



**HAL**  
open science

# Investigation on the organocatalyzed ROP of $\delta$ -tetradecalactone: From polymerization to biodegradation

Peter Mcmichael, Xavier Schultze, Henri Cramail, Frédéric Peruch

► **To cite this version:**

Peter Mcmichael, Xavier Schultze, Henri Cramail, Frédéric Peruch. Investigation on the organocatalyzed ROP of  $\delta$ -tetradecalactone: From polymerization to biodegradation. *European Polymer Journal*, 2024, 208, pp.112859. 10.1016/j.eurpolymj.2024.112859 . hal-04472323

**HAL Id: hal-04472323**

**<https://hal.science/hal-04472323v1>**

Submitted on 22 Feb 2024

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

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



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License



# Investigation on the organocatalyzed ROP of $\delta$ -tetradecalactone: From polymerization to biodegradation

Peter McMichael<sup>a</sup>, Xavier Schultze<sup>b</sup>, Henri Cramail<sup>a</sup>, Frédéric Peruch<sup>a,\*</sup>

<sup>a</sup> Université de Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, 33600 Pessac, France

<sup>b</sup> L'Oréal Recherche et Innovation, 1 avenue Eugène Schueller, 93600 Aulnay sous Bois, France

## ARTICLE INFO

### Keywords:

$\delta$ -Tetradecalactone  
Ring-opening polymerization (ROP)  
Organocatalyst  
Renewable  
Ready biodegradability  
OECD 301

## ABSTRACT

Searching for biobased and biodegradable polymers, we explored the organocatalytic ring-opening polymerization (ROP) of a renewable *n*-alkyl  $\delta$ -lactone, namely  $\delta$ -tetradecalactone ( $\delta$ -TDL) that can be extracted from coconut oil, and we studied the ready biodegradability of the corresponding polyester. As reported for other *n*-alkyl  $\delta$ -lactones, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was used to perform the bulk and room temperature ROP of  $\delta$ -TDL. A study of the purification of the monomer prior to its ROP showed the importance of the combination of a distillation process and an elution through basic alumina to remove most of the impurities and obtain the higher molar masses. Despite this careful purification, capped molar masses were obtained (<40 kg/mol) and attributed by NMR and MALDI-ToF spectroscopy to TBD initiation and other side-initiators contained in the monomer, which were not possible to be identified. Other catalysts such as diphenyl phosphate (DPP) and the phosphazene superbase *t*-BuP<sub>4</sub> combined with a thiourea were also tried. The assessment of poly( $\delta$ -tetradecalactone) (pTDL) ready biodegradability was finally performed using the OECD test guideline 301F and showed the obtention of up to 41 % biodegradation rate in 28 days using a bioavailability improvement method.

## 1. Introduction

Synthetic polymers are versatile, lightweight and, for most of them, low-cost materials that have significantly contributed to many aspects of our modern life. However, a vicious circle has arisen from the rampant production of petroleum-based and non-degradable polymers leading to difficulties in their waste managements and thus their presence in the environment [1–6]. On the path to sustainability, solutions have emerged to produce more environmentally friendly polymers. In the cosmetic industry, L'OREAL is striving to improve its environmental footprint with efforts dedicated, but not limited to the design of biobased polymers combining a green chemistry synthetic process and a favorable end of life. While polymers fulfilling all these requirements are scarce, aliphatic polyesters have been considered as particularly relevant to answer growing environmental concerns. Indeed, polyesters exhibit a broad range of properties from biocompatibility to biodegradability and can be synthesized in a controlled fashion to reach various architectures and microstructures, by the mean of ring-opening polymerization of lactones (ROP), an atom economic reaction [7–11]. Polylactide (PLA) is a prime example of such a polymer, which can be obtained *via* the ROP of renewable lactide and can be biodegraded in industrial compost

[12–16]. The ROP of other renewable lactones in a sustainable manner is also of high interest to achieve polyesters which can biodegrade in the environment. In this regard, *n*-alkyl  $\delta$ -lactones are interesting candidates due to their renewability and industrial availability and can form potentially biodegradable polyesters. These monomers were reported to be mainly produced from fatty acids transformations by Baeyer-Villiger or enzymes oxidation as well as being obtained from biomass extraction [17–23]. ROP of these monomers such as  $\delta$ -decalactone were performed mainly through organocatalysis due to their restrictive thermodynamic characteristics allowing high conversions only at low reaction temperatures and in bulk [24–26]. This feature has interestingly enabled the chemical recovery of  $\delta$ -decalactone by applying a high temperature to its polymer in presence of diphenyl phosphate (DPP) and an external nucleophile (benzyl alcohol) [27]. Among the existing organocatalysts, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and DPP have already been used for the homopolymerization of *n*-alkyl  $\delta$ -lactones and enabled controlled bulk ROP with conversions close to 90 % at room temperature [26–30]. Molar masses targeted were in general below 20 kg/mol with experimental molar masses matching with these values. The major properties of the polyesters stemming from *n*-alkyl  $\delta$ -lactones arise from their pendant alkyl chains that bring hydrophobicity and generates non-

\* Corresponding author.

E-mail address: [peruch@enscbp.fr](mailto:peruch@enscbp.fr) (F. Peruch).

stacking low  $T_g$  amorphous polyesters [25]. From these properties, *n*-alkyl  $\delta$ -lactones have also been used to design block copolymers able to self-assemble and encapsulate hydrophobic drugs or for the obtention of thermoplastic elastomer materials [10,31]. Targeting highly hydrophobic polyesters, we explored the polymerization of  $\delta$ -tetradecalactone ( $\delta$ -TDL), an industrially available, biobased alkyl  $\delta$ -lactone with a nonyl substituent, that can be extracted from coconut oil [32]. While this monomer was hardly studied in the literature with only one article briefly mentioning its ROP through DPP catalysis [25], it has a close structural proximity with the already well-studied  $\delta$ -decalactone or  $\delta$ -dodecalactone. Herein, we studied the bulk ROP of the renewable  $\delta$ -TDL with organocatalysts to produce high molar masses polymers. A deep investigation of the influence of the monomer purification on the molar masses was performed as the presence of protic impurities such as water could influence the control of the reaction. The presence of side-initiation was evidenced during the TBD (and other organocatalysts) catalyzed ROP of  $\delta$ -TDL. To conclude this study, the ready biodegradability of the so-formed polyester was assessed using the OECD test guideline 301F.

## 2. Materials and methods

### 2.1. Materials

$\delta$ -Tetradecalactone (TDL, 98 %, Sigma Aldrich) was purified using various protocols. (i) Percolation through activated basic alumina under inert atmosphere. (ii)  $\text{CaH}_2$ /filtration: dried over  $\text{CaH}_2$  for 48 h prior to filtration under inert atmosphere. (iii)  $\text{CaH}_2$ /distillation: dried over  $\text{CaH}_2$  for 48 h prior to cryo-distillation under reduced pressure. (iv)  $\text{CaH}_2$ /distillation/basic alumina: dried over  $\text{CaH}_2$  for 48 h prior to cryo-distillation under reduced pressure. The distillate was then percolated through activated basic alumina under inert atmosphere. (v)  $\text{CaH}_2$ /distillation/basic alumina + celite: dried over  $\text{CaH}_2$  for 48 h prior to cryo-distillation under reduced pressure. The distillate was then percolated through activated basic alumina and a layer of Celite® 545 under inert atmosphere. 1,3,5-triazabicyclodecene (TBD, 98 %, Sigma Aldrich) was purified by sublimation under vacuum. Diphenyl phosphate (DPP, 99 %, TCI), 1,4-benzenedimethanol (BDM, 99 %, Acros) and biphenyl-4-methanol (B4M, 98 %, Alfa) were dried three times by azeotropic distillation of residual water and toluene (dried and distilled on PS/Bu-Li). *t*-BuP<sub>4</sub> (P<sub>4</sub>, 0.8 M in hexane), was purchased from Sigma Aldrich and used without further purification. 1,3-diisopropyl-2-thiourea (TU, 99 %, Sigma Aldrich) dried three times by azeotropic distillation of residual water and THF (dried and distilled on Na/Benzophenone). All compounds were stored in a glovebox under argon atmosphere ( $\text{O}_2 \leq 0.5$  ppm,  $\text{H}_2\text{O} \leq 0.5$  ppm).

### 2.2. General polymerization methods

**General procedure for the organocatalyzed-ROP of  $\delta$ -TDL:** In a glovebox, previously dried 50 mL round bottom Schlenk tubes were charged with a magnetic stir bar and an appropriate amount of catalyst and alcohol from a stock solution in dry DCM. DCM was then removed by applying vacuum and alkyl  $\delta$ -lactones was added under a flow of argon. A typical polymerization reaction was performed in the following composition:  $[\delta\text{-TDL}]_0:[\text{Cat}]:[\text{B4M}] = 480:4:1$  with Cat being TBD, DPP or *t*-BuP<sub>4</sub>/TU. A stirring rate of 400 rpm was applied at the early stage of the reaction. When the viscosity raised, a 100 rpm rate was applied. At specified times, aliquots were collected and quenched with benzoic acid/triethylamine (TBD-ROP/DPP-ROP) for reaction monitoring by <sup>1</sup>H NMR.

