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Supporting Information to:

A simplified approach for the metal-free polymerization of propylene oxide

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Contents

Experimental

Starting materials and catalyst synthesis

Propylene oxide (PO, TCI Chemicals, > 99.0 %), butylene oxide (BO, TCI Chemicals, > 99.0 %), allyl glycidyl ether (AGE, Sigma-Aldrich, > 99.0 %) and *tert*-butyl glycidyl ether (*t*BuGE, TCI, > 96.0 %) were dried over CaH_2. After distillation of PO and BO under ambient pressure or, in case of AGE and *t*BuAGE, under static vacuum ($1 \cdot 10^{-3}$ mbar) with subsequent degassing, the monomers were stored under protective conditions inside the glove box (LabMaster, *MBraun*, Germany, freezer at -36 °C). The hygroscopic α,ω-dihydroxylated PEO 8k and PEO 20k were dried by dissolving the polymer in dry dichlormethane (glove box) and storage over molecular sieve for at least 48 h, after which the sieve was exchanged and applied for another 48 h. Afterwards the solvent was removed under reduced pressure over several hours. Et_3B (1.0 M in THF) was used as received and stored inside the glove box (freezer, -36 °C). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 4-dimethylaminopyridine (DMAP) and 1,4-diazabicyclo[2.2.2]octane (DABCO) were used as received and stored in the glove box. NHO **1**[1–3], **2**[1,4] and **3**[2] were prepared according to published procedures, identification was confirmed using ^{1}H and ^{13}C NMR analysis; for full characterization please see the cited references. A schematic synthetic route is provided below (Fig. S1). Precursor salt **4'** was received following the general procedure of **3'** by cyclization of the suitable diamine with the orthoester. For synthesis and characterization of NHO **4**, see below.

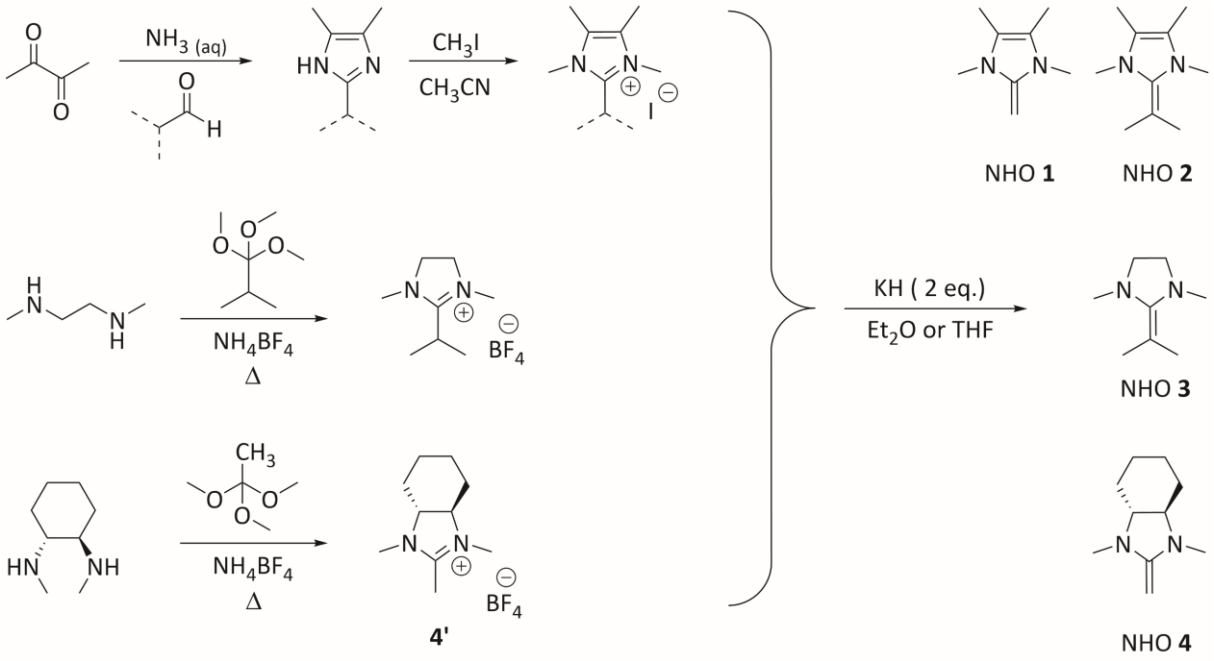

Figure S1 Synthesis of NHO **1**, **2**, **3** and **4**.

Preparation of precursor salt 4'

Trimethyl orthoacetate (6.80 g; 56.6 mmol) and (1*R*, 2*R*)-(-)-*N*,*N*'-dimethylcyclohexane-1,2-diamine (8.05 g; 56.6 mmol) were combined and stirred at room temperature. After subsequently adding NH_4BF_4 (5.93 g; 56.6 mmol), the resulting suspension was heated to 110°C (condenser) for 4h. All volatiles (MeOH) were then removed in vacuo, the residue was dissolved in dichloromethane and filtered before adding THF to the solution in order to precipitate the product, which was filtered off as a white crystalline solid. The precursor salt was washed several times with THF before drying under vacuum. Yield: 4.92 g (29.6 mmol, 52%).

