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N-Heterocyclic Olefins as Initiators for the Polymerization of (Meth)Acrylic Monomers: A Combined Experimental and Theoretical Approach

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The zwitterionic organopolymerization of four different acrylic monomers (*N,N*-dimethylacrylamide, methyl acrylate, methyl methacrylate and *tert*-butyl methacrylate) based on neutral initiators, so-called *N*-heterocyclic olefins (NHOs), is presented. Scope and underlying (deactivation-)mechanisms were studied in a combined experimental and computational effort. From a range of differently structured NHOs it emerged that imidazole-, in contrast to imidazoline- and benzimidazole-derivatives, readily polymerize the selected monomers. While the additive-free reactions proceed with a relatively low degree of control to yield largely atactic material, for the acrylamide the addition of LiCl as μ -type ligand has been shown to result in a rapid and quantitative monomer consumption. The thus generated poly(*N,N*-dimethyl acrylamide) was found to be highly isotactic (>90% isotactic dyads) with high molecular weight ($M_n = 250\,000 - 650\,000$ g/mol, $D_M = 1.3 - 1.6$). Complementing DFT calculations considered the zwitterionic chain growth with respect to competing side reactions, namely spirocycles and enamine formation. It was found that NHOs with unsaturated backbone better support the zwitterionic chain growth, with the spirocycles acting as dormant species that slow down but do not quench the polymerization process. Contrasting this, enamine formation irreversibly terminates the polymerization and is found to be energetically favored. This pathway can be blocked by introduction of substituents on the exocyclic carbon of the NHO, resulting in structures like 2-isopropylidene-1,3,4,5-tetramethylimidazoline (**4**) which consequently deliver the most controlled polymerizations. Finally, a good correlation of the initiation energy barrier with the buried volume (% V_{Bur}) and the Parr electrophilicity index is described, allowing for a quick and reliable screening of potential monomers based on these two readily accessible parameters.

Introduction

The anionic polymerization of (meth)acrylic monomers is a powerful but challenging matter, governed by a complex interplay of initiation- and propagation kinetics, the frequent occurrence of side reactions and the aggregation of active chain ends with its resulting equilibria between different types of aggregates and ion pairs.¹⁻⁴ This is a direct consequence of the presence of activating polar ester or amide groups and renders the anionic polymerization of typical examples like methyl methacrylate or *N,N*-dimethylacrylamide somewhat less robust when compared to hydrocarbon monomers such as styrene. Especially the range of suitable initiators is limited; a compound like butyllithium does not entail a controlled polymerization but has to be attenuated in its reactivity instead.^{1,5-6} To achieve this, 1,1-diphenylethylene is commonly

reacted with butyllithium to generate diphenylhexyllithium (DPHLi) as a delocalized, less aggressive carbanion (Scheme 1).⁷ In combination with further additives (Lewis acids, ligands for the counter ions) and low polymerization temperatures, a controlled polymerization can be conducted.⁸⁻⁹

In view of these difficulties, a range of alternative initiating systems has been investigated with the overall aim of increasing the livingness of the polymerization and reducing the complexity of the reaction setup. Major contributions include tailoring of the aggregation equilibria by application of coordinating additives (both of the counter ion and the enolate),¹⁰ the development of group-transfer polymerization¹¹ and the use of metal-free counter ions,¹²⁻¹⁵ as well as discrete organometallic porphyrin-¹⁶⁻¹⁷ or metallocene-based¹⁸⁻²⁰ catalysts. More recently, Lewis pairs have been described by Lu,²¹ Chen and Cavallo²²⁻²³ as well as Rieger,²⁴ which enable very controlled polymerizations at room temperature, relying on the strong activating power of aluminium compounds such as $Al(C_6F_5)_3$ or $AlPh_3$. Taton reported a silane/phosphine organic Lewis pair for MMA polymerization.²⁵ Finally, considerable effort was dedicated to establish *N*-heterocyclic carbenes (NHCs) as organoinitiators for MMA.²⁶⁻²⁷ In this case, the polymerization is started by conjugate addition of the NHC to the Michael-acceptor system

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of the monomer to form a zwitterionic species (Scheme 1). Strikingly, it was found that the success of this strategy depends strongly on the chemical structure of the NHC: interaction with MMA can result in dimerization, cyclodimerization, monoadduct formation or polymerization (Scheme 1).^{28–32} Chen first disclosed the polymerization of MMA using 1,3-di-*tert*-butylimidazol-2-ylidene, which yielded moderately controlled polymer ($\bar{D}_M = 2.0$, $M_n = 33\ 000$ g/mol).³¹

Scheme 1. a) Preparation of DPHLi as attenuated carbanionic initiator; b) NHC-based polymerization of MMA via a zwitterionic species; c) $\text{Al}(\text{C}_6\text{F}_5)_3$ -assisted polymerization of MMA using asymmetric NHO; d) NHO-initiated polymerization of non-activated acrylic monomers as discussed in this work.