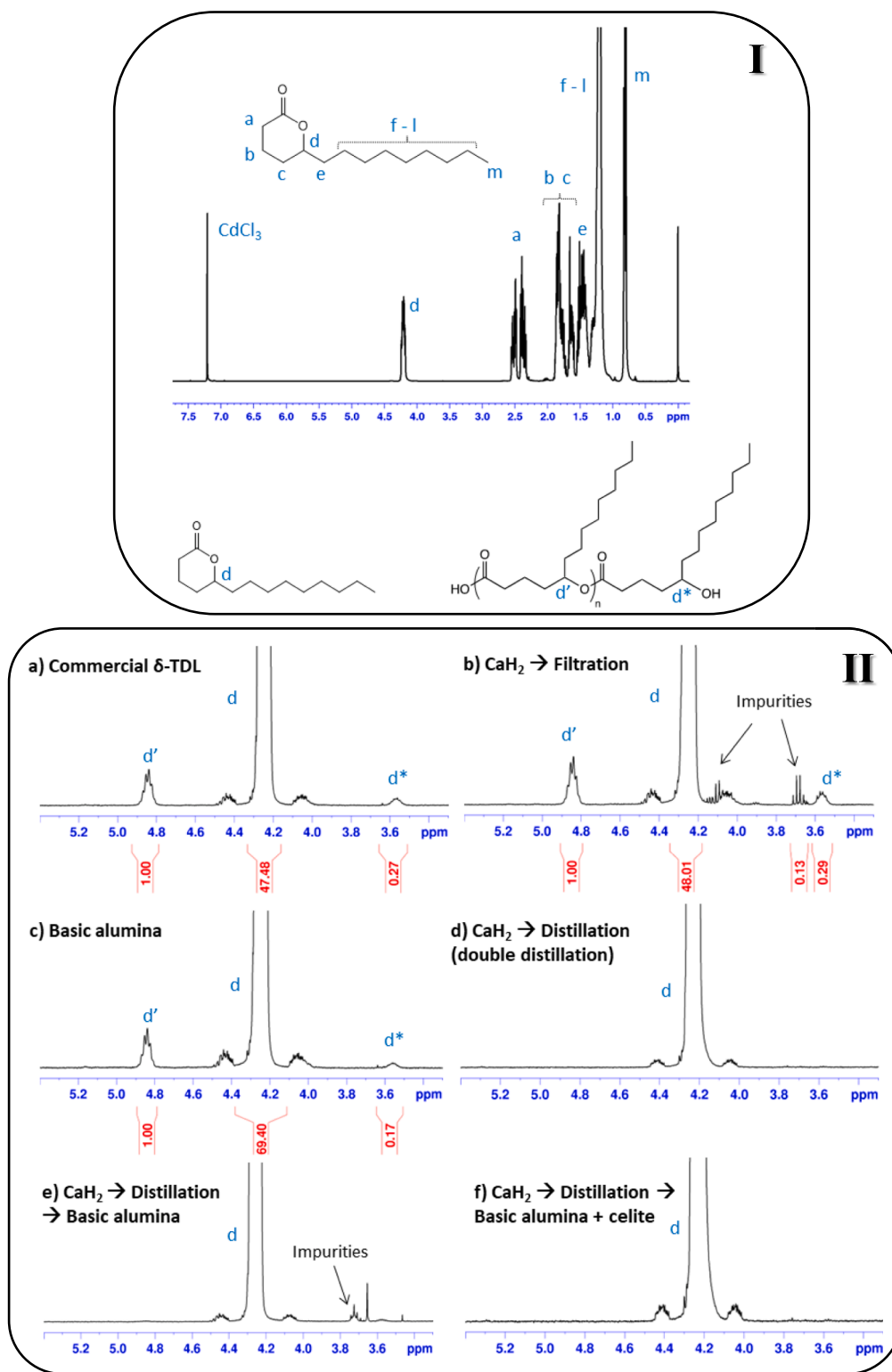
**Chain extension:** As the second monomer feed, the same amount of  $\delta$ -TDL was added to an ongoing polymerization of  $\delta$ -TDL that reached equilibrium conversion. At specified times, aliquots were collected and quenched with benzoic acid for reaction monitoring by <sup>1</sup>H NMR.

In both cases, at the end of the polymerization, the as-obtained

polymers were dissolved in a chloroform solution of benzoic acid to quench the reaction. A minimum of 3 precipitations in extremely cold methanol were performed to remove residual monomer and catalyst. Dynamic vacuum was finally applied for two days to remove residual methanol. The final polymers appear as a highly viscous liquid. The number average molar mass ( $M_n$ ) was determined by <sup>1</sup>H NMR and SEC. The dispersity ( $\mathcal{D}$ ) was evaluated by SEC.

### 2.3. Characterization

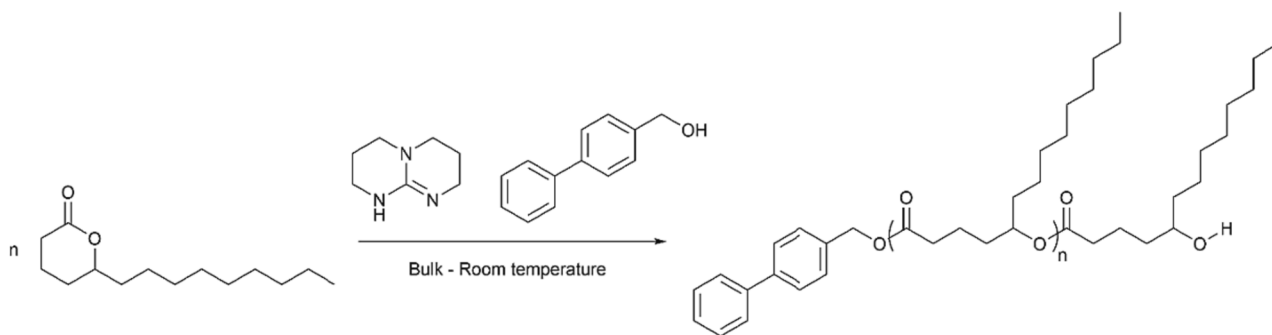
Reactions were monitored by liquid state <sup>1</sup>H NMR recorded at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz in CDCl<sub>3</sub>. Conversions were calculated as follow:  $\text{Conversion} = \frac{I_p}{I_m + I_p}$  with  $I_p$  = Integration of characteristic polymer peak and  $I_m$  = Integration of characteristic peak of the monomer (methine protons at respectively 4.86 ppm and 4.27 ppm). For the identification of the structure, liquid-state <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>H-<sup>13</sup>C HSQC NMR and <sup>1</sup>H-<sup>1</sup>H COSY NMR spectra were recorded at 298 K on a Bruker Prodigy spectrometer operating at 400 MHz in CDCl<sub>3</sub>. All DOSY (Diffusion Ordered Spectroscopy) measurements were performed at 298 K on a Bruker Avance NEO 400 spectrometer operating at 400.33 MHz and equipped with a 5 mm Bruker multinuclear z-gradient direct cryoprobe-head capable of producing gradients in the z direction with strength 53.5 G·cm<sup>-1</sup>. Sample was dissolved in CDCl<sub>3</sub> ( $V = 400 \mu\text{L}$ ) for internal lock. DOSY spectra were acquired with the *dsteppg3s* pulse program (to reduce convection) from Bruker topspin software with spinning. The duration of the pulse gradients and the diffusion time were adjusted to obtain full attenuation of the signals at 95 % of maximum gradient strength. Duration of the gradient pulses was varied around 5 ms and diffusion time around 100 ms. The gradients strength was linearly incremented in 16 steps from 5 % to 95 % of the maximum gradient strength. A delay of 5 s between echoes was used. The data were processed using 8192 points in the F2 dimension and 128 points in the F1 dimension with the Bruker topspin software. Field gradient calibration was accomplished at 25 °C using the self-diffusion coefficient of H<sub>2</sub>O + D<sub>2</sub>O at  $19.0 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ . Size exclusion chromatography (SEC) has been used for the determination of the polymer number-average molar masses ( $M_n$ ) and dispersities ( $\mathcal{D} = M_w/M_n$ ). Measurements were performed using tetrahydrofuran (THF) as the eluent and on an Ultimate 3000 system from ThermoScientific equipped with diode array detector DAD. The system also includes a multi-angles light scattering detector MALS and differential refractive index detector dRI from Wyatt technology. Polymers were separated on three G2000, G3000 and G4000 TOSOH HXL gel columns (300 × 7.8 mm) (exclusion limits from 1000 Da to 400,000 g/mol) at a flowrate of 1 mL/min. Columns temperature was held at 40 °C. Polystyrene was used as the standard. Absolute molar masses were also calculated based on the measured  $dn/dc$  of poly( $\delta$ -tetradecalactone) ( $dn/dc = 0.073 \text{ mL/g}$ ). The polyester molar masses were estimated on precipitated samples using different methods [1]. Based on the monomer conversion and monomer/initiator ratio in the feed ( $M_{n,\text{theo}}$ ), assuming that biphenyl-4-methanol (B4M) is the sole initiator; (2) By calculating the ratio between the peak integration of the methine proton of the polymer (4.86 ppm) with the one of the methylene group of B4M (5.15 ppm), and assuming that all the chains are solely initiated by B4M ( $M_{n,\text{NMR}\omega}$ ); [3] By calculating the ratio between the peak integration of the methine proton of the polymer with the one of the methine group of the chain ends (3.58 ppm) ( $M_{n,\text{NMR}\omega}$ ); [4] By SEC analysis in THF at 40 °C using PS standards ( $M_{n,\text{SEC}}$ ); [5] By SEC analysis in THF at 40 °C using the  $dn/dc$  value of pTDL (0.073 mL/g). MALDI-ToF Mass Spectrometry (MALDI-ToF MS) experiments were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 65  $\mu\text{J}$  delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10,000. All samples were analyzed using *trans*-2-[3-(4-tert-



**Fig. 1.** I:  $^1\text{H}$  NMR spectra of  $\delta$ -TDL purified by the “Distalu” method. II:  $^1\text{H}$  NMR spectra of  $\delta$ -TDL purified by different methods, zoomed in the methine proton chemical shift (small peaks at  $\sim 4.0$  and  $\sim 4.4$  ppm are satellite peaks due to  $^1\text{H}$ - $^{13}\text{C}$  coupling).

butyl-phenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix, which was prepared as a  $40 \text{ mg}\cdot\text{mL}^{-1}$  solution in  $\text{CHCl}_3$ . This solution ( $1 \mu\text{L}$ ) was applied to a stainless-steel target and air-dried. Polymer samples were dissolved in THF to obtain  $1 \text{ mg}\cdot\text{mL}^{-1}$  solutions and  $50 \mu\text{L}$  of  $2 \text{ mg}\cdot\text{mL}^{-1}$  NaI solution in acetonitrile was added to the polymer solution. Therefore,  $1 \mu\text{L}$  of this solution was applied onto the target area already bearing the matrix crystals and air-dried. For the

recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass all the ions of the distribution and they were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.



**Scheme 1.** Bulk TBD-ROP of  $\delta$ -TDL initiated by B4M at room temperature.

**Table 1**

Results of the B4M initiated bulk ROP of  $\delta$ -TDL catalyzed by TBD.

Run	Monomer purification	$[\text{TDL}]_0/[\text{B4M}]_0$	Time (h)	Conv. <sup>a</sup> (%)	$M_{n,\text{theo}}$ <sup>b</sup> (g/mol)	$M_{n,\text{NMR}\alpha}$ <sup>c</sup> (g/mol)	$M_{n,\text{NMR}\omega}$ <sup>d</sup> (g/mol)	$M_{n,\text{SEC}}$ <sup>e</sup> (g/mol)	$M_{n,\text{abs}}^f$ (g/mol)	$\bar{D}$ <sup>e</sup>
1	None	240	–	0	–	–	–	–	–	–
2	Basic alumina		84	81	44,000	52,900	10,300	15,600	10,000	1.10
3	CaH <sub>2</sub> /filtration		24	89	48,300	42,300	7300	14,800	7200	1.30
4	Distillation		24	82	44,800	49,150	18,000	28,500	18,200	1.18
5	Dist/alumina		24	75	40,700	46,600	12,600	18,000	14,000	1.11
6	Dist/alumina/celite		24	86	46,600	49,000	22,400	30,600	21,300	1.11
8	Dist/alumina/celite	60	24	87	11,800	12,500	8700	17,800	12,400	1.07
9	celite	480	52	75	81,400	76,400	28,250	40,100	30,000	1.03
10		960	44	83	163,000	259,000	30,000	51,200	39,700	1.12

$[\text{TBD}]:[\text{B4M}] = 2:1$ ;  $T_{\text{pol.}} = \text{room temperature}$ ;  $m_{\text{TDL}} = 2 \text{ g}$ .

