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Highly Polarized Alkenes as Organocatalysts for the Polymerization of Lactones and Trimethylene Carbonate

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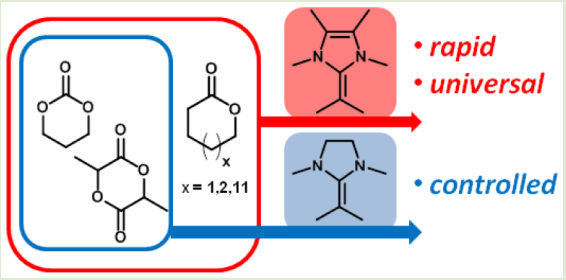
Supporting Information

ABSTRACT: In this work, the activity of N-heterocyclic olefins (NHOs), a newly emerging class of organopolymerization catalyst, is investigated to affect the metal-free polymerization of lactones and trimethylene carbonate (TMC). A decisive structure−activity relationship is revealed. While catalysts of the simplest type bearing an exocyclic $=CH_2$ moiety polymerize L-lactide (L-LA) and δ-valerolactone (δ-VL) in a non-living and non-quantitative manner, the introduction of methyl substituents on the exocyclic carbon radically changes this behavior. 2-Isopropylidene-1,3,4,5-tetramethylimidazoline is found to be highly active for a range of monomers such as L-LA, δ-VL, ε-caprolactone (ε-CL), and TMC, with quantitative conversion occurring within seconds with catalyst loadings of just 0.2 mol %. The high activity of this NHO further enables the ring-opening polymerization (ROP) of the macrolactone ω-pentadecalactone (PDL). However, this broad applicability is offset by a lack of control over the polymerizations, including side reactions as a consequence of its strong basicity. To overcome this, a saturated, imidazolinium-derived analogue was synthesized and subsequently demonstrated to possess a harnessed reactivity which enables it to polymerize both L-LA and TMC in a controlled manner ($Đ_M$ < 1.2). NMR spectroscopic and MALDI-ToF MS experiments highlight the differences in polymerization pathways for 2-methylene-1,3,4,5-tetramethylimidazoline, in which the exocyclic carbon is not substituted, in contrast to 2-isopropylidene-1,3,4,5-tetramethylimidazoline, with the former operating via its nucleophilicity and the latter acting as a base with enolizable δ-VL.



The rapid ascent of organocatalyzed polymerization reactions over the past 15 years has been driven by a number of well-recognized, advantageous properties of this kind of catalysis.[1−3] Among these, a more convenient and less expensive access to the catalysts themselves, the elimination of environmental concerns over toxic metal-based components, and the ability to operate under alternative polymerization mechanisms, compared to the more established organometallic catalysis, are considered to be the key beneficial properties.[4,5] Despite this, in terms of high activity and tunability, readily achieved for metal complexes by skillful manipulation of the ligand sphere, organocatalysts still need further improvement. However, when a strong inherent reactivity can be paired with a facile adaptability of the organocatalyst structure, impressive results have been obtained. This is perhaps best represented by *N*-heterocyclic carbenes (NHCs), which can be tailored to the task at hand and nowadays are useful for a range of monomers.[6,7] Further research into highly active, yet structurally diverse species has recently led to the disclosure of *N*-heterocyclic olefins (NHOs, Figure 1) as organopolymerization catalysts for propylene oxide (PO).[8] Outperforming NHCs, these compounds contain a strongly polarized double bond, which renders the exocyclic carbon partially anionic in character and reactivity. Crucially, the polarity of the olefinic bond can be manipulated in a number of ways, including variation of the ring size, (un)saturation of the backbone, and substituents both on the nitrogen atoms and

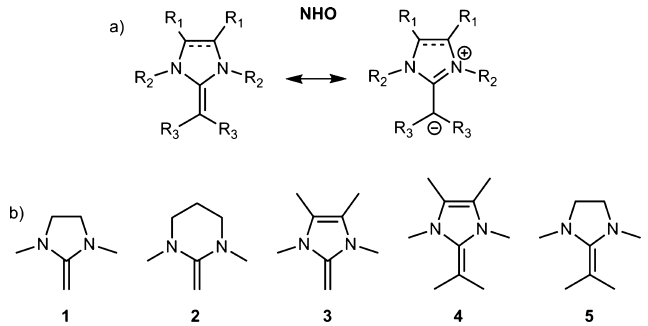


Figure 1. (a) Mesomeric structures for NHOs and (b) organocatalysts used in this study.

directly on the exocyclic carbon.[9−15] While the defining structural prerequisites for efficient PO polymerization have been illuminated, the behavior of NHOs toward other monomers is so far completely unknown.[16] In view of the promising properties of this class of organocatalyst,[17] the activity of five different NHOs with regard to small- and large-ring lactones as well as lactide and trimethylene carbonate was investigated, allowing for a deeper understanding of the

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underlying mechanisms and the structural requirements for successful polymerization.

