1 *N*-Heterocyclic carbene/Lewis acid-mediated ring-opening
2 polymerization of propylene oxide. Part 2: toward
3 dihydroxytelechelic polyethers using triethylborane

4 *Qilei Song,^{†,‡} Junpeng Zhao,[†] Guangzhao Zhang,[†] Daniel Taton,[‡] Frédéric Peruch,[‡]*
5 *and Stéphane Carlotti^{□,‡}*

6 [†]Faculty of Materials Science and Engineering, South China University of
7 Technology, Guangzhou 510640, People's Republic of China

8 [‡]Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France

9 * Corresponding author E-mail: carlotti@enscbp.fr

10 **Abstract:** Propylene oxide (PO) is polymerized by metal-free ring-opening
11 polymerization (ROP) at 25 °C using *N*-heterocyclic carbenes (NHCs) and
12 triethylborane (Et₃B) as a bicomponent catalytic system. Poly(propylene oxide)s with
13 predictable molar mass up to 60 000 g.mol⁻¹ and low dispersity ($\bar{D} < 1.10$) were
14 obtained without the occurrence of undesirable transfer reaction to the monomer. In
15 presence of an alcohol as the initiator, the ROP of PO follows an anionic mechanism
16 assisted by monomer activation improving the efficiency of NHCs for the
17 polymerization of substituted epoxides. Et₃B is involved both in the formation of a
18 complexed active center and in the activation of PO. Interestingly,
19 dihydroxytelechelic PPOs can be readily synthesized not only using 1,4-
20 benzenedimethanol but also water, both serving as difunctional initiators. Block

1 copolyethers are also prepared by PPO chain extension experiments. All
2 (co)polyethers have been thoroughly characterized by ^1H NMR spectroscopy, SEC
3 and MALDI-TOF mass spectrometry as means to elucidate the reaction mechanisms
4 involved in this chemistry.

5 **Keywords:** substituted epoxides, anionic ring-opening polymerization, *N*-heterocyclic
6 carbene, metal-free catalyst, dihydroxytelechelic polyethers

7 1. Introduction

8 Bicomponent catalytic systems based on initiator/chain-end complexation or
9 activation, monomer activation, or combination of both strategies were proposed for
10 the controlled/living ROP of epoxides in order to obtain (co)polyethers with high
11 molar mass and low dispersity. In particular, bicomponent initiating/catalytic systems
12 based on the combination of triisobutylaluminum (*i*-Bu₃Al) as a Lewis acid, and
13 various anionic initiators (*e.g.*, alkali metal alkoxides or ammonium salts) or organic
14 superbases in presence of hydroxyl-containing initiators were shown to rapidly and
15 efficiently control the ROP of various epoxides at 25 °C or below [1-6].

16 The last two decades witnessed the advent of organocatalysts in polymer synthesis to
17 access polymeric materials free of any metallic residues, with a potential use in high-
18 value applications [7-10]. In this context, and to some extent, epoxide monomers
19 distinguish from other heterocyclic compounds, such as lactide, lactones or cyclic
20 carbonates, as just few organocatalysts allows their efficient ROP. Organocatalyzed

1 ring-opening polymerization of epoxides actually found its roots with the use of non-
2 metallic acids to polymerize various monomers, following a cationic-type mechanism.
3 Representative organo-catalysts/initiators for the anionic polymerization or related
4 mechanism of epoxides include onium salts [11-13], phosphazene bases [14-18], *N*-
5 heterocyclic carbenes (NHCs) [19-22] and *N*-heterocyclic olefins (NHOs) [23, 24].
6 Although the polymerization rate can be enhanced relatively to reactions employing
7 alkali metal oxides, there are still some limitations for (co)polyethers synthesis by an
8 organocatalytic pathway, such as long reaction times, elevated temperature (above
9 45 °C), limited molar masses and more generally a lack of universality for different
10 substituted epoxides.

11 Recently, the rapid and controlled/living ROP of epoxides is carried out by using
12 metal-free dual catalysts, which is composed of mild organic bases such as weak
13 phosphazene bases (*e.g.*, *tert*-butylimino tris(dimethylamino)phosphorene, *t*-BuP₁; 1-
14 *tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ⁵,4λ⁵-catenadi(phosphazene), *t*-BuP₂),
15 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *N*-methyl-1,5,7-triazabicyclododecene
16 (MTBD) or onium salts and triethylborane (Et₃B) [25-27]. In these studies, Et₃B is
17 playing a dual role simultaneously, both complexing the initiator/chain-end and
18 activating the monomer substrate, in the same way we have described for *i*-Bu₃Al [1-
19 6]. NHC-catalyzed ROP of epoxides was also investigated in the last decade [19-22].
20 Due to the inherent nucleophilicity and basicity of NHCs, the polymerization can
21 proceed by anionic or zwitterionic mechanism which leads to the formation of PEO
22 with targeted molar mass and low dispersity in dimethyl sulfoxide at 50 °C. However,

as mentioned before, there are still some drawbacks of this one-component-catalyzed polymerization such as low monomer conversion or limited molar mass for PO polymerization. In order to overcome these limitations and following our interest in NHCs and the ROP of epoxides utilizing the concept of basicity decrease and monomer activation, here we report that the association of a NHC with Et₃B achieves efficiently the (co)polymerization of propylene oxide yielding possibly dihydroxytelechelic polyethers.

2. Experimental part

2.1 Chemicals

Tetrahydrofuran (THF; VWR Chemicals BDH, 100%) was dried over sodium/benzophenone before cryo-distillation and use. Benzyl alcohol (BnOH; Sigma Aldrich, 99%) was dried over CaH₂ then distilled and dissolved in purified THF to prepare a 0.5 M solution. Milli-Q water (H₂O), used as an initiator, was dissolved in purified THF into a 0.5 M solution. 1,4-Benzenedimethanol (BDM; abcr GmbH, 99%) was dried by azeotropic distillation of THF then dissolved in THF into a 0.5 M solution. Propylene oxide (PO; Sigma Aldrich, 99%) and 1,2-butylene oxide (BO; Sigma Aldrich, 99%) were stirred over CaH₂ at room temperature overnight before distillation. Triethylborane (Et₃B, 1.0 M in THF) was purchased from Sigma Aldrich and used as received. 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (I^mPh, 98%)

1 and 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu, 98%) were purchased from Strem
2 Chemicals, Inc. and used as received, 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-
3 ylidene (IⁱPr) was prepared according to the previous reference [28].

