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1 *N*-Heterocyclic carbene/Lewis acid-mediated ring-opening  
2 polymerization of propylene oxide. Part 1: triisobutylaluminum  
3 as an efficient controlling agent

4  
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11 **Abstract:** Ring-opening polymerization (ROP) of propylene oxide (PO) is achieved at  
12 25 °C either in bulk or in solution, using *N*-heterocyclic carbenes (NHCs) and  
13 triisobutylaluminum (*i*-Bu<sub>3</sub>Al) as a bicomponent catalytic system. Transfer to monomer  
14 was not observed and poly(propylene oxide)s with predictable molar masses up to 60  
15 000 g.mol<sup>-1</sup> and low dispersities were obtained. In presence/absence of an alcohol as  
16 the initiator, the polymerization of PO follows anionic or zwitterionic ROP mechanisms,  
17 respectively. The addition of the Lewis acid strongly improves the efficiency of NHCs  
18 for the polymerization of substituted epoxides. It is established that *i*-Bu<sub>3</sub>Al is involved  
19 both in the formation of an initiating/propagating complex of moderate

1 basicity/nucleophilicity and in the coordination of PO, enabling the activation of the  
2 monomer towards the complexed nucleophilic active species. Block copolyethers are  
3 also prepared by PPO chain extension experiments. All (co)polyethers were thoroughly  
4 characterized by <sup>1</sup>H NMR spectroscopy, SEC and MALDI-TOF mass spectrometry as  
5 means to prove the control and benefit of this NHC approach for epoxides ROP.

6 **Keywords:** substituted epoxides, anionic ring-opening polymerization, *N*-heterocyclic  
7 carbene, bicomponent catalyst, block copolymers

## 8 **1. Introduction**

9 Aliphatic polyethers such as poly(ethylene oxide) (PEO), poly(propylene oxide)  
10 (PPO) and the related derivatives constitute an important class of polymeric materials  
11 for various applications [1, 2]. The anionic ring-opening polymerization (AROP) of the  
12 corresponding epoxides by alkali metal alkoxides is a common route to the synthesis of  
13 polyethers. However, due to the high nucleophilicity of the propagating alkoxides,  
14 chain transfer reactions to the monomer is always accompanied in the AROP of  
15 substituted epoxides such as propylene oxide (PO), 1,2-butylene oxide (BO) and that  
16 of higher epoxides. This side reaction not only limits the molar masses of resultant  
17 polymers, but also obstructs the access to polyether-based block copolymers [3-5].  
18 With the expanding development of organic catalysis for polymerization [6], some  
19 improvement were made (*e.g.*, phosphazene bases [7-9], *N*-heterocyclic carbenes  
20 (NHCs) [10-13], *N*-heterocyclic olefins (NHOs) [14-16]) with sometimes limitations in

1 terms of kinetics, polymerization temperatures and molar masses in the one-component  
2 organic base-catalyzed polymerization of especially propylene oxide. In particular,  
3 NHCs could catalyze/initiate the controlled/living polymerization of ethylene oxide  
4 (EO) following anionic or zwitterionic ROP mechanisms [10, 11], but it shows limited  
5 performance in polymerization for PO as bulk conditions at 50°C were required to reach  
6 less than 10 000 g/mol in 3 days [12].

7 In order to circumvent the above obstacles and achieve controlled/living ROP of  
8 epoxides especially the substituted ones, initiator/chain-end complexation or activation,  
9 monomer activation or combination of both strategies were proposed to obtain  
10 (co)polyethers with high number-average molar mass ( $\overline{M}_n$ ) and narrow molar mass  
11 distribution. For instance, crown ether or cryptates in conjunction with alkali metal  
12 alkoxides increased the separation of propagating ion-pairs, thus enhancing the  
13 polymerization rate [17-19]. The rapidly and efficiently controlled polymerization of  
14 different epoxides were carried out at 25 °C or lower temperatures by using the  
15 combination of triisobutylaluminum (*i*-Bu<sub>3</sub>Al) and various anionic initiators (*e.g.*, alkali  
16 metal alkoxides, onium salts) or organic superbases/R-OH such as a phosphazene base  
17 [20-25]. In this case, part of the *i*-Bu<sub>3</sub>Al is involved in the interaction with  
18 initiator/chain-end, affording an “ate” complex with moderate basicity/nucleophilicity.  
19 The residual Al-based compound was found to activate the epoxide, leading to the  
20 polymerization in mild conditions. Following this approach, several dual catalysts  
21 based on the association of moderate organic bases and different Lewis acids revealed  
22 high efficiency in the polymerization of epoxides [26-30]. In this article we present that

1 the combination of a NHC with *i*-Bu<sub>3</sub>Al improves the NHC's efficiency for propylene  
2 oxide.

### 3 **2. Experimental part**

4 **Materials.** 2-Methyltetrahydrofuran (MeTHF; Sigma Aldrich, ≥99.5%) was  
5 successively dried over calcium hydride (CaH<sub>2</sub>) and sodium/benzophenone and kept  
6 under vacuum for further distillation until use. Benzyl alcohol (BnOH; Sigma Aldrich,  
7 99%) was dried over CaH<sub>2</sub> then distilled and dissolved in purified MeTHF to prepare a  
8 0.5 M solution. Propylene oxide (PO; Sigma Aldrich, 99%) and 1,2-butylene oxide (BO;  
9 Sigma Aldrich, 99%) were stirred over CaH<sub>2</sub> at room temperature overnight before  
10 distillation. Triisobutylaluminum solution (*i*-Bu<sub>3</sub>Al; 25 wt. % in toluene ≈ 1.0 M in  
11 toluene) was purchased from Sigma Aldrich and used as received. 1,3-Bis(2,4,6-  
12 trimethylphenyl)imidazol-2-ylidene (*I*<sup>m</sup>Ph, 98%) and 1,3-di-*tert*-butylimidazol-2-  
13 ylidene (*I*<sup>t</sup>Bu, 98%) were purchased from Strem Chemicals, Inc. and used as received,  
14 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene (*I*<sup>Pr</sup>) was prepared according to  
15 the previous reference [31].

16 **Instrumentation.** NMR spectra were recorded at 25 °C on a Bruker Avance 400 (<sup>1</sup>H,  
17 400.2 MHz) using deuterated chloroform (CDCl<sub>3</sub>) as the solvent and tetramethylsilane  
18 as the internal standard. Molar masses were determined by size exclusion  
19 chromatography (SEC) in THF (1 mL.min<sup>-1</sup>) at 40 °C with 1,3,5-trichlorobenzene (1  
20 mL in 500 mL of THF) as a flow marker, using both refractive index (RI) and UV

1 detectors. Analyses were performed using a three-column TSK gel TOSOH (G4000,  
2 G3000, G2000 with pore sizes of 20, 75 and 200 Å respectively, connected in series)  
3 calibrated with polystyrene (PS) standards to obtain apparent number-average molar  
4 mass ( $\overline{M}_{n,SEC}$ ) and  $D$  of the polymers. Matrix assisted laser desorption/ionization time  
5 of flight mass spectrometry (MALDI-TOF MS) measurements were performed by the  
6 CESAMO (Bordeaux, France) on an Autoflex mass spectrometer (Bruker). The  
7 instrument is equipped with a laser emitting at 355 nm. Spectra were recorded in the  
8 positive-ion mode using the reflectron. Samples were dissolved in THF (10 mg.mL<sup>-1</sup>),  
9 then mixed with a solution of cationisation agent (NaI) in MeOH (10 mg.mL<sup>-1</sup>) and a  
10 solution of matrix, dithranol (1,8-dihydroxyanthracen-9(10H)-one) in THF (10 mg.mL<sup>-1</sup>),  
11 <sup>1</sup>), in a volume ratio of 1:1:10. Then, 1~2  $\mu$ L of the final solution was deposited onto  
12 the sample target and vacuum-dried.