(3*R*, 7*R*)-1,2,3-trimethyl-3a,4,5,6,7,7a-hexahydro-1*H*-benzimidazol-3-ium tetrafluoroborate (4'): 4.92 g (solid, 52% yield). **^{1}H-NMR** ($CDCl_3$): δ = 3.32-3.30 (m, 2H), 3.08 (s, 6H), 2.31 (s, 3H), 2.23-2.20 (m, 2H), 1.96-1.94 (m, 2H), 1.54-1.51 (m, 2H), 1.40-1.37 (m, 2H) ppm; **^{13}C NMR** ($CDCl_3$): δ = 170, 67.5, 31.3, 27.1, 23.9, 11.2 ppm. **IR** (ATR, cm^{-1}): 2958 (w), 1592 (m), 1534 (w), 1327 (w), 1092 (m), 1026 (s), 628 (m), 520 (m).

General preparation of NHO 4

Precursor salt **4'** (2.0 g, 7.09 mmol, 1.0 eq) was added under nitrogen flow to a Schlenk tube containing 20 mL of dry Et_2O and 570 mg of KH (14.2 mmol, 2.0 eq). Under exclusion of light the suspension was stirred for two days at room temperature (H_2 escapes via open Schlenk line). The product was then extracted from this suspension using dry pentane and the solids were filtered off (both steps inside the glove box). After removal of solvent, a colorless liquid (0.75 g, 4.53 mmol, 64%) remained and was stored at -36 °C in the glove box.

(3*R*, 7*R*)-1,3-dimethyl-2-methyleneoctahydro-1*H*-benzimidazole (4): 750 mg (liquid, 64% yield). **^{1}H-NMR** (C_6D_6): δ = 3.35 (s, 2H), 2.44 (s, 6H), 2.18-2.14 (m, 2H), 1.66-1.63 (m, 2H), 1.49-1.47 (m, 2H), 1.06-0.94 (m, 4H) ppm; **^{13}C NMR** (C_6D_6): δ = 162.4, 66.4, 55.6, 33.6, 28.7, 24.4 ppm; **HRMS (ESI)**: m/z calc. for $C_{10}H_{18}N_2^+$ (cation) = 167.1504, found: 167.1543 $[NHO+H]^+$.

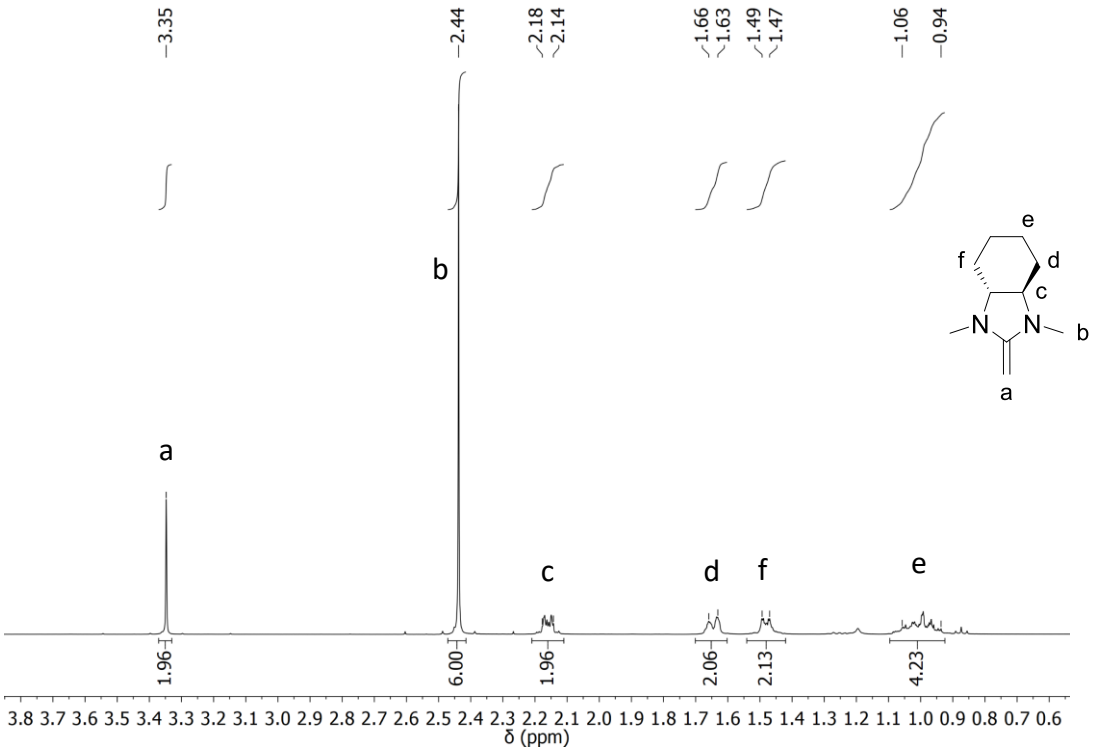

Figure S2 ^{1}H NMR analysis (C_6D_6, 400 MHz, 300K) of NHO **4**.