4 2.2 Instrumentation

5 NMR spectra were recorded at 25 °C on a Bruker Avance 400 (¹H, 400.2 MHz) using
6 deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane as the internal
7 standard. Molar masses were determined by size exclusion chromatography (SEC) in
8 THF (1 mL.min⁻¹) at 40 °C with 1,3,5-trichlorobenzene (1 mL in 500 mL of THF) as
9 a flow marker, using both refractive index (RI) and UV detectors. Analyses were
10 performed using a three-column TSK gel TOSOH (G4000, G3000, G2000 with pore
11 sizes of 20, 75 and 200 Å respectively, connected in series) calibrated with
12 polystyrene (PS) standards to obtain apparent number-average molar mass ($\overline{M}_{n,SEC}$)
13 and $\bar{D}$ of the polymers. Matrix assisted laser desorption/ionization time of flight mass
14 spectrometry (MALDI-TOF MS) measurements were performed by the CESAMO
15 (Bordeaux, France) on an Autoflex mass spectrometer (Bruker). The instrument is
16 equipped with a laser emitting at 355 nm. Spectra were recorded in the positive-ion
17 mode using the reflectron. Samples were dissolved in THF (10 mg.mL⁻¹), then mixed
18 with a solution of cationisation agent (NaI) in MeOH (10 mg.mL⁻¹) and a solution of
19 matrix, dithranol (1,8-dihydroxyanthracen-9(10H)-one) in THF (10 mg.mL⁻¹), in a
20 volume ratio of 1:1:10. Then, 1~2 μL of the final solution was deposited onto the
21 sample target and vacuum-dried.

2.3 General polymerization procedure

Representative procedure for the ROP of PO. A typical procedure of entry 4 in Table 1 is as follows. The Schlenk flask was flamed three times on a vacuum line and transferred in a glovebox, where I^tPr (1.67 mg, 0.0092 mmol), dried THF (1.0 mL), THF solution of BnOH (0.5 M, 93.0 μ L, 0.046 mmol), Et₃B solution (1.0 M in THF, 27.6 μ L, 0.0276 mmol) and PO (0.98 mL, 14.0 mmol) were successively loaded. The flask was then transferred in a fume hood and the reaction mixture was stirred at 25 °C. To obtain the kinetic plot, small aliquots (*ca.* 0.05 mL each) were withdrawn under an argon flow at different time intervals and diluted with 0.6 mL of CDCl₃ containing one drop of acetic acid for ¹H NMR analysis to determine the conversion of PO. After removal of CDCl₃ by evaporation, the sample was re-dissolved in THF for SEC measurement to determine $\overline{M}_{n,SEC}$ and $\overline{D}$. The reaction was quenched after 24 h by addition of a few drops of acetic acid and then an aliquot was withdrawn for ¹H NMR and SEC analysis. Solvent was removed under vacuum, and the product (viscous liquid) was substantially dried under vacuum at room temperature overnight. Conv. (PO) = 87%, $\overline{M}_{n,th}$ = 15.7 kg.mol⁻¹. $\overline{M}_{n,SEC}(THF, PS\ standards) = 16.7\ kg.mol^{-1}$, $\overline{D} = 1.09$. ¹H NMR (400 MHz, 298 K, CDCl₃): δ/ppm = 4.51-4.45 (BnOH, PhCH₂O–), 3.71-3.39 (–OCH₂CH(CH₃)O–), 3.39-3.05 (–OCH₂CH(CH₃)O–), 1.25-0.87 (–OCH₂CH(CH₃)O–).

Chain extension experiments. A typical procedure of entry 9 in Table 1 is as follows. The Schlenk flask was flamed three times on a vacuum line and transferred in a

1 glovebox, where I^{*i*}Pr (5.08 mg, 0.028 mmol), dried THF (0.57 mL), THF solution of
 2 BnOH (0.5 M, 280.0 μ L, 0.14 mmol), Et₃B solution (1.0 M in THF, 168.0 μ L, 0.168
 3 mmol) and PO (0.98 mL, 14.0 mmol) were successively loaded. The flask was then
 4 transferred in a fume hood and the reaction mixture was stirred at 25 °C. After 5 h, the
 5 magnetic stirrer almost stopped spinning due to the increased viscosity of solution and
 6 an aliquot was withdrawn for ¹H NMR and SEC analysis. Conv.(PO) = 100%, $\overline{M}_{n,th}$ =
 7 5.8 kg.mol⁻¹. $\overline{M}_{n,SEC}$ (THF, PS standards) = 6.5 kg.mol⁻¹, D = 1.03. Then a batch of
 8 BO (1.22 mL, 14.0 mmol) was added under an argon flow, after which the magnetic
 9 stirrer gradually started to spin again, and then the flask was kept at 25 °C with
 10 stirring for another 24 h. The reaction was quenched after 29 h by addition of a few
 11 drops of acetic acid and then an aliquot was withdrawn for ¹H NMR and SEC
 12 analysis. Solvent was removed under vacuum, and the product (viscous liquid) was
 13 substantially dried under vacuum at room temperature overnight. Conv.(BO) = 74%,
 14 $\overline{M}_{n,th}$ (diblock) = 11.1 kg.mol⁻¹. $\overline{M}_{n,SEC}$ (THF, PS standards) = 10.7 kg.mol⁻¹, D =
 15 1.06. ¹H NMR (400 MHz, 298 K, CDCl₃): δ /ppm = 4.50-4.46 (BnOH, PhCH₂O–),
 16 3.80-3.15 (PPO, –OCH₂CH(CH₃)O–) and (PBO, –OCH₂CH(CH₂CH₃)O–), 1.60-1.33
 17 (PBO, –OCH₂CH(CH₂CH₃)O–), 1.27-0.86 (PPO, –OCH₂CH(CH₃)O–), 0.90-0.81
 18 (PBO, –OCH₂CH(CH₂CH₃)O–).