### 13 ***General polymerization procedure.***

14 *Representative procedure for the ROP of PO.* A typical procedure of entry 3 in Table  
15 1 is as follows. The Schlenk flask was flamed three times on a vacuum line and  
16 transferred in a glovebox, where I<sup>t</sup>Pr (1.67 mg, 0.0092 mmol), dried MeTHF (0.9 mL),  
17 MeTHF solution of BnOH (0.5 M, 93.0  $\mu$ L, 0.046 mmol), *i*-Bu<sub>3</sub>Al solution (1.0 M in  
18 toluene, 28.0  $\mu$ L, 0.0272 mmol) and PO (0.98 mL, 14.0 mmol) were successively  
19 loaded. The flask was then transferred in a fume hood and the reaction mixture was  
20 stirred at 25 °C. The reaction was quenched after 72 h by addition of a few drops of  
21 acetic acid and then an aliquot was withdrawn for <sup>1</sup>H NMR and SEC analysis.

1 Dimethylformamide was used in this study to solubilize and collect the polymer.  
2 Chloroform can be used for the same purpose. Solvent was removed under vacuum,  
3 and the product (viscous liquid) was substantially dried under vacuum at room  
4 temperature overnight. No specific purification procedure of the catalysts from the  
5 polymer was proposed to keep the crude products for any characterization. Conv. (PO)  
6 = 54%,  $\overline{M}_{n,th} = 9.4 \text{ kg}\cdot\text{mol}^{-1}$ .  $\overline{M}_{n,SEC}(\text{THF, PS standards}) = 10.6 \text{ kg}\cdot\text{mol}^{-1}$ ,  $D = 1.05$ .  $^1\text{H}$   
7 NMR (400 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 4.51\text{-}4.45$  (BnOH,  $\text{PhCH}_2\text{O-}$ ),  $3.71\text{-}3.39$  ( $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O-}$ ),  
8  $3.39\text{-}3.05$  ( $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O-}$ ),  $1.25\text{-}0.87$  ( $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O-}$ ).

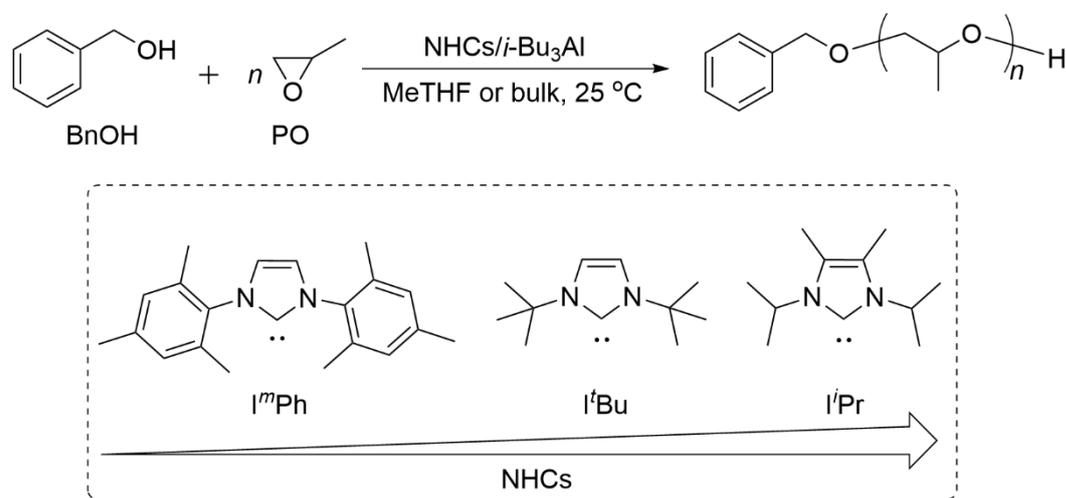
9 *Chain extension experiments.* A typical procedure of entry 11 in Table 2 is as follows.  
10 The Schlenk flask was flamed three times on a vacuum line and transferred in a  
11 glovebox, where *i*Pr (5.08 mg, 0.028 mmol), BnOH (14.5  $\mu\text{L}$ , 0.14 mmol), *i*-Bu<sub>3</sub>Al  
12 solution (1.0 M in toluene, 84.0  $\mu\text{L}$ , 0.084 mmol) were successively loaded. The flask  
13 was then transferred in a fume hood and PO (0.98 mL, 14.0 mmol) was added to the  
14 mixture solution at 0 °C under an argon flow. The reaction mixture was subsequently  
15 stirred at 25 °C. After 24 h, the magnetic stirrer almost stopped spinning due to the  
16 increased viscosity of solution and an aliquot was withdrawn for  $^1\text{H}$  NMR and SEC  
17 analysis. Conv.(PO) = 100%,  $\overline{M}_{n,th} = 5.9 \text{ kg}\cdot\text{mol}^{-1}$ .  $\overline{M}_{n,SEC}(\text{THF, PS standards}) = 8.2$   
18  $\text{kg}\cdot\text{mol}^{-1}$ ,  $D = 1.08$ . Then a batch of BO (1.22 mL, 14.0 mmol) was added under an  
19 argon flow, after which the magnetic stirrer gradually started to spin again, and then the  
20 flask was kept at 25 °C with stirring for another 24 h. The reaction was quenched after  
21 48 h by addition of a few drops of acetic acid and then an aliquot was withdrawn for  $^1\text{H}$   
22 NMR and SEC analysis. Solvent was removed under vacuum, and the product (viscous

1 liquid) was substantially dried under vacuum at room temperature overnight. Conv.(BO)  
2 = 83%,  $\overline{M}_{n,th}$  (diblock) = 11.9 kg.mol<sup>-1</sup>.  $\overline{M}_{n,SEC}$  (THF, PS standards) = 12.7 kg.mol<sup>-1</sup>,  
3  $D = 1.12$ . <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–),  
4 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  
5 (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  
6 (PBO, –OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)O–).