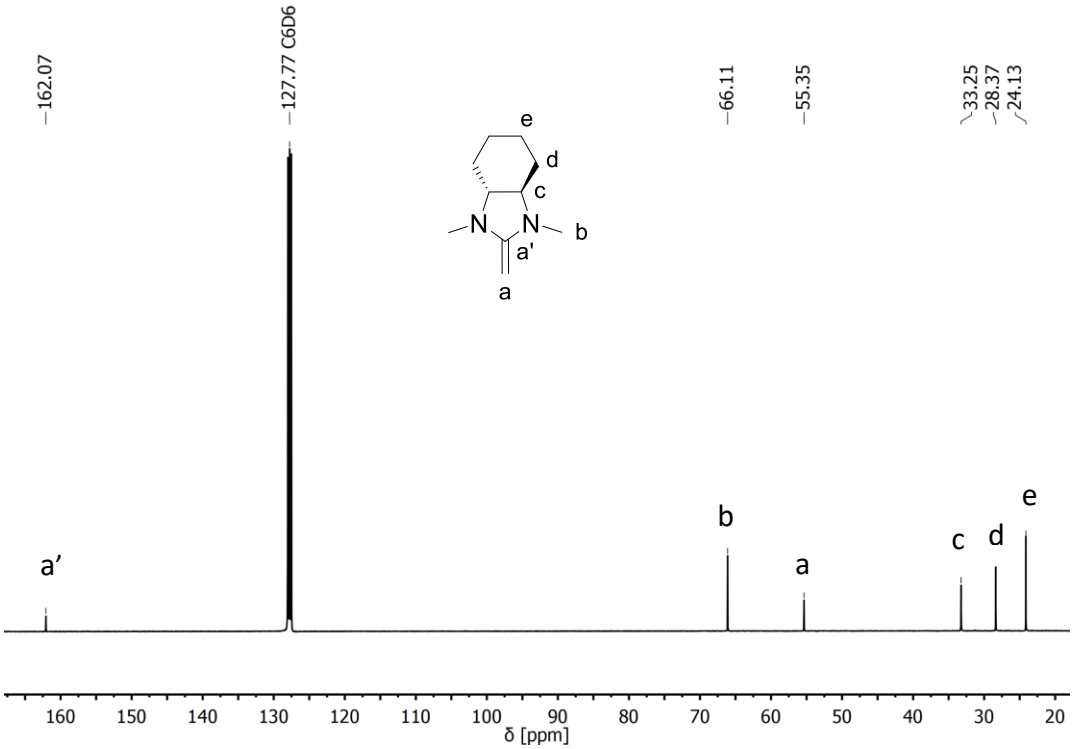

Figure S3 ^{13}C NMR analysis (C_6D_6, 100 MHz, 300K) of NHO **4**.

General procedure for the preparation of $PPO_{n/2}$-PEO_m-$PPO_{n/2}$

All polymerizations were assembled inside the glove box. The reactions were prepared in glass pressure tubes, which were then removed from the glove box and placed in the preheated oil bath (50 °C or 80 °C). For a typical polymerization, the organobase (i.e., NHO **1**, 3.5 mg, 0.025 mmol, 1.0 eq.) was combined with macroinitiator (PEO 8k, 500 mg, 0.0625 mmol = 0.125 mmol OH-end groups, 5.0 eq.) and PO (2.18 g, 37.5 mmol, 1500 eq.). When using triethyl borane (50 µL, 0.125 mmol, 2 eq.), it was added dropwise to the reaction mixture prior to removal from the glove box. The polymerization was quenched by evaporation of the PO. The residue was dissolved in DCM and precipitated from *n*-pentane. The received white polymer was dried under reduced pressure. Polydispersity (PDI) of the polyether was determined *via* GPC analysis ($CHCl_3$). The number of PO-repeating units was calculated from ^{1}H NMR ($CDCl_3$), monitoring the PO(-CH_3)- (δ = 1.17 – 1.09 ppm) and EO-signals (δ = 3.68 – 3.60 ppm) of the resulting polymer (Fig. S4). Conversion of PO is determined from the initial [PO]/[-OH] ratio and the thus calculated number of incorporated PO units.