19 **3. Results and discussion**

20 Following the conclusion of a parallel work using NHC's combined with
 21 triisobutylaluminum (*i*-Bu₃Al) [29], efficient 1,3-bis(isopropyl)-

4,5(dimethyl)imidazol-2-ylidene, *I*^{*i*}Pr; Figure S1) due its higher nucleophilicity [30] was chosen to be combined with Et₃B for the ROP of PO in the presence of different alcohols as initiators. Other NHC's, *e.g.* 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, *I*^{*m*}Ph and 1,3-di-*tert*-butylimidazol-2-ylidene, *I*^{*t*}Bu were shown to be less reactive (ESI Table S1). The initial feed ratio of [PO]₀/[OH]/[NHC]/[Et₃B] was fixed at 300/1/0.2/0.6, targeting relatively high-molar mass PPOs (17.5 kg.mol⁻¹). Use of a threefold excess of Et₃B relatively to NHC was based on previous investigations regarding the Lewis pair-mediated ROP of epoxides [26, 27]. When the *I*^{*i*}Pr/*i*-Bu₃Al system is giving a single PPO population, the SEC trace of the resultant PPO showed a bimodal molar mass distribution, with a small side peak having twice the molar mass of the main population (discussed after) despite exact similar experimental conditions and same solvent, monomer, NHC batches.

Scheme 1. Illustration for ROP of PO catalyzed by *I*^{*i*}Pr + Et₃B in the presence of alcohols.

Influence of the [Et₃B]/[I^{*i*}Pr] feed ratio/loading. The effect of [Et₃B]/[I^{*i*}Pr] molar ratios was first investigated, keeping the [PO]₀/[-OH]/[I^{*i*}Pr] ratio constant at 300/1/0.2 (entries 1-4, Table 1). Importantly, I^{*i*}Pr alone could not induce the polymerization (entry 1). A stepwise increase of the [Et₃B]/[I^{*i*}Pr] molar ratio was then evaluated. When the amount of Et₃B was less than that of I^{*i*}Pr ([Et₃B]/[I^{*i*}Pr] = 0.6, entry 2), PO polymerization proceeded slowly, with only 7% of PO being converted after 88 h. Increasing the molar amount of Et₃B can increase the monomer conversion reaching 39% after 96 h (entry 3, [Et₃B]/[I^{*i*}Pr] = 1). For [Et₃B]/[I^{*i*}Pr] = 3 (entry 4, Table 1), the conversion in PO reached 87% after 24h. In all cases, the resulting PPO showed a bimodal molar mass distribution by SEC with low dispersities (Figure S2).

A low molar mass PPO was synthesized by increasing the amount of initiator (entry 5, Table 1 and Figure 1), and the chain-end fidelity of corresponding product was analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The $\overline{M}_{n,SEC}$ of the main population was found in good agreement with the theoretical molar mass ($\overline{M}_{n,th}$) calculated from the [PO]₀/[BnOH] ratio and the monomer conversion. Intriguingly, the $\overline{M}_{p,SEC}$ of the smaller population was twice that of the main one. Careful examination of the isolated sample by ¹H NMR spectroscopy did not reveal any occurrence of transfer to monomer, as attested by the absence of signals from allylic unsaturated product (CH₂=CHCH₂O-) that would have located at 5.0-6.0 ppm. Through the MALDI-TOF MS analysis, two distinct populations corresponded to the two different PPO chain-ends, *i.e.* α-PhCH₂O/ω-OH (of lower molar mass) and α-HO/ω-OH (higher molar

1 mass). These two populations could eventually be ascribed to the BnOH and the H₂O-
2 initiated ROP of PO, respectively. These data were also consistent with SEC results,
3 where the $\overline{M}_{p,SEC}$ of the smaller population (H₂O-initiated, 3.8 kg.mol⁻¹) was roughly
4 twice that of the main population (BnOH-initiated, 2.0 kg.mol⁻¹). That also explained
5 why no UV signal was observed for the population of higher molar mass in
6 corresponding SEC traces. This means that despite a careful drying of all components,
7 residual water that we believe was trapped in the NHCs can act as a bifunctional
8 initiator. In presence of NHCs alone, so using a mono-component approach, water
9 could not initiate the PO polymerization in such conditions (entry 1, Table 1) due to
10 its low reactivity. In our activated and parallel work using *i*-Bu₃Al instead of Et₃B,
11 water could not initiate PO as well. The highly reactive trialkylaluminum is known to
12 react with water forming inactive aluminum hydroxide. The trialkylboron is shown
13 here to not trap adventitious residual water. To take benefit of this unexpected
14 observation and to check this assumption, a series of experiments were carried out in
15 presence of precise amounts of water. A polymerization was thus conducted in
16 presence of 0.5 equiv. H₂O (entry 6, Table 1). SEC traces of the resultant PPOs
17 showed a clear increase of the peak intensity of the population of the highest molar
18 mass, *i.e.* assigned to the H₂O-initiated PPO (Figure S3). Water was then chosen as a
19 bifunctional initiator for PO polymerization (entries 7, Table 1). SEC traces showing a
20 monomodal mass distribution was thus obtained (Figure 2a), validating that H₂O can
21 act as a bifunctional initiator for the NHC/Et₃B-catalyzed ROP of PO in this
22 chemistry. 1,4-benzenedimethanol (BDM) was also proposed and shown to act as a

1 bifunctional initiator (entry 8, Table 1 and Figure 2b).

