

Mesoionic N-Heterocyclic Olefins as Initiators for the Lewis Pair Polymerization of Epoxides

Iris Haug, Justus Reitz, Célia Ziane, Michael R. Buchmeiser, Max M. Hansmann,* and Stefan Naumann*

Mesoionic N-heterocyclic olefins (mNHOs) have recently emerged as a novel class of highly nucleophilic and super-basic σ -donor compounds. Making use of these properties in synthetic polymer chemistry, it is shown that a combination of a specific mNHO and a Mg-based Lewis acid (magnesium bis(hexamethyldisilazide), Mg(HMDS)₂) delivers poly(propylene oxide) in quantitative yields from the polymerization of the corresponding epoxide (0.1 mol% mNHO loading). The initiation mechanism involves monomer activation by the Lewis acid and direct ring-opening of the monomer by nucleophilic attack of the mNHO, forming a zwitterionic propagating species. Modulation of the mNHO properties is thereby a direct tool to impact initiation efficiency, revealing a sterically unencumbered triazole-derivative as particularly useful. The joint application of mNHOs together with borane-type Lewis acids is also outlined, resulting in high conversions and fast polymerization kinetics. Importantly, while molar mass distributions remain relatively broad, indicating faster propagation than initiation, the overall molar masses are significantly lower than found in the case of regular NHOs, underlining the increased nucleophilicity and ensuing improved initiation efficiency of mNHOs.

unique reactivity has been central for the realization of unusual or difficult to access polymer structures. Examples include the zwitterionic ring-opening polymerization of cyclic (di)esters to form macrocyclic polymers,^[1] the synthesis of exclusively linear poly(γ -butyrolactone)^[2] or the preparation of well-defined, multi-block copolymers using (meth)acrylic monomers.^[3,4] In those examples, either the well-established N-heterocyclic carbenes (NHCs, typically imidazole-2-ylidenes)^[5] or N-heterocyclic olefins (NHOs,^[6–8] Scheme 1A) served as neutral carbon nucleophiles.

In 2019, the Naumann group published a method to generate high-molar mass aliphatic polyethers using NHO initiators.^[9] Focusing on poly(propylene oxide) (PPO), the catalytic action was found to rely on the specific Lewis acid magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂) which activates the monomer for ring-opening while the propagating, oxyanionic chain end is simultaneously deactivated via complexation (Scheme 1B). The latter fully

suppresses basicity-related side reactions (transfer to monomer), thus enabling molar masses (M_n) of $>10^6$ g mol⁻¹.^[9] This polymerization method is thus located in the context of Lewis pair polymerization (LPP),^[4] “ate”-complexes^[10] and retarded anionic polymerization (RAP).^[11,12] Later, it was shown that also copolymers of EO and PO can be prepared this way, enabling high molar masses and a blocky gradient structure.^[13]

However, even though nucleophilic NHOs were employed, the high molar masses were also down to low initiation efficiency (NHO/PO ratio = 1:5000, yet resulting in average degrees of polymerization (DP) of 9000–24 000).^[9] Slow initiation coupled with a fast propagation correspondingly also broadened the molar mass distribution.

Hence, alternative initiators with higher nucleophilicity are an attractive subject for further investigations, and in this regard, mesoionic variants (mNHOs) of the aforementioned NHOs offer intriguing perspectives. These compounds, first described by Hansmann and co-workers in 2020,^[14] are overall neutral but best represented as hybrids of several dipolar (charge-separated) canonical Lewis structures (Scheme 1A). mNHOs are exceptionally strong σ -donors,^[14,15] easily outperforming regular NHOs.^[16] A recent kinetic investigation allowed to accurately quantify the Mayr nucleophilicity parameter^[17] N of mNHOs being in the

1. Introduction

Carbon-centered, neutral nucleophiles have become an impactful addition to the synthetic toolbox in polymer chemistry. Forming charge-separated species after addition to the monomer, their

