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P O L I M E R Y

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

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N-Heterocyclic carbene catalysis — from simple organic reactions to polymerization of cyclic esters

Summary — This contribution aims at reporting on very recent advances achieved in controlled ring-opening polymerization of dilactones as promoted by easily accessible *N*-heterocyclic carbenes (NHCs). Even though carbenes have been known as very unstable species for long, more recently discovered NHC derivatives proved to display higher stability making their handling much easier and allowing their use as efficient catalysts in various organic reactions. Remarkably, these metal-free catalysts display high reactivity in synthesis of aliphatic polyesters such as polylactides and poly(β-butyrolactone)s all characterized by well-tailored compositions, molecular weight, tacticity, and end--group fidelity while presenting narrow to very narrow molecular weight distribution. Interestingly, novel macromolecular architectures based on such aliphatic polyester building blocks have been made available, *e.g.* multi-armed star shaped copolyesters, H-shaped copolyesters or macrocyclic polyesters paving the way to new biomedical applications for this family of important biocompatible and biodegradable aliphatic polyesters.
Key words: *N*-heterocyclic carbene, Stetter reaction, benzoin condensation, L,L-lactide, β-lactones, ring-opening polymerization, aliphatic polyesters, cyclic polyesters.

KATALIZA ZA POMOCĄ *N*-HETEROCYKLICZNYCH KARBENÓW — OD PROSTYCH REAKCJI ORGANICZNYCH DO POLIMERYZACJI ESTRÓW CYKLICZNYCH

Streszczenie — Na podstawie przeglądu literatury opisano osiągnięty ostatnio postęp w dziedzinie kontrolowanych reakcji polimeryzacji z otwarciem pierścienia di(laktonów) aktywowanych za pomocą łatwo dostępnych karbenów *N*-heterocyklicznych (NHC). Karbeny długo uważano za bardzo niestabilne, ale ostatnio odkryte NHC charakteryzują się większą stabilnością ułatwiającą posługiwanie się nimi, co pozwala na ich użycie jako wydajnych katalizatorów do różnych reakcji organicznych. Te niemetaliczne katalizatory wykazują szczególnie dużą aktywność w syntezie poliestrów alifatycznych takich jak polilaktydy i poli(β-butyrolaktony) cechujące się precyzyjnie zaprojektowanym składem, ciężarem cząsteczkowym, taktycznością i zawartością grup końcowych. Umożliwia to syntezę makrocząsteczek o oryginalnej architekturze składających się z takich bloków poliestrów alifatycznych np.: kopoliestrów o kształcie gwiazd wieloramiennych lub litery H, czy poliestrów makrocyklicznych torujących drogę do nowych zastosowań biomedycznych tej rodziny biokompatybilnych i biodegradowalnych poliestrów.
Słowa kluczowe: karben *N*-heterocykliczny, reakcja Stetter'a, kondensacja benzoinowa, L,L-laktyd, β-lakton, polimeryzacja z otwarciem pierścienia, poliestry alifatyczne, poliestry cykliczne.

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Chemistry of carbenes has never been easy since such structures have traditionally been transient, highly reactive and short live species. Their reactivity comes mainly from their electronic unsaturation, *i.e.* carbon as group 14 element has four electrons, four valence orbitals and as carbene two valence bonds. It is therefore left with the choice to place either one parallel electron into each of the two remaining orbitals (triplet carbene) or both electrons into one orbital and leaving the fourth orbital empty (singlet carbene) [1]. Considering a prototype carbene –C̈–, the carbon atom can be either linear or bent, each geometry describable by a certain degree of hybridization. The linear geometry implies a *sp*-hybridized carbene center with two nonbonding degenerate orbitals (p_x and p_y). Bending the molecule breaks this degeneracy and the carbon atom adopts a sp^2-type hybridization: the p_y orbital remains almost unchanged (it is usually called p_π), while the orbital that starts as pure p_x orbital is stabilized since it acquires some *s* character (it is therefore called σ) (Fig. 1).

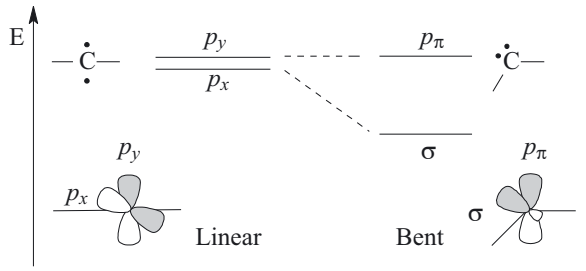
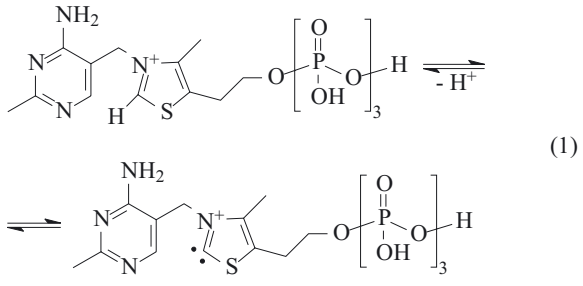


Fig. 1. Relationship between the carbene bond angle and the nature of the frontier orbitals

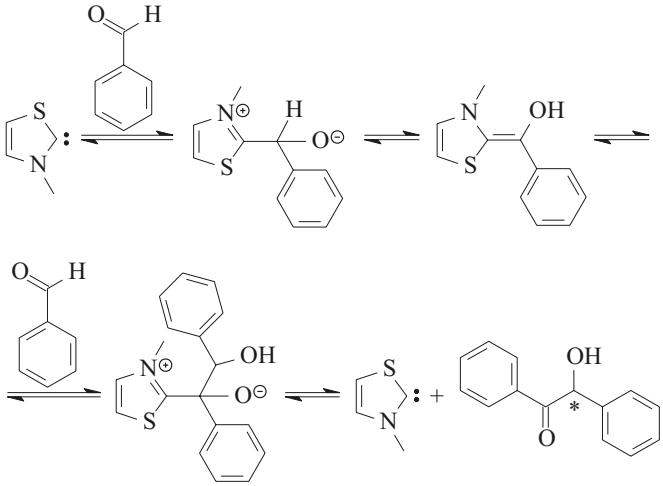
Although a triplet carbene is more stable than a singlet carbene, both are highly reactive and cannot be isolated. For over a century, all attempts to do so proved unsuccessful, although Fischer and Schrock were able to generate stable carbenes in the coordination sphere of transition metals [2]. Clearly the discovery of the first stable free carbene by Arduengo in 1991 [3] and the realisation that these *N*-heterocyclic carbenes NHC can be used instead of phosphines in catalysis sparked a great interest in them [2]. They were found to be more electron-rich ligands than phosphines and more firmly bound to the metal catalyst [2]. Both are highly desirable properties and the main reasons for their success in catalytic applications. However, applications using carbenes as organocatalysts are not as prevalent. In biological systems, the thiazolium salt thiamine (vitamin B_1), in the form of its pyrophosphate, catalyzes important biochemical reactions, such as the decarboxylation of pyruvic acid [4]. Breslow showed that the biochemical mechanism of thiamine action involves formation of the C-2 anion in the thiazolium ring [equation (1)] [5, 6]. Such observation allowed the possibility to use such thiazolium- and triazolium-based carbenes as catalysts for various "simple" organic reactions such as Stetter and benzoin condensation reactions [7, 8].



