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N-Heterocyclic Carbenes as Organocatalysts for Polymerizations: Trends and Frontiers

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This review spotlights current areas of high interest for NHC-based polymerization research. A compact overview about the underlying mechanistic aspects is given, while the main focus is put on more recent developments and emerging new approaches in NHC-mediated polymerization chemistry. Contemporary frontiers in research, such as the preparation of macrocyclic polymers, the polymerization of activated olefins and new types of NHC delivery are discussed and put into perspective. Finally, an outlook is given on where future industrial applications might arise.

Introduction

Polymer chemistry has profited doubly from the rise of *N*-heterocyclic carbenes (NHCs) [1,2] in the last two decades. For one, the discovery of their unique properties as ligands[3] has led to considerable improvements in catalyst design, perhaps best represented by ruthenium-based metathesis catalysts, where the introduction of NHCs enabled a step change in stability and activity.[4] Furthermore, beyond this example, NHC-complexes nowadays play a beneficial role in different types of polymerizations, including controlled radical polymerizations[5] or the oligomerization of ethylene[6] or hexene[7].

A second wave of success came after it had been realized that NHCs are powerful organocatalysts, which is related to their inherent high Brønsted-basicity[8] and nucleophilicity.[9] In combination with their facile preparation and especially their near unlimited structural diversity,[10] this has led to a situation where NHCs are recognized today as some of the most important organocatalysts.[11] In sharp contrast to the specialized organometallic polymerization catalysts and also many other organocatalysts, NHC-mediated polymerizations are characterized by an unparalleled width of applications, which encompass a steadily expanding range of very different monomers, including some of the most commercially important ones. Intensive research continues to adapt NHCs to ever more challenging polymerization setups, and consequently one emphasis of this review is directed at the limits of the current capabilities of NHC-mediated polymerizations. Interestingly, by combining the nucleophilic power of NHCs and Lewis acid activation (*via* co-catalyzing metal ions), dual/cooperative mechanisms have recently emerged.[12] Halfway between “metal-based” and purely organocatalytic reactions, this type of polymerization has been shown to frequently result in dramatically increased rates of monomer consumption. This third way of NHC-dependent polymerizations, which is closely connected to the chemistry of frustrated Lewis pairs,[13] thus adds another attractive alternative for future development. The present review, however, will deal exclusively with metal-free examples and is dedicated to pure organocatalysis only. Indeed, the ability of NHC-mediated polymerizations to provide polymer free of metal-based residues is another advantage that weighs especially heavily for health-related applications, but is also beneficial in view of the cost of precious or rare metals and might increase the competitiveness of NHCs for large-scale production.

Despite its recent emergence, NHC organopolymerization can already be seen as a well established method with a number of monomers. A detailed review on this matter has been published in early 2013;[14] consequently, only a very condensed overview will be given in the following, concentrating on the mechanistic aspects in order to provide a background for understanding the recent advances in this area. Subsequently, newly emerged polymerizations, namely the direct polymerization of acrylates, lactams, and the preparation of duroplastics will be discussed. Finally, the third part of this review will present frontiers in NHC organocatalysis research, including the preparation of cyclic polymers, NHC delivery, a first glimpse on future NHC-mediated polymerization of (activated) olefins and the current state of patent literature. In

Figure 1, some of the catalysts that will be discussed in this paper are depicted. In order to avoid a somewhat cumbersome nomenclature, the NHCs are abbreviated by a sequence consisting of ring size and substituents. Though the most frequently used NHCs, *e.g.*, imidazol-2-ylidenes, imidazolin-2-ylidenes, triazol-5-ylidenes, thiazol-2-ylidenes and tetrahydropyrimidin-2-ylidenes, will be met in this review, it must be kept in mind that the structural diversity of NHCs is much larger than that, including for example diamidocarbenes[15] or alkyl(amino)carbenes,[16] not to speak of so-called mesoionic, abnormal or remote NHCs.[17] Finally, for the sake of simplicity, the NHCs in this work usually are referred to as catalysts, though in some instances initiator (or even pre-initiator) would be the more accurate term.

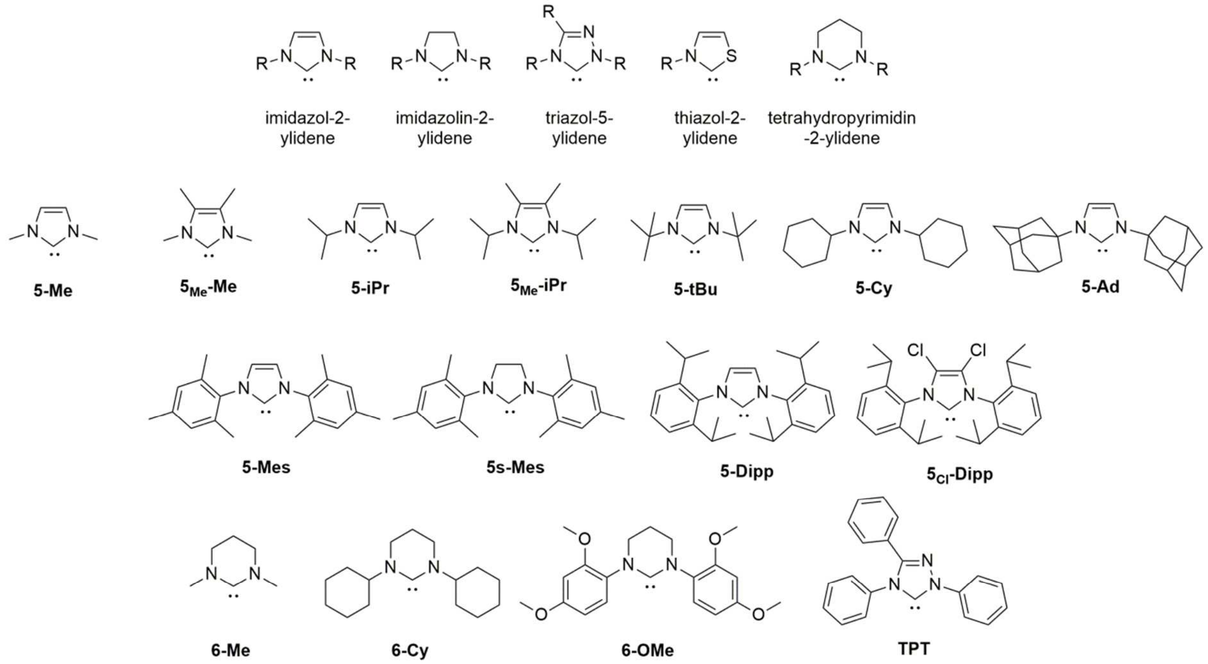


Figure 1. The most common types of NHCs (top) and structures of catalysts discussed in this paper. TPT = 1,3,4-Triphenyl-triazol-5-ylidene.

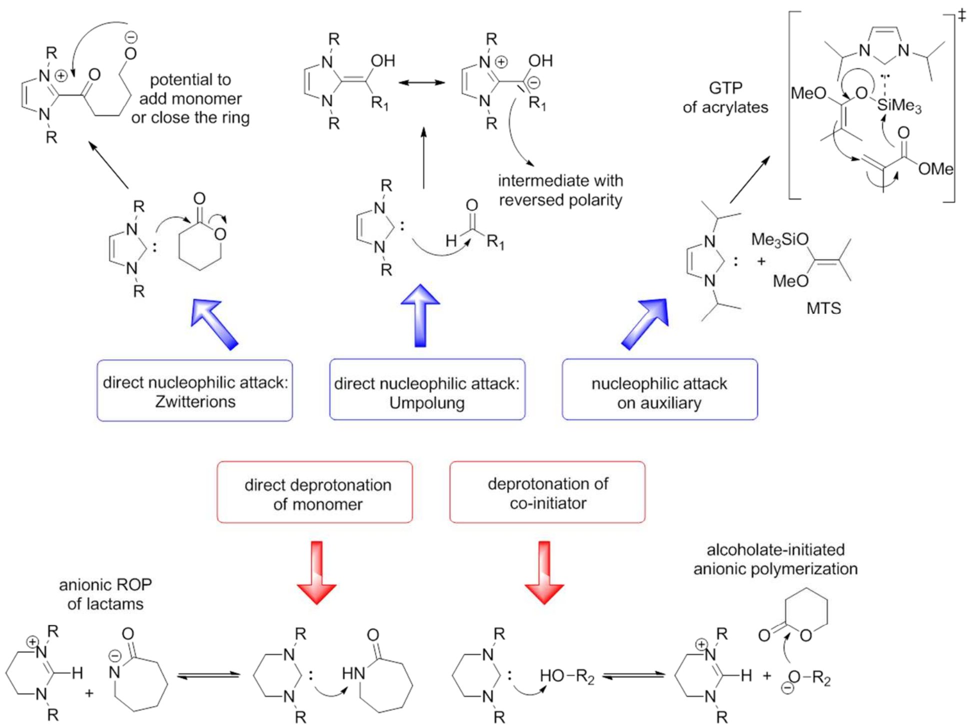
Fundamental mechanisms of NHC organopolymerizations

In principle, NHCs can be exploited in two ways to achieve the polymerization of suitable monomers: mechanisms can be based on nucleophilicity or (Brønsted-)basicity. These can be further subdivided into cases where direct attack on monomer occurs and cases where an auxiliary substance or co-initiator forms the active species after reacting with the NHC (Scheme 1).