### 7 **3. Results and discussion**

8 Three NHCs with different steric hindrance and nucleophilicity (*i.e.*, 1,3-bis(2,4,6-  
9 trimethylphenyl)imidazol-2-ylidene (*I<sup>m</sup>Ph*), 1,3-di-*tert*-butylimidazol-2-ylidene (*I<sup>t</sup>Bu*),  
10 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene (*I<sup>i</sup>Pr*)) were chosen to be combined  
11 with *i*-Bu<sub>3</sub>Al for the polymerization of PO, where the reaction was carried out in  
12 MeTHF at 25 °C with benzyl alcohol (BnOH) as the initiator (Scheme 1). The initial  
13 choice to use a threefold excess of *i*-Bu<sub>3</sub>Al relatively to NHC was based on our previous  
14 investigations regarding the Al-based dual catalysts-mediated ROP of epoxides [25, 32].  
15 The combination of a sterically hindered NHC (*I<sup>m</sup>Ph*) and *i*-Bu<sub>3</sub>Al revealed low  
16 catalytic efficiency, as the monomer conversion was limited to 36% after 72 h (entry 1,  
17 Table 1). While the more electron-rich NHCs, *I<sup>t</sup>Bu* and *I<sup>i</sup>Pr*, used in conjunction with  
18 *i*-Bu<sub>3</sub>Al were found to convert more than 50% of PO after 72 h (entries 2-3, Table 1).  
19 This was also consistent with the different steric hindrance/nucleophilicity of the  
20 employed NHCs, *i.e.*, combination of *i*-Bu<sub>3</sub>Al and NHC of higher basicity led to faster  
21 polymerization rates ( $pK_a^{DMSO}$  (*I<sup>m</sup>Ph*) = 17.0,  $pK_a^{DMSO}$  (*I<sup>t</sup>Bu*) = 22.8,  $pK_a^{DMSO}$  (*I<sup>i</sup>Pr*) =

1 24.7) [33]. Therefore, considering its high catalytic and control efficiencies, catalysts  
2 combining *I*'Pr with *i*-Bu<sub>3</sub>Al was employed for further experiments.



4 **Scheme 1. Illustration for ROP of PO catalyzed by *I*'Pr + *i*-Bu<sub>3</sub>Al**

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11 **Table 1. ROP of PO catalyzed by NHCs + *i*-Bu<sub>3</sub>Al (in MeTHF, [PO]<sub>0</sub> = 7 M, 25 °C,**

1 **BnOH as the initiator)**

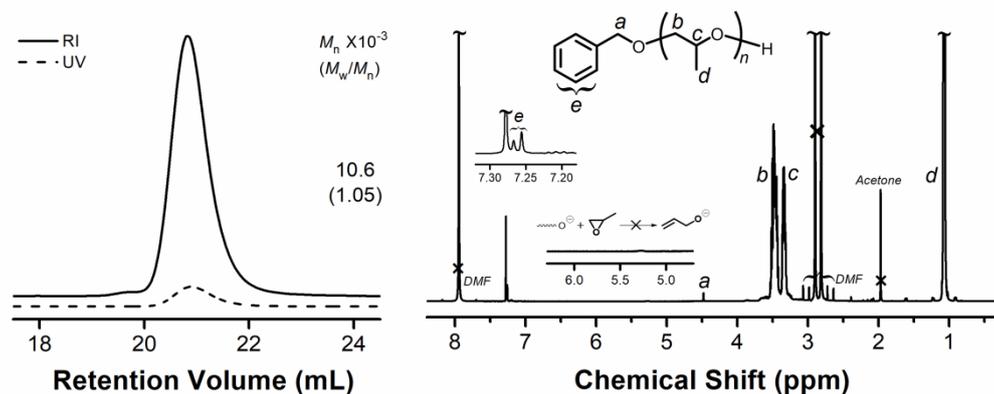
entry	[PO] <sub>0</sub> /[-OH]/ [NHC]/[ <i>i</i> -Bu <sub>3</sub> Al]	NHC	Time (h)	Conv. <sup>a</sup> (%)	$\overline{M}_{n,th}^b$ (kg.mol <sup>-1</sup> )	$\overline{M}_{n,NMR}^c$ (kg.mol <sup>-1</sup> )	$\overline{M}_{n,SEC}^d$ (kg.mol <sup>-1</sup> )	<i>D</i> <sup>d</sup>
1	300/1/0.2/0.6	I <sup>m</sup> Ph	72	36	6.4	6.5	6.8	1.07
2	300/1/0.2/0.6	I <sup>t</sup> Bu	72	62	10.9	12.3	15.2	1.21
3	300/1/0.2/0.6	I <sup>i</sup> Pr	72	54	9.4	10.7	10.6	1.05
4	300/1/0.2/0.2	I <sup>i</sup> Pr	96	–	–	–	–	–
5	300/1/0.2/0.12	I <sup>i</sup> Pr	96	–	–	–	–	–

<sup>a</sup>Conversion of PO calculated from <sup>1</sup>H NMR spectrum of the crude product. <sup>b</sup>Theoretical number-average molar mass calculated from feed ratio and monomer conversion. <sup>c</sup>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>d</sup>Obtained from SEC analysis (THF, 40 °C, polystyrene standards).

2

3 All the SEC traces of the resultant PPOs showed a unimodal molar mass distribution  
 4 (Figure 1). The  $\overline{M}_{n,SEC}$  was found to be in good agreement with the theoretical molar  
 5 mass ( $\overline{M}_{n,th}$ ) calculated from the [PO]<sub>0</sub>/[BnOH] ratio and the monomer conversion. The  
 6 <sup>1</sup>H NMR spectroscopy of isolated product did not reveal any occurrence of transfer to  
 7 monomer, as attested by the absence of signals from allylic unsaturated product  
 8 (CH<sub>2</sub>=CHCH<sub>2</sub>O–) that would be located at 5.0-6.0 ppm (Figure 1). Excess loading of  
 9 *i*-Bu<sub>3</sub>Al was compulsive for this dual catalyst, as no polymerization occurred in other  
 10 molar ratios such as [I<sup>i</sup>Pr]/[*i*-Bu<sub>3</sub>Al] = 0.2/0.2 or 0.2/0.12 (entries 4-5, Table 1).

11



1

2 **Figure 1.** SEC traces (left) and  $^1\text{H}$  NMR spectrum (right) of the isolated PPO (entry  
3 3, Table 1)

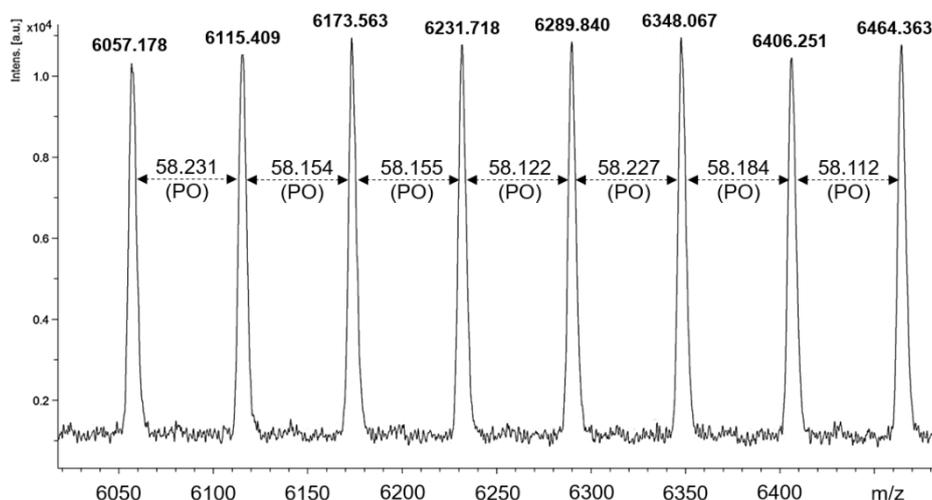
4 To improve the catalytic efficiency of “ $\text{I}^t\text{Pr} + i\text{-Bu}_3\text{Al}$ ” catalytic system, two different  
5 strategies were employed. One pathway is to increase the monomer concentration,  
6 where the bulk polymerization produced controlled PPO with higher molar mass after  
7 48 h (entry 6, Table 2). On the other hand, the enhanced molar ratio of  $[i\text{-Bu}_3\text{Al}]/[\text{I}^t\text{Pr}]$   
8 could also increase the polymerization rate. For instance, when the  $[i\text{-Bu}_3\text{Al}]/[\text{I}^t\text{Pr}]$  feed  
9 ratio was increased to 1.2/0.2 and other conditions (*e.g.*, monomer concentration,  
10 temperature *etc.*) were kept constant, the conversion of PO reached up to 64% after 24  
11 h (entry 7, Table 2). The same tendency was also observed in the synthesis of low-  
12 molar-mass PPOs (entries 8-10, Table 2). The significant reaction time in this case was  
13 due to the increased feed loading of  $\text{I}^t\text{Pr}$  and  $i\text{-Bu}_3\text{Al}$  even if their molar ratio was kept  
14 constant. One can note that the high increase of the Lewis acid broadened the molar  
15 mass distribution due to side reactions, *e.g.* hydride initiation from  $i\text{-Bu}_3\text{Al}$ , as already  
16 shown in our previous report [22].