(1)

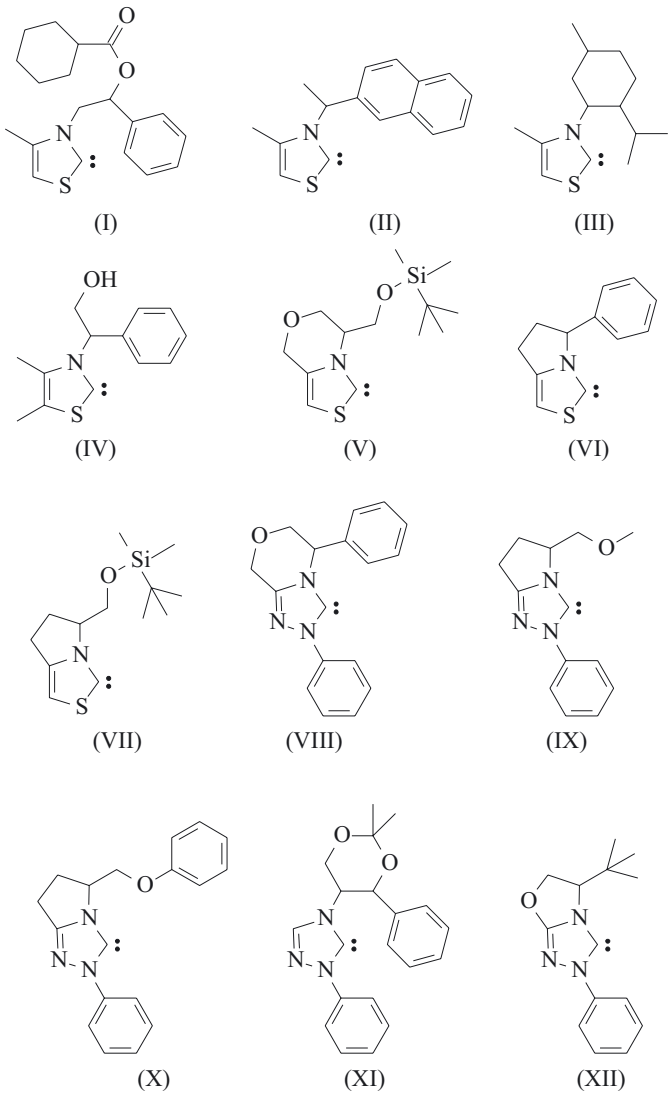
BENZOIN CONDENSATION

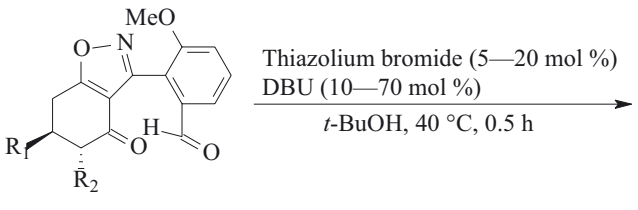
The C-2 conjugate of thiazolium salt thiamine acts also as a nucleophile and activates the carbonyl for condensation in the well-known benzoin condensation (Scheme A). The free carbene reacts first with benzaldehyde *via* nucleophilic addition to the carbonyl group,

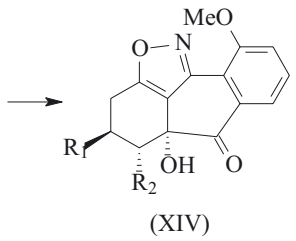


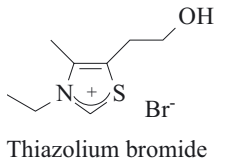
Scheme A. Mechanism for the benzoin condensation using N-methylthiazol-2-ylidene

then subsequently rearranges to the hydroxyenamine (Breslow intermediate), which acts as an acyl anion equivalent for addition to the carbonyl of the second benzaldehyde molecule. A second rearrangement gives rise to benzoin and the free carbene that is ready to participate in a subsequent turnover [9]. Notably, benzoin condensation is an equilibrium reaction and can be reversed. A wide variety of thiazolium, imidazolium, and triazolium salts presenting great structural diversity have been developed over the years, and this has resulted in constant improvements in yield and selectivity [9]. Going beyond the usual focus on central chirality, Pesch *et al.* recently demonstrated that axially chiral *N*-arylthiazoliums catalyze the benzoin condensation [10]. Even though the yields and enantiomeric excess (*ee*) values are low (up to 40—50 %) compared to those of other









R_1	R_2	Yield
H	H	95 %
Me	H	90 %
Me	CO_2Et	90 %

Scheme B. Intramolecular cross-benzoin condensation of ketones and aldehydes

systems, it was shown that axial chirality is a viable approach in this reaction. Triazole-based organocatalysts were shown to give much better *ee* values because of more steric hindrance at both sides of the carbene centre: a bulkier phenyl-substituted *N*-atom instead of the single *S*-atom accounts for their success in the asymmetric benzoin condensation. Formulas (I)—(XII) presents selected organocatalysts that have been used up to date [11]. The most successful catalyst is catalyst (XII) showing a reaction yield of 83 % while the *ee* content is close to 90 % [8].

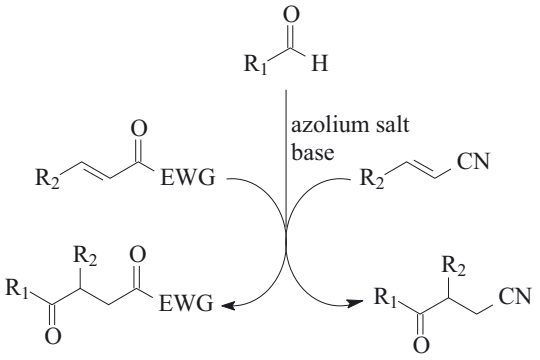
Surprisingly, while numerous catalytic systems have been developed in the last fifty years for intermolecular acyloin condensation, the first intramolecular version appeared only in 2003. Suzuki and co-workers [12] disclosed the facile presented in Scheme B synthesis of functionalized preanthraquinones [formula (XIV)] catalyzed by thiazolium bromide in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) [12].

Noteworthy, the viability of ketones as benzoin-type condensation partners opened new fields of investigation for stereoselective reactions. Subsequently, the groups led by Enders and Suzuki independently reported asymmetric intramolecular cross-benzoin reactions in which they achieved good to high yields and enantioselectivities of α-hydroxyketones [13—16].

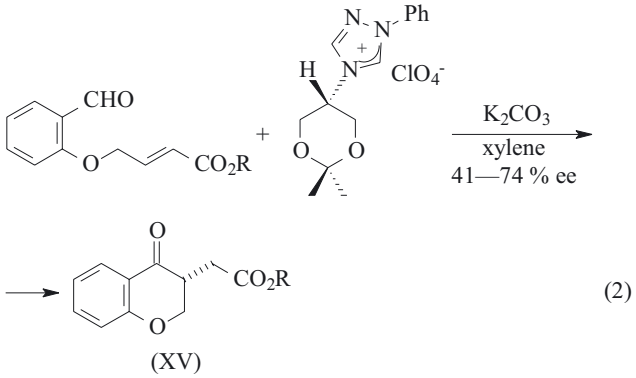
STETTER REACTION

The 1,4-addition of aldehydes to α,β-unsaturated ketones, esters or nitriles to form 4-keto products is known as the Stetter reaction (Scheme C) [4, 7, 17]. Initially catalyzed by cyanide salts, azolium salts derived from thiazoles and imidazoles were quickly adopted as catalytic precursors based on their successful application for benzoin condensation. The use of these catalysts extended the range of substrates to aliphatic as well as aromatic and heterocyclic aldehydes. Catalysis of the Stetter reaction by azolium salts relies on the presence of base to form the active carbenes, which add to aldehydes and induce rearrangement to hydroxyenamine intermediates as in the benzoin condensation. Conjugate addition of this acyl anion equivalent to the α,β-unsaturated carbonyl compound gives the final product and regenerates the *N*-heterocyclic carbene (NHC) catalyst (Scheme C).