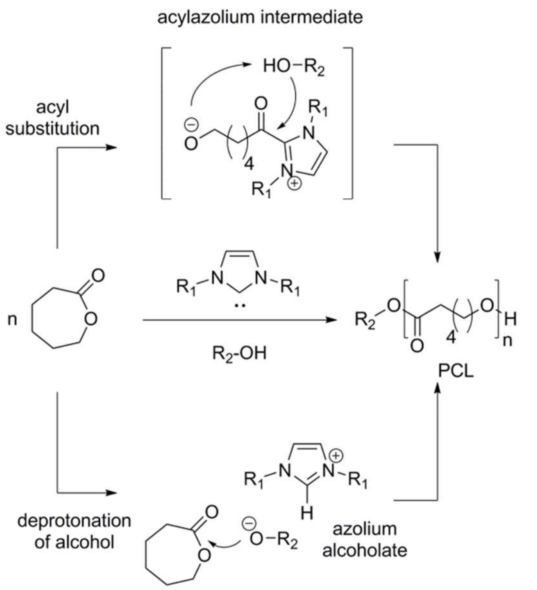
Direct nucleophilic attack on neutral monomer usually results in the formation of a zwitterionic species. These are very important intermediates which have, among other advantages, the potential to form macrocyclic polymers. For example, zwitterions have been proposed for NHC-mediated polymerizations of cyclic esters[18,19] and epoxides,[20] but also for methyl methacrylate (MMA).[21] Alternatively, nucleophilic addition may result in an Umpolung reaction as described first by Breslow.[22] This latter type of reactivity is already widespread in organic synthesis but less so in polymer chemistry, yet it has been applied to prepare polyketones and "polybenzoines".[23,24] Nucleophilic interaction of an NHC with an auxiliary is found in the Group Transfer Polymerization (GTP) of acrylates. This method, independently developed by Taton and Gnanou[25] as well as Waymouth and Hedrick,[26] relies on the formation of hypervalent silicon as a result from the coordination of the NHC on a Si-based transfer agent like 1-methoxy-1-[(trimethylsilyl)oxy]prop-1-ene (MTS, Scheme 1).

NHCs can also act as a base and directly abstract a proton from the monomer. This mechanism of action has been recently disclosed for the anionic polymerization of lactams to form the corresponding polyamides.[27] Similarly, for step-growth polymerization to synthesize polyurethanes[28] and polydimethylsiloxanes[29] from monomers containing –OH functionalities, the NHC was proposed to activate the hydroxyl group by deprotonation or at least bonding to the proton, hence increasing the negative charge on the oxygen and consequently its propensity to undertake nucleophilic attack. Finally, NHCs can deprotonate co-initiators, which then in turn are enabled to start anionic polymerizations (with the protonated NHC as non-innocent counter ion). This situation is especially important for alcoholic co-initiators, which are present in numerous published examples of NHC organopolymerization, but has also been proposed for an incident of MMA polymerization using DMSO as the acidic compound.[30] To date, the complex interactions of alcohols and NHCs in the presence of monomers like cyclic esters are not fully rationalized and the precise reaction mechanisms in a situation where the carbene can potentially both act as a nucleophile (attack on monomer, ring-opening) or base (attack on co-initiator, deprotonation) are still under debate and complicated further by the possibility of adduct formation (Scheme 2).[31,32]

Perhaps the most iconic of NHC-based organopolymerizations is the ring-opening polymerization (ROP) of cyclic esters. First described in 2002,[18] in parallel to findings that NHCs are excellent transesterification agents,[33] it soon became obvious that various cyclic esters could be converted to polymer in high yields and with good control over molecular weight and weight distributions. Extensive studies on the impact of structural changes within the NHC catalysts on their polymerization performance finally led to the formulation of a polymerization mechanism that included the ring-opening of the monomer upon nucleophilic attack by the NHC to form a zwitterionic intermediate (Scheme 3).[19,34] This intermediate is highly activated for nucleophilic substitution, and subsequently captured by the excipient alcohol to liberate the NHC anew alongside the formation of an extended alcohol. Obviously, the ring-opening of the monomer must be much preferred for a sterically not hindered, electron-rich NHC such as **5-Me**. The



Scheme 1. General mechanisms found in NHC-mediated organopolymerizations.



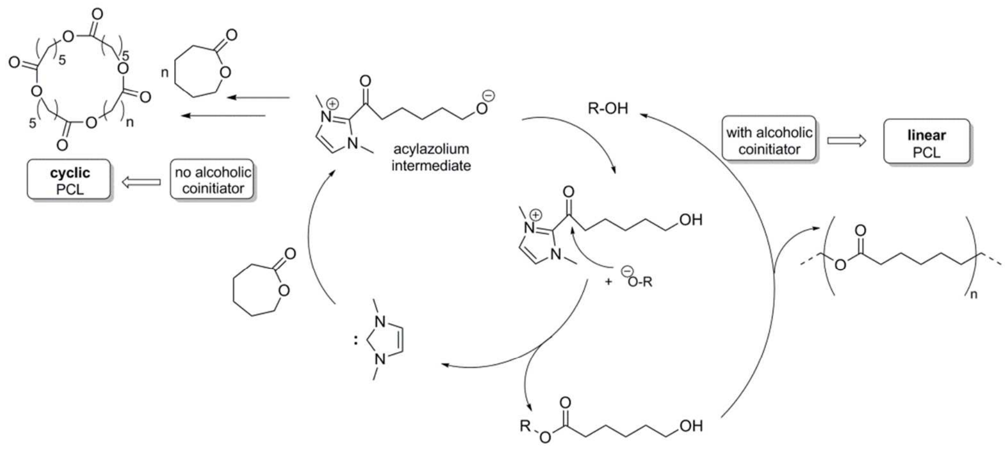
Scheme 2. Competing „nucleophilic“ and „basic“ pathways for the NHC-catalyzed preparation of poly(ε-caprolactone) (PCL) [14,37].

proposed mechanism is thus in good agreement with experimental findings and was recently supported in a study by Buchmeiser and co-workers, who showed that an incremental increase of the size of the *N*-substituent (**5-iPr**, **5-Cy**, **5-tBu**, **5-Ad**) is connected with a stepwise deterioration of the polymerization activity.[35] Direct support for the prevalence of zwitterionic species in this type of polymerization is found in the fact that in the absence of co-initiator cyclic polymer is formed.[36] As no alcohol captures the acylazolium species, which contains a carbonyl carbon with strong positive polarization, it becomes possible for the oxoanionic chain end to substitute the NHC, forming cyclic structures. Despite these findings, it has been argued that it in the presence of –OH functionalities, it might be energetically more favourable for the NHC to deprotonate the alcohol to yield alcoholates, which are well able to start polymerization of lactones (Scheme 2).[37] This potential competition between "nucleophilic" and "Brønsted-basic" mechanisms in one and the same polymerization setup has been discussed for a number of cases, including cyclic esters,[11d,35] epoxides,[20] siloxanes[38,39] or even acrylates.[30]

