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N-Heterocyclic Carbenes: A Powerful Catalyst for Polymerization

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Abstract

As much of the concern is being placed on metal-free polymerization, carbenes are attracting researcher attention. Besides their impact on organic synthesis, they played an integral role in several types of polymerization. This unique class of organocatalyst revives the preparation of polymeric materials that possess functional groups at each carbon atom on the polymer chain, which was hardly reached by conventional methods. This chapter will concern with the contribution of N-heterocyclic carbenes (NHCs) in the preparation of functional polymers from diversified monomers. Also, will discuss the advantages of N-heterocyclic carbenes in some conventional polymerization such as ring-opening and step-growth polymerizations along with the direct zwitterionic polymerization.

Keywords: ring-opening polymerization, step-growth polymerization, zwitterionic polymerization, metal-free polymerization, heterocyclic carbenes

1. Introduction

In the breathtaking development of polymers, the preparation of biocompatible polymers in the economic and environmental friendliness rout has achieved great interests. The synthesis of polymers is usually considered as macromolecular architecture that provides versatile materials in a different application. This includes sophisticated design by different polymerization or post-polymerization techniques [1]. Besides, polymeric materials provided by free radical polymerization, most of the time, the well-known commercial polymers were developed using metal-based catalysts. In this regard, hazardous residual metals and by-products arise as a precarious issue in the biomedical and electronic applications. The cost of precious rare metals, as well as the purification steps, increases the expenditure in large-scale production. In this context, metal-free polymerization by organocatalysts overcomes this obstacle and offers a variety of new synthetic strategies. N-heterocyclic carbenes (NHCs) are classified as one of the most reactive compounds in organocatalysis. In the late 19th and early 20th centuries, NHCs were described as reactive intermediates because the isolation of carbenes was not achieved [2]. N-heterocyclic carbenes have their roots back. Mizuhara et al. [3] reported, in 1954, a natural nucleophilic carbene existence was a catalytically active species of the coenzyme thiamine (**Figure 1**). Ever since the successful isolation of stable NHCs in the early 1990s [2], their contribution has been enlarged rapidly in synthetic chemistry. They

Figure 1.
Coenzyme thiamine.

offer a variety of catalysis and reaction pathways. Besides, their estimated impact on organic synthesis, NHCs are considerable catalysis in the polymer chemist toolbox.

1.1 Polymerization and organocatalysis

In the history of chemistry reactions, catalysis was performed by enzymes and transition metal species. In yet, organocatalysis has emerged to play an integral part in catalysis systems. With regard to other catalytic systems, organocatalysis has been inescapable for many reasons. Beyond their derivation from a variety of organic reagents with plenty of chiral forms, organocatalysis systems are eco-friendly reagents having a low toxicity. Therefore, much of the molecular and macromolecular synthesis relies on it. They were developed to catalysis or initiate polymer synthesis for a variety of sensitive applications like biomedical application, food preserving or packaging, and sophisticated electronic species.

Mainly, polymerization is known to be performed by two categorically mechanisms chain growth and step-growth polymerization. Chain growth polymerization (CGP) is distinguished by the formation of reactive intermediate (anion, cation or radicals) throughout the initiation step. These reactive species transfer the reactive center by reacting with a monomer molecule which is called the propagation stage. The progress of polymer chains is contingent by the continuous reaction of monomer molecules with the formed active center until termination occurs by consuming the active center. In step-growth polymerization (SGP), polymerization starts with the reaction between two molecules that compromise two functional groups. Then another molecule reacts with the formed dimer and so on. Consequently, polymers chain formation depends on the reaction between molecules and/or the formed small chains [4, 5]. Although the difference between these two polymerization mechanisms, they all share using catalytic or initiating systems not only to establish a polymerization process but sometimes to design the macromolecule structure.

Various types of organocatalysts have been employed either in chain growth or step-growth polymerization. It is true that excessive use of organocatalysts was in chain polymerization, in particular, the ring-opening polymerization. However, very recently, many researchers were motivated to use organocatalysts in step-growth polymerization. Given the constantly similar nature of functional groups of ring-opening polymerization, a true example of chain polymerization, with step-growth polymerization, it is nearly to have the same catalytic system for both polymerization mechanisms [6]. Across the field of metal-free polymer preparation catalysis, N-heterocyclic carbenes (NHCs) have affirmed the potential of organocatalysis. This will be presented by revealing NHCs capability to activate certain groups which impact the synthesis of metal-free polymers that are commercially important.