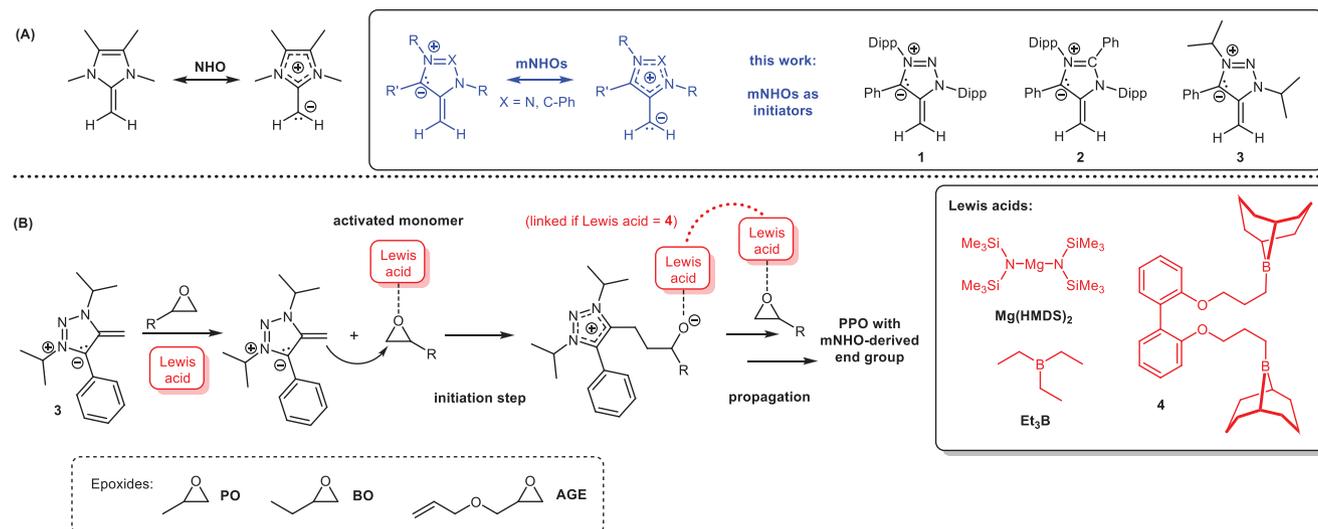
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Scheme 1. A) NHOs and mNHOs, including the investigated compounds 1–3. Dipp = 2,6-diisopropylphenyl. B) Proposed polymerization mechanism, employed Lewis acids (right) and investigated monomers (bottom).

range of $21 < N < 32$, confirming the superior nucleophilicities of mNHOs compared to NHOs.^[18] Alkyl substituted mNHOs belong to the strongest nucleophiles ($N > 30$) reported on the Mayr scale, which currently consists of more than 1000 C-, N-, O-, P-, S-, and Se-nucleophiles.^[17] Since mNHOs are easily accessed and rationally tuneable in their nucleophilic properties, we were interested to test their performance for the zwitterionic polymerization of epoxides. So far, this emergent class of extraordinarily strong carbon nucleophiles has found use mainly in the activation of small molecules or catalysis,^[19–23] but, to the best knowledge of the authors, has not been applied in detail in the field of polymer chemistry.^[24]

2. Results and Discussion

Three structurally different mNHOs (1–3, Scheme 1), based on triazole- or imidazole motifs, were selected and prepared by deprotonation of the salt precursors (see ESI). Based on the kinetics determined for the quantification within the Mayr scale, *N*-alkyl substituted mNHO 3 ($N = 30.25$) is known to be 10 000 times more reactive than mNHO 1 ($N = 22.8$),^[18] while all selected mNHOs are more nucleophilic than typical, regular NHOs ($N \approx 18$).^[25] With the mNHO initiators at hand, a series of initial screening experiments were conducted, whereby the magnesium Lewis acid was used in excess (5 eq.).

Thus, applying compounds 1–3 at room temperature and in the bulk (1000 eq. of PO), it was found that the different basicities and nucleophilicities of the three mNHOs had a significant impact on the outcome of the polymerization (Table 1, entries 1–3). While 1 did not deliver relevant conversion, the more nucleophilic mNHO 2 achieved 10% conversion. In contrast, the most nucleophilic mNHO 3 engendered almost quantitative conversion and a PPO molar mass of $M_n = 40 \text{ kg mol}^{-1}$. The addition of solvent (pentane) slowed down monomer consumption (entries 4–6). Plausibly, this can be attributed to the concomitant lowering of the monomer concentration (see also discussion below), to which Lewis pair-type polymerizations are inherently vulnera-

ble or to the non-polar environment disfavoring charge-separated initiation. Interestingly, at low temperature ($-36 \text{ }^\circ\text{C}$), quantitative conversion was observed while the molar mass distribution broadens (entry 7). At $60 \text{ }^\circ\text{C}$ conversion drastically drops to 3%, indicating a notable temperature-sensitivity of the polymerization setup, most likely on account of the mNHO component (the latter, especially 2 and 3, are known to decompose when held in solution over an extended period of time).^[14,18] Notably, control experiments in the absence of $\text{Mg}(\text{HMDS})_2$ did not result in relevant PO conversion under any conditions, underlining that the mNHO is not able to directly initiate the epoxide polymerization on its own (see Table S2, Supporting Information and discussion below).