Figure 1. a) NHOs employed in this study; b) mesomeric structures for imidazolium-based NHO; c) scope of monomers.

In this context, *N*-heterocyclic olefins (NHOs) seem to offer intriguing potential for application as (organo)initiators for polymerization of acrylic monomers. NHOs contain a strongly polarized double bond, which enables them to act as powerful nucleophiles, organobases or ligands.^{33–41} Indeed, this charge separation is strong enough to describe NHOs as latent, readily tunable zwitterions.^{42–45} In contrast to carbene-like reactivity, this also suggests that NHOs might add much more easily to Michael acceptor systems when compared to NHCs, as a consequence of their partial carbanionic character on the exocyclic carbon. Additionally, the above described attenuation necessary for controlled polymerization seems to be inherent for all NHOs, as the charge separation can be tailored by ring structure and substituents, but will always be limited in comparison to the predominantly ionic butyllithium. Also, the expected formation of zwitterionic growing species is of interest, as the decisively important role of aggregates and ion pairs will be different when the counter ion is part of the polymer chain. Indeed, it has been shown that $\text{Al}(\text{C}_6\text{F}_5)_3$ -activated MMA allows for the direct addition of NHOs and controlled polymerization of the monomer.²¹ Recently, NHO/ $\text{Al}(\text{C}_6\text{F}_5)_3$ has also been described to successfully deliver high molecular weight polyester from lactones.⁴⁶ In all, this underlines the general feasibility of using this class of compounds for initiation but also raises the question whether NHOs can be applied in a more classical sense as direct initiator without activation of the monomer. This would enable a fully metal-free polymerization of acrylates and also further elucidate the structure-dependent reactivity of NHOs towards double bonds. In view of the complexity of the matter, a combined experimental and theoretical approach was chosen in order to gain a more encompassing understanding of the underlying mechanisms. Experimentally, six different NHOs and four acrylic monomers with varying steric and electronic demands were investigated (*N,N*-dimethyl acrylamide (DMAA), methyl acrylate (MA), methyl methacrylate (MMA) and *tert*-butyl methacrylate (tBuMA), Figure 1). The results for metal- and additive-free as well as μ -type ligand-assisted polymerizations are reported here, including information on the stereoconfiguration of the generated polymer. The findings are furthermore correlated with results from theoretical calculations, which specifically focus on deactivation pathways, spirocyclic resting states and the propensity of NHOs to add to acrylic Michael acceptor systems in dependence of the steric congestion and electronic activation of the monomer.

Results and Discussion

Polymerization of DMAA using metal-free and LiCl-containing setups

The NHO initiators were prepared according to published procedures, using potassium hydride to deprotonate precursor salts (see Supporting Information, SI).^{34,37–38,42–45} In all cases this directly led to analytically pure compounds without further workup; while NHOs **1** and **2** were received as liquids, **3–6** are

solids at room temperature. In order to obtain clear structure-activity correlations, the *N*-substituents were identical in all cases (methyl), while a range of different backbones was covered (Figure 1). These include saturated five- and six-membered *N*-heterocyclic rings (**1,2**) as well as imidazolium- (**3,4**) and benzimidazolium-derivatives (**5,6**). Incomplete as the understanding of NHO chemistry currently is, previous work nonetheless suggests that imidazolium-based compounds should display a markedly different behavior from their saturated counterparts.³⁷⁻³⁸ This can be understood as a consequence of the increased charge separation in the former case (mesomeric structures depicted in Figure 1b), which generates favored, aromatic imidazolium moieties. In practice, this has led to a compound like **4** being able to organopolymerize monomers where **1** or **2** have been inactive.³⁷⁻³⁸ Finally, two species with dimethyl-substituted exocyclic carbon are also part of the study (**4** and **6**). Such a manipulation of the initiator may be expected to decrease the initiation efficiency, but it also eliminates a potential site for unwanted side reactions: after addition of the NHO to the acrylic monomer, protons adjacent to the imidazolium moiety (compare Scheme S2) are acidified and might be abstracted by the highly basic propagating enolate. This scenario can be blocked by the introduction of methyl groups. For the polymerization of lactones, a similar effect has been shown to be crucial for controlled polymerization.³⁸

Table 1. Polymerization of DMAA using NHOs **1-6** (NHO/DMAA = 1:200, $[M]_{t=0}$ = 3.33 mol/L, 2h).