2. N-heterocyclic carbenes (NHCs) overview

Nowadays, developing new polymeric material that possesses biocompatible properties has been strongly emerged. Using organic metal-free catalysts became an inevitable approach in today's environmental mindset. Hence, these catalysts can be easily removed from polymers unlike toxic metals in other types of catalytic systems. Carbenes, in particular N-heterocyclic carbenes (NHCs), are considered as a class of organic metal-free catalysts for different types of the polymerization process. Ever since the first successful isolation of N-heterocyclic carbenes by Arduengo, in the early 1990s, the chemistry richness of these compounds has been revealed in many applications. Their chemical structure can be described as heterocyclic moiety having at least one nitrogen atom and of course carbene carbon [7]. These neutral divalent species of carbon owing only four electrons have participated in σ -bonds and two remained at the central carbon. The presence of nitrogen atoms elevates the stability of carbenes by their ability of π donation to the empty carbon π orbital along with σ withdrawing (Figure 2).

This behavior leads to a huge gap of σ - π (Figure 3) that precedes the strong nucleophilic feature of NHCs. Nevertheless, some NHCs would have amphiphilic character. By substituting the amino with σ -donating alkyl group, an increase of electrophilicity and also nucleophilicity is observed. Also, the incorporation of carbonyl groups into the backbone augmented electrophilicity over the nucleophilicity as they compete with the carbene center for the π donation of the nitrogen atom [8].

Therefore, by studying NHCs ability to donate the electron pair (Lewis basicity) it was found that the triazole-ylidene is less nucleophilic by 10^3 than Imidazole and imidazoline-type (Figure 3). Many studies of proton affinity of NHCs, by evaluating the pK_a of their conjugated acid, have been employed. They revealed the great impact of the electron-donating substituent on the nitrogen atom as well as the bulkiness of NHCs on their Bronsted basicity. Also, the increase from 5 to 6 membered ring increases the carbenes angles, and leads to an increase in pK_a [9–11].

Besides, their distinctive coordination chemistry, N-heterocyclic carbenes have other advantages one of them is they can be easily be modulated bearing in mind the large library of heterocyclic chemistry as shown in Figure 4. However, several methods of preparation can be categorized in imidazolium deprotonation, imidazole-thione reduction, and NHCs-adducts thermolysis [12–16].

NHCs have been heavily exploited as ligands for transition metals [17–20]. However, their superiority in metal-free transformations is well recognized in organocatalytic chemistry [21] as well as in macromolecular chemistry [22, 23].

Figure 2.
Ground-state electronic structure of one class of N-heterocyclic carbenes.

Figure 3.
Energy (eV) of border orbitals of classical NHC.

Figure 4.
Examples of N-heterocyclic carbenes polymerization catalysis.

2.1 Ring-opening polymerization (ROP)

Ring-open polymerization has been devoted to developing interesting industrial polymers by synthesis of the analogs of natural as well as biocompatible polymers

by different methods. The sharp improvement in ROP is undoubtedly accelerated by organocatalysis. Mainly, organocatalysis of ROP proceeds according to four activation mechanisms; electrophilic monomer activation, nucleophilic monomer activation, base chain-end activation, or bi-functional activation mechanism. Both electrophilic and nucleophilic monomer activation starts by attacking the carbonyl group of the monomer to obtain a macromolecule that bears two ends having opposite charge starts what is called Zwitterionic ROP (ZROP) (**Figure 5**) [24]. However, they differ in their act for activating the carbonyl group. In electrophilic monomer activation, the carbonyl group is activated by protonation or H- bonding attachment that gives room for a chain end nucleophilic attack. While in nucleophilic monomer activation, the zwitterionic intermediate extends a deprotonation process of the alcohol. Then, the formed alkoxide proceeded with the acylation of the carbonyl group. Consequently, the catalyst is free to act again. The third activation mechanism is the chain-end activation where the nucleophilicity of the alcohol is elevated through deprotonation to form either alkoxide or H-bonding [6].

Figure 5.
 Mechanism of (a) electrophilic and (b) Nucleophilic zwitterionic ring-opening polymerization.