A more detailed investigation of the polymerization kinetics reveals that mNHO 1 is not fully inactive, rather an extremely slow monomer conversion ensued (Figure 1, 5000 eq. of PO at $-36 \text{ }^\circ\text{C}$, 5 m in pentane, 20 eq. of $\text{Mg}(\text{HMDS})_2$). During a reaction time of almost 1000 h, monomer conversion steadily approaches 30% (turnover number (TON) = 1500, here defined as number of PO molecules consumed per mNHO initiator). How-

Table 1. Polymerization results for PO, using different mNHO (I)/ $\text{Mg}(\text{HMDS})_2$ (C) combinations. Solvent = pentane.

#	I	I/C/PO [molar]	[PO]	$T [^\circ\text{C}]$	$t [\text{h}]$	Conv. ^{a)} [%]	$M_n (D_M)^b$ [kg mol ⁻¹]
1	1	1:5:1000	bulk	rt	18.5	<1	—
2	2	1:5:1000	bulk	rt	18.5	10	3.4 (1.36)
3	3	1:5:1000	bulk	rt	18.5	95	40 (1.30)
4	1	1:5:1000	[5 m]	rt	18.5	<1	—
5	2	1:5:1000	[5 m]	rt	18.5	1	—
6	3	1:5:1000	[5 m]	rt	18.5	28	8.2 (2.4)
7	3	1:5:1000	[5 m]	-36	18.5	>99	29 (2.7)

^{a)} determined via $^1\text{H NMR}$ (CDCl_3); ^{b)} determined via GPC (CHCl_3 versus polystyrene (PS, $M_n = 800\text{--}2 \times 10^6 \text{ g mol}^{-1}$)).

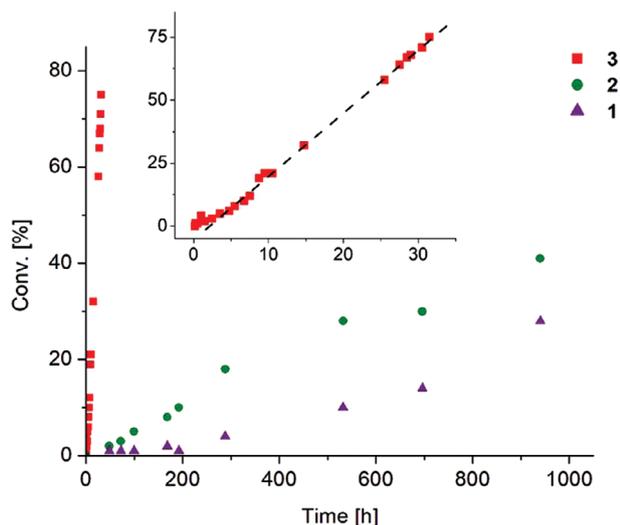


Figure 1. Conversion versus time for 1–3/Mg(HMDS)₂ catalyst pairs (mNHO/Mg(HMDS)₂/PO = 1:20:5000, molar ratio, –36 °C, [M]₀ = 5.0 mol L^{–1} pentane).

ever, a very long induction time of almost 200 h is also found, most likely explaining why the prior screening experiments did not show any conversion. Initiator 2 displays a somewhat faster conversion, in accordance with the results discussed above, yet overall the polymerization is still sluggish with 41% after 940 h (TON = 2050). Obviously, while such polymerization times are impractical, it is conceptually interesting that polyether formation still occurs and that initiation efficiency can be correlated with nucleophilicity/basicity of the mNHO.

Indeed, using the most nucleophilic initiator mNHO 3, the performance is clearly different. A relatively rapid PO enchainment occurs, yielding 75% conversion after 31 h (Figure 1, TON = 3750). Interestingly, the reaction time correlates linearly with conversion of PO, suggesting well-developed zero-order kinetics. This is typical for LPP, where the concentration of activated monomer should be constant.^[4] Also, an induction period of steadily increasing conversion rates can be identified (Figure 1, insert), which is concluded after 7.5 h. From then on the number of propagating chains reaches its final value and the propagation rate is constant and independent from [PO].

