Studies on Design and Synthesis of Efficient Metal Catalysts for Precise Ring-Opening Polymerization of Cyclic Monomers

（精密開環重合に有効な高性能金属触媒の設計・創製に関する研究）

IWASA, Naruhito

岩佐　成人

Graduate School of Materials Science
Nara Institute of Science and Technology

2008

Table of contents

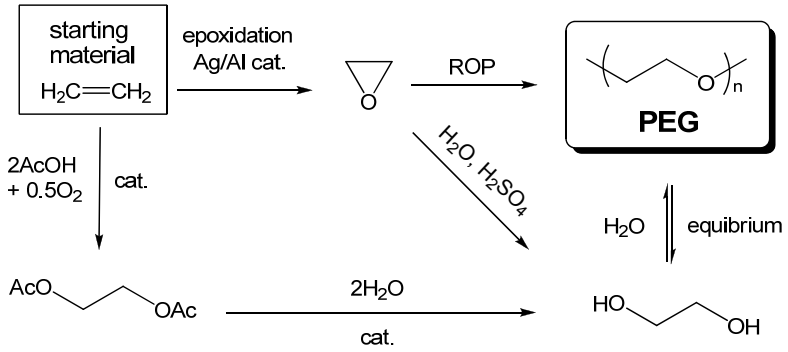
General Introduction

Research Background

Polymers containing functional groups such as heteroatom in the main chain are attractive for various properties of matter derived from the functional groups. Both ring-opening polymerization (ROP) and polycondensation are widely known as synthetic ways for such polymers. In the comparison of these methods, polycondensation accompanies with a by-product, whereas ROP does not yield it. Moreover, polycondensation is an equibrium reaction, for example in the case of polyesters, if the number average of polymerization degree (DP_n) becomes two, then the reaction reaches the equibrium state (the equibrium constant (K) ≈ 1, and $DP_n = 1 + K^{0.5}$). In order to carry out the polymerization, thorough removal of water is indispensable. Therefore, ROP is superior to polycondensation in terms of polymerization for yielding high molecular weight polymer.

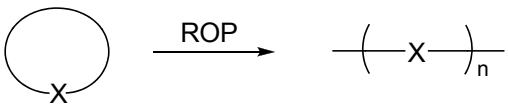
In terms of preparation of monomers, ROP generally has advantage over polycondensation as shown in Scheme 1.[1] Ethylene oxide monomer for ROP is prepared by only epoxidation of ethylene, whereas synthesis of ethylene glycol for polycondensation needs two steps. Therefore, ROP has the advantages in terms of both polymerization and preparation of monomers.

Scheme 1



In 1929, Staudinger examined ROP of EO using various catalysts: Me_3N, Na, $SnCl_4$, $NaNH_2$, ZnO, SrO, CaO.[2] The experiments provided a basis for the catalysts for the ROP. Then, Carothers investigated the polymerizability of various cyclic monomers in 1935.[3] Subsequent to the research, Hall and coworkers made an extensive review of this field in a series of articles published in 1958.[4] Scheme 2 describes the polymerizability of cyclic monomers containing various functional groups by different polymerization of type, anionic, cationic, coordination, and hydrolytic. Note that coordination polymerization column which is promising method for precise ring-opening polymerization. Cyclic ethers, sulfides, and esters afford the polymers by coordination polymerizations. On the other hand, ROPs industrially produce the following polymers: poly(ε-caprolactam), poly(propylene oxide), poly(epichlorohydrin), poly(tetrahydrofuran), poly(ε-caprolactone), poly(lactide), poly(phosphazene), poly(siloxane), etc. (Chart 1).

Scheme 2

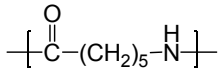


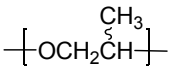
X = —O—, —S—, —NH—, —OCH_2O—, —C(=O)—, —NHC(=O)—, —N=C(R)—, etc.

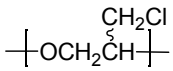
Polymerizability of cyclic monomers containing various functional groups

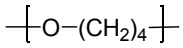
	ether	sulfide	imine	formal	ester	amide	iminoether
anionic	○	○	△	×	○	○	×
cationic	○	○	○	○	○	○	○
coordination	○	○	×	×	○	×	×
hydrolytic	×	×	×	×	×	○	×

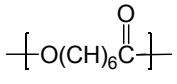
Chart 1

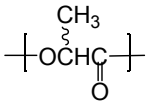

poly(ε-caprolactam)

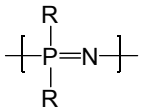

poly(propylene oxide)

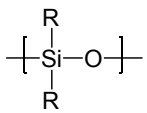

poly(epichlorohydrin)


poly(tetrahydrofuran)


poly(ε-caprolactone)


poly(lactide)


poly(phosphazene)


poly(siloxane)

Polyethers and polyesters especially display the promising characteristics as described below. Polyethrs such as poly(propylene oxide) and poly(epichlorohydrin) are available for synthetic rubbers, coatings, adhesives, raw materials for polyurethane, etc. Moreover, owing to oil resistance, heat-resistance, and ionic conductivity, a lot of novel uses and polymers have been developed recently. On the other hand, polyesters such as polylactone and polylactide possess promising characteristics as biodegradable and bioasimilable materials, not only due to their practical biodegradability in light of recent concerns with the environment, but also due to their biocompatibility for medical and pharmaceutical applications.[5] Therefore, considerable attention has been paid to the ROP of cyclic ethers and esters. Then, the details in the progress of these ROPs are described below.

ROP of cyclic ethers －Polyether－

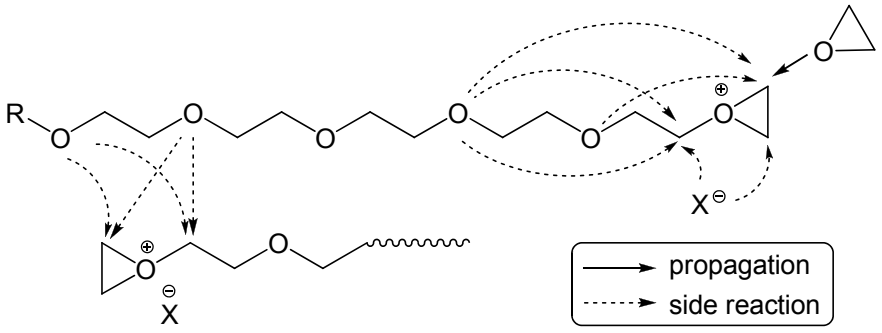
Several inherent characteristics of the ether linkage stimulate extensive research and development of linear polymers with ether linkages in the polymer backbone.[6] The ether linkage has low polarity and low van der Waals interaction characteristics ($\Delta H_{vaporization}$ = 26.4 kJ/mol for pentane *vs.* 26.0 kJ/mol for diethyl ether). The carbon-oxygen bond has a lower barrier to rotation than carbon-carbon bond (11.3 kJ/mol for dimethyl ether *vs.* 13.8 kJ/mol for propane) and thus provides a lower barrier to coiling and uncoiling of polymer chains. The

ether oxygen has an even lower excluded volume than a methylene group (van der Waals radii of 1.4 Å *vs.* 2.1 Å) and thus, of all backbone units, has the smallest "excluded volume". This is also a factor which permits greater chain flexibility. The carbon-oxygen bond has as great a bond energy (355 kJ/mol) as a carbon-carbon bond (343 kJ/mol) and much greater hydrolytic resistance than ester, acetal, or amide links. The ether linkage makes an important contribution to the physical properties and chemical stability on which the utility is based.

Three-membered epoxides have been investigated most extensively and show a wide variety of reactivity. In fact, the epoxides are the only cyclic ethers which may be polymerized by both cationic and anionic mechanisms. This is due to the unusual electronic structure of the strained three-membered ring.

Cationic polymerization of epoxides is brought about by Lewis acids such as BF_3, $AlCl_3$, $SnCl_4$, etc. A protoic compound such as water is often required as the cocatalyst, interacting with the Lewis acid to release protons. Although the principal reaction to form the polymer chain proceeds via the formation of oxonium ion of the monomer, the actual reaction is much more complicated because of side reactions due to the higher basicity of the liner ether group in the polymer chain compared with that of the epoxide monomer (Scheme 3). Therefore, conventional cationic polymerization of epoxides is not suitable for the preparation of the controlled high molecular weight polyethers.

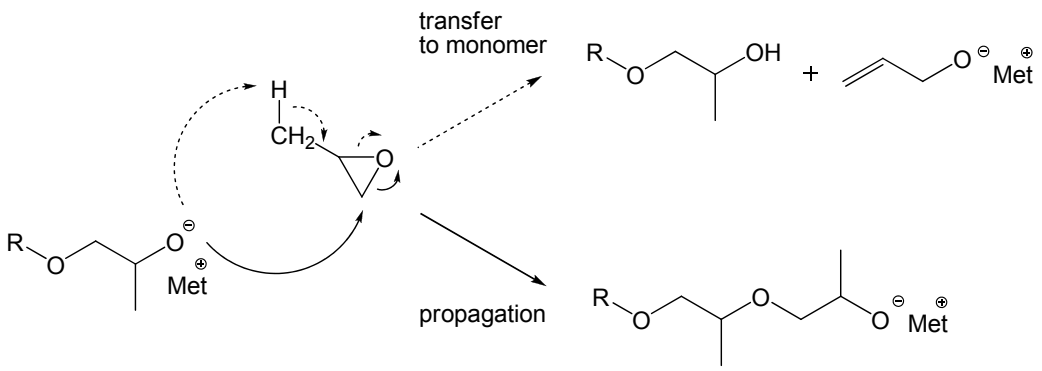
Scheme 3



In contrast, due to the advantage of the rapid polymerization rate, the photoinitiated cationic ring-opening polymerization[7] of epoxides are widely employed in a variety of commercial applications, among which may be mentioned coatings, adhesives, printing inks, microelectronic photoresists, and stereolithography.

The anionic polymerization of ethylene oxide (EO) has been studied for many years, and a large number of anionic initiators have been investigated to improve both the polymerization control and kinetics. Conventional sodium- and potassium-based initiators are used in ether solvent, such as tetrahydrofuran, or in polar media, such as dimethyl sulfoxide, and a controlled polymerization allows synthesis of the end-functional poly(ethylene oxide) (PEO)[8], PEO-based block copolymers[9] as well as PEO chains with more complex architectures like stars[10] or dendrimers.[11] Poly(propylene oxide) (PPO) finds important applications as functional oligomer, block co-oligomer, and high molecular weight elastomer. However, their applications have been still limited due to the lack of control of its polymerization. The high nucleophilicity of the corresponding propagating species using alkali metal derivatives, which are efficient initiators for the ROP of EO, may result in important transfer reactions.[12] In the case of propylene oxide (PO), only low molecular weight polymers are obtained as a consequence of proton abstraction on the PO methyl group, which leads to the formation of hydroxy-ended chains and new allyl alkoxide initiators (Scheme 4).[13]

Scheme 4



Recently, a new polymerization strategy, which allows the fast and controlled anionic polymerization of PO, has been developed by Deffieux *et al*.[14] It is based on the formation of complexes with both the anionic initiator and the monomer. The catalyst systems consisting of ammonium salts in combination with $Al^{i}Bu_3$ have achieved living polymerization with narrow polydispersities and controlled molecular weight, up to 150 000 g/mol, at low temperature, and in short reaction times. The polymerization proceeds with the coordination of the epoxide oxygen toward the metal atom: by coordinate anionic mechanism. The coordination of the monomer to the metal at each propagation step may lead not only to the activation of the monomer but also to a stereospecific reaction.

In the polymerization of racemic PO by alkali catalyst, the distribution of the steric structure with respect to the asymmetric carbon of the monomer unit in the polymer chain is random, and the polymer is atactic stereo regularity. In contrast, multi site catalyst systems, which have some different active sites, such as $FeCl_3$/PO (Fe alkoxide),[15] $ZnEt_2/H_2O$,[16] and $AlEt_3/H_2O$/acetylacetone,[17] Bu_2SnO/Bu_3PO_4,[18] afforded polymers with isotactic structure having long sequences in which the asymmetric carbons of the monomer unit have the same absolute configuration in the ROP of PO. Especially, $AlEt_3/H_2O$/acetylacetone and Bu_2SnO/Bu_3PO_4 catalyst are also effective to other oxirane monomers. These multi site catalysts afforded high molecular weight polymers, however, the catalyst efficiencies (*vs.* metal) were considerably low. Moreover, the polymerization mechanism is not definite even now, although the bimetallic mechanism, that two metals catalyze the propagation reaction, has been proposed.[19] As subsequent important research, Inoue *et al.* developed aluminum porphyrin complex which is available for immortal polymerization of PO. The catalyst made it possible to both control of the molecular weight and the number of polymer chains.[20]

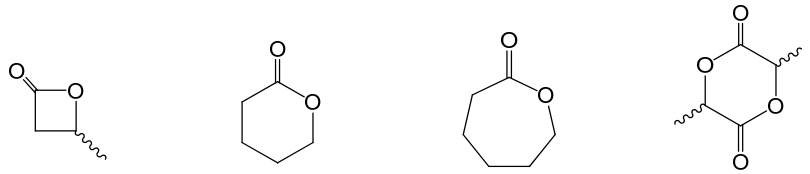
In reference to the isoselectivity of the ROP of PO, Coates *et al.* have recently found that (salph)CoOAc [salph = N,N'-bis(3,5-di-*tert*-butylsalicylidine-1,2-benzenediamine)] catalyzes the isospecific polymerization of racemic PO to form regioregular polyethers with

isotactic triad contents of greater than 99%.[21] On the other hand, there has been considerable interest in double metal cyanide complexes such as the catalyst systems consisting of $Zn_3[Co(CN)_6]_2$ and $ZnCl_2$ in relation to the ROP of PO.[22] The catalyst system is highly active, and gives polymers with narrow molecular weight distribution (< 1.40) as well as with low unsaturation level (< 0.0057 meq/g). Therefore, resultant polymers containing hydroxyl group in the polymer chain ends are available for raw material of polyurethane foams. Incidentally, industrial polyethers mainly from EO and PO are produced and used for many applications, especially, for the production of polyurethane foams. In contrast, polyethers which are derived from epoxides with longer chain substituents or functional groups are rare,[23] although the resultant polymers display attractive properties for promising applications, because such epoxides show a lower reactivity due to a higher steric hindrance and interaction with the catalyst site. In other words, ring-opening polymerization of such epoxides would yield novel polyethers. Therefore, many efforts to such ROP have been undertaken.

ROP of cyclic esters －Polyester－

Polyesters are among the most versatile synthetic polymers, and they have been widely used as fibers, plastics, and coatings. Over the past three decades, of the variety of polyesters known, linear aliphatic polyesters, especially those derived from lactide (LA), ε-caprolactone (CL), δ-valerolactone (VL), β-butyrolactone (β-BL), and their copolymers (Chart 2), have attracted considerable attention due to their new biomedical and pharmaceutical applications such as biodegradable surgical sutures and postoperative support pins and splints, or as a delivery medium for controlled release of drugs.[24]

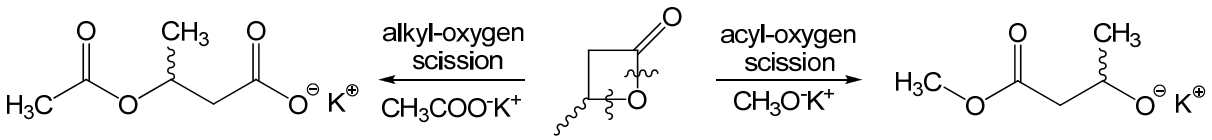
Chart 2



Especially, the starting materials for poly(lactide) (PLA) are derived from corn, beets, and annually renewable resources. As the depletion of petrochemical feedstock comes near, the renewable and environmentally friendly polymers are increasingly important for a sustainable future.[25]

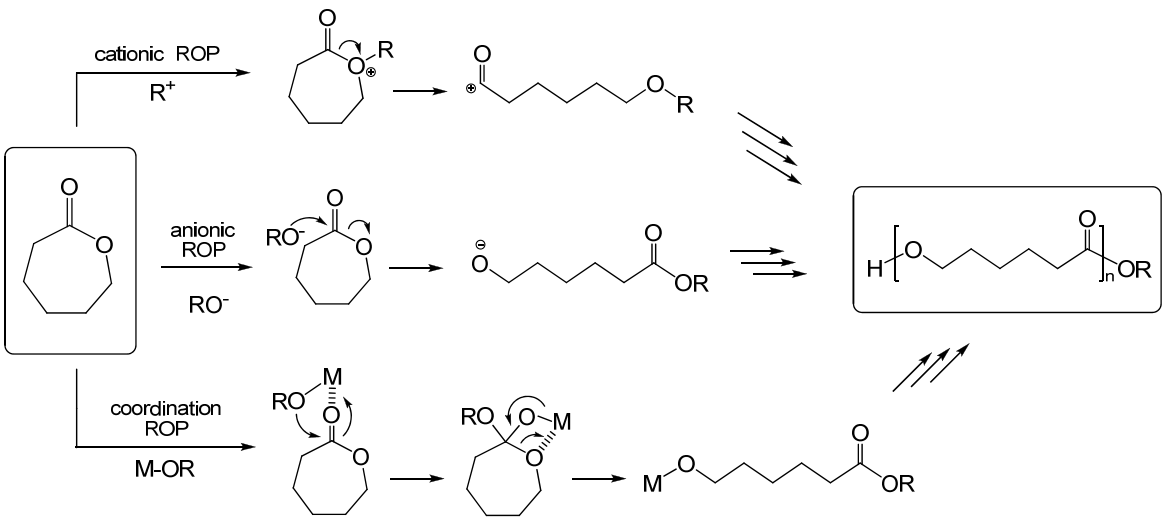
As previously mentioned, a particularly convenient method for the synthesis of polyesters is the ring-opening polymerization of cyclic esters. However, ROPs don't take place if the change of free energy in the polymerization is not enough, and it is depend on the ring-strain of the cyclic esters. Therefore, the ROP of 5-membered lactone don't take place under the mild conditions.[26] On the other hand, two types of cleavage, alkyl-oxygen or acyl-oxygen bond, take place in the ROP of 4-membered β-lactone which has the enough ring-strain, depending on the used initiator (Scheme 5).[27] Then, the ring-opening of large ring derivatives always take place on acyl-oxygen bond. In addition to that, the ring-opening of large ring lactones does not occur by the initiators such as CH_3COONa, pyridine which induce scission of alkyl-oxgen bond in the ROP of β-lactones.

