

Review

Copolymerization of carbon dioxide and epoxides by metal coordination complexes



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ARTICLE INFO

Article history:

Received 7 July 2018

Received in revised form 22 August 2018

Accepted 22 August 2018

Keywords:

Polycarbonates

Carbon dioxide

Epoxides

Homogeneous catalysis

Terpolymers

ABSTRACT

The catalytic copolymerization of CO₂ with epoxides to give polycarbonates was discovered nearly 50 years ago. The last 10 years have been particularly exciting for the development on highly active homogenous catalyst systems, insights into mechanisms and the design of polymers with promising physical properties. Recent work has identified new copolymerization pathways with increasing diversity in the metals and ligands employed. Cooperative mechanisms with binary catalyst systems using exogenous nucleophiles continue to be studied. Elegant ligand design, however, has been used to generate new, highly active bimetallic or bifunctional catalyst systems. The bimetallic systems allow for “shuttling” of growing polymer chains leading to excellent activity under low CO₂ pressures. Bifunctional systems use covalently linked groups that facilitate the role of the nucleophilic co-catalyst. These groups can be neutral Lewis basic sites, such as *N*-donors, or cationic sites, such as ammonium groups, that improve the association of the anionic nucleophilic co-catalyst components. The cationic groups also improve association of any metal-dissociated anionic polymer chain ends and allow more efficient separation of the catalyst from the polymer products via chromatography. This review gives an overview of the developments of homogeneous catalysts for CO₂/epoxide copolymerization grouped by metal site. New mechanistic studies and strategies for future catalyst developments are also discussed.

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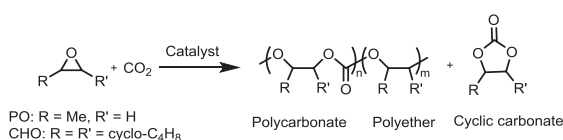
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1. Introduction

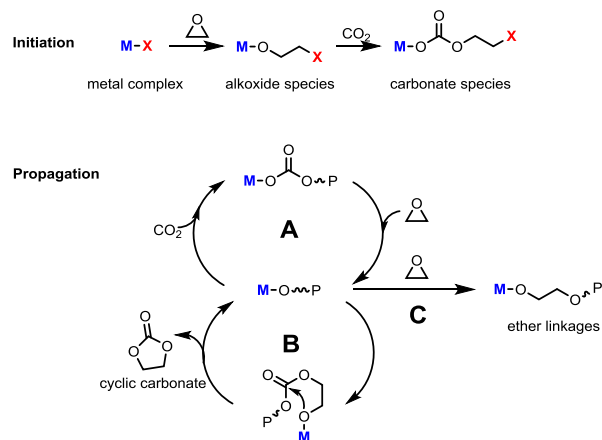
Polycarbonates are durable, transparent, moldable, light and shatter resistant, hence they are widely used for numerous industrial applications [1–4]. The conventional synthesis of polycarbonates involves the reaction of bisphenol A (BPA) with phosgene. This aromatic polycarbonate possesses a high glass transition temperature of 140 to 155 °C and excellent resistance to hydrolysis. Aliphatic polycarbonates, however, typically have lower general heat resistance, as well as higher susceptibility to hydrolysis, which results in more limited commercial applications. Nonetheless, they represent useful materials, particularly if they can be prepared from renewable feedstocks and exhibit biodegradable/biocompatible properties.

The synthesis of polycarbonates from epoxides and CO₂ is a promising route to new materials with highly tunable properties. This process not only uses CO₂ as a carbon feedstock but also provides a potentially sustainable route to produce valuable cyclic and poly(carbonate)s. Furthermore, it uses abundant CO₂ rather than toxic phosgene as a reactant and the polymers generated can contain up to 50 mol% CO₂. In many cases, the epoxide can serve as the solvent, therefore reactions can be run in neat conditions. Copolymerization of CO₂ and epoxide to produce polycarbonate was first identified by Inoue in 1969 [5]. Over the past 20 years, there has been a steady growth in the number of annual publications reporting new details of CO₂/epoxide copolymerization. In general, this reaction is accompanied by the formation of cyclic carbonate byproduct and varying quantities of ether linkages (Scheme 1). Two general observations are also found for this catalytic reaction regardless of the catalyst. First, aliphatic epoxides more easily form cyclic carbonates than alicyclic epoxides. Second, an increase in temperature leads to an increase in the formation of cyclic carbonate [6]. Among the investigated epoxides, propylene oxide (PO) and cyclohexene oxide (CHO) are the most commonly used, of which PO and CO₂ provide the corresponding polycarbonate that has been industrially most developed. On the other hand, CHO affords a polycarbonate that exhibits poor mechanical properties for current industrial needs [7]. However, CHO exhibits low propensity to form cyclic carbonate byproduct in the copolymerization process making it useful for academic studies.