<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy of the crude product; <sup>b</sup>Theoretical molar masses ( $\frac{[\text{TDL}]_0}{[\text{B4M}]} \times M_{\text{TDL}} \times \text{Conv.}$  with  $M_{\text{TDL}}$  being the molar mass of  $\delta$ -TDL);

<sup>c</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR according to B4M initiating chain-end; <sup>d</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR spectroscopy according to hydroxyl  $\omega$ -chain end; <sup>e</sup>Number average molar mass and dispersity of precipitated polymers evaluated by SEC chromatography vs PS standards in THF at 40 °C; <sup>f</sup>Absolute molar mass of precipitated polymers evaluated by SEC chromatography using  $dn/dc$  value of pTDL (0.073 mL/g) in THF at 40 °C.

### 3. Results and discussions

#### 3.1. Purification of $\delta$ -TDL

First the impact of the  $\delta$ -TDL purification process on the poly( $\delta$ -TDL) molar masses of TBD catalyzed ring opening polymerizations was investigated. Prior to their ROP, five methods for the purification of  $\delta$ -TDL were tested and their associated <sup>1</sup>H NMR spectra were recorded (Fig. 1). Resonances of three types of protons, corresponding to the methine protons of the oligomers of  $\delta$ -TDL (4.86 ppm, d'), cyclic  $\delta$ -TDL (4.27 ppm, d) and chain-end of the open form/oligomers of  $\delta$ -TDL (3.58 ppm, d\*), were specifically followed (Fig. 1).

The presence of oligomers in the monomer was observed in the commercial product as well as in the monomer dried over CaH<sub>2</sub> followed by a simple filtration (Fig. 1a & b). A lower amount of these open forms of  $\delta$ -TDL was obtained by eluting  $\delta$ -TDL through basic alumina as attested by a higher integration ratio d/d' compared to the commercial product in <sup>1</sup>H NMR spectroscopy (Fig. 1c). Distillation of the monomer over CaH<sub>2</sub> enabled the obtention of pure  $\delta$ -TDL (Fig. 1d). Percolation of the distilled monomer through basic alumina in an inert atmosphere was further performed to compare with Hillmyer and coll. studies.[26] However, alumina passed through the sintered glass and parasite signals were observed by <sup>1</sup>H NMR (Fig. 1e). Therefore, a layer of celite was added to prevent the monomer pollution and the <sup>1</sup>H NMR spectrum showed a single resonance corresponding to  $\delta$ -TDL (Fig. 1f).

#### 3.2. ROP of $\delta$ -TDL purified by different means

Using these differently purified monomers, room temperature bulk

ROPs of  $\delta$ -TDL were carried out using TBD as the catalyst and biphenyl-4-methanol (B4M) as the initiator under the following conditions:  $[\delta\text{-TDL}]_0:[\text{TBD}]:[\text{B4M}] = 240:2:1$  (Scheme 1). High molar masses were targeted to better observe the discrepancy between theoretical and experimental molar masses. Results of the different synthesis are described in Table 1.

Without purification of the commercial monomer, no polymerization could be obtained (Table 1, run 1). The presence of carboxylic acid moieties and/or traces of water could have deactivated the basic TBD catalyst and thus inhibited the polymerization. When  $\delta$ -TDL was only passed through basic alumina, a very slow polymerization was observed, reaching a conversion of 81 % after 84 h. Again, this can be attributed to the presence of carboxylic acid moieties present at the chain-end of the oligomers as evidenced by <sup>1</sup>H NMR. However, the concentration of –COOH groups must be low enough not to completely deactivate TBD thus enabling a slow polymerization. Residual water remaining in the monomer after filtration on basic alumina could also be detrimental to the polymerization. All the other polymerizations proceeded in 24 h and reached a conversion close to the equilibrium monomer conversion of  $\delta$ -TDL at room temperature (89 %) according to <sup>1</sup>H NMR spectroscopy (Fig. S1). Molar masses determined by <sup>1</sup>H NMR spectroscopy or size exclusion chromatography depicted divergent values. If calculated  $M_n$  values based on B4M methylene signal ( $M_{n,\text{NMR}\alpha}$ ) appeared close to the theoretical  $M_n$  for all synthesized polymers, the ones based on the methine chain-end signal ( $M_{n,\text{NMR}\omega}$ ) are always lower. As, in this latter case, it is considered all the  $\omega$ -chain-ends whatever the initiator, it probably gives more realistic values. In other words, the closer  $M_{n,\text{NMR}\omega}$  and  $M_{n,\text{theo}}$ , the lower the amount of side-initiations. While comparing the  $M_{n,\text{NMR}\omega}$  of pTDL synthesized from  $\delta$ -TDL purified by different

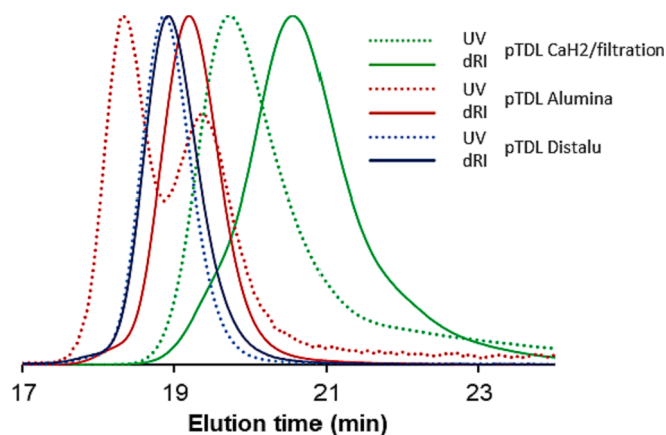


Fig. 2. Normalized dRI and UV traces of precipitated p( $\delta$ -TDL) initiated by B4M, analyses in THF.

treatments, the trend follows the purity of the monomer. With the “CaH<sub>2</sub>/filtration” purified monomer, the lowest  $M_{n,NMR\omega}$  value was obtained due to the remaining high content of  $\delta$ -TDL open forms. “Basic alumina” purified monomers led to slightly higher  $M_{n,NMR\omega}$  which may be explained by the lower amount of oligomers/acid which could act as additional initiators from their –OH end group. Finally, distilled  $\delta$ -TDL led to the highest molar masses. However, even after distillation,  $M_{n,NMR\omega}$  of 18 kg/mol were obtained against  $M_{n,theo}$  of 44.8 kg/mol (Table 1, run 4). An improvement in molar masses was achieved by using a combination of CaH<sub>2</sub>/distillation/basic alumina/celite filtration (abbreviated “Distalu”) for the purification of  $\delta$ -TDL ( $M_{n,NMR\omega}$  = 22.4 kg/mol, Table 1, run 6). Polymerizations of  $\delta$ -TDL purified by the latter mentioned purification system were also performed at a higher targeted degree of polymerization (Table 1, run 9 & 10). Capped molar masses were observed through these experiments, where only a  $M_{n,NMR\omega}$  of 30 kg/mol could be obtained while  $M_n$  up to 163 kg/mol were targeted. In addition,  $M_{n,SEC}$  calculated according to PS calibration confirmed that lower molar masses than targeted were obtained but still with values in accordance with the degree of monomer purity. Interestingly, absolute molar masses determined by SEC in THF with dn/dc calibration, were in very close agreement with  $M_{n,NMR\omega}$ .

These results may not appear in agreement with most results reported in the literature from which distilled monomer generally leads to polymers exhibiting close theoretical and experimental  $M_n$  values. However, in most reported cases, the targeted molar masses were rather low (below 16 kg/mol) thus possibly masking the occurrence of side reactions. Therefore, polymerization of  $\delta$ -TDL (purified from distalu) at a lower targeted molar mass were also performed (Table 1, run 8). A high conversion was obtained (87 %) with molar masses measured by <sup>1</sup>H NMR and SEC in good agreement with theoretical values ( $M_{n,theo}$  = 11.8 kg/mol,  $M_{n,NMR\omega}$  = 8.7 kg/mol,  $M_{n,abs}$  = 12.4 kg/mol).  $M_{n,SEC}$  obtained using PS standards led to higher values (17.8 kg/mol), as generally reported in the literature. All these experiments demonstrate that producing high molar mass p( $\delta$ -TDL) is rather difficult.

### 3.3. Exploration of the nature of side-initiators

To gain insight on the phenomenon that decreased the molar masses of p( $\delta$ -TDL), several characterizations and experiments were performed. SEC traces obtained from RI and UV detections were first compared (Fig. 2). Purification by another mean than distalu (curves in blue), revealed the presence of at least two initiations, one by a chromophore species (most probably B4M) and another by a non-chromophore one (unknown initiator). Indeed, UV and RI traces of p( $\delta$ -TDL) were only superimposed when  $\delta$ -TDL was purified over CaH<sub>2</sub>/distillation/alumina/celite indicating that each polymeric chain bears a biphenyl

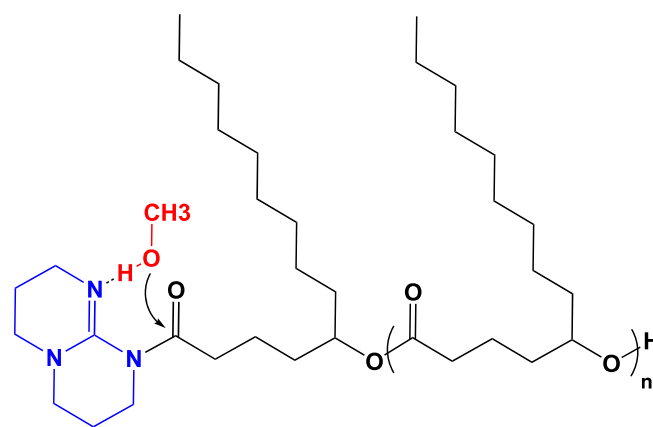


Fig. 3. Transesterification of methanol and TBD- p( $\delta$ -TDL) intermediate species.

