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Ring-Opening Polymerization and Copolymerization of Propylene Oxide Catalyzed by N-Heterocyclic Carbenes

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Herein, we demonstrate the application of adducts of various N-heterocyclic carbenes (NHCs) with CO_2 (i.e., NHC– CO_2) as precatalysts in the ring-opening homopolymerization of propylene oxide (PO) onto diethylene glycol as a chain starter to give well-defined polyether diols. The influence of various

NHCs on the structure of the polymers and the mechanism of this reaction were investigated both experimentally and through DFT calculations. With this methodology, copolymers of PO and the monomers ε -caprolactone and (*S*,*S*)-lactide are accessible.

Introduction

Over the last decade, the metal-free ring-opening polymerization (ROP) of various cyclic monomers, that is, esters, silox-

anes, and epoxides, catalyzed by free N-heterocyclic carbenes (NHCs), such as **1–3** (Figure 1), has gathered considerable attention ("organopolymerization").^[1,2] Surprisingly, despite their high industrial relevance, the NHC-catalyzed ROP of epoxides such as ethylene oxide (EO) and propylene oxide (PO) has only been described by a few authors, such as Taton et al., and only with a limited number of catalysts.^[3–5] Amongst those, for example, 1,3-diisopropylimidazol-2-ylidene (1) was of mediocre activity and stability so that high conversion required long reaction times and low temperature. This is especially true for PO, which is poorly reactive under the reported reaction conditions (\leq 40% conversion after several days), even if it is used as the solvent.

In general, NHCs are strong bases that are prone to decomposition by protonation and hydrolysis.^[6] This makes it necessary to work under strictly water-free conditions. Furthermore, the stability of NHCs with sterically nondemanding substituents is limited, and

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their nucleophilicity might lead to significant side reactions other than the required ROP of epoxides.^[7] The utilization of

free NHCs



Figure 1. Overview of free NHCs 1–3 and NHC precursor 4–11 used in the ROP of PO and DEG.

an NHC precursor that is able to deliver a steady but low concentration of free NHC is therefore an attractive option.^[8] Imidazol(in)ium hydrogen carbonates^[9] or acetates^[10] are NHC precursors with moisture stability that is superior to that of the CO₂ adducts of NHCs, but for high catalytic activity the addition of stoichiometric amounts of base is required.^[11] Carboxylates of N-heterocyclic carbenes (NHC–CO₂), such as **4–11** (Figure 1), have been widely used as NHC precursors in organometallic,^[12] organic, and polymer chemistry.^[13] Furthermore, it was shown by Louie et al. that the decarboxylation reaction is largely influenced by the substituents on the nitrogen atom.^[14] This allows the stereoelectronic factors of an NHC catalyst to be tailored^[15] for a given application.

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Within this work, we therefore investigated the suitability of NHC carboxylates **4–11** for the ROP of PO and compared their performance to that of free NHCs **1–3**. We were especially interested in the effect of different substituents on the activity of the NHC precursor. For this study, we targeted technically relevant reaction conditions, that is, high temperature, neat substrate, and a high conversion of monomer, by using diethylene glycol (DEG) as the chain starter, which should result in the formation of industrially relevant polyether diols.

Results and Discussion

Activity studies of different carboxylate NHC precursors

Initial experiments for the homopolymerization of PO with the DEG chain starter catalyzed by 1,3-dimethyl-imidazolium-2-carboxylate (5) led to the desired polyether diol homopolymer (Scheme 1, Table 1) as observed by gel permeation chromatog-

$$HO \longrightarrow O \longrightarrow OH + O \longrightarrow Conversion H = O \longrightarrow O \longrightarrow O \longrightarrow OH + O \longrightarrow Conversion H = O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow OH + O \longrightarrow O \longrightarrow OH + O \longrightarrow OH$$

Scheme 1. Homopolymerization of PO onto the DEG chain starter. For details, see Table 1.

