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

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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 (Et<sub>3</sub>B) as a bicomponent catalytic system. Poly(propylene oxide)s with  
13 predictable molar mass up to 60 000 g.mol<sup>-1</sup> and low dispersity ( $D < 1.10$ ) 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. Et<sub>3</sub>B 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 <sup>1</sup>H 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*-Bu<sub>3</sub>Al) 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*-BuP<sub>1</sub>; 1-  
14 *tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ<sup>5</sup>,4λ<sup>5</sup>-catenadi(phosphazene), *t*-BuP<sub>2</sub>),  
15 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *N*-methyl-1,5,7-triazabicyclododecene  
16 (MTBD) or onium salts and triethylborane (Et<sub>3</sub>B) [25-27]. In these studies, Et<sub>3</sub>B 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*-Bu<sub>3</sub>Al [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,

1 as mentioned before, there are still some drawbacks of this one-component-catalyzed  
2 polymerization such as low monomer conversion or limited molar mass for PO  
3 polymerization. In order to overcome these limitations and following our interest in  
4 NHCs and the ROP of epoxides utilizing the concept of basicity decrease and  
5 monomer activation, here we report that the association of a NHC with Et<sub>3</sub>B achieves  
6 efficiently the (co)polymerization of propylene oxide yielding possibly  
7 dihydroxytelechelic polyethers.

8

## 9 **2. Experimental part**

### 10 *2.1 Chemicals*

11 Tetrahydrofuran (THF; VWR Chemicals BDH, 100%) was dried over  
12 sodium/benzophenone before cryo-distillation and use. Benzyl alcohol (BnOH; Sigma  
13 Aldrich, 99%) was dried over CaH<sub>2</sub> then distilled and dissolved in purified THF to  
14 prepare a 0.5 M solution. Milli-Q water (H<sub>2</sub>O), used as an initiator, was dissolved in  
15 purified THF into a 0.5 M solution. **1,4-Benzenedimethanol** (BDM; abcr GmbH,  
16 99%) was dried by azeotropic distillation of THF then dissolved in THF into a 0.5 M  
17 solution. Propylene oxide (PO; Sigma Aldrich, 99%) and 1,2-butylene oxide (BO;  
18 Sigma Aldrich, 99%) were stirred over CaH<sub>2</sub> at room temperature overnight before  
19 distillation. Triethylborane (Et<sub>3</sub>B, 1.0 M in THF) was purchased from Sigma Aldrich  
20 and used as received. 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (I<sup>m</sup>Ph, 98%)

1 and 1,3-di-*tert*-butylimidazol-2-ylidene (*I*<sup>t</sup>Bu, 98%) were purchased from Strem  
2 Chemicals, Inc. and used as received, 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-  
3 ylidene (*I*<sup>p</sup>Pr) 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 (<sup>1</sup>H, 400.2 MHz) using  
6 deuterated chloroform (CDCl<sub>3</sub>) 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<sup>-1</sup>) 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  $\mathcal{D}$  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<sup>-1</sup>), then mixed  
18 with a solution of cationisation agent (NaI) in MeOH (10 mg.mL<sup>-1</sup>) and a solution of  
19 matrix, dithranol (1,8-dihydroxyanthracen-9(10H)-one) in THF (10 mg.mL<sup>-1</sup>), 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.

### 1 2.3 General polymerization procedure

2 *Representative procedure for the ROP of PO.* A typical procedure of entry 4 in Table  
3 1 is as follows. The Schlenk flask was flamed three times on a vacuum line and  
4 transferred in a glovebox, where *i*Pr (1.67 mg, 0.0092 mmol), dried THF (1.0 mL),  
5 THF solution of BnOH (0.5 M, 93.0  $\mu$ L, 0.046 mmol), Et<sub>3</sub>B solution (1.0 M in THF,  
6 27.6  $\mu$ L, 0.0276 mmol) and PO (0.98 mL, 14.0 mmol) were successively loaded. The  
7 flask was then transferred in a fume hood and the reaction mixture was stirred at  
8 25 °C. To obtain the kinetic plot, small aliquots (*ca.* 0.05 mL each) were withdrawn  
9 under an argon flow at different time intervals and diluted with 0.6 mL of CDCl<sub>3</sub>  
10 containing one drop of acetic acid for <sup>1</sup>H NMR analysis to determine the conversion  
11 of PO. After removal of CDCl<sub>3</sub> by evaporation, the sample was re-dissolved in THF  
12 for SEC measurement to determine  $\overline{M}_{n,SEC}$  and *D*. The reaction was quenched after 24  
13 h by addition of a few drops of acetic acid and then an aliquot was withdrawn for <sup>1</sup>H  
14 NMR and SEC analysis. Solvent was removed under vacuum, and the product  
15 (viscous liquid) was substantially dried under vacuum at room temperature overnight.  
16 Conv. (PO) = 87%,  $\overline{M}_{n,th} = 15.7 \text{ kg}\cdot\text{mol}^{-1}$ .  $\overline{M}_{n,SEC}(\text{THF, PS standards}) = 16.7 \text{ kg}\cdot\text{mol}^{-1}$ ,  
17 *D* = 1.09. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 4.51\text{-}4.45$  (BnOH,  
18 PhCH<sub>2</sub>O–), 3.71-3.39 (–OCH<sub>2</sub>CH(CH<sub>3</sub>)O–), 3.39-3.05 (–OCH<sub>2</sub>CH(CH<sub>3</sub>)O–), 1.25-  
19 0.87 (–OCH<sub>2</sub>CH(CH<sub>3</sub>)O–).