2

3 **Table 1 ROP of PO catalyzed by *i*Pr + Et₃B with BnOH as the initiator^a**

Entry	[PO] ₀ /[-OH]/ [<i>i</i> Pr]/[Et ₃ B] ^b	Solvent	Time (h)	Conv. ^c (%)	$\overline{M}_{n,th}$ ^d (kg.mol ⁻¹)	$\overline{M}_{n,NMR}$ ^e (kg.mol ⁻¹)	$\overline{M}_{n,SEC}$ ^f (kg.mol ⁻¹)	<i>D</i> ^f
1	300/1/0.2/-	THF	24	0	—	—	—	—
2	300/1/0.2/0.12	THF	88	7	1.2	1.4	1.7 [1.6]	1.09 (10/90)
3	300/1/0.2/0.2	THF	96	39	6.8	7.1	8.1 [7.7]	1.08 (10/90)
4	300/1/0.2/0.6	THF	24	87	15.7	16.6	16.7 [15.6]	1.09 (12/88)
5	300/7.5/0.2/0.6	bulk	44	67	1.5	1.4	2.0 [1.9]	1.07 (5/95)
6 ^g	300/2/0.2/0.6	THF	24	21	—	—	3.0 [2.3]	1.14 (44/56)
7 ^h	50/1/0.2/0.6	THF	24	98	5.8	—	6.8	1.02
8 ^h	50/1/0.2/0.6	THF	24	100	5.9	7.8	8.3	1.03
9-1	100/1/0.2/1.2	THF	4	100	5.8	6.3	6.5 [6.4]	1.03 (2/98)
9-2 ⁱ	100/1/0.2/1.2	THF	24	74	11.1	11.4	10.7 [11.8]	1.06 (2/98)
10	300/3/0.2/0.6	THF	24	14	0.9	0.8	1.1	1.09
11	300/0.3/0.2/0.6	bulk	4	89	51.8	71.8	49.9 [43.0]	1.13 (21/79)
12	300/0.15/0.2/0.6	bulk	7	78	90.7	118.5	67.3 [59.6]	1.18 (23/77)

^aPerformed in THF ([PO]₀ = 7 M) or in bulk at 25 °C with BnOH as the initiator. ^bMolar feed ratio of PO, hydroxyl, *N*-heterocyclic carbene and triethylborane. ^cConversion of PO calculated from ¹H NMR spectra of the crude product.

^dTheoretical number-average molar mass calculated from feed ratio ([PO]₀/[BnOH]) and monomer conversion. ^eNumber-average molar mass calculated from ¹H NMR spectra of the isolated product by comparing signal integrals of the end group (PhCH₂O-) and polymer. ^fNumber-average molar mass, **dispersity** obtained from SEC analysis (THF, 40 °C, polystyrene standards). **For bimodal mass distributions, number in square brackets denotes the molar mass of main peak determined by the UV trace, and the values in parenthesis denotes the percentage of each population calculated by deconvolution.**

^gMolar ratio of [BnOH]/[H₂O] = 1/0.5 is used as initiators. ^hH₂O (entry 7) and BDM (entry 8) are used as an initiator, respectively.

ⁱChain extension following entry 9-1 using BO as the second monomer.

Figure 1. SEC traces (upper left), ^1H NMR spectrum (bottom left) and MALDI-TOF MS spectrum (right) of the isolated PPO (entry 5, Table 1). Signals in MALDI-TOF MS correspond to BnOH/ H_2O -initiated PPOs ionized by sodium cations ($\text{BnO-PO}_n\text{-H}$ and $\text{HO-PO}_n\text{-H}$).

1

2 **Figure 2.** (a) SEC traces (left) and ^1H NMR spectrum (right) of the isolated PPO
 3 (entry 7, Table 1, H_2O -initiated). (b) SEC traces (left) and ^1H NMR spectrum (right)
 4 of the isolated PPO (entry 8, Table 1, BDM-initiated).

5 As discussed above, NHCs can either behave as Brønsted bases or as nucleophiles,
 6 which have been widely proposed in organic catalysis of polymerization [31, 32].
 7 Corresponding mechanisms mostly depend on the structure of the NHC, in particular
 8 its $\text{p}K_{\text{a}}$ value and its steric hindrance but also on the initial experimental conditions
 9 including the presence or the absence of an initiator and the nature of the solvent. In
 10 absence of any initiator, some cyclic monomers can undergo a direct polymerization
 11 by a nucleophilic attack of the NHC, *via* the so-called zwitterionic ROP (ZROP)
 12 mechanism [20, 33-36]. Here PO polymerization induced by $\text{I}^t\text{Pr} + \text{Et}_3\text{B}$ in absence of

1 initiator yielded PPOs with uncontrolled molar masses and low dispersity (entries S4-
2 6, Table S1). The ^1H NMR spectrum of the isolated product clearly indicated that no
3 transfer to monomer occurred during the polymerization (Figure S4). The related
4 ZROP mechanism was illustrated in Scheme S1.

5 **Kinetic study.** The kinetic study of the ROP of PO was carried out using three
6 different reaction conditions. Two distinct parameters, namely, the monomer
7 concentration and the molar ratio of $[\text{Et}_3\text{B}]/[\text{I}^*\text{Pr}]$ were chosen to investigate the
8 polymerization kinetics. The ROP of PO exhibited an apparent first kinetic order with
9 respect to the monomer, a linear increase of $\overline{M}_{n,\text{SEC}}$ values with PO conversion in all
10 cases and low dispersities (Figure 3). Compared with the polymerization performed in
11 THF, where PO was almost consumed after 8 h, it only took 4 h for PO to be almost
12 quantitatively converted when the ROP was conducted in bulk. Keeping the monomer
13 concentration constant at $[\text{PO}]_0 = 7 \text{ mol.L}^{-1}$ and increasing the feed ratio of
14 $[\text{Et}_3\text{B}]/[\text{I}^*\text{Pr}]$ to 6/1 enabled to enhance the polymerization rate to reach similar
15 reaction times in bulk condition. These results were also consistent with their apparent
16 propagation rate constants (k_{app}), which equaled to the slope of the linear fits based on
17 the equation $\ln([\text{M}]_0/[\text{M}]_t) = k_{\text{app}}t$. Thus, increasing the monomer concentration and/or
18 the amount in Lewis acid allowed to accelerate the ROP of PO.