Scheme 5

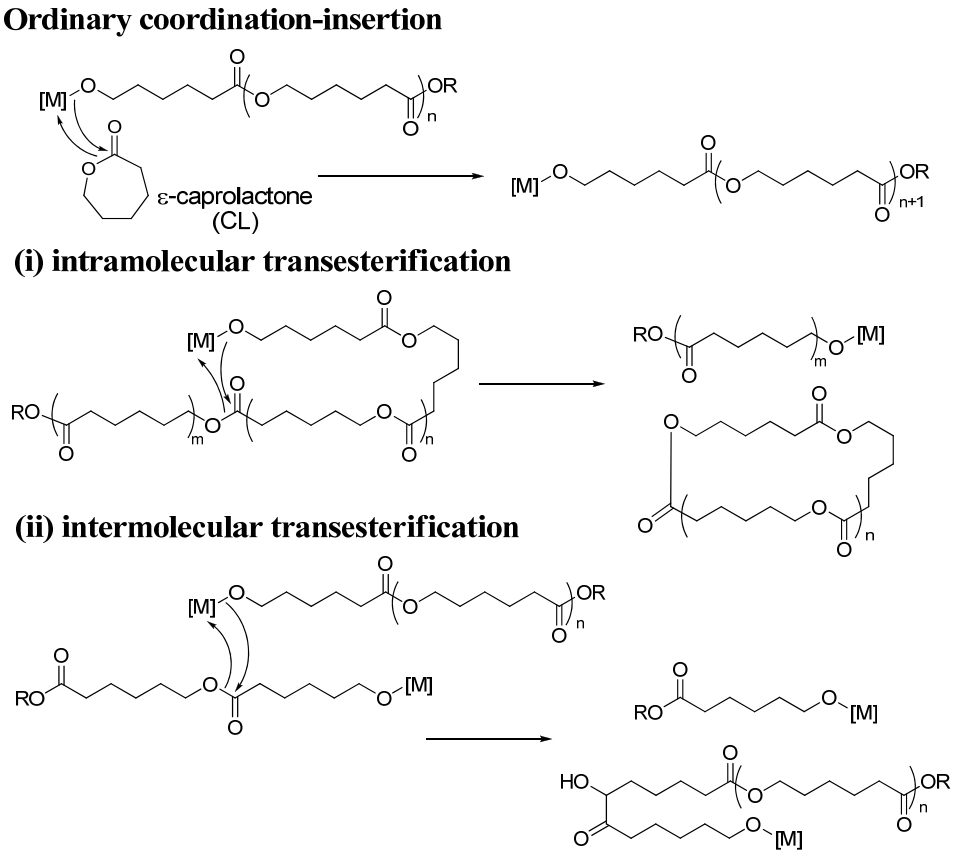


Among the three mechanisms in Scheme 6, most attention is devoted to the coordination polymerization using well-defined metal complexes, due to the advantages of well controlled molecular weight and low molecular weight distribution. The efficiency of the molecular weight control in such coordination polymerizations depends on the ratio $k_{propagation}/k_{initiation}$ and on the extent of transesterification side reactions. These transesterification reactions can occur both intramolecularly (backbiting leading to macrocyclic structures and short chains) and intermolecularly (chain redistribution) (Scheme 7).[28]

Scheme 6



Scheme 7

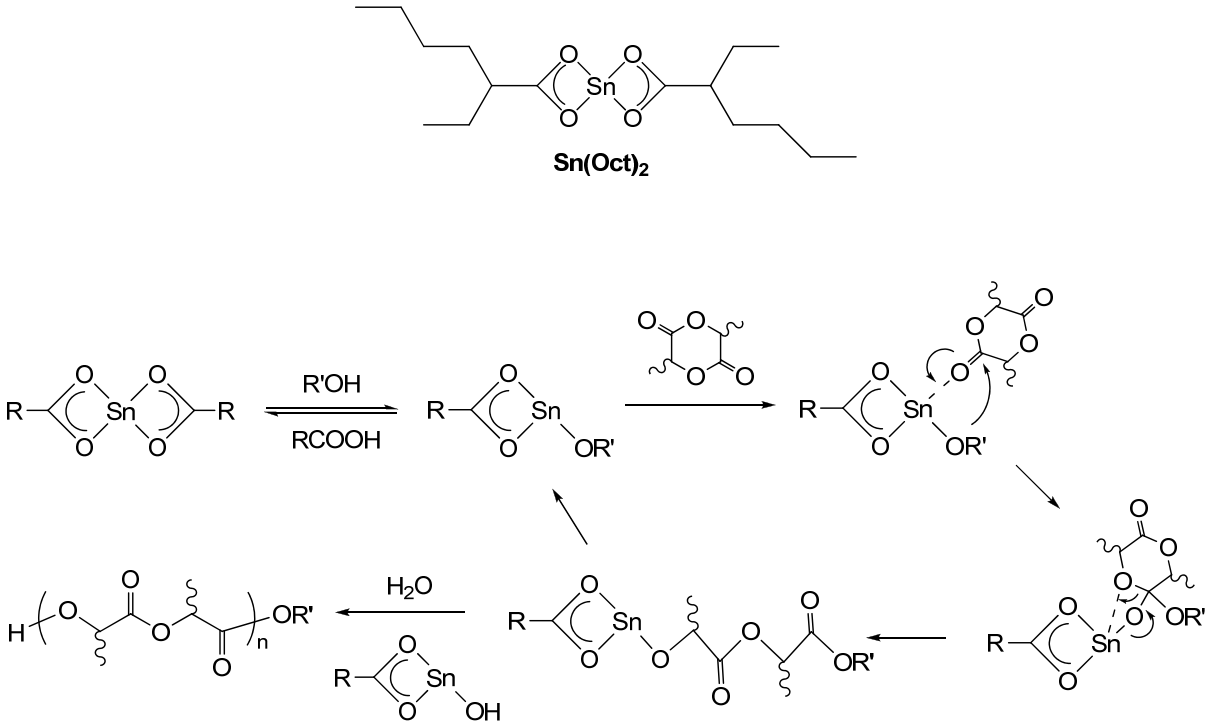


These side reactions result in polymers rather with broad molecular weight distributions, and the molecular weights of the resulting polymers may not be reproducible. The extent of these undesirable transesterification reactions was found to strongly depend on the metallic initiator.[28,29]

The most widely used complex for the industrial preparation of PLA is undoubtedly tin(II) bis(2-ethylhexanoate) (Scheme 8). This derivatives, usually referred to as tin(II) octanoate, $Sn(Oct)_2$, is commercially available, easy to handle, and soluble in common organic solvents. It is highly active (typical reaction times in bulk at 125-180 °C range from minutes to a few hours) and allows for the preparation of high molecular weight polymers (up to 10^5 or even 10^6 Dalton in the presence of an alcohol).[30] However, side reactions occur from the very beginning of the polymerization with $Sn(Oct)_2$, leading to rather broad

molecular weight distributions (M_w/M_n around 2). Moreover, the toxicity associated with most tin compounds in the resultant polymer is a considerable drawback in the case of biomedical applications.[31]

Scheme 8



Aluminum alkoxide have also proved to be efficient catalysts for the ROP of cyclic esters. The archetypal example, namely, $Al(O^iPr)_3$, has been largely used for mechanistic studies. However, it has been revealed to be significantly less active than $Sn(Oct)_2$ (in bulk at 125-180 °C, reaction times of several days are usually required and molecular weights are generally lower than 10^5 Da).[30] Moreover, an induction period of a few minutes is systematically observed with $Al(O^iPr)_3$. This feature has been attributed to aggregation phenomenon.[32] Then, side reactions occur at high or even complete conversion with $Al(O^iPr)_3$, yielding lower molecular weight distribution (less than 1.5).[30] For all these reasons, $Al(O^iPr)_3$ is much less used for the preparation of biodegradable polyesters.

However, toxicity of aluminum is much lower than tin compounds,[33] and the concerning about the safety of the resultant polymers has given rise to a growing interest in the other green catalysts (metal catalysts and organocatalysts without metals) for the ROP of cyclic esters as described below (Figure 1).[34] Aluminum, zinc, and iron complexes etc. are reported as the low toxic metal catalysts. They have merits and demerits, for example aluminum salen complex reported by Spassky *et al.* indicate stereospecificity in ROP of *rac*-lactide (LC), however, extremely low activity [TOF {(molar amount of LC reacted)/(molar amount of Al)·h^{-1}} = 0.6 h^{-1}, under the condition: [LC]/[Al] = 75, initala LC concentration = 0.80 mmol/mL, in toluene, 70 ºC].[34(a)] On the other hand, high nucleophilic organocatalysts such as N-heterocyclic carbenes and phospazenes are reported.[34(d),(e)] These catalysts are only available at low ratio [LC]/[Cat.] (≈ 100), thus high molecular weight polymers cannot be yielded.

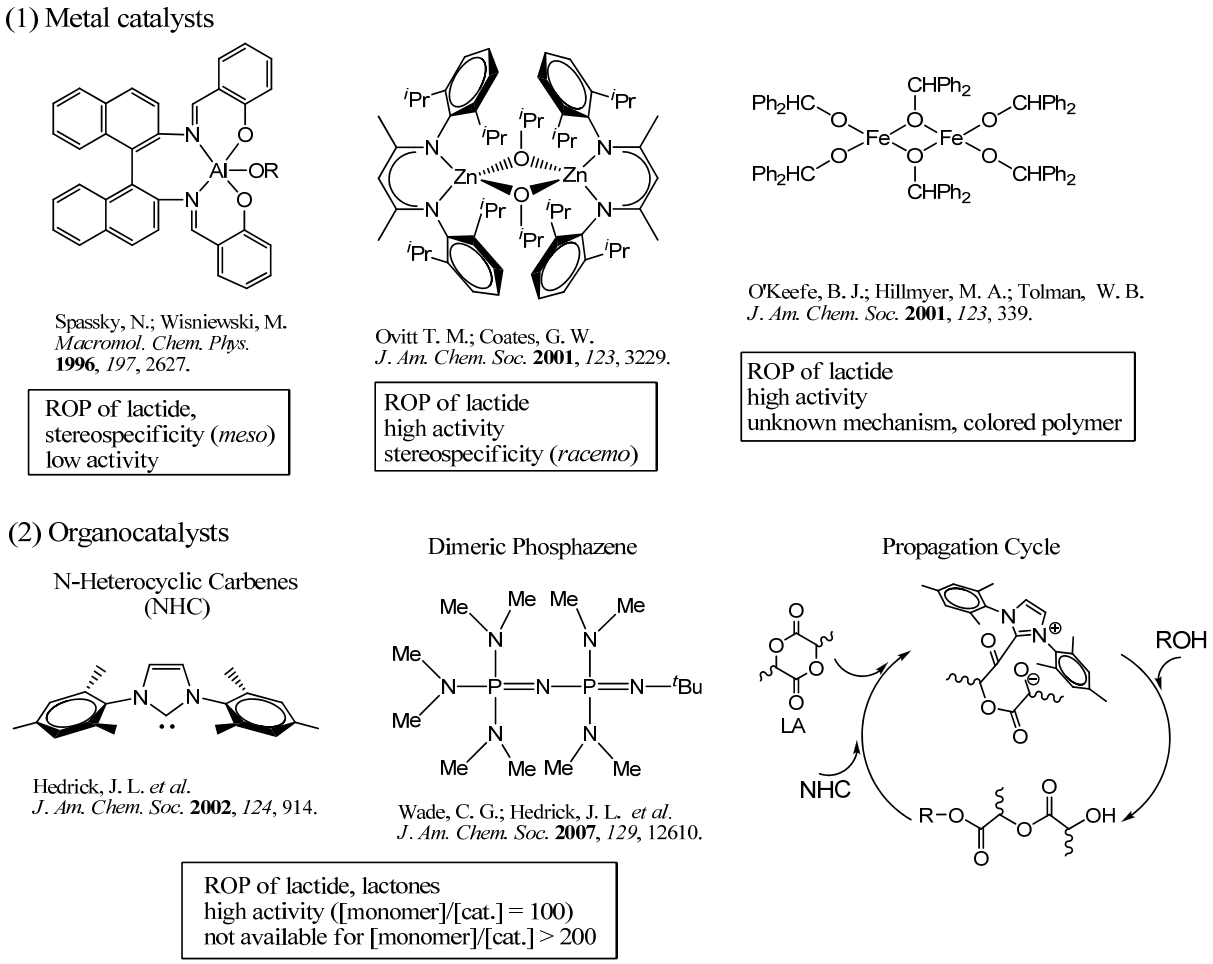


Figure 1. Green catalysts for the ROP of cyclic esters

As above described, aluminum complexes are reported as one of the effective green catalysts for the ROP. However, there were no examples for design of catalysts and only a few examples for effect of ligand using isolated Al complexes (Figure 2).[35] These research only reported general effect of substituents for the ROP of cyclic esters: electron-withdrawing groups lead to high activity and big steric bulk substituents bring about low activity. However, any catalysts were not efficient due to low activity. On the other hand, Nomura *et al.* reported that *in situ* mixed catalyst systems consisting of $AlEt_3$ and 2.0 equiv. of salicylaldimine, [2,4-R_2-6-{(2,4,6-$R^1{}_3C_6H_2$)N=CH}C_6H_2OH, R^1, R^2= alkyl, aryl, halogen], showed high catalytic activity for ROP of CL in the presence of $PhCH_2OH$.[35(d)] However, no studies were made concerning the catalytically active species including isolation of the Al

complexes. Therefore, considerable attention is paid to the synthesis, and structural determinations as well as design for an efficient Al initiator (catalyst) in the ROP of cyclic esters.

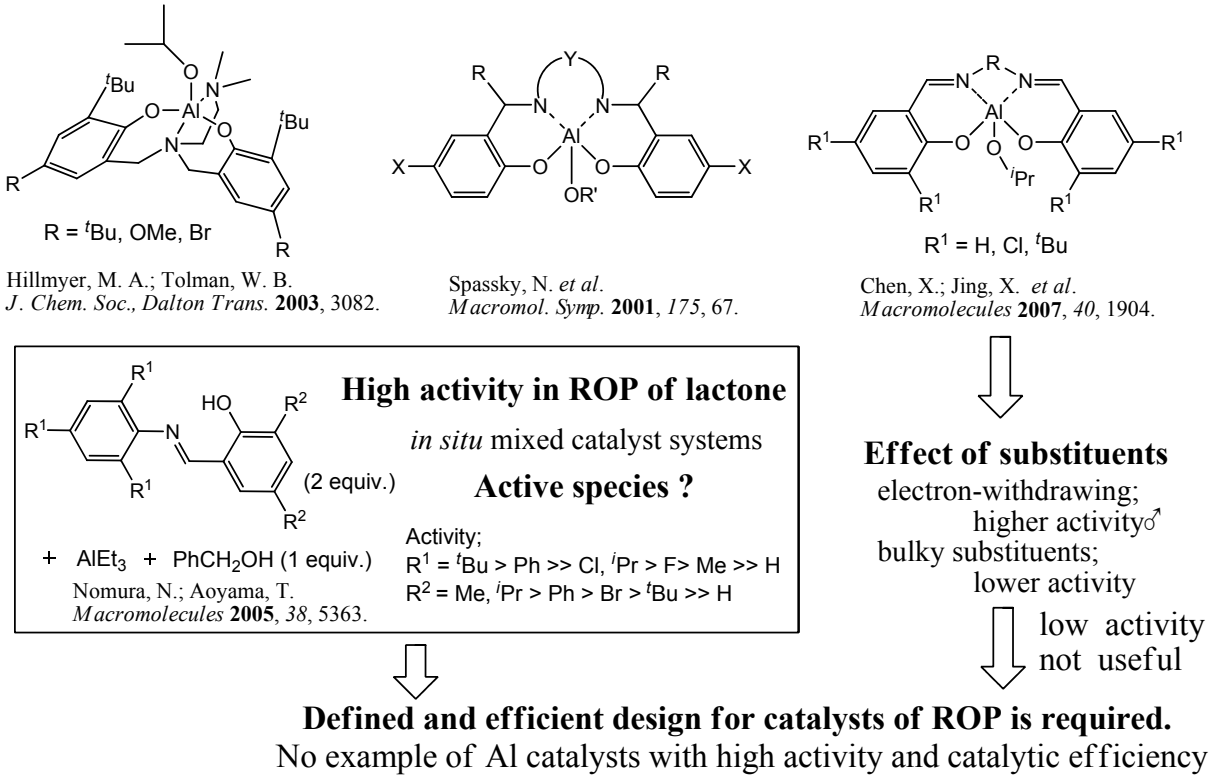


Figure 2. Examples for effect of ligand using Al complexes.

Objectives of This Thesis

As above mentioned, precisely controlled ring-opening polymerization (ROP) of propylene oxide has been achieved recently. On the other hand, it is difficult to carry out the ROP of functionalized epoxides, although it is one of the most promising means to yield notable polymers. Hence, the present thesis highlights precise synthesis of the polyethers containing functional groups, especially, establishes methodology which introduces a highly reactive oxirane ring in the polymer side chain. The oxirane ring in the side chain is useful for modification of the polymer, and various functional polymers would be obtained from the precursor polymers. The results of selective polymerization are presented in Chapter 1.

As demonstrated above mentioned, aluminum compounds are expected as an alternative to $Sn(Oct)_2$, and much attention has been paid to the exploration of monomeric or dimeric Al complex catalysts for the efficient polymerization.[36] Although it is known that an introduction of extremely bulky aryloxide ligands to aluminum generates monomeric Lewis acid catalysts that can be used in various organic reactions,[37] reports concerning ligand effect toward the catalytic activity in the ROP of cyclic esters using a series of 'isolated' Al complexes were rare. Therefore, as an efficient high-performance Al complex catalyst, monomeric Al complex containing chelete ligand is focused, and I aim to expand basic knowledge concerning ligand effect for the design of catalyst, and to confirm polymerization mechanism of cyclic esters using Al complexes.

References

1. Weissermel, K.; Arpe, H. –J. *Weissermel, Arpe : Industrial Organic Chemistry. Fourth Completely Revised Edition*; WILEY-VCH:Germany, 2003.
2. Staudinger, H.; Schweitzer, O. *Ber. Deut. Chem. Ges.* **1929**, *62*, 2395.
3. (a) Hill, J. W.; Carothers, W. H. *J. Am. Chem. Soc.* **1935,** *57*, 925. (b) Mark, H.; Whitby, G. S. *The collected papers of W. H. Carothers, High Polymers Vol. I, Page 81-140;* Wiley: New York, 1940.
4. (a) Hall, H. K. Jr.; Schneider, A. K. *J. Am. Chem. Soc.* **1959**, *81*, 6409. (b) Hall, H. K. Jr. *J. Am. Chem. Soc.* **1959**, *81*, 6412. (c) Hall, H. K. Jr.; Brandt M. K.; Mason, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 6420. (d) Hall, H. K. Jr.; Zbinden, R. *J. Am. Chem. Soc.* **1959**, *81*, 6428.
5. (a) Vert, M.; Albertsson, A.; Scott, G.; Chiellini, E. Eds. *Biodegradable Polymers and Plastics;* The Royal Society of Chemistry: Cambridge, UK, 1992; p 95. (b) Vert, M.; Feijen, J.; Albertsson, A.; Scott, G.; Chiellini, E. eds. *Biodegradable Polymers and Plastics*; The Royal Society of Chemistry: Cambridge, UK, 1992; p 139. (c) Okada, M. *Prog. Polym. Sci*. **2002**, *27*, 87.
6. Price, C. C. *Acc. Chem. Res.* **1974**, *7*, 294.
7. (a) Tasdelen, M. A.; Kumbaraci, V.; Jockusch, S.; Turro, N. J.; Talinli, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 295. (b) Yonet, N.; Bicak, N.; Yagci, Y. *Macromolecules* **2006**, *39*, 2736. (c) Bulut, U.; Crivello, J. V. *Macromolecules* **2005**, *38*, 3584.
8. (a) Yokoyama, M.; Okano, T.; Sakurai, Y. *Bioconjugate Chem.* **1992**, *3*, 275. (b) Schlaad, H.; Kukula, H.; Rudloff, J.; Below, I. *Macromolecules* **2001**, *34*, 4302.
9. (a) Quirk, R.; Kim, J.; Kausch, C.; Chun, M. *Polym. Int.* **1996**, *39*, 3. (b) Hillmeyer, M. A.; Bates, F. S. *Macromolecules* **1996**, *29*, 6994. (c) Ekizoglou, N.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1198. (d) Ekizoglou, N.; Hadjichristidis, N.

J. Polym. Sci., Part A: *Polym. Chem.* **2002**, *40*, 2166.

10. (a) Knischka, R.; Lutz, P.; Sunder, A.; Mülhaupt, R.; Frey, H. *Macromolecules* **2000**, *33*, 315. (b) Taton, D.; Saule, M.; Logan, J.; Duran, R.; Hou, S.; Chaikof, E.; Gnanou, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1669.
11. Feng, X.; Taton, D.; Chaikof, E. L.; Gnanou Y. *J. Am. Chem. Soc.* **2005**, *127*, 10956.
12. Boileau, S. In *Compr. Polym. Sci.* **1989**, *3*, 467.
13. Price, C. C.; St. Pierre, L. E. *J. Am. Chem. Soc.* **1956**, *78*, 3432.
14. (a) Labbe, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. *Macromolecules* **2007**, *40*, 7842. (b) Rejsek, V.; Sauvanier, D.; Billouard, C.; Desbois, P.; Deffieux, A.; Carlotti, S. *Macromolecules* **2007**, *40*, 6510.
15. (a) Pruitt, M. E.; Baggett, J. M. U. S. Patent, 2706181, 1955. (b) Price, C. C.; Osgan, M. *J. Am. Chem. Soc.* **1956**, *78*, 690.
16. Furukawa, J.; Tsuruta, T.; Sakata, R.; Saegusa, T. *Makromol. Chem.* **1959**, *32*, 90.
17. Vandenverg, E. J. *J. Polym. Sci.* **1960**, *47*, 486.
18. (a) Otera, J.; Yano, T.; Kunimoto, E.; Nakata, T. *Organometallics* **1984**, *3*, 426 (b) Miura, K.; Kitayama, T.; Hatada, K.; Nakata, T. *Polym. J*. **1990**, *22*, 671.
19. (a) Vandenberg, E. J. *J. Polym. Sci., A-1* **1969**, *7*, 525. (b) Vandenberg, E. J. *J. Polym. Sci.,* **1960**, *47*, 486. (c) Ishimori, M.; Nakasugi, O.; Takeda, N.; Tsuruta, T. *Makromol. Chem.* **1968**, *115*, 103. (d) Nakaniwa, N.; Ozaki, J.; Furukawa, J. *Makromol. Chem.* **1970**, *138*, 197. (e) Osgan, M.; Teyssie, Ph. *Polym. Lett.* **1967**, *5*, 789. (f) Osgan, M.; Teyssie, Ph. *Polym. Lett.* **1968**, *6*, 559.
20. Asano, S.; Aida, T.; Inoue, S. *Chem. Commun.* **1985**, *17*, 1148.
21. Peretti, K. L.; Ajiro, H.; Cohen, C. T.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 11566.
22. (a) Chen, S.; Zhang, P.; Chen, L. *Prog. Org. Coat*. **2004**, *50*, 269. (b) Chen, S.; Chen, L. *Coll. Polym. Sci.* **2004**, *282*, 1033. (c) Chen, S.; Xia, X. W.; Xu, N. *Polym. Prep.* **2003**,

44, 774. (d) Baek, S. T.; Anas, K.; Park, D.-W.; Ha, C.-S.; Kim, I. *Div. Fuel Chem.* **2006,** *51*, 843. (e) Lu, Y.; Tu, J.; Jin, H.; Cai, L.; Wang, R. *Polym. Prep*. **2002**, *43*, 1183. (f) Zhang, X.-H.; Hua, Z.-J.; Chen, S.; Liu, F.; Sun, X.-K.; Qi, G.-R. *App. Cat. A: Gene.* **2007**, *325*, 91. (g) Kim, I.; Byun, S. H.; Ha, C.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4393.