#	NHO	T [°C]	Solvent	Conversion ^{a)} [%]	M_n ^{b)} [g/mol]	$\bar{D}_M$ ^{b)}
1	1	RT	toluene	0	-	-
2	2	RT	toluene	0	-	-
3	3	RT	toluene	62 ^{c)}	16 800	9.4
4	3	-36°C	toluene	50 ^{d)}	8 600	2.2
5	4	RT	toluene	69 ^{d)}	18 400	2.6
6	4	-36°C	toluene	37 ^{e)}	1 500	3.2
7	5	RT	toluene	0	-	-
8	6	RT	toluene	0	-	-
9	3	-36°C	THF	32	5 100	4.0
10	3	-36°C	DME	46	11 100	2.5
11	3	RT	benzene	75	13 700	11.8

a) determined via ^1H spectroscopy; b) according to GPC (CHCl_3); c) 0.5 h; d) 1 h; e) 3d.

First experiments were conducted in toluene, using 0.5 mol-% NHO loading and a relatively high monomer concentration (3.33 M). Without any further additives, the initiator was added to the monomer solution and the homogeneous reactions were left stirring at room temperature. These investigations immediately revealed which NHO structures were suitable for further polymerization (Table 1). Strikingly, no conversion at all was observed for initiators **1, 2, 5** and **6**; in contrast, imidazolium derivatives **3** and **4** readily delivered PDMAA. In the latter case, the polymerization solutions turned a pale yellow after addition of the NHOs, which coloration

again disappeared after quenching with methanol. Throughout the reaction solutions remained clear, which already hinted at the stereoconfiguration of the PDMAA prepared (see below).

At room temperature, addition of the NHO **3** resulted in a noticeably exothermic reaction, favored also by the high monomer concentration. Expectedly, this led to a very broad distribution of molecular weights, which was significantly improved by lowering the reaction temperature to -36°C (box freezer, entries 3-4). In notable contrast, polymerizations conducted at lower initial monomer concentrations did not result in relevant conversions. This may be related to a competition between propagation and deactivation (see below), whereby propagation is favored by high concentration of monomer.

Using the more sterically hindered compound **4**, at room temperature a steady consumption of monomer was observed over several hours up to a conversion of 90% (Figure 2). Polydispersity was better than found for **3** under identical conditions (see entries 3 and 5), however, the polymerizations clearly did not proceed in a living manner as evidenced by non-quantitative consumption and $\bar{D}_M$ = 2-3. Cooling of the reaction to -36°C for this NHO resulted in a very sluggish polymerization, with only 37% conversion after three days, yielding low molecular weight PDMAA with broad molecular weight distribution.

Figure 2. Conversion vs. time for the polymerization of DMAA using NHO **4**. Room temperature, toluene, $M_{t=0}$ = 3.33 mol/L, NHO/DMAA = 1:200.

Table 2. Polymerization of DMAA using NHOs **3** or **4** in the presence of LiCl (NHO/LiCl/DMAA = 1:5:100, -36°C, 2 min, THF).

#	NHO	NHO/LiCl /DMAA	$[M]_{t=0}$ [mol/L]	Conversion ^{a)} [%]	M_n ^{b)} [g/mol]	$\bar{D}_M$ ^{b)}
1	3	1:5:100	0.25	99	152 000	1.73
2	3	1:5:100	0.33	100	138 000	1.54
3	3	1:5:100	0.67	100	95 000	1.76
4	3	1:5:100	1.0	100	67 000	2.1
5	4	1:5:100	0.25	99	654 000	1.59
6	4	1:5:100	0.33	100	508 000	1.39
7	4	1:5:100	0.67	100	353 000	1.32
8	4	1:5:100	1.0	100	254 000	1.57
9	3	1:20:100	0.33	46	63 000	3.8
10	3	1:1:100	0.33	100	185 000	2.1
11	3	1:5:100 ^{d)}	0.33	99	73 000	2.4

a) determined via ^1H spectroscopy; b) according to GPC (CHCl_3); c) Solvent: DME.

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Figure 3. GPC traces (CHCl_3) for PDMAA prepared by **4**/LiCl at -36°C . Data from Table 2, entries 5-8.

Initial efforts to rectify this situation by using more coordinating solvents like THF or DME at -36°C still afforded rather uncontrolled polymerizations (Table 1, entries 9-10), while room temperature reaction in benzene again led to ill-defined results (entry 11).

