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# Ring Opening Polymerization Of Lactide And Synthesis Of Polycarbonates Directly From Carbon Dioxide And Diols

Shi Bian

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# Ring Opening Polymerization of Lactide and Synthesis of Polycarbonates Directly from Carbon Dioxide and Diols

By

Shi Bian
Bachelor of Science, Sun Yat-Sen University, 2010

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for the degree of

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This dissertation, submitted by Shi Bian in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done, and is hereby approved.

Dr. Guodong Du

Dr. Harmon Abrahamson

Dr. Lothar Stahl

Dr. Alena Kubátová

Dr. Edward Kolodka

This dissertation meets the standards for appearance, conforms to the style and format requirements of the Graduate School at the University of North Dakota, and is hereby approved.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| ACN | Acetonitrile |
| BDI | B-diketiminate |
| BINAP | Bis(diphenylphosphino)-1,1'-binaphthyl |
| $^t$Bu | *tert*-Butyl |
| CHO | Cyclohexene oxide |
| $CO_2$ | Carbon dioxide |
| dba | Dibenzylideneacetone |
| DCM | Dichloromethane |
| DMAP | 4-dimethylaminopyridine |
| ee | Enantiomeric excess |
| Et | Ethyl |
| EtOAc | Ethyl acetate |
| EtOH | Ethanol |
| FTIR | Fourier transform infrared spectroscopy |
| GC | Gas Chromatography |
| GPC | Gel permeation chromatography |
| HRMS | High resolution mass spectrometry |
| LA | Lactide |
| MeOH | Methanol |
| $M_n$ | Number average molecular weight |
| $M_w$ | Weight average molecular weight |

| | |
|---|---|
| NMR | Nuclear magnetic resonance |
| PC | Poly(carbonate) |
| PCHC | Poly(cyclohexene carbonate) |
| $Pd(OAc)_2$ | Palladium acetate |
| PDI | Polydispersity |
| PE | Polyethylene |
| Ph | Phenyl |
| PLA | Polylactide |
| PO | Propylene oxide |
| $^{i}Pr$ | Isopropyl |
| ROP | Ring-opening polymerization |
| Salen | *N,N*-bis(salicylidene)-1,2-diaminoalkene |
| SO | Styrene oxide |
| TLC | Thin-layer chromatography |
| $T_g$ | Glass transition temperature |
| $T_m$ | Melting point |
| THF | Tetrahydrofuran |
| TOF | Turnover frequency |
| TON | Turnover number |
| $Zn(OAc)_2$ | Zinc acetate |
| $Zn(Et)_2$ | Diethylzinc |

# ABSTRACT

A series of dimethylaluminum complexes **(L**)$AlMe_2$ (where **HL**= 2-(2’-ArNH)phenyl-4-$R_1$-oxazoline) bearing chiral, bidentate anilido-oxazolinate ligands have been prepared and characterized. Six of the complexes, in the presence of an alcohol cocatalyst, are shown to be active initiators for the stereoselective ring opening polymerization of *rac*-lactide in toluene solution and under bulk conditions, yielding polylactides with a range of tacticity from slightly isotactic to moderately heterotactic. The reactivity and selectivity of these catalysts are discussed based on their substituents.

Polycarbonates have attracted considerable recent interest because of their potential biodegradability and sustainability. Two direct routes were developed for the synthesis of polycarbonates and poly(ether carbonate)s from carbon dioxide ($CO_2$) and diols, promoted by either $Cs_2CO_3$/dihalide or $CeO_2$/2-cyanopyridine. While benzylic diols lead to predominantly carbonate linkage, aliphatic diols result in the incorporation of methylene or ethylene unit of dihalides. Moreover, the formation of different linkages was impacted by the dihalides used in the reactions.

# CHAPTER I

# GENERAL INTRODUCTION

## I.1 Development of the Polymer Industry

Along with the significant development of polymer industry, the materials based on synthetic polymers started to play a very important role in our life during the last several decades.[1] The total world plastic production was continuously growing from 1.7 Mton/year in 1950 to 288 Mton/year in 2012. Advanced technologies in the polymer industry make it possible to produce versatile polymers with highly tunable properties. Depending on the request, polymers now can be stiff or soft, transparent or opaque, conducting or insulating, permeable or impermeable, and stable or degradable. Now, people's living styles have been changed by the widely application of synthetic polymers, and they have contributed a lot to the advance of human civilization.[2] From some daily used items such as the microelectronics in cell phones and high-strength fibers used in the farm to some special materials with highly technical applications, for example, the light weight engineering plastics used in aircraft, polymers have become more and more indispensable and irreplaceable in the modern society.[3] A huge number of traditional metal and glass-based materials have even replaced by synthetic polymers in our life due to their ease of processing, low cost, and availability. Modern life would be impossible without polymeric materials, since other classes of materials won’t have such diverse properties and versatile applicability.[4]

On the other hand, the industrial production of a wide range of synthetic polymers heavily relies on fossil resources, as only 5% of polymers are currently produced from renewable feedstocks. In the past, the low price of petroleum made it possible that petroleum-based polymers could be much cheaper than other commodity products. However, the competitive price advantage of fossil fuels during the last century has been diminishing.[5] The global depletion of petroleum resources will eventually become a significant problem in the polymer industry. In addition, neither the industrial approach of producing petroleum-based materials nor the most of the petroleum-based polymer is environmentally friendly. The unsustainability of petroleum-based polymer production and pollution caused by it have limited the development of the polymer industry.[6] In the past few years, a dramatic shift occurred in the development of novel materials derived from biorenewable resources.

## I.2 Polymer Synthesized from Renewable Resources

### I.2.1 Introduction of Lignocellulosic Biomass

Due to its sustainability and low cost, biomass derived materials have been pointed out to be one of the most promising feedstock of the synthetic alternatives to petroleum-based polymers. Promotion of using synthetic polymers from biomass and other natural resources would decrease the current dependence on fossil resources.[7]

Lignocellulose is one component of the abundant biomass produced from cell walls of land plants.[8] It has crucial advantages over other biomass because it comes from the non-edible portion of the plant and therefore does not interfere with food supplies.[9] Moreover, lignocellulose could be recovered from the waste streams of multiple industries such as food processing and paper production. Therefore, from an economic point of view, lignocellulosic biomass can be produced quickly and at a lower cost than other agriculturally important biofuel feedstocks such as corn starch, soybeans, and sugar cane. It is also significantly cheaper than crude oil. The main compositions of lignocellulosic biomass are three different polymers: cellulose, hemicelluloses, and lignin,[10] which are mainly composed of carbon, hydrogen, and oxygen.[11] Usually, the percentage of these three polymers are various in the lignocellulose from different plants. For example, woody biomass has more lignin and cellulose than herbaceous biomass.[12] Cellulose and hemicelluloses are both formed by sugar moieties. Cellulose is an isotactic polymer of cellobiose that contains two *D*-glucose units linked by a $\beta$-1-4 bond.[13] Hemicellulose is a heteropolysaccharide and has more complicated chain structure. More than one kind of sugar units can be found in the main chain of hemicelluloses, such as galactomannan and glucuronoxylan, and the side of the chain can be occupied by some other units as well.[14] Different from cellulose and hemicellulose, lignin is a three-dimensional polymer of phenylpropanoid units. It is formed by three different phenylpropane building monolignols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units are identified as the corresponding phenylpropanoid monomeric units in the lignin polymer, respectively.[15]

Cellulose, hemicellulose, and lignin can be transformed into various biomass-based chemicals through depolymerization and further treatment. These chemicals provide the opportunity for transformations toward promising alternative monomers for polymer production. Five- or six-carbon sugars are the main degradation products of cellulose and hemicellulose. Glucose, a six-carbon sugar, is the only product of the degradation of cellulose. Meanwhile, the depolymerization of hemicellulose results in the formation of glucose as well as the other five (xylose, arabinose) and six (mannose, galactose, rhamnose) carbon sugars.[16] The degradation products of lignin are different from cellulose and hemicellulose, which are mostly phenolic chemicals such as toluene, xylene, phenols and hydroxybenzoic acids. Many platform chemicals can be derived from these C5 and C6 sugars, include 5-hydroxymethylfurfural (HMF) and furfural, levulinic acid and lactic acid.[17] The production of 5-hydroxymethylfurfural and furfural relies on the dehydration of glucose and xylose under acidic conditions with subsequent treatment. These two compounds not only are essential intermediates that lead to furan resins but also can be transformed to various aliphatic diols. The further subsequent hydrogenation of the aldehyde function of HMF yields 2,5-bis(hydroxymethyl)-tetrahydrofuran or 2,5-dimethylfuran, which can be ring opened and further converted to 1,6-hexanediol or 2,5-hexanediol.[18] The similar selective hydrogenation of the aldehyde function of furfural results in the formation of furfuryl alcohol; further hydrogenation of the furan ring can lead to 2-(hydroxymethyl)-tetrahydrofuran. Ring opening of 2-(hydroxymethyl)-tetrahydrofuran can produce either 1,5-pentanediol or 1,2-pentanediol.[19] Levulinic acid is another interesting compound, and it can be made by rehydration of 5-hydroxymethylfurfural.[20] Some widely used monomers, such as α-angelica lactone, are synthesized from levulinic acid. It is noteworthy that another important monomer derived from levulinic acid, diphenolic acid, is synthesized from the coupling of levulinic acid and phenols derived from lignin. The production of lactic acid is mainly achieved from the fermentation of glucose and sucrose by lactic acid bacteria, and the production of enantiopure *L*-lactic acid or *D*-lactic acid depends on the microbial strain used during the fermentation process.[21]

### I.2.2 Polymerization of Lactic Acid and Lactide

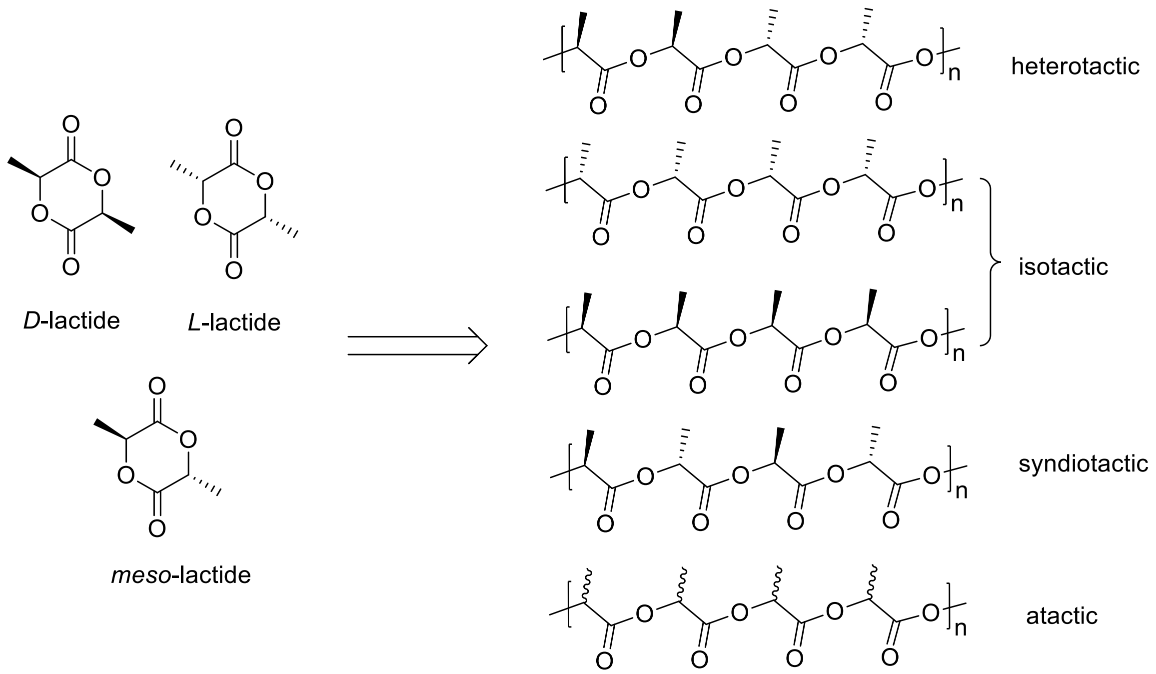
Lactic acid (LA) is one of the most popular lignocellulosic biomass products in the world.[22] The Swedish chemist ScheeleIt first isolated LA in 1780 from sour milk, and it was first produced commercially in 1881.[23] The fermentation of simple sugars is the general approach to make lactic acid. Some of these simple sugars such as glucose, sucrose, and lactose can be collected from the byproducts of agricultural and other industry.[24] The production of LA increased significantly between 1998 to 2004 when PGLA-1 (USA), B&G (China) and Cargill Dow (USA) plants started up their production of LA for food packaging and industrial purposes.[25] Polymerization of LA leads to the formation of poly(lactic acid) (PLA), which is a biodegradable polymer that can degrade into nontoxic compounds in landfills.[26] In last decades, a number of studies indicated its excellent renewability, biocompatibility, and biodegradability.[27] In 2002, NatureWorks first produced PLA commercially. Since then, many applications of PLA have been widely reported. On the area of commodity applications, the product of PLA, such as flexible films, drink cups and bottles are already available in the marketplace and became more and more popular. As high-performance compostable materials and biomedical devices, PLA was also widely used on the delivery carrier and tissue engineering scaffold.[28]

Two different synthetic routes were developed for PLA by now. The first route is direct polycondensation of LA. The process occurred in the presence of organic solvent while water is continually removed by distillation. Due to the very slow diffusion of moisture out of the highly viscous polymer, the challenge of this route is the removal of water at a high degree of polymerization.[29] Importantly, the presence of water decreases the molecular weight of PLA. Therefore, condensation of lactic acid only yields a brittle or glassy polymer with low molecular weight, most of which is unusable for any applications. The second route of producing PLA is ring-opening polymerization (ROP) of lactide. To achieve pure lactide, the lactic acid needs to be oligomerized first to remove water. The resulting oligomers are then depolymerized to yield lactide. After further purification, the lactide is converted to the polymer via catalytic ring-opening polymerization. ROP is a living polymerization process, by which PLA with high molecular weight can be achieved[18] as well as a narrow polydispersity index. Currently, the ROP of lactide is the only dominant method of producing pure and high molecular weight PLA.[30]

In practice, an appropriate catalyst is necessary for ROP of lactide with reasonable conditions, and the properties of PLA are controlled by the catalyst as well. In the 1950s, Kleine first reported an ROP of lactide catalyzed by the metal complex. Since then, considerable attention has been paid to the study of metal complex catalysts in this area.[31] A broad range of catalysts has been prepared and evaluated in the last several decades,[32] which indicated the interesting impact of the nature of the metal center as well as surrounding ligands on the catalytic performance of ROP. Spectacular improvements have also been achieved in terms of catalytic activity as well as polymerization control. These well-defined complexes have contributed significantly to a better understanding of the factors that govern the polymerization. Along with metal complexes, a number of organocatalysts were also developed for the ROP of lactide. The recent results on ROP of lactide with these metal-free promoters (include anionic, cationic and nucleophilic) was rather promising.[33] The organocatalysts could be a better choice than a metal complex, especially when the resulting polymers are intended for biomedical applications.

The three-step coordination-insertion mechanism for the ROP of cyclic esters, such as lactide, was first formulated in1971 by Dittrich and Schulz,[34] and the first experimental proof for such a mechanism was independently reported in the late 1980s by Kricheldorf and Teyssie from the Al(O*i*Pr)$_3$ initiated polymerization of lactide.[35] Further support for such a mechanism has also been provided by experimental[36] as well as theoretical[37] studies. Based on these studies, the coordination of the monomer to the Lewis-acidic metal center is the first step of the coordination-insertion mechanism. After that, the monomer subsequently inserts into one of the aluminum-alkoxide bonds via nucleophilic addition of the alkoxy group on the carbonyl carbon. The final step is ring opening via acyl-oxygen cleavage. The hydrolysis of the active metal alkoxide bond resulted in a hydroxide chain end. Both the isopropyl ester and the hydroxide were identified as an ending group by $^1$H NMR of the resulting polymers. The living character of the polymerization in toluene at 70 °C has also confirmed by the linear dependence of the mean degree of polymerization on the molar ratio of monomer/initiator calculated for the actual monomer conversion.[32]

Moreover, lactide exists as three different stereoisomers (Scheme 1), which makes it possible to produce materials that vary from amorphous to semicrystalline with a broad range of physical properties. The microstructures of polylactide can be impacted by the sequence of chiral centers in the polymer chain.[38] Both poly(*L*-lactide) and poly(*D*-lactide) are considered as isotactic polylactide, which contains sequential stereocenters of the same relative configuration. On the other hand, syndiotactic polylactide contains sequential stereocenters of opposite relative configuration. The regular alternation of *L*- and *D*-lactide units in the polymer chains results in heterotactic polylactide, which is also named as disyndiotactic polylactide. The stereo sequence distribution in polylactide samples is usually determined by NMR spectroscopy through inspection of the methine and/or carbonyl regions ($^{13}$C NMR and homonuclear decoupled $^{1}$H NMR).[39] The physical properties of polylactide are strongly dependent on its stereochemical composition. Sometimes, the melting, as well as the glass-transition, temperatures of PLA can be used to characterize the stereoregularity of polylactide. For example, highly crystalline pure isotactic poly-(*L*-lactide) has a $T_m$ around 180 °C. When the isotactic polymer chain is contaminated with units of *meso*-lactide and the stereochemical defects of the resulting polymer reach to 15%, the melting point ($T_m$) of the polymer decreases to 130 °C as well as the crystallinity.[40]



**Scheme 1** Tacticity of Polylactide

### I.2.3 Synthesis of Polycarbonate

Polycarbonates is another raw material attracting increased research attention as petroleum-based alternatives in polymer synthesis due to their high abundance, low toxicity, and structural diversity. From electronic components to aircraft canopies, polycarbonates are widely used in many different applications due to their excellent physical properties. From 2004 to 2010, the global PC demand increased about 100 ktons, which indicated the significant growth of PC market in the last few decades.[41]

Commercially, the main polycarbonate is produced by the reaction of bisphenol A (BPA) and phosgene ($COCl_2$). Due to the very high demand of polycarbonates from a petroleum-derived monomer (BPA), great attention is paid to elaborating technologies to displace BPA by diphenolic acid (DPA) (derived from lignocellulosic biomass). The synthetic approach of polycarbonates from DPA and phosgene has been reported.[42] To prevent branching, the carboxyl group of DPA is protected by esterification before the polymerization.[43] The polycarbonates were prepared by interfacial polymerization using phosgene in the gaseous phase and the DPA ester in pyridine solution. The studies of the properties of polycarbonates based on DPA and BPA indicated that the polymers have nearly the same molecular weight (about 40 kg/mol) and a similar PDI. However, the glass transition temperature of BPA-based polycarbonates (150 °C) was much higher than polycarbonate obtained from DPA (108 °C). This is probably due to the very stiff backbone and minimal molecular rotation of BPA-based polycarbonates.

Compared to phenolic polycarbonates, aliphatic polycarbonates have much better biodegradability and biocompatibility, which make them attractive materials for biomedical applications such as tissue engineering scaffolds and vehicles for drug delivery.[44] Unfortunately, aliphatic polycarbonates cannot be achieved by the traditional approach with diphenolic substrates. Therefore, the study of synthetic polycarbonate is now focused on a new approach with different monomers. Currently, the new approach of synthetic polycarbonate is either based on the direct copolymerization of $CO_2$ with epoxides or based on the polymerization of organic carbonates. Since Inoue and co-workers first reported the synthesis of polycarbonate via the copolymerization of $CO_2$ and epoxides catalyzed by Al-porphyrin complexes in 1969,[45] many efficient catalyst systems were developed with decent catalytic activity and polymer selectivity.[46] Among these studies, the catalysts based on transition metal salen complexes currently gain a resurgence of interest due to their great catalytic performance and easy handling. In 2002, a completely alternating poly(cyclohexene carbonate) (PCHC) was achieved by Darensbourg and coworkers using Cr(III)-salen catalysts on the copolymerization $CO_2$/cyclohexene oxide (CHO).[47] The excellent catalytic performance was also obtained from some catalyst systems such as β-diiminate zinc complexes.[48] Using a variety of epoxides characterized by a different molecular structure can be very interesting as polymers with different structural properties are obtained. The great success was achieved by the copolymerization of $CO_2$ and epoxides; however, this route is significantly limited by choice of backbone structure from the available epoxide. As an alternative to this route, instead of using epoxide, people started to use diols in the copolymerization with $CO_2$. The first synthetic approach was reported in 1998 by Kadokawa and co-workers. The polycarbonates were successfully made from the direct polycondensation of $CO_2$ with alkane diols in the presence of trisubstituted phosphines, carbon tetrahalides, and an organic base.[49] Recently, the heterogeneous catalyst system (using $CeO_2$) and heterogeneous promoters (using $Cs_2CO_3$/dihalides) were both reported with a decent activity on the polycondensation of $CO_2$ with alkane diols.[50]

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# CHAPTER II

# RING OPENING POLYMERIZATION OF *rac*-LACTIDE WITH ALUMINUM CHIRAL ANILIDO-OXAZOLINATE COMPLEX[a]

## II.1 INTRODUCTION

Synthetic aliphatic polyesters, such as polylactide (PLA), and their copolymers have attracted considerable attention due to their biocompatibility and biodegradability.[1] These features are important in biomedical applications, such as tissue engineering and drug delivery,[2] and in agricultural and packaging applications.[3] Furthermore, PLA is derived from renewable resources and is considered a viable alternative to petrochemical based materials. Although PLA can be produced by the polycondensation of lactic acids, ring opening polymerization (ROP) of lactide (LA) with an initiator/catalyst is the method of choice because it offers higher degree of reaction control.[a] Due to the presence of two chiral centers in a lactide monomer, a range of microstructures, including atactic, isotactic, heterotactic, and syndiotactic, are possible for PLA derived from lactide. The tacticity has a significant effect on the physical and thermo properties of bulk materials. For example, atatic PLA is amorphous, while isotactic PLA is a crystalline polymer that melts at ~170 °C.[4] Alongside the structure of lactide monomers, catalysts play a vital role in determining the stereo outcome of ROP. Much effort has currently been devoted to the design and synthesis of single-site catalysts/initiators for the ROP of *rac*-lactide with high activities and stereoselectivities.[5]