It is constructive to consider the polymerization kinetics with 1000 eq. of PO instead of 5000 eq., but under otherwise identical conditions (Figure 2). Now less diluted, monomer consumption gets disproportionately faster. Hence, initiator 3 achieves quantitative monomer conversion after less than 0.5 h of polymerization time, while the same is true for compound 2 after less than 4 h.

Interestingly, even mNHO 1 can entail high conversion in this case: in accordance with the subdued reactivity of the latter, the rate of polymerization increases over the whole observation time, revealing that initiation is still very slow and new propagating polyether chains are continuously generated. It should be noted that these experiments were conducted with a significant excess of the magnesium catalyst relative to the mNHO (20 eq.); using only 5 eq. of Mg(HMDS)₂, initiator 1 does not lead to any relevant conversion even at room temperature in the bulk (Table 1, entry 1). MALDI MS analysis reveals the

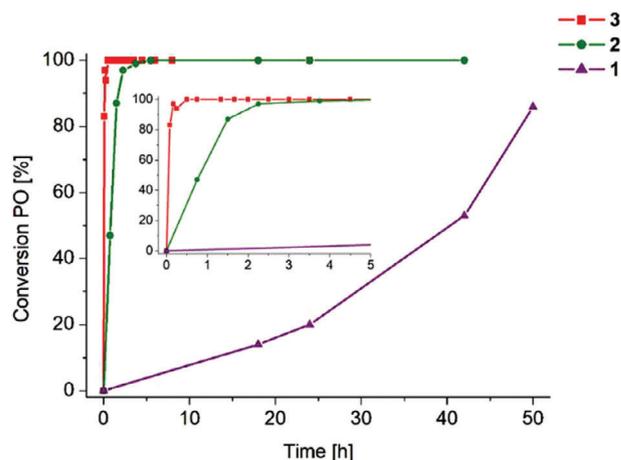


Figure 2. Conversion versus time for 1–3/Mg(HMDS)₂ catalyst pairs (mNHO/Mg(HMDS)₂/PO = 1:20:1000, molar ratio, –36 °C, pentane [5 M], including enlargement (insert).

dominant population to be mNHO-terminated polyether chains (see Figure 3). This end group cationizes the polymer chain. It should be noted that it is a beneficial characteristic of NHO-type initiators to stay attached to the polymer chain even during workup – their presence as end group is thus diagnostic^[9,26] for the occurrence of the expected zwitterionic polymerization mechanism. In sum, kinetic profile and determined end groups indeed suggest a zwitterionic LPP mechanism. This agrees with earlier work using “regular” NHOs.^[9] However, importantly, the obtained molar masses are smaller by two orders of magnitude, reflecting the superior nucleophilicity of mNHOs and the ensuing higher initiation efficiency. Still, the observed polydispersity ($\bar{D}_M = 1.3$ –2.7, Table 1) indicates that slower initiation, compared to the rate of propagation, is responsible for the relative broadening of molar mass distribution. Coherently, a non-polar environment, which disfavors charge-separation as required in the initiation step (e.g., pentane, Table 1, entries 4–7), not only slows down polymerization but also broadens the PDI. In contrast, polyethers received from polymerization in the bulk are significantly better defined ($\bar{D}_M = 1.30$ –1.36).

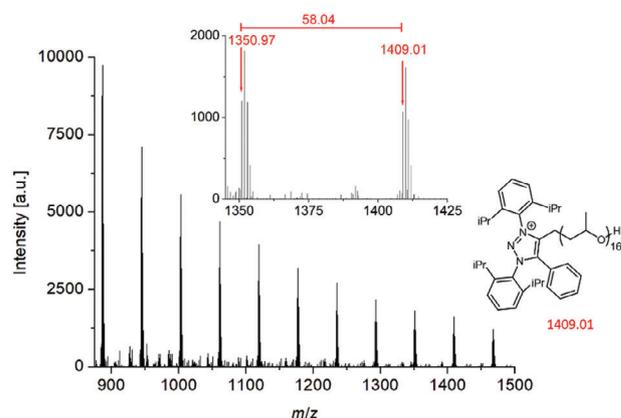


Figure 3. MALDI MS analysis of PPO derived by the action of 1/Mg(HMDS)₂. The polyether is cationized by the positively charged, mNHO-derived end group.