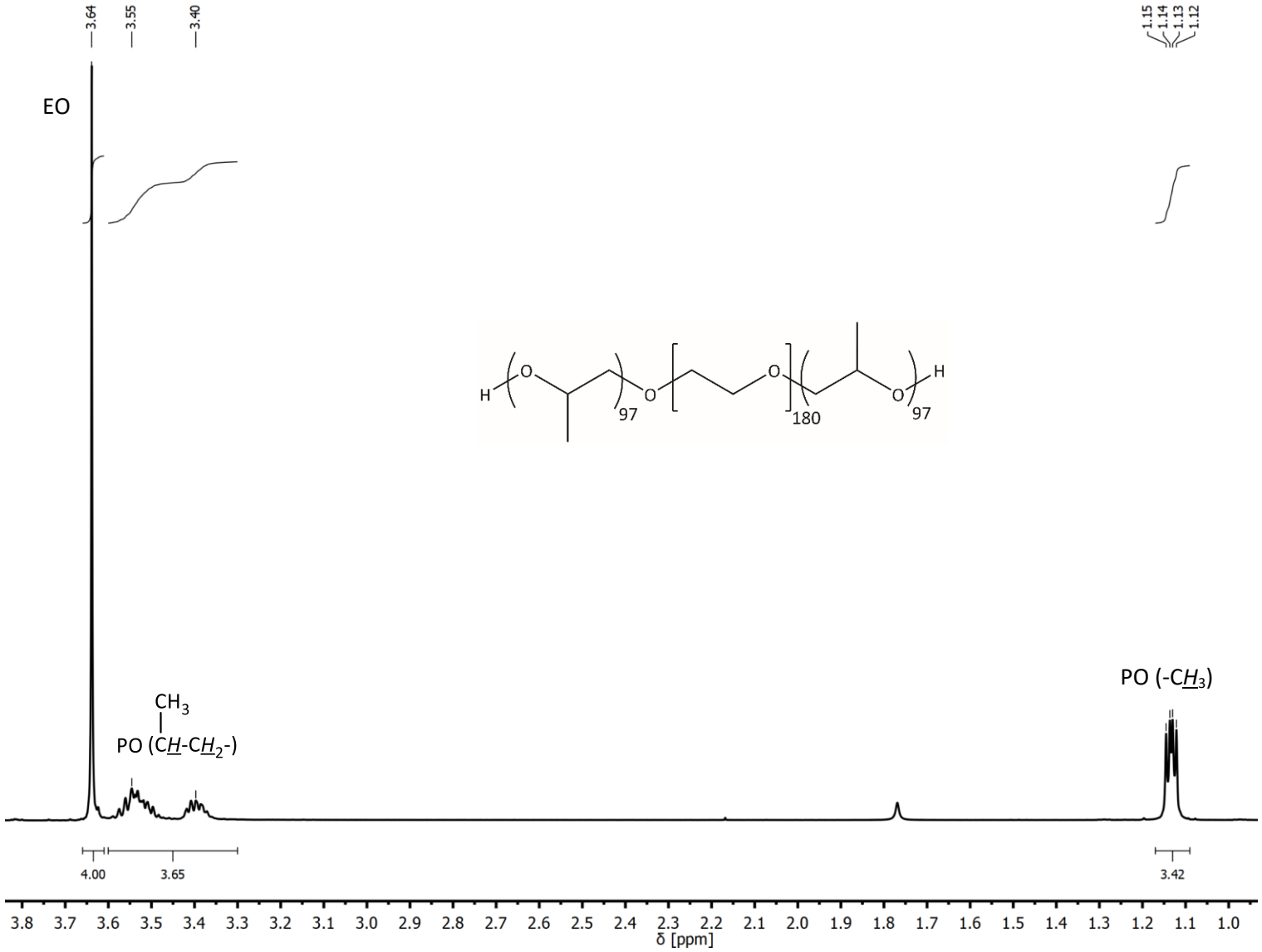

Figure S4 ^{1}H NMR analysis ($CDCl_3$, 400 MHz, 300 K) of a ‘‘*Reverse Pluronic*‘‘ prepared by action of NHO **1**.

Characterization and analysis

^{1}H and ^{13}C NMR spectra were recorded on a *Bruker* Avance III 400 spectrometer. All chemical shifts are reported relative to the reference peak of deuterated chloroform (δ = 7.26 ppm for ^{1}H / δ = 77.16 ppm for ^{13}C) or deuterated benzene (δ = 7.16 ppm for ^{1}H / δ = 128.1 ppm for ^{13}C).

Molecular weights and polydispersity of the different polymers were determined via gel permeation chromatography (GPC), employing a calibration versus polystyrene in the range of 800 g/mol – $2 \cdot 10^{6}$ g/mol. GPC measurements (40 °C) were carried out in $CHCl_3$ using an Agilent 1200 Series G1362A RI-detector. The separation system was equipped with a *PSS* SDV 5 µm 8*50mm precolumn and three *PSS* SDV 100 000 Å 5 µm 8*50mm columns. A flow rate of 1 ml/min and a sample concentration of 2 mg/mL was applied (100µL injection).

MALDI-ToF (matrix-assisted laser desorption ionization-time of flight) mass spectrometry measurements were conducted on a *Bruker* Autoflex III (337 nm, reflector mode). The samples were prepared by mixing matrix solution (2,5-dihydroxybenzoic acid, 5 mg/mL in THF), PPO solution (10 mg/ml in THF), and sodium trifluoromethanesulfonate solution used as cationization agent (0.1 M in 90% acetone/water = 9:1) with a ratio of 2:1:2. For calibration, a polystyrene standard was employed.

Representative GPC analysis

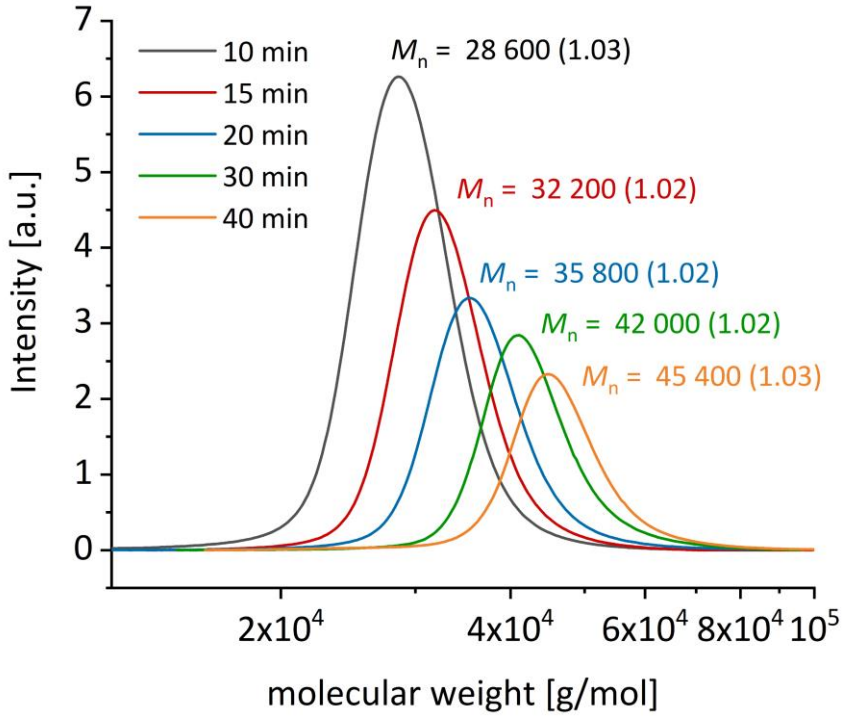

Figure S5 Representative GPC traces of **1**/Et_3B/-OH/PO = 1:4:5:1500. Reaction conditions: 80 °C, PEO 8k.