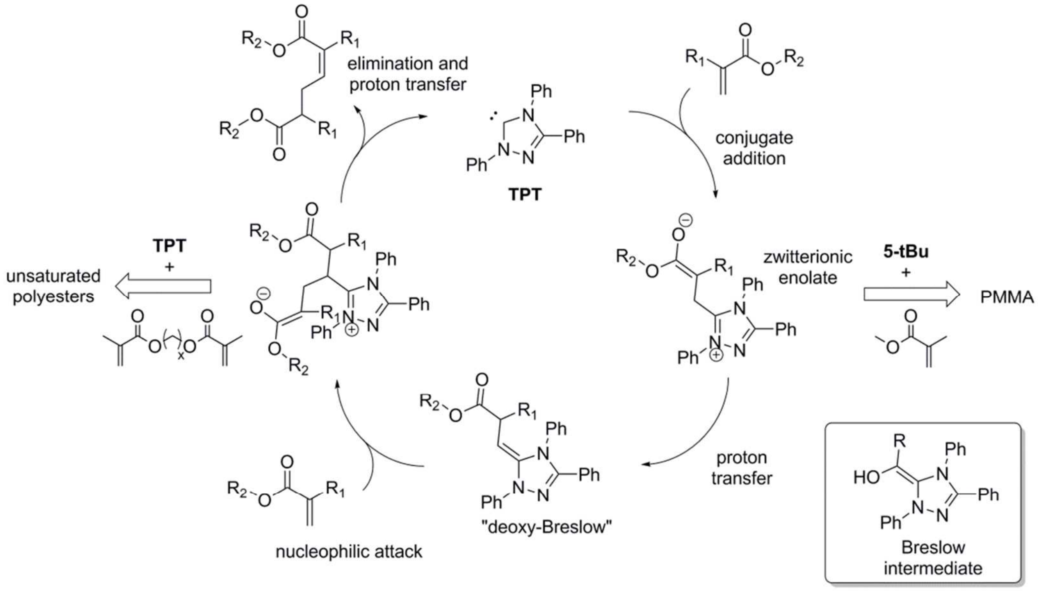
While it is as yet not fully clear which mechanism is dominant in a given case, it seems reasonable to assume that the chemical structure of the NHC plays a decisive role. Indeed there is evidence that the six-membered tetrahydropyrimidin-2-ylidenes, which are about 10^7 stronger bases than their five-membered counter parts,8 act preferentially in the "basic" mode.[35] This suggests that NHCs are capable to access both pathways of this mechanistic dualism, while the extent of each is governed mainly by parameters like NHC structure, acidity of the co-initiator and solvent polarity. Importantly, it was also found that a strongly basic abnormal NHC can even outperform the more commonly used NHCs in the ROP of lactones.[40]

New types of polymerizations using NHCs

The addition of NHCs to double bonds is of high interest both in organic as well as polymer chemistry. Unlike the ROP of heterocyclic compounds, advances in this area were only recently made, based on insights from organic chemistry.[11,14] Addition of nucleophiles to double bonds is much facilitated in the presence of activating conjugation and electron-withdrawing groups, so not



Scheme 3. Polymerization of ε-CL with co-initiator according to [19], and the formation of macrocycles in the absence of alcohols [36].



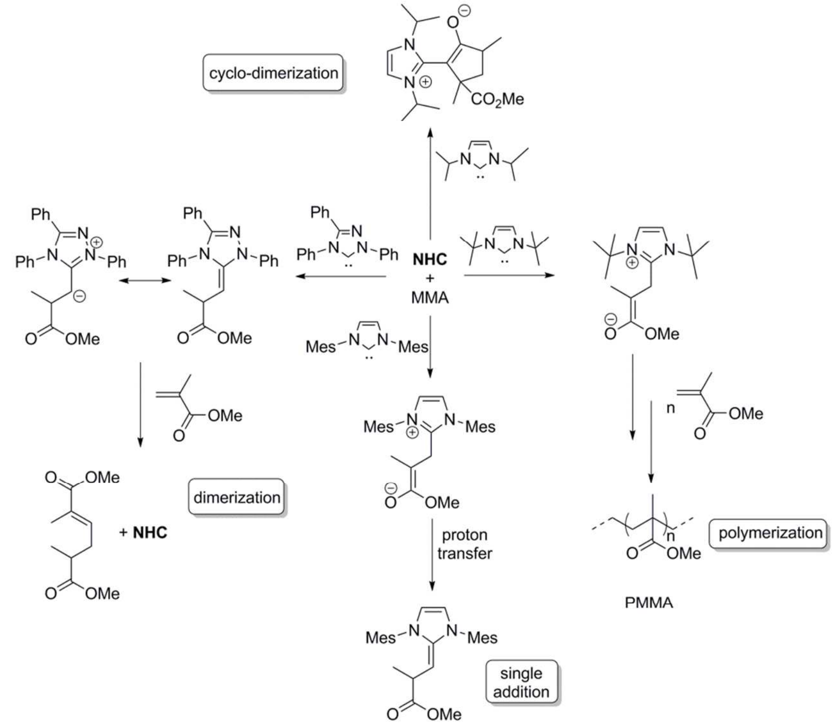
Scheme 4. Tail-to-tail dimerization according to Matsuoka and Glorius (centre) [42] and two ways to use key steps of this mechanism for polymerization-enabling systems [21,43].

surprisingly the first examples of NHC conjugate addition were reported on Michael acceptor systems such as **α,β-unsaturated esters**.[41]

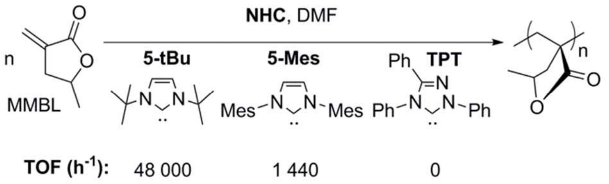
TPT (Figure 1), a very suitable agent to bring about umpolung reactions, was later exploited by Glorius and Matsuoka to dimerize MMA.[42] The proposed mechanism (Scheme 4) crucially involves 1,4-conjugate addition of the NHC to the monomer to form a zwitterionic enolate, which undergoes H-transfer to yield a so-called "deoxy-Breslow" intermediate. This compound is nucleophilic enough to subsequently attack a second molecule of MMA to yield the dimerized product and set the NHC free after elimination.

This process obviously does not enable polymerization, however, intelligent manipulation of the setup allows to render this system fit for polymerization in at least two ways, both of which were recently employed by Chen.[21,43] Firstly, one possibility is to conserve the zwitterionic species, which contains the crucial enolate moiety needed for propagation and polymerization. To do this, H-transfer and subsequent formation of deoxy-Breslow intermediates must be suppressed. One method by which to realize this was found by Chen and coworkers in 2012, who showed that by moving from **TPT** to **5-tBu** rapid polymerization of γ-methyl-α-methylene-γ-butyrolactone (MMBL, Scheme 6) could be achieved.[21]

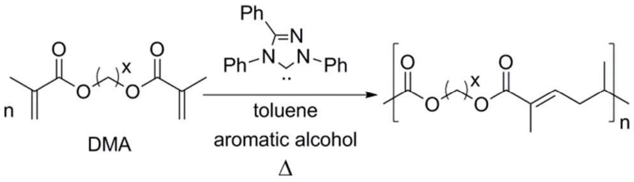
Consistently, **TPT** fails under these conditions and does not yield polymer. While MMBL is very reactive, the commercially much more important MMA is less so. Here, the application of **5-tBu** resulted in a much slower reaction. Three hours reaction in DMF at room temperature resulted in yields around 80% with much reduced TOFs of 50-150 h^{-1}, compared to MMBL. Molecular weights of more than 30 000 $g.mol^{-1}$ were realized this way with a $Đ_M$ of 2. **5-Mes** and **TPT** proved to be inactive under these conditions, hinting at a very strong susceptibility of this type of polymerization on the chemical structure of the NHC initiator. This was supported by the extensive study of



Scheme 5. Reactivity of NHCs **5-iPr**, **5-tBu**, **5-Mes** and **TPT** towards MMA [21,42,44].



Scheme 6. Polymerization of MMBL using different NHCs [21].



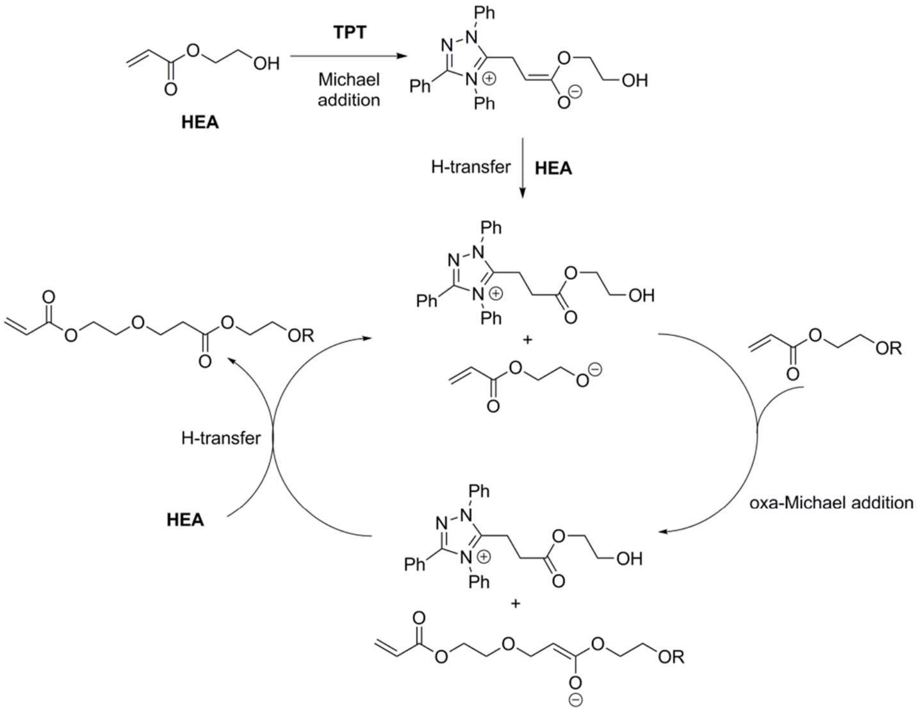
Scheme 7. NHC catalyzed HTP-process to yield unsaturated polyester [43].