The importance of the Stetter reaction products as valuable precursors in the synthesis of cyclopentanone derivatives [7, 18] and heterocycles [19—21], explains its now very common use in total synthesis [23—26] in solid-phase organic synthesis [27—31] and in the preparation of extended heterocyclic systems [32—34]. An asymmetric version of the intramolecular Stetter reaction employing a chiral azolium salt for the synthesis of the benzopyran derivative [formula (XV)] was first reported by Enders *et al.* [equation (2)] [35, 36]. Independently, Kerr and Alaniz showed that the use of a



Scheme C. The Stetter reaction (EWG — electron-withdrawing group)



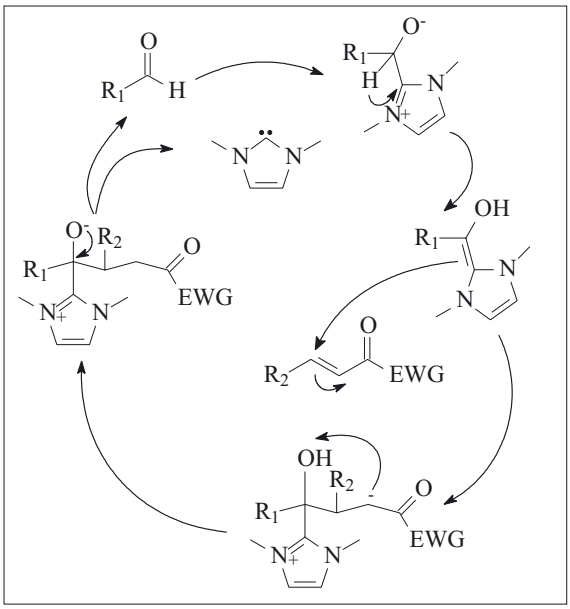
(2)

fused chiral triazolium salt leads to the product in higher yield and enantioselectivity [37].

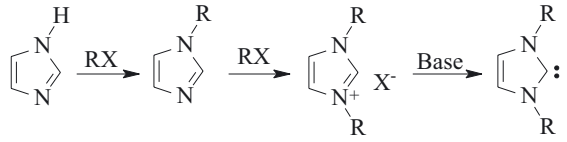
More recently, designed thiazolium salts were applied to the Stetter reaction. Fused menthyl-substituted thiazoliums reported by Pesch *et al*. [38] catalyzed intramolecular Stetter reactions in 75 % yield with 50 % *ee*. The artificial amino acid β-(*N*-benzylthiazolyl)alanine (Taz) introduced by Mennen *et al*. [39] catalyzes the Stetter reaction in modest yield (40 %) and good *ee* (80 %), especially considering the distance of the chiral centre from the nucleophilic carbon. Furthermore, its formulation as an amino acid allows facile incorporation into small peptides, permitting combinatorial studies towards optimizing yield and selectivity. For instance, simple modification of Taz improves the yield (67 %) at a slight cost to the *ee* (73 %) [39].

CARBENE GENERATION, REACTIVITY AND STABILITY

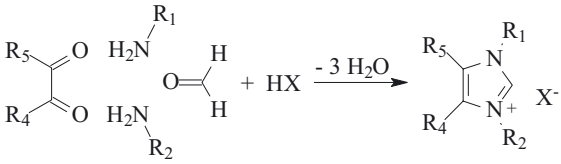
N-Heterocyclic carbenes are synthesized from triazolium, thiazolium or imidazolium salts which might be easily functionalized on both nitrogen atoms (Scheme D). In 1988, a commercial need arose for catalysts in various polymer cross-linking applications [40]. The imidazol-2-thiones seemed well suited to these applications



because they proved very powerful nucleophiles without being too strong bases. Existing syntheses of the imidazol-2-thiones were not well suited for large-scale manufacturing processes because of material costs, yield, separation, and by-product problems. A more con-



Scheme D. General procedure for the N-heterocyclic carbene synthesis



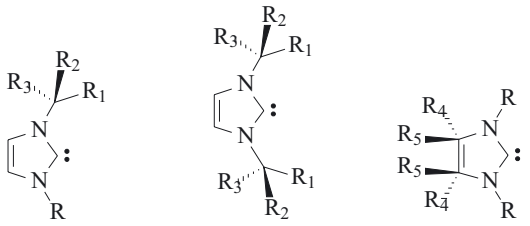
(3)

venient synthesis of imidazol-2-thione was developed [40], along with a new one-step synthesis of imidazolium ions that allowed the production of substituted imidazolium ions that were not accessible by conventional routes [equation (3)] [41].

As progress toward commercialization of imidazol-2--thiones continued, reactions with a very wide range of substituents that again seemed to underscore the extreme stability and tolerance of carbene have been run. Pilot-tests were not always conducted with the same attention to detail that one can achieve when working on a small laboratory scale. Nonetheless the ease with which these reactions succeeded served to bolster the belief that the carbene intermediates were remarkably stable. A stable carbene is defined as a carbene that is persistent at ambient temperature (and often does not decompose even at temperature higher than 200 °C), but requires an

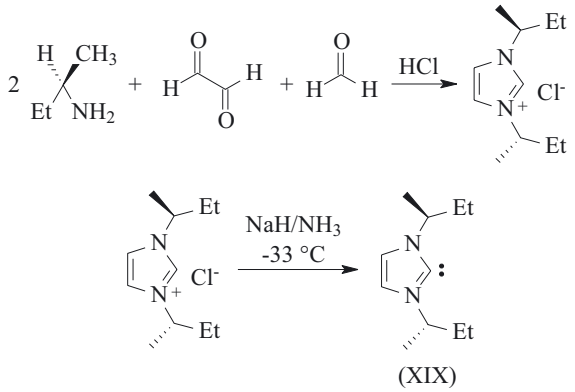
inert gas atmosphere and is extremely sensitive to moisture and chlorinated solvents. One of the best representing examples is the imidazol-2-ylidene substituted by 1-adamentyl group. A solution of this carbene in THF-d_8, sealed under a few atmospheres of CO, has shown no decomposition or change after 7 years at room temperature [3].

The simplest method to introduce chirality in carbene is to use a naturally occurring and commercially available chiral amine in the synthesis of the imidazole ring or to use a chiral alkyl halide to quaternise the second



(XVI) (XVII) (XVIII)

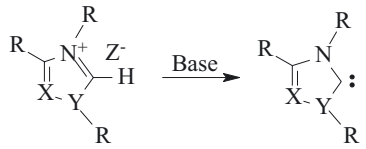
nitrogen in the synthesis of the imidazolium salt [formulas (XVI)—(XVIII)] [42, 43]. The synthesis of chiral carbene has been described by Herrmann *et al*. [44] as exemplified by Scheme E for the synthesis of molecule (XIX). Reaction of two equivalents of commercially available enantiopure *sec*-butylamine with paraformaldehyde,



Scheme E. Proposed synthesis of chiral carbene (XIX) using the Herrmann synthesis

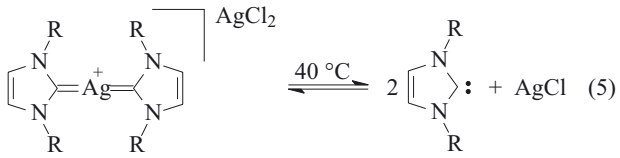
glyoxal, and hydrochloric acid will generate the corresponding chiral imidazolium salt, with retention at the chiral carbon. Subsequent deprotonation of the salt with NaH in a mixture of THF and liquid ammonia at low temperature will provide enantiomerically pure carbene (XIX) without racemisation or decomposition.