23. Inoue, S.; Aida, T. *Polyethers.* in *Handbook of polymer synthesis, Part A.*: New York, 1991.
24. (a) Langer, R. *Nature* **1998**, *392*, 5. (b) Uhrich, K. E.; Cannizzaro, S. M.; Langer, R. S.; Shakesheff, K. M. Chem. Rev. **1999**, *99*, 3181. (c) Jacoby, M. *Chem. Eng. News* **2001**, *79*, 30.
25. Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.
26. Korte, F.; Flet, W. *J. Polym. Sci., Part B: Polym. Lett.* **1966**, *4*, 685.
27. (a) Grobelny, Z.; Stolarzewicz, A.; Morejko, B.; Pisarski, W.; Maercker, A.; Skibinski, A.; Krompiec, S.; Rzepa, J. *Macromolecules* **2006**, *39*, 6832. (b) Kricheldorf, H. R.; Scharnagl, N. *J. Macromol. Sci., Chem.* **1989**, *A26*, 951. (c) Jedliński, Z.; Kowalczuk, M.; Główkowski, W.; Grobelny, J.; Szwarc, M. *Macromolecules* **1991**, *24*, 349. (d) Kurcok, P.; Matuszowicz, A.; Jedliński, Z. *Macromol. Rapid Commun.* **1995**, *16*, 201. (e) Duda, A. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 21. (f) Sosnowski, S.; Słomkowski, S.; Penczek, S. *Macromolecules* **1993**, *26*, 5526. (g) Słomkowski, S.; Penczek, S. *Macromolecules* **1976**, *9*, 367. (h) Deffieux, A.; Boileau, S. *Macromolecules* **1976**, *9*, 369. (i) Jedliński, Z.; Kowalczuk, M.; Kurcok, P. *Macromolecules* **1991**, *24*, 1218. (j) Jedliński, Z.; Kurcok, P.; Kowalczuk, M. *Macromolecules* **1985**, *18*, 2679. (k) Jedliński, Z.; Kowalczuk, M. *Macromolecules* **1989**, *22*, 3244.
28. (a) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Symp.* **1997**, *123*, 93. (b) Penczek, S.; Duda, A.; Szymanski, R. *Macromol. Symp.* **1998**, *132*, 441.

29. Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286.

30. (a) Degée, P.; Dubois, P.; Jérôme, R.; Jacobsen, S.; Fritz, H.-G. *Macromol. Symp.* **1999**, *144*, 289. (b) Dege´e, P.; Dubois, P.; Jérôme, R. *Macromol. Symp.* **1997**, *123*, 67. (c) Degée, P.; Dubois, P.; Jérôme, R. *Macromol. Chem. Phys.* **1997**, *198*, 1973.

31. The data for applications by Food Safety Commission, Hydrolysis Study on DABCO T-9. $Sn(Oct)_2$ is stoichiometrically converted to 2-ethylhexanoic acid and Sn^{2+} at 37 °C for 10 minutes in stomach. NOAEL (No observed Adverse Effect Level) of 2-ethylhexanoic acid = 25 mg/kg/day for rabbit, PTWI (Provisional Tolerable Weekly Intake) of Sn^{2+} = 14 mg/kg/week).

32. $Al(O^iPr)_3$ is known to exist as a mixture of at least two aggregates, namely, a trimer and a tetramers, see: Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114.

33. WHO (World Health Organization) and FAO (Food and Agriculture Organization) reported TDI (Tolerable Daily Intake) of aluminum ion is 50 mg/kg/day reported by. As a supplementary explanation associated with low toxic catalysts, TDI of zinc ion is 20-30 mg/kg/day reported by International Zinc Association.

34. (a) Spassky, N.; Wisniewski, M.; Pluta, C.; Borgne, A. L. *Macromol. Chem. Phys.* **1996**, *197*, 2627. (b) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (c) O'Keefe, B. J.; Monnier, S. M.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2001**, *123*, 339. (d) Connor, E. F.; Nyce, G. W.; Myers, M.; Mock, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 914. (e) Zhang, L.; Nederberg, F.; Messman, J. M.; Pratt, R. C.; Hedrick, J. L.; Wade, C. G. *J. Am. Chem. Soc.* **2007**, *129*, 12610.

35. (a) Roman, L. M. A.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2003**, 3082. (b) Jhurry, D.; Luximon, A. B.; Spassky, N. *Macromol. Symp.* **2001**, *175*, 67. (c) Du, H.; Pang, X.; Yu, H.; Zhuang, X.; Chen, X.; Cui, D.; Wang, X.; Jing, X. *Macromolecules* **2007**, *40*, 1904. (d) Nomura, N.; Aoyama, T.; Ishii, R.; Kondo,

T. *Macromolecules* **2005**, *38*, 5363.

36. (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem.* **1996**, *35,* 63. (b) Qian, B.; Ward, D. L.; Smith III., M. R. *Organometallics* **1998**, *17*, 3070. (c) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (d) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883. (e) Munoz-Hernandez, M.-A.; Keiser, T. S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416. (f) Liu, S.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Organomet. Chem.* **2000**, *596*, 109. (g) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A. *J. Chem. Soc.*, *Dalton Trans.* **2001**, 1472. (h) Hill, M. S.; Hutchison, A. R.; Keiser, T. S.; Parkin, S.; VanAelstyn, M. A.; Atwood, D. A. *J. Organomet. Chem.* 2001, *628*, 71. (i) Redshaw, C.; Elsegood, M. R. J.; *Chem. Commun.* **2001**, 2016. (j) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 415. (k) Chakraborty, D.; Chen, E. Y.-X. *Macromolecules* **2002**, *35*, 13. (l) Lewiński, J.; Zachara, J.; Starowieyski, K. B.; Ochal, Z.; Justyniak, I.; Kopec, T.; Stolarzewicz, P.; Dranka, M. *Organometallics* **2003**, *22*, 3773. (m) Lewinski, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (n) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P.; Jaouen, G. *Organometallics* **2003**, *22*, 3732. (o) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64. (p) Zhu, H.; Chen, E. Y.-X. *Inorg. Chem.* **2007**, *46*, 1481. (q) Yao, W.; Mu, Y.; Gao, A.; Liu, Q. Su, Y.; Zhang, Y. *Polymer* **2008**, *49*, 2486.

37. (a) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.,* **1988**, *110*, 3588. (b) Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 6431. (c) Maruoka, K.; Conception, A. B.; Murase, N.; Oishi, M.; Hirayama, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 3943. (d) Maruoka, K.; Imoto, H.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 4131. (e) Saito, S.; Yamamoto, H. *J. Chem. Soc., Chem. Commun.* **1997**, 1585.

Part I

Precise Synthesis of the Polyether containing Oxirane Ring in the Side Chain by Selective Ring-Opening Polymerization

Chapter 1

Ring-opening polymerization of various oxirane derivatives using organotin phosphate condensate; selective synthesis of the polyether containing oxirane ring in the side chain

Abstract

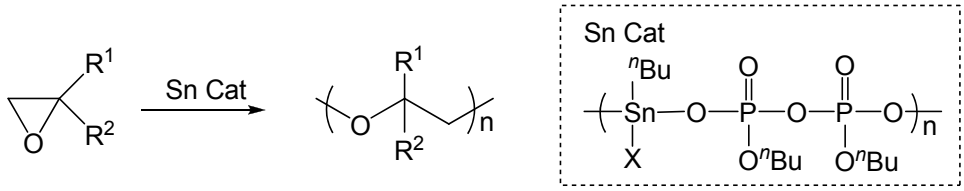
Ring-opening polymerization (ROP) of various oxirane derivatives of the type, 2,2-R^1,R^2-CCH_2O [R^1 = H (**1**), CH_3 (**2**); R^2 = CH_3 (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)], using organotin phosphate ($^n Bu_2SnO$-$^n Bu_3PO_4$) condensate has been explored. The ROP of monosubstituted oxiranes (**1a-c**) afforded ring-opened polymers in high yields (**1a, 1c** = 99% and **1b** = 69%); the resultant polymers from monomers **1a** and **1b** possessed high molecular weights (M_n = 9.49×10^4, 10.60×10^4, respectively). In contrast, both polymer yields and molecular weights for resultant polymers in the polymerization of disubstituted oxiranes (**2a-c**) were considerably lower than those in the polymerization of monosubstituted monomers (**1a-c**). ROP of glycidyl 2-methylglycidyl ether (**3**) possessing two oxirane groups with different reactivity was thus conducted by organotin catalyst; the high molecular weight polyether (M_n = 9.17×10^4) containing oxirane ring in the side chain has successfully been obtained in moderate yield.

Introduction

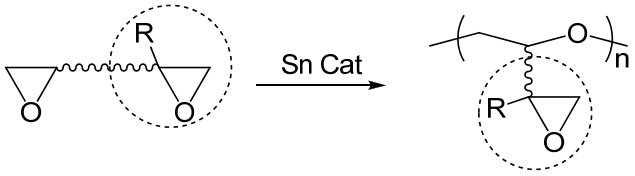
Ring-opening polymerization (ROP) of oxiranes has recently emerged as a subject of substantial interest since the initial report on the polymerization of propylene oxide (PO) using a catalyst system composed of $FeCl_3$ with PO in 1955 by Pruitt,[1] which enhanced a rapid development in the design of catalyst systems/initiators for the ROP of a wide variety of monomers.[2-13] Above-mentioned Pruitt-Baggett catalyst[1,3] was followed by the development of aluminum- and zinc-based catalyst systems (for example; $AlEt_3$-H_2O-acetylacetone and Et_2Zn-H_2O, respectively),[2] double metal cyanide (DMC) catalysts[4] and organotin phosphate condensate catalysts such as $^{n}Bu_2SnO$-$^{n}Bu_3PO_4$.[5] Among various oxirane monomers, ROP of PO has been often studied from the viewpoint of stereochemical control during the polymerization.[1-3,5-6] Recently, Coates and coworkers achieved the synthesis of isotactic poly(PO) ([*mm*] > 99%) with high molecular weight by using cobalt catalyst.[6] However, the catalytic activity was not so high in comparison with Fe-, Al-, Zn- and Sn-based catalyst. Moreover, the application of the cobalt catalyst was restricted to PO, because other oxirane monomers were not polymerizable with this system. The polymerization of oxirane monomers other than PO is highly desirable because of attractive properties and promising applications in the resulting polymers; many effective catalysts for this purpose have been thus reported.[7-12] High molecular weight poly(isobutylene oxide) was prepared by using a ternary catalyst system composed of $ZnEt_2$, H_2S and cyclohexylamine.[8] Moreover, various organotin phosphate condensate catalysts were effective for ROP of epichlorohydrin,[9] the ROP of 3,3,3-trifluoro-1,2-epoxypropane using organozinc compound[11] or aluminate complex[12] afforded polyether which possessed unique properties derived from fluorine atoms. In this chapter, the effect of steric bulk of various oxirane monomers toward their reactivity in the ROP using the organotin phosphate condensate catalyst has been examined (Scheme 1-1). Moreover, I wish to demonstrate a selective synthesis of polyether containing oxirane ring in the side chain by adopting selective ROP of the bifunctional monomer containing two oxirane

moieties with different reactivity (Scheme 1-2).

Scheme 1-1



Scheme 1-2



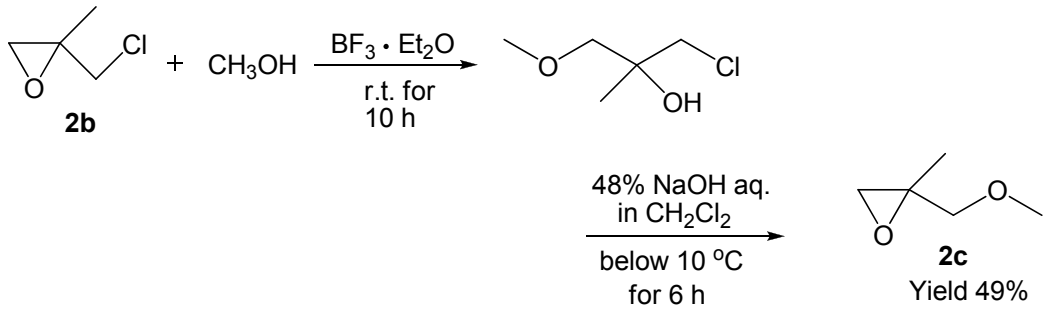
Results and Discussion

1. Synthesis of oxirane monomers

1-1. Synthesis of methyl 2-methylglycidyl ether (2c)

Methyl 2-methylglycidyl ether (**2c**) was prepared by acid-catalyzed ring-opening of oxirane (**2b)** with methanol and subsequent intramolecular nucleophilic substitution leading to ring closure (Scheme 1-3). The product resulting from the nucleophilic substitution of Cl atom was by-produced if reaction of **2b** with methanol is carried out in alkaline medium leading to the lower yield of **2c**. Monomer **2c** was characterized by ^{1}H and ^{13}C NMR spectra, FT-IR spectrum and mass spectrometry. The IR spectrum showed characteristic vibrations of epoxide (ν_{asym} = 899, ν_{sym} = 1263 cm^{-1}).

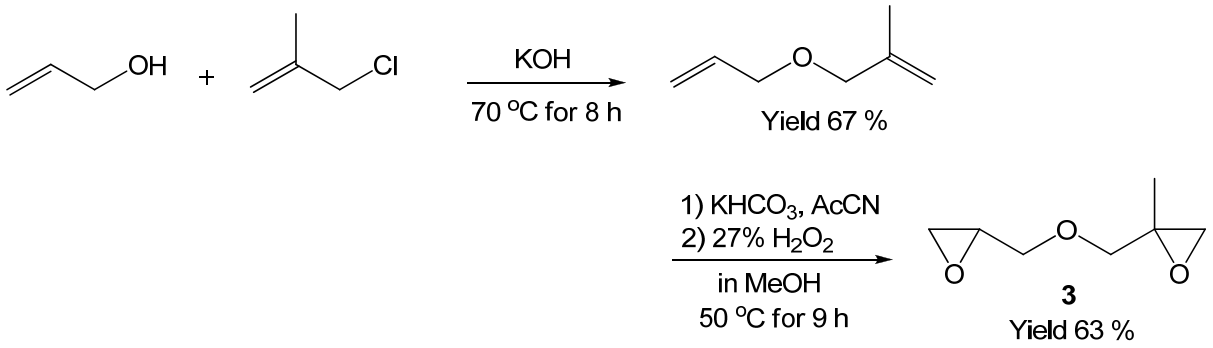
Scheme 1-3



1-2. Synthesis of glycidyl 2-methylglycidyl ether (3)

Allyl methallyl ether, the product in the first step, was prepared in 67% yield by Williamson ether synthesis, and the subsequent epoxidation with hydrogen peroxide afforded glycidyl 2-methylglycidyl ether (**3**) in 63% yield (Scheme 1-4). The yield decreased (yield 43%) if the epoxidation of allyl methallyl ether was conducted by using peracetic acid. The monitoring the epoxidation by gas chromatography revealed that no significant differences were seen in the epoxidation rates of both allyl ether and methallyl ether (Figure 1-1). The structure of **3** was confirmed by ^{1}H and ^{13}C NMR spectra, FT-IR spectrum and mass spectrometry. The IR spectrum showed characteristic vibrations of epoxide; ν_{asym} = 899, ν_{sym} = 1261 cm^{-1}.

Scheme 1-4



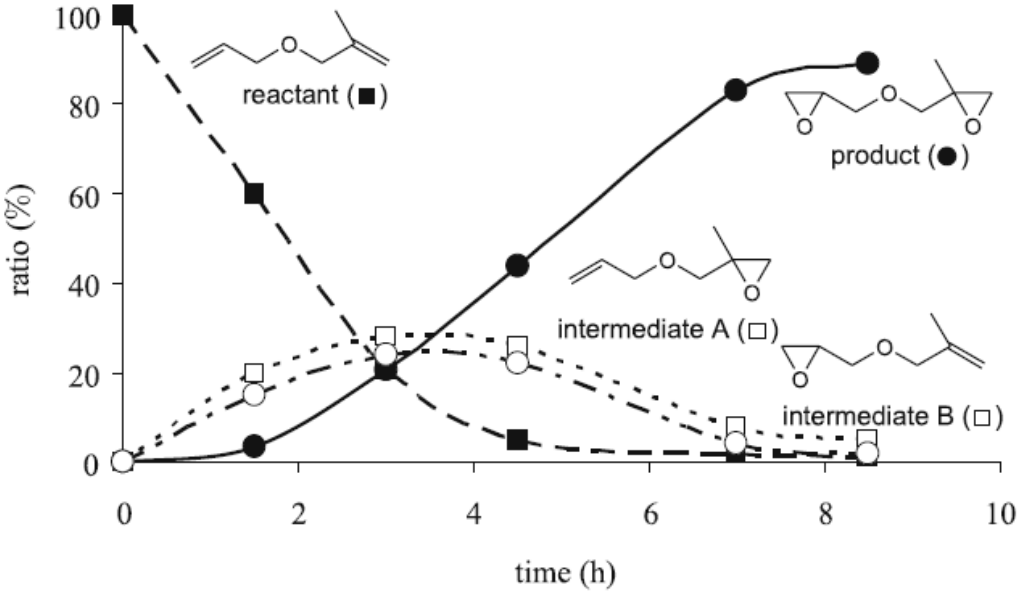
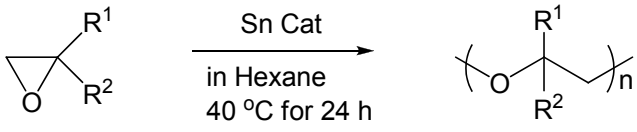


Figure 1-1. Monitoring of epoxidation by GC (■: reactant, □: intermediate A, ○: intermediate B, ●: product)

2. Ring-opening polymerization (ROP) of various epoxide monomers using organotin phosphate condensates

As depicted in Scheme 1-5, polymerizations of various epoxide monomers of the type, 2,2-R^1,R^2-CCH_2O [R^1 = H (**1**), Me (**2**); R^2 = Me (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)] were conducted in the presence of organotin phosphate condensate. The results are summarized in Table 1-1.

Scheme 1-5



R^1= H (**1**), Me (**2**)
R^2= Me (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)

The resultant polymers possessed ring-opened structure confirmed by ^1H and ^{13}C NMR spectra. Ring-opening polymerization (ROP) of monosubstituted epoxide **1a** reached to completion after 24 h, affording high molecular weight polymer (M_n = 9.49×10^4). In

contrast, the polymer yield as well as the molecular weight in the resultant polymer was considerably lower in ROP of disubstituted monomer **2a**, which would be explained due to the greater steric bulk of **2a** than that of **1a**.

Table 1-1. Ring-opening polymerization of oxiranes, 2,2-R^1,R^2-CCH_2O [R^1 = H (**1**), Me (**2**); R^2 = Me (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)] and glycidyl 2-methylglycidyl ether (**3**) by organotin phosphate condensate.[a]

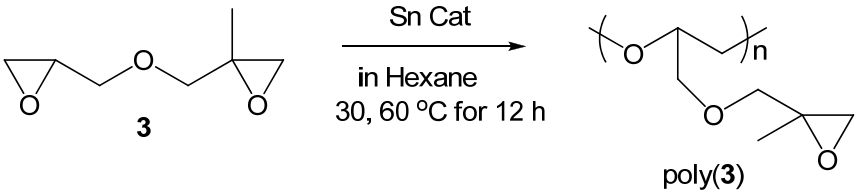
run	monomer (R^1, R^2)	temp. / ºC	time / h	yield / g (%)	M_n[b] $\times 10^{-4}$	M_w/M_n[b]
1	**1a** (CH_3, H)	40	24	3.95 (99)	9.49	4.9
2	**2a** (CH_3, CH_3)	40	24	0.66 (17)	0.25	2.0
3	**1b** (CH_2Cl, H)	40	24	2.76 (69)	10.60	4.8
4	**2b** (CH_2Cl, CH_3)	40	24	trace	--	--
5	**2b** (CH_2Cl, CH_3)	60	24	trace	--	--
6	**1c** (CH_2OCH_3, H)	40	24	3.94 (99)	1.63	3.0
7	**2c** (CH_2OCH_3, CH_3)	40	24	trace	--	--
8	**2c** (CH_2OCH_3, CH_3)	60	24	trace	--	--
9	**3**	30	12	3.40 (85)	9.17	3.6
10	**3**	60	12	3.83 (96)	5.60	5.7

[a]Conditions: Sn cat 1.0 wt% for monomers (runs 1-8), 1.5 wt% (runs 9-10), monomer 4.0 g, initial monomer conc.= 4.2 mol/L, *n*-hexane. [b]GPC data in DMF *vs.* polystyrene standards.

The steric effect was pronounced in the ROP of disubstituted monomers **2b**, **2c** with increased steric bulk; the ROP did not take place with the present catalyst system (runs 4,7), moreover at the higher temperature (runs 5,8). Although it was widely known that the ROP of oxiranes strongly depends on the temperature,[14] the effect of the temperature was not seen in this range (40-60 ºC). On the other hand, ROP of monosubstituted monomers **1b** and **1c** afforded the polymers in 69% and 99% yields, respectively. The results clearly suggest that monosubstituted oxirane monomers display higher reactivity toward the present catalyst system than their disubstituted counterparts. The molecular weights of poly(**1a**) and poly(**1b**) were close, whereas the M_n value for poly(**1c**) was much low, although I do not have

any appropriate reason to explain the observed difference at this moment. Taking into account the above results, selective synthesis of polyethers containing epoxy ring in the side chain was considered by the selective ROP of bifunctional monomer containing both mono- and disubstituted epoxide moieties in the presence of organotin catalyst. The ROPs of **3** were thus examined in *n*-hexane and polymers were obtained in 85 % (30 ºC, run 9) and 96 % (60 ºC, run 10), respectively (Scheme 1-6).

