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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*-Bu₃Al) 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⁻¹ 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*-Bu₃Al 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 ¹H 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*-Bu₃Al) 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*-Bu₃Al 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*-Bu₃Al 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 (CaH₂) and sodium/benzophenone and kept
6 under vacuum for further distillation until use. Benzyl alcohol (BnOH; Sigma Aldrich,
7 99%) was dried over CaH₂ 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 CaH₂ at room temperature overnight before
10 distillation. Triisobutylaluminum solution (*i*-Bu₃Al; 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*^mPh, 98%) and 1,3-di-*tert*-butylimidazol-2-
13 ylidene (*I*^tBu, 98%) were purchased from Strem Chemicals, Inc. and used as received,
14 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene (*I*^{Pr}) was prepared according to
15 the previous reference [31].

16 **Instrumentation.** NMR spectra were recorded at 25 °C on a Bruker Avance 400 (¹H,
17 400.2 MHz) using deuterated chloroform (CDCl₃) 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⁻¹) 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⁻¹),
9 then mixed with a solution of cationisation agent (NaI) in MeOH (10 mg.mL⁻¹) and a
10 solution of matrix, dithranol (1,8-dihydroxyanthracen-9(10H)-one) in THF (10 mg.mL⁻¹),
11 ¹), in a volume ratio of 1:1:10. Then, 1~2 μ 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^tPr (1.67 mg, 0.0092 mmol), dried MeTHF (0.9 mL),
17 MeTHF solution of BnOH (0.5 M, 93.0 μ L, 0.046 mmol), *i*-Bu₃Al solution (1.0 M in
18 toluene, 28.0 μ 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 ¹H 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%, $\overline{M}_{n,th} = 9.4 \text{ kg}\cdot\text{mol}^{-1}$. $\overline{M}_{n,SEC}(\text{THF, PS standards}) = 10.6 \text{ kg}\cdot\text{mol}^{-1}$, $D = 1.05$. ^1H
7 NMR (400 MHz, 298 K, 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 $3.39\text{-}3.05$ ($-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O-}$), $1.25\text{-}0.87$ ($-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O-}$).

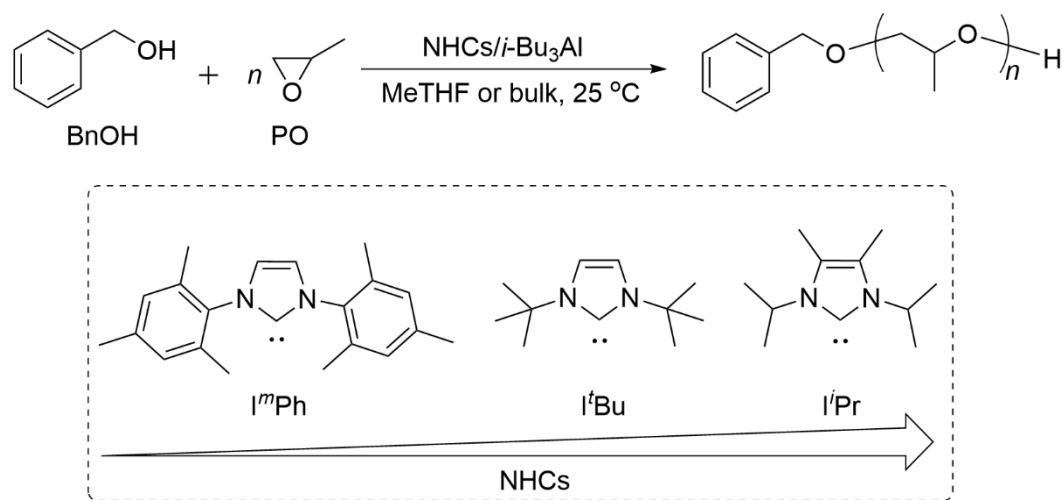
9 *Chain extension experiments.* A typical procedure of entry 11 in Table 2 is as follows.
10 The Schlenk flask was flamed three times on a vacuum line and transferred in a
11 glovebox, where *i*Pr (5.08 mg, 0.028 mmol), BnOH (14.5 μL , 0.14 mmol), *i*-Bu₃Al
12 solution (1.0 M in toluene, 84.0 μL , 0.084 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 ^1H 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 ^1H
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⁻¹. $\overline{M}_{n,SEC}$ (THF, PS standards) = 12.7 kg.mol⁻¹,
3 $D = 1.12$. ¹H NMR (400 MHz, 298 K, CDCl₃): $\delta/ppm = 4.50-4.46$ (BnOH, PhCH₂O–),
4 3.80-3.15 (PPO, –OCH₂CH(CH₃)O–) and (PBO, –OCH₂CH(CH₂CH₃)O–), 1.60-1.33
5 (PBO, –OCH₂CH(CH₂CH₃)O–), 1.27-0.86 (PPO, –OCH₂CH(CH₃)O–), 0.90-0.81
6 (PBO, –OCH₂CH(CH₂CH₃)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^mPh*), 1,3-di-*tert*-butylimidazol-2-ylidene (*I^tBu*),
10 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene (*IⁱPr*)) were chosen to be combined
11 with *i*-Bu₃Al 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*-Bu₃Al 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^mPh*) and *i*-Bu₃Al 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^tBu* and *IⁱPr*, used in conjunction with
18 *i*-Bu₃Al 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*-Bu₃Al and NHC of higher basicity led to faster
21 polymerization rates (pK_a^{DMSO} (*I^mPh*) = 17.0, pK_a^{DMSO} (*I^tBu*) = 22.8, pK_a^{DMSO} (*IⁱPr*) =