Buchmeiser and co-workers, who employed 13 different NHC-CO_2 adducts in an attempt to map out a correlation of structure and activity in the polymerization of MMA.[30] Strikingly, only **5-tBu-CO_2** was found to be active in the direct, zwitterionic polymerization. Notably the reactions were successful not only in the presence of highly polar DMF, but also in toluene and in bulk, where very high molecular weights were generated. Interestingly, all six-membered NHCs failed in the direct polymerization, but led to PMMA in the presence of DMSO, most probably by deprotonating solvent molecules, which then started a more typical anionic polymerization.

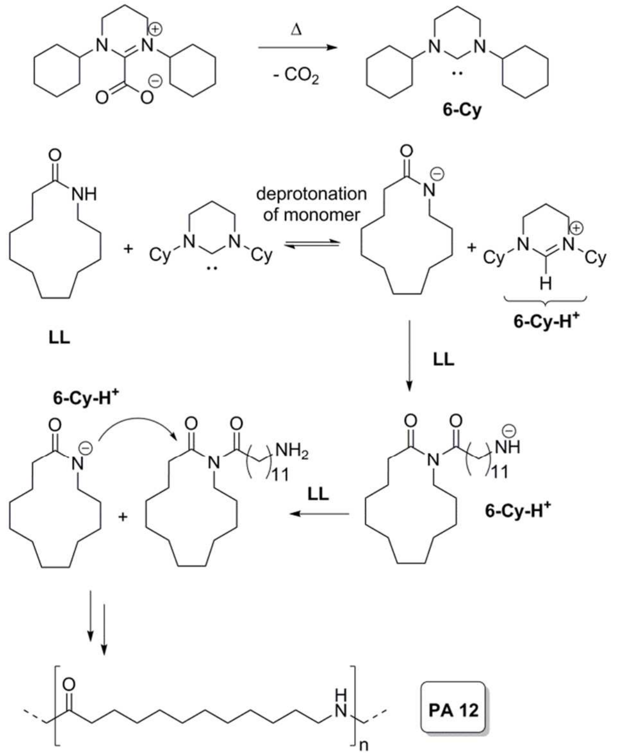
Taton *et al.* recently underlined those findings by showing that a very small change of the NHC structure, from **5-tBu** to **5-iPr**, completely quenched the polymerization activity and resulted in cyclodimerized product instead,[44] while Chen had shown earlier that **5-Mes** undergoes only a single addition.[21] These surprisingly sensitive relations (Scheme 5) have also been subject of theorectical considerations.[44,45] It should be noted that this polymerization *via* conjugate addition of the NHC is completely different from the GTP approach, yet NHCs can be successfully adapted to both very different requirements. It should be stressed, however, that the high degree of control over molecular weights that can be realized with the NHC-based GTP process has not yet been achieved in the direct polymerization *via* conjugate addition. Furthermore, it is instructive to consider recent work by Bertrand and co-workers, where it was clearly outlined that the typical NHCs that are used for polymerization reactions actually represent only a limited part of the full bandwidth of reactivity that can be realized with NHCs.[46] *Electrophilic* NHCs were shown to behave in a completely different manner from the well-known imidazol-2-ylidenes when combined with methyl acrylate, though no polymerizations were reported so far.[46]

A second way of expanding the MMA dimerization mechanism (Scheme 4) for polymerizations is to exploit the apparent weakness of **TPT**-based systems, *e.g.* the favored formation of Breslow intermediates followed by dimerization, as an actual means to couple monomer in a step-growth polymerization.[43] Using dimethacrylates (DMA) in toluene with 5 mol% of **TPT** and traces of radical scavengers (4-methoxyphenol or catechol) at 80 °C, unsaturated polyester was produced with M_w =17 600 g.mol^{-1} and $Đ_M$ of 1.9. The polymerization consists of repeated cycles of conjugate addition, H-transfer and NHC-release and was thus coined as proton transfer polymerization (HTP, Scheme 7). Importantly it was noted that the addition of aromatic alcohols not only suppressed the undesired radical vinyl polymerization, but also increased activity of the whole process (more than tenfold). The thus created unsaturated polyester was also subjected to cross-linking reactions.

In a further demonstration of acrylate polymerization by



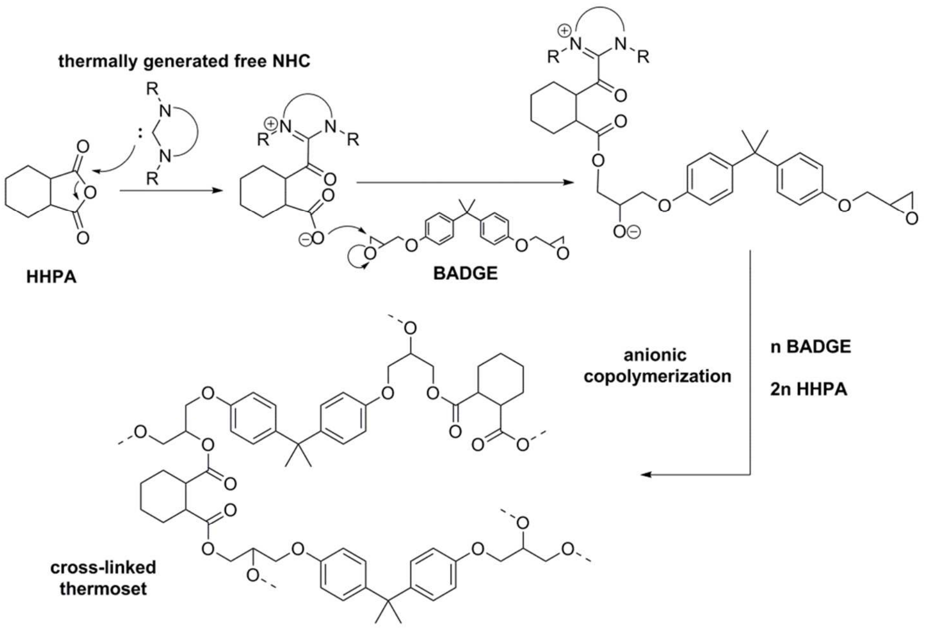
Scheme 8. Proposed mechanism for the NHC-mediated oxa-Michael addition polymerization according to Matsuoka [47].



Scheme 9. Anionic polymerization of lactams using NHCs as thermally liberated bases [48]. Laurolactam = LL.

NHCs, Matsuoka and co-workers reported the first NHC-mediated oxa-Michael addition polymerization of hydroxyl functionalized acrylate monomers.[47] Application of **TPT** or **5-Dipp** to monomers like 2-hydroxyethyl acrylate (HEA, Scheme 8) resulted in poly(ester-ether)s after 24 h at room temperature. By using appropriate monomers it was also possible to introduce functional groups in the polymer main chain, like alkyne or cycloalkane moieties. The proposed mechanism favors addition of the NHC to the activated double bond, with subsequent quenching of the zwitterionic enolate by the hydroxyl group of another monomer molecule. The thus created alcoholate adds to another double bond (oxa-Michael addition) and is protonated in turn. In this scenario, the NHC acts as initiator by forming Lewis basic intermediates, rather than directly activating the alcohol functionalities. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) experiments have been cited to support this mechanism.[47] Although the polymerization is relatively slow and requires high NHC loadings to give moderate yields (up to 81%) and molecular weights (500-2 500 g.mol^{-1}), the ability of this process to work at room temperature is clearly advantageous in comparison with other catalysts that require heat and can thus entail undesired cross-linking reactions.