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

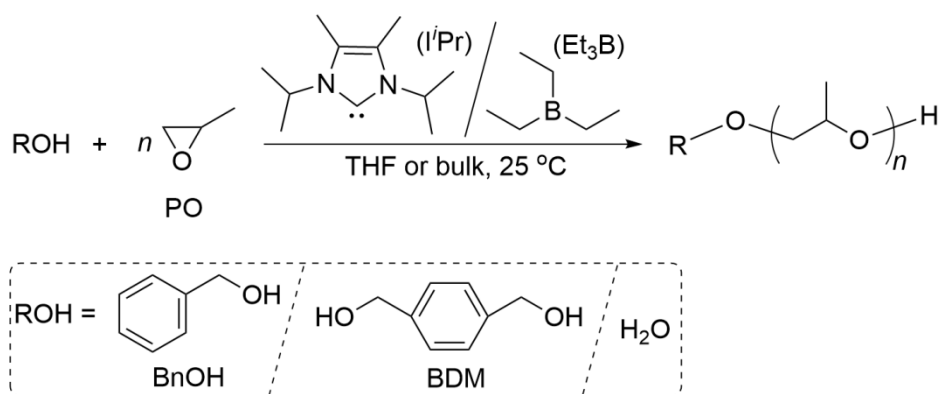
1 glovebox, where *i*Pr (5.08 mg, 0.028 mmol), dried THF (0.57 mL), THF solution of  
2 BnOH (0.5 M, 280.0  $\mu$ L, 0.14 mmol), Et<sub>3</sub>B solution (1.0 M in THF, 168.0  $\mu$ L, 0.168  
3 mmol) and PO (0.98 mL, 14.0 mmol) were successively loaded. The flask was then  
4 transferred in a fume hood 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 <sup>1</sup>H NMR and SEC analysis. Conv.(PO) = 100%,  $\overline{M}_{n,th}$  =  
7 5.8 kg.mol<sup>-1</sup>.  $\overline{M}_{n,SEC}$  (THF, PS standards) = 6.5 kg.mol<sup>-1</sup>,  $D$  = 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 <sup>1</sup>H 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<sup>-1</sup>.  $\overline{M}_{n,SEC}$  (THF, PS standards) = 10.7 kg.mol<sup>-1</sup>,  $D$  =  
15 1.06. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$ /ppm = 4.50-4.46 (BnOH, PhCH<sub>2</sub>O-),  
16 3.80-3.15 (PPO, -OCH<sub>2</sub>CH(CH<sub>3</sub>)O-) and (PBO, -OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)O-), 1.60-1.33  
17 (PBO, -OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)O-), 1.27-0.86 (PPO, -OCH<sub>2</sub>CH(CH<sub>3</sub>)O-), 0.90-0.81  
18 (PBO, -OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)O-).

### 19 3. Results and discussion

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



1 4,5(dimethyl)imidazol-2-ylidene, *I*<sup>*i*</sup>Pr; Figure S1) due its higher nucleophilicity [30]  
 2 was chosen to be combined with Et<sub>3</sub>B for the ROP of PO in the presence of different  
 3 alcohols as initiators. Other NHC's, e.g. 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-  
 4 ylidene, *I*<sup>*m*</sup>Ph and 1,3-di-*tert*-butylimidazol-2-ylidene, *I*<sup>*Bu*</sup> were shown to be less  
 5 reactive (ESI Table S1). The initial feed ratio of [PO]<sub>0</sub>/[-OH]/[NHC]/[Et<sub>3</sub>B] was fixed  
 6 at 300/1/0.2/0.6, targeting relatively high-molar mass PPOs (17.5 kg.mol<sup>-1</sup>). Use of a  
 7 threefold excess of Et<sub>3</sub>B relatively to NHC was based on previous investigations  
 8 regarding the Lewis pair-mediated ROP of epoxides [26, 27]. When the *I*<sup>*i*</sup>Pr/*i*-Bu<sub>3</sub>Al  
 9 system is giving a single PPO population, the SEC trace of the resultant PPO showed  
 10 a bimodal molar mass distribution, with a small side peak having twice the molar  
 11 mass of the main population (discussed after) despite exact similar experimental  
 12 conditions and same solvent, monomer, NHC batches.



14 **Scheme 1.** Illustration for ROP of PO catalyzed by *I*<sup>*i*</sup>Pr + Et<sub>3</sub>B in the presence of  
 15 alcohols.

16

1 **Influence of the [Et<sub>3</sub>B]/[I<sup>i</sup>Pr] feed ratio/loading.** The effect of [Et<sub>3</sub>B]/[I<sup>i</sup>Pr] molar  
2 ratios was first investigated, keeping the [PO]<sub>0</sub>/[-OH]/[I<sup>i</sup>Pr] ratio constant at 300/1/0.2  
3 (entries 1-4, Table 1). Importantly, I<sup>i</sup>Pr alone could not induce the polymerization  
4 (entry 1). A stepwise increase of the [Et<sub>3</sub>B]/[I<sup>i</sup>Pr] molar ratio was then evaluated.  
5 When the amount of Et<sub>3</sub>B was less than that of I<sup>i</sup>Pr ([Et<sub>3</sub>B]/[I<sup>i</sup>Pr] = 0.6, entry 2), PO  
6 polymerization proceeded slowly, with only 7% of PO being converted after 88 h.  
7 Increasing the molar amount of Et<sub>3</sub>B can increase the monomer conversion reaching  
8 39% after 96 h (entry 3, [Et<sub>3</sub>B]/[I<sup>i</sup>Pr] = 1). For [Et<sub>3</sub>B]/[I<sup>i</sup>Pr] = 3 (entry 4, Table 1), the  
9 conversion in PO reached 87% after 24h. In all cases, the resulting PPO showed a  
10 bimodal molar mass distribution by SEC with low dispersities (Figure S2).