19

Figure 3. Conversion and $\ln([PO]_0/[PO])$ vs time plots for PO polymerization with I'Pr/Et₃B systems.

Chain extension reactions. To further explore the living character of I'Pr + Et₃B-catalyzed ROP of PO and thus expand the scope of application of this bicomponent catalyst, 1,2-butylene oxide (BO) was employed as representative substituted epoxides for chain extension reactions (entry 9, Table 1). A $[PO]_0/[-OH]/[I'Pr]/[Et_3B]$ feed ratio of 100/1/0.2/1.2 in THF ($[PO]_0 = 7$ M) was chosen based on the kinetic study discussed above. After full conversion of PO was achieved to grow the first block based on PPO, 100 equiv. of another monomer (BO) were added. After 24 h of reaction at 25 °C, the parent SEC trace clearly shifted to the higher molar masses, with no trace of dead polymer (Figure 4), attesting to the effective crossover reaction

1 from PPO to the other block. Diblock copolymers (PPO-*b*-PBO) with predictable
 2 molar mass and low $\bar{D}$ could thus be achieved, as also evidenced by ^1H NMR analysis
 3 confirming the presence of both blocks. From the relative integrations of
 4 characteristic signals of both blocks at 1.07 ppm and at 0.85 ppm for PPO and PBO
 5 blocks, respectively, a value of 11.1 kg.mol⁻¹ vs 11.3 kg.mol⁻¹ by SEC analysis, was
 6 thus calculated. In addition, BO polymerized more slowly compared to PO under
 7 otherwise similar conditions, in agreement with a lower reactivity of the former
 8 monomers.

Figure 4. Chain extension reactions, SEC traces (left) of crude PPO-*b*-PBO (orange line) and ^1H NMR spectrum (right) of the isolated product (entry 9, Table 1).

Synthesis of PPOs of different molar masses. Maintaining $[\text{PO}]_0/[\text{I}^*\text{Pr}]/[\text{Et}_3\text{B}] = 300/0.2/0.6$, PPOs with various molar masses were targeted (entries 10-12, Table 1) by adjusting the molar ratio of the monomer to the initiator (BnOH). When a low-molar mass PPO is targeted ($\overline{DP}_n = 100$, 5.8 kg.mol⁻¹), it is found that directly enhancing the amount of initiator by 3 times leads to a much slower polymerization, the conversion of PO being only 14% after 24 h in THF (entry 10, Table 1).

1 Consistently with the above discussion, the synthesis of PPO with low molar mass (
2 $\overline{DP}_n = 40$, 2.3 kg.mol⁻¹) was achieved by polymerizing PO in bulk to enhance the
3 reaction rate (entry 5, Table 1). Under such conditions, the conversion of PO reached
4 67% after 44 h. For a higher molar mass PPO targeted ($\overline{DP}_n = 1000$, 58.1 kg.mol⁻¹),
5 an even faster polymerization rate was noted (entry 11, Table 1), with a conversion of
6 89% in PO being reached after 4h. For the highest targeted molar mass ($\overline{DP}_n = 2000$,
7 116.2 kg.mol⁻¹) 7h was required to achieve 78% conversion of PO (entry 12, Table 1).
8 These results suggested that a higher concentration in hydroxyl groups caused a lower
9 conversion of PO for the same time. In the meantime, a slight increase of the small
10 H₂O-initiated population was observed by SEC, owing to the decrease in
11 concentration of BnOH.

12 **Mechanism.** Et₃B is believed to play an activating role for the monomer and to
13 complex the base, similarly to the metal-based *i*-Bu₃Al used as strong Lewis acid in
14 the ROP of epoxides [1-6] or metal-free Et₃B in the Lewis pair-mediated ROP of
15 epoxides and its copolymerization with other cyclic monomers [25-27, 37-41]. For a
16 molar ratio of [Et₃B]/[IPr] equals to 3/1, Et₃B would play a dual role by being
17 involved both in the formation of an activated-hydroxyl complex (AH) and an
18 activated monomer (AM). Interestingly, H₂O is yielding twice the molar mass in
19 agreement with a double initiation (Scheme 2).

20 The specific amount of Et₃B used for the formation of two complexes is not shown in
21 the proposed scheme as there is an open discussion about the specific ratio of Et₃B in

1 these two functions, which means whether 1 equiv. of Et₃B is used for the formation
2 of AH complex and the monomer is activated by the residual Et₃B (2 equiv.), or *vice*
3 *versa* [27, 37]. In fact, when the amount of [Et₃B] ≤ [IⁱPr], the ROP of PO indeed
4 occurred even at a slow polymerization rate (entries 2-3, Table 1, [Et₃B]/[IⁱPr] = 0.6,
5 1, respectively) as shown previously [26]. The PO monomer could coordinate to Et₃B
6 which would be more favourable than the formation of AH complex, due to the higher
7 concentration in monomer relatively to the initiator. In the present case, the minimum
8 feed ratio of [Et₃B]/[IⁱPr] = 0.6 was still effective for the ROP of PO, due to the
9 formation of a weak AH complex, corresponding to the activation by H-bonding of
10 the hydroxyl function by the NHC and complexed with Et₃B. Therefore, coexistence
11 of both an activated-hydroxyl complex, preventing transfer to monomer, and an
12 activated monomer enables the polymerization to proceed, even when [Et₃B] < [IⁱPr],
13 achieving high molar mass PPOs.