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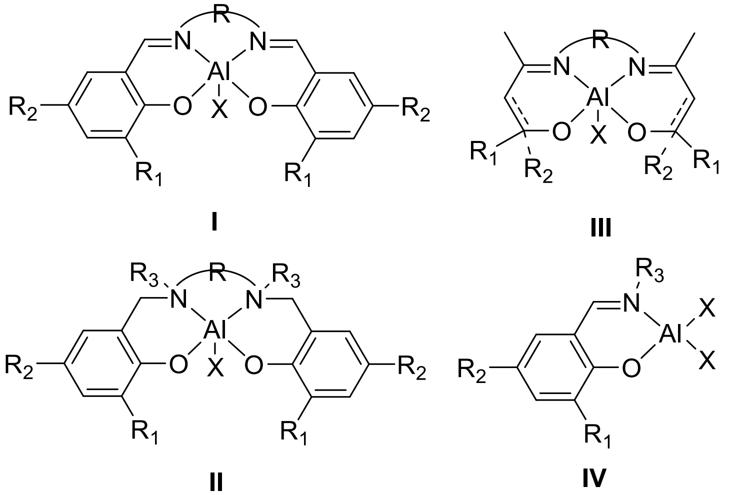
A wide array of catalytic systems for ROP of lactides have been developed in the literature, ranging from homoleptic metal salts such as Sn(Octanoate)$_2$, Ca[N(SiMe$_3$)$_2$]$_2$, and Sc(OTf)$_3$ in combination with alcohols as chain transfer reagents,[6] to well-defined single-site catalysts such as Zn and Mg complexes supported by $\beta$-diketiminate,[7] and Y and Sc complexes supported by pyridine-diamide type ligands.[8] In particular, group 13 metal complexes are of special interest because of their effective stereo control, and low toxicity.[9] The pioneering works by Spassky[10] in the control of PLA microstructure showed that a chiral salen aluminum complex (Scheme 1, **I**, where R = (*R*)-2,2'-binaphthyl, R$_1$ = R$_2$ = H, X = OMe) is highly isoselective for ROP of *rac*-lactide. This system was further exploited[11] and expanded to other salen,[12] their reduced derivatives such as salan (**II**, Scheme 1)[13] and salalen,[14] and related N$_2$O$_2$ (**III**, Scheme 1) and N$_4$ type ligands.[15] These initiators typically feature a five-coordinate aluminum center supported by dianionic, tetradentate ligands. A range of stereoselectivity has been achieved, from highly isospecific to highly heterospecific, even by simply varying the substituent groups in the same ligand framework.[13a] Al complexes supported by related bidentate half salen ligands are usually 4-coordinate (**IV**, Scheme 1) and exert less stereocontrol for ROP of *rac*-lactide.[16] Al complexes supported by bidentate ligands can take on a pentacoordinate geometry and induce high isoselectivity.[17] It should also be mentioned that initiators based on heavier group 13 elements have been shown to be stereoselective for the ROP of *rac*-lactide.[18]



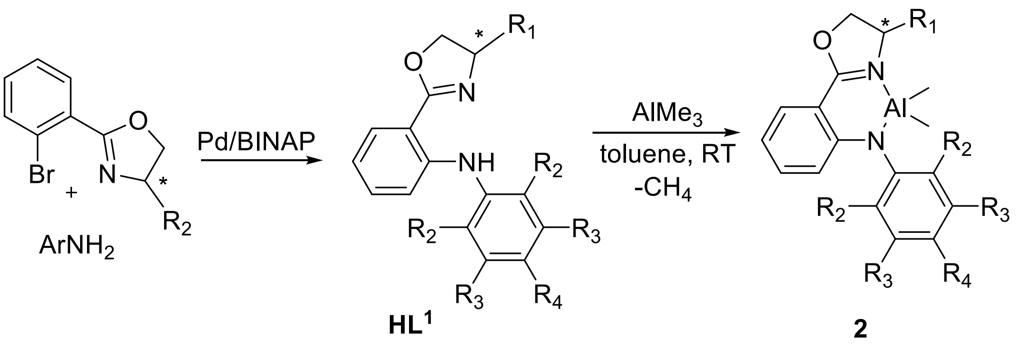
**Scheme 2** Examples of stereoselective Al-based initiators for ROP of rac-lactide

Bidentate and monoanionic β-diketiminate ligands are analogous to the half salen ligands, and have been successfully employed in ROP reactions.[5a, 19] We have been interested in a chiral variation based on the anilido-oxazolinate framework,[20] and turned our attention to aluminum complexes incorporating these chiral ligands. The achiral version of the anilido-oxazolinate aluminum complexes in the ROP of *L*-lactide has been reported.[21] It is expected that the new chiral complexes are active initiators for the ROP of *rac*-lactide and may induce appreciable stereoselectivity to control the microstructure of the product. Herein we report a series of dimethyl aluminum complexes and their application as initiators for the ROP of *rac*-lactide. Both hetero and isotactic selectivities could be achieved by modulation of the substituent groups.

## II.2 RESULTS AND DISCUSSION

### II.2.1 Synthesis of Ligands

As mentioned earlier, the bidentate anilido-oxazolinate ligands (**HL$^1$**, Scheme 2) can be viewed as a chiral variation of the conventional β-diketiminate ligands. The oxazoline ring is conveniently formed from chiral amino alcohols and 2-bromobenzaldehyde, and the coupling between oxazolines and anilines using a palladium-catalyzed amination protocol gave the ligands as orange oily or crystalline materials in good to high yields (69-88%). In addition to addressing the question if the chiral version could induce stereoselectivity in the ROP of *rac*-lactide, this particular series of ligands was targeted to investigate the steric and electronic influences of the substituents (see Scheme 2), because such factors may drastically affect the stereoselectivity toward the ROP of *rac*-lactide.[13a] The stereogenic center is introduced at the oxazoline $R_1$ position and is expected to exert a substantial steric influence. The aniline $R_3$ and $R_4$ positions are mostly electronic. On the other hand, the $R_2$ position is in closer proximity to the metal center, as compared to the *ortho* position in related bidentate half-salen ligands (see the $R_1$ group in **IV** in Scheme 1), and it can also influence the metal center electronically. Based on these considerations, (*S*)-$^i$Pr, (*R*)-Ph, and (*R*)-$^i$Bu at $R_1$ position, and a methyl group at the $R_2$ position were incorporated to test the steric factors on the reactivity and selectivity of the catalysts. The trifluoromethyl group on the $R_3$ position and methoxy group on the $R_4$ position were used to probe the electronic effect.



| | R$_1$ | R$_2$ | R$_3$ | R$_4$ |
|---|---|---|---|---|
| **a** | (*S*)-$^i$Pr | H | H | H |
| **b** | (*S*)-$^i$Pr | Me | H | H |
| **c** | (*R*)-Ph | H | H | H |
| **d** | (*R*)-Ph | Me | H | H |
| **e** | (*R*)-$^i$Bu | H | H | H |
| **f** | (*R*)-$^i$Bu | Me | H | H |
| **g** | (*S*)-$^i$Pr | H | CF$_3$ | H |
| **h** | (*S*)-$^i$Pr | H | H | OMe |
| **i** | (*S*)-$^i$Pr | OPh, H | H | H |

**Scheme 3** Preparation of Ligands and Their Aluminum Complexes

### II.2.2 Synthesis and Characterization of Aluminum Complexes

Reaction of the free ligands **HL$^1$** with 1.5 equivalent of AlMe$_3$ in toluene at ambient temperature yields the dimethyl aluminum complexes **2a-i** (Scheme 2). The compounds were normally isolated as yellow powders in good yields (68%-87%). Characterization by $^1$H NMR and $^{13}$C NMR revealed the formation of the expected dimethylaluminum complexes, and was consistent with the mononuclear structures. For instance, the NH peak of the free ligand (around 10 ppm) disappeared upon reaction, and the $^1$H NMR signals for the oxazoline moiety shift downfield compared to that in the free ligands, indicative of the formation of the six-membered chelation ring. Furthermore, two separate singlets in the upfield region around -1 ppm were observed and attributed to the aluminum methyl (Al*Me*$_2$) protons. These observations are in agreement with the unsymmetrical nature of the complexes and the two methyl groups are non-equivalent. The latter is relevant in the context of stereoselective catalysis, as the growing polymer chain will occupy one of the coordination sites during polymerization. In complexes **2b**, **2d**, and **2f**, two singlets corresponding to the two *o*-methyl groups on the aniline phenyl moiety were observed, indicative of restricted rotation due to steric bulk of *o*-methyl groups. In line with these observations, two sets of $^1$H and $^{13}$C NMR signals were observed for compound **2i** in which a bulky phenoxy group occupies one of the *ortho* positions ($R_2$ in Scheme 2), presumably due to the presence of a pair of isomers with *anti* and *syn* configurations. The ratio of ~1.5 remains largely unchanged upon dilution or heating up to 60 °C.[22] We were also able to obtain crystals of **2d** for single crystal X-ray diffraction analysis that confirmed the mononuclear, distorted tetrahedral geometry around the aluminum center, despite the low quality of the data.[22] Attempts at obtaining pentacoordinate Al complexes by using 2:1 ratio of ligand:$AlMe_3$ have been unsuccessful.

### II.2.3 Polymerization of *rac*-Lactide

The aluminum complexes were tested as initiators for *rac*-lactide ROP, and the results are summarized in Table 1. The polymerizations were typically conducted in dry toluene at 80 °C with concentrations of *rac*-lactide (0.50 M), catalyst (10 mM), and benzyl alcohol (10 mM). The reaction progress was monitored by taking regular aliquots which were analyzed by NMR spectroscopy. During the catalysis, the benzyl alcohol reacts with the aluminum compound to generate an alkoxide complex, which is believed to be the actual initiating species; such a protocol is typical for polymerizations using aluminum initiators. In the absence of an exogenous alcohol, these complexes led to very little conversion of lactide. Indeed, mixing of stoichiometric amounts of compound **2c** and *rac*-LA showed no sign of reaction. Complexes (**2b**, **2d**, and **2f**) with 2,6-dimethyl substituents were not effective; less than 15% conversion was observed after 24 h (entries 3, 6, 10), while the rest of the aluminum catalysts achieved >93% conversion under identical conditions.

**Table 1**: Polymerization of rac-Lactide with Al complexes **2a-i**[a]

| Entry | Catalyst | Cat. Loading (mol %) | Time ( h) | Conversion (%)[b] | $M_n$[c] (kg/mol) | $M_n$[d](kg/mol) | PDI[d] | $P_r/P_m$[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | Al1(**2a**) | 2 | 24 | 96 | 6.92 | 7.7 (4.4) | 1.20 | $P_r = 0.69$ |
| 2 | Al1(**2a**) | 0.5 | 48 | 97 | 28.0 | 12.1 (7.0) | 1.45 | $P_r = 0.51$ |
| 3 | Al2(**2b**) | 2 | 24 | 15 | - | - | - | - |
| 4 | Al3(**2c**) | 2 | 24 | 95 | 6.85 | 10.8 (6.3) | 1.23 | $P_m = 0.60$ |
| 5 | Al3(**2c**)[f] | 2 | 20 | 95 | 6.85 | 7.7 (4.5) | 1.29 | $P_m = 1.0$ |
| 6 | Al4(**2d**) | 2 | 24 | 12 | - | - | - | - |
| 7 | Al5(**2e**) | 2 | 24 | 95 | 6.85 | 8.3 (4.8) | 1.28 | $P_r = 0.74$ |
| 8 | Al5(**2e**) | 1 | 48 | 98 | 14.1 | 23.6 (13.7) | 1.69 | - |
| 9 | Al5(**2e**)[g] | 1 | 48 | 40 | - | - | - | - |
| 10 | Al6(**2f**) | 2 | 24 | 12 | - | - | - | - |
| 11 | Al7(**2g**) | 2 | 24 | 95 | 6.85 | 4.9 (2.8) | 1.64 | $P_m = 0.57$ |
| 12 | Al8(**2h**) | 2 | 24 | 93 | 6.70 | 9.7 (5.6) | 1.25 | $P_r = 0.62$ |
| 13 | Al9(**2i**) | 2 | 24 | 98 | 7.06 | 9.0 (5.2) | 1.53 | $P_r = 0.61$ |

[a]Reaction conditions: see Experimental section for details. [b]Monomer conversion determined by $^1H$ NMR spectroscopy. [c]Calculated molecular weight based on conversion, $[LA]_0/[Al]_0$ x conv.% x 144 g/mol. [d]Experimental molecular weight determined by GPC vs polystyrene standards. The values in parenthesis are corrected by a factor of 0.58.[23] [e]Probability of *racemo* ($P_r$) or *meso* ($P_m$) enchainment, determined by homonuclear decoupled $^1H$ NMR spectroscopy. [f]L-Lactide was used. [g]Reaction was carried out in THF at 60 ˚C.

Presumably the steric bulk played a considerable role in inhibiting the polymerization.[21] However, in the case of **2i** where only one $R_2$ substituent (see Scheme 2) was present, comparable reactivity was observed as unsubstituted complexes (entry 13). Furthermore, experiments conducted in THF at 60 °C were much slower than in toluene, likely due to the coordinating nature of THF and lower temperatures (entry 9). When an *L*-

lactide was employed with **2c**, a perfectly isotactic PLA (PLLA) with $P_m = 1$ was obtained and no epimerization was detected (entry 5). The observed molecular weights of PLA are typically lower than or close to the calculated values based on conversion, and the polydispersity indexes (PDI) are somewhat broad (1.2-1.7). MALDI-TOF mass spectrometry analysis of the polymer generated by **2c** revealed the presence of benzyloxy initiating group and a series of peaks separated by 72 mass unit, indicative of considerable transesterification during the polymerization.

One of our main goals was to investigate if these chiral catalysts could induce stereoselectivity in the ROP of *rac*-lactide. Thus the microstructure, or tacticity of the resulting PLA, in particular the probability of isotactic enchainment at the diad level, $P_m$, was assessed by integration of the methine region of the homonuclear decoupled $^1$H NMR spectrum (Table 1). It is noteworthy that a range of stereoselectivities was observed. While two of the initiators (**2c** and **2g**) lead to isotactic enrichment, the rest leads to heterotactic enrichment. Among this series of catalysts, **2c** showed the highest isoselectivity ($P_m = 0.61$), while **2a** ($P_r = 0.69$) and **2e** ($P_r = 0.74$) were heterotactically inclined. Apparently the bulkiness and the electron withdrawing ability of the phenyl group at $R_1$ may be responsible for the increase in isoselectivity. Compound **2g** also exhibited a slight isotactic bias ($P_m = 0.57$), which again was attributed to the presence of a strong electron-withdrawing group at $R_3$. Based on these considerations, **2i** with a phenoxyl group at $R_2$ position was expected to have high heteroselectivity. However, a $P_r$ of 0.58 was observed. This might be accounted for by the presence of *anti* and *syn* isomers of **2i**. Although the stereoselectivity observed was not particularly high, the findings here are interesting because the change of selectivity was due to the variation of substituents on $R_1$, $R_3$ and $R_4$ in the similar initiator structures. Such a strategy of modulation of tacticity by changing substituents has been utilized in other aluminum[13] and zirconium[24] systems.

**Table 2**: Polymerization of rac-Lactide with Al complexes under bulk conditions[a]

| Entry | Catalyst | Cat.Loading (mol %) | Time( h) | Conversion (%)[b] | $M_n$[c] (kg/mol) | $M_n$[d] (kg/mol) | PDI[d] | $P_r/P_m$[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | Al1(**2a**) | 2 | 1.5 | 74 | 5.33 | 3.9 (2.3) | 1.74 | Pr=0.52 |
| 2 | Al1(**2a**) | 0.25 | 1.0 | 81 | 46.7 | 23.1(13.4) | 1.45 | Pr=0.52 |
| 3 | Al3(**2c**) | 0.25 | 1.0 | 65 | 37.5 | 13.1 (7.6) | 2.02 | Pm=0.61 |
| 4 | Al5(**2e**) | 0.25 | 1.0 | 61 | 35.2 | 4.2 (2.5) | 1.82 | Pr=0.57 |
| 5 | Al6(**2f**) | 0.25 | 2.0 | 31 | 17.9 | 19.6(11.3) | 1.95 | Pr=0.60 |
| 6 | Al9(**2i**) | 0.25 | 1.5 | 75 | 43.2 | 207 (120) | 1.84 | Pr=0.58 |

[a]Reaction conditions: see Experimental section for details. [b]Monomer conversion determined by $^1$H NMR spectroscopy. [c]Calculated molecular weight based on conversion, $[LA]_0/[Al]_0$ x conv.% x 144 g/mol. [d]Experimental molecular weight determined by GPC vs polystyrene standards. The values in parenthesis are corrected by a factor of 0.58. [e]Probability of *racemo* ($P_r$) or *meso* ($P_m$) enchainment, determined by homonuclear decoupled $^1$H NMR spectroscopy.

We also tested representative catalysts under bulk/melt conditions at 130 °C, since such conditions require no solvent and allow high temperature and high monomer concentration, leading to shorter reaction time and higher turnover frequency.[25] Selected results are summarized in Table 2. Indeed, these aluminum compounds functioned as initiators for ROP of *rac*-lactides with low catalyst loads (0.25 mol%) and much shorter reaction times (1 - 1.5 h). In addition, the alcohol co-catalyst was not required under bulk conditions, and therefore not employed in the above runs. The actual nature of initiating groups is uncertain, but likely external nucleophilic impurities. Even **2f** with the bulky 2,6-dimethylphenyl group showed a higher conversion (31% vs 12% in solution). The molecular weights were typically lower than the theoretical values (except for **2i**, where a much higher $M_n$ is obtained) and the molecular weight distributions tended to be broader than the solution polymerizations. This may be due to diffusional constraints imposed by the elevated viscosities found in bulk polymerizations, particularly at high conversions. However, the conversion of *rac*-lactide in these reactions seems to reach a limit of around 70-80%. One likely reason is that the mobility of the monomer is reduced due to viscosity induced diffusional constraint, and the reaction slows down considerably. Another interesting observation is the variation of selectivity as judged by $P_m$. For example, **2a** and **2e** showed a moderate heteroselectivity under normal conditions, but become essentially nonselective under bulk conditions. In contrast, isoselectivity for **2c** remained the same under both normal and bulk conditions.

To further probe the catalyst factors that may influence the activity in ROP of *rac*-lactide, the polymerization kinetics were monitored for the six active initiators (**2a, 2c, 2e, 2g, 2h,** and **2i**) in combination with one equiv. of BnOH. All of them showed a first order dependence on lactide concentration up to 80% conversion, as judged by the linear relationship of $\ln([LA]_0/[LA]_t)$ versus time (Figure 1). The pseudo-first-order rate constants, $k_{obs}$, were obtained from the slope of these linear plots and are listed in Table 3. Among the six Al complexes, the apparent first order rate constants follow the order **2a** > **2h** > **2e** ~ **2g** ~ **2i** > **2c**. The trend can be understood in part on the basis of steric and electronic considerations. In the **2a**, **2c**, and **2e** series where the aniline arm is constant, **2a** with an isopropyl at the $R_1$ position is fastest, likely due to its smaller steric bulk in comparison with isobutyl (**2e**) and phenyl (**2c**) groups, which would usually be anticipated to facilitate the polymerization reaction. In the **2a**, **2g**, **2h**, **2i** series where the oxazoline moiety is the same, both the electron withdrawing groups at $R_3$ and electron donating groups at $R_4$ give rise to lowered reactivity, which may suggest a delicate sensitivity of reactivity *vs* Lewis acidity of the metal center.[26]

**Table 3**: Apparent Rate Constants ($k_{obs}$) for the Polymerization of rac-Lactide[a]

| Entry | Catalyst | $k_{obs}$ ($h^{-1}$) | Entry | Catalyst | $k_{obs}$ ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 | Al1(**2a**) | 0.248 (± 0.009) | 5 | Al7(**2g**) | 0.173 (± 0.006) |
| 2 | Al3(**2c**) | 0.11 (± 0.04) | 6 | Al8(**2h**) | 0.21 (± 0.04) |
| 3[b] | Al3(**2c**) | 0.09 (± 0.02) | 7 | Al9(**2i**) | 0.17 (± 0.06) |
| 4 | Al5(**2e**) | 0.16 (± 0.01) | | | |

[a]Reaction conditions: in the presence of 1 equiv. of BnOH; see Experimental section for details.
[f]L-Lactide was used.

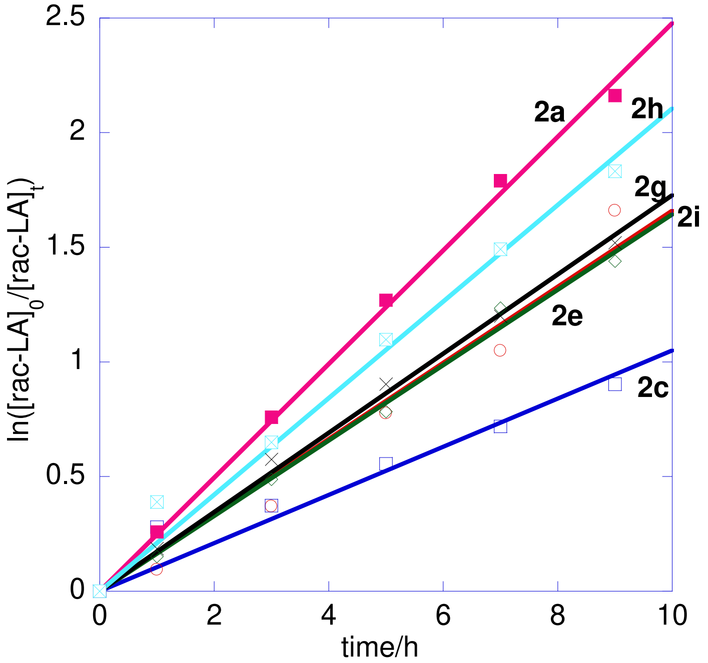


**Figure 1** Semilogarithmic plot of rac-lactide conversion vs time catalyzed by complexes **2** in toluene at 80 °C

The enhanced Lewis acidity induced by electron withdrawing groups may lead to preferred coordination of lactide monomer, but it could also inhibit the subsequent insertion step. It is also worth noting that the two catalysts (**2c** and **2g**) with a preference for isotacticity are two of the less active catalysts. In addition, kinetic measurements for the polymerization of *L*-lactide by **2c** revealed very similar rate as that for *rac*-lactide. Analogous results have been observed for a highly isoselective aluminum complex.[12a]

## II.3 CONCLUSIONS

In conclusion, a series of aluminum complexes containing chiral, bidentate anilido-oxazolinate ligands have been synthesized and characterized. These complexes were tested in the ring opening polymerization of *rac*-lactide in the presence of benzyl alcohol, and six of them were effective in promoting the polymerization, while the other three with 2,6-dimethylphenyl substituents showed low catalytic reactivity. The microstructure of the resulting polylactides ranged from slightly isotactic to moderately heterotactic. The reactivity and selectivity can be roughly understood on the basis of steric and electronic factors of substituents on several specific positions of the ligand framework. Taken together, these results indicate that the bulky, electron withdrawing groups on this series of aluminum compounds tend to give slower, but isoselective catalysts for the ROP of *rac*-LA. Studies further delineating these factors in catalysis are underway.

## II.4 EXPERIMENTAL SECTION

**General.** All reactions that involved compounds sensitive to air and/or moisture were carried out under a dry nitrogen atmosphere using freshly dried solvents and standard Schlenk line and glove box techniques. All chemicals were purchased from commercial sources. Toluene was distilled under nitrogen from Na/benzophenone. $CDCl_3$ was dried over $CaH_2$, distilled and degassed prior to use. *rac*-LA was recrystallized from dry toluene, sublimed under vacuum and stored under a dry nitrogen atmosphere.

NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer ($^1$H, and $^{13}$C), and referenced to residual solvent peak. Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar, using PLgel 5 μm Mixed-D column, a Prostar 355 RI detector, and THF as eluent at a flow rate of 1 mL/min (20 °C). Polystyrene standards were used for calibration. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were obtained on Applied Biosystems/MD SCIEX 4800 equipment using α-cyano-4-hydroxycinnamic acid as a matrix and 5 mM sodium acetate as an ionization agent. The HR-MS was performed using high resolution time of flight G1969A instrumentation (Agilent).

