

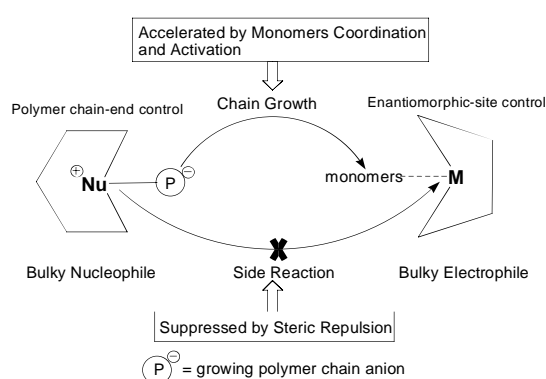
# ON THE DESIGN OF HIGHLY ACTIVE BINARY CATALYST SYSTEMS FOR CO<sub>2</sub>/EPOXIDES COPOLYMERIZATION: POLYMER SELECTIVITY, ENANTIOSELECTIVITY AND STEREOCHEMISTRY CONTROL

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Conversion of carbon dioxide (CO<sub>2</sub>) to desirable, economically competitive products has received much attention, because CO<sub>2</sub> is naturally abundant, relative non-toxic and inexpensive, and also the major greenhouse gas.<sup>1</sup> One of the most promising green reactions in this area is the alternating copolymerization of CO<sub>2</sub> and epoxides to generate biodegradable polycarbonates,<sup>2</sup> which was first reported by Inoue et al. in the late 1960's.<sup>3</sup> This process represents an environmentally benign approach compared to the alternative route of condensation polymerization involving the use of toxic phosgene. In recent decades, numerous catalyst systems, including heterogeneous catalysts mainly based on diethyl zinc combined with a modifier having at least two labile hydrogen atoms, and homogeneous catalysts associated with discrete zinc-based complexes, magnesium, aluminum, manganese, cobalt, chromium, and rare-earth metals, have been developed for this transformation<sup>4</sup>. Although the advances have been significant, high catalyst loading, elevated CO<sub>2</sub> pressure, and long reaction time are usually prerequisite for obtaining appreciable amounts of polymer, which are often not perfectly alternating and exhibit broad molecular weight distributions. Prominent among these are single-site homogeneous catalysts being the most efficient for CO<sub>2</sub>/epoxides copolymerization and in some cases approach to the regio- and/or stereo-selective polymerization.<sup>5</sup>

On the other hand, the simultaneous control of polymer chain length and relative stereochemistry remains an important goal in polymerization catalysis.<sup>6</sup> For CO<sub>2</sub>/aliphatic epoxides copolymerization, there exists much interesting information, such as polymer/cyclic product selectivity, ether and dicarbonate linkages, regiochemistry of epoxide ring-opening, and stereochemistry of carbonate unit sequence in a polymer, which bears a memory of the reaction pathway leading to its formation.<sup>7</sup>



**Scheme 1** Schematic representation of high-speed asymmetric copolymerization of CO<sub>2</sub> and rac-epoxide by a synergistic catalysis of binary electrophile-nucleophile system.

Herein, we will describe the design principle of highly active binary electrophile-nucleophile catalyst systems for CO<sub>2</sub>/epoxides copolymerization by outlining optimized systems. Both properties of the electrophile and the nucleophile significantly affect catalyst activity, polymer selectivity, enantioselectivity and stereochemistry. A continuous determination of a polymer end group (initiating and chain-growth species) at various time was firstly achieved by in situ electrospray ionization mass spectrometry (ESI/MS), which in combination with kinetic

study reveal a copolymerization mechanism, in which the electrophile plays an important role for activating epoxides and the nucleophile plays an initiator of polymer-chain growth during the copolymerization (Scheme 1). Both enantiomorphic-site effect resulted from the chiral electrophile

and polymer chain-end effect mainly from the bulky nucleophile cooperatively control the stereochemistry of the CO<sub>2</sub>/epoxides copolymerization. Furthermore, approach to precisely control polycarbonate regio- and stereochemistry was realized by altering catalyst properties with respect to polymer end growth paths.

Stimulated by our success with binary chiral electrophile-nucleophile catalyst systems for the asymmetric alternating copolymerization of aliphatic epoxides and CO<sub>2</sub>,<sup>8</sup> we also apply these systems to the asymmetric copolymerization of alicyclic cyclohexene oxide (CHO) and CO<sub>2</sub> for yielding isotactic-enriched poly(cyclohexene carbonate) (PCHC) with a narrow molecular distribution. Of importance, the binary catalyst systems are very effective in the ter-polymerization of CO<sub>2</sub> with CHO and propylene oxide (PO) to selectively provide polycarbonates with a narrow polydispersity (*M<sub>w</sub>/M<sub>n</sub>* ratio) of 1.24, and >99% carbonate linkages. The resulting ter-polymer has only one glass transition temperature (*T<sub>g</sub>*) and one thermolysis peak. The unprecedented results are tentatively assumed that an alternating nature of the two different carbonate units predominantly exists in the resulting polycarbonate. Furthermore, the *T<sub>g</sub>* of the PO/CHO/CO<sub>2</sub> ter-polymer can be easily adjusted by controlling the proportion of cyclohexene carbonate linkages and propylene carbonate linkages.

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