1 **Table 2. ROP of PO catalyzed by I'Pr+ *i*-Bu<sub>3</sub>Al<sup>a</sup>**

entry	[PO] <sub>0</sub> /[-OH]/ [I'Pr]/[ <i>i</i> -Bu <sub>3</sub> Al] <sup>b</sup>	Solvent	Time (h)	Conv. <sup>c</sup> (%)	<i>M</i> <sub>n,theor</sub> <sup>d</sup> (kg.mol <sup>-1</sup> )	<i>M</i> <sub>n,NMR</sub> <sup>e</sup> (kg.mol <sup>-1</sup> )	<i>M</i> <sub>n,SEC</sub> <sup>f</sup> (kg.mol <sup>-1</sup> )	<i>D</i> <sup>f</sup>
6	300/1/0.2/0.6	bulk	48	78	13.6	16.5	15.7	1.05
7	300/1/0.2/1.2	MeTHF	24	64	11.1	15.0	12.1	1.31
8	100/1/0.2/0.6	MeTHF	72	99	5.7	7.2	7.2	1.06
9	100/1/0.2/0.6	bulk	24	99	5.9	7.4	8.7	1.14
10	100/1/0.2/1.2	MeTHF	1	99	5.7	10.9	8.7	2.07
11-1	100/1/0.2/0.6	bulk	24	100	5.9	8.8	8.2	1.08
11-2 <sup>g</sup>	100/1/0.2/0.6	bulk	24	83	10.7	12.8	12.7	1.12
12	300/-/0.2/0.6	MeTHF	0.7	84	73.2	–	62.1	1.56
13	300/-/0.4/1.2	MeTHF	0.7	96	41.8	–	30.3	1.81
14	300/0.3/0.2/0.6	MeTHF	0.7	89	51.7	59.2	40.9	1.40
15	300/0.15/0.2/0.6	MeTHF	0.7	81	94.1	189.1	47.8	1.39

<sup>a</sup>Performed in MeTHF ([PO]<sub>0</sub>= 7 M) or in bulk with BnOH as the initiator, except for entries 8-11 ([PO]<sub>0</sub>= 10 M). <sup>b</sup>Molar feed ratio of PO, hydroxyl, *N*-heterocyclic carbene and triisobutylaluminum. <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 and monomer conversion. <sup>e</sup>Number-average molar mass calculated from <sup>1</sup>H NMR spectra of the isolated product. <sup>f</sup>Number-average molar mass, molar mass distribution from SEC analysis (THF, 40 °C, polystyrene standards) and bimodal distribution (number in parentheses denotes the percentage of each population calculated by SEC peak areas). <sup>g</sup>Chain extension following entry 11-1 using BO as the second monomer.

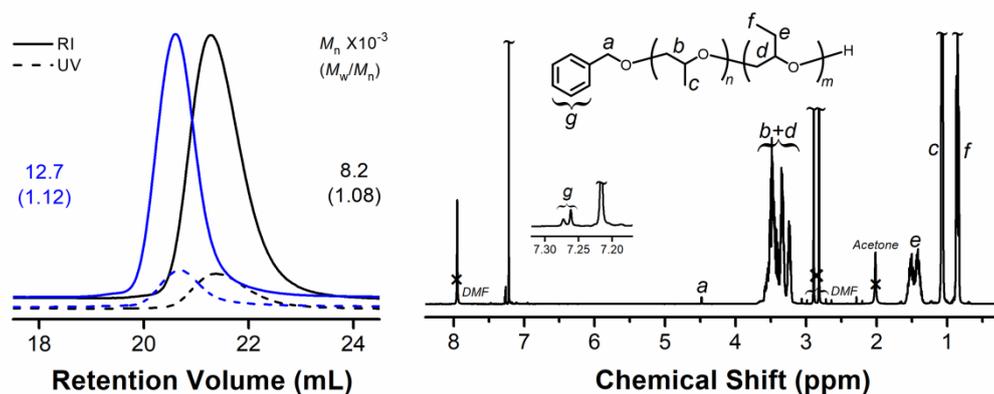
2 The chain-end fidelity of resultant PPOs was analysed by MALDI-TOF mass  
3 spectrometry (Figure 2). Despite slightly broad peaks probably certainly due to an  
4 isotopic distribution, one main distinct population corresponding to the desired PPO  
5 chain-ends, *i.e.* α-PhCH<sub>2</sub>O/ω-OH was observed. These data were also consistent with  
6 <sup>1</sup>H NMR and SEC results. Signals in MALDI-TOF MS correspond to BnOH-initiated  
7 PPOs ionized by sodium cations. Transfer reaction to an isobutyl group, which can be  
8 seen sometimes when using triisobutylaluminum in high amount or high monomer  
9 concentration or temperature [24], cannot be totally excluded (see ESI)



1

2 **Figure 2.** MALDI-TOF MS spectrum of a low-molar mass PPO (enlarged region  
 3 around 6000 g/mol, entry 9, Table 2 ; full spectrum in ESI ).

4 The living character of  $I'Pr + i-Bu_3Al$ -catalyzed polymerization of propylene oxide was  
 5 confirmed by the sequential ROP of PO and 1,2-butylene oxide (BO) (entry 11, Table  
 6 2). The initial feed ratio of  $[PO]_0/[-OH]/[I'Pr]/[i-Bu_3Al]$  was kept constant at  
 7 100/1/0.2/0.6 in bulk, and the full conversion of PO was achieved after 24 h.  
 8 Subsequently, 100 equiv. of BO was added to conduct the chain extension reaction  
 9 based on the first PPO-block. After another 24 h of reaction at 25 °C, the parent SEC  
 10 trace clearly shifted to the higher molar masses, with no trace of dead polymer (Figure  
 11 3), attesting the effective crossover reaction from PPO to the other block. Diblock  
 12 copolymers (PPO-*b*-PBO) with predictable molar mass and narrow  $\mathcal{D}$  could thus be  
 13 achieved, as also evidenced by  $^1H$  NMR analysis confirming the presence of both  
 14 blocks.