[5] [mol %] ^[a]	T [°C]	Conv. [%] ^[b]	[5] [mol%]	T [°C]	Conv. [%] ^[b]		
10	80	30	0	120	3		
10	100	58	0.6	120	24		
10	120	69	5	120	52		
10	140	63	10	120	69		
10	160	51	20	120	78		
[a] $n(5)/n(DEG)/n(PO) = 0.1:1:20$, 4 h. [b] Conversion (conv.) determined gravimetrically after 4 h by precipitation of the polymer with Et ₂ O. Conv = $[m(\text{product}) - m(\text{catalyst}) - m(DEG)/m(PO) - [c] n(DEG)/n(PO) - 1:20]$							

catalyst loading with respect to DEG, 120°C, 4 h.

raphy (GPC), NMR spectroscopy, and ESIMS. The activity of the catalyst was measured by the conversion of PO after 4 h, which was determined gravimetrically in these homopolymerization experiments.

The decarboxylative release of the free carbene from NHC-CO₂ adduct **5** as well as the polymerization reaction itself were found to be very sensitive to temperature (Table 1): Interestingly, the highest conversion (69%) was obtained at 120 °C after 4 h. At 160 °C, the conversion dropped to 51%, which might be a consequence of the decomposition of the catalyst at higher temperatures. For conversions >50%, a catalyst loading of at least 5 mol% (relative to DEG) was required (Table 1). In the absence of the NHC precursor, only very minor amounts of the ROP product were formed. To obtain maximal conversion, a relatively high catalyst loading of 10 mol% with respect to DEG was chosen for further activity studies. Under those opti-

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mized reaction conditions, the influence of the carbene backbone as well as the N-substituents in the 1,3-positions on conversion was investigated with selected NHC precursors **4–11** (Figure 1) and free carbenes **1** (R/R' = iPr/iPr), **2** (R/R' = Mes/Mes, Mes = 2,4,6-trimethylphenyl), and **3** (R/R' = tBu/tBu).

In general, the activity of NHC precursors **4**, **7**, and **10** correlated well with the activity of the "free" NHCs (**4** vs. **1**=71:74, **7** vs. **3**=46:42, and **10** vs. **2**=46:44; see Table 2). Diimidazolidin-2-ylidene **11** was slightly less active than corresponding diimidazol-2-ylidene **10** (39 vs. 46% conversion), which might be a consequence of the fact that **11** is more prone to hydrolysis and oxidation.^[16] Clearly advantageous for catalyst activity was symmetric or even asymmetric substitution by small alkyl substituents R=Me/Et/*i*Pr in the 1,3-positions (**4**/**5**/**6**=71:69:75% conversion), whereas electronic effects seemed to be less important. As soon as steric bulk (R=*t*Bu/*t*Bu, i.e., **7**) or aryl substituents came into play (R=Mes/Mes, i.e., **10**), the activity dropped, even in the case of asymmetric derivative **9** (R=Me/

> Mes). Detrimental to catalyst activity was the benzimidazole backbone, as demonstrated by the huge reactivity difference of **8** and **5** (R=Me/Me). In most cases, molecular-mass distributions with small polydispersity indices (D=1.23–1.08) were obtained, as analyzed by GPC. Furthermore, the number average molar mass (M_n) was found to correlate well with the conversion of PO (Table 2).

Quantum chemical calculations at the DFT level support the slightly endergonic character of the CO_2 dissociation reaction from adducts **4**, **5**, **7**, and **10** at 120 °C (Scheme 2). The computed Gibbs free energies of dissociation reflect the tendency observed by Louie et al. and others that the decarboxylation temperature of NHCs with bulky N-substituents is as low as 72 °C for *t*Bu-substituted derivative **7**.^[14] However, those experiments were performed in the solid state, and significant differences might arise in the liquid phase, in which the actual polymerization reaction takes place. To inves-