11 A low molar mass PPO was synthesized by increasing the amount of initiator (entry 5,  
12 Table 1 and Figure 1), and the chain-end fidelity of corresponding product was  
13 analyzed by matrix-assisted laser desorption/ionization time-of-flight mass  
14 spectrometry (MALDI-TOF MS). The  $\overline{M}_{n,SEC}$  of the main population was found in  
15 good agreement with the theoretical molar mass ( $\overline{M}_{n,th}$ ) calculated from the  
16 [PO]<sub>0</sub>/[BnOH] ratio and the monomer conversion. Intriguingly, the  $\overline{M}_{p,SEC}$  of the  
17 smaller population was twice that of the main one. Careful examination of the isolated  
18 sample by <sup>1</sup>H NMR spectroscopy did not reveal any occurrence of transfer to  
19 monomer, as attested by the absence of signals from allylic unsaturated product  
20 (CH<sub>2</sub>=CHCH<sub>2</sub>O-) that would have located at 5.0-6.0 ppm. Through the MALDI-TOF  
21 MS analysis, two distinct populations corresponded to the two different PPO chain-  
22 ends, *i.e.* α-PhCH<sub>2</sub>O/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 H<sub>2</sub>O-  
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 (H<sub>2</sub>O-initiated, 3.8 kg.mol<sup>-1</sup>) was roughly  
4 twice that of the main population (BnOH-initiated, 2.0 kg.mol<sup>-1</sup>). 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*-Bu<sub>3</sub>Al instead of Et<sub>3</sub>B,  
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. H<sub>2</sub>O (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 H<sub>2</sub>O-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 H<sub>2</sub>O can  
21 act as a bifunctional initiator for the NHC/Et<sub>3</sub>B-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

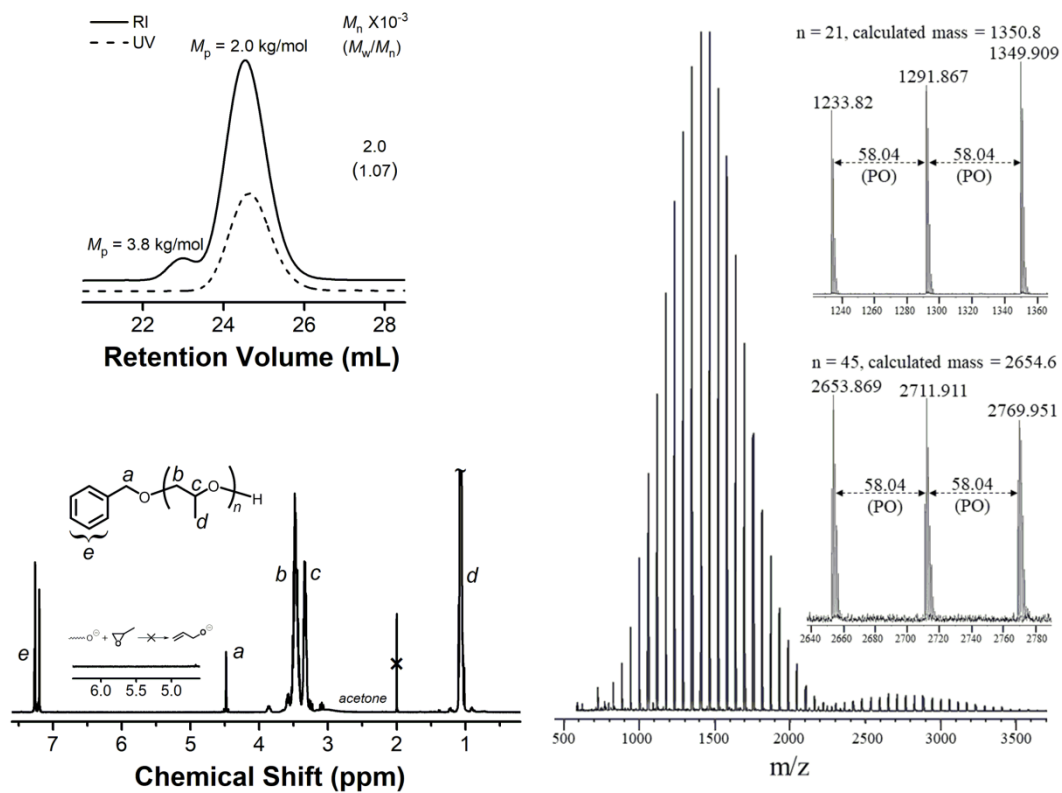
3 **Table 1 ROP of PO catalyzed by *I*Pr + Et<sub>3</sub>B with BnOH as the initiator<sup>a</sup>**

Entry	[PO] <sub>0</sub> /[-OH]/ [ <i>I</i> Pr]/[Et <sub>3</sub> B] <sup>b</sup>	Solvent	Time (h)	Conv. <sup>c</sup> (%)	$\bar{M}_{n,th}$ <sup>d</sup> (kg.mol <sup>-1</sup> )	$\bar{M}_{n,NMR}$ <sup>e</sup> (kg.mol <sup>-1</sup> )	$\bar{M}_{n,SEC}$ <sup>f</sup> (kg.mol <sup>-1</sup> )	<i>D</i> <sup>f</sup>
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 <sup>g</sup>	300/2/0.2/0.6	THF	24	21	-	-	3.0 [2.3]	1.14 (44/56)
7 <sup>h</sup>	50/1/0.2/0.6	THF	24	98	5.8	-	6.8	1.02
8 <sup>h</sup>	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 <sup>i</sup>	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)

<sup>a</sup>Performed in THF ([PO]<sub>0</sub> = 7 M) or in bulk at 25 °C with BnOH as the initiator. <sup>b</sup>Molar feed ratio of PO, hydroxyl, *N*-heterocyclic carbene and triethylborane. <sup>c</sup>Conversion of PO calculated from <sup>1</sup>H NMR spectra of the crude product.