Results

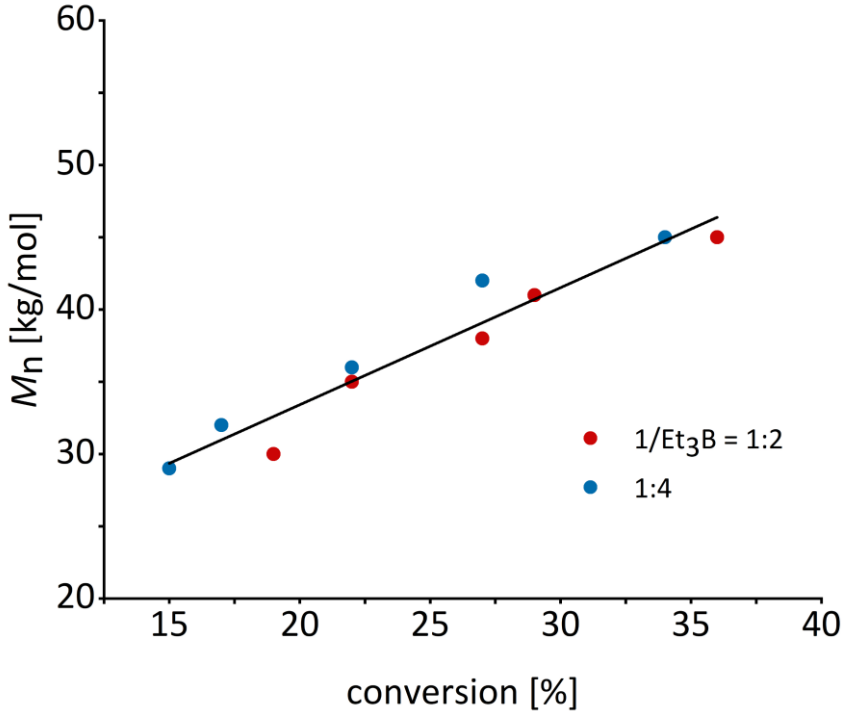

Figure S6 Conversion vs. M_n for PO polymerization with PEO 8k as macroinitiator using different **1**/Et_3B ratios.

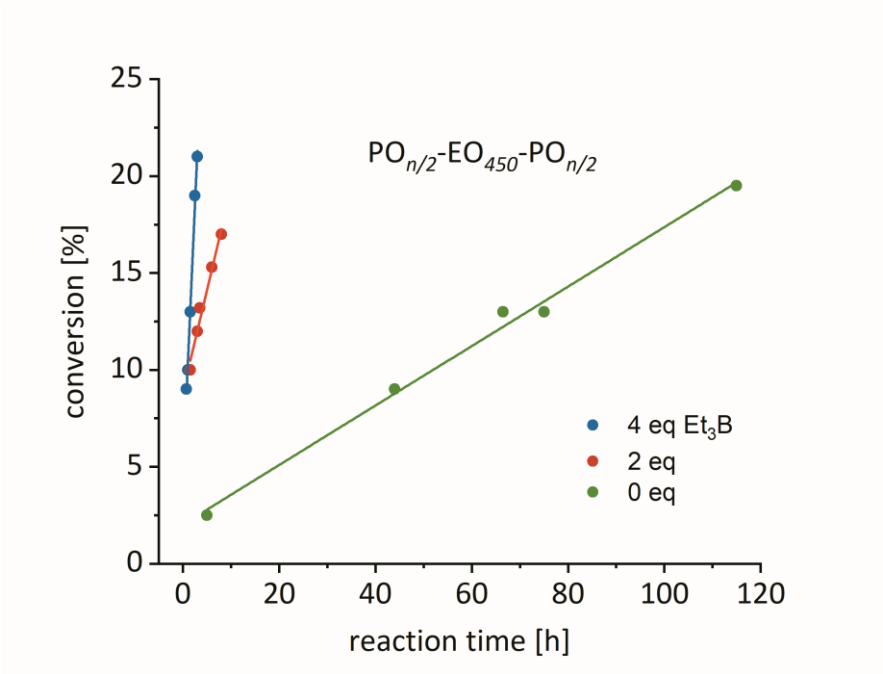

Figure S7 Reaction time vs. conversion (^{1}H NMR) for polymerization of PO at 80 °C using NHO **1** and different equivalents of BEt_3 as cocatalyst: **1**/PEO 20k[-OH]/PO = 1:5:1500.