**Synthesis of ligands.** Similar ligands have been obtained previously;[20] the following example is typical: To a round bottom flask were added 2-bromobenzaldehyde (6.5 mmol), 1 equivalent of amino alcohols, and 25 mL of toluene. After stirring the mixture for 24 h, $K_3PO_4$ (19.5 mmol) and NBS (13.0 mmol) were added and stirring was continued for 5 h at room temperature. After filtration, the mixture was washed with $NaHCO_3$ and $H_2O$ 3 times. The organic fraction was dried with $Na_2SO_4$ and purified by column to the give the oxazoline precursors. The product was mixed with 120 mol% aniline, 5 mol% $Pd(OAc)_2$, 5 mol% *rac*-BINAP, 140 mol% sodium tert-butoxide and 15 mL dry toluene in a schlenk flask under nitrogen. The mixture was heated at 100 °C for 48 h, and then filtered and purified by column. The desired ligands were usually obtained as yellow-orange oil (**HL$^{1a-c}$** and **HL$^{1e-h}$**) or crystalline solids (**HL$^{1d}$** and **HL$^{1i}$**) in ~66-89% yields. Characterizations of **HL$^{1b, d, f}$** have been reported previously.[20]

**(4*S*)-4,5-Dihydro-2-(2’-anilinophenyl)-4-*iso*-propyloxazole** (**HL$^{1a}$**). Yield: 86 %. $^1$H NMR ($CDCl_3$, 298K): $\delta$ 10.55 (1H, s, N*H*), 7.73 (1H, d, Ar*H*), 7.28 (4H, m, Ar*H*), 7.20

(2H, d, Ar*H*), 6.97 (1H, t, Ar*H*), 4.29 (1H, m, NCH(R)C*H*$_2$O), 4.05 (1H, m, NC*H*(R)CH$_2$O), 3.96 (1H, m, NCH(R)C*H*$_2$O), 1.71 (1H, m, C*H*CH$_3$), 0.97 (3H, d, CHC*H*$_3$), 0.88 (3H, d, CHC*H*$_3$). $^{13}$C NMR(CDCl$_3$, 298K): $\delta$ 163.75 (*C*=N), 145.73, 141.74, 132.09, 130.12, 129.51, 122.77, 121.55, 117.10, 113.28, 110.59, 73.16 (N*C*H(R)CH$_2$O), 69.28 (NCH(R)*C*H$_2$O), 33.59 (*C*HMe$_2$), 19.24 (CH*Me*$_2$), 19.02 (CH*Me*$_2$). GC/MS: *m/z* 280.0 [M]$^+$, 237.0 (100), 206.9, 193.9, 179.9, 166.9. HRMS (EI$^+$): *m/z* cald for $C_{18}H_{21}N_2O$ [M+H]$^+$ 281.16539; found 281.16457.

**(4*R*)-4,5-Dihydro-2-(2’-anilinophenyl)-4-phenyloxazole** (**HL$^{1c}$**).[27] Yield: 88%. $^1$H NMR (CDCl$_3$, 298K): $\delta$ 10.39 (1H, s, N*H*), 7.80 (1H, d, Ar*H*), 7.22 (6H, m, Ar*H*), 7.17-7.15 (3H, m, Ar*H*), 7.08 (2H, t, Ar*H*), 6.96 (1H, t, Ar*H*), 6.69 (1H, t, Ar*H*), 5.39 (1H, m, NCH(R)C*H*$_2$O), 4.63 (1H, m, NC*H*(R)CH$_2$O), 4.06 (1H, m, NCH(R)C*H*$_2$O). $^{13}$C NMR(CDCl$_3$, 298K): $\delta$ 165.25, 146.25, 142.69, 141.44, 132.48, 130.40, 129.45, 128.97, 127.78, 126.73, 123.21, 122.32, 117.11, 113.36, 110.10, 73.31 (N*C*H(R)CH$_2$O), 70.32 (NCH(R)*C*H$_2$O). GC/MS: *m/z* 314 [M]$^+$, 283, 205, 194 (100), 167, 91. HRMS (EI$^+$): *m/z* cald for $C_{21}H_{18}N_2O$ [M]$^+$ 314.14191; found 314.14866.

**(4*R*)-4,5-Dihydro-2-(2’-anilinophenyl)-4-*iso*-butyloxazole** (**HL$^{1e}$**). Yield: 86%. $^1$H NMR (CDCl$_3$, 298K): $\delta$ 10.48 (1H, s, N*H*), 7.73 (1H, d, Ar*H*), 7.26 (4H, m, Ar*H*), 7.18 (2H, t, Ar*H*), 6.97 (1H, t, Ar*H*), 6.67 (1H, t, Ar*H*), 4.35 (2H, m, NCH(R)C*H*$_2$O), 3.82 (1H, t, NC*H*(R)CH$_2$O), 1.80 (1H, m C*H*$_2$CH), 1.59 (1H, m, C*H*$_2$CH), 1.36 (1H, m, CH$_2$C*H*), 0.93 (6H, m, CHC*H*$_3$). $^{13}$C NMR(CDCl$_3$, 298K): $\delta$ 163.45, 145.54, 141.49, 131.86, 129.90, 129.27, 122.66, 121.56, 116.93, 113.11, 110.44, 71.48 (N*C*H(R)CH$_2$O), 65.17 (NCH(R)*C*H$_2$O), 45.65 (*C*H$_2$CHMe$_2$), 25.84 (CH$_2$*C*HMe$_2$), 22.98 (CH$_2$CH*Me*$_2$), 22.64

($CH_2CHMe_2$). GC/MS: *m/z* 294 $[M]^+$ (100), 263, 237, 194, 167, 139. HRMS ($EI^+$): *m/z* cald for $C_{19}H_{23}N_2O$ $[M+H]^+$ 295.18104; found 295.18182.

**(4*S*)-4,5-Dihydro-2-(2'-(3,5-bis(trifluoromethyl)anilino)phenyl)-4-*iso*-propyloxazole** (**HL$^{1g}$**). Yield: 87%. $^1$H NMR ($CDCl_3$, 298K): $\delta$ 11.00 (1H, s, N*H*), 7.74 (1H, d, Ar*H*), 7.50 (2H, s, Ar*H*), 7.30-7.27 (3H, m, Ar*H*), 6.80 (1H, t, Ar*H*), 4.28 (1H, m, NCH(R)C$H_2$O), 4.04 (1H, m, NC*H*(R)$CH_2$O), 3.95 (1H, m, NCH(R)C$H_2$O), 1.70 (1H, m,C*H*$CH_3$), 0.93 (3H, d, CHC$H_3$), 0.84 (3H, d, CHC$H_3$). $^{13}$C NMR($CDCl_3$, 298K): $\delta$ 163.66, 143.79, 143.49, 133.01, 132.74, 132.40, 130.50, 124.66, 122.48, 119.65, 118.89, 114.82, 114.30, 112.59, 72.99 (N*C*H(R)$CH_2$O), 69.47 (NCH(R)*C*$H_2$O), 33.47 (*C*H$Me_2$), 19.14 (CH*Me*$_2$), 18.88 (CH*Me*$_2$). GC/MS: *m/z* 416 $[M]^+$ , 373 (100), 345, 316, 291, 234, 182. HRMS ($EI^+$): *m/z* cald for $C_{20}H_{19}N_2OF_6$ $[M+H]^+$ 417.14016; found 417.14115.

**(4*S*)-4,5-Dihydro-2-(2'-(4-methoxyanilino)phenyl)-4-*iso*-propyloxazole** (**HL$^{1h}$**). Yield: 88%. $^1$H NMR ($CDCl_3$, 298K): $\delta$ 10.36 (1H, s, N*H*), 7.80 (1H, d, Ar*H*), 7.22 (3H, d, Ar*H*), 7.11(1H, d, Ar*H*); 6.93(2H, d, Ar*H*); 6.70(1H, t, Ar*H*); 4.38(1H, t, NCH(R)C$H_2$O); 4.15 (1H, m, NC*H*(R)$CH_2$O); 4.06(1H, t, NCH(R)C$H_2$O); 3.83(3H, s, ArO*Me*); 1.82(1H, m, C*H*$CH_3$); 1.06(3H, d, CHC$H_3$); 0.96 (3H, d, CHC$H_3$). $^{13}$C NMR($CDCl_3$, 298K): $\delta$ 163.36 (*C*=N), 156.28, 147.33, 134.47, 132.13, 130.03, 125.10, 116.19, 114.76, 112.46, 109.58, 73.08 (N*C*H(R)$CH_2$O), 69.10 (NCH(R)*C*$H_2$O), 55.75 (ArO*Me*), 33.50 (*C*H$Me_2$), 19.26 (CH*Me*$_2$), 18.97 (CH*Me*$_2$). GC/MS: *m/z* 310 $[M]^+$ (100), 267, 237, 209, 182, 154. HRMS ($EI^+$): *m/z* cald for $C_{19}H_{23}N_2O_2$ $[M+H]^+$ 311.17595; found 311.17612.

**(4*S*)-4,5-Dihydro-2-(2'-(2-phenoxyanilino)phenyl)-4-*iso*-propyloxazole** (**HL$^{1i}$**). Yield: 88%. $^1$H NMR ($CDCl_3$, 298K):: $\delta$ 10.63 (1H, s, N*H*), 7.79 (1H, d, Ar*H*), 7.63 (3H, d, Ar*H*), 7.46(1H, d, Ar*H*), 7.29(2H, m, Ar*H*), 7.11(1H, m, Ar*H*), 7.03(2H, m, Ar*H*), 6.97(4H, m, Ar*H*), 6.78(1H, m, Ar*H*), 4.31(1H, t, NC*H*(R)$CH_2O$), 4.00 (2H, m, NCH(R)$C\mathit{H}_2O$), 1.65(1H, m, C*H*$CH_3$), 0.93(3H, d, CHC$\mathit{H}_3$), 0.85 (3H, d, CHC$\mathit{H}_3$). $^{13}$C NMR($CDCl_3$, 298K): *δ* 163.33 (*C*=N), 157.78, 148.29, 144.95, 133.89, 131.84, 130.12, 129.69, 124.08, 122.89, 122.71, 120.92, 120.40, 118.20, 117.50, 113.75, 111.59, 73.15 (N*C*H(R)$CH_2O$), 69.18 (NCH(R)$\mathit{C}H_2O$), 33.29 (*C*$HMe_2$), 19.17 (CH$\mathit{Me}_2$), 18.86 (CH$\mathit{Me}_2$). GC/MS: *m/z* 372 $[M]^+$, 329, 299, 286 (100), 245, 209, 167. HRMS ($EI^+$): *m/z* cald for $C_{24}H_{25}N_2O_2$ $[M+H]^+$ 373.19160; found 373.18851.

**Synthesis of Aluminum Complexes.** In a typical procedure, ligand **HL$^1$** (2.0 mmol) was mixed with 1.5 equivalents of $AlMe_3$ in toluene. The mixture was stirred under nitrogen at room temperature for 12 h. After removal of toluene in vacuo, the resulting yellow-orange residue was extracted with dry hexanes multiple times and combined. The solvent was then removed in vacuo at low temperature, affording the product as a yellow powder. The products can be further purified by recrystallization from a dichloromethane-hexane solution.

**($L^{1a}$)$AlMe_2$ (2a).** Yield: 69 %. $^1$H NMR($CDCl_3$, 298K): *δ* 7.59 (1H, d, J = 10, Ar*H*), 7.30 (3H, m, Ar*H*), 7.11 (1H, t, J = 10, Ar*H*), 7.02 (2H, m, Ar*H*), 6.37 (2H, m, Ar*H*), 4.38 (3H, m, NC*H*(R)$C\mathit{H}_2O$), 2.25 (1H, m, C*H*$Me_2$), 0.91 (3H, d, J= 10, CH$(C\mathit{H}_3)_2$), 0.84 (3H, d, J =10, J = CH$(C\mathit{H}_3)_2$), -0.95 (3H, s, Al*Me*), -0.97 (3H, s, Al*Me*). $^{13}$C NMR($CDCl_3$, 298K): *δ* 169.93 (*C*=N), 157.14, 147.16, 135.33, 130.73, 129.92, 128.35, 124.79, 117.23, 105.03, 67.99 (NCH(R)$\mathit{C}H_2O$), 67.61 (N*C*H(R)$CH_2O$), 29.93 (*C*$HMe_2$), 19.50 (CH$\mathit{Me}_2$), 14.37 (CH$\mathit{Me}_2$), -7.55 (Al$\mathit{C}H_3$), -9.91 (Al$\mathit{C}H_3$).

**($L^{1b}$)$AlMe_2$ (2b).** Yield: 69 %. Anal. Calcd. for $C_{22}H_{29}N_2OAl$: C, 71.41; H, 7.49; N, 8.33. Found: C, #; H #; N, #. $^1$H NMR ($CDCl_3$, 298K): *δ* 7.70 (1H, d, J = 10, Ar*H*), 7.13 (2H, m, Ar*H*), 7.08 (2H, m, Ar*H*), 6.45 (1H, t, J = 5, Ar*H*), 6.05 (1H, d, J = 5, Ar*H*), 4.50 (3H, m, NC*H*(R)C*H*$_2$O), 2.34 (1H, m, C*H*Me$_2$), 2.12 (Ar*Me*), 2.10 (Ar*Me*), 0.99 (3H, d, J= 10, CH(C*H*$_3$)$_2$), 0.90 (3H, d, J =10, J = CH(C*H*$_3$)$_2$), -0.89 (3H, s, Al*Me*), -0.93 (3H, s, Al*Me* ). $^{13}$C NMR(CDCl$_3$, 298K): $\delta$ 170.01, (*C*=N), 156.24, 143.28, 137.07, 136.75, 135.70, 130.92, 129.27, 128.88, 125.34, 116.12, 113.57, 104.46, 67.72 (NCH(R)*C*H$_2$O), 67.50 (N*C*H(R)CH$_2$O), 29.84 (*C*HMe$_2$), 19.40 (CH*Me*$_2$), 18.65 (Ar*C*H$_3$), 18.60 (Ar*C*H$_3$), 14.19 (CH*Me*$_2$), -8.31 (Al*C*H$_3$), -8.97 (Al*C*H$_3$).

**(L$^{1c}$)AlMe$_2$ (2c).** Yield: 53 %. $^1$H NMR (CDCl$_3$, 298K): $\delta$ 7.78 (1H, d, J = 10, Ar*H*), 7.5-7.3 (8H, m, Ar*H*), 7.15 (2H, m, Ar*H*); 7.06 (1H, m, Ar*H*), 6.50 (1H, t, J = 10, Ar*H*), 6.44 (1H, d, J = 10, Ar*H*), 5.36 (1H, m, NC*H*(R)CH$_2$O), 4.99 (1H, m, NCH(R)C*H*$_2$O), 4.58 (1H, m, NCH(R)C*H*$_2$O), -0.94 (3H, s, Al*Me*), -1.55 (3H, s, Al*Me*). $^{13}$C NMR (CDCl$_3$, 298K): $\delta$ 170.18 (*C*=N), 157.35, 146.94, 138.46, 135.60, 130.90, 129.93, 129.45, 129.37, 128.26 128.06, 124.84, 117.34, 113.82, 104.55, 75.34 (NCH(R)*C*H$_2$O), 67.03 (N*C*H(R)CH$_2$O), -9.05 (*Me*Al), -9.83 (*Me*Al). Anal. Calcd. for C$_{23}$H$_{23}$N$_2$OAl·0.15CH$_2$Cl$_2$: C, 72.57; H, 6.13; N, 7.31. Found: C, 72.92; H 6.38; N, 7.28.

**(L$^{1d}$)AlMe$_2$ (2d).** Yield: 50 %. $^1$H NMR (CDCl$_3$, 298K): $\delta$ 7.80 (1H, d, J = 10, Ar*H*), 7.40 (3H, m, Ar*H*), 7.35 (2H, m, Ar*H*), 7.11 (3H, m, Ar*H*), 7.05 (1H, m, Ar*H*), 6.49 (1H, t, J = 10, Ar*H*), 6.06 (1H, d, J = 10, Ar*H*), 5.37 (1H, m, NCH(R)C*H*$_2$O), 5.00 (1H, m, NC*H*(R)CH$_2$O), 4.57 (1H, m, NCH(R)C*H*$_2$O), 2.11 (3H, s, Ar*Me*), 2.04 (3H, s, Ar*Me*), -0.92 (3H, s, Al*Me*), -1.62 (3H, s, Al*Me*). $^{13}$C NMR (CDCl$_3$, 298K): $\delta$ 170.30 (*C*=N), 138.82, 136.92, 136.62, 136.01, 131.06, 130.90, 129.36, 129.35, 128.88, 127.94, 125.44, 124.53, 116.23, 113.69, 104.09, 75.40 (NCH(R)*C*H$_2$O), 66.96 (N*C*H(R)CH$_2$O), 18.67 (*Me*Ph), -9.39 (*Me*Al), -10.38 (*Me*Al).

**(L$^{1e}$)AlMe$_2$ (2e).** Yield: 67 %. $^1$H NMR (CDCl$_3$, 298K): ): *δ* 7.68 (1H, d, J = 10, Ar*H*), 7.38 (2H, m, Ar*H*), 7.19 (1H, m, Ar*H*), 7.10 (3H, m, Ar*H*), 6.45 (2H, m, Ar*H*), 4.72 (1H, m, NC*H*(R)CH$_2$O), 4.41 (1H, m, NCH(R)C$\mathit{H}_2$O), 4.23(1H, m, NCH(R)C$\mathit{H}_2$O), 1.95 (1H, m, C*H*CH$_3$), 1.64 (2H, m, C$\mathit{H}_2$CH), 0.99 (6H, m, CH(C$\mathit{H}_3$)$_2$), -0.85 (3H, s, Al*Me*), -0.90 (3H, s, Al*Me*). $^{13}$C NMR (CDCl$_3$, 298K): *δ* 157.06, 147.57, 147.10, 135.28, 130.70, 129.97, 128.30, 124.79, 117.28, 113.83, 105.20, 73.31 (NCH(R)*C*H$_2$O), 62.12 (N*C*H(R)CH$_2$O), 44.12 (*C*H$_2$CHMe$_2$), 25.94 (*C*H$_2$*C*HMe$_2$), 24.02 (CH*Me$_2$*), 21.82 (CH*Me$_2$*), -7.08 (*Me*Al), -9.95 (*Me*Al). Anal. Calcd. for $C_{21}H_{27}N_2OAl{\cdot}0.2CH_2Cl_2$: C, 69.30; H, 7.52; N, 7.62. Found: C, 69.64; H 7.78; N, 7.28.

**(L$^{1f}$)AlMe$_2$ (2f).** Yield: 90 %. $^1$H NMR (CDCl$_3$, 298K): *δ* 7.71 (1H, d, J = 10, Ar*H*), 7.15 (3H, m, Ar*H*), 7.08 (1H, d, J = 10, Ar*H*), 6.45 (1H, t, J = 10, Ar*H*), 6.05 (1H, d, J = 10, Ar*H*), 4.73 (1H, m, NC*H*(R)CH$_2$O), 4.42 (1H, m, NCH(R)C$\mathit{H}_2$O), 4.25 (1H, m, NCH(R)C$\mathit{H}_2$O), 2.12 (3H, s, Ar*Me*), 2.10 (3H, s, Ar*Me*), 1.96 (1H, m, C*H*CH$_3$), 1.62 (2H, m,C$\mathit{H}_2$CH), 1.00 (6H, m, CHC$\mathit{H}_3$), -0.88 (3H, s, Al*Me*), -0.89 (3H, s, Al*Me*). $^{13}$C NMR (CDCl$_3$, 298K): *δ* 169.79 (*C*=N), 156.05, 143.15, 137.08, 136.73, 135.69, 130.81, 128.93, 128.83, 125.37, 116.13, 113.59, 104.66, 73.18 (NCH(R)*C*H$_2$O), 61.94 (N*C*H(R)CH$_2$O), 44.05 (C*C*HCH$_3$), 25.91 (CH*C*H$_2$CH), 24.00 (CH*Me*), 21.70 (CH*Me*), 18.76 (*Me*Ph), -7.17 (*Me*Al), -9.28 (*Me*Al). Anal. Calcd. for $C_{23}H_{31}N_2OAl{\cdot}0.2CH_2Cl_2$: C, 70.46; H, 8.00; N, 7.08. Found: C, 70.79; H, 8.31; N, 6.97.

**(L$^{1g}$)AlMe$_2$ (2g).** Yield: 95 %. $^1$H NMR (CDCl$_3$, 298K): *δ* 7.75 (1H, d, J = 5, Ar*H*), 7.61 (1H, s, Ar*H*), 7.54 (2H, s, Ar*H*), 7.24 (1H, m, Ar*H*), 6.65 (1H, t, J = 5, Ar*H*), 6.57 (1H, d, J = 5, Ar*H*), 4.54 (2H, m, NCH(R)C$\mathit{H}_2$O), 4.44 (1H, m, NC*H*(R)CH$_2$O), 2.32 (1H, m, C*H*CH$_3$), 1.00 (3H, d, J = 5, CHC$\mathit{H}_3$), 0.91 (3H, d, J = 5, CHC$\mathit{H}_3$), -0.84 (3H, s, Al*Me*), -

0.88 (3H, s, Al*Me*). $^{13}$C NMR ($CDCl_3$, 298K): $\delta$ 169.87 (*C*=N), 155.55, 150.20, 135.86, 133.24 (*C*$F_3$), 131.10, 127.55, 124.66, 117.75, 116.12, 107.33, 68.13 (NCH(R)*C*$H_2$O), 68.08 (N*C*H(R)$CH_2$O), 30.03 (*C*HMe$_2$), 19.38 (CH*Me*$_2$), 14.37 (CH*Me*$_2$), -6.84 (Al*C*$H_3$), -8.73 (Al*C*$H_3$).

**($L^{1h}$)AlMe$_2$ (2h).** Yield: 84 %. $^1$H NMR ($CDCl_3$, 298K): $\delta$ 7.67 (1H, d, J = 10, Ar*H*), 7.11 (1H, m, Ar*H*), 6.98 (4H, m, Ar*H*), 6.43 (1H, t, J = 10, Ar*H*), 6.37 (1H, d, J = 10, Ar*H*), 4.48 (3H, m, NC*H*(R)C*H*$_2$O), 3.86 (3H, s, ArO*Me*), 2.33 (1H, m, C*H*$CH_3$), 1.00 (3H, d, J = 10, CHC*H*$_3$), 0.91 (3H, d, J = 10, CHC*H*$_3$), -0.87 (3H, s, Al*Me*), -0.89 (3H, s, Al*Me*). $^{13}$C NMR ($CDCl_3$, 298K): $\delta$ 169.90 (*C*=N), 157.62, 157.08, 139.33, 135.34, 130.75, 129.50, 125.07, 116.77, 115.20, 114.81, 113.36, 104.59, 67.94 (NCH(R)*C*$H_2$O), 67.48 (O*C*$H_3$), 55.60 (N*C*H(R)$CH_2$O), 29.92 (C*C*H$CH_3$), 19.50 (CH*Me*), 14.33 (CH*Me*), -7.76 (*Me*Al), -9.91 (*Me*Al). Anal. Calcd. for $C_{21}H_{27}N_2O_2Al{\cdot}0.3CH_2Cl_2$: C, 65.28; H, 7.10; N, 7.15. Found: C, 65.46; H, 7.67; N, 6.84.