Of the various ways to generate *N*-heterocyclic carbenes, the most common strategy is the deprotonation of imidazolium, triazolium or thiazolium salts. Typically, the free carbenes can be generated using a base such as triethylamine or potassium *t*-butoxide, depending on the pK_a of the salt [equation (4)] [11, 45]. For many reasons, *e.g.*, the deprotonation can be carried out *in situ*, this technique is a versatile method of screening carbene compounds for activity and selectivity. Because of the interest in NHCs as ligands for transition metals, various strategies have been devised for ligating carbenes to transition metals. The use of silver(I) carbene complexes as transfer agents in the generation of transition metal complexes prompted the investigation of these silver complexes as potential delivery agents for free carbenes



(4)

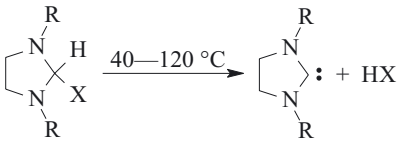
with X = N, $CH_{(2)}$; Y = N or S; Z = Cl, I, BF_4



(5)

[46]. Complexes of this type are already prepared by reaction of imidazolium chloride with silver(I) oxide, and this was shown to be a general method for various unsaturated imidazol-2-ylidene compounds [equation (5)] [11]. Delivery of free carbene was demonstrated by differential scanning calorimetry and thermogravimetric analysis.

Carbene adducts containing electron-withdrawing substituents were easily generated in good yield by the reaction of a diamine with benzaldehyde derivative or a hemiacetal [47]. Upon heating, the fluoroaryl adducts

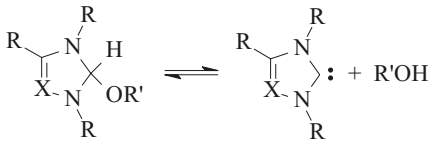


(6)

where X = Fluoroaryl, CF_3, CCl_3

degrade to free carbene and fluorobenzene, and the transition temperature depends on the fluorination degree of the aryl group [equation (6)] [11].

Adducts with weak electron-withdrawing groups such as trifluoromethane, benzene, and 2,3,4-trifluorobenzene are thermally very stable and do not readily degrade to the free carbene even at 100 °C. The pentafluorobenzene adduct is readily generated from the aldehyde and the diamine and thermally generates the carbene at 60 °C. Chloroform adducts can be readily accessed through reaction of chloroform with the free carbene [47] or by treatment of the imidazolinium salt with



(7)

where X = N or CH_2; R' = Alkyl

sodium hydroxide and chloroform [48]. The use of alcohol adducts of carbenes has been more widely investigated as a delivery method for free carbenes [equation (7)]. Both imidazolin- and triazolin-2-ylidenes form stable alcohol adducts. Enders *et al.* [49] demonstrated that heating the alkoxytriazolylidene under vacuum at 80 °C led to the generation of free carbene and more recently Coulembier *et al.* [50] have demonstrated that amino-adducts in solution at elevated temperature are also useful precursors for carbene generation.

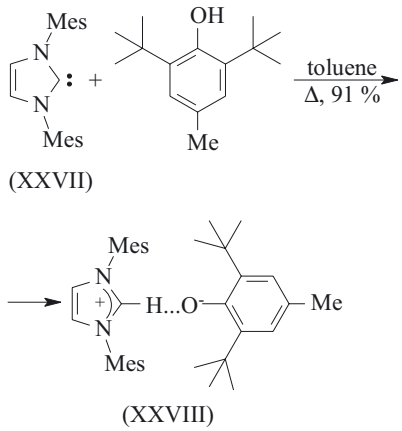
In 1996, Heinemann *et al.* [51] addressed the question whether the C=C unsaturated Arduengo-type imidazol-2-ylidene carbenes [formula (XX)] benefit from "aromaticity", *i.e.* from cyclic 6π-electron delocalization. A critical role of the C=C double bond in stabilizing carbene (XX) might have been suspected intuitively from the fact that in the carbon case the corresponding imidazolin-2-ylidenes [formula (XXI)], in which the olefinic backbone of the five-membered ring is transformed into a saturated hydrocarbon moiety, had not been isolated until mid 1995 despite numerous attempts [52]. The different approaches show consistently that cyclic electron delocalization does indeed occur in the C=C unsaturated imidazol-2-ylidene systems, in particular with respect to the corresponding C-C saturated imidazolin-2-ylidenes. However, the conclusion of authors regarding the degree of conjugation and aromaticity depends on the criteria used, being quite small according to the "atoms-in-molecules" charge analysis but more significant according to the energetic and the magnetic properties. According to all criteria, the aromatic character of imidazol-2-ylidenes is less pronounced compared to benzene or the imidazolium cation.

(XX) (XXI)

Interestingly, Alder *et at.* [53] determined the nucleophilicity and basicity of various aminocarbenes based on the Broensted-Lowry concept. They reported that pK_a of 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene [formula (XXII) in Fig. 2] as 24 in DMSO-d_6 and found that it is a much stronger base than 1,5-diazabicyclo[3.4.0]-non-5-ene [DBN, formula (XXIII) in Fig. 2], 1,8-diazabicyclo[5.4.0]undec-7-ene [DBU, formula (XXIV) in Fig. 2], and proton sponge 1,8-bis(dimethylamino)naphthalene [formula (XXV) in Fig. 2] but weaker than phosphazene bases [formula (XXVI) in Fig. 2].

Recently, Kim and Streitweiser [54] calculated the pK_a of 1,3-di(*tert*-butyl)imidazol-2-ylidene in THF as 20, which is much less than that of the dimesityl derivative reported by Alder [53]. The pronounced basicity of the *N*-heterocyclic carbene (XXVII) is attested by the isolation of crystalline compounds with organic acids such as 2,6-di-*tert*-butyl-4-methylphenol [equation (8)].

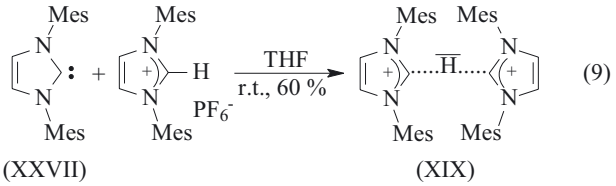
Similarly, Arduengo *et al.* [55] reported the isolation according equation (9) of stable hydrogen-bonded bis(carbene) complex [formula (XXIX)] by the interaction



(XXVII) (XXVIII)

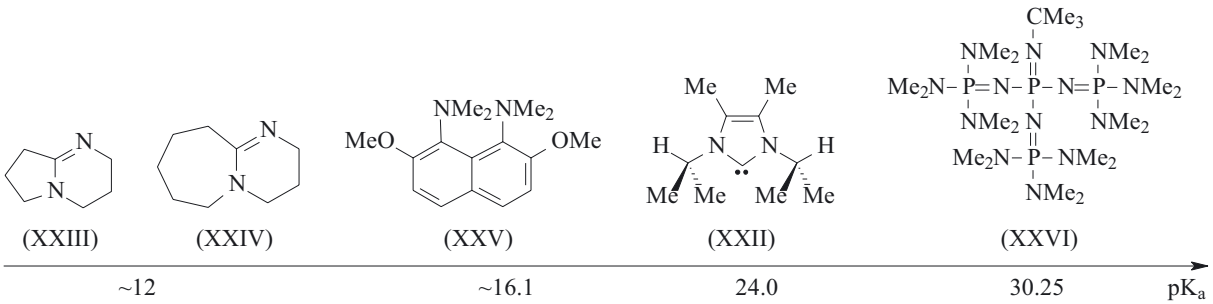
(8)

Mes = C_6H_2-2,4,6,-Me_3



(XXVII) (XIX)

(9)



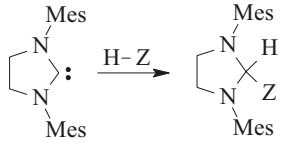
(XXIII) (XXIV) (XXV) (XXII) (XXVI)

~12 ~16.1 24.0 30.25 pK_a

Fig. 2. pK_a value of 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene [formula (XXII)] compared to those of well-known structures [53]

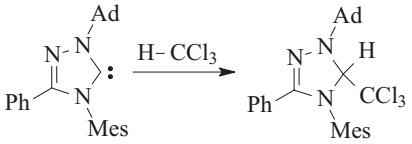
of carbene (XXVII) with its azolium salts. Stable carbene (XXVII) also forms C-H···C (π) complexes with hydrocarbons such as indene and fluorine [56].