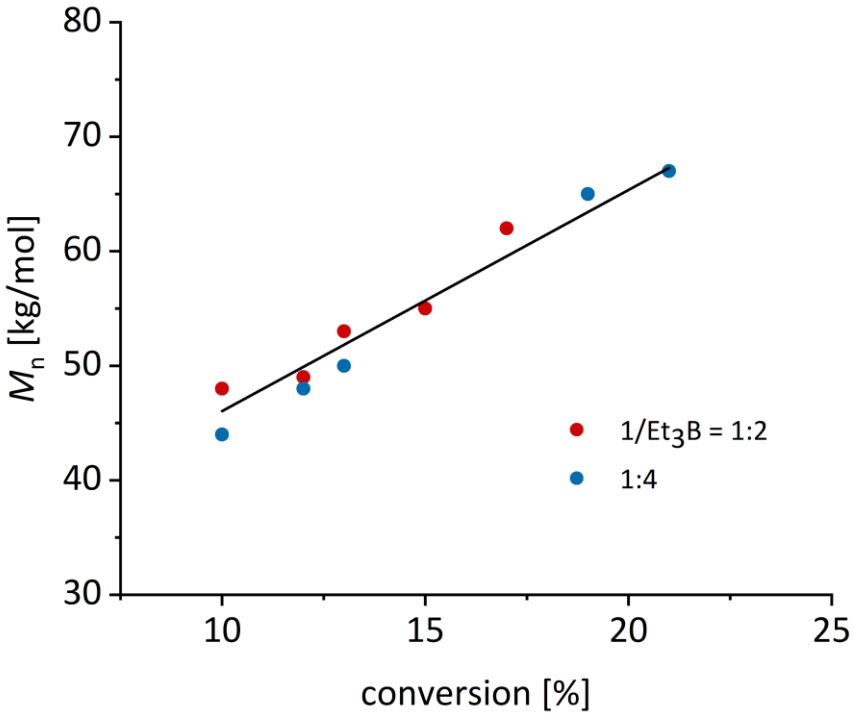

Figure S8 Conversion vs. M_n for PO polymerization with PEO 20k as macroinitiator using different **1**/Et_3B ratios.

Table S1 Additional examples: Polymerization of PO with variation of organobase and Et_3B loading. Content of side product (SP) approximated via integration of GPC signal.

#	OB	Initiator	OB/-OH/Et_3B/PO molar ratio	*T* [°C]	*t* [h]	Conv [%][a]	PO [a] *n/2*	M_n (calc.)[a] [kg mol^{-1}]	$Đ_M$ [b]	SP[b] [%]
1	**2**	PEO 8k	1:5:0:1500	50	2.5	0	0	-	-	-
2	**2**	PEO 8k	1:5:0:1500	50	22	12	35	12.0	1.02	0
3	**2**	PEO 8k	1:5:2:1500	50	2	43	130	23.0	1.03	0
4	**2**	PEO 8k	1:5:2:1500	80	2	31	94	18.9	1.03	0
5	**2**	PEO 8k	1:5:4:3000	80	2	29	174	28.1	1.04	0
6	**2**	PEO 8k	1:5:4:3000	80	22	47	282	40.6	1.04	2
7	**1**	PEO 8k	1:5:0:1500	50	22	21	63	15.2	1.04	12
8	**1**	PEO 8k	1:5:2:1500	50	2	41	122	22.1	1.03	1
9	**1**	PEO 8k	1:5:0:1500	80	22	27	80	17.2	1.03	10
10	**1**	PEO 8k	1:5:2:1500	80	3	39	116	21.4	1.02	2
11	**1**	PEO 8k	1:5:4:1500	80	1	35	105	20.1	1.02	1
12	**1**	PEO 8k	1:5:4:3000	80	2	22	129	22.9	1.02	2
13	**1**	PEO 8k	1:5:4:3000	80	3	38	229	34.5	1.03	14
14	**1**	PEO 8k	1:5:4:3000	80	22	47	284	40.9	1.02	6
15	**3**	PEO 8k	1:5:2:1500	80	1.5	25	76	17.0	1.03	1
16	**3**	PEO 8k	1:5:4:1500	80	2	42	127	22.7	1.03	4
17	**3**	PEO 8k	1:5:4:1500	80	22	48	145	24.7	1.03	n.d
18	**4**	PEO 8k	1:5:4:1500	80	2	6	18	10.0	1.02	0
19	**4**	PEO 8k	1:5:4:1500	80	22	26	79	17.1	1.03	5
20	**4**	PEO 8k	1:5:4:1500	80	72	34	101	19.6	1.03	5
21	**5**	PEO 8k	1:5:4:1500	80	2	30	90	18.4	1.02	n.d.
22	**5**	PEO 8k	1:5:4:1500	80	22	45	135	23.6	1.02	9
23	**6**	PEO 8k	1:5:2:1500	80	22	10	31	11.6	1.02	2
24	**6**	PEO 8k	1:5:4:1500	80	22	22	65	15.5	1.02	2
25	**6**	PEO 8k	1:5:4:1500	80	48	35	106	20.2	1.02	3
26	**7**	PEO 8k	1:5:4:1500	80	22	5	16	9.8	1.03	0
27	**7**	PEO 8k	1:5:4:1500	80	48	16	49	13.6	1.03	1
28	**1**	PEO 20k	1:5:0:3000	80	115	19	117	33.5	1.04	10
29	**1**	PEO 20k	1:5:2:3000	80	1.75	13	79	29.1	1.04	1

[a] Determined via ^{1}H NMR analysis ($CDCl_3$); [b] SP = side product, approximately determined from GPC ($CHCl_3$) integration.