For a first series of experiments, NHOs **1**−**3** (Figure 1) were prepared. These compounds were received as liquids (**1**−**2**) or as a solid (**3**) in analytically pure form, following a convenient procedure using potassium hydride to deprotonate the precursor salts (see SI, Scheme S1), precluding the need for any further purification. These structures were chosen to map out the influence of different ring structures, while the exocyclic methylene moiety remained unchanged in its simplest and sterically least hindered form. NHOs **1**−**3** were then applied for polymerization reactions with L-lactide (L-LA) and δ-valerolactone (δ-VL), both in the absence and presence of initiator (benzyl alcohol, BnOH) at room temperature under nitrogen ($[M]_0$ = 1.0 M), immediately revealing the strong influence of the heterocyclic ring system on performance. In the absence of initiator, L-LA was not polymerized at all by NHO **1**, while six-membered NHO **2** delivered 29% monomer conversion, followed by the imidazolium derivative NHO **3**, use of which delivered a monomer conversion of 47% after 1.5 h (Table 1). In conjunction with BnOH ([NHO]/[BnOH] = 1:2 in order to prevent undesired NHO-initiated ring-opening polymerization (ROP)), monomer consumption was noticeably faster, enabling NHO **1** to effect a moderate conversion, while NHOs **2** and **3** consumed more than 70% and 80% of L-LA, respectively (Table 1, entries 4−6). However, in spite of the reasonably controlled molecular weight distributions, quantitative conversion remained elusive as an extension of the polymerization time to 4 h did not result in a relevant increase of monomer consumption (Table 1, entry 7). An increase of the NHO/BnOH ratio to 1:25 and a lowering of the target degree of polymerization (DP) led to a higher overall turnover, but full conversion was still not achieved (Figure S1). Indeed, closer inspection of the correlation of time and monomer consumption revealed that the polymerization proceeded very rapidly in the beginning (see Figure S1), to then quickly plateau with minimal subsequent conversion and no increase in dispersity ($Đ_M \approx 1.2$), which suggests that a deactivation of the highly active catalyst occurred. Polymerization of δ-VL in combination with BnOH demonstrated similar behavior with the same order of activity (**3** > **2** > **1**), non-living monomer consumption (see Table S1, entries 4−6), and low dispersity ($Đ_M \leq 1.3$). In the absence of initiator, however, even the most active NHO only delivered a monomer conversion of 5% (Table S1, entry 7).

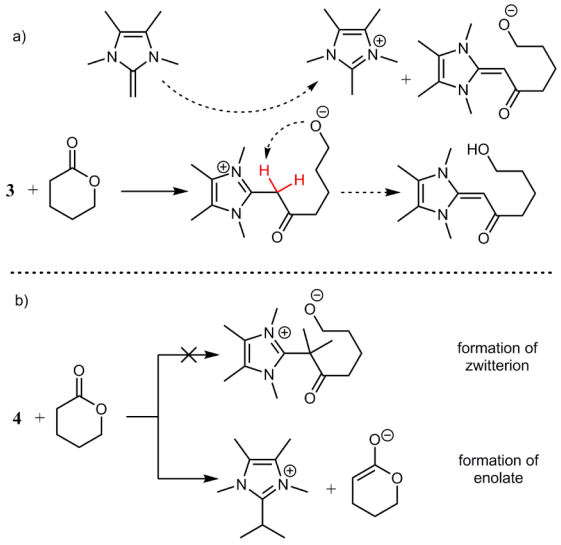
Table 1. Polymerization of L-LA Using Different NHOs in the Presence and Absence of BnOH (rt, THF, $[M]_{t0}$ = 1.0 M)

#	NHO	t [h]	NHO/BnOH/M	conversion [%][a]	M_n ($Đ_M$) [g mol^{-1}][b]
1	**1**	1.5	1:0:100	0	-
2	**2**	1.5	1:0:100	29	2800 (1.59)
3	**3**	1.5	1:0:100	47	4700 (1.27)
4	**1**	1.5	1:2:100	37	2300 (1.26)
5	**2**	1.5	1:2:100	74	4600 (1.30)
6	**3**	1.5	1:2:100	83	4000 (1.37)
7	**3**	4.0	1:2:100	86	3900 (1.46)

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by GPC (THF against PS standards).

