

Review

Carbon dioxide-based functional polycarbonates: Metal catalyzed copolymerization of CO₂ and epoxides

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ABSTRACT

Proof of principles studies by Inoue and coworkers in the late 1960s clearly illustrated the poorly controlled coupling of CO₂ and epoxides to provide polycarbonates. These early studies utilizing inadequately defined zinc catalysts derived from diethyl zinc and water have led to the development of a variety of catalysts for these processes over the last two decades. Numerous catalyst systems have been shown to be very effective and selective at affording perfectly alternating copolymers, including those with high levels of regio- and stereo-selectivity. The vast majority of the current literature reports upon the synthesis of hydrophobic polycarbonates which lack functionalities. In this review we will summarize the reports which utilize these well-developed metal-catalyzed CO₂/epoxides copolymerization processes to prepare high value-added functionalized polymeric materials for a variety of applications.

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1. Introduction

Polycarbonates (PCs) are a class of thermoplastic polymers containing carbonate units in their chemical structure. The most common type of polycarbonates on the market is bisphenol A (BPA) polycarbonate. It is an aromatic polycarbonate with a high glass transition temperature (T_g) of 140–155 °C. BPA polycarbonate is widely used in numerous industrial applications including automotive interiors, sunglasses, bulletproof windows, medical devices [1] et al. Compared to aromatic polycarbonates, aliphatic polycarbonates have received little commercial attention due to their low heat resistance and high susceptibility to hydrolysis. Their industrial applications are mostly limited to low molecular weight polycarbonate polyols for polyurethane production. Recently, aliphatic polycarbonates have attracted significant attention in the biomedical field due to their biocompatibility and biodegradability. One of the most investigated aliphatic polycarbonates is poly(trimethylene carbonate) (PTMC). Unlike other degradable polymers like polyester, PTMC degrades into non-acidic diols and carbon dioxide which are less likely to cause adverse effects such as inflammation. PTMC and its copolymers have been fabricated into nanoparticles [2,3], sutures [4,5] and hydrogels [6,7] for applications in tissue engineering and drug delivery.

One attractive method to produce polycarbonates is the catalytic coupling of CO₂ and epoxides (Scheme 1), first discovered by Inoue in 1969 [8,9]. This synthetic route provides many advantages. It uses the nontoxic and inexpensive CO₂ as a carbonyl source instead of the toxic phosgene employed in traditional polycondensation methods. Polycarbonates made from this route can contain up to 50% (by moles) of CO₂ and therefore will rely less on fossil-based feedstocks and will have a significantly reduced carbon footprint. This process usually does not require extraneous solvent as many epoxides themselves are liquid and can dissolve the catalyst and the resulting polymer. Several side reactions that can occur in the process include the formation of ether linkages due to consecutive ring-opening of epoxides and production of cyclic carbonates due to a backbiting process. Along with the normal chain propagation process, chain transfer reactions also need to be considered. Chain transfer reactions, while reduce the chain length of the final products, can be exploited to achieve precise control of molecular weights which are determined by the concentration of both the catalyst and chain transfer agents.

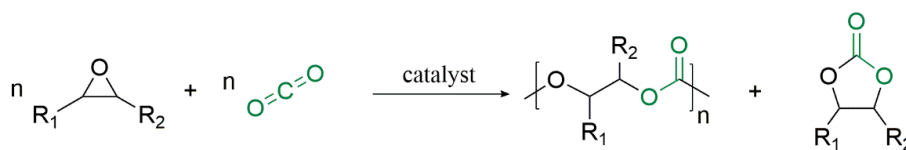
Two of the most investigated epoxides are cyclohexene oxide and propylene oxide (PO). Generally, copolymerization of CHO and CO₂ can proceed readily using a variety of catalysts under mild conditions and exhibits a high polycarbonate selectivity even at high temperatures. PO can also react with CO₂ quite easily to form polycarbonate. However, in the latter instance, judicious

choice of catalysts and reaction temperatures are usually required to eliminate formation of the cyclic by-products. Poly(cyclohexene carbonate) (PCHC) and poly(propylene carbonate) (PPC) burn cleanly and completely in air without emitting harsh residues, and thus can be used as sacrificial binders in electronics and ceramics manufacturing. Compared to PCHC, PPC exhibits more favorable mechanical properties and have found wider applications. For instance, PPC is already finding use as a degradable packaging material, and its low M_w polyols can substitute traditional petro-based polymers in polyurethane production. To date, PPC and PCHC have been commercially synthesized from CO₂ by many companies such as Saudi Aramco [10], Empower Materials [11], Eonic Technologies [12] and Covestro [13].

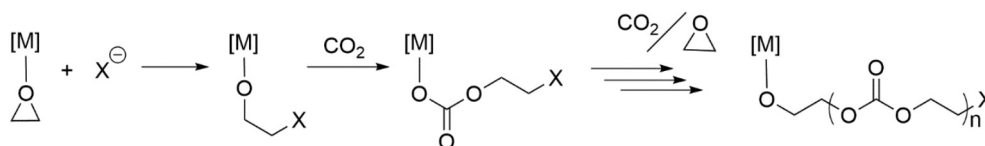
Despite the advantages of PPC and PCHC, their lack of functionalities and relatively low glass transition temperatures ($T_g = 37$ °C for PPC, 115 °C for PCHC) have limited their use in high value-added and functional materials. In order to expand the application scope of CO₂-based polycarbonates, two topics are of current interest. One is the synthesis of more diverse polycarbonates with different functionalities. For clarification, functional polycarbonates discussed here are not characterized by their thermal properties, but rather by their inherent functionalities. Both pendant and terminal functional groups can be incorporated into the polymer. The second topic of interest is the preparation of CO₂-PCs with high thermal resistance, characterized with a high glass transition temperature (T_g) and/or melting temperature (T_m). This report will focus on the current development of more diverse CO₂-derived polycarbonates with improved performance. In particular, synthetic strategies to expand polymer functionalities and to improve the thermal properties will be presented. Finally, recent applications of CO₂-based polycarbonates will be highlighted.

2. Catalysts development for the copolymerization of CO₂ and epoxides

The coupling reaction between CO₂ and an epoxide usually requires the application of a metal catalyst. The generally accepted mechanism for production of polycarbonates is depicted in Scheme 2. The copolymerization is initiated by the coordination of the epoxide and its subsequent ring-opening by the nucleophilic cocatalyst (X^-) to provide a metal-alkoxide species. This metal alkoxide intermediate then undergoes CO₂ insertion to form a metal-carbonate. The successive alternating incorporation of epoxides and CO₂ produces linear polycarbonates. It is generally proposed that the rate-determining step involves epoxide ring-opening by the growing anionic polymer chain rather than CO₂ insertion [14].



Scheme 1. Coupling between epoxide and CO₂ to yield the desired copolymer, and cyclic carbonate side-product.



Scheme 2. Generalized mechanism for the production of polycarbonates.

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