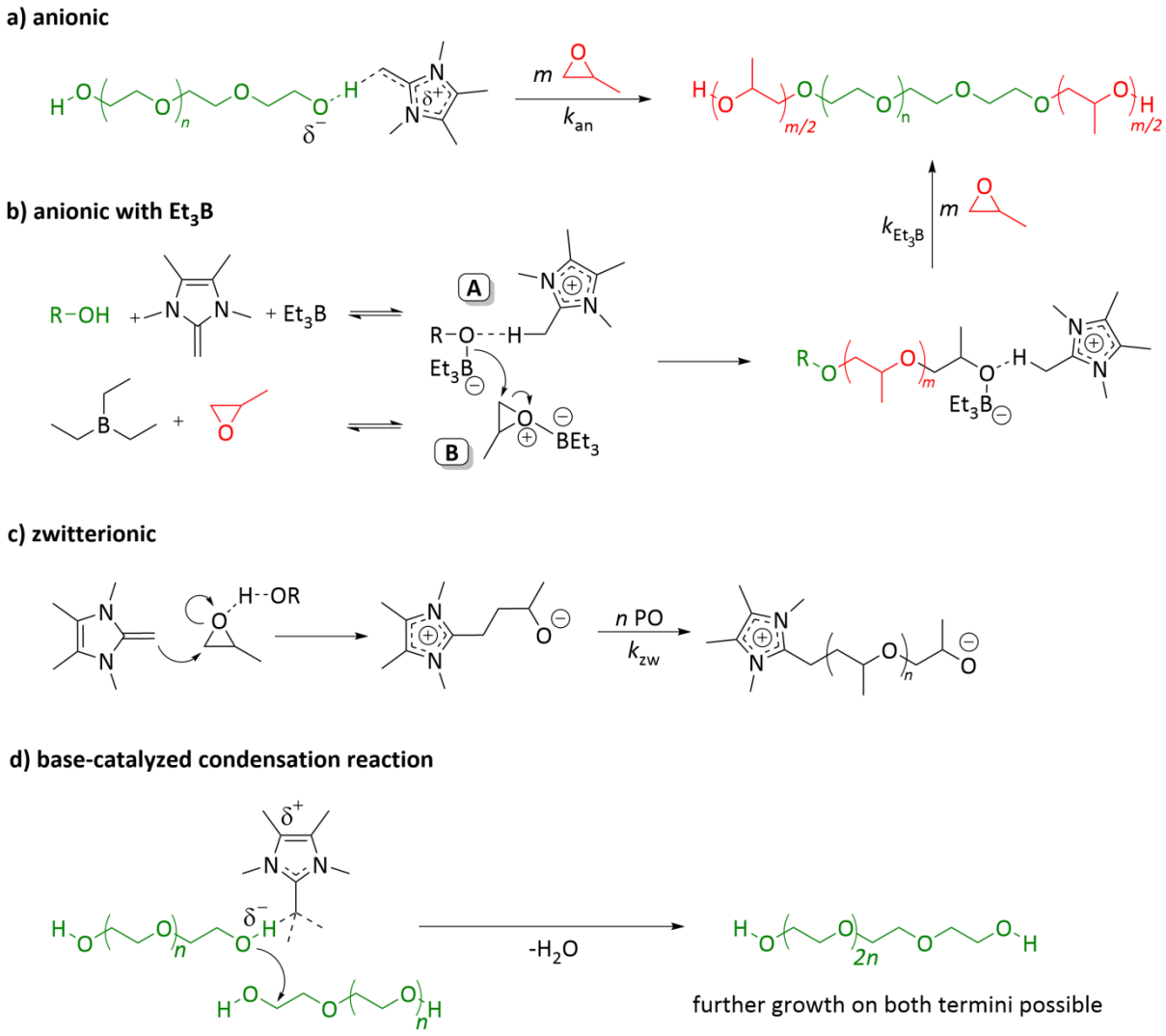

Figure S9 Reaction scheme for the a) NHO-based anionic polymerization of PO in presence of an alcohol initiator;[3,5] b) desired, anionic mechanism by adding Et_3B to form activated hydroxyl (A) and activated monomer (B) which enables a fast and controlled polymerization to prepare a BAB-type block copolyether;[6] c) zwitterionic ring-opening polymerization as side reaction, initiated by the organobase;[3,5] d) Proposed NHO-mediated condensation reaction by using PEO8k or PEO20k as macroinitiator.[7]