**($L^{1i}$)AlMe$_2$ (2i).** Yield: 80%. The compound exists as two isomers in ~1.5:1.0 ratio, presumably the *anti* and *syn* isomers due to the orientation of the *ortho*-PhO group. $^1$H NMR ($CDCl_3$, 298K): *anti*-**2i**: $\delta$ 7.47 (1H, d, J = 5, Ar*H*), 6.58 (1H, d, J = 10, Ar*H*), 6.52 (2H, d, J = 10, *o*-$C_6H_5O$), 6.48 (m, 1H, Ar*H*), 4.02 (m, 1H, oxazoline-C*H*), 2.12 (m, 1H, C*H*Me$_2$), 0.85 (d, 3H, J = 5, CH*Me*$_2$), 0.76 (d, 3H, J = 5, CH*Me*$_2$), -0.91 (s, 3H, Al*Me*), -1.06 (s, 3H, Al*Me*). *syn*-**2i**: $\delta$ 7.56 (1H, d, J = 10, Ar*H*), 6.80 (1H, d, J = 5, Ar*H*), 6.70 (2H, d, J = 5, *o*-$C_6H_5O$), 6.48 (m, 1H, Ar*H*), 2.18 (m, 1H, C*H*Me$_2$), 0.85 (d, 3H, J = 5, CH*Me*$_2$), 0.66 (d, 3H, J = 5, CH*Me*$_2$), -0.87 (s, 3H, Al*Me*), -1.06 (s, 3H, Al*Me*). The rest of signals at 7.22-6.82 for aromatic protons and at 4.42-4.20 for oxazoline protons show considerable overlap and are not resolved. $^{13}$C NMR ($CDCl_3$, 298K): *anti*-**2i**: $\delta$ 169.29

(*C*=N), 157.08 (*ipso-C*), 155.54 (*ipso-C*), 151.32 (*ipso-C*), 139.04 (*ipso-C*), 134.58, 129.87, 129.03 (*m-C*$_6$H$_5$O), 128.81, 124.88, 124.68, 122.17, 121.07, 119.13, 118.38 (*o-C*$_6$H$_5$O), 115.03, 107.22 (*ipso-C*), 67.95, 67.81, 30.05 (*C*HMe$_2$), 19.35 (CH*Me*$_2$), 14.49 (CH*Me*$_2$), -7.51 (Al*Me*), -11.16 (Al*Me*). *syn*-**2i**: $\delta$ 169.37 (*C*=N), 156.54 (*ipso-C*), 156.03 (*ipso-C*), 152.79 (*ipso-C*), 138.90 (*ipso-C*), 134.65, 130.16, 129.61 (*m-C*$_6$H$_5$O), 127.92, 124.35, 124.07, 123.47, 119.80 (*o-C*$_6$H$_5$O), 119.03, 118.63, 114.91, 107.07 (*ipso-C*), 68.16, 67.69, 29.80 (*C*HMe$_2$), 19.48 (CH*Me*$_2$), 14.30 (CH*Me*$_2$), -8.78 (Al*Me*), -9.53 (Al*Me*). Anal. Calcd. for $C_{26}H_{29}N_2O_2Al$: C, 72.88; H, 6.82; N, 6.54. Found: C, 72.70; H, 6.76; N, 6.43.

**Polymerization of *rac*-Lactide.** A typical solution polymerization procedure was exemplified by the following: *rac*-Lactide (0.71 g, 4.9 mmol), benzyl alcohol (10.3 μL, 0.10 mmol), Al complex (0.10 mmol) and toluene (8.0 mL) were added into a Schlenk flask. The reaction mixture was heated in an oil bath preset at 80 °C. The conversion of *rac*-lactide was monitored by periodically taking samples via $^1$H NMR spectroscopic analyses. Typical conversions were 92%- 99% after 24 h (except compounds **2b**, **2d**, and **2f**). At the end of the reaction, the polymer was isolated by precipitation from a $CH_2Cl_2$ solution. The tacticity was determined by homonuclear decoupled $^1$H NMR spectrum at the methine region (5.25-5.15 ppm), which can be assigned according to the literature.[28]

The bulk polymerization was performed by heating *rac*-lactide (2.84 g, 19.8 mmol) and an Al catalyst (0.050 mmol) in a Schlenk flask under nitrogen with an oil bath preset at 130 °C. The heating was discontinued when the melt became very viscous and stirring stopped, usually within 2 h. The resulting reaction mixture was analyzed by $^1$H NMR to determine the conversion of lactide and tacticity of PLA.

**Kinetic Runs**. A Schlenk flask was loaded with *rac*-lactide, Al catalyst (2 mol%), and benzyl alcohol (2 mol%, one equivalent *vs* catalyst) and toluene such that [*rac*-LA] = 0.50 M under nitrogen. The flask was then heated to 80 ºC via an oil bath. At preset time intervals, an aliquot (0.1 mL) was withdrawn and quenched with MeOH or $CH_2Cl_2$. The solvent was then removed in vacuo and the conversion of lactide was determined by $^1H$ NMR. The apparent first order rate constants were obtained by the slope of linear fit of semilogarithmic plot of *rac*-lactide conversion *vs* time, using the KaleidaGraph program.

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# CHAPTER III

# SYNTHESIS OF POLYCARBONATES AND POLY(ETHER CARBONATE)S DIRECTLY FROM CARBON DIOXIDE AND DIOLS PROMOTED BY A $Cs_2CO_3/CH_2Cl_2$ SYSTEM[a]

## III.1 INTRODUCTION

Polymers are important materials widely used in modern society. Examples of synthetic polymers include commodity plastics, synthetic fabrics, rubbers, and so on.[1,2] Polymer science has grown into a major research area in both industry and academia; however, the nearly exclusive utilization of petroleum-based feedstocks for the synthesis will ultimately become an issue.[3,4,5,6] Therefore, the development of effective processes for the manufacture of polymers from renewable resources has attracted significant attention. One prominent example is the production of polycarbonates from carbon dioxide ($CO_2$), which is considered an attractive renewable carbon source because of its low cost, non-toxicity, and availability in nature and from many industrial processes.[7,8] Polycarbonates represent a class of polymers that is potentially biodegradable and biocompatible.[9] Earlier studies have shown that aliphatic polycarbonates undergo slow hydrolytic degradation in vitro and accelerated enzymatic degradation in vivo.[10] Some of the polycarbonates have been applied in the synthesis of engineering thermoplastics and resins and may be useful as coatings, adhesives, ceramic binders, and packaging materials.[11]

Typical synthetic pathways for polycarbonates are summarized in Scheme 1. The classical method is the condensation of a diol with highly toxic phosgene ($COCl_2$) or its

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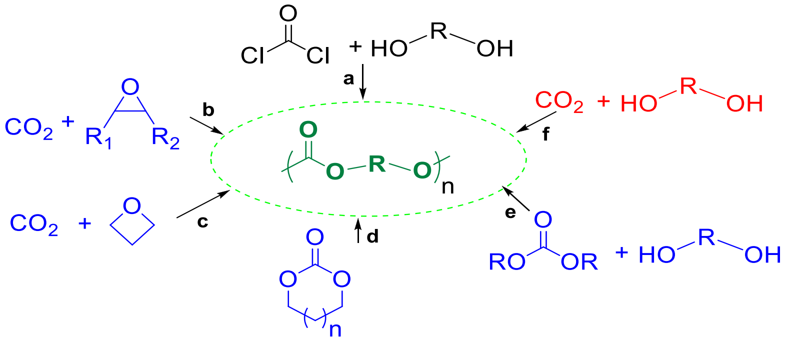
derivatives (route **a**), by which the conventional polycarbonate, poly(oxocarbonyloxy-1,4-phenylene isopropylidene-1,4-phenylene), is produced industrially.[12] The alternating copolymerization of $CO_2$ with epoxides/oxetanes (routes **b**, **c**), in the presence of catalysts/cocatalysts, has been widely studied.[13,14] In particular, homogeneous single site catalysts derived from Co, Cr and Zn are among the most effective systems.[15] Similarly, the catalytic ring opening polymerization of cyclic carbonates is another promising approach for polycarbonates (route **d**).[16] However, these routes (**b-d**) are restricted more or less by epoxides/cyclic carbonates monomers that are available. In comparison, diols provide much greater flexibility because various structurally diverse diols are readily available for incorporation. Along this line the condensation/metathesis of diols with organic dicarbonates such as dimethyl and diphenyl carbonates have been recently developed (route **e**).[17] However, dimethyl and diphenyl carbonates still need to be produced from phosgene or $CO_2$. Thus a direct approach from $CO_2$ and diols for the synthesis of polycarbonates would be highly desirable, but this approach (route **f**) is less explored.[18]

**Scheme 4**: Synthesis of Polycarbonates



In the context of $CO_2$ utilization, significant progresses have been made for the direct synthesis of organic carbonate from $CO_2$ and alcohols, in part because $CO_2$ is used directly and water is the only byproduct.[19] One typical approach involves the three-component coupling of $CO_2$, alcohols and halides, in the presence of organic or inorganic base promoters.[20] While asymmetrical dialkyl carbonates are produced in general, symmetrical dicarbonates can be obtained by choosing appropriate combination of alcohols and halides. For example, dimethyl carbonate (DMC) has been synthesized from methanol and $CO_2$ mediated by inorganic bases and methyl iodide.[19a,21] In another approach, direct coupling of $CO_2$ and alcohols leads to the formation of symmetrical dialkyl carbonates, again in the presence of a base promoter and an appropriate reagent that can serve as a leaving group.[22] We are particularly drawn to the work of Saito and coworkers, in which various alcohols were converted to dialkyl carbonates using a combination of $Cs_2CO_3$ and dichloromethane (DCM).[23] DCM plays an essential role for the transformation, yet is not incorporated into the dialkyl carbonate products. Also noteworthy is that the synthesis was achieved under 1 atm of $CO_2$. Prompted by these advances, we reason that the carbonate linkage would be generated when a diol is employed under the similar conditions, thus leading to the formation of oligo- and polycarbonates. During the preparation of this manuscript, a $Cs_2CO_3$-promoted synthesis of polycarbonates from $CO_2$, diols and dihalides has been described.[18f] In the present study, we report our efforts that utilize Saito's method towards various diols and $CO_2$ in the presence of $Cs_2CO_3$ and DCM, yielding polymers with polycarbonates and poly(ether carbonate)s main chains.

## III.2 RESULTS AND DISCUSSION

### III.2.1 Copolymerization of $CO_2$ and 1,4-Benzenedimethanol

In our study, 1,4-benzenedimethanol was first chosen as a representative diol that is unlikely to form cyclic carbonate on account of its rigid backbone structure. The combination of $Cs_2CO_3$/DCM in a solvent NMP (N-Methyl-2-pyrrolidone) was investigated as the reagents, as the system has been found effective in the synthesis of organic carbonates from $CO_2$ and alcohols.[23] The reaction was initially carried out under optimized conditions for organic dicarbonates: one equiv of 1,4-benzenedimethanol, 4 equiv of $Cs_2CO_3$, 6.2 equiv of DCM and 1 ml of NMP under 1 atm of $CO_2$ at 100 $^{o}$C for 12 h (Table 4, entry 1). Excellent conversion of diol (>99%), as determined by NMR, was achieved under these conditions. Not surprisingly, the conversion was lowered with less loading of $Cs_2CO_3$ or DCM, or both (entries 2-4). When a polar, aprotic, high-boiling solvent DMSO (dimethyl sulfoxide) was used as an alternative solvent to NMP, a significant decrease of the diol conversion was observed under otherwise identical conditions (entry 5 vs 1). Concerning the role of $Cs_2CO_3$ in the synthesis, $Cs_2CO_3$ was often considered as a strong base and could also be used to absorb small amount of water. Therefore, $Cs_2CO_3$ was replaced by a strong organic base, DBU (1,8-diazabicycloundec-7-ene), in combination with molecular sieves (entry 6). However, no conversion of diol was observed in the reaction, which suggested that $Cs_2CO_3$ served as more than just a base or dehydration agent in the reaction. In this context, it was noted that alkoxides conjugated with cesium ion can exhibit enhanced nucleophilicities that facilitate the attack to carbon dioxide.[24]

**Table 4**. Copolymerization of $CO_2$ and 1,4-benzenedimethanol with $Cs_2CO_3$/DCM[a]

| entry | $Cs_2CO_3$(equiv.) | DCM(equiv.) | Time (h) | Conv.(%)[b] |
|---|---|---|---|---|
| **1** | 4 | 6.2 | 12 | >99[c] |
| **2** | 2 | 6.2 | 12 | 24.5 |
| **3** | 4 | 3.1 | 12 | 26.8 |
| **4** | 2 | 3.1 | 12 | 9.5 |
| **5[d]** | 4 | 6.2 | 12 | 30.2 |
| **6[e]** | 0 | 6.2 | 24 | 0 |
| **7** | 4 | 0 | 24 | 0 |

[a]Reactions were performed with 1 mmol 1,4-benzenedimethanol at 100 °C under 1 atm of $CO_2$ in 1 ml of NMP, unless noted otherwise. [b]Determined by $^1H$ NMR spectroscopy. [c]The pure polymeric product was isolated from the mixture with 63.7% yield. [d]The reaction was run in 1 ml of DMSO instead of NMP. [e]The reaction was run with molecular sieves 4 Å and DBU (4 equiv) without $Cs_2CO_3$.

The product generated in the reaction (entry 1, Table 4) was isolated in decent yields (63.7%) by precipitation as an off-white solid, and characterized via various spectroscopic techniques including $^1H$ and $^{13}C$ NMR, FT-IR, and ESI-MS and GPC, which suggest the formation of a short chain polycarbonate with alcohol end groups. According to the literature study, the carbonate linkage of the polymer results from the coupling of alcohols and $CO_2$, not from $Cs_2CO_3$.[20,25] The $^1H$ and $^{13}C$ NMR spectra are comparable with the reported data,[18b] in which the carbonyl carbon exhibits a characteristic peak at 156 ppm in the $^{13}C$ NMR spectrum. The presence of carbonyl group was also confirmed by the absorbance at 1740 $cm^{-1}$ in the FT-IR spectrum, similar to those in other polycarbonates.[26] The ESI-ToF mass spectrum features a main series of peaks at $164n + 138 + 18$, which can be assigned to $n(C_9H_8O_3)$ + 1,4-benzenedimethanol + $NH_4^+$. The molecular weight is determined by GPC to be $M_n = 1700$ g/mol with $M_w/M_n = 1.2$. These observations support the assignment of a short chain polycarbonate diol structure. The thermal property of the isolated product was studied with differential scanning calorimetry (DSC) and a melting transition at ~188 °C was observed.

### III.2.2 Copolymerization of $CO_2$ and 1,4-Cyclohexanedimethanol

Benzylic alcohols tend to behave quite differently compared to other aliphatic alcohols, so we then chose a fully aliphatic diol, 1,4-cyclohexanedimethanol, as the coupling partner with $CO_2$. The reaction was carried out using 4 equiv of $Cs_2CO_3$ and 6.2 equiv of DCM under 1 atm of $CO_2$ at 100 °C, and the conversion of 1,4-cyclohexanedimethanol reached 100 % within 12 h, as determined by the $^1H$ NMR spectroscopy. The product has been isolated as a light colored, soft material with 52.9% yield, and characterization by NMR and FT-IR spectroscopies revealed some remarkable features of the polymeric product. The most striking is the resonance at 5.35 ppm in the $^1H$ NMR spectrum (Figure 2) that is assignable to the methylene (**a**) protons between two oxygen atoms, suggesting both carbonate linkage and ether linkage are present in the polymer backbone. The methylene group (**c**) connected to the other side of the carbonate group is represented by the peaks around 4.0 ppm and the methylene group (**f**) connected to the opposite side of the cyclohexyl linkage was represented by the peaks around 3.5 ppm. The peaks between 1.0 ppm and 2.0 ppm belong to the cyclohexane ring. The structure of the polymer was also corroborated by the $^{13}C$ NMR spectrum (Figure 3), featuring a peak around 155 ppm, assignable to the carbonate carbon, and a peak around 92 ppm, assignable to the methylene (**a**) carbon. These assignments were supported by the 2D COSY and HSQC NMR spectra of the isolated products. Furthermore, the existence of carbonyl group was confirmed by the absorbance at 1740 $cm^{-1}$ in the FT-IR spectrum.

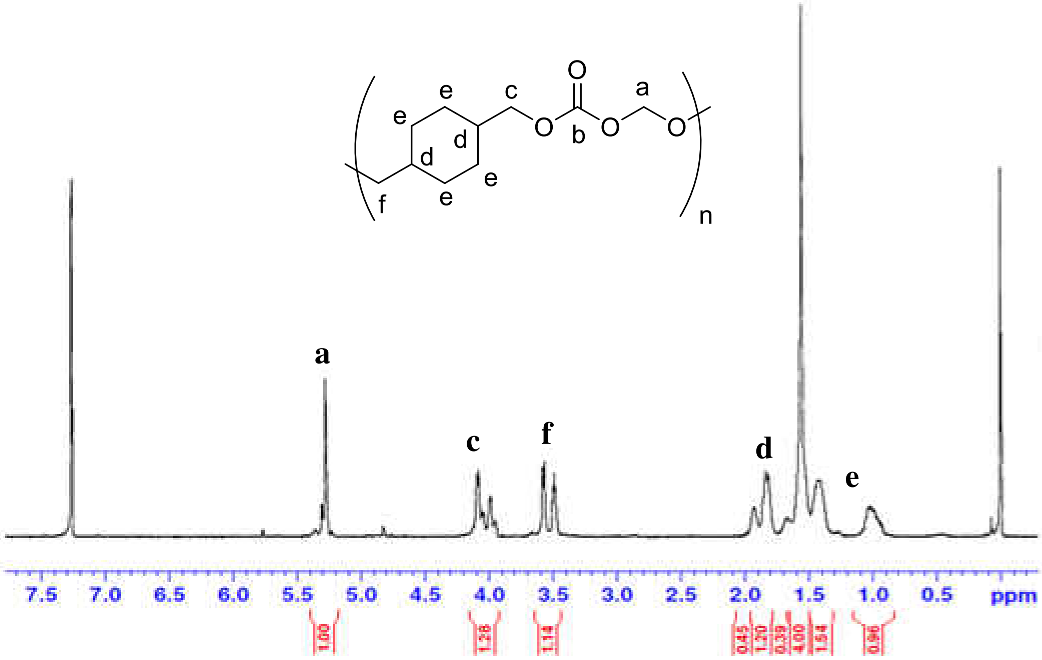


**Figure 2**. $^{1}H$ NMR spectra of poly(ether carbonate) from 1,4-cyclohexanedimethanol.

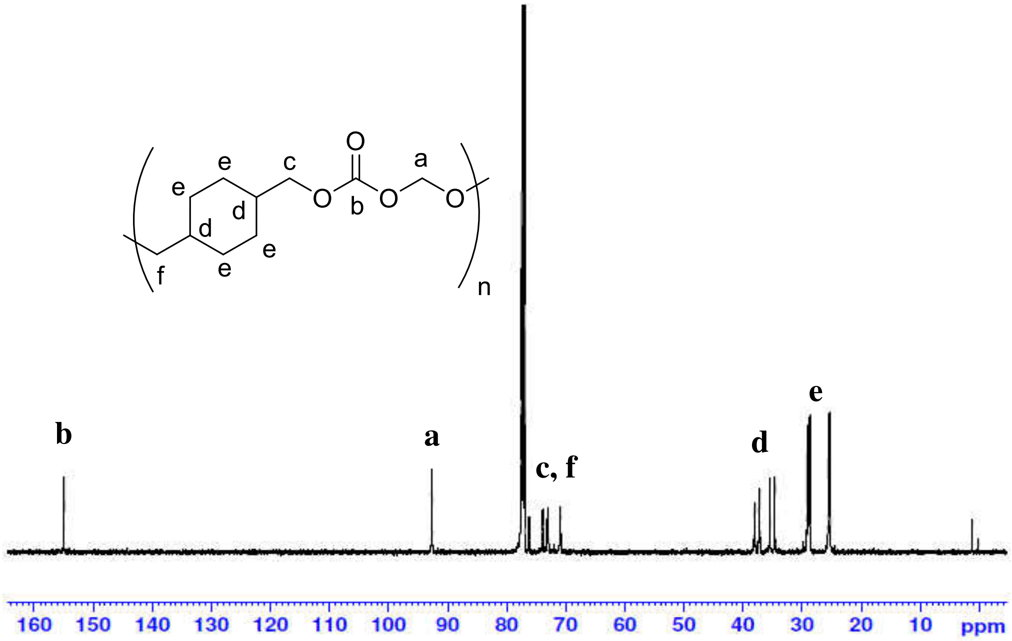


**Figure 3**. $^{13}C$ NMR spectra of poly(ether carbonate) from 1,4-cyclohexanedimethanol.

On the basis of these analyses, the structure of the polymeric product from 1,4-cyclohexanedimethanol and $CO_2$ is characterized as poly(ether carbonate)s. The ratio of the integration of the set of peaks at 4.0 ppm (linked to carbonate) and the set of peaks at

3.5 ppm (linked to ether) was 1.07:1, and they were both close to the integration of the methylene peak at 5.3 ppm. These important observations suggested that about 93% of the repeating unit of the polymer consists of an ether-carbonate linkage. The rest was believed to be the pure carbonate linkage without incorporation of the $OCH_2O$ ether moiety, which is consistent with the slightly larger integration of the set of peaks at 4.0 ppm. The ether-carbonate connectivity was mostly alternating in nature, as suggested by an HMBC NMR experiment (Figure 3). The observed three sets of cross peaks clearly demonstrate the connection of C3-C1-C2-C4 that are interspersed with oxygen atoms. The ether-carbonate repeating unit of ~200.1 *Da* was also detected in the ESI-MS (Figure 4), in agreement with the alternating nature of the structure. The minor incorporation of methylene group of $CH_2Cl_2$ was observed in the reaction of $CO_2$ with alcohols for the synthesis of organic carbonates,[23,27] which is believed to result from the reaction between DCM and alkoxide CsOR or carboxylate CsO(C=O)OR under the reaction conditions. It is worth mentioning that the formation of the alternating ether carbonate linkage is quite unique and has not been observed in other similar systems. In the polycondensation reaction of $CO_2$ with diols and α,ω-dihalides promoted by $K_2CO_3$[18a] or $Cs_2CO_3$,[18f] ether linkage was not detected and both the diol and dihalide units were incorporated as carbonate linkages.