1 24.7) [33]. Therefore, considering its high catalytic and control efficiencies, catalysts
2 combining *I*'Pr with *i*-Bu₃Al was employed for further experiments.



4 **Scheme 1. Illustration for ROP of PO catalyzed by *I*'Pr + *i*-Bu₃Al**

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11 **Table 1. ROP of PO catalyzed by NHCs + *i*-Bu₃Al (in MeTHF, [PO]₀ = 7 M, 25 °C,**

1 **BnOH as the initiator)**

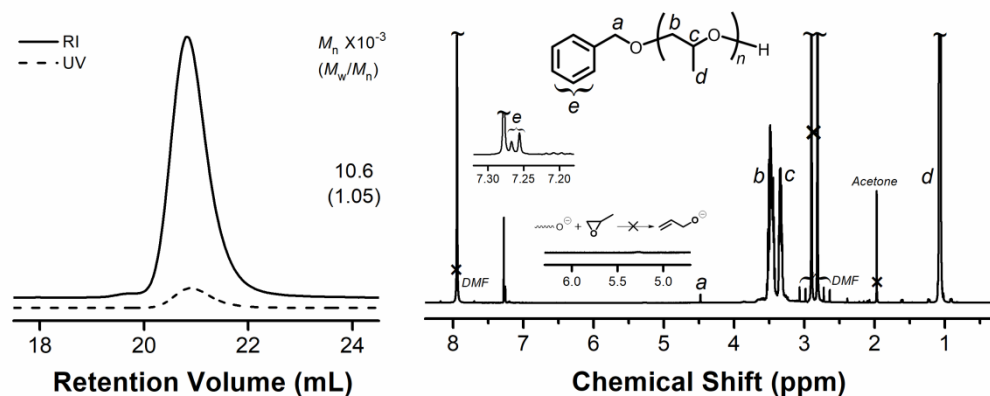
entry	[PO] ₀ /[-OH]/ [NHC]/[<i>i</i> -Bu ₃ Al]	NHC	Time (h)	Conv. ^a (%)	$\overline{M}_{n,th}^b$ (kg.mol ⁻¹)	$\overline{M}_{n,NMR}^c$ (kg.mol ⁻¹)	$\overline{M}_{n,SEC}^d$ (kg.mol ⁻¹)	<i>D</i> ^d
1	300/1/0.2/0.6	I ^m Ph	72	36	6.4	6.5	6.8	1.07
2	300/1/0.2/0.6	I ^t Bu	72	62	10.9	12.3	15.2	1.21
3	300/1/0.2/0.6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