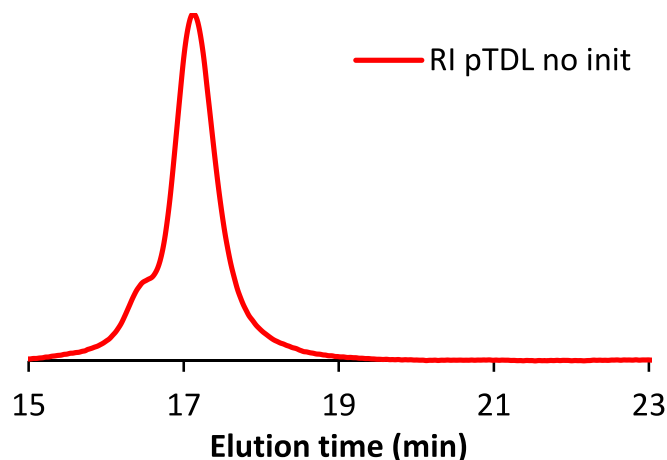
moiety (from B4M initiator) at its chain-end. However, the molar masses are lower than expected, meaning that non-chromophore side-initiated chains are superimposing at the same elution time. When  $\delta$ -TDL was purified over CaH<sub>2</sub>/filtration, UV traces show to superimpose with RI traces only for the higher molar masses which correspond to the polymer chains initiated by B4M initiator. Moreover, the broad shape of the RI trace indicate that a large proportion of the polymer chains have been initiated by other non-UV absorbing initiating species and, most probably, by adventitious water despite CaH<sub>2</sub> filtration, or by the remaining open form of  $\delta$ -TDL, as discussed in the previous section. For “Alumina” pTDL (Table 1, run 2), the UV trace displayed a bimodal distribution, with the lower molar mass peak corresponding more or less to the RI trace. The higher molar mass fraction could have been initiated by alumina impurities as we observed the presence of alumina particles after filtration and according to several reports, aluminum is a chromophore species and absorbs in the UV domain. [33,34].

To assign the nature of the polymer chain-ends, MALDI-TOF was performed on p( $\delta$ -TDL) obtained from the “Distalu”  $\delta$ -TDL (Table 1, run 8) (details in Fig. S2). A monomodal distribution was obtained. Nevertheless, 3 populations could be observed on the spectrum, one corresponding to B4M initiation, one to a methoxy chain-end and a last one remaining unidentified. This methoxy chain-end could have appeared during precipitation step where transesterification reactions might have occurred in presence of excess methanol and TBD. [35] However, the narrow dispersity and unimodal distribution of this p( $\delta$ -TDL) did not really correspond to intermolecular transesterification reactions. Another hypothesis could be that a part of TBD initiated the polymerization (as described by Bansal [36]) and underwent chain-scission during the precipitation step towards the formation of that methoxy chain-end, also as a result of a transesterification reaction (Fig. 3).

The absence of macrocyclic p( $\delta$ -TDL)L was further confirmed through the obtention of a single diffusion coefficient for a p( $\delta$ -TDL) with a  $M_{n,NMR\omega}$  = 22.3 kg/mol in DOSY NMR (Fig. S3). Indeed, diffusion of cyclic polymers is approximately twice as fast as linear polymer of similar molar masses [37,38]. Finally, deeper NMR analyses were carried out as <sup>1</sup>H NMR spectrum of precipitated p( $\delta$ -TDL) always showed a broad signal at 4.04 ppm, that was never assigned in the literature (Fig. S4) [26,27]. <sup>13</sup>C NMR, 2D COSY, 2D HSQC and 2D HMBC were thus performed (Figs. S5 to 8, respectively). This signal was then assigned to methylene protons near an ester functional group (CH<sub>2</sub>-CH<sub>2</sub>-O-CO-R) or to methylene protons of an ethoxy group (CH<sub>3</sub>-CH<sub>2</sub>-O-CO). As a confirmation, methylene protons of octanol in  $\alpha$ -position of an ester function (*i.e.* initiating octanol for the ROP of  $\delta$ -TDL) was located at 4.04 ppm (Fig. S9). However, such sequence would normally never happen according to the reagents used during this reaction. Moreover, the molar mass of the unknown side-initiating species observed in MALDI-ToF was not matching with any possible molecule with this kind of structure.

**Table 2**Results of bulk TBD-ROP of  $\delta$ -TDL initiated by B4M or without initiator at room temperature.

Run	[TDL] <sub>0</sub> : [TBD]: [B4M]	Reaction time	Conv. <sup>a</sup> (%)	M <sub>n,theo</sub> <sup>b</sup> (g/mol)	M <sub>n,NMR<math>\alpha</math><sup>c</sup> (g/mol)</sub>	M <sub>n,NMR<math>\omega</math><sup>d</sup> (g/mol)</sub>	M <sub>n,SEC</sub> <sup>e</sup> (g/mol)	M <sub>n,abs</sub> <sup>f</sup> (g/mol)	D <sup>e</sup>
1	240:2:1	24 h	86	46,600	49,000	22,400	30,600	21,300	1.11
2	240:2:0	72 h	89	–	–	31,300	52,600	35,000	1.18

[TDL]/[TBD] = 120; T<sub>pol.</sub> = room temperature; m<sub>TDL</sub> = 2 g;  $\delta$ -TDL purified from “distalu”.<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy (Cf. calculation in SI); <sup>b</sup>Theoretical molar masses ( $\frac{[TDL]_0}{[B4M]} \times M_{TDL} \times \text{Conv.}$  with M<sub>TDL</sub> being the molar mass of  $\delta$ -TDL);<sup>c</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR according to B4M initiating chain-end (cf. calculation in SI); <sup>d</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR spectroscopy according to hydroxyl  $\omega$ -chain end (cf. calculation in SI); <sup>e</sup>Number average molar mass and dispersity of precipitated polymers evaluated by SEC chromatography vs PS standards in THF at 40 °C; <sup>f</sup>Absolute molar mass of precipitated polymers evaluated by SEC chromatography using dn/dc value of p( $\delta$ -TDL) (0.073 mL/g) in THF at 40 °C.**Fig. 4.** SEC chromatogram of p( $\delta$ -TDL) catalyzed by TBD and synthesized without initiator, analysis in THF.

Despite all the efforts held to understand the obtention of low molar masses, only one side-initiation was partially evidenced with TBD. The possibility of TBD to act as an initiator was investigated further through a TBD-catalyzed ROP of  $\delta$ -TDL performed without initiator and using monomers purified from the “distalu” method. The results of this polymerization are reported in Table 2.

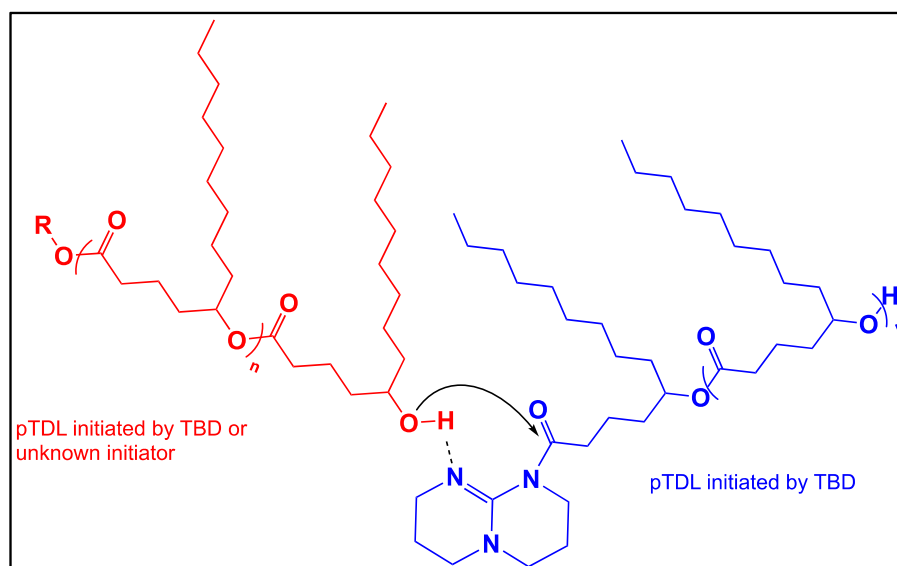
Remarkably, without initiator, the TBD-ROP of  $\delta$ -TDL enabled the

synthesis of p( $\delta$ -TDL) in 72 h with 89 % conversion. A longer reaction time was however needed to reach such a conversion (72 h vs. 24 h with B4M). Monitoring of the reaction was performed using <sup>1</sup>H NMR and showed the good conversion of the monomer throughout the reaction (Fig. S10). The parasite peak at 4.04 ppm appeared at 24 h and kept growing until the end of the reaction. <sup>1</sup>H NMR also enabled the calculation of M<sub>n,NMR $\omega$</sub>  based on the chain-end methine proton of the precipitated p( $\delta$ -TDL) and showed a M<sub>n</sub> of 31.3 kg/mol. Moreover, M<sub>n,abs</sub> calculated with the dn/dc value of p( $\delta$ -TDL) showed a value of 35 kg/mol, in good agreement with M<sub>n,NMR $\omega$</sub> . A shoulder could be observed at short elution times (Fig. 4). One hypothesis could be that long reaction times favored potential coupling reactions. Indeed, the molar mass at the peak of this shoulder indicated twice the molar mass of the main population's peak (65 kg/mol vs. 33 kg/mol). Coupling reaction might have involved hydroxy chain-end polymers that reacted with TBD initiated polymer, possibly due to the viscosity increase and the lower monomer concentration at high reaction time (Fig. 5).

### 3.4. Chain-extension

To get more insight in this polymerization route, chain-extension experiments were achieved to confirm the living character of the  $\delta$ -TDL ROP, but also to try to increase p( $\delta$ -TDL) molar masses (Table 3).

Chain-extension reactions showed an increase of the conversion over time to reach 67 % in 48 h (Fig. S11). Interestingly, M<sub>n</sub> calculated from the  $\omega$ -chain-end methine proton decreased after chain extension demonstrating that new chains were initiated. As a confirmation of side-initiations, a bimodal distribution was observed by SEC for the

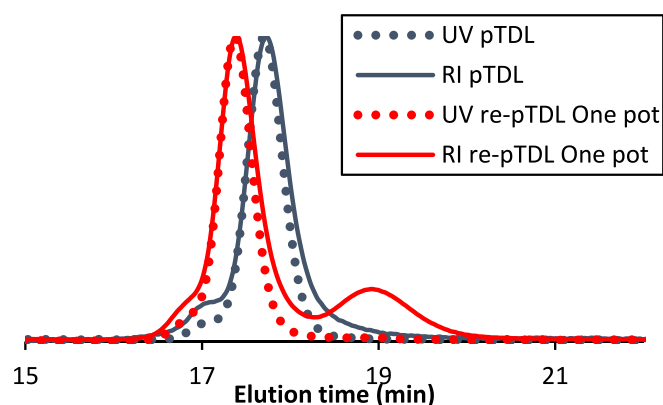
**Fig. 5.** Proposed mechanism for the coupling of two p( $\delta$ -TDL) chains.