From these initial insights, important conclusions for a further improvement of the NHO-initiated polymerization of DMAA could be drawn. Firstly, all subsequent reactions were to be limited to NHOs **3** and **4**; the superiority of these compounds is most probably explained by their increased nucleophilicity along the lines discussed above. Secondly, the need to cool down polymerizations is evident from Table 1, a typical feature found for many anionic polymerizations of acrylic monomers (in contrast to group-transfer polymerization).^{1,2} Most importantly, the non-living character and comparably slow monomer consumption under the previous conditions, irrespective of any NHO-induced side reactions, was expected to result from unfavorable ion pairing and aggregation dynamics. Generally, the equilibria between different kinds of ion pairs determine propagation rates, while the speed of interconversion between differently aggregated species controls the molecular weight distributions.¹ Addition of LiCl was therefore investigated, a frequently used “ μ -type” ligand.¹⁰ The beneficial effect of this additive is related to the coordination of lithium to the enolate species, breaking up aggregates and stabilizing the growing polymer chain end, although the effects are complex and also depend on the acrylic monomer.^{1-2,47}

Consistently, polymerization with a fivefold excess of LiCl relative to the NHO in THF at -36°C progressed very differently when compared to the additive-free reactions. Seconds after addition of the NHO solution, the polymerization mixtures solidified under formation of precipitate with high molecular weight (Table 2). Reactions were quenched and re-dissolved with methanol. Investigations via NMR after just two minutes polymerization time showed very high or even quantitative conversion with no trace of monomer left. Interestingly, the molecular weights found with NHO **3** were high (entries 1-4), indicating fast propagation relative to initiation. This

Figure 4. Tacticity of PDMAA obtained by NHO initiation as found by ^{13}C NMR analysis (carbonyl region, 100 MHz, 300 K, MeOD).^[48,49] Top: Metal-free polymerization, NHO/DMAA = 1:200. Bottom: With LiCl as additive, NHO/LiCl/DMAA = 1:5:100.

assumption is further supported by the effect of dilution on molecular weights, whereby a stepwise increase of the initial monomer concentration from 0.25 mol/l to 1.0 mol/L likewise suppresses M_n in stages while full conversion is maintained. Application of NHO **4** resulted in even higher molecular weight, with M_n ranging from 250 000 - 650 000 g/mol under identical conditions, again displaying the same correlation with the initial concentration of DMAA (Figure 3 and Table 2, entries 5-8). Importantly, GPC analysis also underlined that molecular weight distribution was narrowed significantly by addition of LiCl, with $\mathcal{D}_M = 1.5\text{--}2.1$ for **3** and $\mathcal{D}_M = 1.3\text{--}1.6$ for application of **4**. The somewhat improved polydispersity found for initiator **4** might indicate that dimethyl-substitution of the exocyclic carbon indeed limits side reactions related to proton transfer—an assumption that is also supported by results from DFT calculation (see below). The generally very high molecular weights, in view of a NHO/DMAA molar ratio of only 1:100, highlight the limited initiation efficiency of the NHOs investigated in this work, which is expectedly lower for the sterically encumbered initiator **4**. More LiCl relative to initiator (20:1) reduced conversion and was accompanied by much broader molecular weight distribution (entry 9), while equimolar amounts of LiCl retained high conversion at increased molecular weight (compare entries 2 and 10) with a limited loss of control over polydispersity. Polymerization in DME was much less defined than results obtained from reaction in THF (entry 11).

The PDMAA generated by NHO organopolymerization is largely atactic (Figure 4, top) and well soluble in toluene, while

addition of LiCl entails highly isotactic material (>90% isotactic triads) which is soluble in methanol or chloroform, but only very limited so in THF.⁴⁸⁻⁴⁹ **3**/LiCl and **4**/LiCl display practically identical ¹³C NMR spectra (see Figure S3-S4).

Table 3. Polymerization of several acrylic monomers using NHO **3** (NHO/M = 1:200, [M]₀ = 3.33 mol/L, toluene).

#	M	T [°C]	Time [min]	Conversion ^{a)} [%]	M _n ^{b)} [g/mol]	Đ _M ^{b)}
1	MA	RT	30	73	22 000	2.0
2	MA	-36	30	94	62 000	1.63
3	MMA	RT	30	31	79 000	4.0
4	MMA	-36	5	65	111 000	3.1
5	tBuMA	RT	5	71	325 000	4.3
6	tBuMA	-36°C	5	91	294 000	4.1

a) determined via ¹H spectroscopy; b) according to GPC (CHCl₃).