Table 2. [scaffold.	Dependency o	f conversion and	d polymer	properties	on NHC
NHC ^[a]	R/R′	Conv. [%] ^[b]	$M_{\rm p}^{\rm [c]}$	$M_n^{[d]}$	$D^{[d]}$
1	<i>i</i> Pr/ <i>i</i> Pr	73.7	878.4	1236	1.08
2	Mes/Mes	43.5	356/1059	589	1.18
3	tBu/tBu	41.5	646.2	642	1.12
4	<i>i</i> Pr/ <i>i</i> Pr	70.6	820.4	1091	1.17
5	Me/Me	69.3	762.3	1032	1.15
6	Me/Et	75.1	878.5	1193	1.16
7	tBu/tBu	45.9	588.3	819	1.20
8	Me/Me	19.3	-	-	-
9	Me/Mes	61.8	762.3	1017	1.19
10	Mes/Mes	46.4	588.2	713	1.20
11	Mes/Mes	38.7	298/419	315	1.23

[a] Reaction conditions: $n_{cat}/n_{DEG}/n_{PO} = 0.1:1:20$, $120 \,^{\circ}$ C, 4 h. [b] Conversion determined gravimetrically after 4 h by precipitation of the polymer with Et₂O. Conv. = [m(product) - m(catalyst) - m(DEG)]/m(PO). [c] Maximum peak of ESIMS mass distribution [polymer+NH₄+]. [d] Molar masses and dispersity index (*D*) obtained by GPC in THF by using polystyrene as a standard for calibration.



Scheme 2. Computed Gibbs free energies for the dissociation of CO $_2$ from NHC–CO $_2$ adducts 4, 5, 7, and 10 at 120 $^\circ$ C.

tigate the decarboxylation reaction in solution, changes in the C=O band of polyethylene glycol (PEG) were followed by in situ IR spectroscopy.

Although both asymmetric and symmetric C=O vibrations were diagnostic for carboxylates **4** ($\tilde{v} = 1693$ and 1321 cm⁻¹), **5** ($\tilde{\nu}$ = 1696 and 1317 cm⁻¹), **7** ($\tilde{\nu}$ = 1689 and 1327 cm⁻¹), **8** ($\tilde{\nu} = 1703$ and 1314 cm⁻¹), and **10** $(\tilde{v} = 1700 \text{ and } 1323 \text{ cm}^{-1})$, **7** (R = tBu/tBu) was the only one of sufficient solubility in PEG. The decay of the band at $\tilde{\nu} = 1689 \text{ cm}^{-1}$ was followed over time at 80, 100, 120, and 140 °C (Figure 2). The decarboxylation reaction proceeded rather slowly at 100 °C and below (86 and 97% of 7 present after 4 h). Significant decomposition of 7 started at 120 °C, although after the typical reaction time of 4 h, 61% of 7 still remained. At 140 °C, the decarboxylation reaction again accelerated and approximately 9% of 7 remained in the mixture after 4 h. The NHC carboxylate precursor should be therefore considered as a NHC reservoir that continuously delivers a small amount of NHC during the reaction. This is remarkable, as the PO conversion for this carboxylate was found to be similar to that for its analogue, free NHC 3 (\approx 46 vs. 42%).

Mechanism of the NHC-catalyzed ROP of PO and DEG

Three different basic reaction mechanisms have been discussed for the NHC-catalyzed ROP of various substrates,^[5] which could, in principle, also apply for the ROP of epoxides (Scheme 3): A zwitterionic mechanism, as observed for cyclic esters, such as lactide [route (3)],^[2,17] a slightly modified mechanism as proposed by Waymouth and Taton et al. for lactones and epoxides [route (2)],^[3,18] and finally, anionic polymerization by nucleophilic attack of the free alkoxide chain on the epoxide. Such alkoxides can be formed through direct proton transfer from the chain starter to either the NHC or the activated monomer [route (1)]. In order not to bias experiments on propagation by a superimposed decarboxylation reaction, the dependence of the polymerization of PO on the amount of DEG chain starter was studied for the free NHC 1,3-diisopropylimidazol-2-ylidene (1). Its activity was strongly dependent on the concentration of DEG, and only a minor conversion was found in the absence of DEG (Figure 3). This excludes route (3) as the exclusive reactive pathway, for which the chain starter



Figure 2. Decay of the C=O band in **7** in PEG over time at 80–140 °C.



Scheme 3. Possible reaction mechanisms (1)–(3) for the NHC-catalyzed ROP of PO in the presence of a chain starter.