14 As mentioned, the hydroxyl concentration has dramatically affected the
15 polymerization rate as the content in Et₃B available for epoxide activation depends on
16 the amount of alcohol added. Therefore, the difference in the monomer activation
17 process also explains the different polymerization rates caused by the variation of
18 targeted $\overline{DP}_n$ (e.g., entry 5 vs entry 11, Table 1). With a similar [PO]₀/[IⁱPr]/[Et₃B]
19 ratio, a lower concentration of the AM complex is formed, due to the presence of
20 higher amount of alcohol (lower targeted $\overline{DP}_n$), promoting the complexation of
21 activated/dormant hydroxyl functions by Et₃B, which slows down the polymerization.
22 Fast interconversion between AM and uncomplexed hydroxyl functions (dormant

1 chain-end or alcohol) enables a complete initiation efficiency.

3 **Scheme 2.** Proposed mechanism for the synthesis of dihydroxytelechelic PPO by
 4 ROP of PO initiated by H_2O and catalyzed by I'Pr + Et_3B (1/3).

5 4. Conclusions

6 *N*-heterocyclic carbenes (NHCs) used in association with triethylborane (Et_3B) enable
 7 to efficiently trigger the metal-free ring-opening polymerization (ROP) of propylene
 8 oxide (PO) and the synthesis of polyether-based block copolymer. PPOs with
 9 predictable molar masses over a wide molar mass range and low dispersity ($\mathcal{D} < 1.1$)
 10 can be achieved under rather mild conditions, including solvent-free conditions at
 11 room temperature. Depending on the presence of hydroxyl functions or not, an

anionic or a zwitterionic ROP mechanism operates, respectively. Water can act as a bifunctional initiator providing α,ω -hydroxytelechelic PPOs. Compared with NHCs alone for the PO polymerization (bulk, 50 °C), the presence of Et₃B improves its performance in terms of efficiency and molar masses, highlighting the advantages of this bicomponent system.

Acknowledgement

Q. Song gratefully thanks the China Scholarship Council for offering the scholarship to work in LCPO, University of Bordeaux, France.

Data in brief

The raw data will be shared upon request.

References

- [1] C. Billouard, S. Carlotti, P. Desbois, A. Deffieux, “Controlled” High-Speed Anionic Polymerization of Propylene Oxide Initiated by Alkali Metal Alkoxide/Trialkylaluminum Systems, *Macromolecules* 37(11) (2004) 4038-4043.
- [2] S. Carlotti, C. Billouard, E. Gautriaud, P. Desbois, A. Deffieux, Activation Mechanisms of Trialkylaluminum in Alkali Metal Alkoxides or Tetraalkylammonium Salts / Propylene Oxide Controlled Anionic Polymerization, *Macromol. Symp.* 226(1) (2005) 61-68.
- [3] A. Labbé, S. Carlotti, C. Billouard, P. Desbois, A. Deffieux, Controlled High-Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of Triisobutylaluminum, *Macromolecules* 40(22) (2007) 7842-7847.
- [4] V. Rejsek, D. Sauvanier, C. Billouard, P. Desbois, A. Deffieux, S. Carlotti, Controlled Anionic Homo- and Copolymerization of Ethylene Oxide and Propylene Oxide by Monomer Activation, *Macromolecules* 40(18) (2007) 6510-6514.
- [5] V. Rejsek, P. Desbois, A. Deffieux, S. Carlotti, Polymerization of ethylene oxide initiated by lithium derivatives via the monomer-activated approach: Application to the direct synthesis of PS-*b*-PEO and PI-*b*-PEO diblock copolymers, *Polymer* 51(24) (2010) 5674-5679.
- [6] A.-L. Brocas, A. Deffieux, N. Le Malicot, S. Carlotti, Combination of phosphazene base and triisobutylaluminum for the rapid synthesis of polyhydroxy

- telechelic poly(propylene oxide), *Polym. Chem.* 3(5) (2012) 1189-1195.
- [7] M.K. Kiesewetter, E.J. Shin, J.L. Hedrick, R.M. Waymouth, *Organocatalysis: Opportunities and Challenges for Polymer Synthesis*, *Macromolecules* 43(5) (2010) 2093-2107.
- [8] W.N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle, D. Taton, Update and challenges in organo-mediated polymerization reactions, *Prog. Polym. Sci.* 56 (2016) 64-115.
- [9] S. Hu, J. Zhao, G. Zhang, H. Schlaad, Macromolecular architectures through organocatalysis, *Prog. Polym. Sci.* 74 (2017) 34-77.
- [10] A. Dove, H. Sardon, S. Naumann, *Organic Catalysis for Polymerisation*, Royal Society of Chemistry 2018.
- [11] H. Morinaga, B. Ochiai, T. Endo, Metal-Free Ring-Opening Polymerization of Glycidyl Phenyl Ether by Tetrabutylammonium Fluoride, *Macromolecules* 40(16) (2007) 6014-6016.
- [12] H. Morinaga, Y. Ujihara, T. Yamanaka, D. Nagai, T. Endo, Metal-free ring-opening polymerization of glycidyl phenyl ether initiated by tetra-n-butylammonium acetate and its application to the hydroxyl-terminated telechelic polymer, *J. Polym. Sci., Part A: Polym. Chem.* 49(18) (2011) 4092-4097.
- [13] J. Zhang, Q. Liu, H. Ren, N. Zhang, P. Li, K. Yang, Phosphoniums as catalysts for metal-free polymerization: Synthesis of well-defined poly(propylene oxide), *J. Mol. Struct.* 1148 (2017) 421-428.
- [14] B. Eßwein, N.M. Steidl, M. Möller, Anionic polymerization of oxirane in the presence of the polyiminophosphazene base t-Bu-P₄, *Macromol. Rapid Commun.* 17(2) (1996) 143-148.
- [15] S. Boileau, N. Ily, Activation in anionic polymerization: Why phosphazene bases are very exciting promoters, *Prog. Polym. Sci.* 36(9) (2011) 1132-1151.
- [16] J. Zhao, N. Hadjichristidis, Y. Gnanou, Phosphazene-promoted anionic polymerization, *Polimery* 59(01) (2014) 49-59.
- [17] H. Misaka, E. Tamura, K. Makiguchi, K. Kamoshida, R. Sakai, T. Satoh, T. Kakuchi, Synthesis of end-functionalized polyethers by phosphazene base-catalyzed ring-opening polymerization of 1,2-butylene oxide and glycidyl ether, *J. Polym. Sci., Part A: Polym. Chem.* 50(10) (2012) 1941-1952.
- [18] Y. Satoh, H. Matsuno, T. Yamamoto, K. Tajima, T. Isono, T. Satoh, Synthesis of Well-Defined Three- and Four-Armed Cage-Shaped Polymers via “Topological Conversion” from Trefoil- and Quatrefoil-Shaped Polymers, *Macromolecules* 50(1) (2016) 97-106.
- [19] J. Raynaud, C. Absalon, Y. Gnanou, D. Taton, N-heterocyclic carbene-induced zwitterionic ring-opening polymerization of ethylene oxide and direct synthesis of alpha,omega-difunctionalized poly(ethylene oxide)s and poly(ethylene oxide)-b-poly(epsilon-caprolactone) block copolymers, *J. Am. Chem. Soc.* 131(9) (2009) 3201-9.
- [20] J. Raynaud, C. Absalon, Y. Gnanou, D. Taton, N-Heterocyclic Carbene-Organocatalyzed Ring-Opening Polymerization of Ethylene Oxide in the Presence of Alcohols or Trimethylsilyl Nucleophiles as Chain Moderators for the Synthesis of