Rationalization of these results proved crucial for the development of an improved generation of NHOs. The order of activity essentially follows the expected nucleophilicity (and basicity) on the exocyclic carbon. This property is somewhat stronger in saturated six-membered NHOs compared to their five-membered counterparts, as shown by Pittman and co-workers.[18] Likewise, it is reasonable to assume that on changing to an unsaturated, imidazolium-based backbone the charge separation will be supported by aromatization, potentially explaining the superiority of NHO **3**. The observed non-living behavior in polymerization, proposed to be a result of deactivation of the NHO, was interpreted as the consequence of a proton transfer (Scheme 1a). It is proposed that the free NHO in solution is able to attack the monomer, which undergoes ring opening to form a zwitterionic intermediate. In this intermediate, the methylene unit is positioned between a positively charged *N*-heterocyclic ring structure and a carbonyl functionality, both of which will acidify the $-CH_2-$ moiety. Deprotonation in this position by another NHO molecule or a propagating oxoanionic chain end will then effectively quench any polymerization activity. A similar effect has been demonstrated for isocyanate−NHO adducts.[18] Notably, this proposed deactivation mechanism is markedly different from the behavior of NHCs with lactones.[7,19]

Scheme 1. Proposed Mechanisms (No BnOH) for (a) Deactivation of NHO 3 by Acidified Protons (Red) and (b) Enolate Formation in Preference to Zwitterionic Ring Opening for NHO 4



On the basis of the above assumptions, NHO **4**, bearing exocyclic methyl groups, was synthesized.[20] This compound combines dimethyl substitution at the exocyclic carbon to avoid deactivation with an imidazolium-derived backbone to achieve high performance. As a consequence of these structural changes, a much increased activity was observed (Table 2). Polymerization of L-LA was found to proceed to monomer conversions of 88% and 98% in the absence and presence of BnOH, respectively. Control over the molecular weight distribution was much better in the latter case, which could be further improved by reduction of the polymerization time to 30 min (Table 2, entry 3). A lowering of the catalyst loading to 0.2 mol % and variation of the NHO/BnOH ratio showed an increase of turnover and molecular weight control in the case of

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Table 2. Polymerization of Different Monomers Using NHO 4[a]

#	M	t [min]	4/BnOH/M	conversion [%][b]	M_n ($Đ_M$) [g mol^{-1}][c]
1	L-LA	90	*1:0:100*	88	*4900 (1.92)*
2	L-LA	90	*1:2:100*	98	*6800 (1.33)*
3	L-LA	30	1:2:100	92	7600 (1.24)
4	L-LA	90	1:2:500	57	4300 (1.73)
5	L-LA	90	1:10:500	77	5300 (1.28)
6	L-LA	90	1:25:500	98	3700 (1.32)
7	δ-VL	240	1:0:100	96	4500 (4.26)
8	δ-VL	240	1:2:100	95	4300 (2.04)
9	δ-VL	5	1:2:500	95	11400 (3.29)
10	δ-VL	5	1:25:500	95	1900 (2.59)
11	δ-VL	0.25	1:2:100	94	8800 (2.53)
12	ε-CL	240	1:2:100	86	6500 (2.15)
13	PDL	240	1:0:100	4	-
14	PDL	240	1:2:100	47	6300 (2.36)
15	TMC	25 s	1:2:100	>99	7600 (1.89)
16	TMC	10 s	1:2:500	98	22900 (2.05)

[a]Reactions conducted in THF at room temperature ($[M]_0$ = 1.0 M) except where stated otherwise. [b]Determined by ^{1}H NMR spectroscopy. [c]Obtained from GPC ($CHCl_3$, entries 7−16; or THF, entries 1−6; against PS standards). [d]δ-VL and ε-CL polymerized in toluene. [e]Polymerization of PDL in toluene at 110 °C. [f]Polymerization of TMC with $[M]_0$ = 0.83 M.