Figure 3. Effect of the amount of DEG on ROP conversion. Reaction conditions: n(1)/n(DEG)/n(PO) = 0.1:n(DEG):20, 120 °C, 4 h.

neither plays a role in initiation nor chain growth in the polymerization. Differentiation between pathways (1) and (2) would require determination of the presence/absence of propoxylated NHCs, which is difficult at realistic catalyst concentrations.

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Scheme 4. Computed Gibbs free energies for elementary steps (1)-(4).

By means of DFT calculations, additional information about the different proposed mechanisms, that is, activation barriers as well as Gibbs free energies, were obtained for selected steps (see Scheme 4). In this study, MeOCH₂CHCH₃OH was chosen as a model for the chain ends of the propagating polymers. We assumed that the DEG starter would not behave significantly different, which was not explicitly verified for all reactive steps. The most probable initiation represents nucleophilic attack of the NHC at the PO monomer. Despite the significant activation barrier of this step ($\Delta G^{\neq} = 132.8 \text{ kJ mol}^{-1}$), it is exergonic enough to be irreversible [$\Delta G = -86.3 \text{ kJ mol}^{-1}$, scenario (1)]. Deprotonation of the polymer end group as well as the chain starter by the NHC is significantly endergonic [$\Delta G =$ 48 kJ mol⁻¹, scenario (2)], which makes it unlikely in comparison to scenario (1); for chain propagation, this already very rare alkoxide species has to overcome a barrier of more than 110 kJ mol⁻¹ [scenario (3)], and consequently, the effective barrier for propagation by this base catalysis would add up to approximately 165 kJ mol⁻¹ (sum of ΔG for proton transfer and ΔG^{\neq} of propagation). The observed propagation at all starter OH groups requires a proton transfer between the alkoxide and the alcohol end groups, which however should be fast and thermoneutral as soon as growing chains have reached a length of one to a few PO units. This then leads to 1,2,3-trialkylimidazolium cations and starter alkoxide anions. Furthermore, we consider the transfer of a 2-hydroxypropyl group (or longer chains), which was proposed by Taton et al.^[3] from the above-mentioned cation to anionic polymer chains, as rather unlikely in view of the extremely high activation barrier $\Delta G^{\neq} =$ 229.2 kJ mol⁻¹ and the poor leaving-group character of the NHC [scenario (4)].

Consequently, mechanistic scenario (1), which corresponds also to scenario (1) of Scheme 3, prevails, and the product will contain a certain amount of polymer chains grown on the NHC catalyst (or therefore rather acting as a "NHC starter").

NHC-catalyzed copolymerization of PO and cyclic esters

Carboxylate 5 was also capable of a ROP copolymerization with benzyl alcohol as the chain starter. The reactions were performed in two modes: In the stepwise reaction (conditions A), the chain starter was mixed with NHC-carboxylate 5, the first monomer (monomer 1), and diglyme as an additive to keep the NHC catalyst in solution. After heating for the given time, the unreacted monomer was removed by evaporation. Then, the second monomer (monomer 2) and a new batch of 5 were added, and the mixture was heated again. In the onepot reaction (conditions B), the chain starter, both monomers, and the catalyst were mixed, and the polymerization of the reaction mixture was initiated by heating to the given temperature. All copolymers were analyzed by GPC, ESIMS, and NMR spectroscopy (Scheme 5, Table 3). The linkages between the polyether and polyester part of the polymer were analyzed by NMR spectroscopy (Figure 4). The resonance for proton I on the tertiary C atom of the PO unit (CH₂CHCH₃O) was shifted by 1.5 ppm if the PO unit was connected to a carbonyl group (CH₂CHCH₃OCOR, i.e., I*). Integration of this CH signal and



Scheme 5. Conversion of monomer and analytical data for copolymerization experiments. For details, see Table 3.