<sup>d</sup>Theoretical number-average molar mass calculated from feed ratio ([PO]<sub>0</sub>/[BnOH]) and monomer conversion. <sup>e</sup>Number-average molar mass calculated from <sup>1</sup>H NMR spectra of the isolated product by comparing signal integrals of the end group (PhCH<sub>2</sub>O-) and polymer. <sup>f</sup>Number-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.**

<sup>g</sup>Molar ratio of [BnOH]/[H<sub>2</sub>O] = 1/0.5 is used as initiators. <sup>h</sup>H<sub>2</sub>O (entry 7) and BDM (entry 8) are used as an initiator, respectively. <sup>i</sup>Chain extension following entry 9-1 using BO as the second monomer.



1

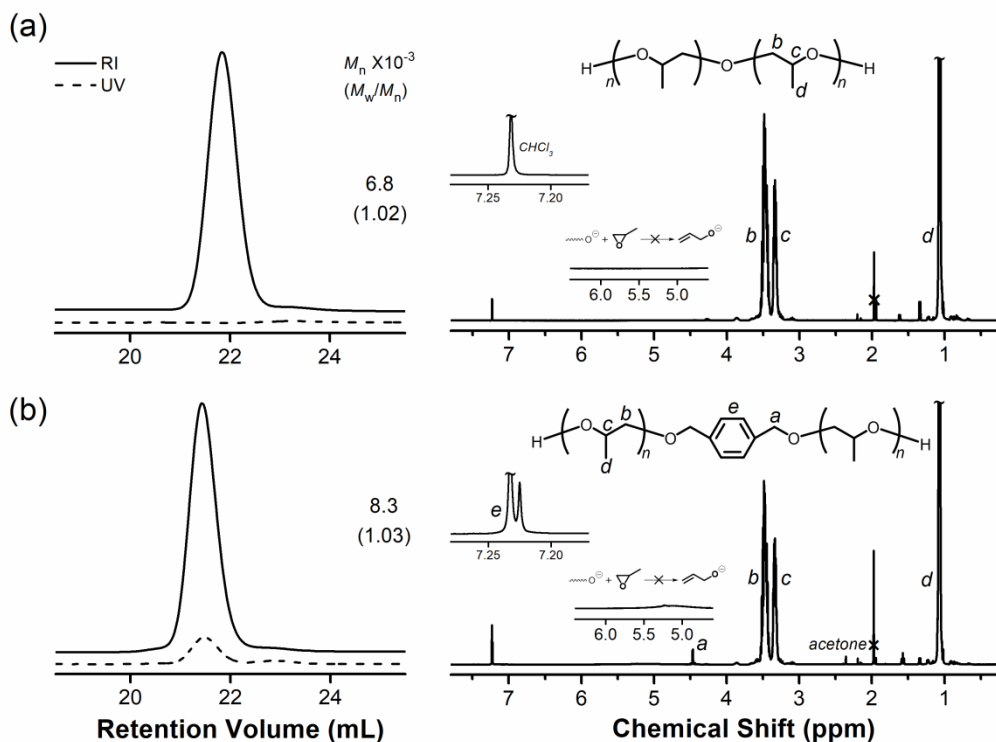
2 **Figure 1.** SEC traces (upper left),  $^1\text{H}$  NMR spectrum (bottom left) and MALDI-TOF

3 MS spectrum (right) of the isolated PPO (entry 5, Table 1). Signals in MALDI-TOF

4 MS correspond to BnOH/ $\text{H}_2\text{O}$ -initiated PPOs ionized by sodium cations (BnO- $\text{PO}_n\text{-H}$

5 and HO- $\text{PO}_n\text{-H}$ ).

6



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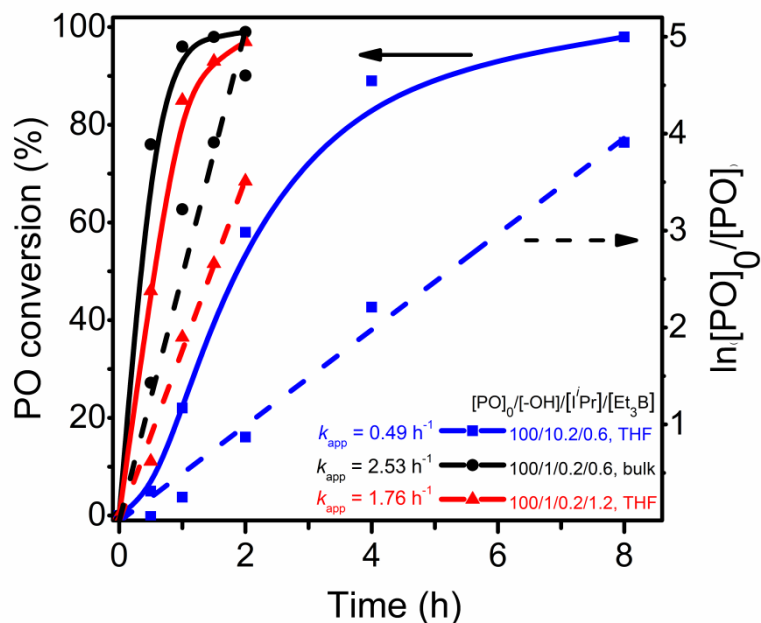
2 **Figure 2.** (a) SEC traces (left) and  $^1\text{H}$  NMR spectrum (right) of the isolated PPO  
 3 (entry 7, Table 1,  $\text{H}_2\text{O}$ -initiated). (b) SEC traces (left) and  $^1\text{H}$  NMR spectrum (right)  
 4 of the isolated PPO (entry 8, Table 1, BDM-initiated).