Organopolymerization of MA, MMA and tBuMA

¹H NMR experiments using MMA and NHO **2** or **3** in equimolar ratio (C₆D₆, 300K) again highlighted the striking differences in reactivity. While NMR analysis showed that combination of **3** with the monomer resulted in quantitative disappearance of all olefinic signals, saturated compound **2** coexisted with MMA without any observable change to shifts or integrals (see Figure S5). NHO **3** was subsequently applied for the polymerization of acryl esters, using both acrylic and methacrylic monomers. Again a yellow discoloration was observed after initiator and monomers had been combined, which disappeared after quenching with methanol. With all three substrates polymerization occurred, although the outcome was markedly different for each of the monomers (Table 3). The relatively highest control over polymerization and lowest molecular weights were found for MA. At -36°C, reactions in toluene progressed moderately controlled in a non-living manner, reaching high conversion (entry 2), without achieving quantitative monomer consumption. Under identical conditions, molecular weights were found to be significantly higher for MMA (100 000 g/mol, entries 3-4) and again for tBuMA (300 000 g/mol, entries 5-6). This clearly reflects the propensity of the NHO to add to the differently activated Michael acceptor systems. The apparent initiation efficiency of **3** for MA>MMA>tBuMA mirrors the reactivity, and thus the destabilization, of the growing enolate species. For a conventional, anionic initiator like DPHLi this is of minor importance as addition to the double bond always creates a less reactive anionic species than the starting compound was. For the neutral NHOs these substitution effects are more keenly felt and directly influence the initiation kinetics. This effect is also nicely mirrored in the activation energies necessary for addition of the NHO to the different monomers (see below).

The PMMA prepared by organopolymerization using compound **3** displayed triad intensities as found by ¹³C NMR integration of 54% rr, 40% mr and 6% mm (see Figure S6),⁵⁰ revealing the polymer to be moderately syndiotactic-rich and similar to NHC-derived PMMA in its stereoconfiguration.^{31,51} Polymerized tBuMA was found to be largely heterotactic

(Figure S7).⁵² Similarly, ¹³C NMR analysis of the correspondingly synthesized PMA showed signal patterns typical for atactic material.^{53,54} In this context it is noteworthy that the PMMA derived from classical anionic initiators in THF is predominantly syndiotactic (with the expected increase of heterotactic placement when temperature is increased), while in toluene highly isotactic material is received.⁵⁵ This obviously contrasts with the NHO-initiated polymerization in toluene which delivers PMMA where syndiotactic placement is slightly predominant (see above), with almost no isotactic triads. It is tempting to relate these differences to the absence of a coordinating counterion, typically Li⁺ from lithiumorganyl-based initiators, in case of the NHO organopolymerization. Since isotactic PMMA has a low T_g and is therefore only of limited use for thermoplastic applications,^{56,57} these metal-free alternatives might offer an attractive access to more suitable, toluene-borne material once polymerizations can be conducted in a more controlled manner. Another field of potential application might be the polymerization of divinyl monomers, an area traditionally challenging for conventional anionic polymerization.⁵⁸ The decisive influence of the solvent is also underlined by the fact that reactions run in THF at -36°C using **3**/tBuMA/LiCl, **3**/MA/LiCl and **3**/MMA did not result in any conversion. While ¹H NMR or MALDI-ToF MS techniques have not delivered conclusive data for end-group analysis, we have employed DFT calculations to shed light on prospective side reactions.

DFT calculations for the organopolymerization of MA, MMA, tBuMA and DMAA

From above experimental results it is clear that NHO-catalysis displays some characteristics which are inherently found in anionic (meth)acrylate polymerization, like the need for low-temperature conditions and the notorious aggregation phenomena which can be partly resolved by coordinating additives. However, several other aspects seem to originate specifically from the presence of NHOs. A deeper understanding of the peculiarity of NHO catalysis could lead to the rational design of more tailored NHOs, and could contribute to the development of one of the current frontiers of organopolymerization, which is the direct polymerization of double bond-containing monomers.²⁷

To this end, the general reaction pathway (Scheme 2) was investigated by DFT calculations (see SI for computational details). This setup considers the initiation event, where the NHO adds to the free monomer forming a zwitterionic species (**B**), and the further chain growth through addition of another monomer unit to the thus formed enolate (via 1,4-addition), generating structure **C**. A repeated monomer addition leads to polymer by an approximately "classic" enolate-based anionic mechanism. Importantly, in this case, the counter ion (the positively charged NHO-moiety) is part of the growing chain.

In addition to this straightforward process, two side reactions were also considered, specifically the formation of spirocyclic structures and the H-transfer process leading to enamine species. Spirocycles are increasingly identified as crucial resting states or deactivation products for both NHC- and NHO-based

Scheme 2. Polymerization pathway and its side reactions as considered in this study.