Entry	Mon. 1	Mon. 2	Poly. 1 ^[a]		Poly. 2 ^[a]		T_1	T_{2}	Add. 1	Add. 2	Conv. 1 ^[c]	Conv. 2 ^[c]	n(PO*)/
			M _n	D	M _n	D	[°C]	[°C]			[%]	[%]	<i>n</i> (BnO)
1	PO	CL	608	1.38	1863	1.38	120	100	-	diglyme	39	48	0.93
2	CL	PO	3998	1.58	3690	1.76	100	100	diglyme	_	> 95	22	1.9
3	PO	LA	608	1.38	1890	1.57	120	50	-	diglyme	39	>95	1.46
4	LA	PO	1378	1.70	749	1.61	100	100	diglyme	-	> 95	4	0.74
5	PO + LA		2168	1.77			120		-		30	>95	1.72



Figure 4. ¹H NMR of a PO-CL block copolymer (see Table 3, entry 1).

comparison with the aromatic signal of the chain starter was used to determine the number of such connections per polymer chain. Similar information was derived from the resonance of the methyl group of a PO unit, that is, II (CH_2CHCH_3O) and II* (CH_2CHCH_3OCOR).

Under our ROP reaction conditions, each of the cyclic esters, ε -caprolactone (CL) and (3*S*,6*S*)-lactide (LA), that is, (3*S*,6*S*)-3,6-dimethyl-1,4-dioxane-2,5-dione, were quantitatively converted with PO into the corresponding copolymers of the esters and PO. This increased reactivity of the copolymerization reaction compared to the homopolymerization of PO has already been discussed.^[1-3] In contrast, the copolymerization of PO and CL and/or LA resulted in polymers with significantly broader molecular mass distribution ($D_{\text{homop.}} = 1.08 - 1.23$, $D_{\text{cop.}} = 1.38 - 1.76$). This might originate from transesterification reactions, which are known to be catalyzed by NHCs at this temperature.^[19]

The linkage of a poly(ethylene oxide) chain to a poly(*ɛ*-caprolactone) chain was demonstrated by Taton et al.^[4] In our experiments, especially the NMR spectroscopic data suggest that the polyester blocks of CL or LA were connected to the PO blocks (Table 3, entries 1 and 3). Attempts to polymerize a PO block onto a polyester block resulted in the insertion of the PO unit into the polyester in the case of CL (Table 3, entry 2), as shown by the ratio of the signals I*/Bn. A similar situation that probably results from transesterification reactions was observed for the one-pot polymerization of PO and LA (Table 3, entry 5). For experiments in which the polymerization of PO on a block of LA was attempted, no conversion of PO was observed (Table 3, entry 4).

This difference in reactivity of PO on an already existing block of CL or LA might again be explained by DFT results, which suggest the formation of a stable, cyclic anion (six-membered ring) originating from backbiting. This prevents further propagating steps in the case of LA, in contrast to CL for

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which the analogous 10-membered ring is not very stable (see Scheme 6).

Conclusions

We have shown that carboxylates of N-heterocyclic carbenes are suitable catalyst precursors for the ROP of PO and that they exhibit activities close to that of the "free" NHC. NHCs with imidazolium-type structures were by far the most active ones. More active precursors are those with less-bulky substituents on the heterocyclic N atoms, whereas electronic effects seem to be less important. Our experiments indicate that the decarboxylation reaction is slow, which results in a continuous delivery of free carbene catalyst over the investigated reaction time. In contrast to the literature, our experimental results as well as our results from quantum chemical calculations indicate a free anionic polymerization mechanism. The same catalysts are also efficient in the copolymerization by sequential



Scheme 6. Different reactivity of PO on an already existing block of LA (left) and CL (right).

ROP of PO and ε -caprolactone as well as PO and (*S*,*S*)-lactide. The sequential polymerization of ε -caprolactone and PO led to an insertion of PO into the polyester block under formation of a statistical copolymer.