The reactivity of stable diaminocarbenes towards water, oxygen, and hydrogen has also been investigated. Imidazolin-2-ylidenes underwent instant hydrolysis on exposure to moist THF, whereas hydrolysis of the aromatic congeners such as l,3-di(*tert*-butyl)imidazol-2-ylidene to the corresponding aldehydes took days [57]. These carbenes were found to be inert towards oxygen



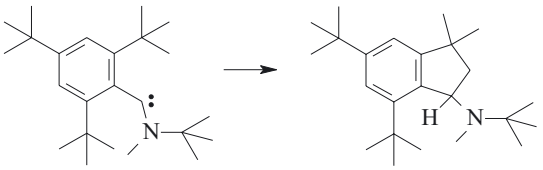
(10)

Z = CCl_3 or CH_2SO_2Ph or CH_2CN or CCR



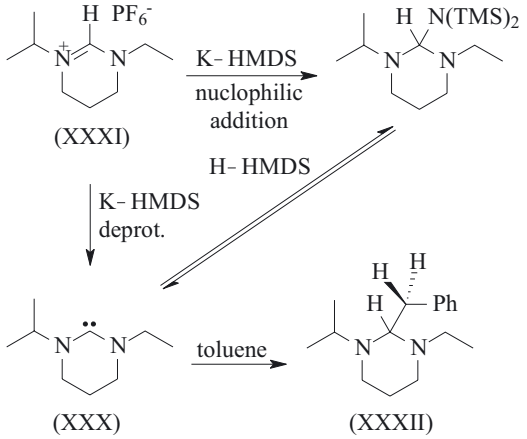
(11)

Ad = adamantyl



(12)

and hydrogen, but in the presence of hydrogen and a platinum or palladium catalyst, they underwent slow hydrogenation. Finally, aminocarbenes such as triazolylidene have been shown to insert into strongly polar X-H bonds (X = OR', NR_2) to afford the corresponding 1,1-addition product [58]. To date only few works report



Scheme F. Side/co-products arising from generation of carbene (XXX) by reaction of salt (XXXI) with commercial solution of (K-HMDS)$_2$ in toluene

the reaction of stable carbenes with "acidic" C-H bonds ($pK_a \leq 25$) which to the best of our knowledge are limited to the following examples [equation (10)—(12)] [59].

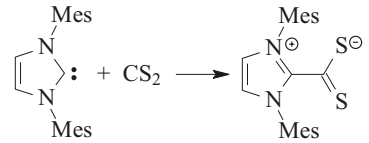
Interestingly Owen-Smith [59] reported recently the possibility of an intermolecular insertion of an *N*-heterocyclic carbene into a non acidic C-H bond (Scheme F). He shows that when carbene (XXX) is produced in toluene by deprotonation of tetrahydropyrimidum salt with PF_6^- (XXXI) using dimeric potassium hexamethyldisilazide ["(K-HMDS)$_2$"] the by-product (XXXII) initially identified as a minor component (content lower than 2.5 %) was found to increase with the time to become the major product. The reaction of carbene (XXX) with toluene ($pK_a \approx 22$—44) was surprising since there is a significant mismatch between reactants [ΔpK_a of salt (XXXI) and toluene *ca*. 16—18] while reaction was found to be catalyzed by (K-HMDS)$_2$.

RING-OPENING POLYMERIZATION USING *N*-HETEROCYCLIC CARBENES

Linear polyesters obtained by *N*-heterocyclic carbene catalysis

Ring-opening polymerization (ROP) of cyclic esters is a particularly convenient method for the synthesis of polyesters. These versatile polymers are widely used as fibres, plastics, coatings, and more especially, as biodegradable surgical sutures and in compounding medicines for the controlled release of drugs [60]. The ROP is most often promoted by metal-based catalysts or initiators. However, their applications as biomaterials raised concerns about the removal of the contaminant metal bound to the chain end or physically trapped into the structure.

Metal-free approaches to polyesters based on tertiary amines or phosphines [61, 62] were followed by the use of *N*-heterocyclic carbenes as catalysts for the polymerization of lactides and lactones [63]. The representative imidazol-2-ylidene [IMes, formula (XXVII)] proved to be far more active than phosphines and even amines [63]. For initial monomer concentrations around 1 mol/dm^3 and monomer-to-initiator ratios ranging from 50 to 200, quantitative conversions were achieved in less than 1 h at room temperature in THF. Polymerization can be terminated by deactivation of the carbene with addition of acetic acid, CO_2 or CS_2, the latter of which forms a zwitterionic species [equation (13)] that is readily removed from polymer upon precipitation. The catalyst to initiator ratio has a strong influence on the polymerization



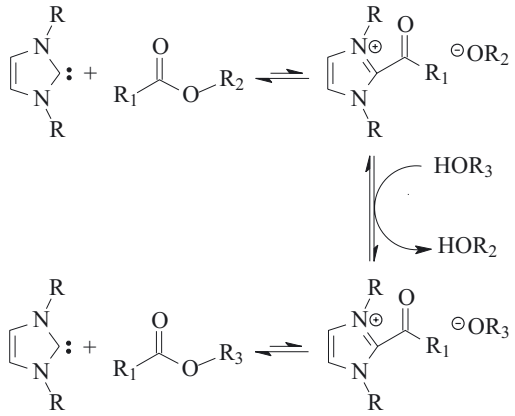
(13)

(XXVII)

control. Ratios from 0.25 to 1.5 allow for the preparation of polylactides with high molecular weights [degree of polymerization (*DP*) is higher than 100] and low polydispersity index (PDI), whereas much lower ratios on the order of 0.0125 are necessary to obtain oligomers ($DP \approx 15$) with low PDI.

As the ROP is fundamentally a transesterification reaction, two possible mechanisms have been envisaged:

— monomer-activated mechanism mediated by the nucleophilic attack of the carbene on lactone (Scheme G),

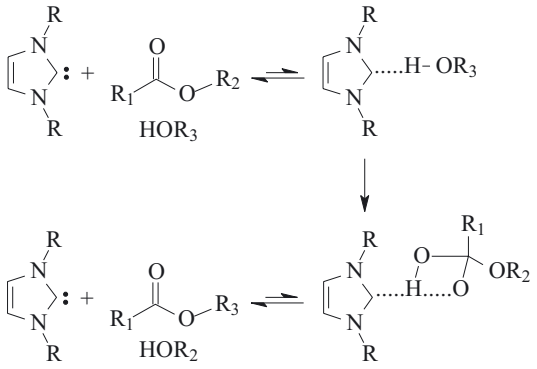


Scheme G. Nucleophilic mechanism of transesterification

— a chain-end activated mechanism whereby the carbene activates the alcohol toward nucleophilic attack (Scheme H).