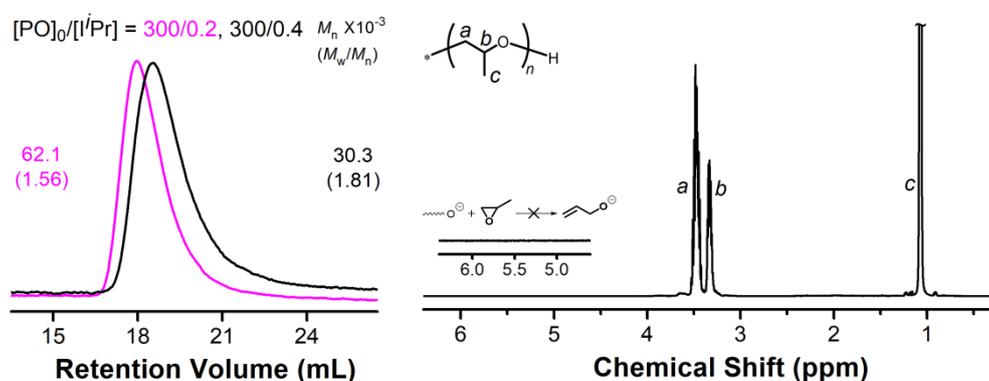


1

2 **Figure 3.** Chain extension reactions: SEC traces (left) of crude PPO-*b*-PBO (blue line)  
 3 and <sup>1</sup>H NMR spectrum (right) of the isolated product (entry 11, Table 2).

4 The zwitterionic ROP of PO was also achieved in absence of initiators by using I<sup>+</sup>Pr +  
 5 *i*-Bu<sub>3</sub>Al (entries 12-13, Table 2). The molar masses of obtained PPOs could be adjusted  
 6 by the initial feed ratio of [PO]<sub>0</sub>/[I<sup>+</sup>Pr]. The polymerization process was inferred to be  
 7 initiated by the NHC through the nucleophilic attack of PO, similar to other zwitterionic  
 8 ROP of cyclic monomers [11, 28, 34-36]. <sup>1</sup>H NMR spectra of the isolated PPOs  
 9 indicated that no transfer to monomer occurred during the polymerization (Figure 4).  
 10 Side reactions probably still occurred as broad SEC chromatograms were obtained  
 11 particularly when high amount of Lewis acid was used. In addition, high-molar mass  
 12 PPOs were also targeted by adjusting the loading of initiators (BnOH) (entries 14-15,  
 13 Table 2). Maintaining [PO]<sub>0</sub>/[I<sup>+</sup>Pr]/[*i*-Bu<sub>3</sub>Al] = 300/0.2/0.6, it was found that by directly  
 14 decreasing the amount of initiator by 10 times led to a much faster polymerization, the  
 15 conversion of PO being up to 89% after 0.7 h (entry 14, Table 2). These results  
 16 suggested that a lower concentration in hydroxyl groups induced the faster

1 polymerization of PO, which would be further explained in the below proposed  
 2 mechanism.



3  
 4 **Figure 4.** Left: SEC traces of PPOs synthesized with  $I^{tPr} + i-Bu_3Al$  in absence of the  
 5 initiator corresponding to entries 12 (pink line), 13 (black line) in Table 2. Right:  $^1H$   
 6 NMR spectrum of the isolated product of entry 12.

7  
 8 Considering the roles of  $i-Bu_3Al$  used in other bicomponent catalysts we established for  
 9 the polymerization of epoxides,<sup>20-25</sup> a similar mechanism was proposed here. For the  
 10 excess loading of aluminium compound compared to  $I^{tPr}$  ( $[i-Bu_3Al]/[I^{tPr}] = 3/1$ ),  $i-$   
 11  $Bu_3Al$  is involved both in the formation of an activated-hydroxyl complex (AH) and an  
 12 activated monomer (AM), accounting for the high efficiency of this catalytic system.  
 13 Through the formation of the hydroxyl- $I^{tPr}$ - $i-Bu_3Al$  active centre, the oxyanion  
 14 deriving from the BnOH initiator exhibited a decreased basicity, which was well suited  
 15 for the nucleophilic attack onto the monomer in its activated form as  $i-Bu_3Al$  was used  
 16 in excess. The less reactive alkoxide was thus not capable to cause any transfer reaction  
 17 to the monomer, which permitted the synthesis of high molar mass PPOs. As mentioned,

1 the concentration in hydroxyls dramatically affected the polymerization rate as the  
2 content in *i*-Bu<sub>3</sub>Al available for epoxide activation depends on the amount of alcohol  
3 added. Therefore, the difference in the monomer activation process also explained the  
4 different polymerization rates caused by the variation of targeted  $\overline{DP}_n$  (e.g., entry 3  
5 Table 1 vs entry 14, Table 2). With a similar [PO]<sub>0</sub>/[I<sup>*i*</sup>Pr]/[*i*-Bu<sub>3</sub>Al] ratio, the presence  
6 of higher amount of alcohols (low targeted  $\overline{DP}_n$ ), meaning higher amount of AH, led  
7 to the decreased concentration of the AM complex, and thus slows down the  
8 polymerization rate. To achieve the 100% initiation efficiency, it was inferred that fast  
9 interconversion occurred between activated monomer and hydroxyl functions (dormant  
10 chain-end or alcohol), which led to polyether chains growing from all the added alcohol  
11 initiators in equal rates, achieving synthesis of PPO with targeted  $\overline{M}_n$  and narrow *D*.  
12 This exchange may be facilitated by the reversible formation of AH/AM complexes  
13 (Scheme 2).

14



1 designed function. Therefore, this bicomponent catalyst not only improves the NHC-  
2 ROP of PO and its derivatives, but also expands the scope on the use of Lewis pairs in  
3 polymerization reactions.

#### 4 **Acknowledgement**

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#### 7 **Data in brief**

8 The raw data will be shared upon request.

#### 9 **References**

- 10 [1] S. Thomas, P. Visakh, Handbook of Engineering and Specialty Thermoplastics,  
11 Volume 3: Polyethers and Polyesters, John Wiley & Sons2011.
- 12 [2] M. Ionescu, Chemistry and Technology of Polyols for Polyurethanes, Smithers  
13 Rapra2016.
- 14 [3] M. Hans, H. Keul, M. Moeller, Chain transfer reactions limit the molecular weight  
15 of polyglycidol prepared via alkali metal based initiating systems, Polymer 50(5)  
16 (2009) 1103–1108.
- 17 [4] A.-L. Brocas, C. Mantzaridis, D. Tunc, S. Carlotti, Polyether synthesis: From  
18 activated or metal-free anionic ring-opening polymerization of epoxides to  
19 functionalization, Prog. Polym. Sci. 38(6) (2013) 845–873.
- 20 [5] J. Herzberger, K. Niederer, H. Pohlit, J. Seiwert, M. Worm, F.R. Wurm, H. Frey,  
21 Polymerization of Ethylene Oxide, Propylene Oxide, and Other Alkylene Oxides:  
22 Synthesis, Novel Polymer Architectures, and Bioconjugation, Chem. Rev. 116(4) (2016)  
23 2170–243.
- 24 [6] A. Dove, H. Sardon, S. Naumann, Organic Catalysis for Polymerisation, Royal  
25 Society of Chemistry2018.
- 26 [7] B. Eßwein, N.M. Steidl, M. Möller, Anionic polymerization of oxirane in the  
27 presence of the polyiminophosphazene base t - Bu - P4, Macromol. Rapid Commun. 17(2)  
28 (1996) 143–148.
- 29 [8] S. Boileau, N. Illy, Activation in anionic polymerization: Why phosphazene bases  
30 are very exciting promoters, Prog. Polym. Sci. 36(9) (2011) 1132–1151.
- 31 [9] J. Zhao, N. Hadjichristidis, Y. Gnanou, Phosphazene-promoted anionic

1 polymerization, *Polimery* 59(01) (2014) 49–59.