This chain-end attacks the carbonyl carbon triggering a ring-opening reaction to form an ester allowing the activated alcohol species to reform. The last mechanism for ROP is the bifunctional activation mechanism. It comprises activation of the monomer carbonyl carbon through electrophilic activation along with the activation of the chain end/initiator [25].

Ever since, knowing the benefits of NHCs in transesterification reactions [26–28], they were intensely employed in ring-opening polymerization (ROP). NHCs play a role in producing polymers with low disparities as they are able to provide living polymerization that control the polymer molecular weight. Furthermore, they facilitate the ROP for production of linear and cyclic aliphatic polyesters [29].

2.2 ROP of cyclic ester

Thanks to Nyce *et al.* in 2002, through their navigation for an efficient nucleophilic catalyst, they discovered the effectiveness of NHCs as organocatalysts for ROP [28]. They also succeeded to polymerize cyclic monomers to deliver Poly (L-lactide) (PLA) (**Figure 6**), poly(ϵ -caprolactone) (PCL), and poly(b-butyrolactone) (PBL) with dispersity near to unity and definite chain ends which help to control the polymers molecular weight [26]. The polymerization was initiated by alcohols (benzyl alcohol or 4-(pyrene-1-yl)butan-1-ol) which provoke an α -end group address the ester from the initiating alcohol upon ring-opening a hydroxyl functional ω -chain end that propagates the chain. Hedrick's team first suggestion for the transesterification reaction mechanism was activated monomer mechanism. Considering the steric effect and the higher pKa of the alcohol compared to the conjugated acid of NHC in DMSO, deprotonation of less acidic alcohol by NHC is unlikely the beginning step of the catalysis act. Therefore, they assumed a direct attack of the monomer by the nucleophilic NHC to form a zwitterionic intermediate that interacts with the other monomer molecules pursued by the reaction with alcohol. Another initiation mechanism proposed by the theoretical study assumed the occurrence of an active chain-end mechanism. Lia *et al.* suggest the hydrogen bonding between NHC and alcohol, then deprotonation of alcohol which attacks the cyclic monomer [30]. This assumption was based on the lower energy of the H-bonded adduct than the zwitterionic intermediate. Several studies follow to

Figure 6. Ring-opening polymerization of L-lactide through path: (A) monomer activation mechanism and (B) active-chain end mechanism.

find out the predominant mechanism. This dispute most likely has been resolved by Patel *et al.* manifesting the ability of NHC to act as bifunctional catalysts in the presence of alcohol and the two mechanisms are likely participating in [31].

The catalytic behavior NHCs in the absence of alcohol was investigated. At a relatively high LA concentration and ambient temperatures, a very fast polymerization was reported (5 s–900 s) yielding a cyclic polymer. In this case, NHC acts as an initiator that generates zwitterionic intermediate by a direct nucleophilic attack of NHC to the LA monomer. The ring-closure occurred by trapping the NHC within a zwitterionic NHC–CS₂ adduct.

Engaging the spirit of the suggested mechanism of cyclic esters polymerization, remarkable turnovers were observed for the ROP of a variety of other cyclic monomers including cyclosiloxanes, epoxides, and N-carboxyanhydrides. NHCs proved extreme activeness, although the usage of low concentration and temperature.

2.3 ROP of siloxanes

Taking the advantage of NHCs silicophilicity [32], the ROP of cyclic (carbo) siloxanes has been investigated [33]. A rapid polymerization of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (TMOSC) occurred in less than a minute [34]. The polymerization was activated by electron-rich NHC in toluene (**Figure 7**). The product, poly(carbosiloxane), the molar mass of 10,200 g mol⁻¹ was controlled with dispersity equal to 1.19. This was observed if the polymerization stopped in high conversion otherwise broadening was detected due to undesired transesterification side reactions.

The authors reported a decrease in the polymerization rate when bulky, and less basic NHC is involved. Also, they revealed through mechanistic studies that the polymerization process is activated by hydrogen bonding instead of nucleophilic ring-opening of TMOSC by the NHC.

Figure 7.
 the proposed mechanism of ROP of TMOSC.