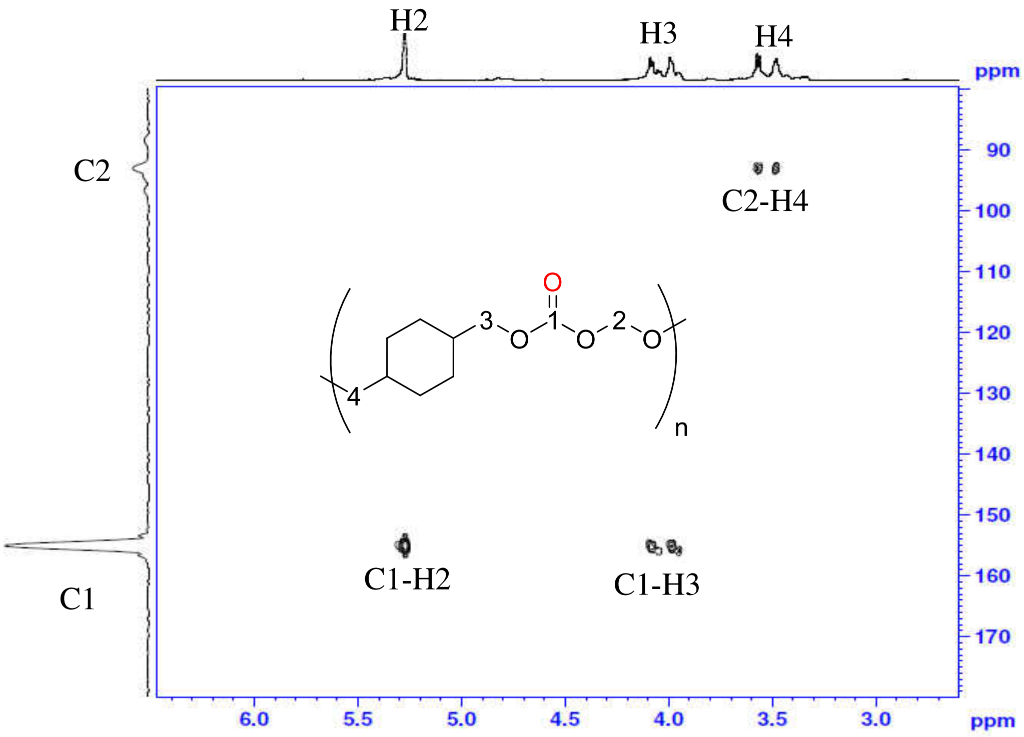


**Figure 4.** HMBC NMR of Poly(ether carbonate) from 1,4-cyclohexanedimethanol

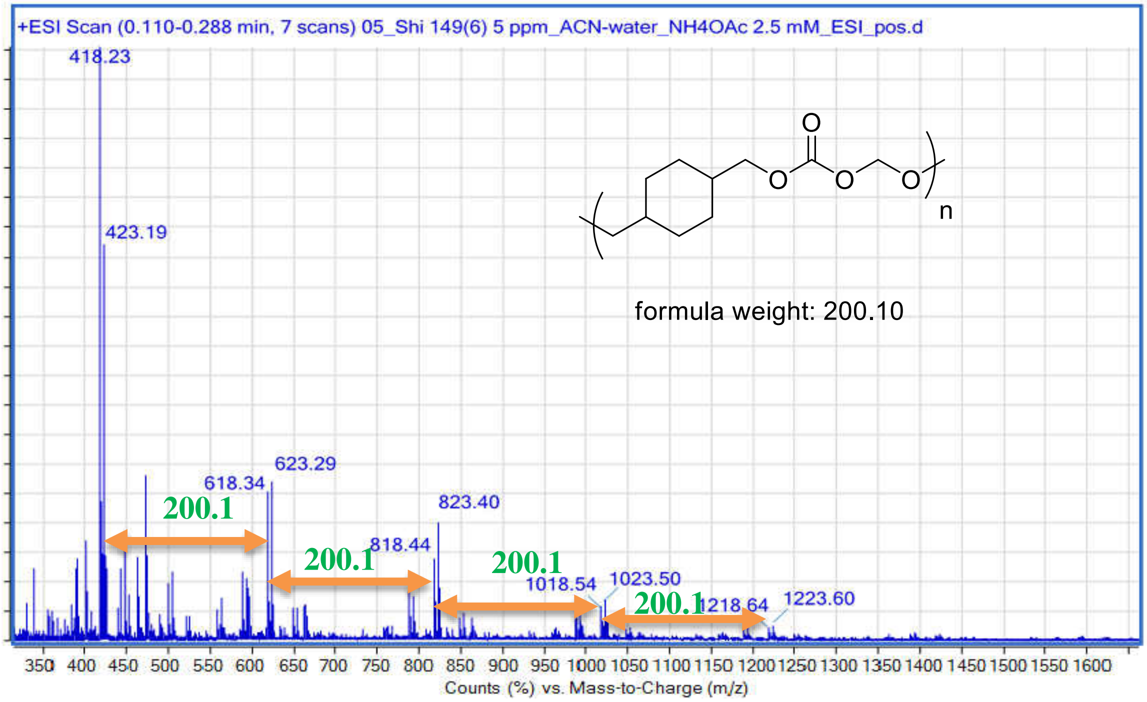


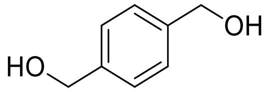
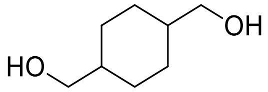
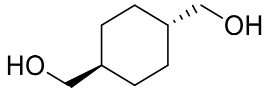
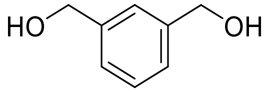
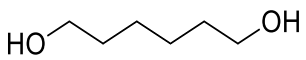
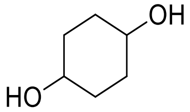
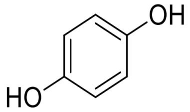
**Figure 5.** ESI-TOF-MS of Poly(ether carbonate) from 1,4-cyclohexanedimethanol

Another notable observation of the NMR spectra of the polymer is that the hydrogen and carbon signals associated with the 1,4-cyclohexanedimethanol moiety are represented by two separate sets of peaks. This is due to the *cis*- and *trans*- isomers of the 1,4-cyclohexanedimethanol, because our starting material is a mixture of *cis*- and *trans*-1,4-cyclohexanedimethanol. The assignment was verified by synthesizing polymer from *trans* 1,4-cyclohexanedimethanol and comparing the respective NMR spectra.

### III.2.3 Copolymerization of $CO_2$ and a Variety of Diols

Next we investigated a variety of diols in the direct copolymerization with $CO_2$ under similar conditions (Table 5). For most of the diol substrates, high conversions and decent yields were achieved. The characterizations data of the products, including the NMR and IR spectra, were compiled in the SI. As observed earlier, when another benzylic diol, 1,3-benzenedimethanol, was used (entry 4), the resulting polymer consisted of predominantly carbonate linkage (>95%) with no methylene incorporation; while regular aliphatic diols afforded polymers with alternating polycarbonate/ether repeating units, as judged by the presence of a singlet around 5.3 ppm assignable to the methylene group in the $^1$H NMR. When 1,6-hexanediol, a linear aliphatic diol that is potentially bio-derived, was employed in the reaction, up to 86% diol conversion was achieved (Table 5, entry 5). The incorporated $OCH_2O$ unit is identified by the NMR signals at 5.29 ppm ($^1$H) and 92.6 ppm ($^{13}$C). However, the isolated yield (36.0%) of the reaction was somewhat low, probably due to the formation of short chain oligomers that were not readily precipitated out from the mixture during the isolation. Nearly quantitative conversion was obtained when 1,4-cyclohexanediol was employed as the starting diol, and the which indicated that secondary alcohols can be used in this synthesis (Table 5, entry 6). The corresponding poly(ether carbonate) was isolated in good yield (63.1%) and showed a moderate molecular weight ($M_n$ 5.1 kg/mol). However, when 1,4-hydroquinone, an aromatic diol, was used, only a small amount (~8%) of low molecular weight polymeric material ($M_n$ ~800 g/mol) was isolated despite the high conversion of the starting diol (entry 7). Spectroscopic analysis of this isolated product showed the incorporation of the methylene unit (5.6 ppm in $^1$H NMR) and the absence of carbonate linkage (no peak at ~1740 cm$^{-1}$ in FT-IR, see Figure S19), and the product is therefore characterized as an oligomeric -($OCH_2OC_6H_4$)$_n$-. This is consistent with the literature report that the acetal $PhOCH_2OPh$ was the predominant product in the reaction of phenol and $CO_2$ under the $Cs_2CO_3$/DCM conditions.[23] Obviously the reaction of phenoxide ($ArO^-Cs^+$) with DCM is preferred over the incorporation of $CO_2$.

**Table 5**. Synthesis of polycarbonates and poly(ether carbonate)s from $CO_2$ and various diols with $Cs_2CO_3$/DCM[a]

| entry | Diol | Conv. (%)[b] | Yield (%) | $M_n$ (kg/mol)[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|
| **1** |  | >99 | 63.7 | 1.8 | 1.23 |
| **2** |  | >99 | 52.9 | 5.0 | 1.84 |
| **3** |  | >99 | 53.6 | 5.1 | 1.77 |
| **4** |  | >99 | 57.2 | 3.4 | 1.22 |
| **5** |  | 85.8 | 36.0 | 6.6 | 1.41 |
| **6** |  | >99 | 63.1 | 5.1 | 1.62 |
| **7**[d] |  | 94.4 | 8.0 | 0.78 | 1.13 |

[a]Reactions were performed with 1 mmol diol at 100 °C under 1 atm of $CO_2$ for 12 h. [b]Determined by $^1$H NMR spectroscopy [c]Determined by GPC [d]Polyether was formed instead of polycarbonate.

Since the incorporation of the $OCH_2O$ unit was identified in the isolated products from all the aliphatic diols, we thought it would be interesting to investigate the influence of the loading of DCM, from 1.6 to 12.3 equivalents (vs 1,4-cyclohexanedimethanol) on the outcome of the reactions. The isolated yields of polymers (Table 3) increase with the loadings of DCM (from 1.6 equiv. to 9.3 equiv.) and the highest yield (71.7%) was achieved with 9.3 equivalent of DCM. Further increase in DCM seems to be not helpful for the isolated yield. GPC analysis shows that most of the isolated polymers exhibit decent number average molecular weights ($M_n$) between 3800 and 7600 g/mol, with a broad PDI from 1.8 to 2.5 (Table 6). We suspect that a considerable portion of the products is oligomers that are not readily isolated by the precipitation method. To support this notion, the methanol soluble components during precipitation were collected and analyzed. The $^1H$ NMR spectrum was very similar to the precipitated polymeric products, and GPC analysis showed a $M_n$ of ~700 g/mol. Furthermore, the combined yield of the methanol soluble components and the precipitated polymers was >90%. In accord with this notion, the yield of polymers could be improved by extending the reaction time (entry 2). With 6.2 equiv. of DCM and 72 h of reaction time, we were able to obtain a polymer with $M_n$ of 11 kg/mol in 75.2% isolated yield.

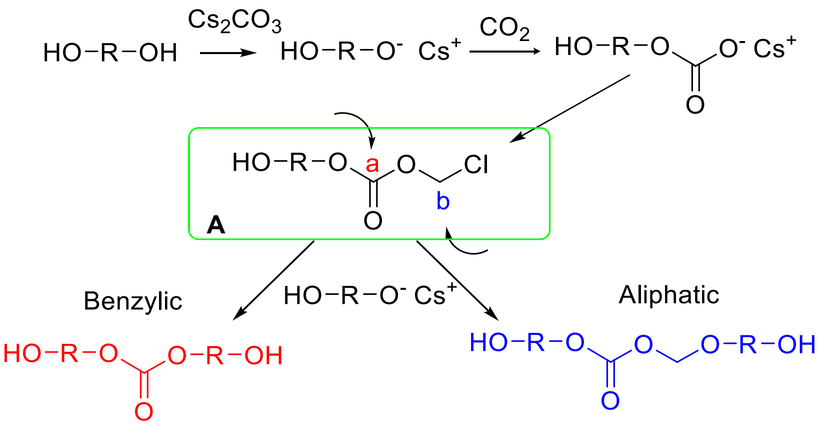
**Table 6**. Copolymerization of $CO_2$ and 1,4-cyclohexanedimethanol under various conditions[a]

| entry | DCM (equiv.) | $M_n$ (g/mol)[b] | $M_w/M_n$ | Yield (%) |
|---|---|---|---|---|
| **1** | 1.6 | 4400 | 1.8 | 14 |
| **2**[c] | 3.1 | 6400 | 2.2 | 43 |
| **3** | 6.2 | 5000 | 1.8 | 52 |
| **4** | 9.3 | 3800 | 2.2 | 71 |
| **5** | 12.4 | 7600 | 2.5 | 49 |
| **6**[d] | 6.2 | 11100 | 2.7 | 75.2 |

[a]Reactions were performed with 1 mmol 1,4-cyclohexanedimethanol and 4 mmol $Cs_2CO_3$ at 100 °C under 1 atm of $CO_2$ in 1 ml of NMP for 12 h. [b]Determined by gel permeation chromatography. [c]The reaction was performed for 24 h. [d]The reaction was performed for 72h.

With the excellent reactivity and selectivity achieved for the copolymerization of $CO_2$ and diols promoted by the current $Cs_2CO_3$/DCM system, comparison can be made with the recent procedures reported. [18] In the $CeO_2$/2-cyanopyridine system, carbonate linkage is formed with >90 % selectivity, however, the molecular weights are low ($M_n$ about 0.5 k ~1.7 k) and the procedure works poorly for the secondary alcohols. [18e] In a more closely related $Cs_2CO_3$-dihalide system,[18f] higher molecular weights up to 43 k have been achieved. However, it requires high pressure of $CO_2$ (instead of 1 atm used in this study) and more significantly, the polymers obtained consist of mostly carbonate linkage incorporating both the diol and dihalides moieties, similar to $K_2CO_3$-promoted reactions,[18a] but distinctly different from the results presented here.

Based on these results and the related studies in the literature,[23, 25] a possible, simplified pathway was proposed in Scheme 5. The nucleophilic attack on $CO_2$ by the alkoxide generated from deprotonation of diol by $Cs_2CO_3$ results in the formation of a carboxylate, which reacts with DCM to yield an intermediate **A**, again aided by $Cs_2CO_3$. The preference of methylene incorporation into aliphatic diols over benzylic diols might stem from the difference in their acidity (p*K*a ~14.0 for benzylic diols, ~14.8-14.9 for aliphatic diols in this study). While the attack at the carbonate position *a* by the less basic benzylic alkoxide leads to pure polycarbonate, the more basic aliphatic alkoxide seems to prefer to attack at the methylene position *b*, affording methylene-incorporated poly(ether carbonate).



**Scheme 5**: A possible pathway for the copolymerization of the diols and $CO_2$

## III.3 CONCLUSIONS

In summary, a new procedure for the synthesis of polycarbonate and poly(ether carbonate) directly from diols and $CO_2$ has been reported under 1 atm pressure of $CO_2$ using the combination of $Cs_2CO_3$ and $CH_2Cl_2$ as the reagents. The excellent conversions and isolated yields are achieved with various diols including benzylic and aliphatic alcohols. Both primary and secondary aliphatic diols have proven to be suitable substrates for the copolymerization. The isolated polymers have been fully investigated by IR, NMR, GPC, and ESI-MS, by which the structure of the products are confirmed. Notably, the polycarbonates from benzylic diols contain more than 90% of the carbonate linkage, while the polymers from aliphatic diols contain mainly the alternating carbonate/ether linkage. In addition, attempts at expanding the substrate scope and controlling the type of the linkage formed in the reaction are now underway in our laboratory.

## III.4 EXPERIMENTAL SECTION

**Materials.** Organic compounds including all diols are commercially available and were purchased from Sigma-Aldrich. The diols were dried under vacuum overnight. Dichloromethane was dried over activated molecule sieves (4 Å) overnight. The pre-dried $Cs_2CO_3$ and N-Methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich and used without further purification. All of the compounds were stored inside of a Glove box under nitrogen atmosphere.

**General Methods.** NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer ($^1H$ and $^{13}C$). Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar, using a PLgel 5 μm Mixed-D column, a Prostar 355 RI detector, and THF as eluent at a flow rate of 1 mL/min (20 °C). Polystyrene standards were used for calibration. The HR-MS (ESI TOF) was performed on a high resolution time of flight G1969A instrumentation (Agilent) using 2.5 mM ammonia acetate as an ionization agent. The DSC data were collected on a Perkin Elmer Pyris DSC using 10.0 °C/min heating rate with 20mL/min nitrogen flow. The FT-IR spectrum was recorded on a Perkin-Elmer Spectrum 400 FT-IR spectrophotometer.

**Typical Procedure for Polymerization.** A 100 ml Schlenk flask was dried by heating under vacuum and then transferred into a dry nitrogen glove box. Inside of the glove box, the flask was loaded with 1 mmol of a diol, 4 mmol of $Cs_2CO_3$, 6.2 mmol of dichloromethane and 1 mL of N-methyl-2-pyrrolidone. The flask was then transferred out of the glove box, the reaction mixture was frozen by liquid $N_2$, and the $N_2$ atmosphere was replaced by dry $CO_2$ with three evacuation-refill cycles. The reaction mixture was heated at 100 °C for 12 h with stirring. The conversion was checked by $^1H$ NMR of the crude mixture. The isolation procedure of polymeric products depended on the substrates. For benzylic diols, the reaction mixture was first treated with water (10 mL), and the insoluble solid was collected by filtration or centrifugation, and washed with methanol (2 mL) for three times. For aliphatic diols, the reaction mixture was filtered and washed with DCM (5 mL) for three times. The filtrate was collected and concentrated to ~ 1 mL under vacuum. Methanol (5 mL) was then added, and the precipitate formed was collected by centrifugation and washed further with methanol (1 mL x 3). Finally the solid product was dried under vacuum to constant weight to determine the yield.

**Polycarbonate from 1,4-benzendimethanol,** Yield: 63.7%, $^1$H NMR ($CDCl_3$, 298K): $\delta$ 7.38 (s, Ar*H*), 5.17 (s, $ArCH_2OCOO$), 4.71 (d, $ArCH_2OH$, *J* = 7.0). $^{13}$C NMR ($CDCl_3$, 298K): $\delta$ 155.19 (*C*=O), 128.84, 127.35, 69.74 ($ArCH_2OCOO$), 65.22 ($ArCH_2OH$).

**Polycarbonate from 1,3-benzendimethanol,** Yield: 57.2%, $^1$H NMR ($CDCl_3$, 298K): $\delta$ 7.38 (m, Ar*H*, 11H), 5.15 (s, $ArCH_2OCOO$, 10H), 4.72 (s, $ArCH_2O$, 1H). $^{13}$C NMR ($CDCl_3$, 298K): $\delta$ 155.22 (*C*=O), 135.77, 129.15, 128.77, 128.33, 69.68 ($ArCH_2OCOO$), 69.15($ArCH_2O$).

**Poly(ether carbonate) from 1,4-cyclohexanedimethanol**, Yield: 52.9%, $^1$H NMR ($CDCl_3$, 298K): $\delta$ 5.31 (s, $OCH_2O$, 1H), 4.10 (d, *J* = 5.0, $COOCH_2CH$, 1H), 4.00 (s, $COOCH_2CH$, 0.6 H), 3.58 (d, *J* = 5.0, $OCH_2CH$, 0.8H), 3.50 (s, $OCH_2CH$, 0.7H), 1.93 (s, $CH_2CHCH_2$, 0.6H), 1.84 (d, *J* = 10, $CH_2CHCH_2$, 1.5 H), 1.67 (s, $CHCH_2CH_2$, 0.5H), 1.43 (s, $CHCH_2CH_2$, 2H), 1.01 (m, $CHCH_2CH_2$, 1H). $^{13}$C NMR ($CDCl_3$, 298K): $\delta$ 154.93 (*C*=O), 92.72 ($OCH_2O$), 76.32 ($OCH_2CH$), 73.94 ($OCH_2CH$), 73.19 ($OCH_2CH$), 70.93 ($OCH_2CH$), 38.15 ($CH_2CHCH_2$), 37.37 ($CH_2CHCH_2$), 35.48 ($CH_2CHCH_2$), 34.66 ($CH_2CHCH_2$), 29.20 ($CHCH_2CH_2$), 25.42 ($CHCH_2CH_2$).

**Poly(ether carbonate) from 1,4-cyclohexanedimethanol (*trans*),** Yield: 53.6%, $^1$H NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 5.28 (s, $\mathrm{OC}H_2\mathrm{O}$, 1H), 4.00 (d, $J$ = 5.0, $\mathrm{COOC}H_2\mathrm{CH}$, 1H), 3.50 (d, $J$ = 5.0, $\mathrm{OC}H_2\mathrm{CH}$, 1H), 1.85 (m, $\mathrm{CH_2C}H\mathrm{CH_2}$, $\mathrm{CHC}H_2\mathrm{CH_2}$, 2H), 1.68 (s, $\mathrm{CHC}H_2\mathrm{CH_2}$, 1H), 1.04 (m, $\mathrm{CHC}H_2\mathrm{CH_2}$, 2H). $^{13}$C NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 154.95 ($C$=O), 92.77 ($\mathrm{O}C\mathrm{H_2O}$), 76.33 ($\mathrm{O}C\mathrm{H_2CH}$), 73.22 ($\mathrm{O}C\mathrm{H_2CH}$), 38.13 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 37.37 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 35.48 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 34.66 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 29.20 ($\mathrm{CH}C\mathrm{H_2CH_2}$).

**Poly(ether carbonate) from 1,4-cyclohexanediol (*trans*),** Yield: 63.1%, $^1$H NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 5.34 (s, $\mathrm{OC}H_2\mathrm{O}$, 1H), 4.74 (s, br, $\mathrm{COOC}H\mathrm{CH_2}$, 0.5H), 3.77 (s, br, $\mathrm{CH_2OC}H\mathrm{CH_2}$, 0.5H), 1.93 (s, $\mathrm{CHC}H_2\mathrm{CH_2}$, 1H), 1.81 (s, $\mathrm{CHC}H_2\mathrm{CH_2}$, 2H), 1.70 (s, $\mathrm{CHC}H_2\mathrm{CH_2}$, 1H). $^{13}$C NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 154.25 ($C$=O), 90.61 ($\mathrm{O}C\mathrm{H_2O}$), 75.06 ($\mathrm{O}C\mathrm{HCH_2}$), 74.12 ($\mathrm{O}C\mathrm{HCH_2}$), 28.18 ($\mathrm{CH}C\mathrm{H_2CH_2}$), 27.35 ($\mathrm{CH}C\mathrm{H_2CH_2}$).

**Poly(ether carbonate) from 1,6-hexanediol,** Yield: 36.0%, $^1$H NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 5.29 (s, $\mathrm{OC}H_2\mathrm{O}$, 1H), 4.17 (m, $\mathrm{COOC}H_2\mathrm{CH_2}$, 1H), 3.67 (m, $\mathrm{CH_2OC}H_2\mathrm{CH_2}$, 1H), 1.71(s, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, 1H) 1.62 (s, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, 1H), 1.43 (s, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, 2H). $^{13}$C NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 154.90 ($C$=O), 92.55 ($\mathrm{O}C\mathrm{H_2O}$), 70.81 ($\mathrm{O}C\mathrm{H_2CH_2}$), 68.26 ($\mathrm{O}C\mathrm{H_2CH_2}$), 29.64 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 28.79 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 25.92 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$).

**Polyether from Hydroquinone,** Yield: 8.0%, $^1$H NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 7.01 (m, Ar$H$, 4H), 5.60 (s, $\mathrm{OC}H_2\mathrm{O}$, 2H). $^{13}$C NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 152.51 ($C_{Ar}\mathrm{O}$), 118.00 (Ar-$C$), 92.51 ($\mathrm{O}C\mathrm{H_2O}$).

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# CHAPTER IV

# DIRECT COPOLYMERIZATION OF CARBON DIOXIDE AND DIOLS PROMOTED BY $Cs_2CO_3$ WITH VARIOUS DIHALIDES

## IV.1 INTRODUCTION

Using $CO_2$ as a material for the production of chemicals and materials is a particularly interesting and valuable study. On the one hand, carbon dioxide is a great C1 feedstock since it is abundant, inexpensive and renewable. Some widely used toxic C1 building blocks (like phosgene) could be successfully replaced by $CO_2$ in many syntheses.[1] The chemicals and materials using $CO_2$ as a carbon feedstock would also be potentially alternative toward the compounds that are currently derived from fossil fuel-based resources.[2] On the other hand, high level of $CO_2$ in the atmosphere is one of the major contributors to the climate change.[3] Transforming $CO_2$ and using it as a precursor for commodity chemicals, such as salicylic acid, would reduce its emission.[4]

In the area of polymers, the aliphatic polycarbonates with decent biodegradability and biocompatibility were considered as attractive materials for many applications such as tissue engineering scaffolds and vehicles for drug delivery.[5] Using $CO_2$ as a feedstock for the aliphatic polycarbonates is incredibly promising. Specifically, the alternating copolymerization of $CO_2$ with epoxides is on the top of current interest. In 1969, Inoue and co-workers first reported biodegradable $CO_2$-based polycarbonates generated by copolymerization of epoxides and $CO_2$.[6] In the last several decades, many interesting catalysts were discovered for this synthesis including both homogeneous and hetereogeneous systems. Not only the high activity but also the excellent regio- and/or stereoselectivity were achieved in the copolymerization of $CO_2$ with epoxides by these catalysts. [7] Along with this approach, another synthetic route would give access to the polycarbonates by ring opening polymerization (ROP) of cyclic carbonates. The developments in the catalysis for ROP have enabled polymerizations to proceed in a controlled fashion under mild conditions.[8] Furthermore, advances in organocatalytic ROP have provided alternatives to traditional heavy-metal-based catalysis that dominated the catalytic copolymerization of $CO_2$ with epoxides.[9] However, both of the two approaches were limited on the design of backbone by the small ring structure of the starting materials.