- 1 α,ω -Heterodifunctionalized Poly(ethylene oxide)s, *Macromolecules* 43(6) (2010)
- 2 2814-2823.
- 3 [21] J. Raynaud, W.N. Ottou, Y. Gnanou, D. Taton, Metal-free and solvent-free
- 4 access to α,ω -heterodifunctionalized poly(propylene oxide)s by N-
- 5 heterocyclic carbene-induced ring opening polymerization, *Chem. Commun.* 46(18)
- 6 (2010) 3203-5.
- 7 [22] R. Lindner, M.L. Lejkowski, S. Lavy, P. Deglmann, K.T. Wiss, S. Zarbakhsh, L.
- 8 Meyer, M. Limbach, Ring-Opening Polymerization and Copolymerization of
- 9 Propylene Oxide Catalyzed by N-Heterocyclic Carbenes, *ChemCatChem* 6(2) (2014)
- 10 618-625.
- 11 [23] S. Naumann, A.W. Thomas, A.P. Dove, N-Heterocyclic Olefins as
- 12 Organocatalysts for Polymerization: Preparation of Well-Defined Poly(propylene
- 13 oxide), *Angew. Chem. Int. Ed. Engl.* 54(33) (2015) 9550-4.
- 14 [24] A. Balint, M. Papendick, M. Clauss, C. Muller, F. Giesselmann, S. Naumann,
- 15 Controlled preparation of amphiphilic triblock-copolyether in a metal- and solvent-
- 16 free approach for tailored structure-directing agents, *Chem. Commun.* 54(18) (2018)
- 17 2220-2223.
- 18 [25] L. Ye, H. Peng, G. Yang, D. Zhang, Z. Xia, Well Controlled Living Anionic
- 19 Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of
- 20 Triethyl Borane, *Gaofenzi Cailiao Kexue Yu Gongcheng/Polymeric Materials*
- 21 *Science and Engineering* 34(1) (2018) 1-5.
- 22 [26] Y. Chen, J. Shen, S. Liu, J. Zhao, Y. Wang, G. Zhang, High Efficiency Organic
- 23 Lewis Pair Catalyst for Ring-Opening Polymerization of Epoxides with
- 24 Chemoselectivity, *Macromolecules* 51(20) (2018) 8286-8297.
- 25 [27] C.J. Zhang, H.Y. Duan, L.F. Hu, C.H. Zhang, X.H. Zhang, Metal-Free Route to
- 26 Precise Synthesis of Poly(propylene oxide) and Its Blocks with High Activity,
- 27 *ChemSusChem* 11(24) (2018) 4209-4213.
- 28 [28] N. Kuhn, T.J.S. Kratz, Synthesis of imidazol-2-ylidenes by reduction of
- 29 imidazole-2 (3H)-thiones, 1993(06) (1993) 561-562.
- 30 [29] Q. Song, J. Zhao, G. Zhang, F. Peruch, S. Carlotti, N-Heterocyclic carbene/Lewis
- 31 acid-mediated ring-opening polymerization of propylene oxide. Part 1:
- 32 triisobutylaluminum as an efficient controlling agent, *Eur. Polym. J.* submitted
- 33 (2020).
- 34 [30] A.M. Magill, K.J. Cavell, B.F. Yates, Basicity of nucleophilic carbenes in
- 35 aqueous and nonaqueous solvents-theoretical predictions, *J. Am. Chem. Soc.* 126(28)
- 36 (2004) 8717-24.
- 37 [31] M. Fevre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, N-Heterocyclic carbenes
- 38 (NHCs) as organocatalysts and structural components in metal-free polymer
- 39 synthesis, *Chem. Soc. Rev.* 42(5) (2013) 2142-72.
- 40 [32] S. Naumann, A.P. Dove, N-Heterocyclic carbenes as organocatalysts for
- 41 polymerizations: trends and frontiers, *Polym. Chem.* 6(17) (2015) 3185-3200.
- 42 [33] D.A. Culkin, W. Jeong, S. Csihony, E.D. Gomez, N.P. Balsara, J.L. Hedrick,
- 43 R.M. Waymouth, Zwitterionic polymerization of lactide to cyclic poly(lactide) by
- 44 using N-heterocyclic carbene organocatalysts, *Angew. Chem. Int. Ed. Engl.* 46(15)

(2007) 2627-30.