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  $i\text{Pr} + \text{Et}_3\text{B}$  in absence of

1 initiator yielded PPOs with uncontrolled molar masses and low dispersity (entries S4-  
2 6, Table S1). The  $^1\text{H}$  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  $[\text{Et}_3\text{B}]/[\text{I}^i\text{Pr}]$  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  $[\text{Et}_3\text{B}]/[\text{I}^i\text{Pr}]$  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 ( $k_{\text{app}}$ ), 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



1

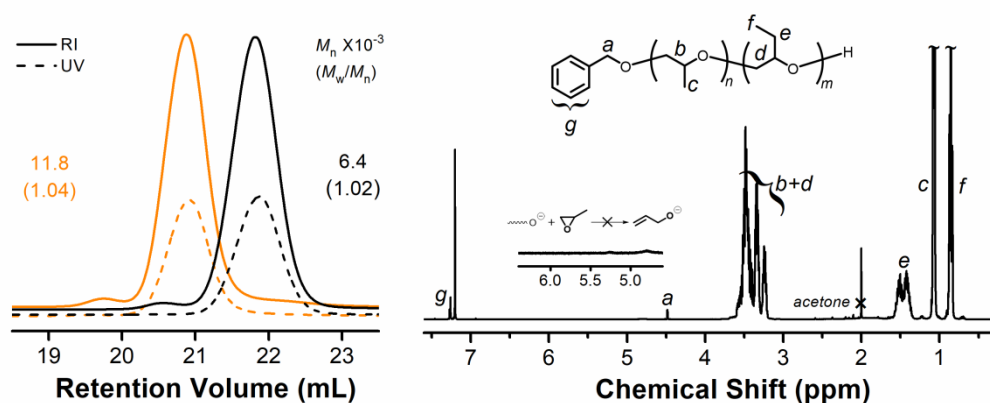
2 **Figure 3.** Conversion and  $\ln([PO]_0/[PO])$  vs time plots for PO polymerization with  
 3  $I^iPr/Et_3B$  systems.

4

5 **Chain extension reactions.** To further explore the living character of  $I^iPr + Et_3B$ -  
 6 catalyzed ROP of PO and thus expand the scope of application of this bicomponent  
 7 catalyst, 1,2-butylene oxide (BO) was employed as representative substituted  
 8 epoxides for chain extension reactions (entry 9, Table 1). A  $[PO]_0/[-OH]/[I^iPr]/[Et_3B]$   
 9 feed ratio of 100/1/0.2/1.2 in THF ( $[PO]_0 = 7$  M) was chosen based on the kinetic  
 10 study discussed above. After full conversion of PO was achieved to grow the first  
 11 block based on PPO, 100 equiv. of another monomer (BO) were added. After 24 h of  
 12 reaction at 25 °C, the parent SEC trace clearly shifted to the higher molar masses,  
 13 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  $\mathcal{D}$  could thus be achieved, as also evidenced by  $^1\text{H}$  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  $11.1 \text{ kg}\cdot\text{mol}^{-1}$  vs  $11.3 \text{ kg}\cdot\text{mol}^{-1}$  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.



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

12 **Synthesis of PPOs of different molar masses.** Maintaining  $[\text{PO}]_0/[\text{I}^*\text{Pr}]/[\text{Et}_3\text{B}] =$   
 13  $300/0.2/0.6$ , PPOs with various molar masses were targeted (entries 10-12, Table 1)  
 14 by adjusting the molar ratio of the monomer to the initiator (BnOH). When a low-  
 15 molar mass PPO is targeted ( $\overline{DP}_n = 100$ ,  $5.8 \text{ kg}\cdot\text{mol}^{-1}$ ), it is found that directly  
 16 enhancing the amount of initiator by 3 times leads to a much slower polymerization,  
 17 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<sup>-1</sup>) 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<sup>-1</sup>),  
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<sup>-1</sup>) 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 H<sub>2</sub>O-initiated population was observed by SEC, owing to the decrease in  
11 concentration of BnOH.

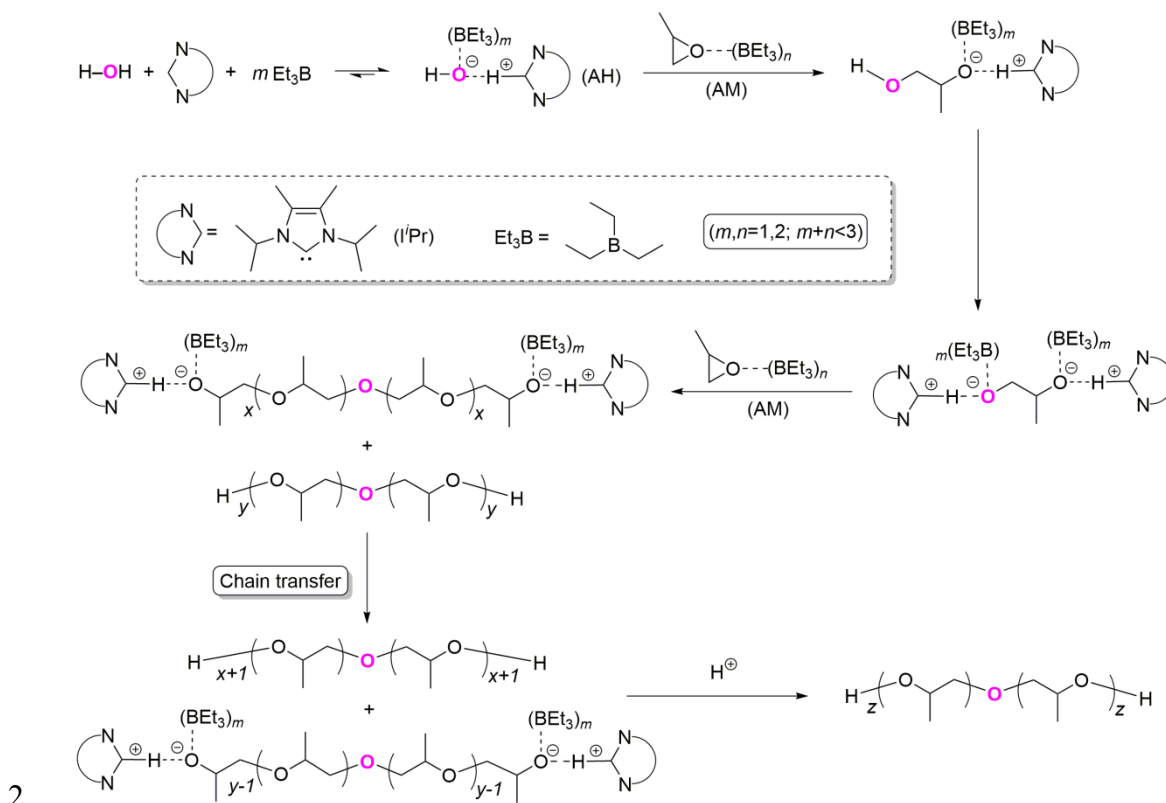
12 **Mechanism.** Et<sub>3</sub>B is believed to play an activating role for the monomer and to  
13 complex the base, similarly to the metal-based *i*-Bu<sub>3</sub>Al used as strong Lewis acid in  
14 the ROP of epoxides [1-6] or metal-free Et<sub>3</sub>B in the Lewis pair-mediated ROP of  
15 epoxides and its copolymerization with other cyclic monomers [25-27, 37-41]. For a  
16 molar ratio of [Et<sub>3</sub>B]/[I'Pr] equals to 3/1, Et<sub>3</sub>B 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, H<sub>2</sub>O is yielding twice the molar mass in  
19 agreement with a double initiation (Scheme 2).