polymerization catalysis.⁵⁹⁻⁶² In the present case, ring formation can, in principle, take place after the first monomer addition (**B**) to either form a four-membered spirocycle via the enolate carbon (**Bspiro_C**) or a six-membered ring via the enolate oxygen (**Bspiro_O**). Likewise, the formation of a six-membered C-bonded species is explored after the first chain growth step (**Cspiro_C**).⁶³ The above described reaction pathways were investigated for NHOs **1**, **3** and **4** in the polymerization of MMA, the commercially most eminent acrylic monomer. Additionally, for NHO **3** the discussion is extended to DMAA, tBuMA and MA (Table 4). Direct comparison of **1**/MMA and **3**/MMA thereby allows to determine the influence of the substitution at the NHO backbone (i.e. saturated versus non-saturated), while contrasting **3**/MMA and **4**/MMA highlights the importance of exocyclic substituents on the carbon-carbon double bond of NHOs. Finally, the evaluation of the whole monomer series with compound **3** will reveal how the different electronic and steric configurations of the monomers shape their propensity towards NHO-addition and influence the propagation scheme. The formation of the zwitterionic species **B** is clearly sensitive to the chemical nature of the NHO. The zwitterionic adduct is considerably less stable with **1** (11.1 kcal/mol, Table 4) than with **3** (5.1 kcal/mol), despite similar initiation barriers. This clearly reflects the much reduced ability of **1** to stabilize the positive charge on the catalyst ring with respect to **3**, which aromatizes upon charge separation (see Fig. 1b). As a consequence, system **1**/MMA promotes an easier formation of the neutral spirocyclic adducts. While six-membered **Bspiro_O** seems to be in equilibrium with **B** (relative energies 11.7 and

11.1 kcal/mol with an interconversion barrier of about 2 kcal/mol), **Bspiro_C** is more stable than the zwitterionic compound. The same trend is found after the first propagation step, where species **C** is more stable for **3**, while the spirocycle is relatively more stable for **1**. Overall, this means that polymerization with the saturated, five-membered NHO would be very challenging, with any global reactivity prone to be quenched by the formation of unreactive spirocycles. This is in full agreement with the non-existent activity observed in our polymerization experiments (see previous chapter) and reminiscent of the recently described NHO-mediated polymerization of propylene oxide, where likewise imidazole-derivatives clearly outperformed imidazoline-derived NHOs.^[37,61]

Further significant differences appear when the exocyclic carbon bears two methyl groups. In spite of its increased steric hindrance, **4** displays an improved propensity to polymerize MMA. The energy barrier for the formation of the zwitterion **B** is relatively low (5.0 kcal/mol, relative to 16 kcal/mol for **3**) and the stability of this species considerably higher (-5.4 vs. 5.1 kcal/mol). Moreover, both spirocyclic alternatives are higher in energy than the zwitterion. In the same manner, the first propagation step **B**-**C** is more than 10 kcal/mol lower than for **3**. As for **3**, polymerization-inactive resting states (**Cspiro_C**) can be formed and are somewhat more stable than **C**, with a relatively low barrier between both structures. Importantly, the system **4**/MMA differs from **3**/MMA in a further point, namely the blocking of any enamine formation (**D**). This process occurs by an intramolecular⁶⁴ H-transfer from the C2 of the NHO to the strongly basic enolate C- α carbon of the last

Table 4. Free energies in toluene (reported in kcal/mol). NHO and free monomer (A) were chosen as the base line, to which all data are referenced. X-Y denotes a transition state from species X to species Y. n. l. = not localized

	NHO 1	NHO 3				NHO 4
	MMA	MMA	tBuMA	MA	DMMA	MMA
A	0.0	0.0	0.0	0.0	0.0	0.0
A-B	17.3	16.3	17.3	11.4	14.4	5.0
B	11.1	5.1	5.3	1.7	5.2	-5.4
B-Bspiro _o	13.1	17.7	n. l.	n. l.	14.3	2.6
Bspiro _o	11.7	16.4	n. l.	n. l.	12.3	-2.6
Bspiro _c	7.0	10.4	9.7	7.5	9.8	0.3
B-C	24.4	16.7	17.8	11.1	14.8	5.4
C	4.0	-2.1	-2.6	-9.8	-6.8	-7.2
C-Cspiro _c	9.9	4.6	7.1	-7.9	-4.6	-2.5
Cspiro _c	-11.1	-7.9	-9.9	-20.0	-17.2	-14.0
C-D	16.8	10.7	10.9	4.0	7.8	---
D	-17.0	-16.7	-15.5	-22.6	-20.6	---

inserted unit, see step C to D in Scheme 2 (see Figure S2 also). The process is favored by the presence of the neighboring, positively charged *N*-heterocyclic ring that acidifies the $-\text{CH}_2-$ unit, as already reported for similar NHC- and NHO-mediated polymerizations.^{32,38,64} The resulting enamine is structurally identical to an NHO with one R substituent on its exocyclic carbon, which itself is structurally the same as the so-called deoxy-Breslow intermediates.⁶⁵ Although that means a considerable nucleophilicity will be engendered in the end group formed by such an H-transfer process, the steric demand will most likely block any further reaction of the newly formed NHO structure with other monomer molecules. Species D must therefore be considered as an irreversible termination of the polymerization process due to the comparably high stability of D relative to C (13-14 kcal/mol more stable). This result fits well to the experimental findings. The noticeably narrower molecular weight distribution of the polymer obtained with 4 (Table 2), in the presence of LiCl, might be related to the impossibility to form deactivated enamines with this NHO. Moreover, the higher monomer concentration required to promote polymerization by 3 is in accordance with enamine-formation as termination pathway: the competition between propagation and H-transfer will be shifted towards the chain growth event by increasing the concentration of monomer. One of the advantages of adding LiCl is most likely a partial suppression of this side reaction: the enolate is complexed by Li^+ and thus less prone to engage in acid-base reactions (compare Table 1 and 2).