Scheme 1-6



The both resultant polymers were almost easily soluble in common organic solvents such as, benzene, toluene and DMF. The solubility of the poly(**3**) in DMF allowed the determination of its M_n by GPC {9.17×10^4 (run 9), 5.60×10^4 (run 10)}, and the M_n value (9.17×10^4) was not very different from those of poly(**1a**) and poly(**1b**). The result suggests that polymer is formed by ring opening of (most probably the less bulky) one oxirane group selectively. On the other hand, the lower M_n value (5.60×10^4) would be due to increased active sites for the ROP by higher temperature (60 ºC), not cross-linking by the ring-opening of both mono- and disubstituted epoxide, because the ROP of both **2b** and **2c** at 60 ºC (runs 5,8) afforded negligible amount of polymer. In addition, the better solubility of the resultant polymer should rule out the possibility of any cross-linking accompanied due to ring opening of both the oxirane moieties. The fact was also confirmed by the ^{1}H and ^{13}C NMR spectra as well as the FT-IR spectrum of the polymer (Figure 1-2, Figure 1-3).

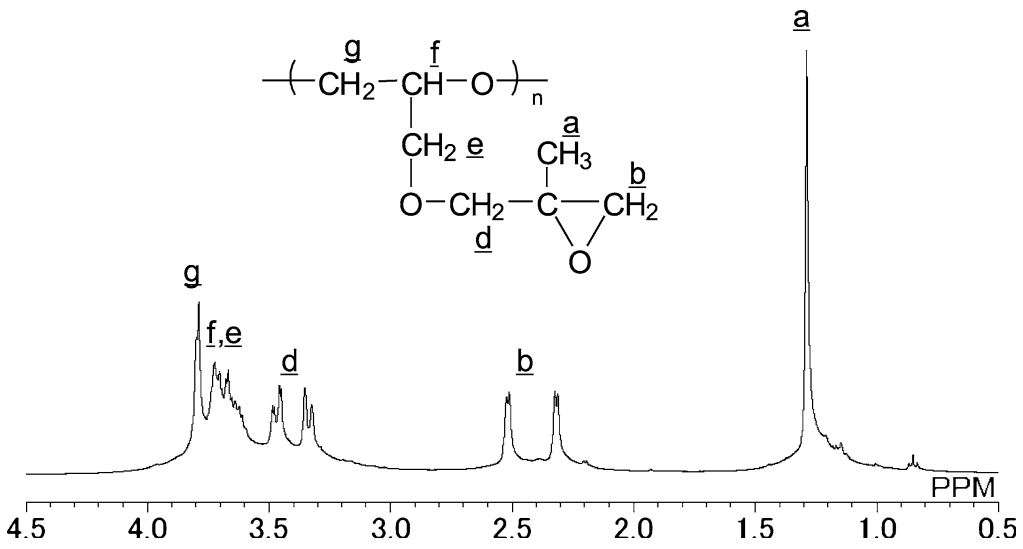


Figure 1-2. ^{1}H NMR spectrum of poly(**3**) (400 MHz, benzene-d_6, 50 ºC).

The two doublet peaks around 2.32 and 2.52 ppm are observed in ^{1}H NMR spectrum of the polymer with integration ratio of 1:1. The presence of these peaks clearly indicates the presence of disubstituted oxirane moiety in the resulting polymer thus suggesting the selective ROP of the bifunctional monomer **3**.

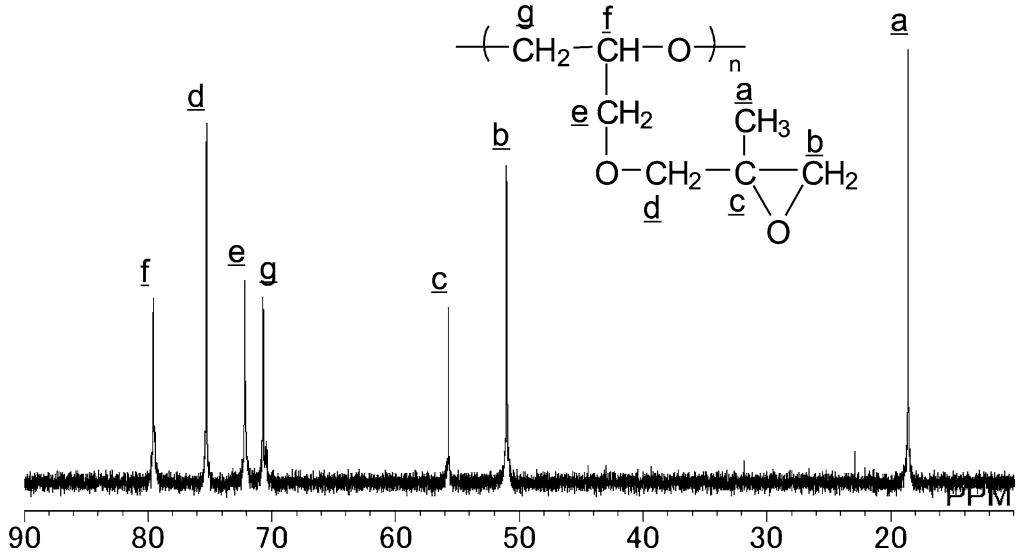


Figure 1-3. ^{13}C NMR spectrum of poly(**3**) (100 MHz, benzene-d_6, 50 ºC).

Moreover, the peak at 51.0 ppm in ^{13}C NMR is also assigned to methylene carbon in the intact epoxy ring. IR spectrum of the polymer furnished further evidence for the presence of epoxy ring the polymer as showed by the presence of peaks around ν_{sym} = 1261, ν_{asym} = 897 cm^{-1}. DSC of the resultant polymer indicated that ΔH_m could not be detected and glass transition point (T_g) was found to be -48 ºC. The polyether is expected to act as the precursor for the formation of various functional polymers by the introduction of a variety of substitutents in the side chain using the reaction chemistry of epoxide moiety. Moreover, this kind of polymer is anticipated to find application as elastomer without the requirement of cross-linkers.

Conclusions

Organotin phosphate ($^{n}Bu_2SnO$-$^{n}Bu_3PO_4$) condensate mediateded the ring-opening polymerization of **1a-c** and **2a-c**. The ROP of monosubstituted oxiranes (**1a-c)** reached to high conversion, whereas the conversion of the bisubstituted (**2a-c**) was considerably lower. Consequently, the polymerization of glycidyl 2-methylglycidyl ether (**3**) with both mono- and disubstituted oxirane groups was carried out resulting in the formation of polyether containing oxirane ring in the side chain in moderate yield.

Experimental Section

General Procedures.

Dibutyltin oxide, tributyl phosphate, 2-propen-1-ol and 3-chloro-2-methyl-1-propene were purchased from Aldrich Chemical Co. and were used as received. Racemic propylene oxide (**1a**) and 2,2-dimethyloxirane (**2a**) were refluxed over a mixture of potassium hydroxide and calcium dihydride, and then fractionally distilled under nitrogen atmosphere. Epichlorohydrin (**1b**), β-methylepichlorohydrin (**2b**), 2-methylglycidyl ether (**2c**) and glycidyl 2-methylglycidyl ether (**3**) were transferred into bottles containing molecular sieves (a

mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 stream, the solution was shaken for 10 min, and passed through a short alumina column. Glycidyl methyl ether (**1c**) was purified by vacuum distillation using fractionating column and the same purification procedure was employed for **1b, 2b,** and **2c**. All other chemicals used were of reagent grades and purified by standard purification procedures. All ^{1}H and ^{13}C NMR spectra of the resultant polymers were measured in benzene-d_6 at 50 ºC on a JEOL ECP-400 spectrometer (^{1}H 400 MHz and ^{13}C 100 MHz). Chemical shifts were referred to the peak of benzene-d_6 at 7.15 ppm for ^{1}H, and 128.0 ppm for ^{13}C. Gel permeation Chromatography (GPC) measurements were performed on an Shimadzu gel permeation chromatography system equipped with the columns Shodex KD807, KD806, KD806M and KD803 at 60 ºC using DMF as the eluent with a flow rate of 1.0 mL/min. All measurements were calibrated *vs.* polystyrene standards. Infrared spectroscopy (IR) spectra were measured on a FT-730 spectrometer (HORIBA) at room temperature. Differential scanning calorometry (DSC) thermograms were measured on Perkin-Elmer 7 Series Thermal Analysis System. High resolution mass spectrometry (HRMS) was measured using positive electrospray ionization (m/z values are given) on JMS-700 (JEOL).

Preparation of Bu_2SnO-Bu_3PO_4 condensates

A mixture of $^{n}Bu_2SnO$ (4.0 g, 16 mmol) and $^{n}Bu_3PO_4$ (8.5 g, 32 mmol) was stirred and heated at 250 ºC for 20-30 min under dry nitrogen atmosphere. Removal of the by-products (butane, butene, 1-butanol, and dibutyl ether) from the mixture afforded the titled condensate (white solid) until the by-products didn't evolve any more. The condensate was insoluble in a variety of organic solvents because of the formation of network structure. The condensate is assumed to have the following structure (Figure 1-4).[9]

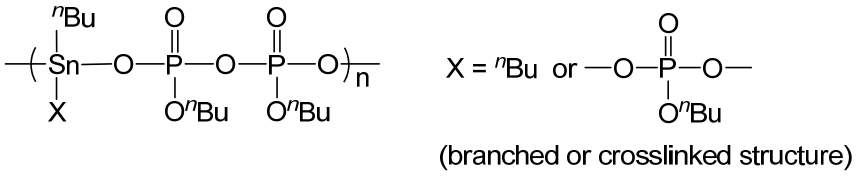


Figure 1-4. Plausible structure of organotin phosphate condensate.

Synthesis of methyl 2-methylglycidyl ether (2c)

Into a 3L separable flask containing MeOH (481 g, 15.0 mol) and $BF_3{\cdot}Et_2O$ (4.74 g, 30.0 mmol), which was precooled to 10 ºC, β-methylepichlorohydrin (**2b**) (320 g, 3.0 mol) was added dropwise over a period of 2 h. The solution was stirred for 8 h at the same temperature (10 ºC), and the organic solvents in the mixture were then removed *in vacuo* using rotary evaporator. The resultant liquid was added CH_2Cl_2 (980 mL) and cooled to 10 ºC, and 48% NaOH aq. (292 g, 3.5 mol) was then added dropwise over 2 h; the resultant suspension was stirred for 4 h at the same temperature. The organic layer was then separated and the aqueous layer was extracted with CH_2Cl_2 (150 mL × 3). All organic layers were combined and washed with 3% HCl aq. (200 mL × 2). Removal of CH_2Cl_2 afforded the crude product **2c**, which was further purified by distillation *in vacuo* equipped with a fractionating column (yield 49%). Purified **2c** was a colorless liquid (boiling point 39 ºC/47 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 3H, *Me*), 2.18 (d, *J* = 5 Hz, 1H, *CH2* in epoxy ring), 2.34 (d, *J* = 5 Hz, 1H, CH_2 in epoxy ring), 3.03 (d, *J* = 11 Hz, 1H, CH_2OCH_3), 3.09 (s, 3H, OCH_3), 3.17 (d, *J* = 11 Hz, 1H, CH_2OCH_3). ^{13}C NMR ($CDCl_3$): δ 18.3, 50.7, 55.4, 58.7, 76.3. IR (neat): 806, 899, 1115, 1196, 1263, 2927, 2987, 3047 cm^{-1}. HRMS Calcld. for $C_5H_{10}O_2$, 102.0681; Found, 101.0604 $[M\text{-}H]^+$.

Synthesis of glycidyl 2-methylglycidyl ether (3)

Preparation of 3-allyloxy-2-methyl-1-propene

3-propenol (482 g, 8.3 mol) and KOH (628 g, 11.2 mol) were added into a 3L separable flask and the mixture was stirred at room temperature for 1 h. The resultant suspension was heated up to 70 ºC and 3-chloro-2-methylpropene (996 g, 11.0 mol) was

added slowly over a period of 5 h. The reaction mixture was further stirred under the same reaction conditions for 3 h, and the flask was cooled to room temperature. The salt formed was filtered off using a glass filter, and the filtrate was rinsed with diethyl ether (200 mL). The filtrate was washed with water (100 mL × 3) and the organic layer was dried over Na_2SO_4. 3-Allyloxy-2-methyl-1-propene with pure form was obtained by distillation (Yield 67%).

Preparation of glycidyl 2-methylglycidyl ether (3)

Into a 3L separable flask, 3-allyloxy-2-methyl-1-propene (150 g, 1.34 mol), acetonitrile (330 g, 8.04 mol), $KHCO_3$ (107 g, 1.07 mol) and methanol (300 mL) were added. The mixture was heated up to 50 ºC, and 27 % H_2O_2 (438 g, 3.48 mol) aq. was then added slowly over a period of 6 h. The resulting heterogeneous mixture was stirred for 3 h under the same reaction conditions, and the solution was cooled to room temperature. Cold water (300 mL) was then added into the mixture, and the resulting suspension was extracted with CH_2Cl_2 (150 mL × 2); the organic layer was washed with water (100 mL × 3), and then 0.1N $NaHSO_3$ aq. (100 mL × 3) and was dried over Na_2SO_4. The vacuum distillation of the crude **3** afforded a pure sample in 63% yield as colorless liquid (boiling point 85 ºC/8 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.16 (s), 1.18 (s, total 3H), 2.13-2.19 (m, 2H), 2.26-2.28 (m, 1H), 2.35-2.38 (m, 1H), 2.78-2.84 (m, 1H), 3.06-3.21 (m, 2H), 3.29-3.47 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 18.27, 18.30, 43.37, 43.40, 50.52, 50.58, 50.68, 50.78, 55.48, 55.52, 72.07, 72.30, 74.79, 75.08. IR (neat): 800, 899, 1105, 1261, 1286, 2927, 2964, 3054 cm^{-1}. HRMS Calcld. for $C_7H_{12}O_3$, 144.0786; Found, 143.0707 $[M-H]^+$.

Polymerization of 1a-c and 2a-c

Polymerizations of monomers **1a-c** and **2a-c** were conducted as follows: ^{n}Bu_2SnO-^{n}Bu_3PO_4 condensate (40 mg) was dried in a glass ampoule at 150 ºC for 1 h *in vacuo* prior to use. Into a Schlenk tube containing the pretreated ^{n}Bu_2SnO-^{n}Bu_3PO_4 condensate (40 mg), *n*-hexane (9.1 mL) and **1a** (4.0 g) were added at room temperature.

Polymerization was conducted at 40 ºC for 24 h. The polymerization was then terminated by adding methanol, and the resultant polymer was dissolved in benzene and insoluble initiator residue was removed by centrifugation. The ring-opened polymer was then collected from the benzene solution by removing the volatiles *in vacuo*.

Polymerization of glycidyl 2-methylglycidyl ether (3)

Polymerization of glycidyl 2-methylglycidyl ether (**3**) was conducted as follows: $^{n}Bu_2SnO$-$^{n}Bu_3PO_4$ condensate (60 mg) was dried in a glass ampoule at 150 ºC for 1 h *in vacuo* prior to use. Into a Schlenk tube containing the pretreated condensate, *n*-hexane (9.1 mL) and **3** (4.0 g) were added, and polymerization was performed at 30 ºC for 12 h. The polymerization was quenched by adding methanol, and the resultant polymer was dissolved in benzene and insoluble initiator residue was removed by centrifugation. The polymer was collected from the benzene solution by removing volatiles *in vacuo*. ^{1}H NMR (C_6D_6): δ 1.29 (s, 3H), 2.32 (d, 1H), 2.52 (d, 1H), 3.33-3.49 (m, 2H), 3.62-3.80 (m, 5H). ^{13}C NMR (C_6D_6) : δ 18.59, 51.04, 55.72, 70.72, 72.20, 75.31, 79.59. IR (solid) 804, 897, 1082, 1105, 1261, 2924, 2958 cm^{-1}.

References

1. Pruitt, M. E.; Jackson, L. J.; Baggett, M. U.S. Patent 2706181, 1955.
2. (a) Furukawa, J.; Tsuruta, T.; Sakata, R.; Saegusa, T.; Kawasaki, A.; Makromol. Chem. **1959**, *32*, 90. (b) Tani, H.; Takeo, A.; Oguni, N.; Ueyama, N. *J. Am. Chem. Soc.* **1967**, *89*, 173. (c) Vandenverg, E. J. *J. Polym. Sci. A-1* **1969**, *7*, 525. (d) Oguni, N.; Watanabe, S.; Maki, M.; Tani, H. *Macromolecules* **1973**, *6*, 195. (e) Coulon, C.; Spassky, N.; Sigwalt, P. *Polymer* **1976**, *17*, 821. (f) Buys, H. C. W. M.; Overmars, H. G. J.; Noltes, J. G.; Price, C. C.; Vandenverg, E. J. *Coordination Polymerization*; Plenum Publishing Corporation: New York, 1983. (g) Wu, B.; Harlan, C. J.; Lenz, R. W.; Barron, A. R. *Macromolecules* **1997**, *30*, 316. (h) Öktem, Z.; Alyürük, K. *Polymer* **1998**, *39*. 583.
3. Takrouri, F.; Alyürük, K. *Polymer* **1994**, *35*, 1518.
4. (a) Herold, R. J. U. S. Patent 3278459, 1966. (b) Kuyper, J.; Boxhoorn, G. *J. Catal.* **1987**, *105*, 163. (c) Wu, L. C.; Yu, A. I.; Zhang, M.; Liu, B. H.; Chen, L. B. *J. Appl. Polym. Sci.* **2004**, *92*, 1302. (d) Kim, I.; Ahn. J. T.; Ha, C. S.; Yang, C. S.; Park, I. *Polymer* **2003**, *44*, 3417.
5. (a) Miura, K.; Kitayama, T.; Hatada, K.; Nakata, T. *Polym. J.* **1993**, *25*, 685. (b) Schütz, C.; Dwars, T.; Schnorpfeil, C.; Radnik, J.; Menzel, M.; Kragl, U. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3032.
6. Peretti, K. L.; Ajiro, H.; Cohen, C. T.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 11566.
7. Kamio, K.; Kuwana, M.; Nakada, S. U.S. Patent 3509074, 1970.
8. Boor, J.; Bauer, S. *J. Appl. Polym. Sci.* **1974**, *18*, 3699.
9. Otera, J.; Yano, T.; Kunimoto, E.; Nakata, T. *Organometallics* **1984**, *3*, 426.
10. Xie, H. Q.; Guo, J. S.; Yu, G. Q.; Zu, J. *J. Appl. Polym. Sci.* **2000**, *80*, 2446.
11. (a)Umezawa, J.; Hagiwara, T.; Hamana, H.; Narita, T.; Furuhashi, K.; Nohira, H. *Macromolecules* **1995**, *28*, 833. (b) Ikeda, Y.; Yoshida, Y.; Ishihara, K.; Hamana, H.;

Narita, T.; Hagiwara, T. *Macromol. Rapid Commun.* **1996**, *17*, 713.

12. Sakakibara, K.; Nakano, K.; Nozaki, K. *Macromolecules* **2007**, *40*, 6136.

13. (a) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013. (b) Rexin, O.; Mülhaupt, R. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 864. (c) Braune, W.; Okuda, J. *Angew. Chem. Int. Ed.* **2003**, *42*, 64. (d) Chakraborty, D.; Rodriguez, A.; Chen, E. Y. X. *Macromolecules* **2003**, *36*, 5470. (e) Huang, Y. J.; Qi, G. R.; Wang, Y. H. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1142. (f) Labbe, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. *Macromolecules* **2007**, *40*, 7842.

14. (a) Vinogradova, L. V.; Sgonnik, V. N.; Ilina, A. A. *Macromolecules* **1992**, *25*, 6733. (b) Nelles, G.; Tsvetanov, C. *et al.* EP 1840150 A1, 2007.

Part II

Design and Synthesis of Efficient Aluminum Complex Catalysts for Precise Ring-Opening Polymerization of Cyclic Esters

Chapter 2

Synthesis of Al complexes containing phenoxy-imine ligands and their use as the catalyst precursors for efficient living ring-opening polymerisation of ε-caprolactone

Abstract

Al complexes containing phenoxy-imine ligands of type, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^1 = Me, R^2 = 2,6-$^{i}Pr_2C_6H_3$ (**1a**), ^{t}Bu (**1b**); R^1 = ^{t}Bu, R^2 = 2,6-$^{i}Pr_2C_6H_3$ (**2a**), ^{t}Bu (**2b**), cyclohexyl (**2c**), adamantyl (**2d**), C_6H_5 (**2e**), 2,6-$Me_2C_6H_3$ (**2f**), C_6F_5 (**2g**)] have been prepared in high yields from $AlMe_3$ by treating with 1.0 equiv. of 2-R^1-6-$(R^2N{=}CH)C_6H_3OH$ in *n*-hexane. Structures for **1a**, **1b**, **2a–e** and **2g** were determined by X-ray crystallography, and these complexes have a distorted tetrahedral geometry around Al; both the Al–O and the Al–N bond distances were influenced by substituents in both the aryloxo and the imino groups. $Me_2Al[\mu_2\text{-}O\text{-}2\text{-}(R^2N{=}CH)C_6H_4](AlMe_3)$ [R^2 = 2,6-$^{i}Pr_2C_6H_3$(**3a**), ^{t}Bu (**3b**)] were prepared exclusively by reaction of $AlMe_3$ with 2-$(R^2N{=}CH)C_6H_4OH$, and these complexes form a distorted tetrahedral geometry around each Al centre with additional $AlMe_3$ coordinating to the oxygen in the phenoxy-imine ligand. Complexes **1a**, **1b** and **2a–g** were tested as catalyst precursors for ring-opening polymerisation (ROP) of ε-caprolactone (CL) in the presence of ^{n}BuOH (1.0 equiv. to Al), and their catalytic activities were strongly influenced by the imino substituent (R^2). The efficient ROP has been achieved using the C_6F_5 analogue (**2g**), with the ROP taking place in a living manner.