Experimental Section

General procedures

All reactions and manipulations were performed under an argon atmosphere by using standard Schlenk techniques. THF was dried with an MBraun solvent purification system. Et_2O , propylene oxide, and diglyme were stored over molecular sieves (4 Å). All deuterated solvents for NMR measurements were degassed by freeze–pump–thaw cycles and stored over molecular sieves (4 Å). ¹H NMR and ¹³C(¹H) NMR spectra were recorded with Bruker Avance 200 and 500 MHz spectrometers, with chemical shifts reported relative to the solvent peaks (¹H NMR, ¹³C NMR). Elemental analyses and mass spectra were obtained from the Organic Chemistry Institute of the University of Heidelberg. ESIMS was performed by using

a Finnigan LCQ with a quadrupole ion trap (positive ion-channel). To facilitate reproducible ionization, the polymer sample was dissolved in a solution of NH₄OAc in MeOH ($\approx 10^{-4}$ M). GPC was performed by using a three-column set of TSK gel TOSOH (G4000, G3000, G2000 with pore sizes of 20, 75, and 200 Å respectively, connected in series). The system was calibrated with polystyrol/ heptylbenzene standards (3000000-580/176 Da). THF was used as the eluent (1.2 mLmin^{-1}) by using a refractometric (ERC-RI-101) and UV detector (Waters 2487 UV). Isothermic in situ FTIR spectroscopy was performed by using a Bruker Vertex 70 instrument equipped with a heatable diamond ATR unit (Golden Gate Single Reflection, Specac). Compound 7 (44.8 mg, 0.200 µmol) was dissolved in commercial polyethylene glycol (1 mL, Sigma-Aldrich, $M_{\rm p} = 400$, dried by heating to 150 °C at 5 kPa for 3 h). Concentration of the carboxylate was followed by decay of the C=O band (1689 cm⁻¹) on a heated attenuated total reflectance (ATR) crystal. Measurements were performed at 80, 100, 120, and 140 $^\circ\text{C}.$

All calculations at the Becke-Perdew-86 functional (BP86) level of theory were performed with the program package Turbomole by employing the efficient RI-J approximation.[20] This comprises all structure optimizations for which an SV(P)^[21] basis set was used in combination with the assumption of an electric conductor (dielectric constant $\epsilon\!=\!\infty\!$) according to the solvation model COSMO. $^{[22]}$ Thermodynamic functions were evaluated according to standard statistic thermodynamic expressions for a temperature of 120°C. Owing to the size of the species involved, this was done by only considering the lowest-energy conformer of each species involved. As systems with too many atoms typically exhibit very low energy vibrations for which a computation of the vibrational partition function within the harmonic approximation would lead to artifacts, the entropic contributions from vibrational partition functions were computed instead for small models. Solvation treatment was performed by using the COSMO-RS method, [23] which implies explicit consideration of electrostatic effects on intermolecular interactions for multinary mixtures.^[24] This requires further calculations at the BP86 level with a TZVP basis set,^[25] assuming both a gas and an electric conductor environment. As a model solvent, diethylene glycol was chosen. As DFT method for a more accurate description of the actual chemical activation and reaction energetics in the gas phase, the M06 functional^[26] was used. These computations were done with the program package NWChem.[27] For these calculations, the def2-TZVP^[28] basis set was used, which also represents a slight improvement over the aforementioned TZVP.

The literature-known compounds 1,3-diisopropyl-imidazol-2-ylidene (1),^[29] 3-ethyl-1-methylimidazolium carboxylate (**6**),^[12b,13d] and 1,3-dimesitylimidazolium carboxylate (**10**)^[14b] were synthesized according to the published procedure, whereas the literature-known compounds 1,3-diisopropylimidazolium carboxylate (**4**),^[13c,14a] 3-mesityl-1-methylimidazolium carboxylate (**9**),^[30] and 1,3-di-*tert*-butylimidazolium carboxylate (**7**)^[31] as well as the new compound 1,3-dimethylbenzimidazolium carboxylate (**8**) were synthesized according to the procedure described in this work. All other starting materials were purchased in reagent-grade purity from Acros, Aldrich, Fluka, or Strem and used without further purification.