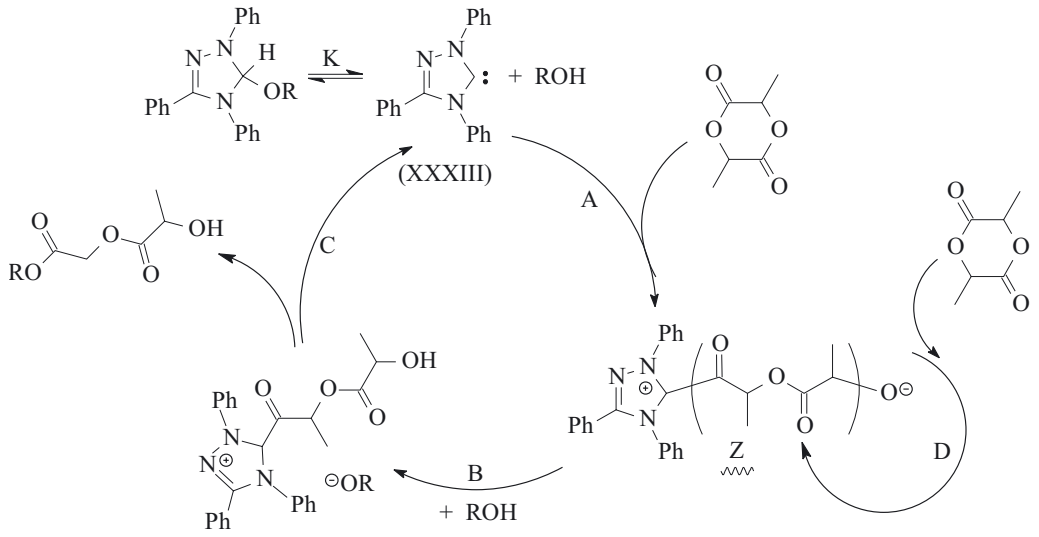
In analogy to the known behaviour of pyridine derivatives in acylation reactions [64], a nucleophilic mechanism has been proposed in accordance to the Breslow's nucleophilic mechanism for the benzoin and formoin condensation reactions [5].

The nucleophilic mechanism was favoured as it was argued on the basis of the relative pK_a's that the alcohol was unlikely to protonate the carbene IMes to initiate an anionic polymerization from the alkoxide [63]. Subsequently, it was proposed that hydrogen-bonding between the carbene and the alcohol could activate the alcohol toward nucleophilic attack [65, 66]. For the ROP, this would correspond to a chain-end activation mechanism. A monomer-activated mechanism was proposed for the *N*-heterocyclic-catalyzed ROP of lactide [63, 67]. Nucleophilic opening of the lactide monomer by the carbene (for example IMes) was proposed to generate a



Scheme H. Alcohol-activated mechanism of transesterification

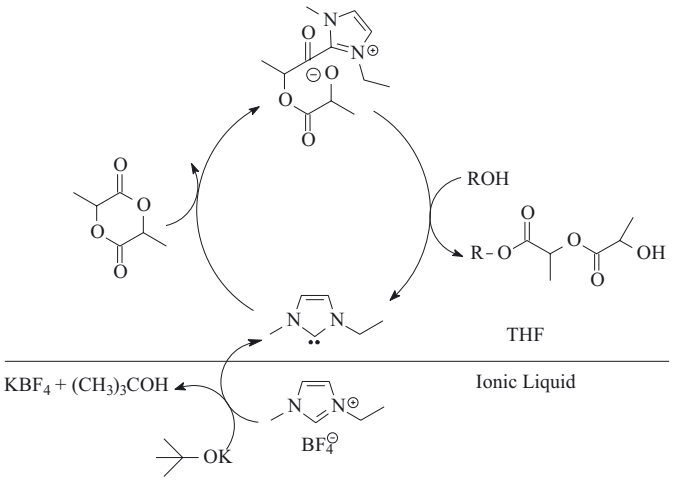
zwitterionic intermediate that undergoes a proton transfer with an alcohol to generate an alkoxide. Attack of the alkoxide on the acyl imidazolium intermediate liberates the ester and regenerates the carbene. Following acylation of the initiating alcohol, propagation entails acylation of the alcohol chain-ends by the activated monomer. As the activated monomer has an equal probability of acylating any chain-end, all chains grow with equal probability, leading to narrow polydispersites (Scheme I, ways A-B-C). Recently, they also observed that when L-lactide is polymerized with excess of 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene [formula



Scheme I. Proposed mechanism for ROP of lactide with carbene (XXXIII)

(XXXIII) in Scheme I] compared to the alcohol, the polymerization is less well controlled, with competing mechanisms able to produce poly(L-lactide) without alcohol initiator (Z), leading to the formation of linear and/or macrocyclic oligomers (Scheme I, way D) [68].

The scope and generality of these nucleophilic polymerizations was also investigated by varying the structure and substituents of the carbene catalyst [69]. Imidazol-2-ylidenes as well as thiazol-2-ylidenes and imidazolin-2-ylidenes featuring various substituents both at the nitrogen atoms and the carbon-based framework have been tested. The diaminocarbenes proved to be the most active catalysts, sterically demanding and electron--withdrawing substituents being as expected less favorable. Interestingly, the extreme air and moisture sensitivity of *N*-heterocyclic carbenes can be easily circumvented by their *in situ* generation from their protonated form. The feasibility of solid-supported catalysis has also been established with thiazolium and imidazolium precatalysts, although some restrictions (limited molecular weights, broader PDI), probably associated with solubility problems, were observed [69]. Better results were obtained for THF/ionic liquid biphasic catalysis [69]. Indeed, *in situ* deprotonation of an imidazolium-based



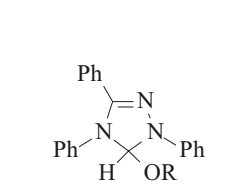
Scheme J. Biphasic N-heterocyclic carbene-catalyzed polymerization

ionic liquid generates the corresponding imidazol-2-ylidene, which then migrates to the THF phase and initiates lactide ROP. Rapid and repetitive polymerizations were achieved, the imidazolium precatalyst being easily regenerated by addition of a tertiary ammonium salt (Scheme J).

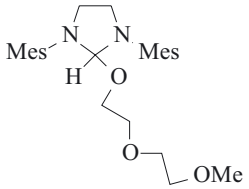
The extraordinarily high activity of carbenes for ROP enables the stereoselective polymerization of *rac*- and *meso*-lactide at low temperatures [70, 71]. For example, polymerization of *rac*-lactide with the sterically hindered carbene Ph_2IMes in CH_2Cl_2 at temp. 70 °C for 2 hours yielded a crystalline polylactide with 91 % conversion with a melting temperature of *ca.* 153 °C. This result was interpreted in terms of a chain-end control mechanism where the stereogenic terminal alkoxide of the growing chain selectively attacks the acyl imidazolium of the same relative stereochemistry, leading to preferential isotactic enchainments (probability of isotactic placement P_i = 0.90). This hypothesis was supported by the stereoselective polymerization of *meso*-lactide with Ph_2IMes at temp. -40 °C to yield a heterotactic polylactide with a P_i = 0.83.

Saturation of the *N*-heterocyclic carbene backbone gives strikingly different reactivity for both free carbenes and carbene-ligated metal complexes [72]. For example saturated *N*-heterocyclic carbenes with less sterically hindered *N*-substituents lead to dimerization of the carbenes [11]. Polymerization of lactide with 1,3-diphenyl--imidazolin-2-ylidenes [SIMes, formula (XXI)] generated *in situ* from the respective hydrochloride salt proceeds rapidly to produce narrowly dispersed polymers with molecular weights that closely track the monomer-to--initiator ratios [69]. The "Wanzlick" dimer, bis(1,3-diphenyl-2-imidazolidinylidene), was shown to be a potent lactide polymerization catalyst, though with slightly broader polydispersities. Application of SIMes and 1,3-diphenyl-imidazolin-2-ylidene (SIPh, from "Wanzlick" dimer) as catalyst for ε-caprolactone polymerization resulted in different polymerization behavior: SIMes gives no polymerization activity, while less hindered SIPh was active for the polymerization of ε-caprolactone and δ-valerolactone.