[34] H.A. Brown, R.M. Waymouth, Zwitterionic ring-opening polymerization for the synthesis of high molecular weight cyclic polymers, *Acc. Chem. Res.* 46(11) (2013) 2585-96.

[35] T.S. Stukenbroeker, D. Solis-Ibarra, R.M. Waymouth, Synthesis and Topological Trapping of Cyclic Poly(alkylene phosphates), *Macromolecules* 47(23) (2014) 8224-8230.

[36] P. Walther, A. Krauss, S. Naumann, Lewis Pair Polymerization of Epoxides via Zwitterionic Species as a Route to High-Molar-Mass Polyethers, *Angew. Chem. Int. Ed. Engl.* 58(31) (2019) 10737-10741.

[37] S. Liu, T. Bai, K. Ni, Y. Chen, J. Zhao, J. Ling, X. Ye, G. Zhang, Biased Lewis Pairs: A General Catalytic Approach to Ether-Ester Block Copolymers with Unlimited Ordering of Sequences, *Angew. Chem. Int. Ed. Engl.* 58(43) (2019) 15478-15487.

[38] S. Pappuru, D. Chakraborty, Progress in metal-free cooperative catalysis for the ring-opening copolymerization of cyclic anhydrides and epoxides, *Eur. Polym. J.* 121 (2019) 109276.

[39] H.-Y. Ji, D.-P. Song, B. Wang, L. Pan, Y.-S. Li, Organic Lewis pairs for selective copolymerization of epoxides with anhydrides to access sequence-controlled block copolymers, *Green Chem.* 21(22) (2019) 6123-6132.

[40] D. Zhang, S.K. Boopathi, N. Hadjichristidis, Y. Gnanou, X. Feng, Metal-Free Alternating Copolymerization of CO₂ with Epoxides: Fulfilling "Green" Synthesis and Activity, *J. Am. Chem. Soc.* 138(35) (2016) 11117-20.

[41] J.L. Yang, H.L. Wu, Y. Li, X.H. Zhang, D.J. Darensbourg, Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides by Metal-Free Lewis Pairs, *Angew. Chem. Int. Ed. Engl.* 56(21) (2017) 5774-5779.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

--

CRediT author statement

Qilei Song: Conceptualization, Methodology, Investigation, Visualization, Writing.

Others: Conceptualization, Resources, Validation, Supervision.

N-Heterocyclic carbene/Lewis acid-mediated ring-opening polymerization of propylene oxide. Part 2: toward dihydroxytelechelic polyethers using triethylborane

Qilei Song,^{†,‡} Junpeng Zhao,[†] Guangzhao Zhang,[†] Daniel Taton,[‡] Frédéric

Peruch,[‡] and Stéphane Carlotti^{□,‡}

[†]Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

[‡]Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France

Figure S1. Overview of NHCs employed in Lewis pairs-catalyzed ROP of PO.

Table S1 ROP of PO catalyzed by NHC + Et₃B with **BnOH** as the initiator^a

Entry	[PO] ₀ /[-OH]/ [NHC]/[Et ₃ B] ^b	NHC	Time (h)	Conv. ^c (%)	$\overline{M}_{n,th}^d$ (kg mol ⁻¹)	$\overline{M}_{n,NMR}^e$ (kg mol ⁻¹)	$\overline{M}_{n,SEC}^f$ (kg mol ⁻¹)	$\mathcal{D}^g$
S1	300/1/0.2/0.6	I ^m Ph	24	—	—	—	—	—
S2	300/1/0.2/0.6	I ^t Bu	24	55	9.6	9.5	10.5 [9.2]	1.09 (16/84)

S3	300/1/0.2/0.6	I ^t Pr	24	90	15.7	16.6	16.7 [15.6]	1.09 (12/88)
S4	300/–/0.2/0.6	I ^t Pr	24	86	74.9	–	99.0	1.52 (39/61)
S5	200/–/0.2/0.6	I ^t Pr	48	96	55.7	–	45.5	1.18 (12/88)
S6	1000/–/0.2/1.2	I ^t Pr	24	50	58.1	–	136.6	1.24 (34/66)

^aPerformed in THF ([PO]₀ = 7 M) at 25 °C with BnOH as the initiator. ^bMolar feed ratio of PO, hydroxyl, *N*-heterocyclic carbene and triethylborane. ^cConversion of PO calculated from ¹H NMR spectrum of the crude product. ^dTheoretical number-average molar mass calculated from feed ratio ([PO]₀/[BnOH] or [PO]₀/[I^tPr] when no BnOH) and monomer conversion. ^eNumber-average molar mass calculated from ¹H NMR spectra of the isolated product by comparing signal integrals of the end group (PhCH₂O–) and polymer. ^fNumber-average molar mass, molar mass distribution obtained from SEC analysis (THF, 40 °C, polystyrene standards). For bimodal mass distribution, number in square brackets denotes the molar mass of the main peak determined by the UV trace, and the values in parenthesis denotes the percentage of each population calculated by deconvolution.

Figure S2. Left: SEC traces of PPOs corresponding to entries 2 (green line), 3 (blue line), and 4 (red line) in Table 1. Right: ¹H NMR spectrum of the isolated product of entry 4.

Figure S3. Results of control experiments (a) SEC traces (left) and ^1H NMR spectrum (right) of the isolated PPO (entry 6 in Table 1). (b) SEC traces (left) and ^1H NMR spectrum (right) of the isolated PPO (entry 4 in Table 1).

Figure S4. Left: SEC traces of PPOs synthesized with $\text{I}'\text{Pr} + \text{Et}_3\text{B}$ as the catalyst in absence of the initiator corresponding to entries S4 (pink line), S5 (purple line), and S6 (black line) in Table S1. Right: ^1H NMR spectrum of the isolated product of entry S6.

$$\text{*-(CH}_2\text{CH(CH}_3\text{)O)}_y\text{H}$$

**Controlled/living
High molar mass
Dihydroxytelechelic
polyether**