Syntheses

1,3-Diisopropylimidazolium carboxylate (4): 1,3-Diisopropylimidazolium-2-ylidene (100 mg, 657 μ mol) was dissolved in THF (8 mL), and the solution was extensively stirred under a CO₂ atmosphere at normal pressure for 1 h. Decantation of the white precipitate, washing with THF (2×2 mL), and drying under vacuum resulted in **4**. Yield: 39%. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 6.78$ [s, 2H; N(CH)₂N], 5.25 [sept., ³J_{H,H}=6.8 Hz, 2H; CH(CH₃)₂], 1.16 ppm [d, ³J_{H,H}=6.8 Hz, 12H, CH(CH₃)₂]. ¹³C(¹H} NMR (126 MHz, CD₂Cl₂): $\delta = 155.2$ (s, CO₂), 143.9 (s, NCN), 116.3 (s, CH), 51.3 [s, CH(CH₃)₂], 23.1 ppm [s, CH(CH₃)₂]. HRMS (FAB+): *m/z*: calcd for C₁₀H₁₇N₂O₂ 197.1290 [*M*+H⁺]; found: 197.1304.

1,3-Di-*tert*-butylimidazolium carboxylate (**7**): 1,3-Di-*tert*-butylimidazol-2-ylidene (504 mg, 2.80 mmol) was dissolved in Et₂O (28 mL). The solution was cooled to -78 °C and CO₂ was added by condensation. The solution was warmed to RT and a white precipitate was formed. Filtration and washing with Et₂O resulted in **7**. Yield: 99%. ¹H NMR (200 MHz, CD₂Cl₂): δ = 7.50 [s, 2 H; N(CH)₂N], 1.73 ppm (s, 18H; CH₃). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ = 160.0 (s, CO₂), 135.3 (s, NCN), 119.3 (s, CH), 60.7 (s, CCH₃), 30.2 ppm (s, CCH₃).

1,3-Dimethylbenzimidazole carboxylate (8): 1,3-Dimethylbenzimidazolium iodide (1.00 g, 3.65 mmol) and KOtBu (491 mg, 4.38 mmol) were mixed in THF (5 mL). The solution was stirred for 4 h at RT and then filtered through Celite. The resulting solution was extensively stirred under a CO₂ atmosphere at normal pressure for 30 min, and the white precipitate was separated by decantation. Washing of the product with THF (2×1 mL) and drying under vacuum resulted in 8. Yield: 68%. ¹H NMR (50 MHz, CD₂Cl₂): δ = 7.63 (m, 4H; CH), 4.22 ppm (s, 6H; NCH₃). ¹³C{¹H} NMR (50 MHz, CD₂Cl₂): δ = 154.7 (s, CO₂),148.9 (s, NCN), 131.8 (s, C), 127.3 (s, CH), 113.1 (s, CH), 33.4 ppm (s, NCH₃). HRMS (FAB+): *m/z*: calcd for C₁₀H₁₂N₂O₂ 191.0821 [*M*+H⁺]; found: 191.0815.

3-Mesityl-1-methylimidazolium carboxylate (**9**): 3-Mesityl-1-methylimidazolium iodide (1.00 g, 3.05 mmol) and KOtBu (411 mg, 3.66 mmol) were mixed in THF (17 mL). The solution was stirred for 4 h at RT and then filtered through Celite. The resulting solution was extensively stirred under a CO₂ atmosphere at normal pressure for 1 h, and the white precipitate was separated by decantation. Washing with Et₂O (3×20 mL) and drying under vacuum resulted in **9**. Yield: 91%. ¹H NMR (200 MHz, CD₂Cl₂): δ = 7.23 (d, ³J_{H,H} = 2 Hz, 1H; CH) 6.99 (m, 2H; CH), 6.92 (d, ³J_{H,H} = 2 Hz, 1H; CH), 4.16 (s, 3H; NCH₃), 2.34 (s, 3H; CCH₃), 2.03 ppm (s, 6H; CCH₃). ¹³C{¹H} NMR (50 MHz, CD₂Cl₂): δ = 154.2 (s, CO₂), 145.8 (s, NCN), 140.5 (s), 134.9 (s), 133.9 (s), 129.7 (s), 122.5 (s), 121.6 (s), 37.9 (s, NCH₃), 21.4 (s, CCH₃), 17.8 ppm (s, CCH₃). HRMS (FAB +): *m/z*: calcd for C₁₄H₁₇N₂O₂ 245.1290 [*M*+H⁺]; found: 245.1301.