Another new development is found in the polymerization of lactams to the corresponding poly(amide)s (PA) using NHCs as initiators. Buchmeiser and co-workers have investigated the bulk polymerization of ε-caprolactam[27] and laurolactam[48] to PA 6 and PA 12, respectively. Using a variety of NHC-CO$_2$ adducts at temperatures of 180-220 °C it was found that the NHC structure exerts a decisive influence. While most commonly used NHCs like **5-Mes**, **5-iPr** or **5-Cy** delivered little or no polymer, the much more Brønsted-basic six membered NHCs allowed higher or even quantitative yields of polymer. For example, using the CO$_2$-adduct of **6-Cy** in only 0.3 mol% loading at 180 °C resulted in quantitative isolated yields of PA 12. A clear correlation between basicity of the NHCs and their activity was observed, strongly suggesting that the polymerization operates by an anionic mechanism (Scheme 9). This was supported by observation of induction periods and degradation of the molecular weight of the polymer over time (“chain-multiplication”). Both



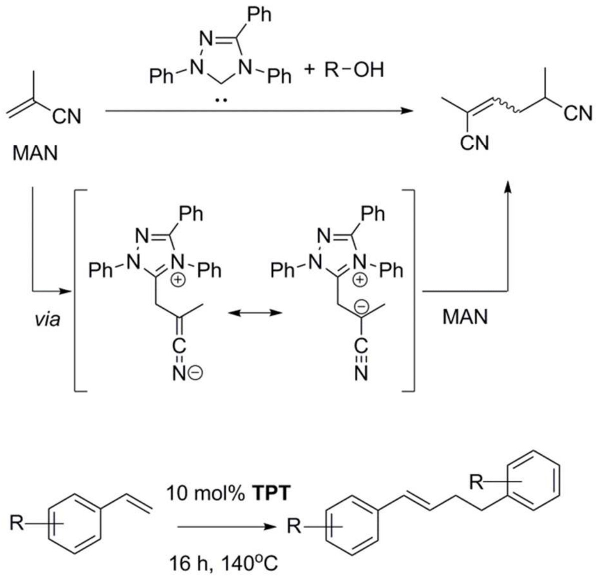
Scheme 10. Proposed mechanism for NHC-induced hardening of epoxy/anhydride resins [49].

findings are typical for the anionic polymerization of lactams. Notably, in the case of lactam polymerization a "nucleophilic" pathway (ring-opening by action of the NHC as found for various lactone polymerizations) is not possible. Consequently, the NHC can only act as Brønsted-base and the six-membered tetrahydropyrimidin-derivatives prevail over their five-membered counterparts. Using this technique, ε-caprolactam and laurolactam have also been copolymerized.[48] Furthermore, the application of CO_2-protected NHCs allowed for the preparation of thermally latent, ready-to-polymerize one component mixtures, which were found to be stable over months without premature reaction starting. This metal-free method represents the first single-component access *via* anionic polymerization to the commercially important poly(amide)s and again nicely illustrates the versatility of NHC-based polymerization systems.

NHC catalysis has also been extended to the curing chemistry of epoxy resins, which constitute a hugely important class of duroplastic materials.[49] One of the incentives for using NHCs in this type of polymerization is that they are inherently superior to any other commonly used catalysts (typically tertiary amines or imidazoles, referred to as "accelerators") by means of nucleophilicity and basicity. In addition, their ability to be generated from thermally latent precursors[32] presents an advantage for their use in an environment where premature setting must be prevented, while at the same time fast curing must occur once the reaction is triggered.[50] Consistent with above reasoning, it was found that protected NHCs (including CO_2 adducts) are well suited for the thermal curing of epoxy resins, using anhydrides as hardeners.[49] Notably, out of 12 NHC-precursors studied, it was found that all were able to effect a complete curing at 160 °C, while the rate of polymerization was easily modulated by the chemical structure of the NHC. Thus, the stability of the carbon dioxide adducts was identified as convenient lever to regulate the reactivity of the protected NHC. For example, by reducing the steric pressure on the CO_2-moiety (*e.g.*, going from **6-Cy** to **6-Me**) the curing exotherm was successfully shifted towards higher temperature. The fastest polymerization was achieved using the *in-situ* liberated electron-rich **6-OMe**, displaying a conversion of 94% after 4 minutes of heating to reach a fully cured state shortly after. Importantly, mixtures based on bisphenol A diglycidylether (BADGE), hexahydrophthalic anhydride (HHPA) and protected NHC were fully homogeneous and remained free-flowing for days or weeks at room temperature. These considerable pot-times were modulated by precursor stability in a similar manner. The single component-mixtures can be handled and stored under air and do not require special precautions; likewise, non-purified commercial educts can be used at low NHC loadings (0.1-1.0% relative to BADGE), underlining the practical potential of this kind of NHC catalysis. The robustness and tolerance of the system with regard to the NHC structure was interpreted to suggest initial attack of the carbene on anhydride moieties instead of on epoxy groups (Scheme 10).

Frontiers in NHC-Organopolymerization

In contrast to the ROP of heteroatom containing cyclic monomers, which is readily realized using NHCs, the polymerization of other types of monomers is still rare; especially the direct interaction with double-bond containing molecules is not yet well developed. As described previously, the GTP approach can be applied to polymerize acrylates and closely related monomers. On the other hand, the direct polymerization *via* conjugate addition has succeeded only in a limited number of cases and the challenge remains to gain full control over the polymerization process. However, a closer understanding of the mechanisms involved seems rewarding as this might allow to extend the scope of NHC organopolymerization even further, for example towards **(activated) olefins**. Indeed organic chemistry is already preparing the ground for this. Matsuoka and co-workers have recently reported on the tail-to-tail dimerization of methacrylonitrile (MAN), using **TPT** in combination with



Scheme 11. Tail-to-tail dimerization of MAN according to Matsuoka [51] and Glorius‘ homodimerization of activated styrenes [53]. R = electron-withdrawing group.

alcohols (Scheme 11).[51]

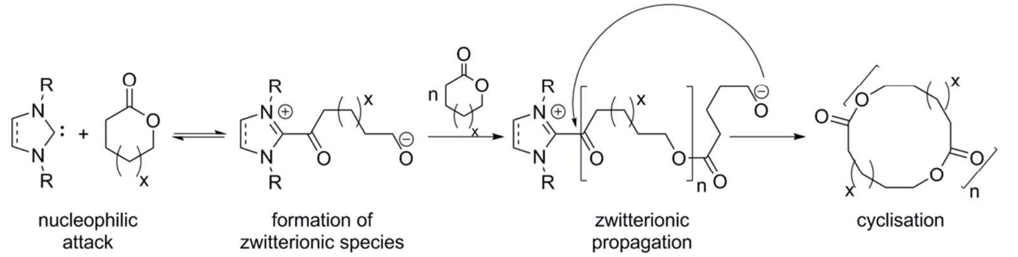
While in this case NHCs were reported to be not effective when applied in the absence of alcohols, it has been proposed that the latter promote intermolecular proton transfer und thus enhance the catalytic turnover. Extensive studies showed that the first addition of the NHC to MAN proceeds swiftly. Potentially this zwitterionic intermediate could be exploited for polymerization, analogously to the situation found with methyl methacrylate (see Scheme 4), and notably patent literature exists where the NHC-mediated polymerization of acrylonitrile (AN) is claimed.[52] There, **5-tBu** is added to AN in toluene to yield polymer of more than 200 repeating units.

Very important in this regard is also recent work by Glorius *et al.*, who investigated the addition of NHCs to styrene and derivatives.[53] Isolation and characterization of mono-adducts of the deoxy-Breslow type was possible when styrene or *p*-cyanostyrene were combined with **TPT**, highlighting for the first time that NHCs can add to non-activated double-bonds as present in styrene. Under optimized conditions the catalytic tail-to-tail dimerization of electron-poor styrene derivatives succeeded, albeit with harsh conditions and high catalyst loadings required (Scheme 11). Polymerizations have not been reported so far, but future breakthroughs can be expected.