**Table 3**  
Results of bulk TBD-ROP of  $\delta$ -TDL before and after chain-extension.

Run	Process	$\frac{[\text{TDL}]}{[\text{B4M}]}$	Reaction time	Conv. <sup>a</sup> (%)	$M_{n,\text{theo}}$ <sup>b</sup> (g/mol)	$M_{n,\text{NMR}\alpha}$ <sup>c</sup> (g/mol)	$M_{n,\text{NMR}\omega}$ <sup>d</sup> (g/mol)	$M_{n,\text{abs}}^e$ (g/mol)	$D$ <sup>e</sup>
1	Bulk - RT	480	48 h	85	92,200	89,500	25,350	33,800	1.04
2	From an ongoing pTDL	+ 480	48 h	67	164,900	137,400	7400	46,500 & 13,200	–

$\frac{[\text{TBD}]}{[\text{OH}]} = 4$ ;  $T_{\text{pol.}}$  = room temperature; <sup>a</sup> $M_{n,\text{theo}} = M_{n,\text{abs}} + M_{n,\text{theo}}$  chain-extension;  $m_{\text{TDL}} = 2$  g.

<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy (Cf. calculation in SI); <sup>b</sup>Theoretical molar masses ( $\frac{[\text{TDL}]_0}{[\text{B4M}]} \times M_{\text{TDL}} \times \text{Conv.}$  with  $M_{\text{TDL}}$  being the molar mass of  $\delta$ -TDL); <sup>c</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR according to B4M initiating chain-end (cf. calculation in SI); <sup>d</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR spectroscopy according to hydroxyl  $\omega$ -chain end (cf. calculation in SI); <sup>e</sup>Absolute molar mass and dispersity of precipitated polymers evaluated by SEC chromatography using dn/dc value of p( $\delta$ -TDL) (0.073 mL/g) in THF at 40 °C.



**Fig. 6.** dRI and UV traces of precipitated pTDL before and after chain-extension.

precipitated chain-extended polymer (Fig. 6). It was hypothesized that the initial peak was shifted to higher molar masses with an increase from 33.8 to 46.5 kg/mol. Indeed, they all had a similar signal in RI and UV detection, the latter being the proof of the role of B4M as an initiator. On the contrary, the other population exhibited no UV response which further confirm that these initiating impurities in the monomer are not absorbing in UV. This observation further confirms that the maximum molar mass that can be reached for these polymerizations is imposed by the amount of non-UV absorbing initiating impurities present in the monomer or still initiation by TBD. In addition, monitoring of the reaction was followed by SEC and showed the formation of this new population from the beginning of the chain-extension (Fig. S12). Besides that, the main population appeared to shift throughout the reaction and demonstrated that all macroinitiator species initiated the reaction.

**Table 4**  
Results of bulk-TBD-ROP of  $\delta$ -TDL initiated by B4M and BDM.

Run	Initiator	$\frac{[\text{TDL}]}{[\text{Init}]}$	Conversion <sup>a</sup> (%)	$M_{n,\text{theo}}$ <sup>b</sup> (kg/mol)	$M_{n,\text{NMR}\alpha}$ <sup>c</sup> (kg/mol)	$M_{n,\text{NMR}\omega}$ <sup>d</sup> (kg/mol)	$M_{n,\text{abs}}^e$ (kg/mol)	$D$ <sup>e</sup>
1	B4M	960	75	163	259	30.0	31.2	1.24
2	BDM		74	161	253	31.8	82.9 – 28.0	–

$\frac{[\text{TBD}]}{[\text{OH}]} = 4$ ;  $\frac{[\text{TDL}]}{[\text{TBD}]} = 120$ ;  $T_{\text{pol.}}$  = room temperature; Reaction time = 48 h;  $m_{\text{TDL}} = 5$  g.

<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy (Cf. calculation in SI); <sup>b</sup>Theoretical molar masses ( $\frac{[M]_0}{[\text{BDM}]} \times M_{\delta\text{-lactone}} \times \text{Conv.}$  with  $M_{\delta\text{-lactone}}$  being the molar mass of the monomer); <sup>c</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR according to BDM initiating chain-end (cf. calculation in SI); <sup>d</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR spectroscopy according to hydroxyl  $\omega$ -chain end (cf. calculation in SI); <sup>e</sup>Absolute molar mass of precipitated polymers evaluated by SEC chromatography using dn/dc value of p( $\delta$ -TDL) (0.073 mL/g) in THF at 40 °C.

### 3.5. TBD-ROP of $\delta$ -TDL initiated by benzenedimethanol

Benzenedimethanol (BDM) initiated TBD-ROP of  $\delta$ -TDL was also conducted in bulk at room temperature, as this initiator (a diol) has been used for most of the reported ROP of  $\delta$ -decalactone (Fig. S13) [26,27,39–41]. It was also expected that the use of a diol would lead to twice the molar masses. A high degree of polymerization was targeted for this reaction and the following conditions were used:  $[\text{TDL}]_0$ : $[\text{TBD}]$ : $[\text{BDM}] = 960$ :4:1. Results of the ROP of  $\delta$ -TDL initiated by BDM (and B4M for comparison) are summarized in Table 4. BDM-initiated ROP of  $\delta$ -TDL was successfully carried out with TBD as the catalyst. A conversion of 74 % was obtained in 48 h, like for the B4M-initiated ROP of  $\delta$ -TDL.  $M_{n,\text{NMR}\alpha}$  of the precipitated telechelic p( $\delta$ -TDL) was found higher than the theoretical molar mass. As for the B4M-initiated p( $\delta$ -TDL), a very small signal of the initiator methylene protons was witnessed and could have led to poor reliability of this signal integration (Fig. S14). Interestingly, integration of the broader signal of  $\omega$ -chain-end p( $\delta$ -TDL) was more reliable and enabled the calculation of  $M_{n,\text{NMR}\omega}$ . A lower molar mass was still obtained and levelled off at 32 kg/mol. The presence of side-initiations was, once again, evidenced by SEC. A bimodal distribution was observed as for the chain-extended polymers (Fig. 7). Two distinct populations were obtained having molar masses of 82.9 and 28 kg/mol according to dn/dc calibration. Even if the UV signal was too low to identify which population was initiated by BDM, it was assumed that the higher molar mass was the telechelic p( $\delta$ -TDL). Indeed, such a molar mass has never been obtained before. Moreover, the shorter population was superimposing with B4M- p( $\delta$ -TDL) RI trace. One hypothesis could be that the amount of side-initiators was the same for both reactions, as the same amount of each reagent was used. Thus, the 2nd population of low molar mass observed for BDM-initiated  $\delta$ -TDL ROP would highlight the side-initiated chains that are hardly seen for B4M initiated ROP of  $\delta$ -TDL. This phenomenon was also observed by Bansal *et al.* for the TBD-ROP of  $\delta$ -DL (42) They witnessed the formation of both pDL initiated by PEG, and pDL homopolymer of lower molar masses. The latter was assigned to initiation by impurities such as moisture or ring-opened  $\delta$ -DL. High molar mass p( $\delta$ -TDL) was thus obtained by using BDM as



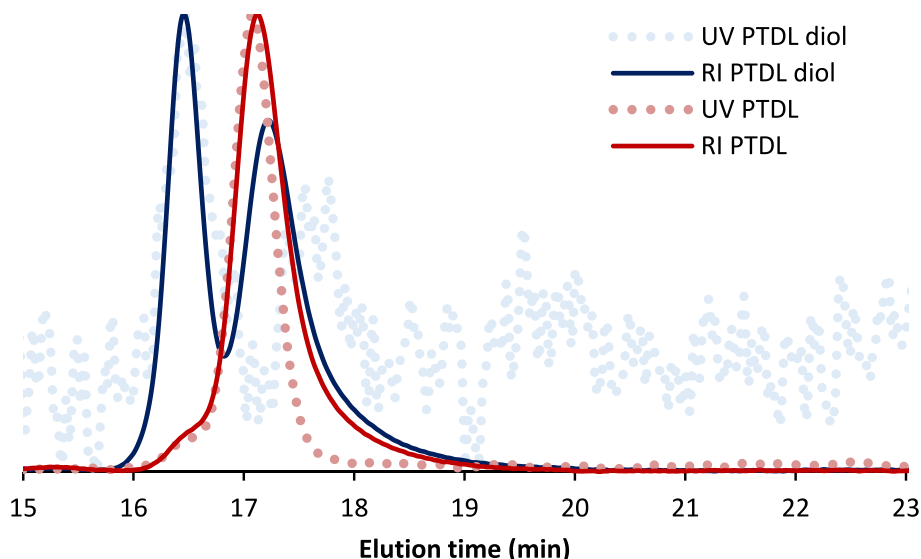


Fig. 7. SEC traces of pTDL initiated by B4M and BDM.

Table 5

Results of bulk DPP-ROP of  $\delta$ -TDL initiated by B4M at room temperature.

Run	$\frac{[\text{TDL}]}{[\text{B4M}]}$	$\frac{[\text{DPP}]}{[\text{B4M}]}$	Reaction time	Conv. <sup>a</sup> (%)	$M_{n,\text{theo}}^b$ (g/mol)	$M_{n,\text{NMR}\alpha}^c$ (g/mol)	$M_{n,\text{NMR}\omega}^d$ (g/mol)	$M_{n,\text{abs}}^e$ (g/mol)	$\bar{D}^e$
1	480	4	17 days	68	74,000	74,700	19,500	30,000	1.08

T<sub>pol.</sub> = room temperature.

<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy (Cf. calculation in SI); <sup>b</sup>Theoretical molar masses ( $\frac{[\text{M}]_0}{[\text{B4M}]} \times M_{\delta\text{-lactone}} \times \text{Conv.}$  with  $M_{\delta\text{-lactone}}$  being the molar mass of the monomer); <sup>c</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR according to BnOH initiating chain-end (cf. calculation in SI); <sup>d</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR spectroscopy according to hydroxyl  $\omega$ -chain end (cf. calculation in SI); <sup>e</sup>Number average molar mass and dispersity of precipitated polymers evaluated by SEC chromatography vs PS standards in THF at 40 °C; <sup>f</sup>Absolute molar mass of precipitated polymers evaluated by SEC chromatography using dn/dc value of p( $\delta$ -TDL) (0.073 mL/g) in THF at 40 °C.

the initiator and TBD as the catalyst. However, the formation of another population was observed and assigned to p( $\delta$ -TDL) initiated by a competing side-initiator.

### 3.6. Other organocatalysts

To evaluate if the side reactions were mainly linked to TBD, other organocatalytic systems were briefly investigated. Diphenyl phosphate

and the phosphazene *t*-Bu-P<sub>4</sub> (associated to a thiourea or not) have already been largely described for the ROP of lactones and were thus tested [42–48].

DPP enabled the polymerization of  $\delta$ -TDL initiated by B4M but in a very slow manner using the following conditions: [TDL]<sub>0</sub>: [DPP]: [B4M] = 480:4:1 (Table 5). Indeed, the reaction was stopped before reaching equilibrium monomer conversion and showed a conversion of 68 % after 17 days. Molar masses were investigated using both <sup>1</sup>H NMR

Table 6

Results and conditions of the ROP of  $\delta$ -TDL catalyzed by P<sub>4</sub>/TU and initiated by B4M in bulk.