Finally, the behavior of different acrylic monomers has been investigated (Table 4). For the two methacrylates MMA and tBuMA no meaningful difference in their reactivity is found. Tellingly, in both cases the barrier for the nucleophilic attack of the NHO to the monomer is 16-17 kcal/mol and the spirocycles derived from B are higher in energy than the zwitterion, so that a major effect on the initiation event seems unlikely. Interestingly, no spiro_o intermediate has been localized for tBuMA. Along the propagation pathway, further monomer addition is almost isoenergetic for the two monomers, both in the kinetic barrier (B-C) and in the energy gain upon formation

of C (7 kcal/mol). After the zwitterionic intermediate C is reached, the system can convert into Cspiro_c with a relatively low energy barrier. Differently from the initiation step, where Bspiro_c requires a strained four-membered ring to be formed, the spirocyclic species after the first propagation step is six-membered and turns out to be 6-7 kcal/mol more stable than C.

Moving to MA, this monomer shows a greater propensity to accept addition by an NHO. Among all the investigated monomers, MA displays the lowest activation barrier for this step (11.4 kcal/mol), with zwitterionic B almost at the same energy level of the starting compounds. As for MMA and tBuMA, the initiation event for MA seems not to be affected by spirocycles. MA monomer addition proceeds with a low barrier (9.4 kcal/mol) and C itself is more stable than for any other NHO/monomer combination. However, for this monomer, the formation of Cspiro_c is essentially barrier free and the cyclic structure is about 10 kcal/mol more stable than the propagating species C. The trend in the speed of interconversion between zwitterionic C and its spirocyclic derivative (i.e. $\Delta G^\ddagger = 1.9, 6.7$ and 9.7 kcal/mol for MA, MMA and tBuMA, respectively) nicely mirrors the differences in the experimentally obtained molecular weights for these three monomers with 3 (see Table 3). This result is directly related to the chemical nature of the monomer: the additional methyl group in MMA and tBuMA increases the electron density in the propagating enolate species, which is thereby higher in energy and more reactive.

Finally, DMAA has been considered. It is interesting to note that the barrier for the nucleophilic attack of the NHO (14.4 kcal/mol) lies between the values found for its direct analogue in the acrylate family (MA) and the methacryl monomers. This pattern is repeated for the subsequent steps: B-DMAA is less stable than B-MA, and starting from B the first propagation step is exergonic by 12 kcal/mol, in comparison to 7 kcal/mol for MMA and tBuMA. The latter difference

Figure 5. Fitting of ΔG_{A-B} using the $\%V_{\text{Bur}}$ and the Parr electrophilicity index, ω , of the eight monomers.

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can be ascribed to unfavorable steric interactions caused by the methyl group on the C- α for MMA and tBuMA; likewise, the somewhat reduced reactivity when compared to MA is a consequence of the reduced activation of the double bond by the less electron-withdrawing amide group compared to the ester moiety.

Overall, for all monomers considered in interaction with **3**, the barrier to back-convert the spirocyclic into the zwitterionic propagating species is well comparable with the monomer addition barrier along the polymerization pathway. Hence, in this case (very much unlike for NHO **1**) the spirocycles can be understood to be dormant species, slowing down the polymerization activity but not killing it. Moreover, the formation of cyclic structures is an intramolecular process and propagation will be favored in an environment of high monomer concentration, as was noted above for enamine formation.

The behavior of different acrylic monomers with regard to NHO addition depends on both their electronic and steric properties. However, a reliable quantification is necessary for a meaningful analysis of the actual contribution of both aspects, and for the screening of suitable monomers for future NHO-mediated polymerizations.