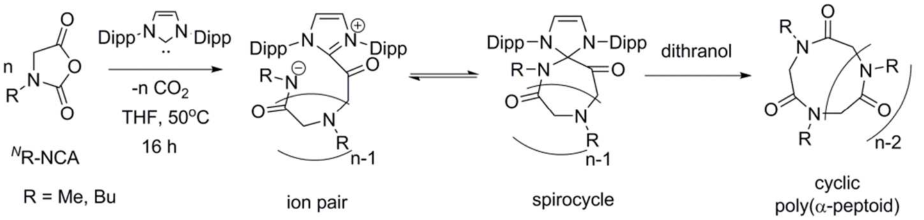
Another focus of recent research activities is directed at the preparation of **macrocyclic polymers**. Though a variety of synthetic strategies exists to gain access to this polymer topology,[54] purification and characterization remain very challenging and new approaches are constantly sought for. In this regard, NHCs have already had considerable impact in this field by virtue of their pronounced propensity to form zwitterionic species. Indeed, especially the zwitterionic ring-opening polymerization (ZROP) has emerged as a powerful tool to construct cyclic polymers of high molecular weight (Scheme 12).[55]

It is beyond the scope of this review to discuss all the difficulties that can thwart attempts at preparation, purification and characterization of cyclic macromolecules, yet some of the main challenges that have to be overcome are the formation of linear impurities as side products, the entropically disfavored ring closure and the need to use lowly concentrated solutions of monomer. Some of these difficulties can be circumvented or attenuated using NHC-based ZROP methods. The synthesis of cyclic α-peptoids is a well-established example for the advantages that can be gained this way. This intriguing example for successful ROP by application of NHCs employs *N*-carboxyanhydrides (^{N}R-NCA) to afford very well defined cyclic poly(α-peptoids).[56] Zhang and co-workers used **5-Dipp** in combination with monomers like ^{N}Bu-NCA or ^{N}Me-NCA in THF at 50 °C (Scheme 13) and demonstrated quasi-living behavior for the polymerization process which enabled the preparation of macrocyclic polymers of molecular weights ranging from 3 000 – 40 000 g.mol^{-1}, all the time maintaining low dispersities (1.04-1.12). The beneficial characteristics of this system are partly due to the release of CO_2 during polymerization, which not only presents a powerful driving force but also renders the monomer structure different from the constitution of the polymer backbone. The latter consists of amide links, which are not attacked by free NHCs, in contrast to the much more reactive anhydride monomers. Secondly, the propagating anionic chain end is “captured” by the positively charged imidazolium terminus, forming ion pairs and spirocycles in an equilibrium. This key feature reduces the concentration of potentially side-reaction inducing moieties and is most probably also responsible for the relatively high initial monomer concentrations (0.4-0.8 M) which can be applied to still deliver high-purity macrocycles.

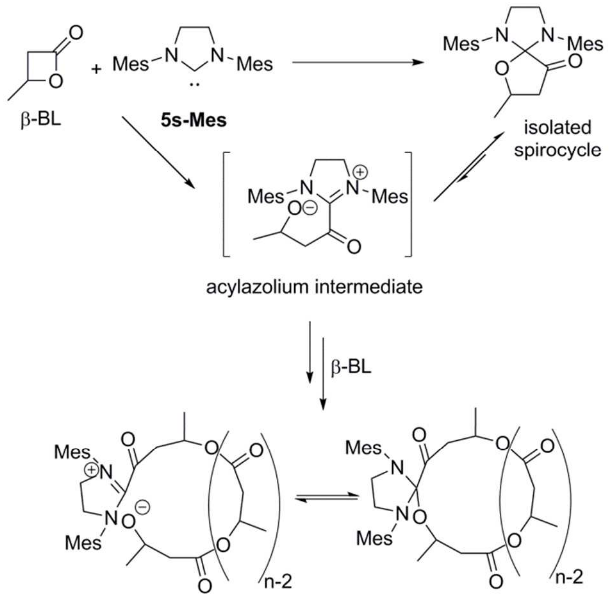
Importantly, this mechanism suggests that NHCs not only initiate the polymerization but also influence the rate of propagation by their action as counter ions. A systematic study employing several NHCs of varying steric congestion and electronic properties highlighted this impact, with a clear correlation occurring between the size of the *N*-substituents and



Scheme 12. Schematic representation of the principal steps of NHC-based ZROP processes using lactones as example.



Scheme 13. Polymerization of ^{N}R-NCA according to Zhang [56,57]. The NHC group can be cleaved off from the spirocycle using suitable MALDI-ToF matrices.



Scheme 14. Formation of cyclic poly(β-BL) using **5s-Mes** *via* spirocyclic intermediates [62].

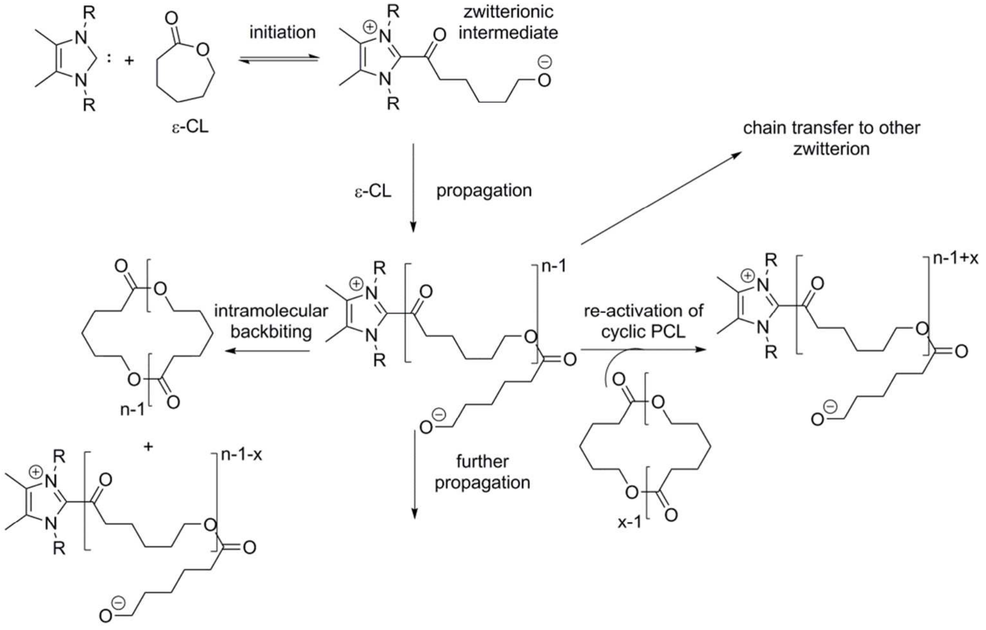
the rates of monomer consumption.[57] Small moieties proved to effect the fastest polymerization, perhaps caused by a lesser steric "shielding" of the ion pair (k_{obs} (**5-iPr**) ≈ 15xk_{obs} (**5-tBu**)). Interestingly, electron withdrawing groups (as present in **5_{Cl}-Dipp**) also accelerated the polymerization, though on a smaller scale.

Fitting to the proposed mechanism (Scheme 13), reactions in strongly polar solvents (DMSO, DMF) lost their well-controlled character by solvation and separation of the ion pairs. Notably, it was also possible to create linear polymers by capping with electrophiles.[57] NHC-mediation was also used for the synthesis of cyclic brush-like macromolecules[58] and amphiphilic cyclic diblock copolypeptoids.[59] Apart from the negligible formation of linear polymer, the key property is the close contact of the cationic chain end and the propagating anionic terminus (including proper bonding in a spirocyclic resting state). Side reactions and scrambling of molecular weight are suppressed, enabling the use of relatively high concentrations. At the same time, the ionic interactions might counterbalance for the entropically disfavored step of closing the macrocycle. Considerable efforts have thus been made to exploit these beneficial traits for other types of polymers.

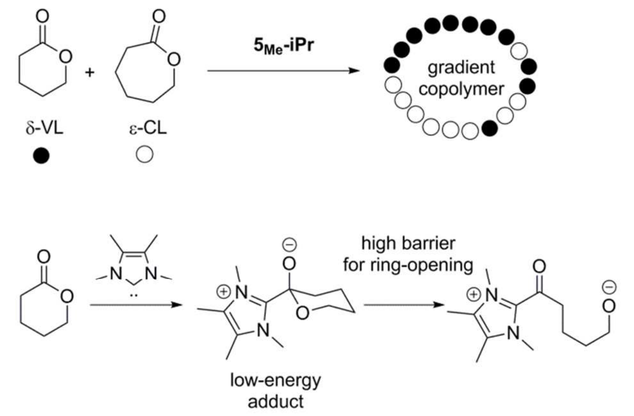
Notably, even before NHCs were used to prepare cyclic α-peptoids, it was found that lactide (LA) can efficiently and rapidly be polymerized to yield macrocyclic polyester.[60,61] In the absence of alcohols, **5-Mes** was used in THF at room temperature to yield cyclics with M_n up to 30 000 g.mol^{-1}. The dispersity remained < 1.35, underlining the well defined manner of the polymerization. The turnover frequencies proved to be high, with yields determined by 1H-NMR to reach 85% after only 24 seconds (NHC/LA = 1/100). Extensive kinetic studies clarified details of the polymerization process.[61] Though the molecular weight of the cyclic polyester grows with growing monomer consumption and the PDI remains small, the polymerization is not fully living. M_n was observed to routinely exceed the theoretical expectations, which was attributed to a slow initiation step (nucleophilic ring-opening to form the zwitterionic species) in combination with swift propagation. Ring-closure, albeit slow, sets an upper limit for the molecular weights. Interestingly, a second-order dependence of the initiation step on [M] keeps the molecular weight distributions narrow, as the NHCs regenerated after cyclisation find themselves in an environment depleted of monomer and are consequently unlikely to initiate growth of another cyclic polymer. Side reactions can occur, mainly inter- or intramolecular backbiting, as evidenced by MALDI-ToF experiments displaying odd- and even-numbered macrocycles.[60]

In contrast to the results obtained from LA polymerization, initiation was found to be fast and quantitative in case of **5s-Mes**-catalyzed ZROP of β-butyrolactone (β-BL).[62] A spirocyclic adduct was isolated, giving rise to a proposed polymerization mechanism similar to the one for ^{N}R-NCA (Scheme 13 and 14), and similarly molecular weights increase linearly with conversion, matching the initial ratios of monomer and NHC. These characteristics underline the positive influence of spirocyclic resting states to minimize side reactions and molecular weight scrambling.