^aConversion of PO calculated from ¹H NMR spectrum of the crude product. ^bTheoretical number-average molar mass calculated from feed ratio and monomer conversion. ^cCalculated from ¹H NMR spectra of the isolated product by comparing signal integrals of the end group (PhCH₂O–) and polymer. ^dObtained 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]₀/[BnOH] ratio and the monomer conversion. The
 6 ¹H 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 (CH₂=CHCH₂O–) that would be located at 5.0-6.0 ppm (Figure 1). Excess loading of
 9 *i*-Bu₃Al was compulsive for this dual catalyst, as no polymerization occurred in other
 10 molar ratios such as [IⁿPr]/[*i*-Bu₃Al] = 0.2/0.2 or 0.2/0.12 (entries 4-5, Table 1).

11



1

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

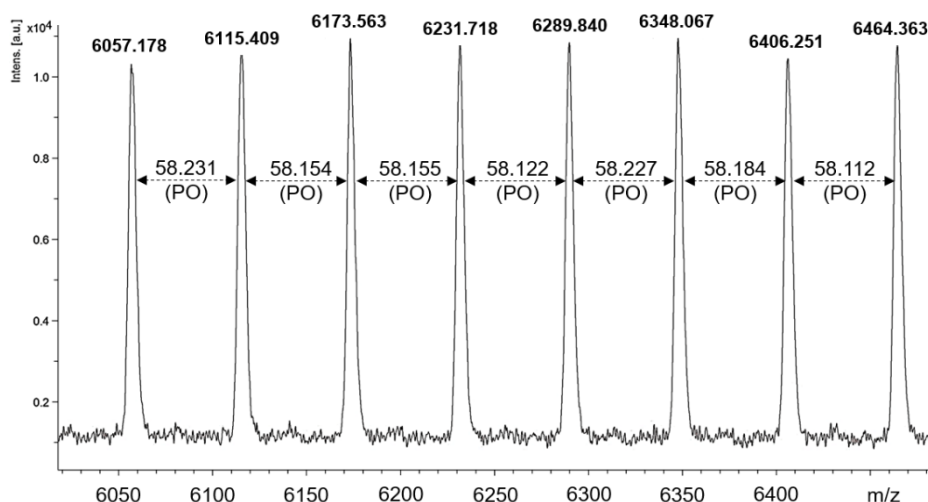
4 To improve the catalytic efficiency of “ $I^tPr + i\text{-Bu}_3\text{Al}$ ” catalytic system, two different
5 strategies were employed. One pathway is to increase the monomer concentration,
6 where the bulk polymerization produced controlled PPO with higher molar mass after
7 48 h (entry 6, Table 2). On the other hand, the enhanced molar ratio of $[i\text{-Bu}_3\text{Al}]/[I^tPr]$
8 could also increase the polymerization rate. For instance, when the $[i\text{-Bu}_3\text{Al}]/[I^tPr]$ 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 I^tPr 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*-Bu₃Al^a**

entry	[PO] ₀ /[-OH]/ [I'Pr]/[<i>i</i> -Bu ₃ Al] ^b	Solvent	Time (h)	Conv. ^c (%)	<i>M</i> _{n,theor} ^d (kg.mol ⁻¹)	<i>M</i> _{n,NMR} ^e (kg.mol ⁻¹)	<i>M</i> _{n,SEC} ^f (kg.mol ⁻¹)	<i>D</i> ^f
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 ^g	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

^aPerformed in MeTHF ([PO]₀= 7 M) or in bulk with BnOH as the initiator, except for entries 8-11 ([PO]₀= 10 M). ^bMolar feed ratio of PO, hydroxyl, *N*-heterocyclic carbene and triisobutylaluminum. ^cConversion of PO calculated from ¹H NMR spectrum of the crude product. ^dTheoretical number-average molar mass calculated from feed and monomer conversion. ^eNumber-average molar mass calculated from ¹H NMR spectra of the isolated product. ^fNumber-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). ^gChain extension following entry 11-1 using BO as the second monomer.