Introduction

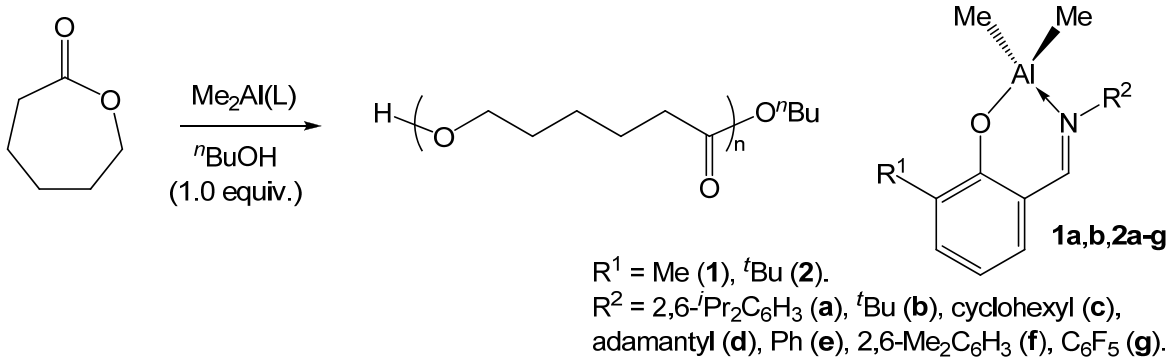
Organoaluminum compounds are known to be important reagents widely employed in organic synthesis,[1] olefin polymerization catalysis,[2] and as initiators for ring-opening polymerization (ROP) of cyclic esters, such as lactones and lactides.[3] It has been observed that the introduction of extremely bulky aryloxide ligands to aluminum generates monomeric Lewis acid catalysts that have been employed in a variety of organic transformations.[4] Moreover, Al alkoxides have been known to polymerize cyclic esters[3] such as lactides,[5] lactones,[5j,5n,6] and certain aliphatic polyesters possessing promising characteristics as biodegradable and bioassimilable materials, not only due to their practical biodegradability in light of recent concerns with the environment, but also due to their biocompatibility for medical and pharmaceutical applications.[7] Therefore, considerable attention has been paid to the synthesis and structural determinations of monomeric/dimeric Al complexes.[8]

Among examples concerning Al-initiated ROP of lactides[5] and lactones,[5j,5n,6] I had an interest in the fact that *in situ* catalyst systems consisting of $AlEt_3$ and 2 equiv. of salicylaldimines, 2,4-R^1_2-6-{(2,4,6-$R^2_2C_6H_3$)N=CH}C_6H_2OH [R^1, R^2 = alkyl, aryl, halogen], in the presence of $PhCH_2OH$ showed moderate catalytic activity for ROP of ε-caprolactone (CL) in a living manner.[6j] This is not only because no detailed mechanistic studies for the catalytically active species including isolation of the Al complexes have been reported,[9] but also because it was reported that an electronic effect of the imino substituent (aromatic or aliphatic *etc.*) was not important; the fact seemed to be related to a description that the electrophilicity of the metal centre is much less important for the ROP of lactones.[6g,i] In contrast, it has been known that the catalytic activity, molecular weight for the resultant polymers, and the polymerization behavior for ethylene (and/or propylene) polymerization using a series of zirconium complexes containing bis(phenoxy)imine ligands were highly affected by substituents on both the phenoxy and the imino groups.[10,11]

This chapter deals with the synthesis and structural analysis of a series of four

coordinate $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^1 = Me (**1**), ^{t}Bu (**2**); R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**a**), ^{t}Bu (**b**), cyclohexyl (**c**), adamantyl (**d**), C_6H_5 (**e**), 2,6-$Me_2C_6H_3$ (**f**), C_6F_5 (**g**)]. Further, the reaction of $AlMe_3$ with 2-$(R^2N{=}CH)C_6H_4OH$ was examined for comparison. This chapter also deals with explored their possibilities as the initiators for ROP of CL in the presence of ^{n}BuOH (1.0 equiv.), including ligand effect toward the catalytic activity (TON) (Scheme 2-1).

Scheme 2-1



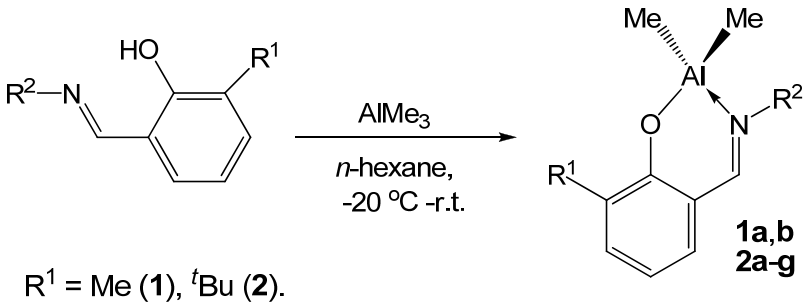
Results and Discussion

1. Synthesis and structural analysis of various aluminum complexes containing phenoxy-imine ligand of type, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$.

A series of aluminum complexes containing phenoxy-imine ligands of the type, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^1 = Me (**1**), ^{t}Bu (**2**); R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**a**), ^{t}Bu (**b**), cyclohexyl (**c**), adamantyl (**d**), C_6H_5 (**e**), 2,6-$Me_2C_6H_3$ (**f**), C_6F_5 (**g**)], were prepared by reaction of $AlMe_3$ with 1.0 equiv. of corresponding 2-R^1-6-$(R^2N{=}CH)C_6H_3OH$ in *n*-hexane as shown in Scheme 2-2. These reactions took place along with evolution of methane, and the analytically pure samples were collected from the chilled concentrated *n*-hexane solution containing Al complexes placed in the freezer (-20 ºC). The resultant complexes were identified by ^{1}H and ^{13}C NMR spectra and elemental analysis. The ^{1}H NMR spectra of these complexes showed no complexity; a sharp single resonance assigned to the Al-*Me* protons (at

-0.16 to -0.30 ppm), a resonance ascribed to the $R^2N=CH$ proton (at 7.22-7.78 ppm, s), as well as resonances corresponding to the ligand were observed. The resultant complexes were also identified by elemental analyses. Crystals suitable for the crystallographic analysis were grown from the chilled concentrated *n*-hexane solution containing **1a,1b, 2a-e** and **2g**, and their structures could be determined by X-ray crystallography as the monomeric four coordinate species as described below.

Scheme 2-2



R^1 = Me (**1**), ^{t}Bu (**2**).
R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**a**), ^{t}Bu (**b**), cyclohexyl (**c**), adamantyl (**d**), Ph (**e**), 2,6-Me$_2$C$_6$H$_3$ (**f**), C$_6$F$_5$ (**g**).

Structures for **1a** and **1b** are shown in Figure 2-1 and the selected bond distances and angles for **1a** and **1b** are summarized in Table 2-1. The crystal structure of **1a** (Figure 2-1 left) showed that **1a** folds a distorted tetrahedral geometry around the Al metal center, as seen in the bond angles for C(1)-Al-C(2) [116.61(15)º], O(1)-Al-C(1) [111.89(11)º], and O(1)-Al-C(2) [111.20(10)º], although the O(1)-Al-N(1) bond angle is somewhat small [93.68(7)º]; these bond angles are somewhat analogous to those in Me$_2$Al[O-2,4-^{t}Bu$_2$-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_2$] reported previously [115.1(2), 114.0(2), 110.4(2) and 93.6(1)º, respectively].[8g] The Al-C bond distances [1.955(2), 1.949(3) Å] are also close to the reported values [1.959(5) and 1.948(5) Å).[8g] The Al-N bond distance in **1a** [1.9821(18) Å] is somewhat close or longer than those in the above 2,4-^{t}Bu$_2$ analogue [1.972 (3) Å],[8g] [ArNC(Me)CHC(Me)O]AlMe$_2$ [1.955(7) Å],[6e] but the distances are significantly

longer than those in EtAl[1,2-{N(PMes$_2$)}$_2$-C$_6$H$_4$] [1.863(1) Å, Mes = 2,4,6-Me$_3$C$_6$H$_2$],[6l] HC[SiMe$_2$N(4-MeC$_6$H$_4$)]$_3$Al(THF) [1.8300(9)-1.8458(9) Å].[8p] The results clearly suggest that the N atom does not form σ-bond with Al. The Al-O bond distance in **1a** [1.7688(17) Å] is somewhat shorter than those in the above reported 2,4-^{t}Bu$_2$ analogue [1.773(3) Å],[8g] [ArNC(Me)CHC(Me)O]AlMe$_2$ [1.795(5)Å].[6e] Although the bond distance is longer than that in Al-O^{i}Pr in {CH$_2$NMeCH$_2$C(CF$_3$)$_2$O}$_2$Al(O^{i}Pr) [1.699(3) Å],[6k] the above results suggest that the oxygen atom strongly coordinates to Al.

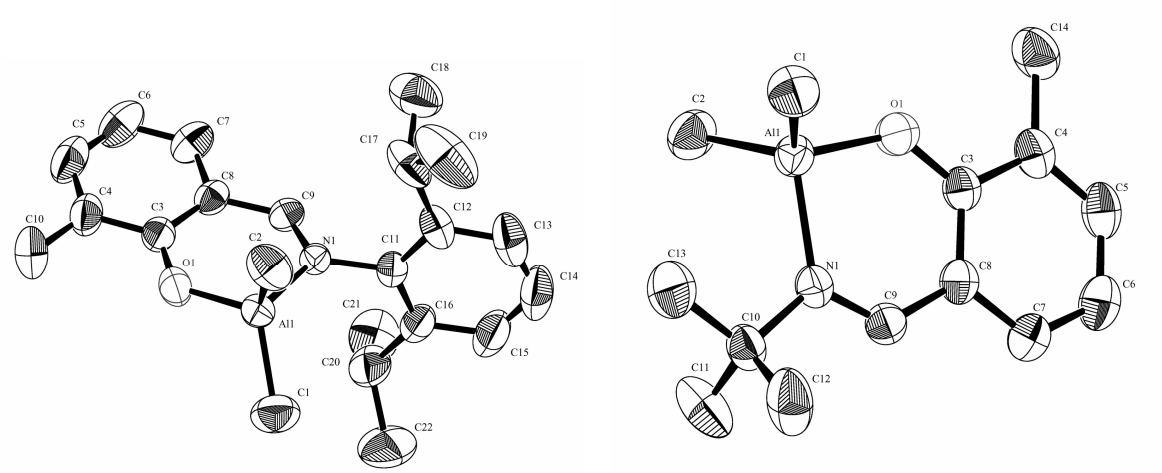


Figure 2-1. ORTEP drawings for Me$_2$Al[O-2-Me-6-(R^{2}N=CH)C$_6$H$_3$] [R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1a**, left), ^{t}Bu (**1b**, right)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

The structure for **1b** around Al atom is similar to that in **1a**, with **1b** forming a distorted four-coordinate tetrahedral geometry around Al. The O(1)-Al-C(1) [109.16(6)º], O(1)-Al-C(2) [110.79(7)º] bond angles are smaller that those in **1a** [111.89(11)º, 111.20(10)º, respectively], whereas the C(1)-Al-C(2) [116.91(8)º] and O(1)-Al-N(1) [95.66(5)º] bond angles are larger than those in **1a** [116.61(15)º and 93.68(7)º, respectively]. The Al-O distance in **1b** [1.7756(11) Å] is longer than in **1a** [1.7668(17) Å] and the Al-N distance [1.9797(13) Å] is shorter than in **1a** [1.9821(18) Å]. The observed differences would be due to an influence from the substituent in the imino group (2,6-^{i}Pr$_2$C$_6$H$_3$ *vs.* ^{t}Bu).

Table 2-1. Selected bond distances (Å) and angles (º) for $Me_2A[O\text{-}2\text{-}Me\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^2 = 2,6-$^{i}Pr_2C_6H_3$ (**1a**) and ^{t}Bu (**1b**)].

$R^1;R^2$	Me;2,6-$^{i}Pr_2C_6H_3$ (**1a**)	Me;^{t}Bu (**1b**)
	Bond Distances (Å)	
Al(1)-O(1)	1.7688(17)	1.7756(11)
Al(1)-N(1)	1.9821(18)	1.9797(13)
Al(1)-C(1)	1.955(2)	1.9607(19)
Al(1)-C(2)	1.949(3)	1.9640(19)
N(1)-C(9)	1.295(2)	1.2935(18)
N(1)-C(11)	1.455(2)	1.5142(18), N(1)-C(10)
	Bond Angles (º)	
O(1)-Al(1)-N(1)	93.68(7)	95.66(5)
C(1)-Al(1)-C(2)	116.61(15)	116.91(8)
Al(1)-O(1)-C(3)	130.81(12)	131.32(9)
Al(1)-N(1)-C(9)	122.24(13)	120.53(9)
Al(1)-N(1)-C(11)	120.69(14)	122.50(9), Al(1)-N(1)-C(10)
O(1)-Al(1)-C(1)	111.89(11)	109.16(6)
O(1)-Al(1)-C(2)	111.20(10)	110.79(7)
N(1)-Al(1)-C(1)	110.71(10)	112.53(6)
N(1)-Al(1)-C(2)	110.44(9)	109.76(6)

The structures for **2a** and **2b** are analogous to those of **1a** and **1b** as shown in Figure 2-2; these complexes also fold a four-coordinate, distorted tetrahedral geometry around Al metal center. The selected bond distances and angles for **2a** and **2b** are summarized in Table 2-2. The Al-O bond distances [1.7592(19), 1.762(2) Å] and the Al-N distances [1.975(2) and 1.972(2) Å] in **2a** and **2b** are somewhat shorter than those in **1a** and **1b** [1.7688(17), 1.7756(11) Å and 1.9821(18), 1.9797(13)Å, respectively], although no significant differences are seen in the Al-C bond distances.

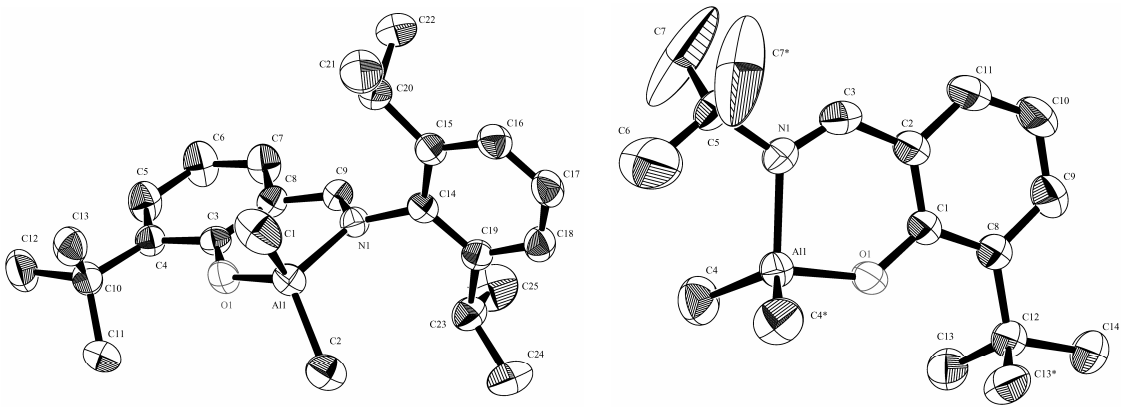


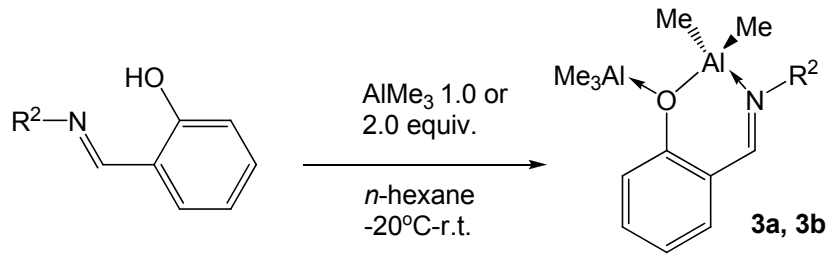
Figure 2-2. ORTEP drawings for $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^2 = 2,6-$^i Pr_2C_6H_3$ (**2a**, left), ^{t}Bu (**2b**, right)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 2-2. Selected bond distances (Å) and angles (º) for $Me_2A[O\text{-}2\text{-}^tBu\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^2 = 2,6-$^i Pr_2C_6H_3$ (**2a**) and ^{t}Bu (**2b**)].

R^1;R^2	Me;2,6-$^i Pr_2C_6H_3$ (**2a**)	Me;^{t}Bu (**2b**)
	Bond Distances (Å)	
Al(1)-O(1)	1.7592(19)	1.762(2)
Al(1)-N(1)	1.975(2)	1.972(2)
Al(1)-C(1)	1.949(3)	1.958(3) Al(1)-C(4)
Al(1)-C(2)	1.943(2)	1.958(3) Al(1)-C(4*)
N(1)-C(9)	1.296(3)	1.289(4) N(1)-C(3)
N(1)-C(14)	1.454(3)	1.526(4), N(1)-C(5)
	Bond Angles (º)	
O(1)-Al(1)-N(1)	93.70(9)	95.52(11)
C(1)-Al(1)-C(2)	115.96(14)	118.99(14), C(4)-Al-C(4*)
Al(1)-O(1)-C(3)	133.84(15)	133.9(2), Al(1)-O(1)-C(1)
Al(1)-N(1)-C(9)	122.24(17)	120.1(2), Al(1)-N(1)-C(3)
Al(1)-N(1)-C(14)	118.14(16)	122.4(2), Al(1)-N(1)-C(5)
O(1)-Al(1)-C(1)	110.41(13)	108.45(10), O(1)-Al(1)-C(4)
O(1)-Al(1)-C(2)	112.40(10)	108.45(10), O(1)-Al(1)-C(4*)
N(1)-Al(1)-C(1)	111.64(11)	111.38(10), N(1)-Al(1)-C(4)
N(1)-Al(1)-C(2)	110.61(11)	111.38(10), N(1)-Al(1)-C(4*)

Note that the reactions of $AlMe_3$ with 1.0 equiv. of 2-(R^2N=CH)C_6H_4OH [R^2 = 2,6-$^{i}Pr_2C_6H_3$ (**3a**), ^{t}Bu (**3b**)] in *n*-hexane afforded a mixture of the reaction product and the free ligand. The ratio was assumed to be 1:1 based on the ^{1}H NMR spectra, with resonances corresponding to protons for the Al-Me bond (in the ^{1}H NMR) were observed as a mixture of Al*Me*$_3$ (s, *ca.* -0.2 ppm, 9H) and the product (s, -0.4 ppm, 6H) identified by the integration ratios. Resonances ascribed to protons in 2-(R^2N=CH)C_6H_4OH were no longer observed when the reaction was performed with 2.0 equiv. of $AlMe_3$ in *n*-hexane. The reaction products were therfore identified as Me_2Al[O-2-(R^2N=CH)C_6H_4]($AlMe_3$) (**3**) based on ^{1}H, ^{13}C NMR spectra and elemental analyses (Scheme 2-3).

Scheme 2-3



R^2 = 2,6-$^{i}Pr_2C_6H3$ (**3a**), ^{t}Bu (**3b**)

Colorless block microcrystals of **3a** suitable for X ray crystallographic analysis were grown from the chilled-concentrated *n*-hexane solution; the structures for **3a** and **3b** were determined (Figure 2-3), and the selected bond distances and angles are summarized in Table 2-3.

The structure of **3a** folds a distorted tetrahedral geometry around each Al metal center, although O(1)-Al(1)-C(1) and O(1)-Al(1)-C(2) bond angles [115.38(11) and 107.66(9)º] are larger than O(1)-Al(2)-C(10) and O(1)-Al(2)-C(11) bond angles [100.81(12), 108.22(10)º]. The Al(1)-O(1) bond [1.8522(16)Å] in **3a** is longer than those in **1**-**2a** [1.7688(17), 1.7592(19) Å, Table 2-1 and Table 2-2), but Al(2)-O(1) bond [1.9761(19) Å] is

much longer than the Al(1)-O(1) bond. These results clearly indicate that the Al(1)-O(1) bond forms σ-bond and Al(2)-O(1) forms a π-bond. The structure for **3b** is analogous to that of **3a**, with $AlMe_3$ coordinating to oxygen in the $Me_2Al[O\text{-}2\text{-}(^tBuN{=}CH)C_6H_4]$ moiety. These results clearly indicate that the *ortho*-substituents in the phenoxy group play an important key role to generate/form mononuclear Al structure.