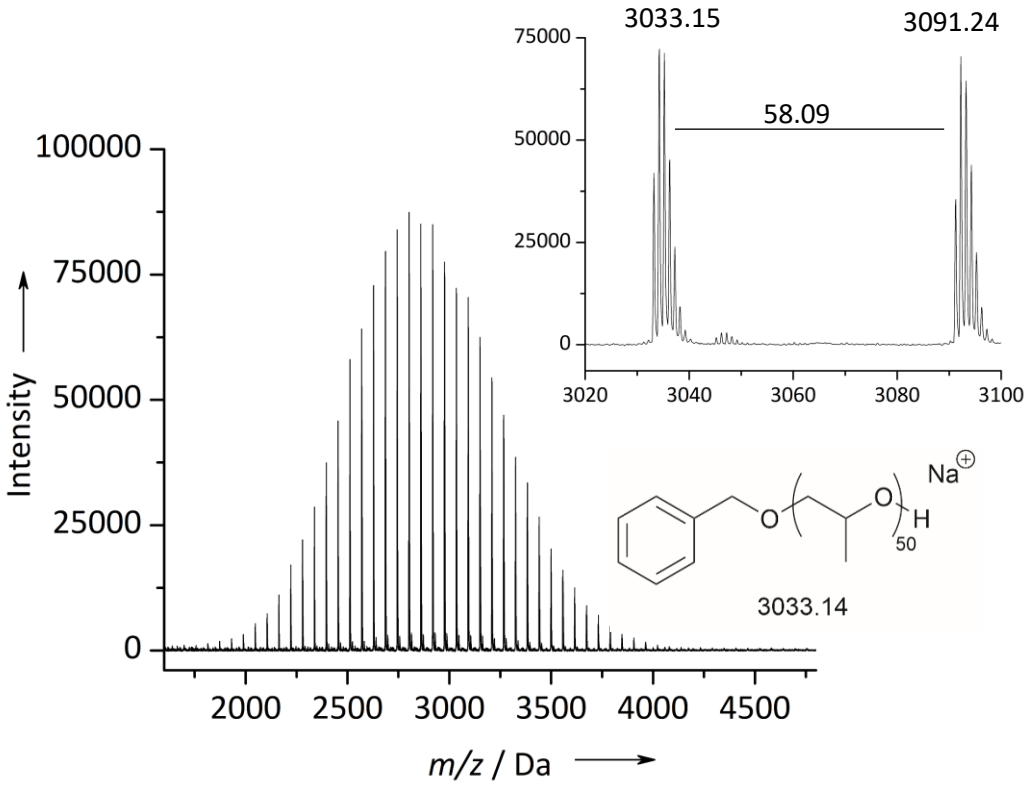

Figure S10 MALDI-ToF MS analysis of PPO prepared by using NHO **2** (Table 1, entry 5), cationized by sodium.

Table S2 Control reactions of PO polymerization with different organobases in the absence of borane cocatalyst.

#	Base	Initiator	Base/-OH/Et_3B/M molar ratio	*T* [°C]	*t* [h]	Conv.[a] [%]
1	**3**	PEO 8k	1:5:0:1500	80	22	0
2	**3**	PEO 8k	0:5:2:1500	80	22	0
3	**4**	PEO 8k	1:5:0:1500	80	22	0
4	**DBU**	PEO 8k	1:5:0:1500	80	22	0
5	**DMAP**	PEO 8k	1:5:0:1500	80	22	0
6	**DABCO**	PEO 8k	1:5:0:1500	80	22	0

[a] Determined via ^1H NMR analysis ($CDCl_3$).

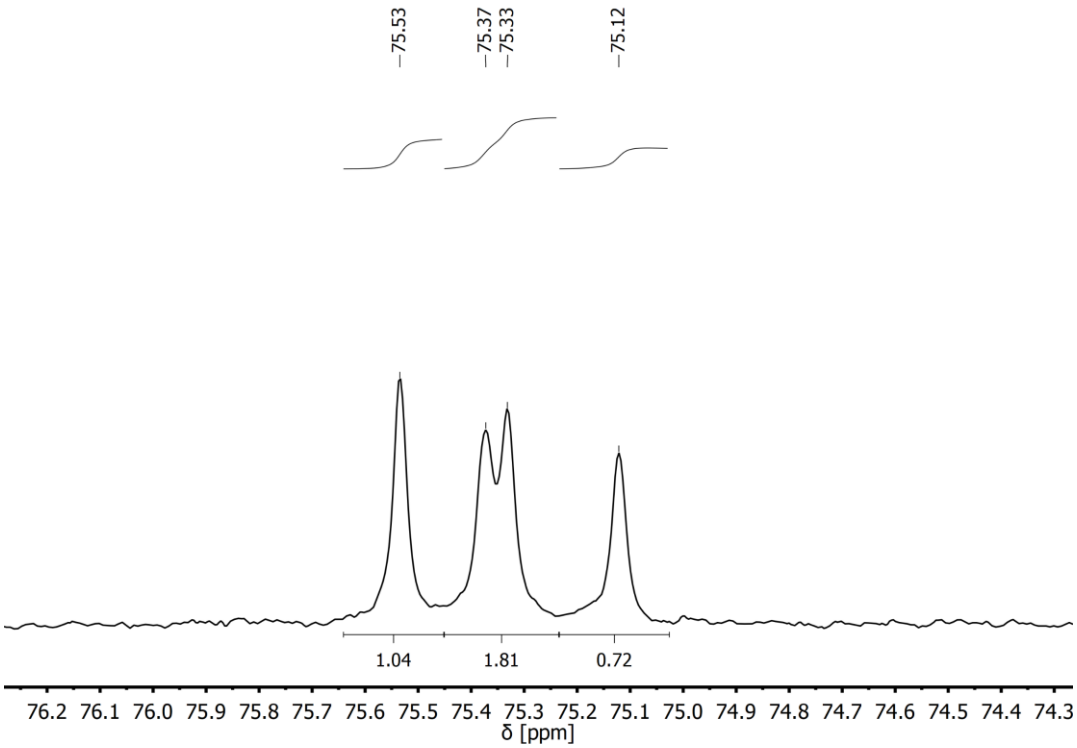

Figure S11 ^{13}C NMR analysis ($CDCl_3$, 100 MHz, ambient) of the methine region of PO_{101}-EO_{180}-PO_{101}. For reaction conditions see Table S1, entry 20.

Table S3 Polymerization of other epoxide monomers using different organobases with Et_3B as cocatalyst (PEG 8k). Reaction conditions: Base/-OH/Et_3B/M = 1:5:4:1500.

#	Base	Monomer	*T* [°C]	*t* [h]	Conv.[a] [%]	PO[a] *n/2*	M_n (calc.)[a] [kg mol^{-1}]	$Đ_M$[b]	SP[b] [%]
1	**3**	BO	80	72	13	38	13.4	1.02	0
2	**3**	AGE	80	72	9	28	14.3	1.03	0
3	**3**	*t*BuGE	80	72	8	24	14.2	1.03	0
4	**DBU**	BO	80	72	7	20	10.8	1.03	0
6	**DBU**	AGE	80	72	8	25	13.6	1.03	0
7	**DBU**	*t*BuGE	80	72	15	45	19.6	1.02	0
8	**DMAP**	AGE	80	72	0	0	-	-	-

[a] Determined via ^{1}H NMR analysis ($CDCl_3$); [b] Determined from GPC ($CHCl_3$). SP = side product.

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