyesters with a composition up to 31% of HBL, could be obtained.

The synthesis of such copolyesters with free pendant hydroxyl groups along the backbone opens the route to many post-modification reactions. In addition, HBL depolymerization is seen as a possibility and advantage of degrading the material under mild conditions.

### **Supplementary Data**

The supporting information is available online at:

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### **Declaration of competing interest**

There are no conflicts of interest.

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