Run	Catalyst ratio (P <sub>4</sub> :TU:Init)	$\frac{[\text{TDL}]_0}{[\text{B4M}]}$	Reaction time	Conv. <sup>a</sup> (%)	$M_{n,\text{theo}}^b$ (g/mol)	$M_{n,\text{NMR}\alpha}^c$ (g/mol)	$M_{n,\text{NMR}\omega}^d$ (g/mol)	$M_{n,\text{abs}}^e$ (g/mol)	$\bar{D}^e$
1*	2:2:1	480	> 1 h	9	9800	–	–	–	–
2*	4:2:1		> 1 h	13	14,100	–	–	–	–
3*	4:4:1		> 1 h	40	43,400	–	–	–	–
4	6:6:1		1 h	91	98,700	102,600	24,600	32,300	1.27
5	4:4:1	240	3 h	84	45,600	46,800	23,300	30,000	1.15
6	4:8:1		0.5 h	81	44,000	55,700	20,700	25,000	1.18
7	6:6:1		3 h	85	46,100	39,900	22,800	26,000	1.52

T<sub>pol.</sub> = room temperature; \* polymers were not precipitated to be further characterized; >1h means no more conversion was obtained for a longer reaction time; m<sub>TDL</sub> = 1 g.

<sup>a</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy of the crude product; <sup>b</sup>Theoretical molar masses ( $\frac{[\text{TDL}]_0}{[\text{B4M}]} \times M_{\text{TDL}} \times \text{Conv.}$  with  $M_{\text{TDL}}$  being the molar mass of  $\delta$ -TDL);

<sup>c</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR according to B4M initiating chain-end; <sup>d</sup>Molar mass of the precipitated polymer calculated by <sup>1</sup>H NMR spectroscopy according to hydroxyl  $\omega$ -chain end; <sup>e</sup>Absolute molar mass of precipitated polymers evaluated by SEC chromatography using dn/dc value of pTDL (0.073 mL/g) in THF at 40 °C.

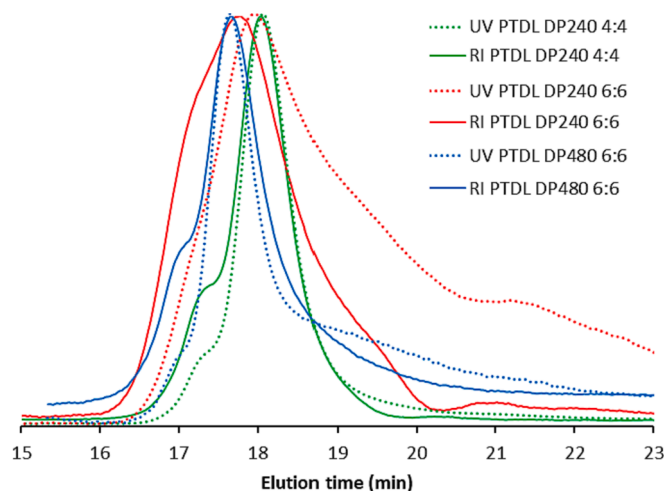


Fig. 8. dRI and UV traces in SEC of precipitated p( $\delta$ -TDL) catalyzed by P<sub>4</sub>/TU.

spectroscopy and SEC. As with TBD, molar masses according to the integration of the methylene protons of B4M showed values close to theoretical ones. However, the same difference appeared when molar masses were calculated from the integration of the methine proton of the  $\omega$ -chain-end. The calculated molar masses were far lower than expected. The unknown peak at 4.04 ppm was still present on <sup>1</sup>H NMR spectra. A precipitated p( $\delta$ -TDL) with an absolute molar mass of 30 kg/mol and narrow dispersity was obtained by SEC. This value was again below theoretical molar mass, meaning that side-initiation is still occurring. Besides that, a monomodal distribution was observed and RI and UV traces overlaid perfectly for precipitated polymers, but also all along the reaction (Fig. S15). Noteworthy, no shoulder was observed for the polymers catalyzed by DPP. Moreover, a good control of the reaction was still observed with the linear increase of molar masses with conversion (Fig. S16). In conclusion, DPP appeared to successfully promote the ROP of  $\delta$ -TDL initiated by B4M in bulk. Moreover, if only a monomodal polymer was obtained, it was again impossible to get molar masses higher than 30 kg/mol, confirming the presence of initiating impurities in the monomer.

The *t*-BuP<sub>4</sub>-catalyzed ROP of  $\delta$ -TDL was carried out in bulk at room temperature. B4M was used as the initiator and the ratio [P<sub>4</sub>]:[B4M] was varied from 1 to 6 at a fixed degree of polymerization of 480. Surprisingly, no conversion was obtained whatever the catalyst amount. Moreover, it can be noted that the deprotonation of B4M was incomplete in all conditions. In this study, a first screening of a dual-catalytic system was performed by using 1,3-diisopropyl-2-thiourea as the thiourea and *t*-BuP<sub>4</sub> as the base. pK<sub>a</sub> of the TU and P<sub>4</sub> are respectively 13.8 (predicted) (48) and 42.1 (in acetonitrile), meaning that the ROP will most probably occur through the anionic mechanism as defined by Waymouth and coll. (49) Several ratios of TU/base were screened for the ROP of  $\delta$ -TDL initiated by B4M in bulk at room temperature (Table 6).

It appeared clearly that a minimum amount of catalysts was needed to reach a decent conversion. Indeed, for a targeted DP of 480, a remarkable 91 % conversion was obtained in only 1 h using [P<sub>4</sub>]:[TU]:[B4M] = 6:6:1, whereas at ratios of 4:4:1 and 2:2:1 only 40 % and 9 % conversion were reached in 1 h respectively (Table 2, runs 4, 3, 1). Furthermore, no polymerization was observed after this time. The reduction of TU amount compared to *t*-BuP<sub>4</sub> decreased even more the conversion (13 %), probably because of less anionic sites (run 2). For a targeted DP of 240, a ratio of 4:4:1 was sufficient to reach a conversion close to the equilibrium monomer conversion in only 20 min and an extension of the reaction time to 3 h, led to only a little increase of the conversion (Table 2, run 5). Interestingly, no effect on the conversion was observed with the increase of TU compared to the base (Table 2, run 6). Moreover, if an increased catalytic amount also showed high

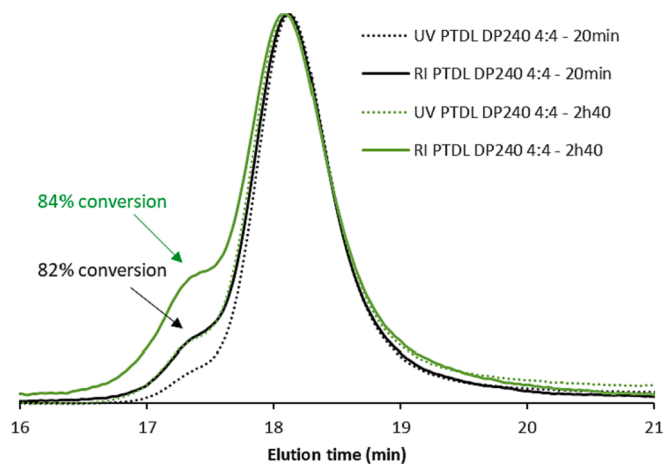


Fig. 9. dRI and UV traces in SEC of a p( $\delta$ -TDL) synthesis catalyzed by P<sub>4</sub>/TU at 20 min and 2 h40.

conversion in 20 min (and no change in 3 h, Table 2, run 7), no clear impact over the conversion rate was noticed due to the fast kinetics of polymerization. It is finally worth mentioning that the unidentified peak at 4.04 ppm was still present during the reactions. Because it was observed for all the catalysts explored for the ROP of  $\delta$ -TDL, the formation of this peak appears to come from the monomer reaction itself. Molar masses of these precipitated p( $\delta$ -TDL) were first calculated according to the initiator and  $\omega$ -chain-end in <sup>1</sup>H NMR spectroscopy (Figures S17 and S18). Molar masses calculated by <sup>1</sup>H NMR from the methine chain-end proton gave closer results for all polymers with molar masses around 20 and 25 kg/mol, as usual below the theoretical ones. By SEC, absolute molar masses were in the range of 25 to 30 kg/mol, in agreement with  $M_{n,NMR\omega}$ . An analysis of the RI and UV traces obtained in SEC of precipitated p( $\delta$ -TDL) was carried out and depicted a second population for lower elution time (Fig. 8). For all the polymerization performed with a 6:6:1 ratio, a broadening of the molar mass distribution curve is obtained with a larger difference between the RI and UV traces compared to the polymerization with a 4:4:1 ratio of P<sub>4</sub>, TU and alcohol. Therefore, too high a dual catalyst concentration results in side-reactions without any positive impact on the polymerization kinetics or final conversion. However, even with a 4:4 P<sub>4</sub>/TU ratio, a high molar mass shoulder is already observed at 20 min (Fig. 9). This shoulder becomes more important after 2h40min with no significant increase of the molar mass of the main peak. This phenomenon was assumed to come from a coupling reaction of chains as the shoulder at short elution time corresponds to a molar mass twice the value of the main peak. In other words, it would mean that transesterification of the polymer chains would only happen between a propagating alkoxide, and the ester group attached to the initiator. At last, these observations showed that extended reaction time led to exacerbated side-reactions.

To conclude, much faster polymerization rates were obtained by using this dual-catalytic system. A minimum amount of catalyst was needed to obtain conversion close to the equilibrium and was decreasing with lower DP targeted. However, this high activity introduced some exacerbated side-reactions such as coupling reactions and transesterification compared to TBD and DPP. Unfortunately, even with such an active catalytic system, molar masses above 32 kg/mol could not be obtained, confirming an issue with the monomer itself rather than the catalysts.