20 The specific amount of Et<sub>3</sub>B 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 Et<sub>3</sub>B in

1 these two functions, which means whether 1 equiv. of Et<sub>3</sub>B is used for the formation  
2 of AH complex and the monomer is activated by the residual Et<sub>3</sub>B (2 equiv.), or *vice*  
3 *versa* [27, 37]. In fact, when the amount of [Et<sub>3</sub>B] ≤ [I'Pr], the ROP of PO indeed  
4 occurred even at a slow polymerization rate (entries 2-3, Table 1, [Et<sub>3</sub>B]/[I'Pr] = 0.6,  
5 1, respectively) as shown previously [26]. The PO monomer could coordinate to Et<sub>3</sub>B  
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 [Et<sub>3</sub>B]/[I'Pr] = 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 Et<sub>3</sub>B. 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 [Et<sub>3</sub>B] < [I'Pr],  
13 achieving high molar mass PPOs.

14 As mentioned, the hydroxyl concentration has dramatically affected the  
15 polymerization rate as the content in Et<sub>3</sub>B 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]<sub>0</sub>/[I'Pr]/[Et<sub>3</sub>B]  
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 Et<sub>3</sub>B, 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.



## 5 4. Conclusions

6 *N*-heterocyclic carbenes (NHCs) used in association with triethylborane ( $\text{Et}_3\text{B}$ ) 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

1 anionic or a zwitterionic ROP mechanism operates, respectively. Water can act as a  
2 bifunctional initiator providing  $\alpha,\omega$ -hydroxytelechelic PPOs. Compared with NHCs  
3 alone for the PO polymerization (bulk, 50 °C), the presence of Et<sub>3</sub>B improves its  
4 performance in terms of efficiency and molar masses, highlighting the advantages of  
5 this bicomponent system.

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8 to work in LCPO, University of Bordeaux, France.

## 9 **Data in brief**

10 The raw data will be shared upon request.

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**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.

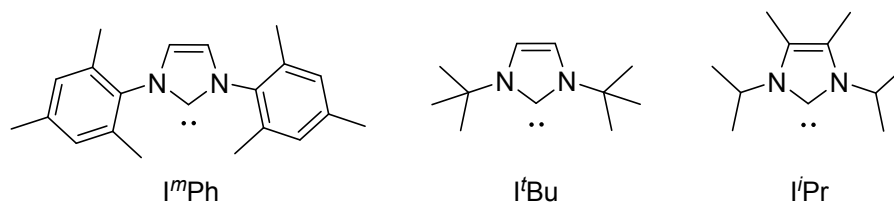
*N*-Heterocyclic carbene/Lewis acid-mediated ring-opening polymerization of propylene oxide. Part 2: toward dihydroxytelechelic polyethers using triethylborane

Qilei Song,<sup>†,‡</sup> Junpeng Zhao,<sup>†</sup> Guangzhao Zhang,<sup>†</sup> Daniel Taton,<sup>‡</sup> Frédéric

Peruch,<sup>‡</sup> and Stéphane Carlotti<sup>□,‡</sup>

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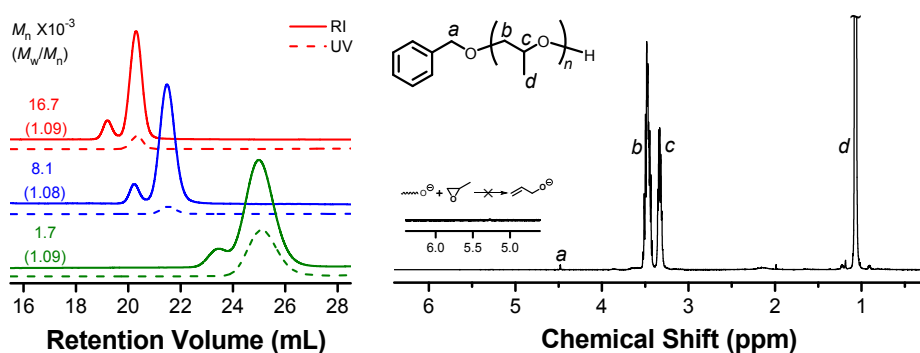
**Figure S1.** Overview of NHCs employed in Lewis pairs-catalyzed ROP of PO.