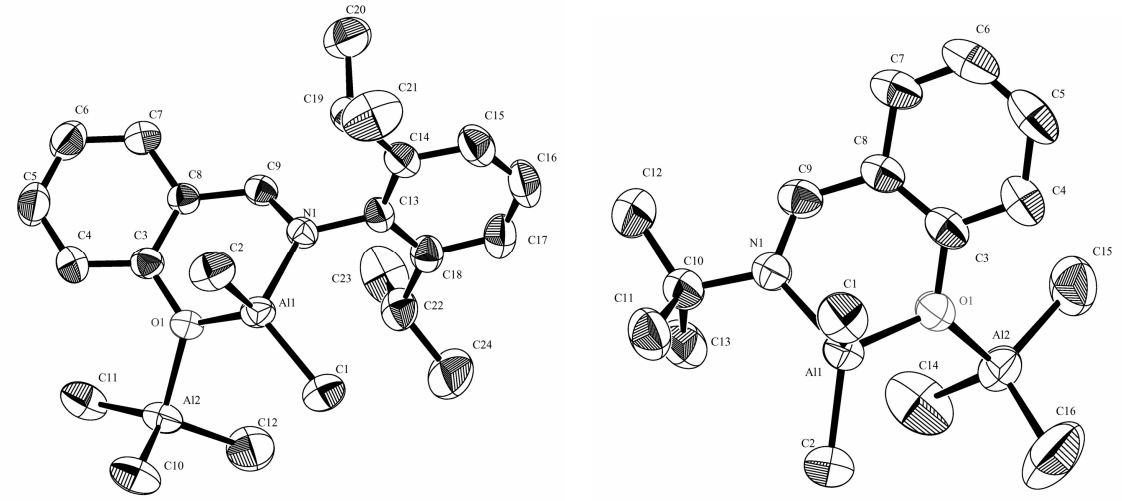


Figure 2-3. ORTEP drawings for $Me_2Al[\mu_2\text{-}O\text{-}2\text{-}(R^2N{=}CH)C_6H_4](AlMe_3)$ [R^2 = 2,6-$^iPr_2C_6H_3$ (**3a**, left), ^{t}Bu (**3b**, right)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

The observed differences in the structures for **1a** and **3a** would provide better explanations for the observed difference in the catalytic activity for the ring-opening polymerization (ROP) of ε-caprolactone using a mixed catalyst system consisting of $AlMe_3$ and iminophenols (1.0 equiv.) in the presence of ^{n}BuOH (1.0 equiv.), as shown in Table 2-4. Moreover, the activities of the catalyst systems consisting of $AlMe_3$ and 2-(^{t}BuN=CH)C_6H_4OH and 2-Me-6-(^{t}BuN=CH)C_6H_3OH were negligible under these conditions (runs 2 and 4); therefore, this suggests that the imino substituent strongly affects the activity.

Table 2-3. Selected bond distances (Å) and angles (º) for $Me_2Al[\mu_2\text{-}O\text{-}2\text{-}(R^2N{=}CH)C_6H_4](AlMe_3)$ [R^2 = 2,6-$^{i}Pr_2C_6H_3$ (**3a**) and ^{t}Bu (**3b**)].

R^1;R^2	Me;2,6-$^{i}Pr_2C_6H_3$ (**3a**)	Me;^{t}Bu (**3b**)
	Bond Distances (Å)	
Al(1)-O(1)	1.8522(16)	1.8477(16)
Al(1)-N(1)	1.9849(17)	1.988(2)
Al(1)-C(1)	1.941(2)	1.943(3)
Al(1)-C(2)	1.940(3)	1.939(3)
N(1)-C(9)	1.288(2)	1.289(2)
N(1)-C(13)	1.462(2)	1.515(3), N(1)-C(10)
Al(2)-O(1)	1.9761(19)	1.9564 (19)
O(1)-C(3)	1.386(2)	1.389(3)
	Bond Angles (º)	
O(1)-Al(1)-N(1)	91.80(6)	92.50(8)
C(1)-Al(1)-C(2)	118.71(12)	118.45(12)
Al(1)-O(1)-C(3)	113.49(15)	112.21(15)
Al(1)-N(1)-C(9)	118.88(13)	116.99(19)
Al(1)-N(1)-C(13)	123.54(11)	122.87(14), Al(1)-N(1)-C(10)
O(1)-Al(1)-C(1)	115.38(11)	109.79(10)
O(1)-Al(1)-C(2)	107.66(9)	110.48(11)
N(1)-Al(1)-C(1)	112.07(10)	104.78(12)
N(1)-Al(1)-C(2)	107.79(10)	117.70(12)
Al(1)-O(1)-Al(2)	124.87(7)	125.88(9)
O(1)-Al(2)-C(10)	100.81(12)	103.71(14), O(1)-Al(2)-C(14)
O(1)-Al(2)-C(11)	108.22(10)	106.66(12), O(1)-Al(2)-C(15)
C(10)-Al(2)-C(11)	115.04(11)	116.4(2), C(14)-Al(2)-C(16)
C(10)-Al(2)-C(12)	115.97(14)	115.41(19), C(15)-Al(2)-C(16)

As described below (in Table 2-4), the imino substituent siginificant affected the activity in the ROP. In contrast, importantly, the *ortho*-substituent in the phenoxide appears to be required for the generation of the catalyst precursors, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}\{(2,6\text{-}^{i}PrC_6H_3)N{=}CH\}C_6H_3]$, by eliminating the possibility of coordination with $AlMe_3$.

Table 2-4. Ring-opening polymerization of ε-caprolactone using catalyst systems consisting of $AlMe_3$ and 2-R^1-6-(R^2N=CH)C_6H_3OH [R^1 = H, Me; R^2 = 2,6-^{i}Pr$_2$$C_6H_3$, ^{t}Bu].[a]

Run	R^1;R^2	time / min	yield / mg (%)	TON[b]	M_n[c] ×10^{-4}	M_w/M_n[c]
1	Me; 2,6-^{i}Pr$_2$$C_6H_3$	60	163 (29)	73	2.4	1.3
2	Me; ^{t}Bu	30	trace	--	--	--
3	H; 2,6-^{i}Pr$_2$$C_6H_3$	60	42 (8)	20	1.1	1.1
4	H; ^{t}Bu	30	trace	--	--	--

[a]Conditions: $AlMe_3$ 20 μmol (in *n*-hexane 19 μL), 2-R^1-6-(R^2N=CH)C_6H_3OH 20 μmol (in toluene 30 μL), ^{n}BuOH 20 μmol, CL 5.0 mmol, 60 ºC. [b]TON = (molar amount of CL reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standards.

The structures of **2c,2d,2e** and **2g** determined by X-ray crystallography are shown in Figure 2-4, with selected bond distances and angles summarized in Table 2-5.

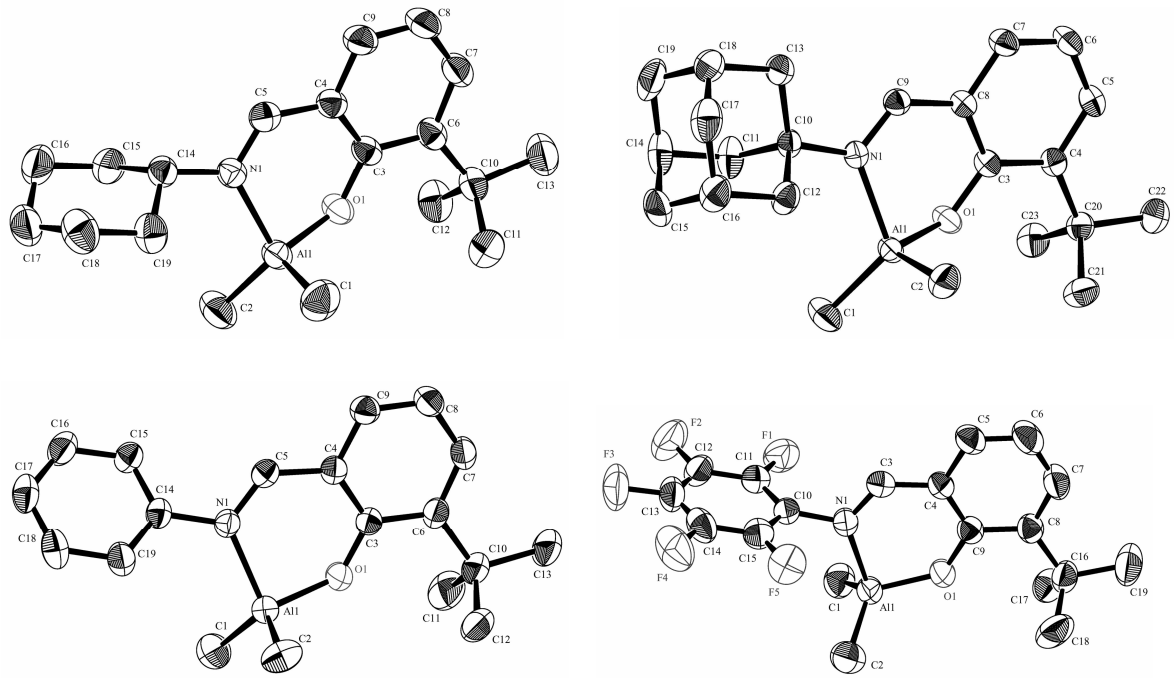


Figure 2-4. ORTEP drawings for Me_2Al[O-2-^{t}Bu-6-(R^2N=CH)C_6H_3] [R^2 =cyclohexyl (**2c**, up left), adamantyl (**2d**, up right), Ph (**2e**, down left), C_6F_5 (**2g**, down right)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

These complexes have a distorted tetrahedral geometry around Al, and no remarkable differences were observed for the bond angles and distances among these complexes, **2a**-**e**, **2g**. The Al-O bond distances in a series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ (**2a**-**e**, **2g**) increased in the order: **2e** [R^2 = Ph, 1.7792(11)Å] > **2c** [cyclohexyl, 1.7746(12) Å], **2g** [C_6F_5, 1.7737(16) Å] > **2d** [adamantyl, 1.7708(11) Å] > **2b** [^{t}Bu, 1.762(2) Å], **2a** [2,6-^{i}Pr$_2$C$_6$H$_3$, 1.7592(19) Å]. The Al-N bond distances increased in the order: **2e** [1.9896(13) Å] > **2d** [1.9859(10)] > **2g** [1.9780(19)], **2a** [1.975(2)], **2b** [1.972(2)] > **2c** [1.9664(14)]. Although I could not find an exact appropriate explanation for the observed difference, I could at least say that the bond distances and angles in $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ are influenced by the substituents in both the imino and aryloxy groups. As demonstrated above, the presence of two substituents in the 2,6-position of the aryloxo ligands are important in folding monomeric four-coordinate (tetrahedral) structures.

The differences in the resonances of the imino protons between the Al complex and the free ligand would also be dependent upon the imino substituent employed [e.g. Δδ (in ppm, C_6D_6) = 0.81 (R^2 = C_6F_5, **2g**) > 0.76 (Ph, **2e**) > 0.65 (^{t}Bu, **2b**) > 0.46 (2,6-^{i}Pr$_2$C$_6$H$_3$, **2a**), 0.45 (2,6-Me$_2$C$_6$H$_3$, **2f**), 0.45 (cyclohexyl, **2c**), > 0.27 (adamantyl, **2d**)]. The differences may be somewhat related to the above bond distances and angles, with the imino nitrogen in certain complexes being partially dissociated partially,[12] which would affect the catalytic activity as described below.

Table 2-5. Selected bond distances (Å) and angles (º) for $Me_2A[O\text{-}2\text{-}^tBu\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^2 = cyclohexyl (**2c**), adamantly (**2d**), Ph (**2e**) and C_6F_5 (**2g**)]

$R^1;R^2$	cyclohexyl (**2c**)	adamantly (**2d**)	Ph (**2e**)	C_6F_5 (**2g**)
		Bond Distances (Å)		
Al(1)-O(1)	1.7746(12)	1.7708(11)	1.7792(11)	1.7737(16)
Al(1)-N(1)	1.9664(14)	1.9859(10)	1.9896(13)	1.9780(19)
Al(1)-C(1)	1.954(2)	1.9578(15)	1.9482(18)	1.951(2)
Al(1)-C(2)	1.956(2)	1.9634(15)	1.9607(18)	1.941(2)
N(1)-C(5)	1.291(2)	1.2971(15), N(1)-C(9)	1.3024(18)	1.300(2), N(1)-C(3)
N(1)-C(14)	1.491(2)	1.4967(17), N(1)-C(10)	1.430(2)	1.436(2), N(1)-C(10)
		Bond Distances (Å)		
O(1)-Al(1)-N(1)	94.75(6)	94.68(4)	93.44(5)	93.17(7)
C(1)-Al(1)-C(2)	117.05(11)	119.32(7)	119.36(8)	118.12(12)
Al(1)-O(1)-C(3)	127.22(11)	124.04(9)	130.64(10)	133.89(14), Al(1)-O(1)-C(9)
Al(1)-N(1)-C(5)	118.85(11)	116.98(9), Al(1)-N(1)-C(9)	119.74(11)	122.97(14), Al(1)-N(1)-C(3)
Al(1)-N(1)-C(14)	124.88(11)	122.22(7), Al(1)-N(1)-C(10)	122.94(8)	120.55(14), Al(1)-N(1)-C(10)
O(1)-Al(1)-C(1)	110.73(8)	107.36(6)	111.93(7)	113.73(10)
O(1)-Al(1)-C(2)	111.54(8)	109.92(5)	110.51(8)	113.71(10)
N(1)-Al(1)-C(1)	107.66(9)	117.15(5)	108.90(6)	105.34(9)
N(1)-Al(1)-C(2)	112.85(8)	105.57(5)	109.59(6)	109.26(10)

2. Ring-opening polymerization (ROP) of ε-caprolactone using $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ (1,2).

Ring-opening polymerization (ROP) of ε-caprolactone (CL) using $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ (**1a**,**1b** and **2a-g**) was conducted upon the addition of ^{n}BuOH (1.0 equiv. to Al), and the results are summarized in Table 2-6. The addition of ^{n}BuOH was essential and the polymerization did not take place in the absence of ^{n}BuOH, suggesting that the polymerization initiated with Al-alkoxide via coordination insertion mechanism as previously proposed and demonstrated.[3]

The catalytic activities [TON values, TON = CL consumed, reacted (mmol)/Al (mmol)] by the 2,6-^{i}Pr$_2$C$_6$H$_3$ analogues (**1-2a**) were higher than the ^{t}Bu analogues (**1-2b**), suggesting that the imino substituents affected the observed catalytic activity. The activity of **1b** was somewhat higher than **2b**, probably due to the increased steric bulk of **2b** containing two ^{t}Bu groups in both the aryloxo and the imino groups. The activity of **2a** was slightly higher than **1a**. It seems that the observed activity was affected by the imino subsituent rather than the phenoxy substituent based on these results (runs 5,6,9 and 10). Therefore, as described below, the ROPs with a series of ^{t}Bu analogues with various susbstuents in the imino group (**2a-g**) were conducted under the same conditions.

The activity (TON after 60 min at 60 ºC) in the ROP of CL with a series of $Me_2Al[O\text{-}2\text{-}^t\text{Bu}\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ increased in the order: $R^2 = C_6F_5$ [**2g**, TON >248 (430) after 30 min, run 17 (run 21)] >> 2,6-$Me_2C_6H_3$ (**2f**, 185 after 30 min, run 8) > 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**, 209, run 6) > C_6H_5 (**2e**, 113, run 16) > cyclohexyl (**2c**, 70, run 13) > ^{t}Bu (**2b**, 20, run 10) > adamantyl (**2d**, trace, run 12).[13] It is thus clear that both electronic and steric factors in the imino substituent (R^2) affected the catalytic activity. This fact would be an interesting contrast to that of the *in situ* catalyst systems consisting of $AlEt_3$ and 2.0 equiv. of salicylaldimines, 2,4-$R^1{}_2$-6-{(2,4,6-$R^2{}_3C_6H_2$)N=CH}C_6H_2OH [R^1, R^2 = alkyl, aryl, halogen], in the presence of $PhCH_2OH$,[6j] because it was described that an electronic effect of the imino

substituent (aromatic or aliphatic etc.) was not important towards the activity.

Table 2-6. Ring-opening polymerization of ε-caprolactone (CL) by [Me_2Al[O-2-R^1-6-(R^2N=CH)C_6H_3] (**1a-b**,**2a-g**) [R^1 = Me (**1**), ^{t}Bu (**2**); R^2 = 2,6-$^i Pr_2C_6H_3$, (**a**), ^{t}Bu (**b**), cyclohexyl (**c**), adamantyl (**d**), C_6H_5 (**e**), 2,6-$Me_2C_6H_3$ (**f**), C_6F_5 (**g**)].[a]

run	complex (R^2)	Al / μmol	CL/Al[b]	temp. / ºC	time / min	yield / mg (%)	TON[c]	M_n[d] $\times 10^{-4}$	M_w/M_n[d]
5	**1a** (2,6-$^i Pr_2C_6H_3$)	20	250	60	60	427 (76)	190	4.50	1.61
6	**2a** (2,6-$^i Pr_2C_6H_3$)	20	250	60	60	472 (84)	209	4.35	1.61
7	**2a** (2,6-$^i Pr_2C_6H_3$)	20	250	60	30	192 (34)	85	2.87	1.24
8	**2f** (2,6-$Me_2C_6H_3$)	20	250	60	30	413 (74)	185	4.84	1.64
9	**1b** (^{t}Bu)	20	250	60	60	106 (20)	50	1.85	1.26
10	**2b** (^{t}Bu)	20	250	60	60	46 (8)	20	1.64	1.10
11	**2b** (^{t}Bu)	20	250	60	90	106 (21)	53	2.04	1.24
12	**2b** (^{t}Bu)	20	250	60	120	227 (41)	100	2.88	1.39
13	**2c** (cyclohexyl)	20	250	60	60	156 (28)	70	2.07	1.19
14	**2d** (adamantyl)	20	250	60	60	trace	--	--	--
15	**2d** (adamantyl)	20	250	60	120	43(8)	19	0.97[e]	1.06
16	**2e** (C_6H_5)	20	250	60	60	258 (45)	113	2.83	1.38
17	**2g** (C_6F_5)	20	250	60	30	551 (99)	248	5.60	1.64
18[f]	**2g** (C_6F_5)	20	250	60	30	551 (99)	248	7.26	1.61
19	**2g** (C_6F_5)	15	333	60	30	549 (99)	330	6.22	1.69
20	**2g** (C_6F_5)	12	417	60	30	515 (92)	383	8.21	1.64
21	**2g** (C_6F_5)	10	500	60	30	481 (86)	430	9.34	1.64
22	**2g** (C_6F_5)	10	500	60	45	538 (95)	475	10.05	1.86
23	**2a** (2,6-$^i Pr_2C_6H_3$)	20	250	50	60	198 (35)	88	2.58	1.27
24	**2f** (2,6-$Me_2C_6H_3$)	20	250	50	60	449 (80)	200	5.39	1.74
25	**2f** (2,6-$Me_2C_6H_3$)	20	250	50	30	193 (34)	85	3.13	1.42
26	**2g** (C_6F_5)	20	250	50	30	456 (81)	203	5.00	1.41

[a]Conditions: Al 10-20 μmol (in toluene 50 μL), ^{n}BuOH 1.0 equiv. to Al, CL 5.0 mmol, 60 ºC. [b]Initial molar ratios of CL/Al. [c]TON = (molar amount of CL reacted)/(molar amount of Al). [d]GPC data in THF vs polystyrene standards. [e]High molecular weight ($M_n = 2.3\times10^4$) shoulder was also observed. [f]$PhCH_2OH$ was used in place of ^{n}BuOH [$M_n = 4.24\times10^4$ (run 18) estimated by ^{1}H NMR spectra].

The ROP with the C_6F_5 analogue (**2g**) reached to completion after 30 min under the same conditions (run 17, Al 20 μmol at 60 ºC); the ROP by **2g** also reached high conversion

of CL (86 % conversion after 30 min, run 21) even when the amount of Al complex was reduced (Al 10 μmol). The M_n values could be controlled by varying the CL/Al molar ratios (runs 17,19,20 and 22), and a linear relationship between the M_n and the TON values was observed (Figure 2-5).

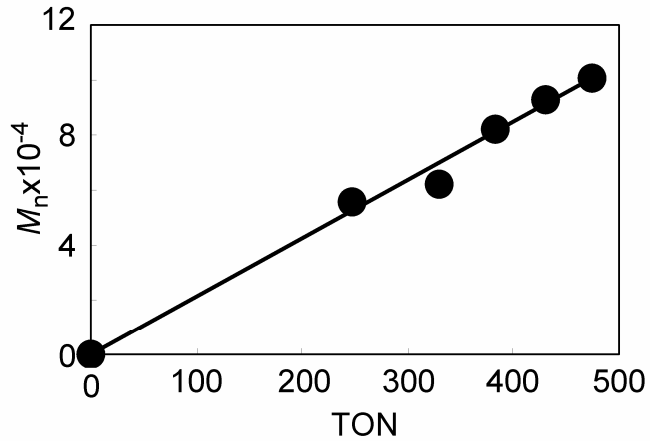


Figure 2-5. Plots of M_n *vs*. TON. Conditions: Al 10-20 μmol (in toluene 50 μL), ^{n}BuOH 1.0 equiv. to Al, CL 5.0 mmol, 60 ºC (Table 2-6, runs 17,19,20 and 22).

The ROP initiated by the **2g**-$PhCH_2OH$ system also reached completion under the same conditions (run 18), and the M_n value [4.24×10^4 (run 18) estimated by the ^{1}H NMR spectrum (based on methylene protons at the polymer chain end derived from $PhCH_2OH$) was very close to the exact value [4.07×10^4 (run 18)] calculated and corrected based on the M_n value by GPC measurement *versus* polystyrene standards.[14] The result thus assumes that the ROP was initiated with Al-OR (R = ^{n}Bu, $PhCH_2$) fragment as proposed.[2a,c,15] The M_n value of the **2g**-$PhCH_2OH$ system was higher than that of the **2g**-^{n}BuOH system, the difference can be explained as the difference in the initiation efficiency. In fact, the initiation efficiency for the ROP by **2g** in the presence of $PhCH_2OH$ estimated from the M_n value by GPC[14e,h] (polymer yields and the M_n value corrected by that measured by GPC) was 68% (run 18), whereas the efficiency of **2g**-^{n}BuOH system (run 17) was 88%.

The ROPs with effective catalysts, **2a**, **2f** and **2g**, were also conducted at 50 ºC, and the observed activities were lower than those performed at 60 ºC (runs 23-26). A similar

trend, the effect of substituent in the imino group toward the activity (**2g** > **2f** > **2a**), was observed, and the polymerization by **2g** reached to high conversion (86 %, run 26) even after 30 min.