higher alcohol concentrations (Table 2, entries 4−6). In contrast, the reactivity of NHO **4** with δ-VL was much more turbulent. Polymerizations on a time scale as used for NHOs **1**−**3** led to a near quantitative conversion in both the presence and the absence of BnOH, yet the molecular weight distribution was found to be broad. A drastic reduction of the reaction time to only 5 min in parallel with a 5-fold increased monomer loading still resulted in 95% monomer conversion without improving control over the polymerization. Similarly, a large excess of BnOH or a rapid quenching of the polymerization after only 15 s still resulted in broad molecular weight distributions at very high conversion; likewise, neither dilution nor cooling improved this situation in a relevant manner. This clearly marked NHO **4** out as a highly active catalyst, which induces extensive transesterification after rapid consumption of the δ-VL monomer, but important conclusions with regard to the polymerization mechanism can also be drawn (see below). Interestingly, NHO **4** was also able to polymerize the macrolactone pentadecalactone (PDL). Polymerization of this monomer, which possesses negligible ring strain, was conducted at 110 °C in toluene to achieve a monomer conversion of 47% after 4 h (entry 14). Notably, triazabicycloundecene, TBD, has previously been demonstrated to be the only organocatalyst from a wide range of screened compounds to be active for this process.[21] Without initiator, the activity of NHO **4** sharply dropped (Table 2, entry 13). Finally, high activity of NHO **4** was also established for polymerization of trimethylene carbonate (TMC). Quantitative conversion was observed after just 10 s, even at catalyst loadings of 0.2 mol % (Table 2, entries 15−16).

The differences in the behavior of NHO **4** toward the various monomers are profound. While the polymerization of lactide is comparatively well-controlled and slow, TMC and δ-VL are consumed rapidly. Furthermore, GPC analysis of the resulting polymers reveals monomodal distributions for the material received from L-LA and TMC, while the polyester derived from δ-VL frequently displayed shoulders or multimodal chromatograms, hinting at several propagating species or alternative initiation mechanisms by interaction of the catalyst directly with the monomer. As NHO **4** can polymerize δ-VL rapidly in the absence of BnOH (Table 2, entry 7), a mechanism must exist for direct polymerization. ^{1}H NMR spectroscopic analysis of the resultant polymer derived from reactions in the absence of BnOH only showed signals that fitted the protonated NHO. No corresponding signals for NHO-terminated polymers (Figures S2−S3) were observed. Methanol washing accordingly completely removed the protonated NHO, providing further weight to this conclusion. To further identify the proton source, repeat experiments were conducted with analysis also under dry conditions, displaying again fully protonated NHO with no other species observable (Figure S4). In contrast to the zwitterionic polymerization that is proposed in the analogous and well-understood NHC-based chemistry of lactone polymerization,[7,22] we postulate that the formation of protonated NHO is consistent with enolate formation via proton abstraction from the lactone by NHO **4** (Scheme 1b). In turn, this is therefore proposed as an initiation process or side reaction that can explain the lack of control over polymerization of δ-VL and the rapid buildup of high molecular weight fractions. On account of the identical molar masses of the postulated enolate-end-capped and cyclic Pδ-VL (that could arise from either enolate or zwitterion formation) MALDI-ToF MS analysis (Figure S5) was inconclusive other than to demonstrate the absence of other end groups.[23] Further evidence to support enolate formation is provided by the ROP of L-LA, which is less prone to enolate formation as a consequence of methyl substitution in α-position to the carbonyl, and TMC, which does not possess an enolizable functionality. Both monomers are polymerized in a more controlled manner, thus favoring the proposed enolate formation.

In an attempt to isolate an NHO enolate, NHO **3** and δ-VL were combined in a 1:20 ratio. Under these conditions, NHO **3** was found not to be protonated, but rather a strong interaction with the monomer was observed (Figure S6). This is in agreement with the above-described manner of deactivation (Scheme 1a), which requires a nucleophilic ring opening of the monomer, and also with the fact that the exocyclic carbon of NHO **3** is much less sterically hindered compared to NHO **4**. Gratifyingly, MALDI ToF MS analysis emphasized these differences in reactivity, as polymer derived from NHO **3**/δ-VL (1:20) shows a multitude of mass distributions, in which the dominating one is a close fit to calculations for NHO-terminated product (Figure S7). Finally, NHO **3** must also be expected to be less basic than NHO **4**, considering the fact that the carbanion in the charge-separated state is primary versus the tertiary one for NHO **4**.[24]

Clearly, the high reactivity of NHO **4** was required to be attenuated in order to maintain a better control over the polymerization. To achieve this, NHO **5**, which contains a saturated heterocyclic ring to decrease the polarization of the olefinic bond, was synthesized.[24] The impact upon the catalytic performance was found to be strong. L-LA was efficiently polymerized (BnOH, 1 mol % catalyst loading), reaching 87% monomer conversion after only 25 s. Interestingly, this is faster than polymerization of the same monomer by NHO **4**, while maintaining better control over the molecular weight distribution. When the reactions were allowed to proceed to reach full conversion and left stirring for additional time, the molecular weight was found to start decreasing with a