### 3.7. Evaluation of the ready biodegradability of p( $\delta$ -TDL)

Biodegradability is an important factor to consider when developing new polymers that are intended to be disposed of in the environment, as it determines how long the material will persist in the environment and

**Table 7**Biodegradation test results of p( $\delta$ -TDL)s with or without HMN.

Homopolymer		Biodegradation (%)	
		Day 14 Mean $\pm$ SD	Day 28 Mean $\pm$ SD
p( $\delta$ -TDL) 10 k	–	4.9 $\pm$ 2.5	5.8 $\pm$ 3.6
	HMN	23.6 $\pm$ 4.9	41.5 $\pm$ 4.8
p( $\delta$ -TDL) 30 k	–	1.7 $\pm$ 1.4	13.6 $\pm$ 2.8
	HMN	15.9 $\pm$ 2.6	35.6 $\pm$ 1.7
Sodium benzoate		88.9 $\pm$ 2.5	95.1 $\pm$ 0.5

what potential impacts it may have on wildlife and ecosystems. Polyesters are a vast class of polymers that have often been considered and reported as biodegradable, sometimes without having been properly evaluated for this property. The ready biodegradability of p( $\delta$ -TDL) was thus assessed using the OECD 301F test guideline in laboratory-scale experiments. This test provides a methodology for evaluating the ready biodegradability of a material in an aqueous medium and under aerobic conditions. The use of activated sludge as the source of microorganisms makes this test particularly relevant to simulate the biodegradation of a material in a wastewater treatment plant (WWTP) and consequently in the environment. Two types of biodegradation test were conducted in this study. The polymer was assessed alone, and a bioavailability improvement method (BIM) was used to improve the biodegradability of our polymers. The mineral oil 2,2,4,4,6,6,8,8-heptamethylnonane (HMN) was used as BIM, according to the work of Sweetlove and coll [49]. A positive result in this highly stringent test would guaranty the ready biodegradability of PTDL. Moreover, a result close to 60 % in 28 days would also indicate that the latter might degrade in the environment. Two p( $\delta$ -TDL) of 10 and 30 kg/mol were assessed in this test. In compliance with OECD 301F validity criteria, all evaluations performed showed a difference between duplicates biodegradation results lower than 20 %. Moreover, the toxicity control biodegradation rate was always above 25 %, indicating the lack of toxicity of the samples towards the inoculum. HMN control test showed no biodegradation in presence of inoculum. Finally, the positive control exceeded 60 % biodegradation rate within 14 days. Degrees of biodegradation were calculated considering the blank correction (Cf. SI). All pTDL evaluated showed a biodegradation rate below 60 % by the end of the test, as resumed in Table 7.

Without HMN, p( $\delta$ -TDL) 30 k showed the highest biodegradation rate with 13.6 % in 28 days. An improvement can be noticed with the use of HMN where all homopolymers showed an increased value of

biodegradation ranging from 35.6 % to 41.5 %. The use of such additive thus appears to increase the bioavailability of the polymers to the microorganisms. The curves of biodegradation over time show the overtaking of the lag phase (biodegradation rate  $>$ 10 %) between day-8 and day-18 only when using HMN (blue curves, Fig. 10). However, even with HMN, the biodegradation rate did not show a sudden increase after the lag phase as it could be observed by Nabeoka *et al.* on other polyesters. (16) Indeed, biodegradation rate appeared to increase slowly and, interestingly, biodegradation was still increasing by day-28 meaning that no plateau phase was reached. It is thus supposed that a longer incubation time might result in a higher biodegradation rate for all the homopolymers tested.

From this biodegradation study, it appeared that p( $\delta$ -TDL) did not reach 60 % of biodegradability after 28 days. However, scores of biodegradations between 35.6 % and 41 % were observed without reaching a plateau after 28 days which is very encouraging for such hydrophobic polyesters under such demanding evaluation conditions. The lack of water solubility of these polyesters would certainly lower the surface contact with microorganisms and thus the biodegradation rate.

#### 4. Conclusion

The impact of several reaction parameters on the  $\delta$ -TDL ring-opening polymerization in bulk at room temperature was investigated: purification of the monomer, chain-extension experiments, variation of the nature of catalysts, etc. With TBD as catalyst and B4M as the initiator, higher molar masses were obtained when the monomer was highly purified through distillation over CaH<sub>2</sub> and filtration through basic alumina and celite. However, a maximal molar mass around 35–40 kg/mol was the upper limit whatever the molar mass targeted. This was attributed to TBD side-initiation and other side-reactions whose nature was not clearly identified. Other organocatalysts led to the same observations. Higher molar masses could have been obtained through chain-extension experiments and initiation with a diol, but in both cases a bimodal distribution was observed by SEC. One population was attributed to chains started by the initiator, whereas the second one was due to side-initiation. The control of the ROP of  $\delta$ -TDL appeared to be very difficult, more than described in the literature for alkyl  $\delta$ -lactones where authors generally synthesize molar masses below 16 kg/mol. Finally, besides being obtained from renewable sources, the biodegradability of p( $\delta$ -TDL) could enhance the sustainability of its entire life cycle. We thus assessed the ready biodegradability of p( $\delta$ -TDL) by using the OECD 301F guideline and have demonstrated that a rate of

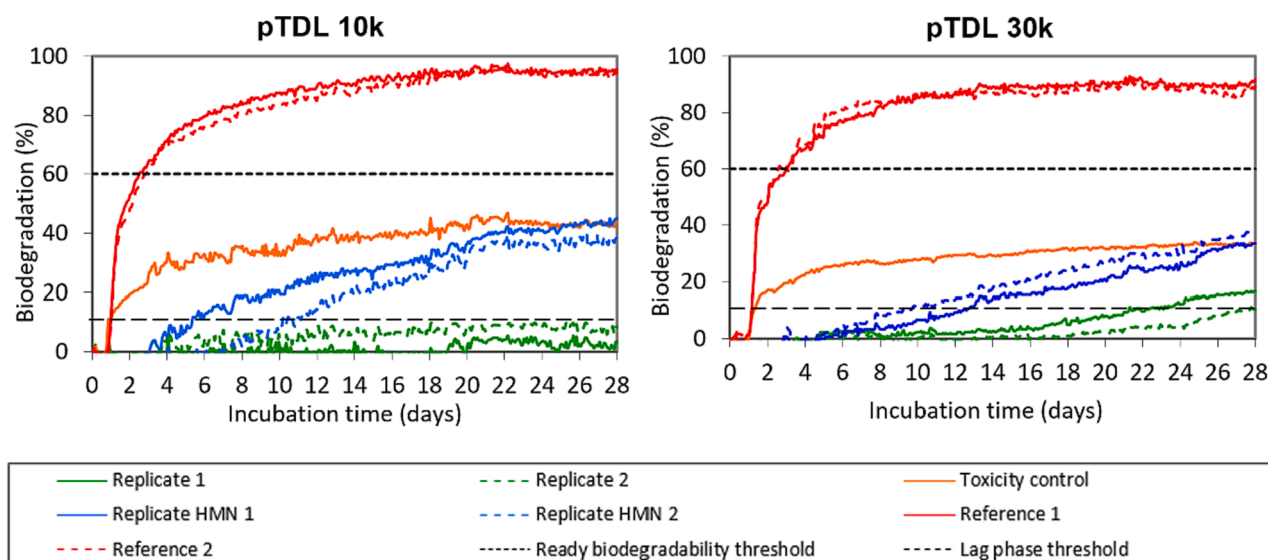


Fig. 10. Biodegradation curves over time of the p( $\delta$ -TDL)s tested, with and without HMN.

biodegradation up to 41 % was obtained in 28 days for p( $\delta$ -TDL) in the presence of a mineral oil. This result is very encouraging for such hydrophobic polyesters. Starting from a biobased monomer, polymerizing it in bulk with an organocatalyst and studying its biodegradability represent a step forward in the design of environmentally friendly polymers. However, stringent monomer purification and uncomplete polymerization remain important challenges to overcome to further improve the synthesis of these polyesters. Further work is underway to tackle these challenges and explore the relation between polymer structure and biodegradability.

### CRedit authorship contribution statement

**Peter McMichael:** Writing – original draft, Methodology, Investigation, Formal analysis. **Xavier Schultze:** Writing – review & editing, Validation, Supervision, Data curation, Conceptualization. **Henri Cramail:** Writing – review & editing, Validation, Supervision, Data curation, Conceptualization. **Frédéric Peruch:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The authors of this publication received research funding from L'OREAL Advanced Research which is developing products related to research described in this review.

### Data availability

The raw/processed data required to reproduce biodegradation studies cannot be shared at this time due to legal reasons.

### Acknowledgements

Financial support of this research by L'Oréal (support to P.M.) is gratefully acknowledged.

### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2024.112859>.