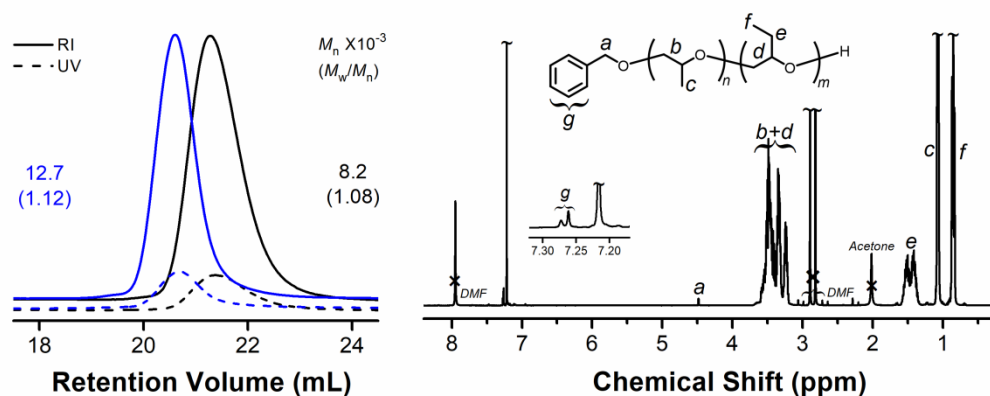
2 The chain-end fidelity of resultant PPOs was analysed by MALDI-TOF mass
3 spectrometry (Figure 2). Despite slightly broad peaks probably certainly due to an
4 isotopic distribution, one main distinct population corresponding to the desired PPO
5 chain-ends, *i.e.* α-PhCH₂O/ω-OH was observed. These data were also consistent with
6 ¹H 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 $I^iPr + i-Bu_3Al$ -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 $[PO]_0/[-OH]/[I^iPr]/[i-Bu_3Al]$ 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.

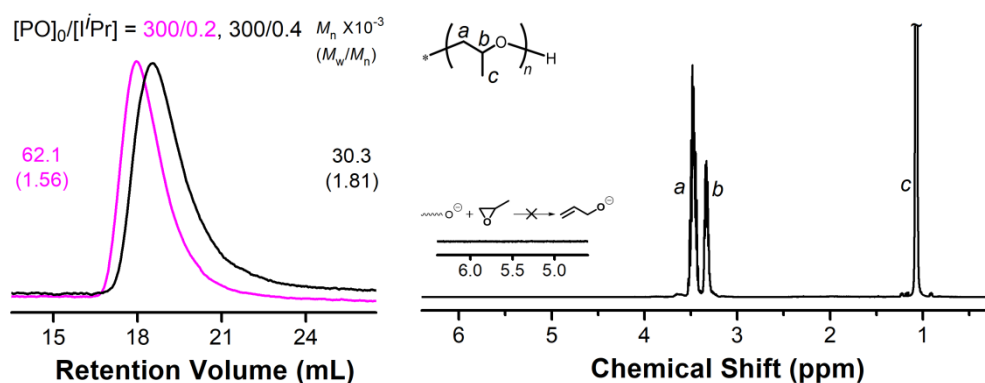


1

2 **Figure 3.** Chain extension reactions: SEC traces (left) of crude PPO-*b*-PBO (blue line)
 3 and ¹H 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^tPr +
 5 *i*-Bu₃Al (entries 12-13, Table 2). The molar masses of obtained PPOs could be adjusted
 6 by the initial feed ratio of [PO]₀/[I^tPr]. 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]. ¹H 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]₀/[I^tPr]/[*i*-Bu₃Al] = 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