2 [10] J. Raynaud, C. Absalon, Y. Gnanou, D. Taton, N-heterocyclic carbene-induced  
3 zwitterionic ring-opening polymerization of ethylene oxide and direct synthesis of  
4 alpha,omega-difunctionalized poly(ethylene oxide)s and poly(ethylene oxide)-b-  
5 poly(epsilon-caprolactone) block copolymers, *J. Am. Chem. Soc.* 131(9) (2009) 3201–9.

6 [11] J. Raynaud, C. Absalon, Y. Gnanou, D. Taton, N-Heterocyclic Carbene-  
7 Organocatalyzed Ring-Opening Polymerization of Ethylene Oxide in the Presence of  
8 Alcohols or Trimethylsilyl Nucleophiles as Chain Moderators for the Synthesis of  
9  $\alpha, \omega$ -Heterodifunctionalized Poly(ethylene oxide)s, *Macromolecules* 43(6) (2010)  
10 2814–2823.

11 [12] J. Raynaud, W.N. Ottou, Y. Gnanou, D. Taton, Metal-free and solvent-free access  
12 to alpha,omega-heterodifunctionalized poly(propylene oxide)s by N-heterocyclic  
13 carbene-induced ring opening polymerization, *Chem. Commun.* 46(18) (2010) 3203–5.

14 [13] R. Lindner, M.L. Lejkowski, S. Lavy, P. Deglmann, K.T. Wiss, S. Zorbakhsh, L.  
15 Meyer, M. Limbach, Ring-Opening Polymerization and Copolymerization of Propylene  
16 Oxide Catalyzed by N-Heterocyclic Carbenes, *ChemCatChem* 6(2) (2014) 618–625.

17 [14] S. Naumann, A.W. Thomas, A.P. Dove, N-Heterocyclic Olefins as Organocatalysts  
18 for Polymerization: Preparation of Well-Defined Poly(propylene oxide), *Angew. Chem.*  
19 *Int. Ed. Engl.* 54(33) (2015) 9550–4.

20 [15] A. Balint, M. Papendick, M. Clauss, C. Muller, F. Giesselmann, S. Naumann,  
21 Controlled preparation of amphiphilic triblock-copolyether in a metal- and solvent-  
22 free approach for tailored structure-directing agents, *Chem. Commun.* 54(18) (2018)  
23 2220–2223.

24 [16] F. Markus, J.R. Bruckner, S. Naumann, Controlled Synthesis of “Reverse Pluronic”  
25 - Type Block Copolyethers with High Molar Masses for the Preparation of Hydrogels  
26 with Improved Mechanical Properties, *Macromol. Chem. Phys.* 221(3) (2020) 1900437.

27 [17] A. Deffieux, S. Boileau, Anionic polymerization of ethylene oxide with cryptates  
28 as counterions: 1, *Polymer* 18(10) (1977) 1047–1050.

29 [18] J. Ding, D. Attwood, C. Price, C. Booth, Use of crown ether in the anionic  
30 polymerization of propylene oxide—3. Preparation and micellization of diblock-copoly  
31 (oxypropylene/oxyethylene), *Eur. Polym. J.* 27(9) (1991) 901–905.

32 [19] J. Ding, F. Heatley, C. Price, C. Booth, Use of crown ether in the anionic  
33 polymerization of propylene oxide—2. Molecular weight and molecular weight  
34 distribution, *Eur. Polym. J.* 27(9) (1991) 895–899.

35 [20] C. Billouard, S. Carlotti, P. Desbois, A. Deffieux, “Controlled” High-Speed  
36 Anionic Polymerization of Propylene Oxide Initiated by Alkali Metal  
37 Alkoxide/Trialkylaluminum Systems, *Macromolecules* 37(11) (2004) 4038–4043.

38 [21] S. Carlotti, C. Billouard, E. Gautriaud, P. Desbois, A. Deffieux, Activation  
39 Mechanisms of Trialkylaluminum in Alkali Metal Alkoxides or Tetraalkylammonium Salts  
40 / Propylene Oxide Controlled Anionic Polymerization, *Macromol. Symp.* 226(1) (2005)  
41 61–68.

42 [22] A. Labbé, S. Carlotti, C. Billouard, P. Desbois, A. Deffieux, Controlled High-  
43 Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the  
44 Presence of Triisobutylaluminum, *Macromolecules* 40(22) (2007) 7842–7847.

1 [23] V. Rejsek, D. Sauvanier, C. Billouard, P. Desbois, A. Deffieux, S. Carlotti,  
2 Controlled Anionic Homo- and Copolymerization of Ethylene Oxide and Propylene Oxide  
3 by Monomer Activation, *Macromolecules* 40(18) (2007) 6510-6514.

4 [24] V. Rejsek, P. Desbois, A. Deffieux, S. Carlotti, Polymerization of ethylene  
5 oxide initiated by lithium derivatives via the monomer-activated approach:  
6 Application to the direct synthesis of PS-b-PEO and PI-b-PEO diblock copolymers,  
7 *Polymer* 51(24) (2010) 5674-5679.

8 [25] A.-L. Brocas, A. Deffieux, N. Le Malicot, S. Carlotti, Combination of phosphazene  
9 base and triisobutylaluminum for the rapid synthesis of polyhydroxy telechelic  
10 poly(propylene oxide), *Polym. Chem.* 3(5) (2012) 1189-1195.

11 [26] Y. Chen, J. Shen, S. Liu, J. Zhao, Y. Wang, G. Zhang, High Efficiency Organic  
12 Lewis Pair Catalyst for Ring-Opening Polymerization of Epoxides with Chemoselectivity,  
13 *Macromolecules* 51(20) (2018) 8286-8297.

14 [27] C.J. Zhang, H.Y. Duan, L.F. Hu, C.H. Zhang, X.H. Zhang, Metal-Free Route to  
15 Precise Synthesis of Poly(propylene oxide) and Its Blocks with High Activity,  
16 *ChemSusChem* 11(24) (2018) 4209-4213.

17 [28] P. Walther, A. Krauss, S. Naumann, Lewis Pair Polymerization of Epoxides via  
18 Zwitterionic Species as a Route to High-Molar-Mass Polyethers, *Angew. Chem. Int. Ed.*  
19 *Engl.* 58(31) (2019) 10737-10741.

20 [29] Y. Chen, S. Liu, J. Zhao, D. Pahovnik, E. Žagar, G. Zhang, Chemoselective  
21 Polymerization of Epoxides from Carboxylic Acids: Direct Access to Esterified  
22 Polyethers and Biodegradable Polyurethanes, *ACS Macro Lett.* 8(12) (2019) 1582-1587.