**Table S1** ROP of PO catalyzed by NHC + Et<sub>3</sub>B with **BnOH** as the initiator<sup>a</sup>

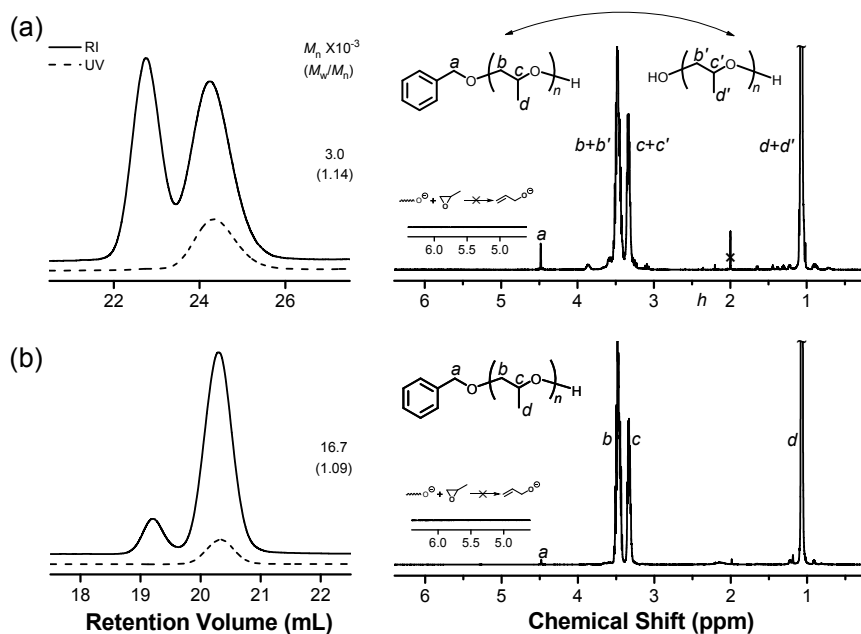
Entry	[PO] <sub>0</sub> /[-OH]/ [NHC]/[Et <sub>3</sub> B] <sup>b</sup>	NHC	Time (h)	Conv. <sup>c</sup> (%)	$\bar{M}_{n,th}$ <sup>d</sup> (kg mol <sup>-1</sup> )	$\bar{M}_{n,NMR}$ <sup>e</sup> (kg mol <sup>-1</sup> )	$\bar{M}_{n,SEC}$ <sup>f</sup> (kg mol <sup>-1</sup> )	$D'$
S1	300/1/0.2/0.6	$I^mPh$	24	–	–	–	–	–
S2	300/1/0.2/0.6	$I^tBu$	24	55	9.6	9.5	<b>10.5 [9.2]</b>	<b>1.09 (16/84)</b>

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

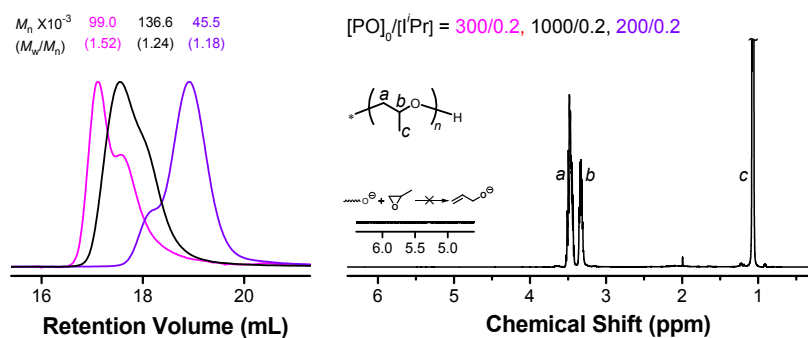
<sup>a</sup>Performed in THF ([PO]<sub>0</sub> = 7 M) at 25 °C with BnOH as the initiator. <sup>b</sup>Molar feed ratio of PO, hydroxyl, *N*-heterocyclic carbene and triethylborane. <sup>c</sup>Conversion of PO calculated from <sup>1</sup>H NMR spectrum of the crude product. <sup>d</sup>Theoretical number-average molar mass calculated from feed ratio ([PO]<sub>0</sub>/[BnOH] or [PO]<sub>0</sub>/[*t*Pr] when no BnOH) and monomer conversion. <sup>e</sup>Number-average molar mass calculated from <sup>1</sup>H NMR spectra of the isolated product by comparing signal integrals of the end group (PhCH<sub>2</sub>O–) and polymer. <sup>f</sup>Number-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.



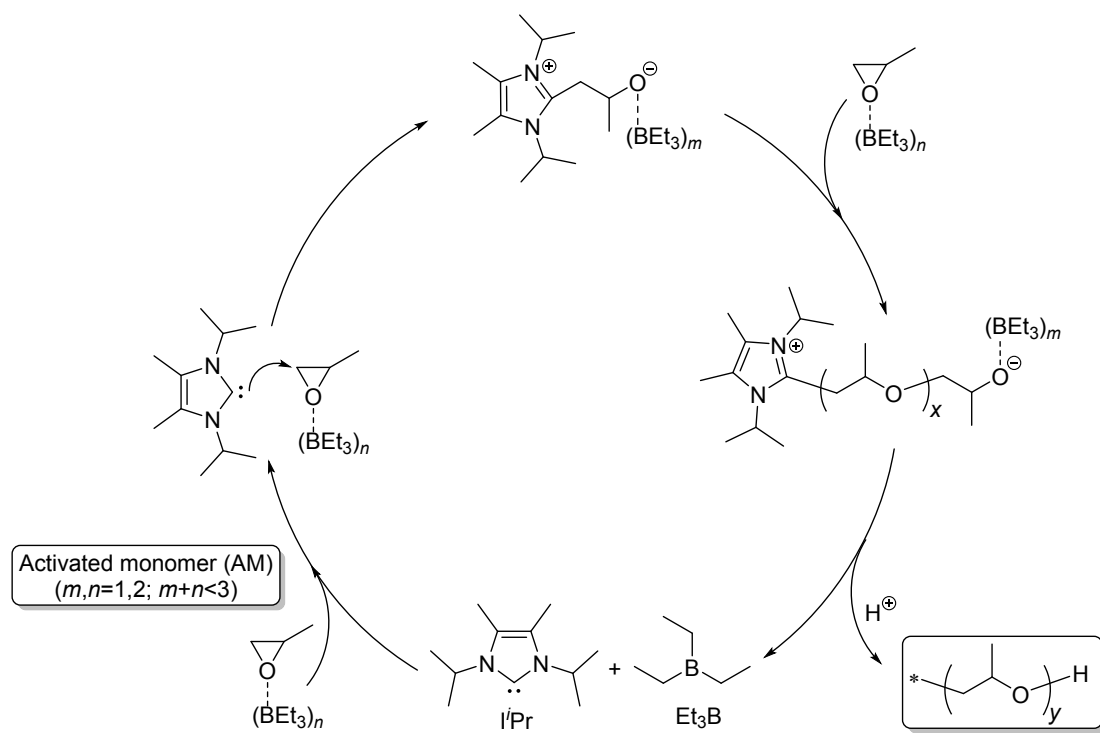
**Figure S2.** Left: SEC traces of PPOs corresponding to entries 2 (green line), 3 (blue line), and 4 (red line) in Table 1. Right: <sup>1</sup>H NMR spectrum of the isolated product of entry 4.