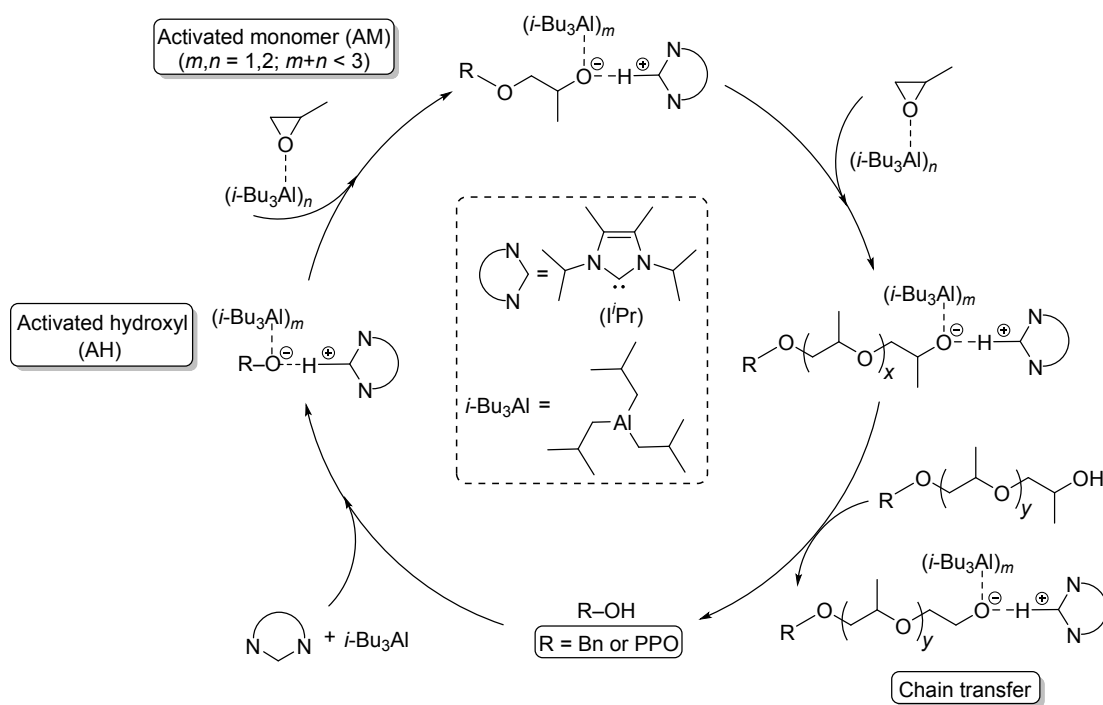
4 **Figure 4.** Left: SEC traces of PPOs synthesized with $I^tPr + i-Bu_3Al$ in absence of the
 5 initiator corresponding to entries 12 (pink line), 13 (black line) in Table 2. Right: 1H
 6 NMR spectrum of the isolated product of entry 12.

7

8 Considering the roles of $i-Bu_3Al$ used in other bicomponent catalysts we established for
 9 the polymerization of epoxides,²⁰⁻²⁵ 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 oxanion
 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*-Bu₃Al 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]₀/[I^{*i*}Pr]/[*i*-Bu₃Al] 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

2 **Scheme 2. Proposed mechanism for ROP of PO catalyzed by I'Pr + *i*-Bu₃Al (1/3).**

3 **4. Conclusion**

4 *N*-heterocyclic carbenes used in conjunction with triisobutylaluminum enables to
 5 efficiently trigger the controlled ring-opening polymerization of propylene oxide
 6 improving the NHC's approach for substituted epoxides. It also enables polyether-
 7 based block copolymer synthesis. PPOs with predictable molar masses over a wide
 8 molar mass range and low dispersities can be achieved under rather mild conditions,
 9 including under solvent-free conditions at room temperature. Depending on the
 10 presence of hydroxyl functions as initiators or not, an anionic or a zwitterionic ROP
 11 mechanism operates, respectively. Considering the rich and diverse structures of NHCs
 12 and its various application in organic ROP, the combination of NHCs and *i*-Bu₃Al also
 13 provides an opportunity for the synthesis of polymers with sophisticated structure and

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.