23 [30] P. Walther, C. Vogler, S. Naumann, Ultrahigh-Molecular-Weight Poly(propylene  
24 oxide): Preparation and Perspectives, *Synlett* 31(07) (2019) 641-647.

25 [31] N. Kuhn, T.J.S. Kratz, Synthesis of imidazol-2-ylidenes by reduction of  
26 imidazole-2 (3H)-thiones, 1993(06) (1993) 561-562.

27 [32] S. Carlotti, A. Labbé, V. Rejsek, S. Doutaz, M. Gervais, A. Deffieux,  
28 Living/Controlled Anionic Polymerization and Copolymerization of Epichlorohydrin  
29 with Tetraoctylammonium Bromide- Triisobutylaluminum Initiating Systems,  
30 *Macromolecules* 41(19) (2008) 7058-7062.

31 [33] A.M. Magill, K.J. Cavell, B.F. Yates, Basicity of nucleophilic carbenes in  
32 aqueous and nonaqueous solvents-theoretical predictions, *J. Am. Chem. Soc.* 126(28)  
33 (2004) 8717-24.

34 [34] D.A. Culkin, W. Jeong, S. Csihony, E.D. Gomez, N.P. Balsara, J.L. Hedrick, R.M.  
35 Waymouth, Zwitterionic polymerization of lactide to cyclic poly(lactide) by using N-  
36 heterocyclic carbene organocatalysts, *Angew. Chem. Int. Ed. Engl.* 46(15) (2007) 2627-  
37 30.

38 [35] H.A. Brown, R.M. Waymouth, Zwitterionic ring-opening polymerization for the  
39 synthesis of high molecular weight cyclic polymers, *Acc. Chem. Res.* 46(11) (2013)  
40 2585-96.

41 [36] T.S. Stukenbroeker, D. Solis-Ibarra, R.M. Waymouth, Synthesis and Topological  
42 Trapping of Cyclic Poly(alkylene phosphates), *Macromolecules* 47(23) (2014) 8224-  
43 8230.



**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.

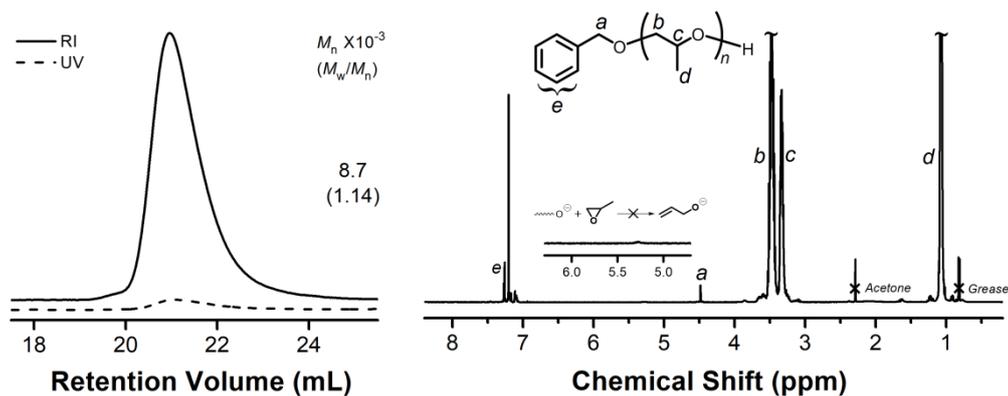
**Others:** Conceptualization, Resources, Validation, Supervision.

*N*-Heterocyclic carbene/Lewis acid-mediated ring-opening polymerization of propylene oxide. Part 1: triisobutylaluminum as an efficient controlling agent

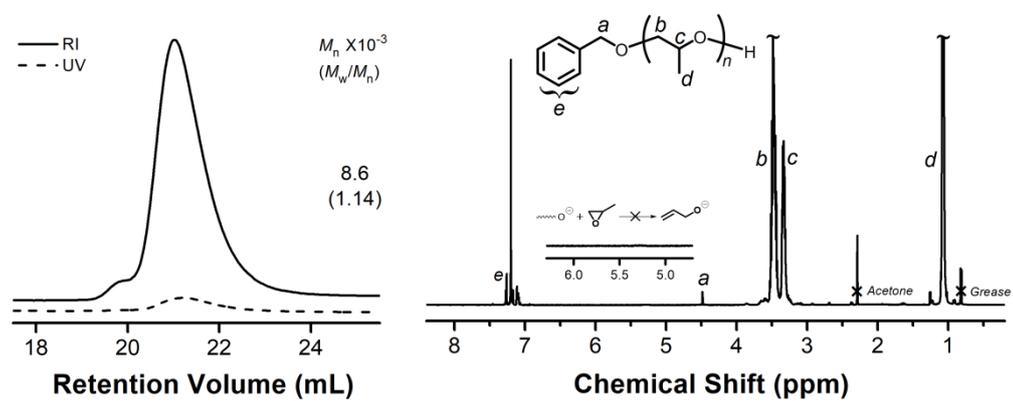
Qilei Song,<sup>†,‡</sup> Junpeng Zhao,<sup>†</sup> Guangzhao Zhang,<sup>†</sup> Daniel Taton,<sup>‡</sup> Frédéric Peruch,<sup>‡</sup>  
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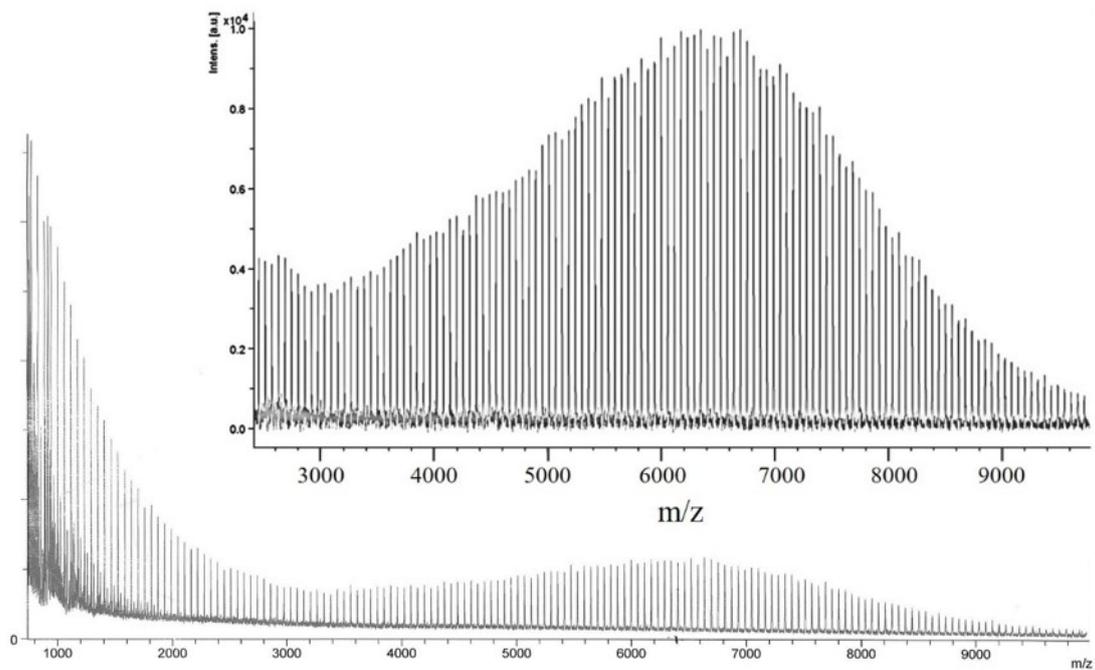
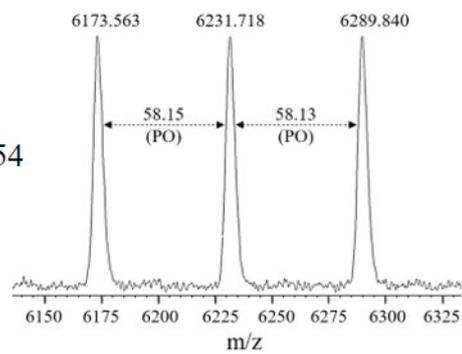