### References

- [1] OECD, Plastic waste by region and end-of-life fate [Internet], 2022. Available from: [https://stats.oecd.org/Index.aspx?DataSetCode=PLASTIC\\_WASTE\\_5](https://stats.oecd.org/Index.aspx?DataSetCode=PLASTIC_WASTE_5).
- [2] P.L. Corcoran, C.J. Moore, K. Jazvac, An anthropogenic marker horizon in the future rock record, *GSA Today* [Internet]. 6 (2014) 4–8. Available from, <http://www.geosociety.org/gsatoday/archive/24/6/abstract/i1052-5173-24-6-4.htm>.
- [3] M. Revel, A. Châtel, C. Mouneyrac, Micro(nano)plastics: a threat to human health? *Curr. Opin. Environ. Sci. Health* [Internet]. 1 (2018) 17–23. Available from, <https://linkinghub.elsevier.com/retrieve/pii/S2468584417300235>.
- [4] L. Lebreton, M. Egger, B. Slat, A global mass budget for positively buoyant macroplastic debris in the ocean, *Sci. Rep.* [Internet]. 9(1) (2019) 12922. Available from: <https://www.nature.com/articles/s41598-019-49413-5>.
- [5] A.E. Schwarz, T.N. Lighthart, E. Boukris, T. van Harmelen, Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study, *Mar. Pollut. Bull.* [Internet]. 143 (May) (2019) 92–100. Available from, <https://linkinghub.elsevier.com/retrieve/pii/S0025326X19302905>.
- [6] M. Kumar, H. Chen, S. Sarsaiya, S. Qin, H. Liu, M.K. Awasthi, et al., Current research trends on micro- and nano-plastics as an emerging threat to global environment: a review, *J. Hazard. Mater.* [Internet]. 5 (409) (2021) 124967. Available from: <https://linkinghub.elsevier.com/retrieve/pii/S0304389420329587>.
- [7] N.E. Kamber, W. Jeong, R.M. Waymouth, R.C. Pratt, B.G.G. Lohmeijer, J. L. Hedrick, Organocatalytic ring-opening polymerization, *Chem. Rev.* [Internet]. 107 (12) (2007) 5813–5840. Available from, <https://pubs.acs.org/doi/10.1021/cr068415b>.
- [8] S. Penczek, M. Cypriak, A. Duda, P. Kubisa, S. Slomkowski, Living ring-opening polymerizations of heterocyclic monomers, *Prog. Polym. Sci.* [Internet]. 32 (2) (2007) 247–282. Available from, <https://linkinghub.elsevier.com/retrieve/pii/S0079670007000056>.
- [9] S. Hu, J. Zhao, G. Zhang, H. Schlaad, Macromolecular architectures through organocatalysis, *Prog. Polym. Sci.* [Internet]. 74 (2017) 34–77. Available from, <https://linkinghub.elsevier.com/retrieve/pii/S0079670017301600>.
- [10] K.K. Bansal, D. Kakde, L. Purdie, D.J. Irvine, S.M. Howdle, G. Mantovani, et al., New biomaterials from renewable resources – amphiphilic block copolymers from  $\delta$ -decalactone, *Polym. Chem.* [Internet]. 6 (40) (2015) 7196–7210. Available from, <http://xlink.rsc.org/?DOI=C5PY01203A>.
- [11] A.P. Dove, Controlled ring-opening polymerisation of cyclic esters: polymer blocks in self-assembled nanostructures, *Chem. Commun.* [Internet]. 48 (2008) 6446. Available from, <http://xlink.rsc.org/?DOI=b813059k>.
- [12] A.C. Albertsson, V.I.K. Aliphatic, Polyesters, Synthesis, properties and applications, in: *Polysaccharides II* [Internet], Springer, Berlin Heidelberg, 2002, pp. 1–40. Available from: [http://link.springer.com/10.1007/3-540-45734-8\\_1](http://link.springer.com/10.1007/3-540-45734-8_1).
- [13] R.A. Auras, S.P. Singh, J.J. Singh, Evaluation of oriented poly(lactide) polymers vs. existing PET and oriented PS for fresh food service containers, *Packag. Technol. Sci.* [Internet]. 18 (4) (2005) 207–216. Available from: <https://onlinelibrary.wiley.com/doi/10.1002/pts.692>.
- [14] R.A. Gross, B. Kalra, Biodegradable Polymers for the Environment, *Science* 99 (4) (1999) 1–36 (1979).
- [15] Y. Tokiwa, B.P. Calabia, Biodegradability and biodegradation of poly(lactide) [Internet], *Appl. Microbiol. Biotechnol.* 72 (2006) 244–51. Available from: <https://link.springer.com/10.1007/s00253-006-0488-1>.
- [16] R. Nabeoka, H. Suzuki, Y. Akasaka, N. Ando, T. Yoshida, Evaluating the ready biodegradability of biodegradable plastics, *Environ. Toxicol. Chem.* [Internet]. 40 (9) (2021) 2443–2449. Available from, <https://onlinelibrary.wiley.com/doi/10.1002/etc.5116>.
- [17] R. Cardillo, Procédé de production microbiologique des gamma- et delta-lactones, Patent EP0412880, 1991.
- [18] R. Cardillo, Procédé pour la préparation de delta lactones saturées par biohydrogénation des composés insaturés naturels correspondants à l'aide de microorganismes, 1993.
- [19] J.J. Brophy, P.I. Forster, R.J. Goldsack, Coconut Laurels: the leaf essential oils from four Endemic Australian *Cryptocarya* Species: *C. Bellendenkerana*, *C. Cocosoides*, *C. Cunninghamii* and *C. Lividula* (Lauraceae), *Nat. Prod. Commun.* [Internet]. 11(2) (2016) 1934578X1601100. Available from: <http://journals.sagepub.com/doi/10.1177/1934578X1601100230>.
- [20] Q. Ma, W. Xing, J. Xu, X. Peng, Baeyer-Villiger oxidation of cyclic ketones with aqueous hydrogen peroxide catalyzed by transition metal oxides, *Catal. Commun.* [Internet]. 53 (2014) 5–8. Available from, <https://linkinghub.elsevier.com/retrieve/pii/S1566736714001630>.
- [21] E. Szczepańska, D. Colombo, F. Tentori, T. Olejniczak, E. Brenna, D. Monti, et al., Ene-reductase transformation of massoia lactone to  $\delta$ -decalactone in a continuous-flow reactor, *Sci. Rep.* [Internet]. 11 (1) (2021) 1–9. Available from: <https://doi.org/10.1038/s41598-021-97585-w>.
- [22] C. Romero-Guido, I. Belo, T.M.N. Ta, L. Cao-Hoang, M. Alchihab, N. Gomes, et al., Biochemistry of lactone formation in yeast and fungi and its utilisation for the production of flavour and fragrance compounds, *Appl. Microbiol. Biotechnol.* 89 (3) (2011) 535–547.
- [23] P.H. van der Schaft, N. ter Burg, S. van den Bosch, A.M. Cohen, Microbial production of natural  $\delta$ -decalactone and  $\delta$ -dodecalactone from the corresponding  $\alpha$ ,  $\beta$ -unsaturated lactones in Massoi bark oil, *Appl. Microbiol. Biotechnol.* 36 (6) (1992) 712–716.
- [24] P. Olsén, K. Odelius, A.C. Albertsson, Thermodynamic presynthetic considerations for ring-opening polymerization, *Biomacromolecules* [Internet]. 17 (3) (2016) 699–709. Available from, <https://pubs.acs.org/doi/10.1021/acs.biomac.5b01698>.
- [25] K.D. Schneiderman, A.M. Hillmyer, Aliphatic polyester block polymer design, *Macromolecules* 49 (7) (2016) 2419–2428.
- [26] M.T. Martello, A. Burns, M. Hillmyer, Bulk ring-opening transesterification polymerization of the renewable  $\delta$ -decalactone using an organocatalyst, *ACS Macro Lett.* 1 (1) (2012) 131–135.
- [27] L. Cederholm, P. Olsén, M. Hakkarainen, K. Odelius, Turning natural  $\delta$ -lactones to thermodynamically stable polymers with triggered recyclability, *Polym. Chem.* (2020) 12–17.
- [28] R. Ferrari, A. Agostini, L. Brunel, L. Morosi, D. Moscatelli, Self-assembling amphiphilic block copolymer from renewable  $\delta$ -decalactone and  $\delta$ -dodecalactone, *J. Polym. Sci. A Polym. Chem.* [Internet]. 55 (22) (2017 Nov 15) 3788–3797. Available from, <https://onlinelibrary.wiley.com/doi/10.1002/pola.28764>.
- [29] D. Bandelli, C. Helbing, C. Weber, M. Seifert, I. Muljajew, K.D. Jandt, et al., Maintaining the hydrophilic-hydrophobic balance of polyesters with adjustable crystallinity for tailor-made nanoparticles, *Macromolecules* 51 (15) (2018) 5567–5576.
- [30] G.W. Fahnhorst, G.X. De Hoe, M.A. Hillmyer, T.R. Hoye, 4-Carboalkoxylated polyvalerolactones from malic acid: tough and degradable polyesters, *Macromolecules* [Internet]. 53 (8) (2020) 3194–3201. <https://pubs.acs.org/doi/10.1021/acs.macromol.0c00212>.
- [31] D. Tang, C.W. Macosko, M.A. Hillmyer, Thermoplastic polyurethane elastomers from bio-based poly( $\delta$ -decalactone) diols, *Polym. Chem.* 5 (9) (2014) 3231–3237.
- [32] Sigma Aldrich. d-tetradecalactone, natural, 98%, FG grade [Internet]. <https://www.sigmaaldrich.com/FR/fr/product/aldrich/w359020>.
- [33] G. Hass, J.E. Waylonis, Optical constants and reflectance and transmittance of evaporated aluminum in the visible and ultraviolet, *J. Opt. Soc. Am.* 51 (7) (1961) 719–722.

- [34] R. Singh, R.K. Soni, Laser synthesis of aluminium nanoparticles in biocompatible polymer solutions, *Appl. Phys. A Mater. Sci. Process.* 116 (2) (2014) 689–701.
- [35] U. Schuchardt, R.M. Vargas, G. Gelbard, Alkylguanidines as catalysts for the transesterification of rapeseed oil, *J. Mol. Catal. A Chem.* 99 (2) (1995) 65–70.
- [36] Bansal KK. Novel Amphiphilic Block Co- polymers from Renewable Feedstocks: “ Synthesis , Characterisation and Applications. Thesis, 2015, (June©).
- [37] D. Kawaguchi, Direct observation and mutual diffusion of cyclic polymers, *Polym. J.* 45 (8) (2013) 783–789.
- [38] Z. Jia, M.J. Monteiro, Synthesis of cyclic polymers via ring closure, *Adv. Polym. Sci.* 262 (2013) 295–328.
- [39] D.K. Schneiderman, C. Gilmer, M.T. Wentzel, M.T. Martello, T. Kubo, J. E. Wissinger, Sustainable polymers in the organic chemistry laboratory: Synthesis and characterization of a renewable polymer from  $\delta$ -decalactone and L-lactide, *J. Chem. Educ.* 91 (1) (2014) 131–135.
- [40] T. Isono, B.J. Ree, K. Tajima, R. Borsali, T. Satoh, Highly ordered cylinder morphologies with 10 nm scale periodicity in biomass-based block copolymers, *Macromolecules* 51 (2) (2018) 428–437.
- [41] Katsuhara S, Takagi Y, Sunagawa N, Igarashi K, Yamamoto T, Tajima K, et al. Enhanced Self-Assembly and Mechanical Properties of Cellulose- Based Triblock Copolymers: Comparisons with Amylose-Based Triblock Copolymers, 2021.
- [42] K. Makiguchi, Y. Ogasawara, S. Kikuchi, T. Satoh, T. Kakuchi, Diphenyl phosphate as an efficient acidic organocatalyst for controlled/living ring-opening polymerization of trimethylene carbonates leading to block, end-functionalized, and macrocyclic polycarbonates, *Macromolecules* 46 (5) (2013) 1772–1782.
- [43] J. Zhao, N. Hadjichristidis, Polymerization of 5-alkyl  $\delta$ -lactones catalyzed by diphenyl phosphate and their sequential organocatalytic polymerization with monosubstituted epoxides, *Polym. Chem.* [Internet]. 6 (14) (2015) 2659–2668. <http://xlink.rsc.org/?DOI=C5PY00019J>.
- [44] C. Thomas, B. Bibal, Hydrogen-bonding organocatalysts for ring-opening polymerization, *Green Chem.* 16 (4) (2014) 1687–1699.
- [45] L. Zhang, F. Norder, R.C. Pratt, R.M. Waymouth, J.L. Hedrick, C.G. Wade, Phosphazene bases: a new category of organocatalysts for the living ring-opening polymerization of cyclic esters, *Macromolecules* 40 (12) (2007) 4154–4158.
- [46] S. Liu, C. Ren, N. Zhao, Y. Shen, Z. Li, Phosphazene bases as organocatalysts for ring-opening polymerization of cyclic esters, *Macromol. Rapid Commun.* 39 (24) (2018) 1–15.
- [47] X. Pan, H. Wang, C. Li, J.Z.H. Zhang, C. Ji, MolGpka: a web server for small molecule pKaPrediction using a graph-convolutional neural network, *J. Chem. Inf. Model.* 61 (7) (2021) 3159–3165.
- [48] B. Lin, R.M. Waymouth, Organic ring-opening polymerization catalysts: reactivity control by balancing acidity, *Macromolecules* 51 (8) (2018) 2932–2938.
- [49] Sweetlove C. Développement de techniques permettant d’améliorer la prédiction de la biodégradabilité en milieu naturel de produits organiques faiblement hydrosolubles dans des tests de laboratoire, 2017.