2.4 ROP of epoxides

An attempt to activate the ROP of ethylene oxide (EO) by NHC was recorded by Raynaud *et al.* [34]. In this work, NHC succeeded to accelerate the ROP of ethylene oxide as a direct initiator and combined with chain regulators of the NuE-type. 1,3-diisopropylimidazol-2-ylidene initiate alone ROP of EO in DMSO at 50°C. linear difunctionalized PEOs were produced, unlike cyclic polymers that formed by ZROP of LA which was previously discussed.

2.5 ROP of carbonates

The ROP of cyclic carbonates was reported in the melt or bulk polymerization [34]. Nederberg et al. investigated the ring-opening polymerization of trimethylene carbonate using varieties of organocatalysts. NHC catalysis yield a quantitative conversion in 30 min and a polymer dispersity of only 1.06, when less electron-rich NHC is employed (**Figure 8**). This study showed that the increased electron-rich nature of NHC leads to an increase in the polymerization rate at the expense of molecular weight control (99% conversion in seconds).

Figure 8.
The ring-opening polymerization of trimethylene carbonate.

2.6 ROP of anhydride

N-carboxyanhydrides have been polymerized using NHC to produce linear poly(α -peptoids) in THF [35]. One of the biggest advantages of this polymerization is the ability to prepare a definite structure with low molecular weight distributions in the range of 1.04–1.12 and the molecular weight ranges (3000–40,000 gmol^{-1}). The authors found that small N-substituents of NHC enhance the reaction rate. They also revealed that the control of molecular weight is strongly dependent on the solvent and the NHC structure. The mechanism of the polymerization followed the ROP mechanism under the loss of CO_2 . Side reactions are significantly suppressed in low dielectric solvents due to the reduced basicity and nucleophilicity of the negatively charged chain ends of the zwitterions, resulting in quasi-living polymerization behavior.

2.7 Step-growth polymerization

Virtually all high-performance polymers (80%) that are currently utilized are products of chain-growth polymerization along with step-growth polymerization. The top valued polymers, polyether ketones, polysulfones, polyimides are step-growth polymerization products. Normally, step-growth polymerization (SGP) compromises the reaction between two different bi-functional groups that might present in one monomer or two different monomers. Amidation, esterification, nucleophilic aromatic substitution, transesterification, and urethane formation with isocyanates are the conventional reaction in step-growth polymerization. They almost proceed with the high conversion that is suitable for polymerization. However, the hard condition, high pressures and temperatures, and side reaction leading to monomers decomposition and limiting the molecular weight [6]. Therefore, almost all step-growth polymerizations require a catalyst to increase the rate of reactions and consequently reduce the potential side reactions.

(NHCs) have been used in step-growth polymerization to achieve high molecular weight polymers. Mostly, they were in-situ developed through deprotonation of imidazolium salts with a base.

Bearing in mind their potential in transesterification reaction, NHCs catalysis was implemented in step-growth polymerization of 6-hydroxyhexanoate, bis(2-hydroxyethyl) terephthalate as well as the polycondensation of dimethylcarbonate (DMC) and a number of diols.

Hedrick et al. polymerized bis(2-hydroxyethyl) terephthalate using only NHCs as a catalytic agent in THF. The polymerization process accomplished almost full conversion within one hour at 250°C. They also, succeeded to prepare aliphatic polyesters by polytransesterification reactions of ethyl 6-hydroxyhexanoate and ethyl glycolate [28]. Poly-(6-hydroxyhexanoate) with dispersity of 1.57 and Mn of 21,000 gmol⁻¹ was obtained by carrying out the SGP at 60°C for 24 h. The polymer in 95% yield was obtained by removing EtOH at low pressure. By this procedure, polyesters (with Mn ranging from 8000 to 20,000 gmol⁻¹) were similar to poly(ϵ -caprolactone) (PCL) and poly-(glycolide) synthesized by ring-opening polymerization (ROP).

NHCs activate the monomers by attacking their carbonyl carbon. This feature was also implemented to prepare a variety of industrial polymers. Plasseraud et al. reported their success to prepare metal-free aliphatic polycarbonates [36]. Dimethylcarbonate and diols in molar mass equal 3:1, respectively, were reacted in bulk at 150°C under reduced pressure. The reactions were conducted at 100°C for 15 min in the first stage to liberate the active NHC by decarboxylation of the NHC-CO₂ adduct that was used as precatalyst. Thereafter, the temperature was elevated to 150°C for one hour under reduced pressure to remove methanol which forceful the polymer formation. Random copolymer with moderately controlled molecular weight distributions and molecular weight (19,000 gmol⁻¹) and homopolymers were produced. Employing a molar equivalent 1: 2 of DMC and aliphatic diols, respectively, hydroxy-terminated polycarbonates could also be achieved.