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7 **Data in brief**

8 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 1: triisobutylaluminum as an efficient controlling agent

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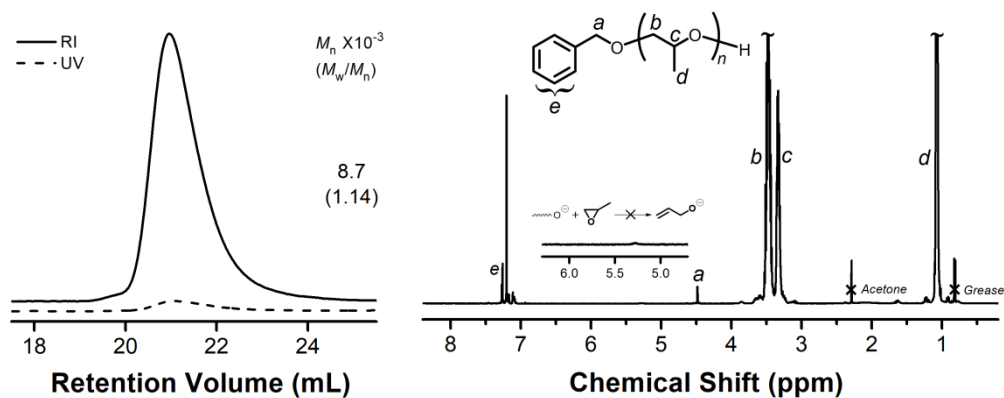


Figure S1. SEC chromatogram and ^1H NMR spectrum of PPO (entry 9, Table 2)

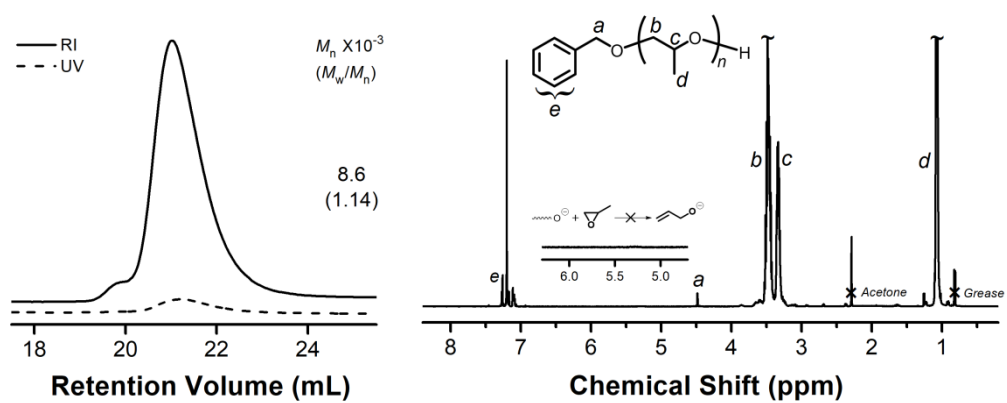


Figure S2. SEC chromatogram and ^1H NMR spectrum of PPO (repeated experience similar to entry 9, Table 2)