To avoid this problem, the direct synthesis of polycarbonates from diols through the polycondensation with $CO_2$ has become more attractive.[10] In 1998, the Kadokawa group first developed a direct polycondensation of $CO_2$ with alkane diols to produce corresponding polycarbonates in the presence of trisubstituted phosphines, carbon tetrahalides and an organic base.[10a,b] The other system using $CeO_2$ as the heterogeneous catalyst in the polycondensation of $CO_2$ and diols with 2-cyanopyridine as the dehydrating agent was recently discovered by Tomishige and co-workers.[10c] Unfortunately, the products of these two systems had relatively low molecular weight (lower than 5000 g/mol). Yves Gnanou and co-workers successfully produced a high molecular weight polycarbonate via the polycondensation of $CO_2$ and diols promoted by $Cs_2CO_3$ and dibromoalkanes.[13] Previously, our group investigated the copolymerization of $CO_2$ with diols in the presence of $Cs_2CO_3$ and dichloromethane, which results decent isolated yield (up to 75%) of a new polymer (poly(ether carbonate)) with moderately high molecular weight (up to 11100 g/mol).[11] In the present study, we focused on the impact of various dihalides on the copolymerization of $CO_2$ with diols in the presence of $Cs_2CO_3$.

## IV.2 RESULTS AND DISCUSSION

According to our previous results, the activity of $Cs_2CO_3$/dichloromethane toward $CO_2$/diols copolymerization was decent under the optimized conditions (100 ºC/1 atm). The reactions were set up with mostly the same conditions on this study. Variation of dihalide loading and reaction time were shown to have a significant impact on the yield of the copolymerization reaction. These effects were considered as the important parameter of the new reactions as well.

**Table 7**. Copolymerization of $CO_2$ and 1,4-cyclohexanedimethanol with $Cs_2CO_3$/dihalides[a]

| Entry | DCM(mmol) | DBM(mmol) | DIM(mmol) | BCM(mmol) | t(h) | Yield (mg) | $M_n$[b] (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 3.1 | - | - | - | 12 | 73 | 6400 | 2.2 |
| 2 | - | 6.2 | - | - | 12 | - | - | - |
| 3 | - | 3.1 | - | - | 48 | - | - | - |
| 4 | - | 6.2 | - | - | 48 | - | - | - |
| 5 | - | 12.4 | - | - | 12 | 43 | 1100 | 1.6 |
| 6 | - | 12.4 | - | - | 36 | 69 | 3310 | 1.2 |
| 7 | - | 12.4 | - | - | 48 | 77 | 3294 | 1.3 |
| 8 | - | 12.4 | - | - | 72 | 91 | 3622 | 1.8 |
| 9 | - | - | 3.1 | - | 24 | 51 | 1566 | 1.5 |
| 10 | - | - | 12.4 | - | 24 | 141 | 2184 | 1.5 |
| 11 | - | - | - | 3.1 | 24 | 79 | 1504 | 2.1 |
| 12 | - | - | - | 6.2 | 24 | 68 | 1326 | 2.3 |

[a]Reactions were performed with 1 mmol 1,4-benzenedimethanol at 100 ˚C under 1 atm of $CO_2$ in 1 ml of NMP with 4 mmol of $Cs_2CO_3$ for 72h, unless noted otherwise. [b]Determined by gel permeation chromatography.

As for the copolymerization of $CO_2$/diols, a yield of 73 mg was achieved from 1 mmol of the starting material (1,4-cyclohexanedimethanol) at 100 ºC under a $CO_2$ pressure of 1 atm (Table 7, entry 1) with $Cs_2CO_3$/dichloromethane (DCM). It is worth noting here that the air in the reaction container was replaced by the purified $CO_2$ without any impurity, and the presence of small quantities of water in the other reagents was also removed by dehydration treatment. Since the copolymerization of $CO_2$/diols was achieved with $Cs_2CO_3$/DCM, other dihalides were applied in the copolymerization as the reagents. Unfortunately, the simple change of reagents led to decrease yield from 73 mg to 0 under the similar conditions (Table 7, entries 2-4). No polymer was produced from the reaction, even with extended reaction time and larger loading of the dibromomethane (DBM). A rise in the loading of the DBM from 6.2 mmol to 12.4 mmol resulted in a dramatic increase of yield from 0 to 43 mg (Table 7, entry 5) , but the yield was significantly lower than the reactions using DCM (Table 7, entry 1). To achieve a high yield and therefore a higher molecular weight, we investigated the reaction at a much longer reaction time with high loading of DBM. When the reaction was carried out under the same conditions, an increase in the reaction time from 12 h to 36 h would increase the yield to 69 mg (entry 6), and even higher yield (77 mg) was achieved on the reaction of 48 h (entry 7). Indeed, the reaction rate of the coupling reaction between short oligomers would be slower than the coupling between monomers, and the polymer with a longer chain would be produced with much longer reaction time. For comparison purposes, the copolymerization was performed at 72 h. The results show that a high yield of 91 mg (entry 8). However, the molecular weight of the resultant polymer has not been improved greatly (entries 6-8). The highest molecular weight is only up to 3622 g/mol which is close to the result from reaction time of 36 h (3310 g/mol), even it is significantly higher than the molecular weight achieved on 12 h (1100 g/mol). The productivity was increased when bromochloromethane (BCM) was employed in the reaction instead of DBM. A yield of 79 mg was achieved on 24 h with 3.1

mmol of BCM. The molecular weight of the product, on the other hand, was only about 1500 g/mol. We also investigated the performance of diiodomethane (DIM) as the reagent in similar reactions. The polymer was formed with lower loading of reagent (3.1 mmol of DIM) and shorter time (24 h) (Table 7, entry 9). However, the molecular weight of the resultant polymer was only 2184 g/mol, even though the yield was up to 141 mg (Table 1, entry 10). Notably, the isolated polymer has a dispersity between 1.2-1.8.

In order to understand the microstructure of the resultant polymers (synthesized with DBM), we fully investigated the polymers by NMR and FT-IR spectroscopies, which revealed some remarkable features of the polymeric products. The two resonances at 5.70 ppm and 4.58 ppm in the $^1$H NMR spectrum (Figure 6) that are assignable to the methylene (**a** ,**b**) protons between two oxygen atoms, suggesting two different methylene protons in the linkage of the polymers. We identified the resonance of the methylene proton between the carbonate linkage and ether linkage in the backbone of the poly(ether carbonate) synthesized with DCM in the previous study. The comparison of $^1$H NMR of the polymer synthesized with DBM and the polymer synthesized with DCM (Figure 8) suggested neither of the two new resonances belong to the methylene between the carbonate linkage and ether linkage. It is possible that the new resonances were assignable to the methylene protons between two carbonate linkages or two ether linkages. The methylene group (**c**) connected to the other side of the carbonate group is represented by the peaks around 4.0 ppm and the methylene group (**d**) connected to the opposite side of the cyclohexyl linkage was represented by the peaks around 3.4 ppm. The peaks between 1.0 ppm and 2.0 ppm belong to the cyclohexane ring. These peaks were found and investigated in poly(ether carbonate) synthesized with DCM in our previous study.

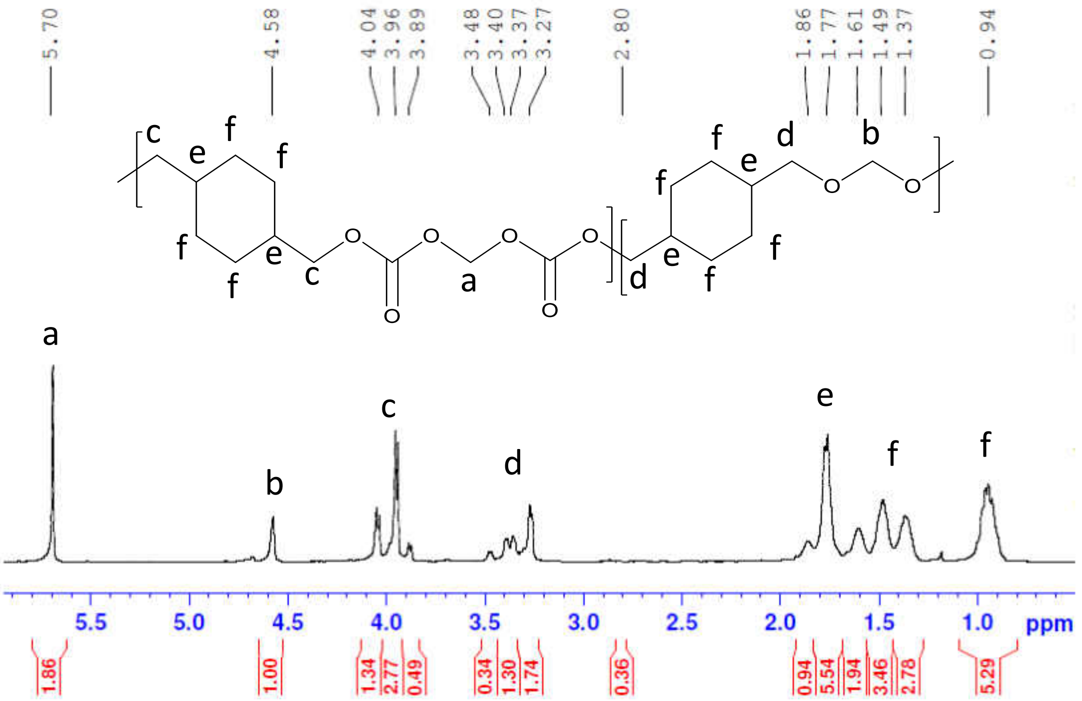


**Figure 6**. $^1$H NMR spectra of polymer from 1,4-cyclohexanedimethanol synthesized with DBM.

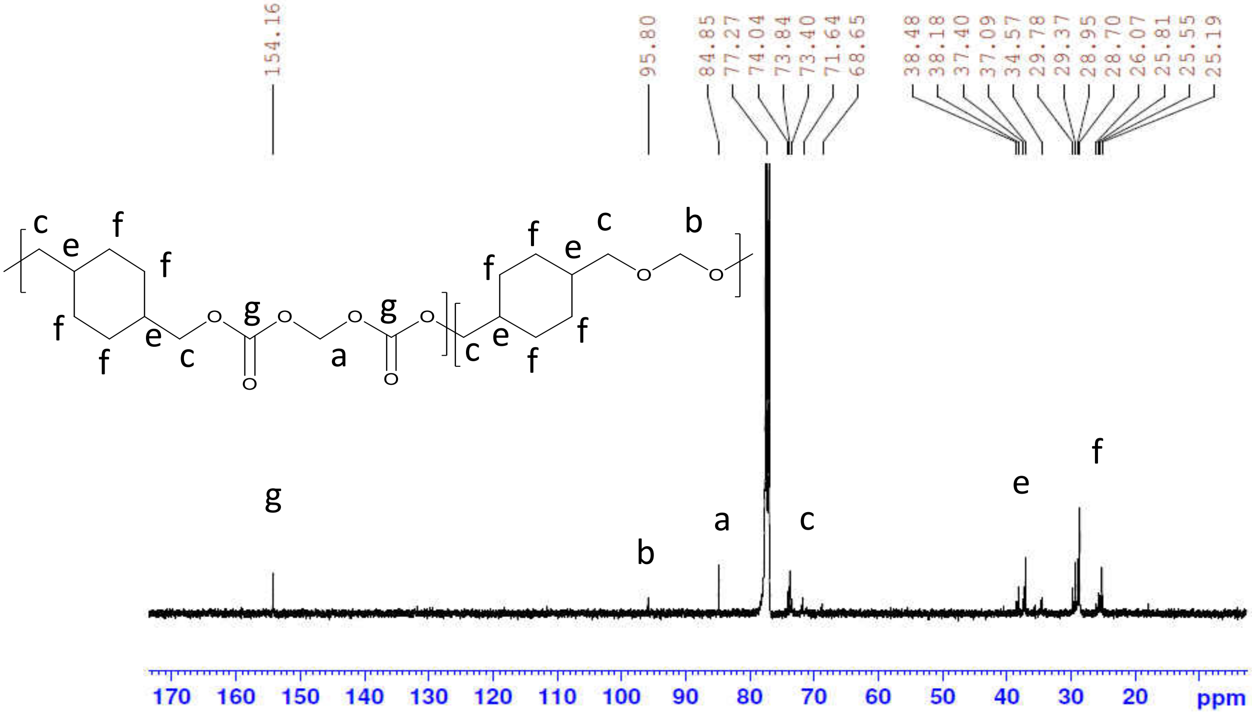


**Figure 7**. $^{13}$C NMR spectra of polymer from 1,4-cyclohexanedimethanol synthesized with DBM.

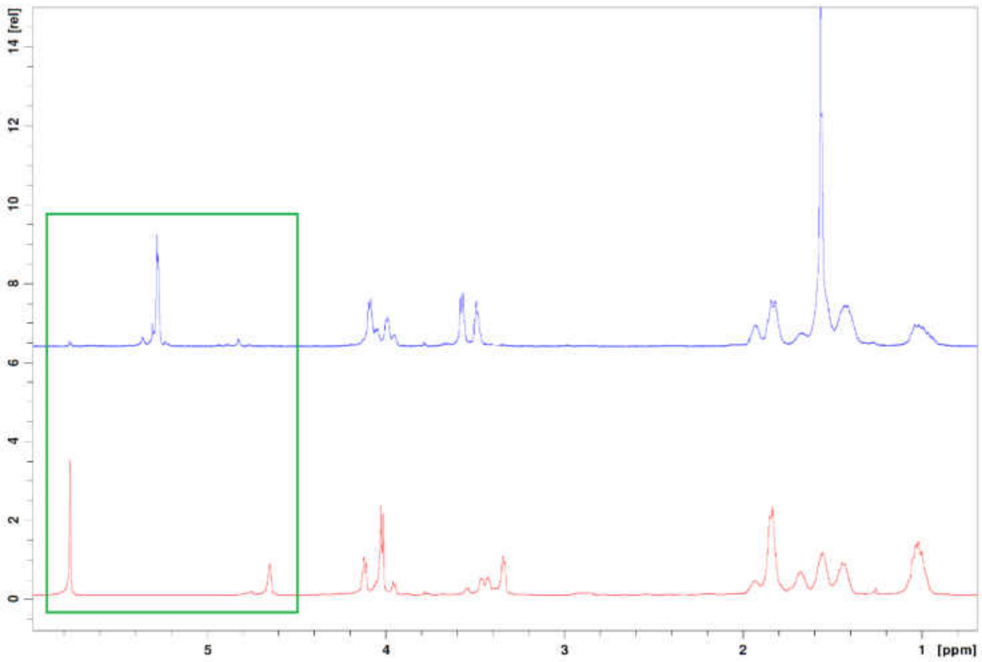


**Figure 8**. Comparison of $^1$H NMR spectra of polymer synthesized with DCM (blue) and DBM (red).

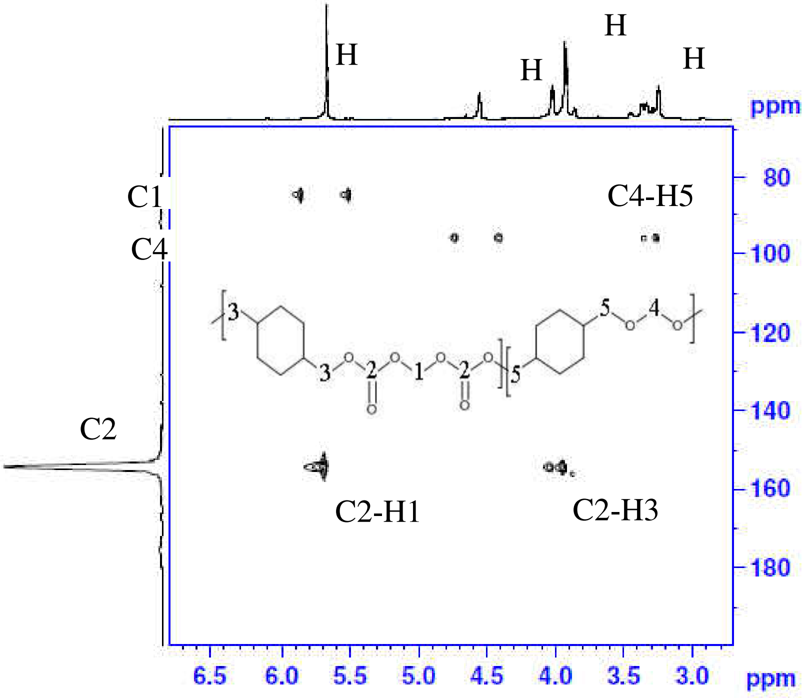


**Figure 9.** HMBC NMR of Polymer from 1,4-cyclohexanedimethanol synthesized with DBM.

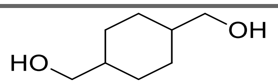
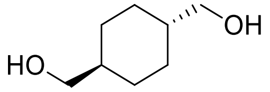
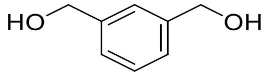
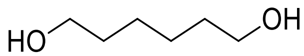
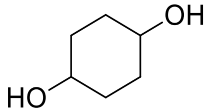
The structure of the polymer was also corroborated by the $^{13}$C NMR spectrum (Figure 7), featuring a peak around 154 ppm, assignable to the carbonate carbon, and two peaks around 96 ppm and 85 ppm, assignable to the methylene (**a, b**) carbon. These assignments were supported by the HSQC NMR spectra of the isolated products. Furthermore, the existence of a carbonyl group was confirmed by the absorbance at 1740 cm$^{-1}$ in the FT-IR spectrum.

On the basis of these analyses, there are two different linkages in the structure of the polymeric product synthesized with DBM. The ratio of the carbonate linkage and ether linkage is 1.9:1, which is indicated by the integrations of the peak at 5.7 ppm (methylene proton linked to carbonate) and the peak at 4.6 ppm (methylene proton linked to ether). Both of these two linkages were confirmed by an HMBC NMR experiment (Figure 9). The connection of C3-C2, and C2-C1 was demonstrated by the cross peaks of C2-H1 and C2-H3, and the connection of C5-C4 was demonstrated by the cross peak of C4-H5. None of the repeating unit was detected in the ESI-MS, which suggested the two linkages were totally random in the structure of the backbone. This interesting structure could only be found from the polymeric product synthesized with DBM. We also investigated the polymer synthesized with DIM, and only the pure ether linkage was found in the structure. Therefore, the current study indicated that the formation of which linkage is significantly dependent on the dihalides used in the reaction.

Next we investigated a variety of diols in the direct copolymerization with $CO_2$ by using DBM (Table 8). For the primary diol substrates, decent yields were achieved. The characterization data of the products, including the NMR and IR spectra, were collected. It is worth mentioning that the reaction using benzylic diol (Table 8, entry 3), 1,3-benzenedimethanol, resulted in polymer consisted of predominantly carbonate linkages

(>95%) with no dihalide methylene incorporation. This observation agrees with our previous study. The regular primary aliphatic diols afforded polymers with both carbonate and ether linkages in the backbone, as judged by the presence of a singlet around 5.70 ppm and 4.58 ppm assignable to the methylene groups in the $^1$H NMR. The reaction using *trans*-1,4-cyclohexanedimethanol (Table 8, entry 2) had slightly lower isolation yield than the reaction using racemic 1,4-cyclohexanedimethanol (Table 8, entry 1), and the polymeric products from these two reactions had similar molecular weight (about 3.0 kg/mol).

**Table 8**. Copolymerization of $CO_2$ and diols with $Cs_2CO_3$/DBM[a]

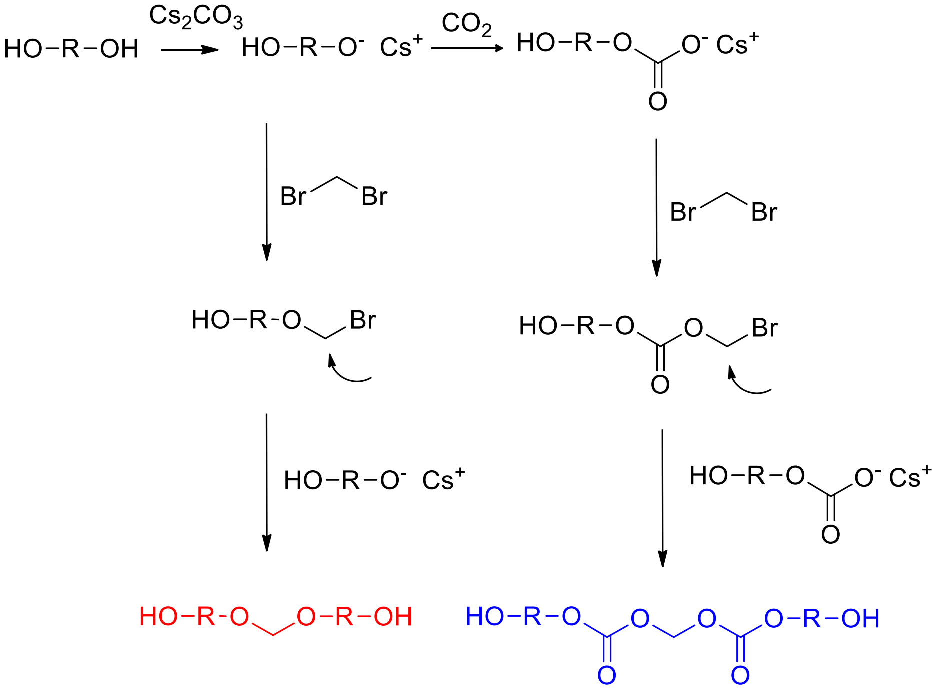
| Entry | Diol | Yield (mg) | $M_n$[b] (g/mol) | PDI |
|---|---|---|---|---|
| 1 |  | 91 | 3622 | 1.8 |
| 2 |  | 74 | 3194 | 1.6 |
| 3 |  | 62 | 2407 | 1.6 |
| 4 |  | 35 | 1490 | 2.1 |
| 5 |  | - | - | - |

[a]Reactions were performed with 1 mmol of diols at 100 °C under 1 atm of $CO_2$ in 1 ml of NMP with 4 mmol of $Cs_2CO_3$ and 12.4 mmol of DBM for 72h, unless noted otherwise. [b]Determined by gel permeation chromatography.

The yield was decreased to 35 mg (Table 8, entry 4) when 1,6-hexanediol, a linear primary aliphatic diol, was employed in the reaction, probably due to the higher percentage of short chain oligomers formed with linear diol than the cyclic diols, which were not readily precipitated out from the mixture during the isolation. This idea was supported by the low number average molecular weight of the polymer from 1,6-hexanediol. None of the polymer was produced from the reaction using the secondary aliphatic diol, 1,6-

cyclohexanediol, which indicated that secondary alcohols cannot be used in this synthesis (Table 8, entry 5).