Table 2. Bulk polymerization results (room temperature) using mNHO 3 (I) and alkyl borane Lewis acids (C).

#	Lewis acid	I/C/PO [molar]	M	t [h]	Conv. ^{a)} [%]	M _n (Đ _M) ^{b)} [kg mol ⁻¹]
1	Et ₃ B	1:4:1000	PO	0.5	25	40 (1.17)
2	Et ₃ B	1:4:1000	PO	1.5	74	52 (1.8)
3	Et ₃ B	1:4:1000	PO	5.5	97	99 (1.6)
4	4	1:2:1000	PO	1.0	>99	55 (2.0)
5	4	1:2:1000	AGE	8.5	99	24 (2.1)
6	4	1:2:1000	BO	8.5	59	14 (1.6)

^{a)} determined via ¹H NMR; ^{b)} determined via GPC (CHCl₃ versus polystyrene (PS, M_n = 800–2 × 10⁶ g/mol).

Next, this polymerization method was extended to 1-butylene oxide (BO) and allyl glycidyl ether (AGE), using mNHO 3 as the most successful initiator. While application of the former monomer did not entail any relevant conversion, AGE was polymerized successfully (Table S1, Supporting Information). Depending on the conditions, 18–77% conversion was achieved (1000 eq. of epoxide) with molar masses in the range of M_n = 14–35 kg mol⁻¹. These molar masses are significantly higher than what is accessible via conventional anionic polymerization,^[27] while at the same time much lower than in the case of regular NHO/Mg(HMDS)₂ catalysis (300–880 kg mol⁻¹, using molar ratios of NHO/Mg(HMDS)₂/AGE = 1:5:1000, T = –36 °C or RT, t = 0.5–72 h),^[9] again highlighting the higher nucleophilicity of mNHOs.

Finally, Mg(HMDS)₂ was exchanged for two different borane-type Lewis acids with a milder electron deficiency, namely the well-available Et₃B as well as diborane catalyst 4 (Scheme 1B). The borane-mediated epoxide (co)polymerization has recently found increasing interest^[28,29] since it allows for low catalyst loadings, rapid polymerizations, novel selectivities and outstanding functional group tolerance.^[30–34] Typically, anionic species such as halides or alkoxides serve as initiators. Mechanistically, the situation is similar to Mg(HMDS)₂ in that two Lewis acidic equivalents are required in the propagation step, serving as (a) complexing agent for the oxyanionic chain end and (b) monomer activator. 4 is advantaged in this regard because the borane moieties are linked via a biphenyl backbone, which ensures that activated monomer is always found in proximity to the propagating polyether chain end (Scheme 1B).^[35,36] The productive interaction of activated monomer and propagating chain end is thus kinetically favored and much less susceptible to dilution or the presence of competing, coordinating species, resulting in a superior performance of diborane structures in comparison to Et₃B.^[4,29,37]

Thus, 3/Et₃B was reacted with PO at RT (bulk), using 4 eq. of borane Lewis acid and 1000 eq. of the epoxide (Table 2, entries 1–3). Monomer consumption increased to 97% conversion (see Figure S5, Supporting Information for reaction time/conversion plot), which resulted in M_n = 99 kg mol⁻¹ (Đ_M = 1.61). This comparatively well-behaved polymerization reaction was additionally accelerated by application of Lewis acid 4, which indeed delivered full conversion in less than 1 h (see Figure S6, Supporting Information for reaction time/conversion plot). Also, in the latter

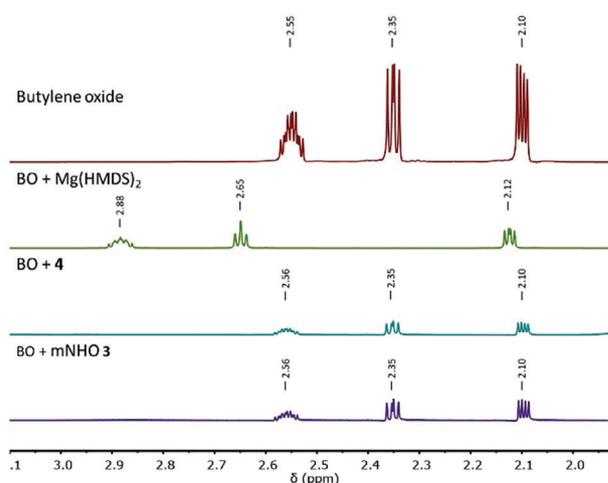


Figure 4. Detail from ¹H NMR spectra (C₆D₆, 400 MHz, 300 K) of BO and its respective combinations with Mg(HMDS)₂, mNHO 3 and diborane 4 (1:1, molar ratio).