Umpolung reactions have their influence on polymer chemistry. The benzoin condensation reaction motivated Pinaud, et al. to synthesis polybenzoin [37]. In this case, the carbonyl group in bis-aldehyde is activated by NHC in THF or DMSO at 40°C to form alkoxide that triggers the formation of “Breslow intermediate”. This intermediate attack the electrophilic carbon of another aldehyde molecule (**Figure 9**). Thereafter, C-C bond formation leads to the step-growth polymerization of bis-aldehyde and cyclic polymers by-products.

In another pathway, NHCs have been used for activation of the alcohol for developing interesting polyurethane (PU) from isocyanates and polyols reaction. A study performed by Bantu et al. showed that the order of addition is a key for successful formation of PU [38, 39]. Hence, first, the alcohol was deprotonated

Figure 9.
 The proposed mechanism of the step-growth polymerization of bis-aldehyde.

by the NHC before the addition of the di-isocyanate monomer. In this investigation, the synthesis of cross-linked polyurethanes was conducted in CH_2Cl_2 at 60–70°C affording in-situ generation of NHC catalyst from NHC– CO_2 adducts. The resulting alkoxides from the reaction of NHC catalyst and ethylene glycol or polyol in a 1/1 ratio at 70°C were detected quantitatively by ^1H NMR analysis. The C2H imidazolium proton and pyridinium proton were detected confirming the proposed mechanism of alcohol activation. Not only the order of addition of reactants is vital but also the nature of the diisocyanate monomer. Coutelier et al., found that when linear aliphatic diisocyanates are employed, soluble, linear PUs (2000–5000 g mol^{-1}) might be derived [40] otherwise crosslinked PU is formed. The SGP polymerizations were carried out in THF using 1 mol% catalyst relative to monomer between 30 and 50°C. The 1/1 ratio was employed for a selected diol and two aliphatic diisocyanates (isophorone diisocyanate and 1,6-diisocyanatohexane). Despite the potency of NHCs as catalysts for the cyclo di or trimerization reaction of phenyl monoisocyanate (70% cyclodimer and 30% cyclotrimer) [41], traces of such uretdione or isocyanurate were detected with alkyl isocyanates. This provides another confirmation of the alcohol activation through H-bonding before nucleophilic addition onto the isocyanate species.

This activation mechanism was utilized by Marrot et al. for the polycondensation of disilanol [42]. In a closed schlenk tube, α,ω -Dihydroxy oligodimethylsiloxanes was mixed with a catalytic amount of isolated NHCs at 80°C for 16 h to yield almost 90%. Interestingly, the water released from the dehydration of the silane did not depress the catalytic activity of NHC. The hydrophobic nature of the developed polydimethylsiloxane seems to prevent direct contact with NHC. Nevertheless, removing the produced water leads to increasing molecular weights of the resulting silicone polymers. This observation suggests another role for NHCs as a catalyst for depolymerization reactions in the presence of H_2O . Therefore, the catalytic amount of NHC and water withdrawal have an effect on regulating the produced polymer molecular weight.

3. Conclusions

Throughout the past two decades N-heterocyclic carbenes (NHCs), have well stood as a true organocatalyst for the production of many industrial polymers. Owing to their rich structural modularity, NHCs can afford highly selective polymerization reaction pathways. A deep awareness of NHC's catalytic activity potential was gained through understanding their activation reaction mechanism that opens pathways for the production of commercial polymers. They have been extensively involved as transesterification agents in the ROP. Also, they showed a tremendous impact on step-growth reactions for the production of high molecular weight polymers (polycarbonates, polyesters, polybenzoins). Besides, their role of accelerating polymerization and their temperature range extends, they have the ability to introduce functionality to polymers. Due to their sensitivity to air and moisture, NHCs were in-situ generated using affordable and air-stable precursors, imidazolium chloride salt as starting source. As the catalyst design field progresses, opportunities for NHC polymerization catalysis can move beyond its current niche to compete in a field currently dominated by heterogeneous metal catalysis.

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