Quite differently, the polymerization of ε-CL (absence of alcoholic initiators) by the action of **5_{Me}-Me** or **5_{Me}-iPr** yielded very high molecular weights, up to 114 000 g/mol^{-1}, which corresponds to a DP of 1000.[36] NHC **5-Mes** did fail to deliver PCL, contrasting its usefulness in the polymerization of lactide, but in line with earlier results suggesting that sterically encumbered catalysts are unsuitable for the polymerization of ε-CL.[34] The high molecular weights were again connected with low initiation efficiency, mirroring the attenuated reactivity of ε-CL compared to the very strained β-BL. Interestingly, recent kinetic modeling investigations have deepened the understanding of the process.[63] The best fit was achieved for a model taking into account the occurrence of transfer reactions, both intra- and intermolecular (Scheme 15). Especially the reactivation of cyclic PCL by a chain transfer reaction and subsequent re-cyclisation seems to be responsible for the very high molecular weights



Scheme 15. Proposed model for the polymerization of ε-CL by the action of NHCs to yield macrocyclic PCL [63].

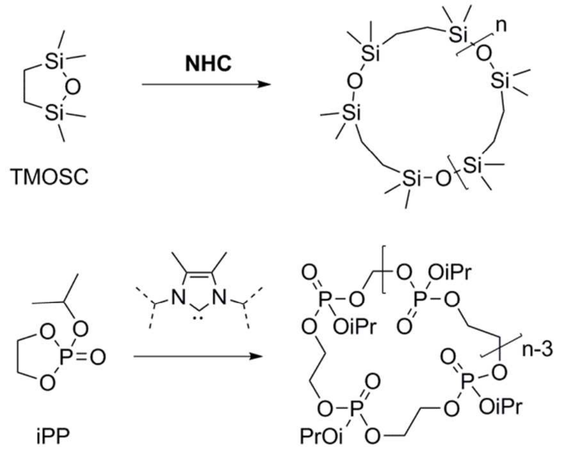


Scheme 16. Synthesis of cyclic gradient block copolymer from lactones (top, [64]) and disfavored ring-opening of a δ-VL-NHC adduct (bottom, [65]).

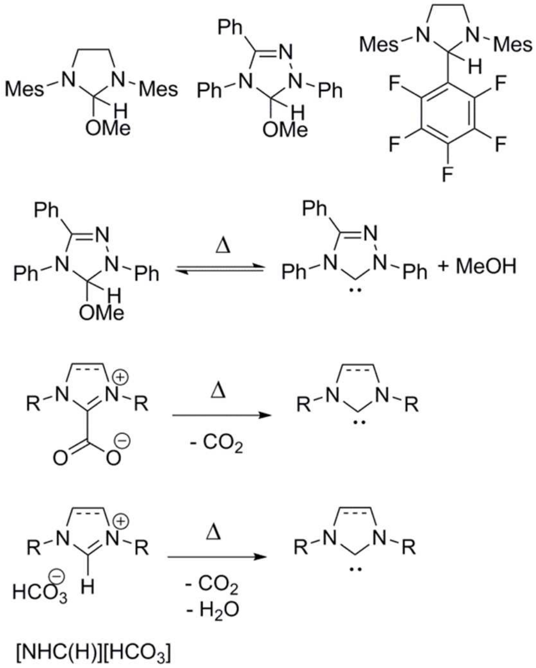
achieved in these polymerizations. It also explains the growing $Đ_{\mathrm{M}}$ values at high conversions.

Overall the system comprises a slow initiation, rapid propagation and several transfer reactions. The latter precluded the preparation of cyclic block copolymers, but the synthesis of macrocyclic gradient copolymers was successful, exploiting the higher propensity of δ-valerolactone (δ-VL) for enchainment relative to ε-CL.[64] Recent DFT studies on the NHC-mediated homopolymerization of δ-VL found that the highest activation barrier in the whole process is located at the ring-opening of the tetrahedral intermediate resulting from nucleophilic attack of the NHC on the carbonyl moiety of the monomer (Scheme 16).[65] The ring-opening requires the development of a partial positive charge (formation of the carbonyl group) next to the already positively charged NHC. This step is strongly disfavored and offers a reasonable explanation why the initiation efficiency is low for some cyclic ester monomers (LA, δ-VL, ε-CL).

Another addition to the ZROP-derived cyclic macromolecules has been published in late 2013, detailing the polymerization of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (TMOSC).[66] Reactions in THF at room temperature were found to deliver very high molecular weight product, with the rates of monomer consumption heavily dependent on the type of NHC that was applied. While **5-Dipp** proved to be inactive under these conditions, the less encumbered **5-Mes** allowed for conversions of 90% after 30 minutes (up to 80 000 g.mol^{-1}). The highly nucleophilic compounds **5_{Me}-iPr** and **5_{Me}-Me** exhibited a much higher reactivity and delivered almost quantitative yields of polymer within seconds (590 000 g.mol^{-1} and 940 000 g.mol^{-1}, respectively). A mechanism was proposed based on zwitterionic propagation and spirocyclic resting states. Especially at higher conversion the occurrence of side reactions is noticeable, entailing a broadening of the molecular weight distribution. Most probably transetherification reactions are responsible for this behavior. Notably, the molecular weights reported in this study are about an order of magnitude higher than found in any other ZROP-based process so far. The results also clearly underline that NHCs can polymerize TMOSC directly by nucleophilic ring-opening without the need of additional alcohol to be present. Published only very recently, the latest report on NHC-mediated ZROP to yield macrocycles describes the polymerization of 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane (iPP) (Scheme 17).[67] Not surprisingly, it was again found that **5_{Me}-Me** and **5_{Me}-iPr** performed well, enabling the synthesis of high molecular weight polymer (50 000- 200 00 g.mol^{-1}) within minutes. Contrasting this, no conversion was observed when **5-Mes** was applied, even over extended times. For small molecular weight fractions, the cyclic nature of the polymer was confirmed by MALDI-ToF MS. As this technique cannot elucidate the architecture of high-molecular weight samples, the cyclic structure was elegantly confirmed for those by entrapping them in a cross-linked matrix. This matrix “threads” the cycles, so they cannot be washed out



Scheme 17. Formation of macrocyclic poly(carbosiloxane) and poly(alkylene phosphate) [66,67].



Scheme 18. Examples for NHCs protected by alcohols or halogenated organic compounds and thermal generation of free NHC (top) [31b,c], as well as liberation from NHC-CO_2-adducts (middle) [73] and from azolium hydrogen carbonates (bottom) [74].

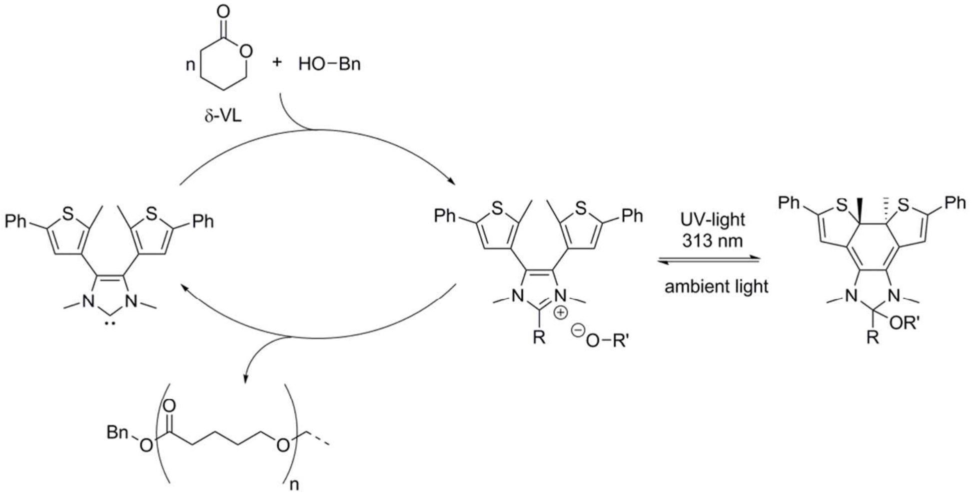
but are held back physically, in contrast to linear polymers.[68] Comparison of the efficiency of the washing out between linear and supposedly cyclic samples can therefore be used to detect macrocyclic structures, especially in cases where the relative intrinsic viscosity is not accessible.[67]

Other than ZROP, NHC-derived macrocyclic polymers are rare. For the zwitterionic polymerization of acrylates, resulting cyclic polymer structures are reasonable to conceive, yet to the best of our knowledge so far no conclusive evidence has been reported.[21,45] Cyclic polymer was also noted when "polybenzoin" was prepared, albeit only as side product.[24] The percentage of cyclics increased at higher conversion, possibly because at lower molecular weight the rigid backbone inhibits cyclisation reactions, and also when poorer solvents were used.