A general catalytic cycle of CO₂/epoxide copolymerization is shown in Scheme 2 [8]. The reaction begins with a ring-opening of the metal-activated epoxide by the initiator X (such as a halide) to generate an alkoxide. The metal alkoxide species subsequently undergoes CO₂ insertion to afford the metal carbonate. The resulting carbonate serves as an initiator to ring-open another coordinated epoxide, followed by CO₂ insertion to generate a carbonate, which continues the polymerization process (Scheme 2, A). During this process, the metal bound polymer chain may backbite to afford the cyclic carbonate product (Scheme 2, B). For some catalysts, the resulting metal alkoxide can also ring-open epoxide or decarboxylate leading to ether linkages in the copolymer backbone (Scheme 2, C). The percentage of carbonate linkages is, therefore, commonly reported. Chain-transfer reactions may also occur, either through intramolecular backbiting or through reaction with an external source of ionizable hydrogens, such as water, alcohols



Scheme 1. Typical copolymerization of epoxide and CO₂ to produce polycarbonate (and ether linkages) and cyclic carbonate byproduct (PO = propylene oxide, CHO = cyclohexene oxide).



Scheme 2. A general catalytic cycle for the catalytic copolymerization of CO₂ and epoxide (P = polymer chain, X = halide or other nucleophile).

or acids. These sources are often contaminants (especially water or alcohols) or otherwise adventitious to the reaction but may also be added intentionally to give precise control over molecular weights or, in the case of polyprotic chain-transfer agents, may yield block copolymers or branched polycarbonates.

The reaction between epoxides and CO₂ is usually carried out with a suitable epoxide, a Lewis acid catalyst, M, and a nucleophile, X, which may be intramolecular (as shown in Scheme 2) or an external nucleophile (referred to in the CO₂/epoxide copolymerization literature as a co-catalyst). The reaction, usually but not always, needs high pressures of CO₂ and high temperature depending on the epoxide species, the desired product and the type of catalyst. The nucleophile can come from the catalyst or can be added externally as co-catalyst, and can be neutral, such as 4-(dimethylamino)pyridine (DMAP) and N-methylimidazole (NMIm) or ionic, such as bis(triphenylphosphine) iminium chloride ([PPN][Cl]) and bis(triphenylphosphine) iminium azide ([PPN][N₃]) (Fig. 1). The Lewis acid catalyst may be a complex of a main group element, such as magnesium or aluminum, or a transition metal. Most catalyst systems are termed “binary” because they require the use of external co-catalysts to facilitate initiation by ring-opening of the epoxide. There is, however, vigorous development of highly active bimetallic or bifunctional catalyst systems. Bimetallic systems often show very high activity at low pressures and negate the need for external nucleophiles as epoxide ring-opening is believed to occur via an

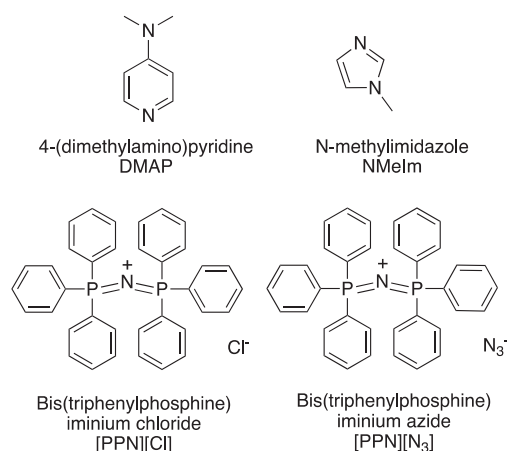


Fig. 1. Structures of commonly used co-catalysts in CO₂/epoxide copolymerization reactions.

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