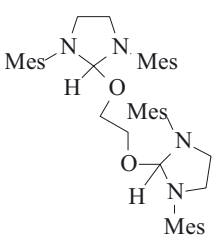
To avoid the presence of a strong base in the reaction mixture, active carbene catalysts can be thermally generated from silver complexes or neutral haloalkane adducts instead of *N*-heterocyclic carbene salts [46, 47]. When these adducts are delivered from alcohols, they play a dual role: catalyst and initiator [formulas (XXXIV)—(XXXVII)]. To demonstrate the versatility of this system, multifunctional carbene adducts were prepared and used to polymerize lactide to produce block



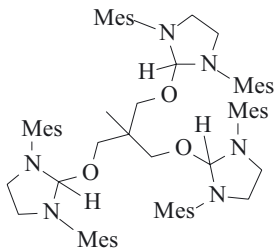
(XXXIV)



(XXXV)



(XXXVI)



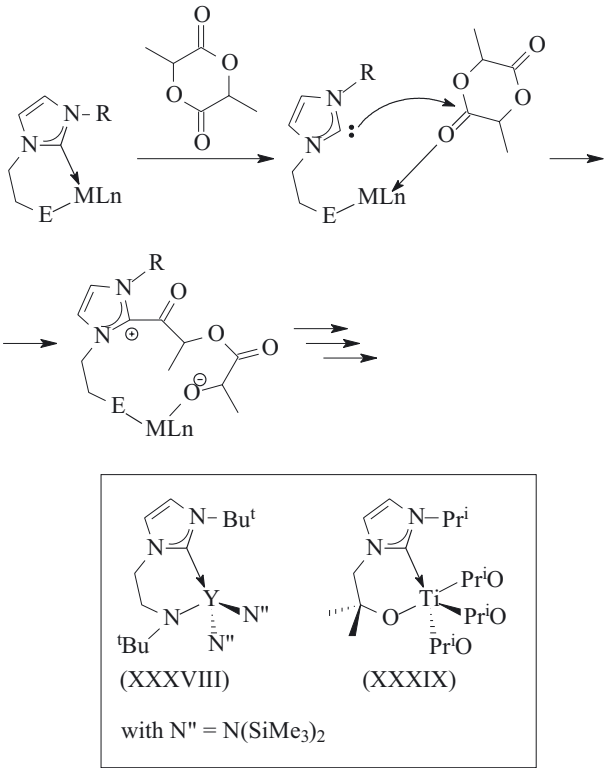
(XXXVII)

copolymers, telechelic polymers and star polymers [73]. The reversible nature of the alcohol adduct formation is partially responsible for the exquisite control observed in this system. The reversible formation of a "dormant" alcohol adduct by combination of free carbene with the propagating alcohol chain ends maintains a low concentration of catalyst in solution, analogous to modern controlled radical polymerization process.

While imidazolidines (XXXV)—(XXXVII) can deliver carbene at room temperature, alkoxytriazolines (XXXIV) dissociate at temp. 90 °C. The reversibility of this process has been exploited for an on-demand polymerization of lactide: an active and dormant form of catalyst can be formed depending on the reaction temperature [67].

Additionally, titanium and yttrium alkoxy-*N*-heterocyclic carbene complexes have been reported to act as bifunctional catalyst that use both Lewis acid and base functionalities to initiate ROP [71, 74]. As shown in Scheme K, an initiating nucleophilic attack on the metal-coordinated monomer by the labilized carbene would be followed by coordination-insertion polymerization of the rest of the lactide monomer. The most effective combination of "protected" hemilabile *N*-heterocyclic carbene and Lewis acidic metal is provided by the Y(III) complex [formula (XXXVIII) in Scheme K], suggesting that further chain growth occurs *via* monomer insertion at the metal center.

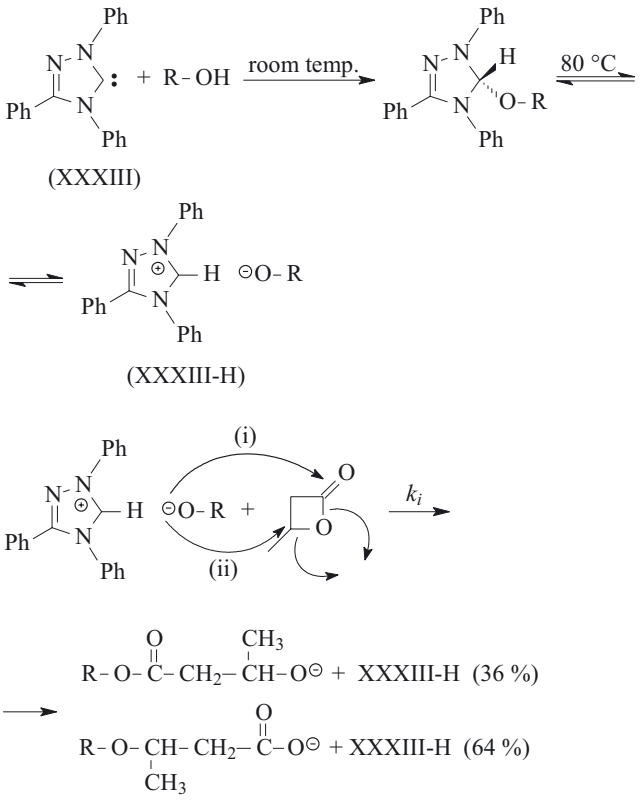
The selectivity of the commercially available carbene (XXXIII) for the ROP of lactide prompted Coulembier *et al*. to investigate its reactivity for the ROP of β-butyrolactone (BL) [68, 75]. When polymerization of BL is initiated from primary alcohol and carbene (XXXIII) at temp. 80 °C in toluene, the expected polymer chains are contaminated by crotonate by-products. Reasoning that the basicity of free carbene (XXXIII) might lead to undesired elimination reactions with unreacted BL, generating crotonate-based initiators, *tert*-butanol has been used as cosolvent to favor adduct formation and minimize the concentration of free carbene (XXXIII). *Tert*-butanol cannot initiate the polymerization of BL, however it does react reversibly with the triazole to form the corresponding adduct. Under these conditions, poly(β-butyrolactone) were obtained having molecular weights matching those predicted from the monomer to initiator ratios and narrow polydispersities (for molecular weights having *DP*'s below 200). For such limited *DP*'s, the plot of the molecular weight *versus* conversion for (XXXIII) catalyzed ROP has been revealed linear, consistent with a thinkable "living" polymerization in which the monomer cleavage proceeds by an *O*-acyl scission. Combined data demonstrate end-group fidelity and predictable molecular weights, particularly for targeted *DP*'s of 200 or less [68, 75, 76]. However, BL polymerization targeting higher molecular weights (*DP*'s ranging from 250 to 450), generally accompanied by long reaction times, tended to show some broadening in the polydispersity. Moreover, for such higher molecular weights, a small amount of crotonate was observed (~25 % of total chain ends), consistent with a second mode of polymerization [68].



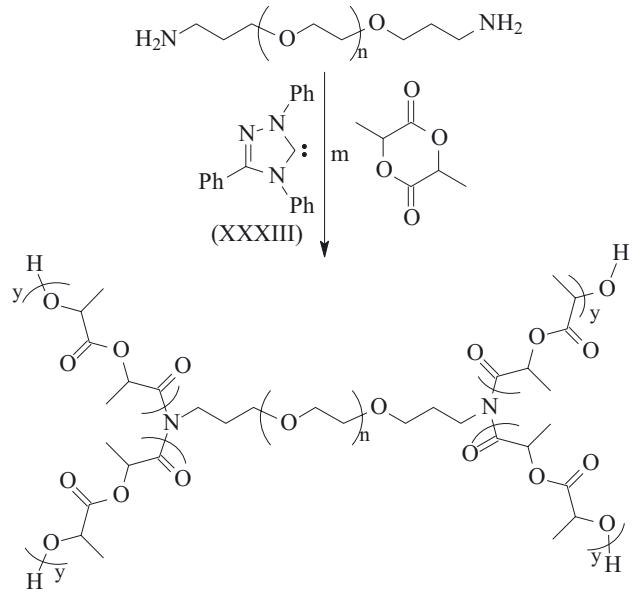
Scheme K. Bifunctional yttrium(III) and titanium(IV) N-heterocyclic carbene catalysts for lactide polymerization

Recently the same authors emphasize the importance of polymerizing BL in anhydrous *t*-BuOH used as the only solvent to get rid of even negligible undesirable crotonate species also able to initiate subsequent propagations leading to the loose of molecular weight and end-group fidelity, especially for high targeted *DP*'s [75]. In such conditions, molar weights higher than 30 000 g/mol were obtained from an equimolar mixture of primary alcohol and carbene (XXXIII) at temp. 80 °C. Interestingly, the end-group analysis of the polyester revealed the presence of a carboxylic acid end-group, meaning that carboxylate were the propagating species in this polymerization reactions. Authors demonstrated that both alkoxy and carboxylic acid groups are present at the early stage of the reaction while the number of carboxylate end groups per polymer chain increased during the course of polymerization to finally represent the only propagating center for *DP*'s higher than 10.