case, the achieved molar mass decreased to 55 kg mol⁻¹, suggesting improved initiation (Table 2, entry 4). With this Lewis acid, it was also possible to convert AGE quantitatively within 8.5 h, while notably the polymerization of BO likewise succeeded (entry 6). In the latter example, 59% conversion was obtained, whereby the resulting polyether was found to have a molar mass of M_n = 14 kg mol⁻¹.

Thus, compared to Mg(HMDS)₂, the borane Lewis acids, in particular diborane 4, enable equally fast or faster monomer consumption using less equivalents of the Lewis acid and are more suitable for AGE and BO. This comes in spite of the significantly less pronounced interaction of monomer and Lewis acid, as exemplified for BO (Figure 4), whereby the magnesium compound entails a strong shift of the monomer signals in ¹H NMR analysis (up to 0.3–0.4 ppm low field shift), while for Et₃B or 4 similar changes are practically absent. Clearly, strong monomer activation alone is not a sufficient guideline for further catalyst design. This can be most likely related to the fact that apart from monomer complexation, the Lewis acid will also coordinate to the propagating chain end (=lowering of alkoxide reactivity) and may form adducts with the mNHO. Both factors may be detrimental for efficient initiation or propagation.

Finally, it should be noted that control experiments (Table S2, Supporting Information), using either the nucleophilic component (mNHO 3) alone or applying only the Lewis acidic components, clearly underline the necessity to employ both for successful and efficient polymerization. Thus, using mNHO/PO, no conversion is observed after 18.5 h. Likewise, usage of Mg(HMDS)₂, Et₃B or diborane 4 entails no or only very sluggish conversion. In a different type of control reaction, 50% of the Mg(II) component was replaced by LiHMDS,^[11] whereby a much weaker monomer activation can be expected (mNHO 3/Mg(HMDS)₂/LiHMDS/PO = 1:2.5:2.5:1000, Table S2, Supporting Information, entry 3). In line with the above mechanistic considerations, the thus decreased concentration of epoxide-coordinating Mg(II) species led to a loss of polymerization activity. In sum, the control reactions not only highlighted the much improved performance by combining suitable mNHOs with se-

lected Lewis acids, but also support the proposed polymerization mechanism as discussed previously.

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3. Conclusion

Three structurally different mNHOs (1–3) were employed as neutral, carbon-centered initiators in conjunction with Lewis acidic catalysts for the polymerization of epoxides. By application of mNHO/Mg(HMDS)₂ pairs, it was demonstrated that indeed high-yielding and rapid consumption of PO can result if certain requirements are fulfilled, namely a) a notable excess of Lewis acid (20 eq.), b) a sterically unencumbered, highly nucleophilic mNHO and c) high monomer concentration. This way, TONs per mNHO of 1000–3750 can be achieved, whereby it was demonstrated that the underlying Lewis pair polymerization mechanism proceeds via a zwitterionic species, resulting in mNHO-terminated poly(propylene oxide). Additionally, it was shown that mNHO initiators combine well with borane-type Lewis acids, which can be considered a milder and more versatile alternative to Mg(HMDS)₂. Overall, the obtained molar masses are up to two orders of magnitude lower than in the case of regular NHO/Mg(HMDS)₂ pairs, reflecting the improved initiation efficiency by the more nucleophilic mNHOs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Iris Haug: polymerization reactions; kinetics; NMR experiments. Justus Reitz: mNHO synthesis. Céilia Ziane: supporting polymerization experiments. Michael R. Buchmeiser: writing original draft & review. Max M. Hansmann: conceptualization, project administration, funding, supervision, writing original draft & review. Stefan Naumann: conceptualization, project administration, funding, supervision, writing original draft & review.

Data Availability Statement

The data that support the findings of this study are available in the [supplementary material](#) of this article.

Keywords

boranes, epoxides, magnesium, organocatalysis, polyethers

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