The calculated energy terms (Table 4) were correlated with the steric and electronic properties of the four monomers employed in this study. Steric properties were assessed via the buried volume descriptor ($\%V_{\text{Bur}}$,⁶⁶⁻⁶⁷ calculated as the space around the terminal $=\text{CH}_2$ -moiety occupied by the rest of the monomer skeleton), while electrophilicity was determined using the Parr index ω (see SI for details).⁶⁸ Initially, an R^2 of 0.84 has been found for the single linear correlation between $\Delta G_{\text{A-B}}$ and the $\%V_{\text{Bur}}$ for the four monomers considered (see Figure S8). The correlation improved to $R^2=0.99$ once a multilinear regression taking into account both $\%V_{\text{Bur}}$ and ω had been conducted, (Figure S9). From these results it emerges that the steric demand of the monomer, most prominently the presence of a methyl group on C- α , meaningfully affects the energy barriers. For instance, even though MMA and tBuMA are more electrophilic than DMAA (ω values in Table S1), they suffer from an increased steric demand (see also $\%V_{\text{Bur}}$ data, Table S1) and, consequently, a higher barrier must be overcome for successful polymerization. It can also be concluded that MA and DMAA are different solely on account of electronic effects, since $\%V_{\text{Bur}}$ is very similar for both monomers. Even though a very good linear correlation has been obtained, only a broadening of the monomer base will reveal whether the chosen variables are a trustable tool to predict reactivity towards NHO-mediated polymerization. To this extend we investigated four additional monomers, namely *N,N*-dimethylmethacrylamide (DMMAA), methacrylamide (MAM), ethyl acrylate (EA), and α -methylene- γ -butyrolactone (MBL) under aforementioned conditions. A plot of the $\Delta G_{\text{A-B}}$ values versus the fitted $\Delta G_{\text{A-B}}$ ($\%V_{\text{Bur}}$, ω) data reveals a good linear correlation, hence the chosen variables can be considered as effective descriptors for substrate screening (Fig. 5).

Conclusions

In this work, a combined experimental and theoretical approach was employed to elucidate the complex interactions of NHOs and acrylic monomers. It was demonstrated for the first time that, under suitable conditions, NHOs can polymerize acrylic and methacrylic esters as well as acrylamides without further additives in a metal-free manner. The generally uncontrolled reactions can be much improved by addition of LiCl, as was demonstrated for DMAA, from which high-Mw (250 000 – 650 000 g/mol), highly isotactic ($\geq 90\%$ isotactic dyads) material can be prepared in short reaction times (≤ 2 min).

Polymerization experiments have shown that, in order to be successful, the NHO should be imidazolium-derived; in contrast, saturated five- and six-membered compounds as well as benzimidazolium-derivatives did not yield any polymer. DFT calculations suggested that this observation is related to the ability to form an aromatic imidazolium-moiety, which stabilizes the zwitterionic species responsible for chain growth. The occurrence of spirocycles is strongly supported by computational results. Their influence on the polymerization reactivity heavily depends on both monomer and NHO. While in the case of saturated NHOs a terminal deactivation of the polymerization can be assumed, initiation by imidazolium derivatives (**3**, **4**) seems to be much less affected. With the latter, spirocycles can be understood as dormant species which are in equilibrium with growing chains, slowing down the polymerization and potentially broadening the molecular weight distribution.

Enamine formation was identified as a further side reaction. Proceeding via H-transfer, this reaction is favored across the whole range of examined combinations of NHO and monomer. Importantly, this process, which was calculated to be practically irreversible, can efficiently be blocked. Substitution at the exocyclic carbon of the initiator not only removes the chemical lability responsible for enamine generation, but can even increase the propensity of the NHO to initiate polymerization. Experimental results broadly corroborate these findings, with the most controlled polymerizations deriving from application of 2-isopropylidene-1,3,4,5-tetramethylimidazoline (**4**). A $=\text{CH}_2$ -group bearing NHO such as 2-methylene-1,3,4,5-tetramethylimidazoline (**3**) is still able to deliver PDMAA, PMMA, PMA or PtBuMA in considerable yields (30-90%, $M_n = 20\,000 - 300\,000$ g/mol), albeit only when high monomer concentration is employed, a condition which favors chain growth over spirocyclization and enamine formation.

Finally, we were able to show how the overall propensity of an acrylic monomer for NHO addition to form a zwitterionic, growth-initiating species depends on a combination of buried volume (steric demand) and electrophilicity. The developed correlation allows for a convenient prediction of monomer reactivity based on these two parameters.

Overall, the insights won from this work will facilitate the search for an improved generation of NHO-based initiators. Apart from an imidazole as backbone and a substituted exocyclic carbon, especially the targeted destabilization of

spirocyclic resting states seems promising. While the reported organopolymerization of acrylic monomers falls well short in terms of control compared to the more elaborate, state of the art metal-based anionic polymerizations, these results seem to render NHOs a structurally more flexible type of organoinitiator when contrasted with the very special behavior of NHCs.

Conflicts of Interest

There are no conflicts of interest to declare.

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The scope and mechanism of *N*-heterocyclic olefin-initiated polymerizations of acrylic monomers is investigated, including deactivation pathways.

657x495mm (96 x 96 DPI)