Interestingly enough, such results allowed authors to initiate the polymerization from an equimolar mixture of carboxylic acid and carbene (XXXIII) at temp. 80 °C in *t*-BuOH to get also access to high molar weigh poly(BL) (M_n > 30 000 g/mol) [75]. Even if the *N*-heterocyclic carbene-catalyzed ROP proceeds *via* a suspected monomer activated mechanism in a toluene/*t*-BuOH mixture [68], the evidence of a clear anionic process has been highlighted when polymerization is conducted in *t*-BuOH as



Scheme L. Proposed initiating anionic process of BL ROP using alkoxytriazolium adduct as initiator in t-BuOH at 80 °C implying both "O-acyl" (i) and "O-alkyl" (ii) cleavages (k_i: initiating rate constant)



Scheme M. Polymerization of lactide initiated by bis(3-aminopropyl) poly(ethylene glycol) in presence of triazole (XXXIII)

the only polymerizing solvent [75]. In such process the triazolium carbene (XXXIII) is suspected to deprotonate the primary alcohol just before the initiation step to give the corresponding alkoxide counter-balanced by the protonated carbene (XXXIII) as complexing cation (Scheme L). The resulting alkoxide might then initiate the BL ROP by both *O*-acyl and *O*-alkyl scission while the number of carboxylate end groups per polymer chain increased during the course of polymerization.

As saturated imidazolinylidenes and triazolylidenes also undergo N-H insertion reactions with amines to yield amino-adducts [77—79] primary amines were investigated as initiators for the ROP of lactide. Remarkably, primary amines act as bifunctional initiators to generate two chains per initiating amine, enabling the facile construction of branched block copolymers from amine-terminated multifunctional macroinitiators. Polymerization of lactide from bis(3-aminopropyl) poly(ethylene glycol) in the presence of triazole (XXXIII) carbene yielded the *H*-shaped block copolymer after 71 hours at temp. 90 °C (Scheme M) [80]. This result is in marked contrast to organometallic promotors where only one chain is initiated from primary amines, generating an amide end-group [81].

Cyclic polyesters obtained by *N*-heterocyclic carbene catalysis

In the field of nanotechnology, macrocyclic polyesters are very promising for the production of heterophase materials with smaller size domains exhibiting distinct properties to their linear counterparts [82]. While numerous methods have been explored for the preparation of these compounds, the general synthesis strategy is similar and can be outlined as follows:

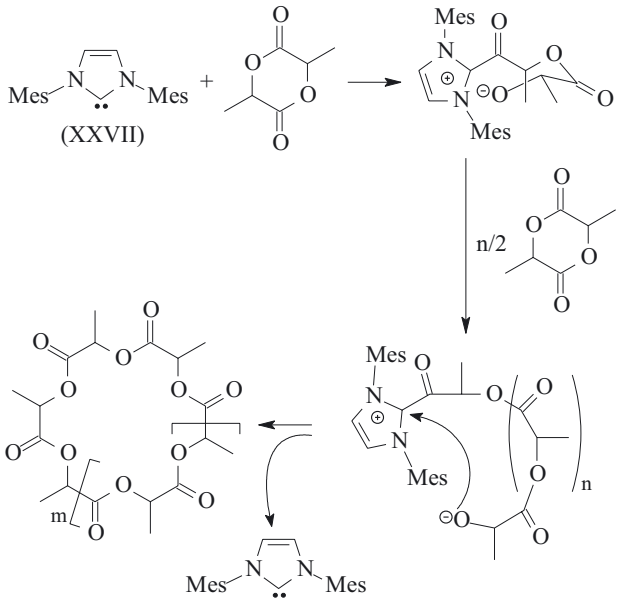
— preparation of a monodisperse α,ω-homodifunctional polymer by controlled "living" mechanism,

— reaction of the α,ω-homodifunctional polymer with a homodifunctional-linking agent,

— fractionation for purification of the cyclic polymer.

In all cases, a high dilution process is required leading to poor cyclization yields and competing reactions, involving tedious purifications to isolate pure macrocycle [83]. In comparison, *N*-heterocyclic carbenes have been demonstrated to be potent transesterification agents able to catalyze the "living" ROP of strained (di)lactones. A key feature of the nucleophilic mechanism involved in the synthesis of linear polyester chains is the formation of a zwitterionic intermediate generated from nucleophilic attack of the carbene on the lactone followed by ROP of the tetrahedral intermediate to generale the acylimidazolium alkoxide zwitterions. To assess the role of the zwitterionic intermediates in these polymerizations and also to get an easy way for the synthesis of macrocyclic structures, the polymerization of lactide was carried out in the absence of alcohol, amine or carboxylic initiators. Remarkably, these conditions led to the formation of cyclic poly(lactide)s of defined molecular weight, even at relatively high monomer concentrations (0.6 to 1.0 mol/dm^3 in THF) [84]. The polymerization of *rac*-lactide with IMes [formula (XXVII)] occurs rapidly (5—900 seconds) at room temperature to yield

cyclic poly(*rac*-lactide)s with molar weights from 7000 to 26 000 g/mol and narrow polydispersities. The cyclic structure of the products was determined by a combination of techniques, including the absence of end-groups by ^{1}H NMR spectroscopy, MALDI-TOF mass spectrometry, and the lower solution viscosities of the cyclic polymers relative to their linear congeners. Polymerization of optically pure L-lactide with (XXVII) generated crystalline cyclic poly(L-lactide), indicating that the polymerization proceeds with retention of stereochemistry. The



Scheme N. Zwitterionic polymerization of lactide to cyclic polylactides

selectivity for the formation of high molecular weight macrolactones, even at relatively high monomer concentrations, was proposed to be a consequence of the enforced proximity of the zwitterionic chain-ends (Scheme N) [85]. Recently, the possibility to control the macrocyclization of β-butyrolactone or β-propiolactone taking advantage of the same mechanism has been also highlighted [86].

CONCLUSION

Undoubtedly, readily accessible *N*-heterocyclic carbenes (NHCs) represent a very important alternative as metal-free catalysts for promoting controlled ring-opening polymerization of (di)lactones. Fine tuning of their reactivity and catalyst efficiency in ROP by simple tailoring of their electronic and steric surroundings, *i.e.*, *via* adequate molecular design and substitution, allows for an almost perfect control over the molecular parameters of the recovered polyester chains. Actually, these metal-free catalysts display unique reactivity in synthesis of aliphatic polyesters such as polylactides and poly(β-butyrolactone)s all characterized by well-tailored compositions, molecular weight, tacticity, and end-group fidelity while presenting narrow to very narrow molecular weight distribution. As a result, novel macromolecular architectures have been made available, *e.g.*, multi-armed star shaped copolyesters, H-shaped copolyesters or macrocyclic polyesters. In very near future, it can be expected heaps of progress in that new catalytic domain allowing for producing various biocompatible and biodegradable materials built upon such metal-deprived aliphatic polyesters with unique applications in the biomedical field.

ACKNOWLEDGMENTS

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