**Figure S1.** SEC chromatogram and <sup>1</sup>H NMR spectrum of PPO (entry 9, Table 2)

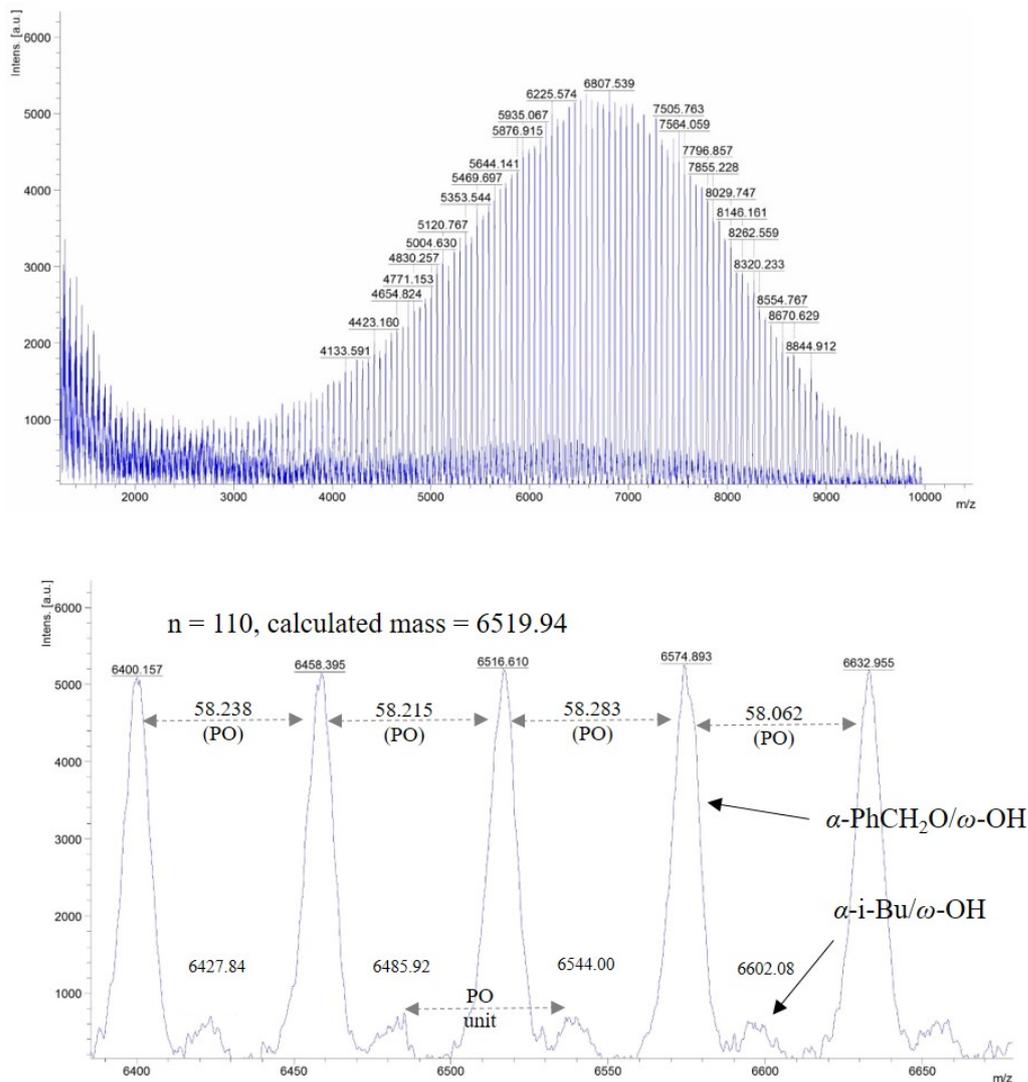


**Figure S2.** SEC chromatogram and  $^1\text{H}$  NMR spectrum of PPO (repeated experience similar to entry 9, Table 2)

$n = 105$ , calculated mass = 6229.54



**Figure S3.** MALDI-TOF MS spectrum of PPO (entry 9, Table 2)

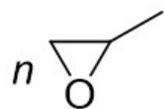
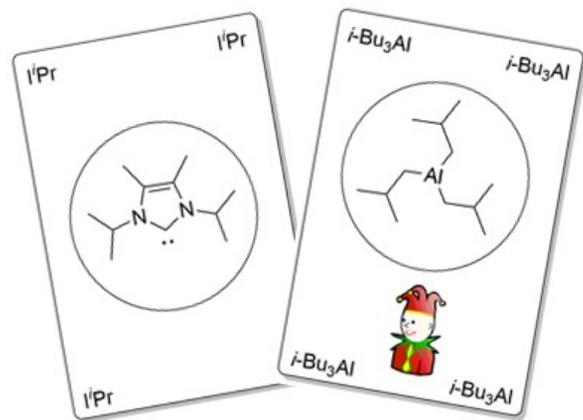


**Figure S4.** MALDI-TOF MS spectrum of PPO (repeated experience similar to entry 9, Table 2)

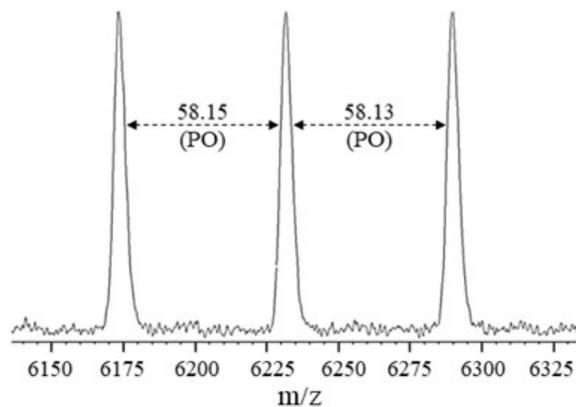
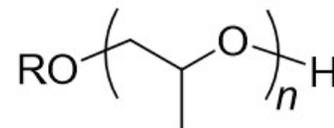
Comments:

The low molar mass fraction appearing in the two MALDI-TOF MS spectra are not explained as their intensity can vary from one experiment to another and do not appear in any SEC analysis.

Transfer to an isobutyl group is detected when polymerizations are mainly conducted in bulk conditions (see particularly the small population on Figure S4).



R-OH, 25 °C



**No transfer to monomer**  
**High molar mass**  
**Mild conditions**