The ROPs of CL by **2b** (R^2 = ^{t}Bu), **2c** (R^2 = cyclohexyl), **2g** (R^2 = C_6F_5) were conducted under rather dilute conditions (initial CL concentration 1.0 mmol mL^{-1} in toluene) in the presence of ^{n}BuOH (1.0 equiv.), and the results are summarized in Table 2-7.

Table 2-7. Ring-opening polymerization of ε-caprolactone (CL) by [$Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^2 = ^{t}Bu (**2b**), cyclohexyl (**2c**), C_6F_5 (**2g**)].[a]

run	complex /μmol	temp. / ºC	time	yield / mg (%)	TON[b]	M_n[c] ×10^{-4}	M_w/M_n[c]	N[d] / μmol
27	**2b** (20)	60	6 h	trace	–	–	–	
28	**2b** (20)	60	12 h	111 (20)	50	1.20	2.61	
29	**2b** (20)	60	24 h	270 (48)	120	1.56	1.67	
30	**2b** (20)	60	48 h	479 (86)	215	3.33	1.72	
31	**2c** (20)	60	3 h	trace	–	–	–	
32	**2c** (20)	60	9 h	138 (25)	63	1.27	1.86	
33	**2c** (20)	60	12 h	447 (80)	200	1.73	3.56	
34	**2g** (10)	60	20 min	413 (74)	370	7.68	1.19	9.6
35	**2g** (10)	60	30 min	481 (86)	430	8.67	1.17	9.9
36	**2g** (10)	50	30 min	208 (37)	185	3.67	1.08	10.1
37	**2g** (10)	50	1 h	299 (53)	265	5.33	1.10	10.0
38	**2g** (10)	50	1.5 h	426 (75)	375	7.33	1.13	10.4
39	**2g** (10)	50	2 h	481 (86)	430	8.15	1.13	10.5

[a]Conditions: Al 10 or 20 μmol (in toluene 100 μL), ^{n}BuOH 1.0 equiv. to Al (in toluene 9 μL), CL 5.0 mmol, toluene 4.37 mL (initial CL concentration 1.0 mmol mL^{-1}), 50 or 60 ºC. [b]TON = (molar amount of CL reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standards. [d]Estimated number of polymer chain (mmol) = polymer yield (mg)/{0.56×$M_{n(GPC)}$}.[14e,h]

The ROP with **2g** proceeded at a significant rate even under the dilute conditions (370 turnovers after 20 min, run 34), affording poly(CL) with a narrow molecular weight distribution (M_w/M_n = 1.19), and the M_n value increased after 30 min with a narrow

distribution (run 35). In contrast, the activities of **2b** (runs 28-30) were significantly lower than those performed under the bulk conditions as described in Table 2-6 (runs 10-12): the monomer conversion reached 86% after 48 h (run 30), and the M_n value increased upon increasing the monomer conversion (runs 29, 30). The monomer conversion reached 80 % after 12 h in the ROP by **2c**, however the molecular weight distribution became broad (M_w/M_n = 3.56, run 33) without any notable increase in the M_n values (runs 32, 33). This fact would suggest a possibility of (probably intramolecular) transesterification accompanied in the catalytic polymerization as the side reaction.[16]

The ROP (at 50 ℃) proceeded at a significant rate at the beginning and the rate gradually decreased; as shown in Figure 2-6, the rates were dependent upon the CL concentration with the first order, suggesting that the polymerization proceeded without deactivation.

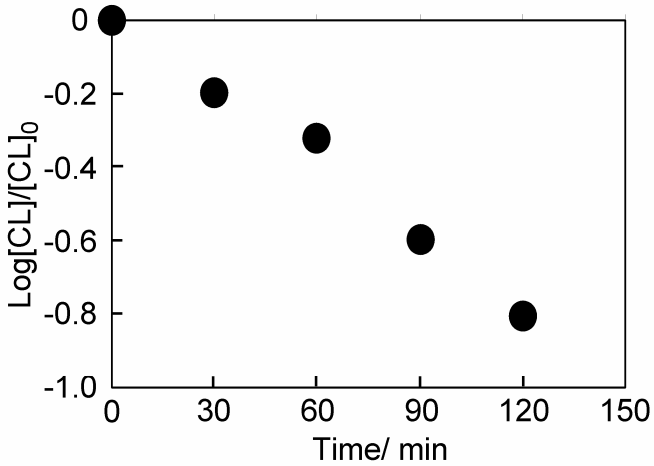


Figure 2-6. Time course plots of $\log[CL]/[CL]_0$. [CL] = concentration of CL in mmol/mL. Conditions are described in Table 2-7.

The M_n value increased linearly upon increasing TON values (M_w/M_n = 1.08-1,13) as described in Figure 2-7. The number of polymer chains estimated from the M_n value by GPC analysis[14] (10.1-10.5 μmol) was close to the Al initiator employed under these conditions (Table 2-7, runs 36-39), and the M_n values could be controlled by varying the CL:

Al molar ratios (runs 17, 19-20 and 22). Taking these facts into account, it is therefore clear that the ROP using **2g** took place in a living manner with executive initiation efficiency under certain optimized conditions.

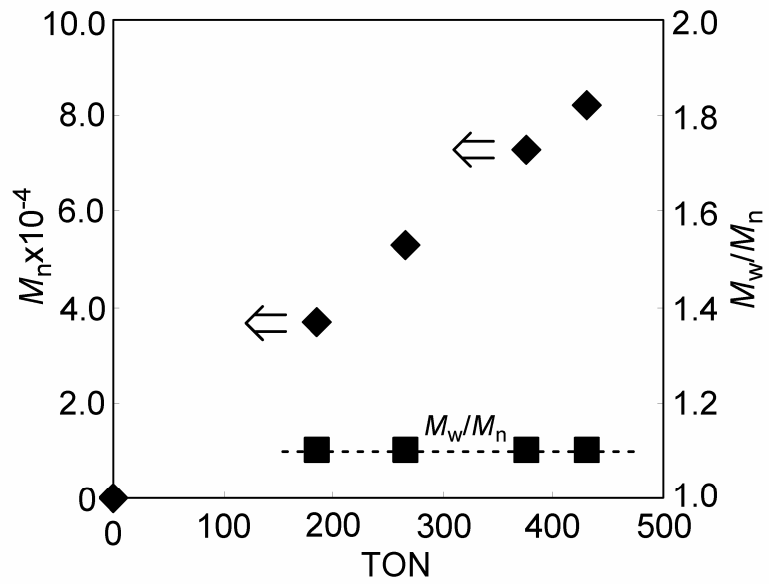


Figure 2-7. Plots of M_n and M_w/M_n values for poly(CL) vs TON for ring-opening polymerization of ε-caprolactone (CL) catalyzed by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**2g**) in toluene. Conditions are described in Table 2-7.

Conclusion

In this chapter, Al complexes containing phenoxy-imine ligands of type, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^1 = Me, R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1a**), ^{t}Bu (**1b**); R^1 = ^{t}Bu, R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**), ^{t}Bu (**2b**), cyclohexyl (**2c**), adamantyl (**2d**), C_6H_5 (**2e**), 2,6-$Me_2C_6H_3$ (**2f**), C_6F_5 (**2g**)] have been prepared in high yields from $AlMe_3$ by treating with 1.0 equiv. of 2-R^1-6-(R^2N=CH)C_6H_3OH in *n*-hexane, and their structures (**1a**,**b** and **2a-e**,**g**) were determined by X-ray crystallography as the mononuclear complexes with tetrahedral geometry around Al. Both the Al-O and the Al-N bond distances were influenced by the substituents in the aryloxo as well as the imino groups. In contrast, the similar reaction of

$AlMe_3$ with 2-(R^2N=CH)C_6H_4OH (0.5 and/or 1.0 equiv. to Al) afforded $Me_2Al[\mu_2$-O-2-(R^2N=CH)C_6H_4](AlMe$_3$) [R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**3a**), ^{t}Bu (**3b**)] exclusively, and their structures fold a distorted tetrahedral geometry around each Al and additional $AlMe_3$ coordinates to oxygen in the phenoxy imine ligand. Complexes **1a**,**b** and **2a-g** were employed as catalyst precursors for ring-opening polymerization (ROP) of ε-caprolactone (CL) in the presence of ^{n}BuOH (1.0 equiv. to Al). The catalytic activity (TON after 60 min at 60 ºC) in the ROP of CL with a series of $Me_2Al[$O-2-^{t}Bu-6-(R^2N=CH)C_6H_3] increased in the order: R^2 = C_6F_5 (**2g**, TON >248 after 30 min) >> 2,6-$Me_2C_6H_3$ (**2f**, 185 after 30 min) > 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2a**, 209) > C_6H_5 (**2e**, 113) > cyclohexyl (**2c**, 70) > ^{t}Bu (**2a**, 20) > adamantyl (**2d**, trace). The results clearly indicate that the imino substituents in **2** strongly affect the activity for the ROP of CL, and the facts presented here should be an interesting contrast to those demonstrated recently.[6g,i,j,15] The C_6F_5 analogue (**2g**) showed the remarkable activity and the M_n values for resultant poly(CL) increased upon increasing the TON values (polymer yields) with narrow M_w/M_n values (M_w/M_n = ca. 1.1) under the optimized conditions (Table 2-7). Moreover, number of the polymer chain estimated was close to the Al initiator employed. These results thus strongly suggest that the ROP took place in a living manner with high initiation efficiency under the certain optimized conditions. I am now exploring in more details for the ROP with Al complexes of this type, including mechanistic details (initiation and propagation mechanism) and effect of ligand toward the activity, and I am also exploring possibilities of these complexes as the catalyst for ROP of other cyclic esters; these results are introduced in the next chapter.

Experimental Section

General Procedures.

All experiments were carried out in a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade *n*-hexane (Kanto Kagaku

Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 stream, and were passed through a short alumina column under a N_2 stream before use. All chemicals used were of reagent grade and were purified by the standard purification procedures. Reagent grade $AlMe_3$ in *n*-hexane (Kanto Kagaku Co. Ltd.) was stored in the drybox and was used as received. Various salicylaldimines (imino-phenols) containing different substituent on both the aryloxo and the imino groups, 2-R^1-6-(R^2N=CH)C_6H_3OH [R^1 = Me (**1**), ^{t}Bu (**2**); R^2 = 2,6-^{i}Pr$_2C_6H_3$ (**a**), ^{t}Bu (**b**), cyclohexyl (**c**), adamantyl (**d**), Ph (**e**), 2,6-$Me_2C_6H_3$ (**f**), C_6F_5 (**g**)] were prepared according to the reported procedures.[10] Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). All ^{1}H, and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted, and chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^{1}H, ^{13}C).

Synthesis of Me_2Al[O-2-Me-6-{(2,6-^{i}Pr$_2C_6H_3$)N=CH}-C_6H_3] (1a).

Into a stirred solution of 2-Me-6-{(2,6-^{i}Pr$_2C_6H_3$)N=CH}C_6H_3OH (0.63 g, 2.15 mmol) in *n*-hexane (3.0 mL), $AlMe_3$ (1.1 M *n*-hexane solution (1.62 g, 2.37 mmol Al) was added drop-wise over a 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h. The reaction mixture was placed in a rotary evaporator, and the solution was concentrated *in vacuo*. The chilled concentrated *n*-hexane solution placed in the freezer (-20 ºC) afforded complex **1a** (0.63 g, 83.5 % yield) as colorless microcrystals. ^{1}H NMR (C_6D_6): δ -0.30 (s, 6H, Al*Me*$_2$), 0.84 (d, *J* = 6.6 Hz, 6H, (*CH*$_3$)$_2$CH-)), 1.19 (d, *J* = 7.0 Hz, 6H, (*CH*$_3$)$_2$CH-)), 2.28 (s, 3H, *Me*), 3.14 (m, 2H, $(CH_3)_2$*CH*-), 6.52 (t, *J* = 7.7 Hz, 1H, aromatic), 6.68 (d, *J* = 7.7 Hz, 1H, aromatic), 7.02-7.11 (m, 4H, aromatic), 7.80 (s, 1H, C*H*=N). ^{13}C NMR (C_6D_6): δ -9.0, 16.4, 22.7, 25.8, 28.5, 117.8, 118.3, 124.5, 128.5, 131.3, 132.8, 138.6, 142.5, 142.6, 164.0, 173.7. Colorless block microcrystals suitable for crystallographic analysis were grown from the chilled concentrated

n-hexane solution containing **1a** and the structures were determined by X-ray crystallography.

Synthesis of $Me_2Al[O\text{-}2\text{-}Me\text{-}6\text{-}(^tBuN{=}CH)C_6H_3]$ (1b).

Synthesis of **1b** was carried out according to the same procedure as that of **1a**, except 2-Me-6-(^{t}BuN=CH)C_6H_3OH (0.41 g, 2.15 mmol) was used. Yield 0.39 g (73.4 %). ^{1}H NMR (C_6D_6): δ -0.22 (s, 6H, Al*Me*$_2$), 1.01 (s, 9H, ^{t}Bu), 2.27 (s, 3H, *Me*), 6.55 (t, *J* = 7.7 Hz, 1H, aromatic), 6.68 (d, *J* = 7.7 Hz, 1H, aromatic), 7.11 (d, *J* = 6.6 Hz, 1H, aromatic), 7.74 (s, 1H, CH=N). ^{13}C NMR (C_6D_6): δ -6.1, 16.3, 29.6, 59.5, 116.9, 118.5, 130.3, 133.0, 137.4, 163.0, 168.2. Anal. Calcd. for $C_{14}H_{22}AlNO$: C, 67.99; H, 8.97; N, 5.66. Found: C, 67.99; H, 9.40; N, 5.62.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N{=}CH\}\text{-}C_6H_3]$ (2a).

An *n*-hexane solution containing 2-^{t}Bu-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$OH (1.0 g, 3.0 mL of *n*-hexane, 3.0 mmol) was added slowly into a stirred *n*-hexane solution containing $AlMe_3$ (220 mg, 15 mL of *n*-hexane, 3.0 mmol) at -20 ºC in a drybox. The solution was allowed to warm slowly to room temperature, and was stirred for a further 3 h. The mixture was then concentrated *in vacuo*, and the chilled solution (-20 ºC) afforded colorless microcrystals of **2a** (926 mg, 77% yield). ^{1}H NMR (400 MHz, C_6D_6): δ -0.30 (s, 6H), 0.80 (d, 6H), 1.18 (d, 6H), 1.52 (s, 9H), 3.13 (septet, 2H), 6.59 (t, 1H), 6.72 (dd, 1H), 7.01-7.03 (m, 2H), 7.08-7.11 (m, 1H), 7.40 (dd, 1H), 7.81 (s, 1H). ^{13}C NMR (400 MHz, C_6D_6): δ -9.06, 22.6, 25.9, 28.4, 29.5, 35.4, 117.7, 119.4, 124.5, 128.5, 133.7, 135.3, 142.0, 142.5, 142.7, 164.9, 174.1. Anal. Calcd. for $C_{25}H_{36}NOAl$: C, 76.30; H, 9.22; N, 3.56 %. Found: C, 76.33; H, 9.46; N, 3.37 %.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(^tBuN{=}CH)C_6H_3]$ (2b).

Synthesis for **2b** was performed according to the same procedure as that of **2a**, except that 2-^{t}Bu-6-(^{t}BuN=CH)C_6H_3OH (1.0 g, 3.0 mL of *n*-hexane, 4.3 mmol) was added slowly into a stirred *n*-hexane solution containing $AlMe_3$ (310 mg, 15 mL of *n*-hexane, 4.3 mmol) at -20 ºC. The off-white microcrystals were then collected from the chilled solution

(942 mg, 76% yield). ^{1}H NMR (C_6D_6): δ -0.23 (s, 6H), 0.98 (s, 9H), 1.55 (s, 9H), 6.61 (t, 1H), 6.69 (dd, 1H), 7.39 (dd, 1H), 7.72 (s, 1H). ^{13}C NMR (C_6D_6): δ -6.41, 29.5, 29.6, 35.2, 59.3, 116.9, 119.8, 133.6, 133.8, 141.1, 163.6, 168.7. Anal. Calcd. for $C_{17}H_{28}NOAl$: C, 70.56; H, 9.75; N, 4.84 %. Found: C, 70.53; H, 10.08; N, 4.73 %.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(cyclohexyl)N{=}CH\}C_6H_3]$ (2c).

Synthesis of **2c** was carried out according to the same procedure as that of **1a**, except that 2-^{t}Bu-6-{(cyclohexyl)N=CH}C_6H_3OH (0.56 g, 2.15 mmol) was used in place of 2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C_6H_3OH. Yield 0.61 g (90 %). ^{1}H NMR (C_6D_6): δ -0.22 (s, 6H, Al*Me*$_2$), 0.90 (m, 3H, cyclohexyl), 0.90-1.51 (m, 7H, cyclohexyl), 1.56 (s, 9H, ^{t}Bu), 2.65 (m, 1H, cyclohexyl), 6.66 (t, *J* = 7.7 Hz, 1H, aromatic), 6.76 (d, *J* = 7.7 Hz, 1H, aromatic), 7.42 (d, *J* = 7.3 Hz, 1H, aromatic), 7.40 (s, 1H, C*H*=N). ^{13}C NMR (C_6D_6): δ -7.5, 25.1, 25.4, 29.5, 33.7, 35.3, 68.5, 116.9, 119.8, 133.2, 133.8, 141.3, 164.0, 170.0. Anal. Calcd. for $C_{19}H_{30}AlNO$: C, 72.35; H, 9.59; N, 4.44. Found: C, 72.28; H, 9.88; N, 4.38.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(adamantyl)N{=}CH\}C_6H_3]$ (2d).

Synthesis of **2d** was performed according to the same procedure as that of **2a**, except that 2-^{t}Bu-6-{(adamantyl)N=CH}C_6H_3OH (0.67 g, 2.15 mmol) was added slowly into a stirred *n*-hexane solution containing $AlMe_3$ (171 mg, 15 mL of *n*-hexane, 2.37 mmol) at -20 ºC. The chilled solution (-20 ºC) afforded yellow microcrystals (0.67 g, 85% yield). ^{1}H NMR (C_6D_6): δ -0.16 (s, 6H), 1.36 (dd, 6H), 1.57 (s, 9H), 1.66 (s or d, 6H), 1.79 (s, 3H), 6.67 (t, 1H), 6.82 (d, 1H), 7.42 (d, 1H), 7.79 (s, 1H). ^{13}C NMR (C_6D_6): δ -6.1, 29.5, 29.7, 35.3, 35.8, 42.4, 60.3, 116.9, 120.0, 133.6, 133.8, 141.3, 163.8, 167.5. Anal. Calcd. for $C_{23}H_{34}AlNO$: C, 75.17; H, 9.33; N, 3.81 %. Found: C, 75.10; H, 8.95; N, 3.84 %.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(PhN{=}CH)C_6H_3]$ (2e).

Synthesis of **2e** was performed according to the same procedure as that of **1a**, except that 2-^{t}Bu-6-(PhN=CH)C_6H_3OH (0.54 g, 2.15 mmol) was used. Yield: 0.57 g (86 %). ^{1}H NMR (C_6D_6): δ -0.21 (s, 6H, Al*Me*$_2$), 1.55 (s, 9H, ^{t}Bu), 6.59-6.67 (m, 2H,

aromatic), 6.90-6.98 (m, 5H, aromatic), 7.41 (dd, *J* = 7.3, 1.8 Hz, 1H, aromatic), 7.47 (s, 1H, C*H*=N). ^{13}C NMR (C_6D_6): δ -8.6, 29.7, 35.5, 117.6, 120.6, 122.6, 130.0, 134.3, 135.2, 141.9, 147.2, 165.0, 170.6. Anal. Calcd. for $C_{19}H_{24}AlNO$: C, 73.76; H, 7.82; N, 4.53. Found: C, 73.68; H, 8.06; N, 4.51 %.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,6\text{-}Me_2C_6H_3)N{=}CH\}\text{-}C_6H_3]$ (2f).

Synthesis of **2f** was performed according to the same procedure as that of **1a**, except that 2-^{t}Bu-6-{(2,6-$Me_2C_6H_3$)N=CH}C_6H_3OH (0.60 g, 2.15 mmol) was used. Yield 0.68 g (94 %). ^{1}H NMR (C_6D_6): δ -0.31 (s, 6H, Al*Me*$_2$), 1.55 (s, 9H, ^{t}Bu), 1.97 (s, 6H, Me), 6.61 (t, *J* = 7.7 Hz, 1H, aromatic), 6.65 (dd, *J* = 7.7, 1.8 Hz, 1H, aromatic), 6.81-6.91 (m, 3H, aromatic), 6.89 (t, *J* = 8.4 Hz, 1H, aromatic), 7.22 (s, 1H, C*H*=N), 7.41 (dd, *J* = 7.4, 1.8 Hz, 1H, aromatic). ^{13}C NMR (C_6D_6): δ -8.6, 18.4, 29.5, 35.3, 117.3, 119.8, 127.4, 129.0, 131.7, 133.8, 135.0, 141.8, 145.1, 164.8, 174.6. Anal. Calcd. for $C_{21}H_{28}AlNO$: C, 74.75; H, 8.36; N, 4.15. Found: C, 74.60; H, 8.47; N, 4.02 %.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (2g).