$n = 105$, calculated mass = 6229.54

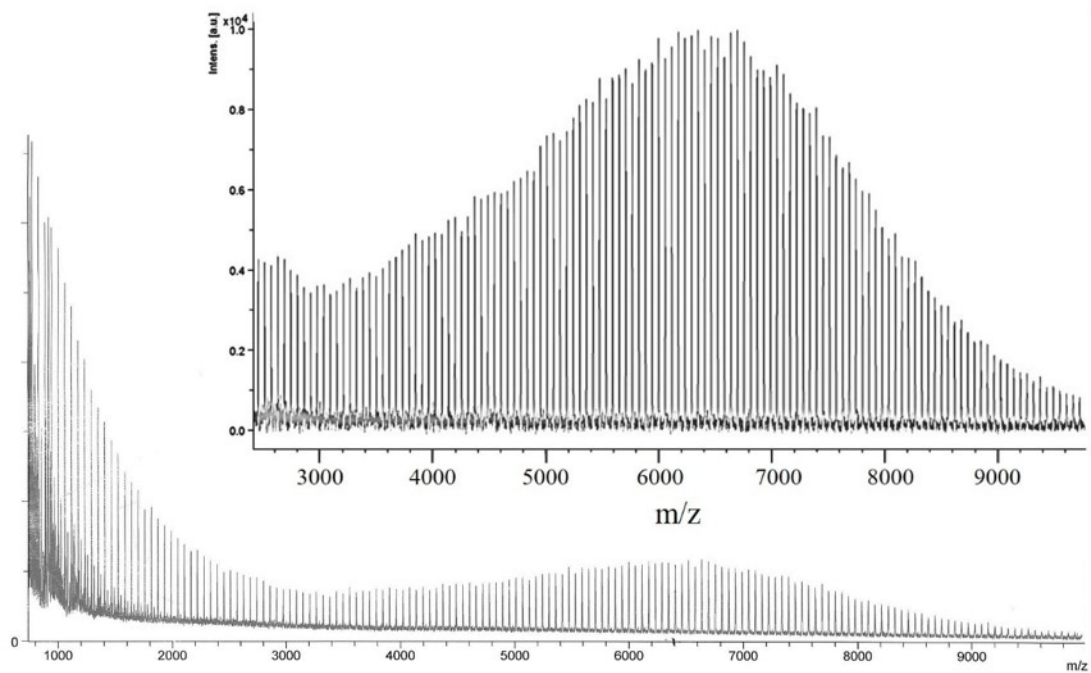
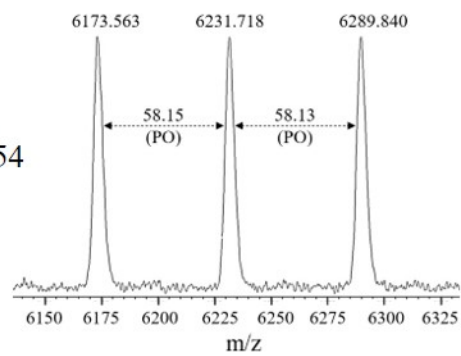


Figure S3. MALDI-TOF MS spectrum of PPO (entry 9, Table 2)