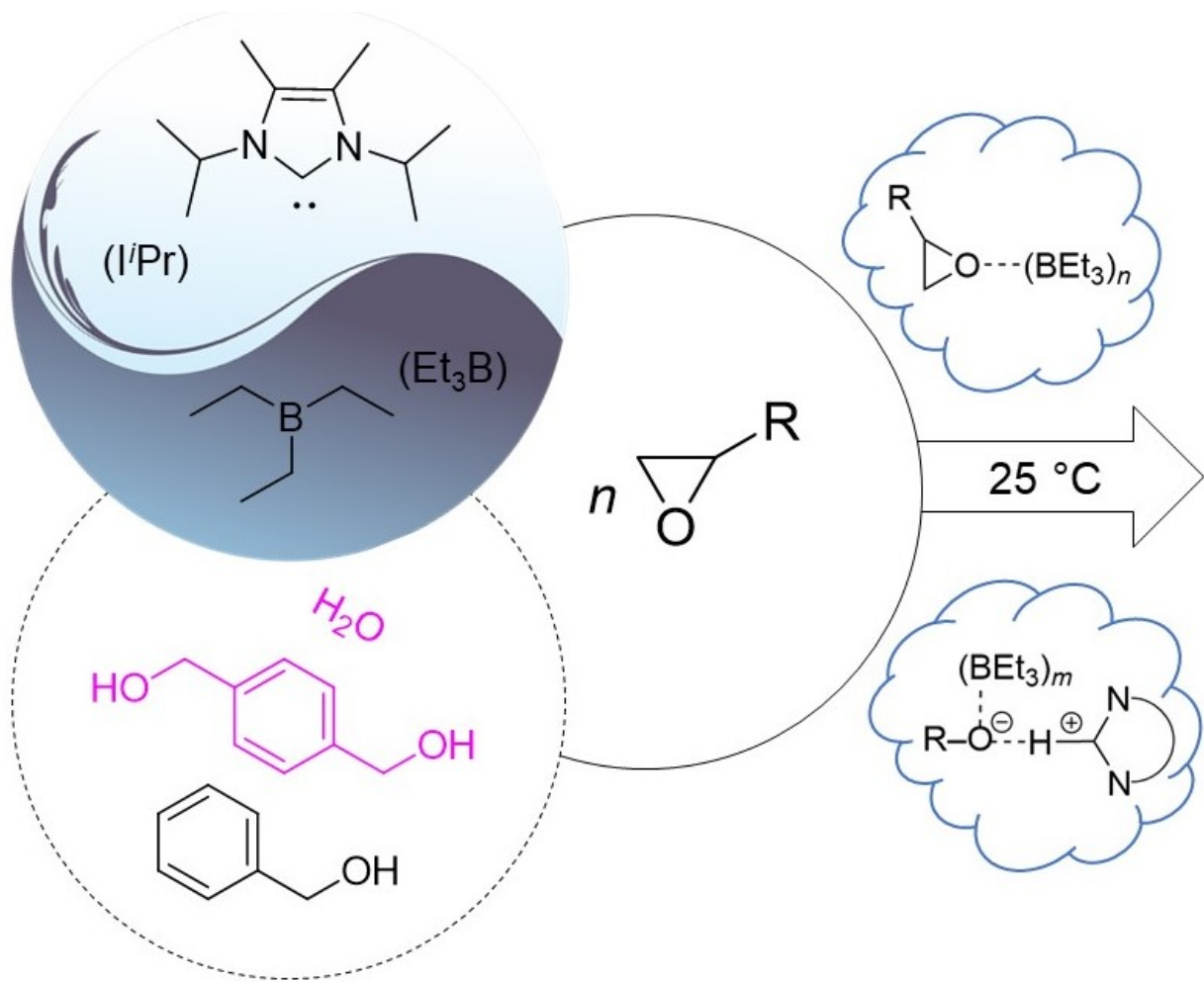
**Figure S3.** Results of control experiments (a) SEC traces (left) and  $^1\text{H}$  NMR spectrum (right) of the isolated PPO (entry 6 in Table 1). (b) SEC traces (left) and  $^1\text{H}$  NMR spectrum (right) of the isolated PPO (entry 4 in Table 1).



**Figure S4.** Left: SEC traces of PPOs synthesized with  $I'Pr + Et_3B$  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:  $^1\text{H}$  NMR spectrum of the isolated product of entry S6.



**Scheme S1.** Proposed zwitterionic ROP of PO catalyzed by  $I'Pr + Et_3B$ .



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