NHC-catalyzed ROP of PO with diethylene glycol

All ring-opening polymerizations were performed under a dry and inert atmosphere by using an autoclave.

a) Dependence of the polymer properties on the NHC precursor scaffold (Table 2): In a typical run, the precatalyst (105.5 µmol), DEG (1.055 mmol, 100 µL), propylene oxide (21.15 mmol, 1.48 mL), and the toluene standard (100 µL) were introduced with syringes in a Premex autoclave (60 mL) in the glove box. The vessel was equipped with a magnetic stirring bar, closed, and heated to 120 °C for 4 h under extensive stirring. Then, the autoclave was cooled to 15 °C, the polymer was collected from the autoclave with Et₂O (3×5 mL), and the monomer was removed by evaporation. The resulting polymer was dried for 1 h at 5 kPa, balanced, and characterized by NMR (¹H, ¹³C) spectroscopy, ESIMS, and GPC.

b) Effect of temperature on ROP conversion (Table 1): The polymerization protocol was similar to a) with the use of 1,3-dimethylimidazolium carboxylate (**5**; 105.5 µmol, 14.8 mg), DEG (1.055 mmol, 100 µL), propylene oxide (21.15 mmol, 1.48 mL), and the toluene standard (100 µL). The autoclave was heated to various tempera-

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tures (80, 100, 120, 140, and 160 $^\circ\text{C}\textsc{)}.$ Workup and analytics were done as described in a).

c) Effect of catalyst loading on ROP conversion (Table 1): The polymerization protocol was similar to a) with the use of DEG (1.055 mmol, 100 μ L), propylene oxide (21.15 mmol, 1.48 mL), and the toluene standard (100 μ L). Various amounts of **5** were used (0, 6.4, 52.8, 158, and 1055 μ mol). Workup and analytics were done as described in a).

d) Effect of amount of DEG on ROP conversion (Figure 3): The polymerization protocol was similar to a) with the use of **5** (105.5 µmol, 14.8 mg), propylene oxide (21.15 mmol, 1.48 mL), and the toluene standard (100 µL). The amount of DEG was varied (0, 528, 1055, and 2110 µmol). Workup and analytics were done as described in a).

Sequential polymerization

a) Table 3, entry 1/3: Benzyl alcohol (110 μ L, 1.06 mmol), propylene oxide (1.48 mL, 21.1 mmol), mesitylene (100 μ L), and **5** (14.8 mg, 106 μ mol) were mixed in an autoclave and heated to 120 °C for 4 h. The vessel was cooled to RT, the mixture was transferred into a round-bottomed flask, and the PO was evaporated under vacuum. Catalyst **5** (14.8 mg, 106 μ mol), diglyme (1 mL), and ϵ -caprolactone (10.6 mmol) or lactide (5.28 mmol) were added, and the mixture was heated to 100 °C (for ϵ -caprolactone) or 50 °C (for lactide) for 4 h.

b) Table 3, entry 2/4: Benzyl alcohol (219 μ L, 2.11 mmol), ε -caprolactone (21.1 mmol) or lactide (10.6 mmol), mesitylene (100 μ L), diglyme (1 mL), and **5** (29.6 mg, 211 μ mol) were mixed in a roundbottomed flask and heated to 100 °C (for ε -caprolactone) or 50 °C (for lactide) for 4 h. The vessel was cooled to RT, and the mixture was transferred into an autoclave. PO and catalyst **5** (29.6 mg, 211 μ mol) were added, and the mixture was heated to 100 °C for 4 h.

One-pot polymerization

Table 3, entry 5: Benzyl alcohol (110 μ L, 1.06 mmol), PO (21.1 mmol, 1.48 mL), ε -caprolactone (5.29 mmol, 559 μ L), mesitylene (100 μ L), and **5** (14.8 mg, 106 μ mol) were mixed in an autoclave and heated to 120 °C for 4 h.

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Keywords: block copolymers · carbenes · density functional calculations · reaction mechanisms · ring-opening polymerization

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