Based on these results and the related studies in the literature,[12] a possible, simplified pathway is proposed in Scheme 6. The nucleophilic attack on $CO_2$ by the alkoxide generated from deprotonation of diol by $Cs_2CO_3$ results in the formation of a carboxylate. The alkoxide and carboxylate would react with DBM on two sides to yield the ether or carbonate linkage. The preference of methylene incorporation into carbonate linkage was indicated by the $^1H$ NMR spectra of the product (ratio of ether/carbonate is about 1/1.9).



**Scheme 6**. A possible pathway for the copolymerization of the diols and $CO_2$ with DBM

Aiming at extending the scope of dihalide, we then replaced dihalomethanes with dihaloethanes (Table 9). Remarkably, the combinations of $Cs_2CO_3$ with dihaloethane, such as 1,2-dichloroethane, also promote the polycondensation of $CO_2$ and diols exhibiting even higher activity. High isolated yield and high molecular weight of the product are now achieved with only 1.5 mmol of 1,2-dibromoethane under the optimized condition (12.4 mmol are needed with DBM), and the reaction time is shorter than with DBM (Table 9, entry 2). 1,2-Dibromoethane proved even more active even at loading of 3.1 mmol and 6.2 mmol (Table 9, entries 1, 3), but the molecular weight of the polymer decreased significantly from 9.8 kg/mol to 2.9 kg/mol. Note that a dramatic drop in activity was observed when 1,2-dibromoethane was replaced by 1,2-dichloroethane (Table 9, entries 4, 5). Even the high yield was achieved with loading of 3.1 mmol of 1,2-dichloroethane, the molecular weight of the products with 1,2-dichloroethane were much lower than with 1,2-dibromoethane on all runs (Table 9, entry 6).

**Table 9**. Copolymerization of $CO_2$ and diols with $Cs_2CO_3$/1,2-dihalide ethane[a]

| **Entry** | **1,2-dichloroethane (mmol)** | **1,2-dibromoethane (mmol)** | **1-bromo-2-chloroethane (mmol)** | **Yield (mg)** | **$M_n$[b] (g/mol)** | **PDI** |
|---|---|---|---|---|---|---|
| 1 | - | 6.2 | - | 283 | 2883 | 1.4 |
| 2 | - | 1.5 | - | 243.7 | 9787 | 1.7 |
| 3 | - | 3.1 | - | 296.1 | 3549 | 1.5 |
| 4 | 6.2 | - | - | 87.4 | 1088 | 1.4 |
| 5 | 1.5 | - | - | 52.3 | 1842 | 1.2 |
| 5 | 3.1 | - | - | 255.3 | 1946 | 1.4 |
| 7 | - | - | 1.5 | 235 | 5040 | 2.0 |
| 8 | - | - | 3.1 | 316 | 1596 | 1.5 |
| 9 | - | - | 1.0 | 153 | 2407 | 1.6 |

[a]Reactions were performed with 1 mmol 1,4-cyclohexanedimethanol at 100 ˚C under 1 atm of $CO_2$ in 1 ml of NMP with 4 mmol of $Cs_2CO_3$ for 24h, unless noted otherwise. [b]Determined by gel permeation chromatography.

The activity of 1-bromo-2-chloroethane was higher than 1,2-dichloroethane but lower than 1,2-dibromoethane in the polycondensation (Table 9, entry 7-9), which agrees with our expectation. Another noteworthy feature of these dual systems is that the best performance of the reaction with 1,2-dichloroethane and 1-bromo-2-chloroethane was not achieved by either the highest or lowest loadings of dihalides.

The characterization data of the products, including the NMR and IR spectra, indicated that there was only carbonate linkage in the polymer, which mostly agrees with the similar polymer reported recently in the literature[13] except that we identified the ending group in the NMR spectra (Figure 10). The two resonances at 4.37 ppm and 3.99 ppm in the $^1H$ NMR spectra (Figure 10) are assignable to the two different methylene groups (**a**, **b**) directly connected to the carbonate, while the two resonances at 4.44 ppm and 3.55 ppm are assignable to the two sides of the ending methylene protons (**c**, **f**). These assignments were supported by the $^{13}C$ NMR and HSQC NMR spectra of the isolated products. The resonances representing the ending methylene protons connected with halide would move to 3.73 when the polymer was produced with 1,2-dichloroethane, which indicated the chemical shift of the ending groups are different with different halides. Furthermore, the NMR spectrum of the polymer produced with 1-bromo-2-chloroethane is as same as the polymer produced with 1,2-dichloroethane. It suggested that there were only chloride ending groups in the polymer, and the system strongly favors the chloride rather than bromide as the ending group.

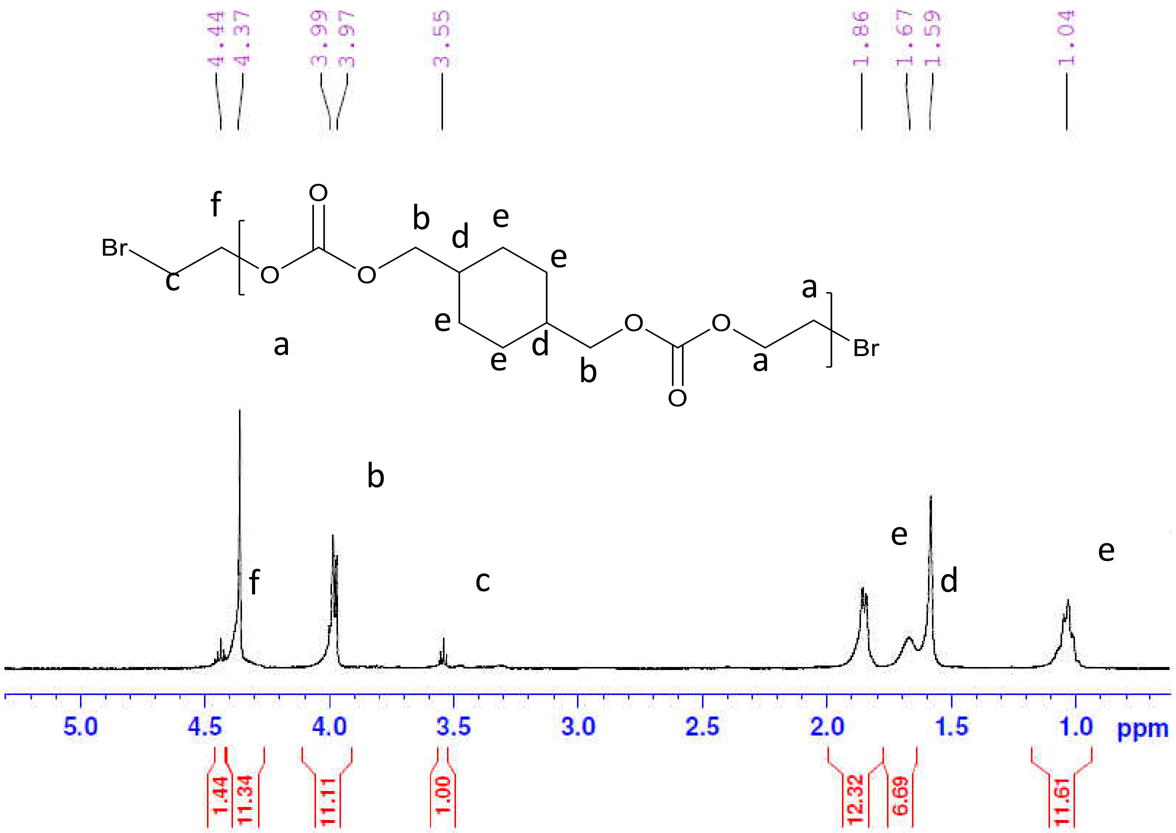


**Figure 10**. $^1$H NMR spectra of polymer from 1,4-cyclohexanedimethanol with 1,2-dibromoethane.

## IV.3 CONCLUSIONS

In summary, a series of dihalides was investigated as the reagent in the copolymerization of $CO_2$ with diols under 1 atm pressure of $CO_2$ in the presence of $Cs_2CO_3$. The decent isolated yields of the polymer are achieved with various dihalides. The isolated polymers have been fully investigated by IR, NMR and GPC by which the structure of the products are confirmed. Notably, the polycarbonates synthesized with DBM contain both carbonate linkages and ether linkages with random appearance in the chain of the polymer, while the polymers synthesized with DIM contain mainly the ether linkage. The polymers containing only carbonate linkage are synthesized successfully with dihaloethane under similar conditions, and the ethyl halide group is identified as the ending group of the polymer.

## IV.4 EXPERIMENTAL SECTION

**Materials.** Organic compounds, including all diols, are commercially available and were purchased from Sigma-Aldrich. The diols were dried under vacuum overnight. Dichloromethane was dried over activated molecular sieves (4 Å) overnight. The pre-dried $Cs_2CO_3$ and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich and used without further purification. All of the compounds were stored inside of a glove box under nitrogen atmosphere.

**General Methods.** NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer ($^1H$ and $^{13}C$). Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar, using a PLgel 5 μm Mixed-D column, a Prostar 355 RI detector, and THF as eluent at a flow rate of 1 mL/min (20 °C). Polystyrene standards were used for calibration. The HR-MS (ESI TOF) was performed on a high resolution time of flight G1969A instrumentation (Agilent) using 2.5 mM ammonium acetate as an ionization agent. The DSC data were collected on a Perkin Elmer Pyris DSC using 10.0 °C/min heating rate with 20mL/min nitrogen flow. The FT-IR spectrum was recorded on a Perkin-Elmer Spectrum 400 FT-IR spectrophotometer.

**Typical Procedure for Polymerization.** A 100 ml Schlenk flask was dried by heating under vacuum and then transferred into a dry nitrogen glove box. Inside of the glove box, the flask was loaded with 1 mmol of a diol, 4 mmol of $Cs_2CO_3$, 12.8 mmol of dibromomethane and 1 mL of N-methyl-2-pyrrolidone. The flask was then transferred out of the glove box, the reaction mixture was frozen by liquid $\mathrm{N_2}$, and the $\mathrm{N_2}$ atmosphere was replaced by dry $\mathrm{CO_2}$ with three evacuation-refill cycles. The reaction mixture was heated at 100 ˚C for 12 h with stirring. The conversion was checked by $^1$H NMR of the crude mixture. The isolation procedure of polymeric products depended on the substrates. For benzylic diols, the reaction mixture was first treated with water (10 mL), and the insoluble solid was collected by filtration or centrifugation, and washed with methanol (2 mL) three times. For aliphatic diols, the reaction mixture was filtered and washed with DCM (5 mL) three times. The filtrate was collected and concentrated to ~ 1 mL under vacuum. Methanol (5 mL) was then added, and the precipitate formed was collected by centrifugation and washed further with methanol (1 mL x 3). Finally the solid product was dried under vacuum to constant weight to determine the yield.

**Polycarbonate from 1,4-cyclohexanedimethanol with DBM**, Yield: 91mg, $^1$H NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 5.70 (s, $\mathrm{OC}H_2\mathrm{O}$, 2H), 4.58 (s, $\mathrm{OC}H_2\mathrm{O}$, 1H), 4.04 (d, $\mathrm{COOC}H_2\mathrm{CH}$, 1H), 3.96 (d, $\mathrm{COOC}H_2\mathrm{CH}$, 3H), 3.89 (d, $\mathrm{COOC}H_2\mathrm{CH}$, 0.5H),3.48 (s, $\mathrm{OC}H_2\mathrm{CH}$, 0.5H), 3.40 (d, $\mathrm{OC}H_2\mathrm{CH}$, 1H), 3.27 (s, $\mathrm{OC}H_2\mathrm{CH}$, 2H), 1.86 (s, $\mathrm{CHC}H_2\mathrm{CH_2}$, 1H), 1.77 (s, $\mathrm{CHC}H_2\mathrm{CH_2}$, 6H), 1.61 (s, $\mathrm{CH_2C}H\mathrm{CH_2}$, 2H), 1.49 (s, $\mathrm{CH_2C}H\mathrm{CH_2}$, 3H), 1.37 (s, $\mathrm{CH_2C}H\mathrm{CH_2}$, 3H), 0.94(m, $\mathrm{CHC}H_2\mathrm{CH_2}$, 5H). $^{13}$C NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 154.16 ($C$=O), 95.80 ($\mathrm{O}C\mathrm{H_2O}$), 84.85 ($\mathrm{O}C\mathrm{H_2O}$), 74.04 ($\mathrm{O}C\mathrm{H_2CH}$), 73.84 ($\mathrm{O}C\mathrm{H_2CH}$), 73.40 ($\mathrm{O}C\mathrm{H_2CH}$), 71.64 ($\mathrm{O}C\mathrm{H_2CH}$), 68.65 ($\mathrm{O}C\mathrm{H_2CH}$), 38.48 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 37.40 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 37.09 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 34.57 ($\mathrm{CH_2}C\mathrm{HCH_2}$), 29.37 ($\mathrm{CH}C\mathrm{H_2CH_2}$), 25.55 ($\mathrm{CH}C\mathrm{H_2CH_2}$).

**Polyether from 1,4-cyclohexanedimethanol with DIM,** Yield: 141mg, $^1$H NMR ($\mathrm{CDCl_3}$, 298K): $\delta$ 4.79 (s, $\mathrm{OC}H_2\mathrm{O}$, 1H), 4.66 (s, $\mathrm{OC}H_2\mathrm{O}$, 3H), 3.47 (m, $\mathrm{OC}H_2\mathrm{CH}$, 1H), 3.34 (d, $\mathrm{OC}H_2\mathrm{CH}$, 8H), 1.83 (m, $\mathrm{CHC}H_2\mathrm{CH_2}$, 13H), 1.54 (s, $\mathrm{CH_2C}H\mathrm{CH_2}$, 4H), 0.99 (m,

$\mathrm{CHC}H_2\mathrm{CH}_2$, 10H). $^{13}$C NMR ($\mathrm{CDCl}_3$, 298K): $\delta$ 95.75 ($\mathrm{O}C\mathrm{H}_2\mathrm{O}$), 74.33 ($\mathrm{O}C\mathrm{H}_2\mathrm{CH}$), 73.47 ($\mathrm{O}C\mathrm{H}_2\mathrm{CH}$), 73.18 ($\mathrm{O}C\mathrm{H}_2\mathrm{CH}$), 68.89 ($\mathrm{O}C\mathrm{H}_2\mathrm{CH}$), 40.77 ($\mathrm{CH}_2C\mathrm{HCH}_2$), 38.43 ($\mathrm{CH}_2C\mathrm{HCH}_2$), 37.45 ($\mathrm{CH}_2C\mathrm{HCH}_2$), 29.65 ($\mathrm{CH}C\mathrm{H}_2\mathrm{CH}_2$).

**Polycarbonate from 1,4-cyclohexanedimethanol with 1,2-dichloroethane,** Yield: 255.3mg, $^{1}$H NMR ($\mathrm{CDCl}_3$, 298K): $\delta$ 4.40 (m, $\mathrm{COOC}H_2\mathrm{CH}_2\mathrm{Cl}$, 1H), 4.36 (s, $\mathrm{COOC}H_2\mathrm{CH}_2$, 4H), 3.98 (m, $\mathrm{COOC}H_2\mathrm{CH}$, 4H), 3.73 (m, $\mathrm{CH}_2\mathrm{C}H_2\mathrm{Cl}$, 1H), 1.85 (d, $\mathrm{CHC}H_2\mathrm{CH}_2$, 4H), 1.68 (s, $\mathrm{CH}_2\mathrm{C}H\mathrm{CH}_2$, 2H), 1.04 (m, $\mathrm{CHC}H_2\mathrm{CH}_2$, 4H). $^{13}$C NMR ($\mathrm{CDCl}_3$, 298K): $\delta$ 155.25 ($C$=O), 73.43 ($\mathrm{O}C\mathrm{H}_2\mathrm{CH}$), 67.32 ($C\mathrm{H}_2\mathrm{CH}_2\mathrm{Cl}$), 65.44 ($\mathrm{O}C\mathrm{H}_2\mathrm{CH}_2$), 41.42 ($\mathrm{CH}_2C\mathrm{H}_2\mathrm{Cl}$), 37.20 ($\mathrm{CH}_2C\mathrm{HCH}_2$), 28.75 ($\mathrm{CH}C\mathrm{H}_2\mathrm{CH}_2$).

**Polycarbonate from 1,4-cyclohexanedimethanol with 1,2-dibromoethane,**Yield: 243.7mg, , $^{1}$H NMR ($\mathrm{CDCl}_3$, 298K): $\delta$ 4.44 (m, $\mathrm{COOC}H_2\mathrm{CH}_2\mathrm{Cl}$, 1H), 4.37 (s, $\mathrm{COOC}H_2\mathrm{CH}_2$, 11H), 3.99 (m, $\mathrm{COOC}H_2\mathrm{CH}$, 11H), 3.55 (m, $\mathrm{CH}_2\mathrm{C}H_2\mathrm{Cl}$, 1H), 1.86 (d, $\mathrm{CHC}H_2\mathrm{CH}_2$, 12H), 1.67 (s, $\mathrm{CH}_2\mathrm{C}H\mathrm{CH}_2$, 7H), 1.04 (m, $\mathrm{CHC}H_2\mathrm{CH}_2$, 12H).

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# CHAPTER V

# DIRECT SYNTHESIS OF POLYCARBONATES FROM CARBON DIOXIDE AND DIOL OVER CERIA CATALYST

## V.1 INTRODUCTION

Polycarbonates are an important class of materials with many applications. On the basis of their favorable thermal, mechanical and optical properties, they have been employed in packaging and engineering thermoplastics.[1] Furthermore, the aliphatic polycarbonates are biodegradable and biocompatible, and could be obtained from synthetic routes based on carbon dioxide ($CO_2$), which renders them an actively pursued target, given the current push for sustainability.[2,3] The commercial synthesis of polycarbonates involves phosgene, a corrosive and highly toxic chemical that is of environmental concern. Recent research in industry and academia has been directed toward developing greener routes and new materials derived from environmentally friendly and renewable resources. $CO_2$ is considered as a valuable starting material because it is nontoxic, nonflammable, and abundant, and could potentially replace the toxic phosgene in the synthesis of polycarbonates.[4]

The alternating copolymerization of $CO_2$ and epoxides has been one of the promising transformations of $CO_2$. Since the first discovery of a $ZnEt_2/H_2O$ system for $CO_2$/propylene oxide copolymerization,[5] many well-defined catalyst systems for $CO_2$ copolymerization have been developed. Among them, Zn and Co based complexes have been shown to be highly effective, and some of them with excellent stereocontrol.[2a,6] In a related approach, polycarbonates can be generated from the catalytic ring opening polymerization of appropriate cyclic carbonate monomers.[7] However, these approaches are limited by the availability of epoxides/cyclic carbonates. In addition, the requirement of a small ring epoxide as co-monomer dictates that the main chain of polycarbonates cannot be easily modified. Alternatively, polycarbonates have also been synthesized by condensation/metathesis of diols with organic carbonates such as dimethylcarbonate and diphenylcarbonate.[8] This approach provides great flexibility in term of monomer choices, since various structurally diverse diols are readily available and can be incorporated into the polycarbonate backbone. Yet another possible pathway is the direct condensation between $CO_2$ and appropriate diols.[9] However, there is not much progress in this direction. Recent advances on direct synthesis from $CO_2$ and alcohols are largely driven toward organic carbonates and cyclic carbonates.[10]

Ceria ($CeO_2$) has seen much interest as a heterogeneous catalyst for various processes.[11] For instance, $CeO_2$ catalyzes the dehydration of alkanediols, affording unsaturated alcohols.[12] In combination with a dehydrating agent, $CeO_2$ catalyzes the efficient synthesis of a series of dialkyl carbonates from $CO_2$ and alcohols.[13] The $CeO_2$/2-cyanopyridine cascade system is among the best catalysts for the synthesis of 5- and 6-membered cyclic carbonates from $CO_2$ and 1,2- and 1,3-diols, respectively.[14] In this reaction $CeO_2$ serves dual roles: it catalyzes the carboxylation of hydroxyl groups, and removes the water byproduct by catalyzing the hydration of 2-cyanopyridine. Inspired by these results, we surmise that polycarbonates may be produced directly from $CO_2$ and a diol in the presence of $CeO_2$ catalyst, provided that the diol is not amenable to cyclic carbonate formation. Herein we report that $CeO_2$ is successfully applied in the direct synthesis of polycarbonate from $CO_2$ and diols under various conditions. The resulting polymer is fully characterized as a short chain polycarbonate diol, which can be used in a wide range of applications such as polyurethane synthesis.

## V.2 RESULTS AND DISCUSSION

The $CeO_2$/2-cyanopyridine cascade system has been used for the synthesis of cyclic carbonates from $CO_2$ and diols.[14] In our study, 1,4-benzenedimethanol was chosen as a representative diol that would not form cyclic carbonate because of the long, rigid backbone. On the basis of optimized reaction conditions in the literature,[14] the polycondensation of $CO_2$ and 1,4-benzenedimethanol was carried out using 0.2 equiv of $CeO_2$ and 10 equiv of 2-cyanopyridine under a 725 PSI of $CO_2$ at 138 °C for 72 h (Table 1, entry 6). The conversion of 1,4-benzenedimethanol was 38.0 %, estimated from the $^1H$ NMR integration of benzylic protons of the reaction mixture. The formation of 2-picolinamide from the hydration of 2-cyanopyridine was detected by $^1H$ NMR. At shorter reaction times, the conversions were expectedly lower, 33.2% (48 h) and 26.2 % (24 h) (entries 4 and 5). Decreasing the loading of 2-cyanopyridine also led to the decreasing of the conversion (entries 2 vs 5), and it was further decreased to 12.5% with even shorter reaction time and less loading of the 2-cyanopyridine (entry 1). The conversion could not be raised with higher loading of the $CeO_2$ (entry 3) or higher reaction temperature (entry 7). At lower reaction temperature, the conversion decreased significantly to 5.6% (entry 8).

**Table 10**. Copolymerization of $CO_2$ and 1,4-benzenedimethanol under various conditions without activation of $CeO_2$[a]

| Entry | $CeO_2$ (equiv) | 2-cyanopyridine (equiv) | t (h) | T (°C) | Conversion (%)[b] |
|---|---|---|---|---|---|
| **1** | 0.2 | 3 | 24 | 138 | 12.5 |
| **2** | 0.2 | 10 | 48 | 138 | 25.2 |
| **3** | 0.4 | 10 | 48 | 138 | 36.4 |
| **4** | 0.2 | 20 | 24 | 138 | 26.2 |
| **5** | 0.2 | 20 | 48 | 138 | 33.2 |
| **6** | 0.2 | 20 | 72 | 138 | 38.0 |
| **7** | 0.2 | 20 | 72 | 150 | 33.3 |
| **8** | 0.2 | 20 | 72 | 100 | 5.6 |

[a]Reactions were performed with 5 mmol (entries 1-3) or 2.5 mmol (entries 4-8) of 1,4-benzenedimethanol in addition to the annotated. [b]Determined by $^1H$ NMR spectroscopy.

Because the conversion seems to max out, as no further conversion of diol was observed even with extended reaction time, we suspected that the catalyst was deactivated. Thus we recovered $CeO_2$ by washing away all the organic components after the reaction of Table 1, entry 3, and reused it for another cycle. Little or no conversion was observed, as expected (Figure 1). When the recovered catalyst was activated by calcination at 600°C for 3 h under air, conversion was again observed, though it was less active with only 28.1% conversion. Obviously the thermal activation of $CeO_2$ is important for the conversion of diol, and the highest conversion of 49.1% was achieved with $CeO_2$ activated by calcination at 800°C for 3 h (Figure 1). Neither higher activation temperature (1000 °C) nor lower activation temperature (600 °C) would improve the conversion. These observations somewhat deviate from the results reported for cyclic carbonates,[14] but may be a reflection of the inherent difficulty in forming linear polymers vs small ring cyclic carbonates.