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broadening $Đ_M$ (Table 3, entries 3–4). This was in sharp contrast with the behavior found for NHOs **1**–**3**, where the monomer conversion stopped increasing, and full conversion was not reached while the molecular weight distribution did not deteriorate (compare Figure S1). These results clearly underline that NHO **5** is not deactivated by side reactions, presumably by virtue of it bearing a substituted exocyclic carbon. Polymerization of TMC markedly differed from what was observed for **4**, enabling a slower reaction yet retaining excellent control over the polymerization (Figure 2). When the catalyst loading was lowered to 0.2 mol %, reaction over extended times was required (Table 3, entry 7), where NHO **4** had delivered full conversion in seconds. Gratifyingly, however, the polycarbonate derived from the action of NHO **5** was found to be very well-defined by GPC ($Đ_M$ < 1.15) and MALDI-ToF MS.

Table 3. Polymerization of Different Monomers Using NHO 5[a]

#	M	t	5/BnOH/M	conversion [%][b]	M_n ($Đ_M$) [g mol^{-1}][c]
1	L-LA	25 s	1:2:100	87	4500 (1.16)
2	L-LA	105 s	1:2:100	92	4400 (1.18)
3	L-LA	5 min	1:2:100	>99	4400 (1.32)
4	L-LA	25 min	1:2:100	>99	3800 (1.64)
5	L-LA	20 min	1:2:500	25	7100 (1.19)
6	TMC	3.5 h	1:2:100	76	5800 (1.12)
7	TMC	18 h	1:2:500	26	7200 (1.12)

[a]Reactions conducted in THF at room temperature ($[M]_{t0}$ = 1.0 mol/L) [b]Determined via ^{1}H NMR spectroscopy; [c]Obtained from GPC ($CHCl_3$, entries 6–7) or THF (entries 1–5).

In conclusion, we have reported the first NHO-mediated polymerizations of several lactones and trimethylenecarbonate. The key structural requirements for successful polymerization have been described. NHO organocatalysts bearing a nonsubstituted methylene moiety are prone to deactivation and are unable to achieve quantitative polymerization of lactide or δ-VL. In contrast, dimethyl substitution at the exocyclic carbon enables high activity and high conversion. In the case of an unsaturated backbone as present in NHO **4**, this leads to a broad applicability with rapid monomer consumption but a loss of control over the polymerization, especially in the case of δ-VL. NMR spectroscopic experiments show that nonsubstituted NHO **3** and the highly active NHO **4** operate under different mechanisms, with the former most probably generating zwitterionic species which ultimately lead to its deactivation, while NHO **4** acts as a base and abstracts a proton from the monomer, inducing enolate-based initiation and side reactions. Finally, the high activity of NHO **4** can be harnessed by saturation of the backbone, allowing for a controlled and gentle polymerization of TMC and lactide. High activity, tunability, and the ability to operate under alternative polymerization mechanisms are key characteristics of NHOs as shown in this work, clearly rendering them a very promising class of organocatalyst to more fully explore.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00873.

Experimental details on synthesis, additional polymerization results, and NMR experiments (PDF)

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Notes

The authors declare no competing financial interest.

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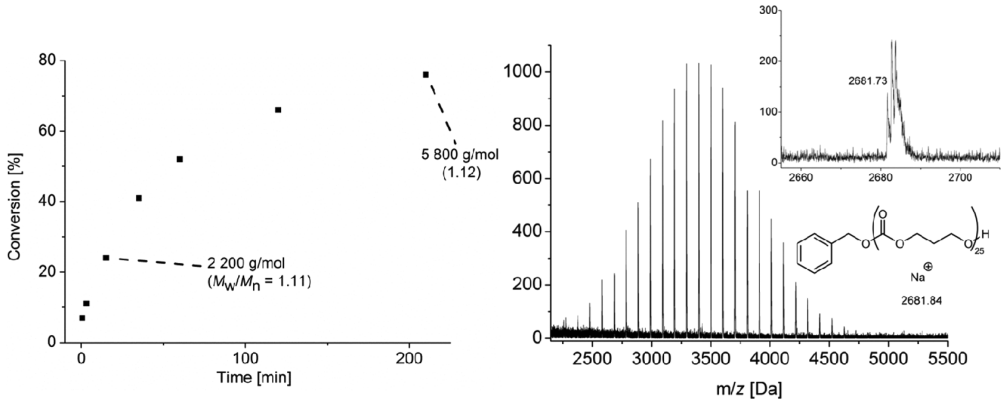

Figure 2. Conversion versus time for polymerization of TMC by NHO **5** (left, for conditions see Table 3, entry 6) and the MALDI-ToF MS analysis for the resulting polycarbonate (right).

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