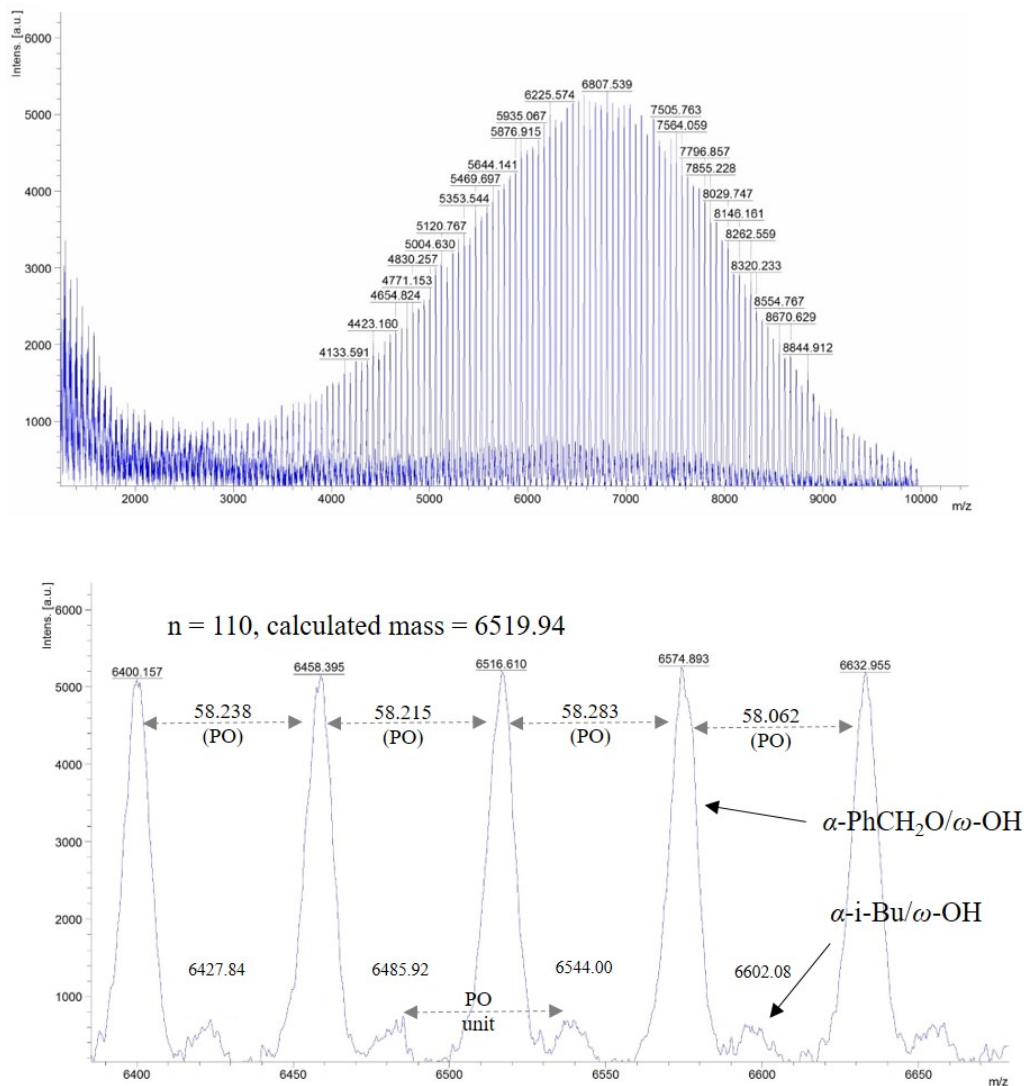
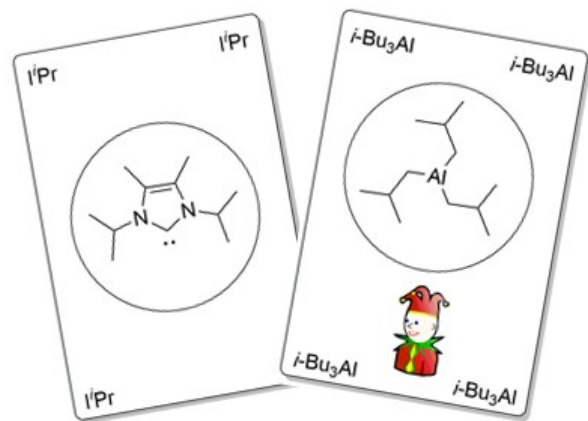


Figure S4. MALDI-TOF MS spectrum of PPO (repeated experience similar to entry 9, Table 2)

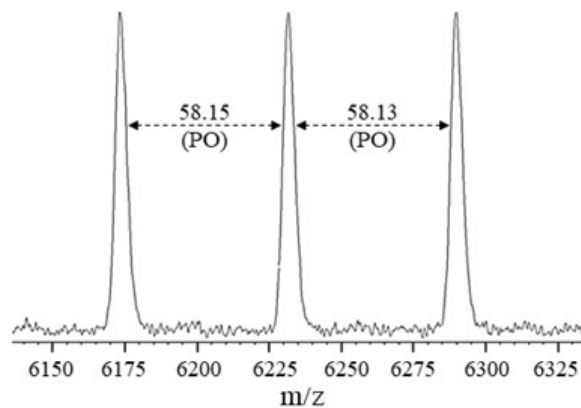
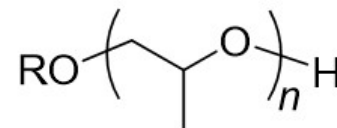
Comments:

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