Another intensely researched area with high relevance for polymer chemistry is the development of new forms of **NHC delivery**. In recent years this field has been mainly driven by the much increased use of *thermally* labile NHC-precursors. This situation has been reviewed recently and will not be reiterated here in detail.[32] The main advantages of this approach are the much increased stability and robustness of the precursors compared to the free NHC and the ability to control the onset of the reaction by using heat in a "switch like" manner. To which extent these beneficial properties are present is defined by the type of NHC-precursor (Scheme 18). One of the oldest methods is to use adducts of NHCs and alcohols or other highly polarized C-H-bonds.[31b,c,69,70] These compounds were shown to readily polymerize lactones and lactide, in some cases it was even possible to stop and restart reactions by changing the temperatures from 90 °C to room temperature and back again. Notably, the alcohol-protected NHCs carry the actual initiator for the polyester synthesis (the alcohol) with them, thus elegantly enabling single-component mixtures. However, the release of protic compounds cannot be tolerated in most anionic polymerizations and many organometallic applications. Consequently, the readily accessible NHC-CO_2-adducts ("NHC-carboxylates") have risen sharply in popularity as evident from the numerous examples found in recent literature, including the synthesis of polyesters[35,71] and polyethers.[72] They provide a high, albeit tunable, stability[73] and can be used for sensitive processes like the zwitterionic formation of PMMA[30] or the anionic polymerization of lactams.[48] A new contribution has been made by Taton and co-workers, who showed that *N*,*N*-dialkylated azolium hydrogen carbonates can serve as cheap and robust NHC-precursors.[74] The precursors can be stored and handled without special precautions, and have been used to initiate polymerizations[71a] (GTP, lactone, lactide) and organocatalytic transformations.[75] However, upon liberation of the NHC also one equivalent of water is released, which may be detrimental for some applications. The high robustness of this type of latent NHC is coupled with a somewhat reduced activity; indeed for standard NHC-organocatalysis a general order of activity was found to be [NHC(H)][HCO_3] < NHC-CO_2 < free NHC.[71a,75]

Related to this topic, in 2013 Bielawski has demonstrated the use of UV-light for changing the chemical structure of NHCs and thus manipulate its activity towards polymerization of δ-VL (Scheme 19).[76] While the active form of the carbene readily yields the polyester, the ring-closed counterpart is about sixty times slower in doing so.

Another approach to facilitate the applicability of NHCs in polymerization processes focuses on ionic liquids (ILs). Many ILs are constituted of 1,3-disubstituted imidazolium salts, and hence identical to the most typical precursors from which NHCs are prepared, usually by addition of a sufficiently strong base (KOtBu, hydrides, KHMDS). As ILs are commercially well available and considered to be "green" solvents, it is reasonable to use them as sources for free NHCs, or even as media in which both the polymerization reaction and in-situ generation of the carbene occurs. The counter ion will be decisive for the ease and degree of carbene formation from imidazolium salts. This is supported by a study which suggests that by tuning the basicity of the anion the concentration of NHCs in solution or gas phase



Scheme 19. UV-switchable NHC-based polymerization setup for the preparation of polyester [76].

might be tailored.[77] Acetate was identified to be a strong enough base to yield detectable amounts of NHC or hydrogen bonded NHC-acetic acid complexes. This neatly ties in with Taton's work described above, where another basic counter ion, HCO_3^-, serves in a similar manner. PET can be depolymerized in a 1-butyl-3-methylimidazolium-based (BMIM) IL after addition of base.[78] Importantly, the *electrochemical* generation of free NHCs from BMIM tetrafluoroborate under evolution of H_2 was successfully used for catalytic transformations in this IL.[79]

As a concluding remark on the growing importance of NHC organopolymerizations, the current **patent situation** shall be highlighted. Nowadays, polymerizations are conducted in optimized, cost-efficient processes that grant very little leeway for new types of catalysts. For NHCs to be successfully introduced in large-scale industrial synthesis, they have to compete with other types of readily available or cheap catalysts, and only stand a chance if they can outperform the alternatives or entail other added value, all the time maintaining the lowest possible cost for preparation and storage. These are steep requirements, yet the large potential of NHC-mediated catalysis is increasingly recognized outside academic research. This is mirrored by a number of patents that have been filed on this topic by eminent companies like Rhodia,[52,80] Evonik,[81] DuPont,[82] Bayer,[83] BASF[84] and Intel[85] since 2006. The inventions mainly describe the polymerization of acrylic monomers,[80a,81a] epoxides,[80b,84] lactones,[81c,82b] lactams[81b,82a] and processes for PU synthesis.[80c,83] As is evident from this review, NHCs can perform very well in these areas; however, some attempts to unify the good lab results with realization on technical scale may be thwarted by the inherent sensitivity of NHCs. This can complicate storage and process steps and thus limit the usefulness of the catalyst. In this regard, the ascent of protected NHCs can be understood. In the optimal case, the superior reactivity of the NHC can be used after selective activation of the precursor, which enables on-demand, robust polymerizations, helps reducing the number of components and enables the prolonged storage of the catalyst or catalyst/monomer mixtures. In addition to being metal-free, this renders NHC-mediated polymerization highly attractive for future industrial application. Likely candidates at the moment are the production of PU, where latent NHCs can substitute very problematic, Hg-based older compounds[28] and of polyamides from lactams,[27,48] where protected NHCs enable single-component compositions, a feature that is unique so far.

Conclusions

NHCs continue to be a hotspot for polymerization catalysis research. Not only do they have a uniquely broad applicability for very different types of monomers – lactones, lactams, epoxides or siloxanes to name but a few- which allows for them to take a special place among polymerization catalysts, but they are also readily tuned and optimized to the task at hand. As a consequence they combine a wide scope with potentially high performance in a given case, not rarely outperforming more established catalytic systems. Deeper insights in the underlying mechanistic processes have enabled NHCs to tackle double bond-containing monomers, an area which is typically challenging for organocatalysts. Progress there seems to depend on intelligent catalysts design, as the polymerization setup is extremely sensitive to changes in the chemical structure of the NHC.

Apart from pushing the limits on accessible monomers, current research focuses on controlling the polymer architecture *via* NHC mediation. As is obvious from the numerous examples above, especially ZROP has emerged as a very promising tool to create macrocyclic material with considerable molecular weight.

Both the expansion of the monomer feed as well as the possibility to create defined (cyclic) polymers path the way to future large-scale application, which is already heralded by an increase in patenting activity over the recent years. This trend is further fuelled by advances in novel forms of NHC delivery, which allow for applying the organocatalysts in a cheaper and more robust forms, or even for on-demand rapid polymerizing systems. Together, this suggests that for polymer science, NHC chemistry will increase in importance in the near future and will stay a rich ground for exciting new developments.

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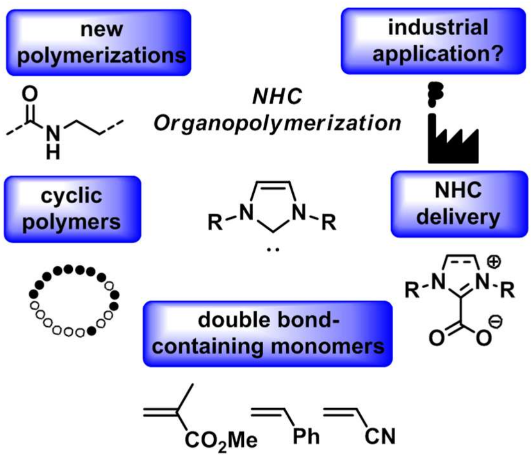
ToC Graph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industrial application?
NHC Organopolymerization
cyclic polymers
NHC delivery
double bond-containing monomers
R-N
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CN