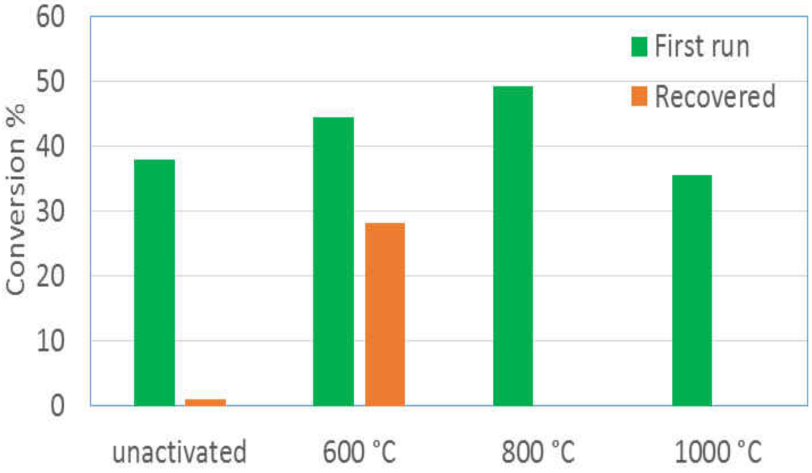

**Figure 11**: Effect of activation and recovery of $CeO_2$ on the activity. Other conditions are same as Table 1, entry 6.

The dehydration agent 2-cyanopyridine was employed in large excess, which also served as a solvent with a high boiling point under the reaction conditions. In an attempt to facilitate the isolation of polycarbonate product, we carried out screening reactions with a few solvents and found that chloroform and chlorobenzene could be suited for the reaction (38.5% and 39.3%, see Figure 2), even though still lower than reactions without solvent (49.1%). In comparison, THF and toluene led to low conversions (<1% and 20.3% respectively). The extremely low activity in THF may be attributed to the coordinating ability of the solvent, but it should be noted that 2-cyanopyridine itself contains two donor atoms. With suitable solvent identified, the reaction was also investigated using molecular sieves 4 Å as a dehydration agent instead of 2-cyanopyridine or without using any dehydration agent. However, no reaction occurred under both conditions (Figure 2). The failure of molecular sieves may be due to the high reaction temperature. Molecular sieves have been applied as dehydration agent in catalytic carbonate synthesis from $CO_2$ and alcohols, but the dehydration step was carried out in a separated vessel at lower temperature.[15]

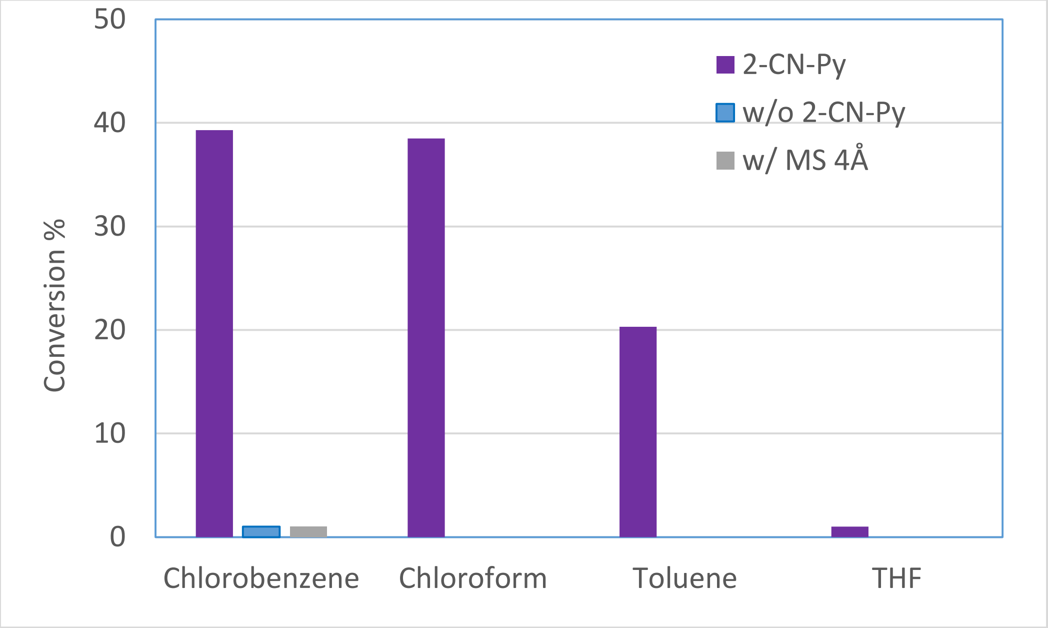

**Figure 12**: Effect of solvent and dehydration agent. Reactions were performed with 2.5 mmol 1,4-benzenedimethanol, 0.5 mmol of $CeO_2$ (calcinated at 800°C for 3h) and 50 mmol of 2-cyanopyridine under 725 PSI of $CO_2$ at 138 °C for 72h.

The molecular weights of the polycarbonates were determined by GPC as shown in Table 2. Most of the $M_n$ were in the range of 1000 to 1300. The polycarbonate with the lowest $M_n$ was obtained from the reaction with shorter reaction time (Table 2, entry 1), in consistent with the step growth of polycondensation reaction. The molecular weight distribution of all polycarbonates were narrow (between 1.07 and 1.15). On the other hand, it appears as if the molecular weights hit a plateau around 1200 g/mol, as activation of $CeO_2$ was unable to increase the $M_n$ of the polycarbonate, even though the conversion of diol increased. We thought that addition of solvent may help with the diffusion of monomer and polycarbonate on the catalyst surface. However, there was no much difference between the $M_n$ of the polycarbonates produced with or without a solvent. The low $M_n$ was probably due to the surface properties of the heterogeneous catalyst, such that the active sites were inaccessible or deactivated once the $M_n$ was around 1200 g/mol. This may explain the narrow molecular weight distribution, but the chemical nature of these interactions is unclear at the moment. It should be mentioned that the $CeO_2$/2-cyanopyridinde system is highly effective for the synthesis of cyclic carbonates from diols[14] and dialkyl carbonates from alcohols,[13b] with typical yields greater than 90%.

**Table 11**. Copolymerization of $CO_2$ and 1,4-benzenedimethanol[a]

| Entry | Activation of $CeO_2$ | Solvent | Conversion [b] (%) | Yield (%) | Mn (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| 1[c] | unactivated | - | 25.2 | 8.6 | 861 | 1.13 |
| 2[d] | unactivated | - | 36.4 | 11.1 | 1044 | 1.15 |
| 3 | unactivated | - | 38.0 | 7.8 | 1085 | 1.15 |
| 4 | 600 °C for 3h | - | 44.5 | 21.5 | 1272 | 1.09 |
| 5 | 800 °C for 3h | - | 49.1 | 23.1 | 1116 | 1.07 |
| 6 | 600 °C for 3h (recovered) | - | 28.1 | 5.6 | 1251 | 1.10 |
| 7 | 1000 °C for 3h | - | 35.6 | 9.2 | 1213 | 1.12 |
| 8 | 800 °C for 3h | Chloroform | 38.5 | 7.1 | 1207 | 1.08 |
| 9 | 800 °C for 3h | Chlorobenzene | 39.3 | 8.2 | 1037 | 1.07 |
| 10 | 800 °C for 3h | Toluene | 20.3 | 5.3 | 1168 | 1.09 |

[a]Reactions were performed with 2.5 mmol 1,4-benzenedimethanol, 0.5 mmol of $CeO_2$ and 50 mmol of 2-cyanopyridine under 725 PSI of $CO_2$ at 138°C for 72h in addition to the annotated. [b]Determined by $^1H$ NMR spectroscopy. [c]Reactions were performed with 5 mmol 1,4-benzenedimethanol, 1 mmol of $CeO_2$ and 50 mmol of 2-cyanopyridine. [d]Reactions were performed with 5 mmol 1,4-benzenedimethanol, 2 mmol of $CeO_2$ and 50 mmol of 2-cyanopyridine.

The polycarbonate products have been isolated as a off-white powder by precipitation with methanol, though the isolated yield was much lower than the conversion. This is attributed to the fact that the polycarbonate could not be completely precipitated out from the reaction mixture. Our attempt at replacing the high boiling 2-cyanopyridine with another dehydration agent (molecular sieves) was unsuccessful. Nevertheless, the isolated polycarbonates have been fully characterized by various techniques such as NMR, IR and ESI-MS. The $^{1}$H NMR and $^{13}$C NMR (Figure 3) spectra of the polycarbonate are similar to the reported data.[9a] In the $^{13}$C NMR spectrum, the resonance at 154.42 ppm corresponds to the carbonyl carbon, whereas the linkage between two carbonyl groups is indicated by the signals at 135.68, 128.33 and 69.05 ppm. The peaks at 142.90, 126.49, 69.05 and 62.58 ppm are assignable to the ending groups.[9a] The existence of carbonyl group in the polymer was also confirmed by the absorbance at 1739 cm$^{-1}$ in the FT-IR spectrum, comparable with those in other polycarbonates.[16] Furthermore, the peak at 3296 cm$^{-1}$ assignable to the chain end OH group is in agreement of the NMR analysis and rules out the possibility of a macrocyclic polycarbonate structure. Therefore, the resulting polymer can be characterized as a short chain polycarbonate diol. Macrodiols have been utilized as macroinitiators in the preparation of multiblock polymers[17] and served as an essential components for thermoplastic polyurethane elastomers,[18] and polycarbonate diols based polyurethanes are widely exploited because of their excellent properties in toughness, durability and flexibility.[19]

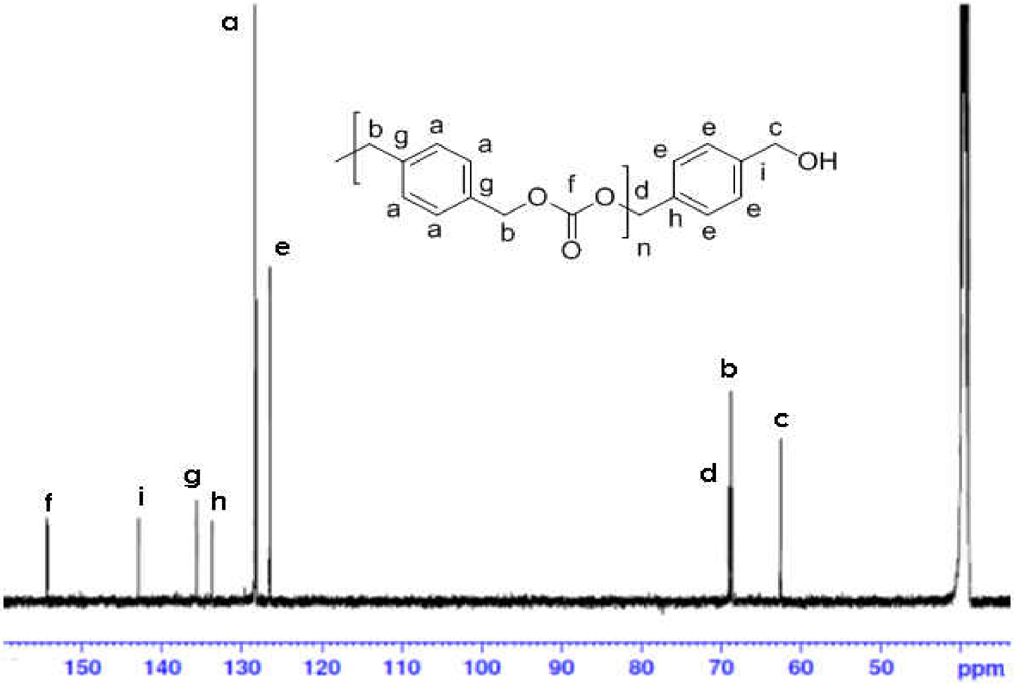

**Figure 13**. Representative $^{13}C$ NMR spectrum in DMSO-$d_6$ of the isolated polymer from entry 3, Table 2.

The thermal property of polycarbonates was studied with differential scanning calorimetry (DSC) and a melting transition at ~168 °C was observed. The ESI-ToF-MS was further employed to analyze the structure of the polycarbonate. The ESI mass spectrum (Figure 4) of the polymer features a series of peaks at 164*n* + 138 + 18 with a charge of +1, which can be assigned to $n(C_9H_8O_3)$ + 1,4-benzenedimethanol + $NH_4^+$. It is to be noted that there is another series of peaks 164*m* + 138 + 23 with a charge of +1, which can be attributed to $m(C_9H_8O_3)$ + 1,4-benzenedimethanol + $Na^+$. Both series of peaks with a difference in molecular mass of 164 *Da* are consistent with the previous NMR and IR analysis and confirm the polycarbonate diol structure.

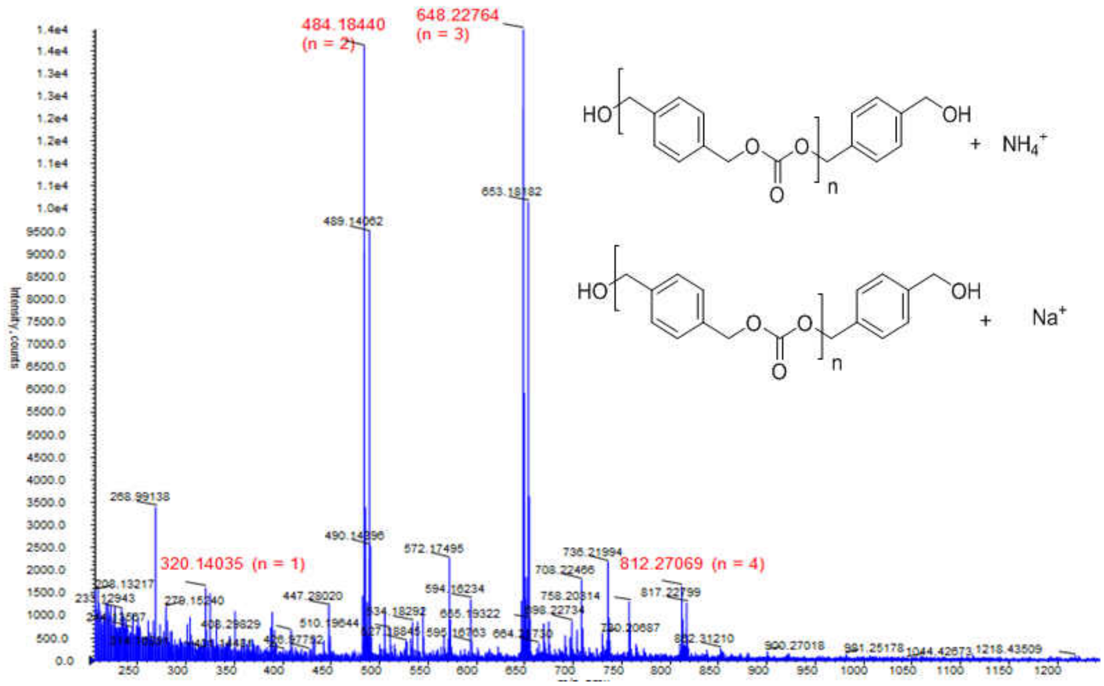

**Figure 14**. Representative ESI-TOF-MS of the isolated polymer from entry 3, Table 2. The major series corresponds to the endcapped polycarbonate.

Promoted by the results with the $CeO_2$/2-cyanopyridine catalyst for the copolymerization of $CO_2$ and 1,4-benzenedimethanol, we applied this system to the copolymerization of 1,6-hexanediol and 1,4-cyclohexanedimethanol using 5 mmol of diol, 1 mmol of $CeO_2$ (activated at 800 °C for 3 h) and 50 mmol of 2-cyanopyridine under 725 PSI of $CO_2$ at 138 °C for 72 h. As expected, the catalytic system is effective in catalyzing the copolymerization of $CO_2$ with 1,6-hexanediol and 1,4-cyclohexanedimethanol to afford the corresponding polycarbonates with 84.8% and 42.1% conversions, respectively. The resultant copolymers have $M_n$ about 2100 g/mol ($M_w/M_n$ = 1.50), and the macrodiol structure was confirmed by the $^1H$ and $^{13}C$ NMR and FT-IR spectroscopies. The aliphatic alcohols such as 1,6-hexanediol are considered as more challenging substrates than benzylic alcohols in these coupling reactions, and our findings suggest the present catalytic system could have broad applications for various diols.

Based on the mechanistic studies for the formation of dialkyl and cyclic carbonates over $CeO_2$,[13b,14] a possible mechanism leading to the polycarbonate from $CO_2$ and diol can be envisioned, which includes the adsorption of the OH group on the $CeO_2$ surface, resulting in a cerium alkoxide, followed by the $CO_2$ insertion giving a cerium carbonate. Attack of the carbonyl in this cerium carbonate species by the OH group from the diol or a (poly)carbonate diol would propagate the polymer chain and generate $H_2O$, which is subsequently consumed in the hydration of 2-cyanopyridine, also aided by the $CeO_2$ catalyst.

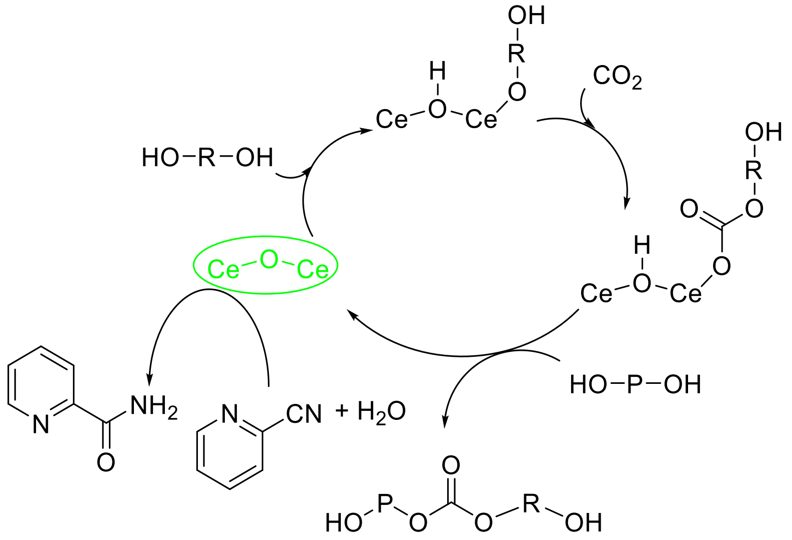

**Figure 15.** A proposed mechanism for polycarbonate formation.

## V.3 CONCLUSIONS

A dual system combining a heterogeneous catalyst ($CeO_2$) with an organic dehydration agent (2-cyanopyridine) has been applied successfully to the direct copolymerization of $CO_2$ and diols, affording short chain polycarbonate diols with decent conversion. The resulting products have been characterized and confirmed by NMR, IR and ESI-MS. Such system offers a direct, environmentally friendly route to polycarbonates, and future work in our laboratory will seek to improve the current system and study its application in copolymerization of $CO_2$ with other diols. Other systems will also be investigated, which may provide better yield and polymers with higher molecule weight.

## V.4 EXPERIMENTAL SECTION

### Materials and methods

All reactions that involved compounds sensitive to air and/or moisture were carried out under a dry nitrogen atmosphere using freshly dried solvents and standard Schlenk line and glove box techniques. All chemicals were purchased from commercial sources. Toluene was distilled under nitrogen from Na/benzophenone. $CDCl_3$ was dried over $CaH_2$, distilled and degassed prior to use.

NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer ($^1H$, and $^{13}C$), and referenced to residual solvent peak. Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar, using PLgel 5 µm Mixed-D column, a Prostar 355 RI detector, and THF as eluent at a flow rate of 1 mL/min (20 °C). The HR-MS and ESI TOF was performed using high resolution time of flight G1969A instrumentation (Agilent). The DSC data was collected from a Perkin Elmer Pyris DSC using 10.0 $^oC$/min heating rate with 20ml/min nitrogen flowing. FT-IR spectra was recorded on a Perkin-Elmer Spectrum 400 FTIR spectrophotometer.

### Copolymerization of 1,4-benzenedimethanol/$CO_2$ with $CeO_2$

A 60 ml Oven dried glass Parr high-pressure reactor vessel was loaded with $CeO_2$ nano-powder (<25nm particle size), 1,4-benzenedimethanol and 2-cyanopyridine. The activation of $CeO_2$ was achieved by heating in the oven with certain temperature for 3 hours. The vessel was loaded in the Parr reactor head and seal tightly. The Parr reactor was set up to the certain temperature and pressure with $CO_2$. Mechanical stirring was also applied in the reactor. The reaction mixture was allowed to cool down to room temperature after the reaction time and a small fraction of the mixture was taken for $^1$H-NMR spectroscopy. The heterogeneous mixture was completely transferred into test tubes, and several milliliters of chloroform were used to help the transportation. $CeO_2$ was separated from the mixture by centrifugation at first. Then, the liquid phase of the original mixture was collected, and the polymer was precipitated from it with addition of methanol. After centrifugation, the polymer was washed by methanol for three times and dried by vacuum to determine yield.

### Copolymerization of 1,4-benzenedimethanol or 1,4-cyclohexanedimethanol and $CO_2$ with $Cs_2CO_3$/DCM

A 100 ml Oven dried Schink flask was loaded with $Cs_2CO_3$, 1,4-benzenedimethanol or 1,4-cyclohexanedimethanol and DCM. The flask was frozen by liquid $N_2$ following by evaporation and refilled by $CO_2$ three times. Then, the flask was heated up to the certain temperature. Magnetic stirring was also applied in the flask. The reaction mixture was allowed to cool down to room temperature after the reaction time and a small fraction of the mixture was taken for $^1$H-NMR spectroscopy. 10 ml of the water was added into the flask, and the heterogeneous mixture was completely transferred into test tubes. Polymer was separated from the mixture by centrifugation at first. Then, the solid phase was collected and washed by methanol for three times. The polymer was dried by vacuum to determine yield.

**Synthesis of ligands.**

Similar ligands have been obtained previously; the following example is typical: To a round bottom flask were added 2-bromobenzaldehyde (6.5 mmol), 1 equivalent of amino alcohols, and 25 mL of toluene. After stirring the mixture for 24 h, $K_3PO_4$ (19.5 mmol) and NBS (13.0 mmol) were added and stirring was continued for 5 h at room temperature. After filtration, the mixture was washed with $NaHCO_3$ and $H_2O$ 3 times. The organic fraction was dried with $Na_2SO_4$ and purified by column to the give the oxazoline precursors. The product was mixed with 120 mol% aniline, 5 mol% $Pd(OAc)_2$, 5 mol% *rac*-BINAP, 140 mol% sodium tert-butoxide and 15 mL dry toluene in a schlenk flask under nitrogen. The mixture was heated at 100 °C for 48 h, and then filtered and purified by column. The desired ligands were usually obtained as yellow-orange oil ($HL^{1a\text{-}c}$ and $HL^{1e\text{-}h}$) or crystalline solids ($HL^{1d}$ and $HL^{1i}$) in ~66-89% yields. Characterizations of $HL^{1b,\ d,\ f}$ have been reported previously.[20]

**Synthesis of Cyclic Carbonate from Epoxides and $CO_2$.**

A typical bulk procedure was exemplified by the following: epoxide, co-catalys and Al complex were loaded into a Parr high-pressure reactor inside of a glovebox. The reaction mixture was then heated under 500 PSI $CO_2$ pressure at 75 $^{o}$C. At the end of the reaction, the conversion was determined by $^1$H NMR spectra of the reaction mixture. The cyclic carbonate was isolated by column.

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