Synthesis of **2g** was carried out according to the same procedure as that of **1a**, except that 2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3OH (0.74 g, 2.15 mmol) was used. Yield 0.70 g (82 %). ^{1}H NMR (C_6D_6): δ -0.29 (s, 6H, Al*Me*$_2$), 1.47 (s, 9H, ^{t}Bu), 6.54 (m, 1H, aromatic), 6.65 (m, 1H, aromatic), 7.30 (s, 1H, C*H*=N), 7.40 (m, 1H, aromatic). ^{13}C NMR (C_6D_6): δ -10.0, 29.3, 35.3, 118.0, 119.3, 121.5, 134.7, 136.8, 137.2, 139.4, 140.6, 141.7, 142.4, 143.0, 166.4, 176.9. Anal. Calcd. for $C_{19}H_{19}AlF_5NO$: C, 57.15; H, 4.80; N, 3.51. Found: C, 57.14; H, 4.66; N, 3.45 %.

Synthesis of $Me_2Al[\mu_2\text{-}O\text{-}2\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N{=}CH\}C_6H_4](AlMe_3)$ (3a).

Into a stirred solution of 2- {(2,6-^{i}Pr$_2C_6H_3$)N=CH}C_6H_4OH (0.60 g, 2.15 mmol) in *n*-hexane (3.0 mL), $AlMe_3$ (1.1 M *n*-hexane, 3.24 g, 4.74 mmol Al) was added drop-wise over a 10 min period at -20 ºC. The solution was then allowed to warm to room temperature and was stirred overnight. The reaction mixture was then placed in a rotary evaporator to

concentrate the reaction mixture under reduced pressure. The chilled solution that was placed in the freezer (-20 ºC) afforded complex **3a** (0.81 g, 92 % yield) as colorless microcrystals. ^{1}H NMR (C_6D_6): δ -0.45 (s, 6H, Al*Me*$_2$), -0.21 (s, 9H, Al*Me*$_3$), 0.90 (d, *J* = 7.0 Hz, 6H, (*CH*$_3$)$_2$CH-)), 1.19 (d, *J* = 7.0 Hz, 6H, (*CH*$_3$)$_2$CH-)), 2.99 (m, 2H, (CH$_3$)$_2$*CH*-), 6.56 (t, *J* = 7.3 Hz, 1H, aromatic), 6.61 (dd, *J* = 7.7, 2.2 Hz, 1H, aromatic), 6.98-7.16 (m, 4H, aromatic), 7.57 (d, *J* = 7.7 Hz, 1H, aromatic), 7.61 (s, 1H, C*H*=N). ^{13}C NMR (C_6D_6): δ -10.2, -5.2, 23.1, 25.1, 28.7, 121.9, 122.9, 124.6, 124.8, 129.0, 133.4, 137.0, 141.8, 157.1, 172.7. Anal. Calcd. for $C_{24}H_{37}Al_2NO$: C, 70.39; H, 9.11; N, 3.42. Found: C, 70.32; H, 9.21; N, 3.30 %.

Synthesis of Me$_2$Al[μ$_2$-O-2-(^{t}BuN=CH)C$_6$H$_4$](AlMe$_3$) (3b).

Synthesis of **3b** was carried out according to the same procedure as that of **3a**, except 2-(^{t}BuN=CH)C$_6$H$_4$OH (0.38 g, 2.15 mmol) was used. Yield 0.68 g (94 %). ^{1}H NMR (C_6D_6): δ -0.37 (s, 6H, Al*Me*$_2$), -0.26 (s, 9H, Al*Me*$_3$), 0.90 (s, 9H, ^{t}Bu), 6.55-6.63 (m, 2H, aromatic), 6.95-7.00 (m, 1H, aromatic), 7.22 (d, *J* = 8.1 Hz, 1H, aromatic), 7.44 (s, 1H, C*H*=N). ^{13}C NMR (C_6D_6): δ -7.7, -5.0, 28.7, 61.5, 121.8, 122.2, 124.5, 133.2, 135.7, 156.5, 165.5. Anal. Calcd. for $C_{16}H_{29}Al_2NO$: C, 62.93; H, 9.57; N, 4.59. Found: C, 62.63; H, 9.86; N, 4.55 %.

Ring opening polymerization (ROP) of ε-caprolactone (CL).

Typical polymerization procedures (Table 2-6, run 5) are as follows. Into a sealed Schlenk tube containing a toluene solution of **1a** (0.020 mmol, 0.050 mL of toluene), ^{n}BuOH (1.8 μL, 0.020 mmol) was added in a drybox at room temperature. The solution was stirred for 10 minutes, and then ε-caprolactone (5.0 mmol) was added to the solution. The reaction mixture was then placed into an oil bath preheated at 60 ºC, and the solution was stirred for the prescribed time (60 min). The polymerization mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into methanol (400 mL). The ring-opened polymer was then collected as the methanol insoluble white precipitates; the

resultant polymer was then collected on filter paper and was dried *in vacuo*. ^{1}H NMR ($CDCl_3$): δ 1.33 (m, 2H), 1.51-1.63 (m, 4H), 2.25 (t, 2H), 4.00 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 24.5, 25.5, 28.3, 34.1, 64.1, 173.5 (C=O). The ROP of CL using a mixed catalyst systems consisting of $AlMe_3$ and $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3OH$ were performed in the analogous procedure for those using **1**,**2**, except that $AlMe_3$ and the imino-phenol was pre-mixed for 10 min before adding ^{n}BuOH.

Crystallographic analysis.

All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The selected crystal collection parameters are listed below (Table 2-8 and 2-9). All structures were solved by direct methods and expanded using Fourier techniques.[17] All calculations were performed using the crystal structure crystallographic software package.[18] The analysis data (including CIF files) were deposited in the Cambridge Crystallographic Data Centre, and the data numbers are summarized in Tables 2-8,9.

Table 2-8. Crystal data and collection parameters of complexes 1a, 2a, 3a, 1b, 2b and 3b.[a]

	1a	**2a**	**3a**	**1b**	**2b**	**3b**
empirical formula	$C_{22}H_{30}NOAl$	$C_{25}H_{36}NOAl$	$(C_{24}H_{37}NOAl_2)_6$	$C_{14}H_{22}NOAl$	$C_{17}H_{28}NOAl$	$C_{16}H_{29}NOAl_2$
fw	351.47	393.55	2529.22	247.32	289.40	305.37
cryst color, habit	colorless, block	colorless, block	colorless, block	colorless, block	colorless, block	colorless, block
cryst dimens (mm)	0.32×0.28×0.14	0.36×0.30×0.14	0.40×0.24×0.14	0.46×0.44×0.34	0.30×0.26×0.24	0.30×0.16×0.12
cryst syst	monoclinic	monoclinic	trigonal	monoclinic	orthorhombic	monoclinic
a (Å)	34.0799(16)	9.8322(5)	38.5672(11)	9.7023(5)	13.4761(6)	11.1926(6)
b (Å)	8.8107(3)	13.4233(5)		9.7378(5)	9.6446(4)	14.3616(7)
c (Å)	15.1777(6)	37.1112(13)	9.3498(3)	15.6108(8)	14.0421(6)	12.9141(8)
β (º)	107.7934(18)	91.9043(13)		92.9412(18)		108.4732(18)
V ($Å^3$)	4339.3(3)	4891.6(4)	12044.0(6)	1472.97(13)	1825.06(14)	1968.89(19)
space group	C2/c (#15)	$P2_1/n$ (#14)	R-3 (#148)	$P2_1/c$ (#14)	Pnma(#62)	$P2_1/n$ (#14)
Z	8	8	3	4	4	4
D_{calc} g/cm^3	1.076	1.069	1.046	1.115	1.053	1.03
F_{000}	1520	1712	4104	536	632	664
no. of reflns measured	Total: 20662	Total: 46794	Total: 58936	Total: 14044	Total: 17111	Total: 19033
R_{int}	0.041	0.057	0.040	0.022	0.025	0.045
Residuals: R_1	0.0430	0.0455	0.0399	0.0449	0.0610	0.0419
Residuals: wR_2	0.1333	0.1220	0.1007	0.1466	0.1899	0.1141
GOF	1.005	1.005	1.013	1.001	1.004	1.012
CCDC No.[b]	666959	645924	666965	666960	645925	666966

[a]Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. [b]CCDC No. at Cambridge crystallographic data center.

Table 2-9. Crystal data and collection parameters of complexes 2c, 2d, 2e, and 2g.[a]

	2c	**2d**	**2e**	**2g**
empirical formula	$C_{19}H_{30}NOAl$	$C_{23}H_{34}NOAl$	$C_{19}H_{24}NOAl$	$C_{19}H_{19}F_5NOAl$
fw	315.43	367.51	309.39	399.34
cryst color, habit	colorless, block	colorless, block	yellow, block	yellow, block
cryst dimens (mm)	0.50×0.44×0.20	0.70×0.70×0.50	0.40×0.24×0.24	0.36×0.24×0.18
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
a (Å)	13.4480(3)	10.1069(3)	12.1416(5)	17.7482(6)
b (Å)	12.7111(4)	19.6741(6)	7.2786(3)	15.6029(6)
c (Å)	22.4540(5)	11.0516(4)	21.0147(9)	14.4394(5)
β (º)		103.9622(10)	100.5986(13)	
V ($Å^3$)	3838.26(17)	2132.63(12)	1825.47(13)	3998.6(2)
space group	Pbca (#61)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	Pccn (#56)
Z	8	4	4	8
D_{calc} g/cm^3	1.092	1.145	1.126	1.327
F_{000}	1376	800	664	1648
no. of reflns measured	Total: 34904	Total: 19914	Total: 17113	Total: 35873
R_{int}	0.034	0.022	0.027	0.044
Residuals: R_1	0.0401	0.0390	0.0394	0.0352
Residuals: wR_2	0.1046	0.1294	0.1195	0.0816
GOF	1.000	1.008	1.012	1.019
CCDC No.[b]	666961	666962,645926	666963	666964

[a]Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. [b]CCDC No. at Cambridge crystallographic data center.

References

1. For example: (a) Yamamoto, H. Ed. *Lewis Acids in Organic Synthesis Volume 1*; Wiley-VCH: Germany, Weinheim, 2000; p 89. (b) Yamamoto, H. Ed. *Lewis Acids in Organic Synthesis*; Wiley-VCH: Germany, Weinheim, 2000; p 191. (c) Yamamoto, H. Ed. *Lewis Acids in Organic Synthesis;* Wiley-VCH: Germany, Weinheim, 2000; p 283.
2. (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev*., **2000**, *100*, 1391. (b) Pedeutour, J.-N.; Radhakrishnan, K.; Cramail, H.; Deffieux, A. *Macromol. Rapid Commun.* **2001**, *22*, 1095. (c) W. E. Piers, *Adv. Organomet.Chem*. **2005***, 52*, 1. (d) Erker, G. *Dalton Trans.* **2005**, 1883.
3. For recent reviewing article: (a) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci*. **1999**, *147*, 1. (b) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc*. *Dalton Trans*. **2001**, 2215. (c) Stridsberg, K. M.; Ryner, M.; Albertsson, A. C. *Adv. Polym. Sci*. **2002**, *157*, 41. (d) Albertsson, A.-C.; Varma, I. *Biomacromolecules* **2003**, *4*, 1466. (e) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147.
4. (a) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc*. **1988**, *110*, 3588. (b) Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc*. **1989**, *111*, 6431. (c) Maruoka, K.; Conception, A. B.; Murase, N.; Oishi, M.; Hirayame, N.; Yamamoto, H. *J. Am. Chem. Soc*. **1993**, *115*, 3943. (d) Maruoka, K.; Imoto, H.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc*. **1994**, *116*, 4131. (e) Saito, S.; Yamamoto, H. *J. Chem. Soc*., *Chem. Commun*. **1997**, 1585.
5. Examples for polymerization of lactide by Al: (a) Trofimoff, L.; Aida, T.; Inoue, S. *Chem. Lett*. **1987**, 991. (b) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys*. **1996**, *197*, 2627. (c) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461. (d) Wisniewski, M.; LeBorgne, A.; Spassky, N. *Macromol*. *Chem. Phys*. **1997**, *198*, 1227. (e) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (f)

Cameron, P. A.; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S. *Macromol. Rapid Commun.* **1999**, *20*, 616. (g) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (h) Bhaw-Luximon, A.; Jhurry, D.; Spassky, N. *Polym. Bull.* **2000**, *44*, 31. (i) Radano, C. P.; Baker, G. L.; Smith, M. R.; *J. Am. Chem. Soc*., **2000**, *122*, 1552. (j) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci.*, *Part A: Polym. Chem*. **2000**, *38*, 4686. (k) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. *Macromolecules* **2001**, *34*, 356. (l) Chisholm, M. H.; Navarro-Llobet, D.; Simonsick, W. J. Jr. *Macromolecules* **2001**, *34*, 885. (m) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (n) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc*. **2002**, *124*, 1316. (o) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2003**, *22*, 769.

6. Examples for ROP of lactones etc.: (a) Ko, B.-T.; Lin, C.-C. *Macromolecules* **1999**, *32*, 8296. (b) Taden, I.; Kang, H.-C.; Massa, W.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem*. **2000**, 441. (c) Chakraborty, D.; Chen, E.Y.-X. *Organometallics* **2002**, *21*, 1438. (d) Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2002**, *35*, 5763. (e) Yu, R.-C.; Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 6450. (f) Zheng, G.; Stöver, H. D. H. *Macromolecules* **2003**, *36*, 7439. (g) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2003**, 3082. (h) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* **2004**, *37*, 7968. (i) Lewinsky, J.; Horeglad, P.; Tratkiewicz, E.; Grzenda, W.; Lipkowski, J.; Kolodziejczyk, E. *Macromol. Rapid Commun.* **2004**, *25*, 1939. (j) Nomura, N.; Aoyama, T.; Ishii, R.; Kondo, T. *Macromolecules* **2005**, *38*, 5363. (k) Amgoune, A.; Lavanant, L.; Thomas, C. M.; Chi, Y.; Welter, R.; Dagorne, S.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 6279. (l) Majoumo-Mbe, F.; Smolensky, E.; Lönnecke, P.; Shpasser, S.; Eisen, M. S.; Hey-Hawkins, E. *J. Mol. Catal*. *A* **2005**, *240*, 91.

7. (a) Vert, M.; Albertsson, A.; Scott, G.; Chiellini, E. Eds. *Biodegradable Polymers and Plastics;* The Royal Society of Chemistry: Cambridge, UK, 1992; p 95. (b) Vert, M.;

Feijen, J.; Albertsson, A.; Scott, G.; Chiellini, E. eds. *Biodegradable Polymers and Plastics*; The Royal Society of Chemistry: Cambridge, UK, 1992; p 139. (c) Okada, M. *Prog. Polym. Sci*. **2002**, *27*, 87.

8 . (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem*. **1996**, *35*, 63. (b) Qian, B.; Ward, D. L.; Smith III., M. R. *Organometallics* **1998**, *17*, 3070. (c) Rad zewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (d) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883. (e) Muñoz-Hernández, M.-A.; Keiser, T. S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416. (f) Liu, S.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Organomet. Chem.* **2000**, *596*, 109. (g) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A. *J. Chem. Soc., Dalton Trans.* **2001**, 1472. (h) Hill, M. S.; Hutchison, A. R.; Keiser, T. S.; Parkin, S.; VanAelstyn, M. A.; Atwood, D. A. *J. Organomet. Chem.* **2001**, *628*, 71. (i) Redshaw, C.; Elsegood, M. R. J. *Chem. Commun.* **2001**, 2016. (j) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 415. (k) Chakraborty, D.; Chen, E. Y.-X. *Macromolecules* **2002**, *35*, 13. (l) Lewiński, J.; Zachara, J.; Starowieyski, K. B.; Ochal, Z.; Justyniak, I.; Kopec, T.; Stolarzewicz, P.; Dranka, M. *Organometallics* **2003**, *22*, 3773. (m) Lewinski, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (n) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P. ; Jaouen, G. *Organometallics* **2003**, *22*, 3732. (o) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64. (p) Zhu, H.; Chen, E. Y.-X. *Inorg. Chem*. **2007**, *46*, 1481.

9. Synthesis of $Me_2Al[O\text{-}2,4\text{-}{}^tBu_2\text{-}6\text{-}(RN{=}CH)C_6H_2]$ (R = 2,6-^{i}PrC_6H_3, ^{t}Bu), structural analysis for $Me_2Al[O\text{-}2,4\text{-}{}^tBu_2\text{-}6\text{-}\{(2,6\text{-}{}^iPr_2C_6H_3)N{=}CH\}C_6H_2]$, and reactions with $B(C_6F_5)_3$ were reported in ref. 8g. NMR study for reactions of $AlEt_3$ with 1.0 or 2.0 equiv. of $2,4\text{-}Me_2\text{-}6\text{-}\{(2,4,6\text{-}{}^tBu_3C_6H_2)N{=}CH\}C_6H_2OH$ in toluene-d_8 was reported in ref

6j, however, no attempts for isolation of Al complexes including structural determinations were made.

10. Syntheses of various salicylaldimines, and Ti, Zr, V complexes containing bis(phenoxy-imine) ligands: Fujita, T.; Tohi, Y.; Mitani, M. European patent EP 0874005A1, 1998.
11. (a) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847, (b) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc*. **2002**, *124*, 3327. (c) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc*. **2003**, *125*, 4293. (d) Terao, H.; Ishii, S.; Saito, J.; Matsuura, S.; Mitani, M.; Nagai, N.; Tanaka, H.; Fujita, T. *Macromolecules* **2006**, *39*, 8584.
12. Related reports concerning synthesis of half-titanocenes containing phenoxy-imine ligands whereas the imino nitrogens were not coordinated to Ti: Zhang, H.; Katao, S.; Nomura, K.; Huang, J. *Organometallics* **2007**, *26*, 5967.
13. As described in text, the Al complexes containing alkyl substituents in the imino group showed low activities (runs 10-12), and the number of polymer chains (N, catalyst efficiencies calculated based on the molar ratio of N/Al) in the resultant poly(CL)s were lower than those in the Al complexes containing aryl substituents in the imino groups under the same conditions (60 ºC after 60 min, runs 6, 8, 13-14). The observed difference may be thus due to the catalyst efficiency. We also speculated that the imino group in the adamantyl analogue (**2d**) may be weakly coordinated to Al estimated by the difference in the chemical shifts of the imino nitrogen between **2d** and the free ligand, presumably leading to the negligible catalytic activity.

14. Reports concerning comparison between exact number average molecular weights and M_n values by GPC *vs*. polystyrene standards: (a) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczel, S. *Macromolecules* **1990**, *23*, 1640. (b) McLain, S. J.; Drysdale, N. E. *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) **1992**, *33*, 174. (c) Pasch, H.; Rhode, K. *J. Chromatogr., A* **1995**, *699*, 24. (d) Kricheldorf, H. R.; Eggerstedt, S. *Macromol. Chem. Phys.* **1998**, *199*, 283. (e) Duda, A.; Kowalski, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (f) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 1964. (g) Chen, H.-L.; Ko, B.-T.; Huang, B.-H.; Lin, C.-C. *Organometallics* **2001**, *20*, 5076. (h) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889. (i) Kricheldorf, H. R.; Rost, S. *Polymer* **2005**, *46*, 3248. In this chapter, the exact M_n values by GPC vs. polystyrene standards according to the following equation: $M_{n(PCL)} = 0.56 \times M_{n(GPC\ vs.\ polystyrene\ standards)}$.[14e,h]

15. Dittrich, W.; Shultz, R. C. *Angew. Macromol.Chem.* **1971**, *15*, 109.

16. Selected reports concerning transesterification in the ROP of CL and DL-lactide: (a) Duda, A.; Penczek, S. *Macromolecules* **1995**, *28*, 5981. (b) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; Le Borgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461. (c) Spassky, N.; Simic, V.; Montaudo, M. S.; Hubert-Pfalzgraf, L. G. *Macromol. Chem. Phys.* **2000**, *201*, 2432. (d) Jhurry, D.; Bhaw-Luximon, A.; Spassky, N. *Macromol. Symp.* **2001**, *175*, 67. (e) Cayuela, J.; Bounor-Legaré, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338.

17. Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, Jan M. M. *The DIRDIF-94 program system,* Crystallography Laboratory, University of Nijmegen, The Netherlands, 1998.

18. (a) Crystal Structure 3.6.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2004) 9009 New Trails Dr. The Woodlands TX 77381 USA. (b) CRYSTALS

Issue 10: Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; & Betteridge, P. W. Chemical Crystallography Laboratory, Oxford, UK, 1996.

Chapter 3

Ring-opening polymerization of various cyclic esters by Al complex catalysts containing a series of phenoxy-imine ligands: Effect of imino substituents for the catalytic activity

Abstract

Ring-opening polymerizations (ROPs) of various cyclic esters [ε-caprolactone (CL), δ-valerolactone (VL), *rac*-lactide (LC)] using Al complexes containing phenoxy-imine ligands of type, $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ [R = ^{t}Bu (**1a**), cyclohexyl (**1b**), adamantyl (**1c**), C_6H_5 (**1d**), 2,6-$Me_2C_6H_3$ (**1e**), 2,6-$^i Pr_2C_6H_3$ (**1f**), 2,4,6-$Me_3C_6H_2$ (**1g**), 2,4,6-$^t Bu_3C_6H_2$ (**1h**), C_6F_5 (**1i**)], have been explored in the presence of ^{n}BuOH. Synthesis and identification of **1g** and **1h** including structural analysis of **1g** by X-ray crystallography have also been explored. Both the catalytic activity and the catalyst efficiency in the ROPs were found to be highly affected by the imino substituent (R) employed. The 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**) showed the notable catalytic activity in spite of its low catalyst efficiency in the ROP of CL, and the C_6F_5 analogue (**1i**) was most effective in terms of both the activity and the efficiency. The C_6F_5 analogue (**1i**) also showed the highest catalytic activity for ROP of VL, and the polymerization proceeded in a living manner. The C_6F_5 analogue also showed relatively high catalytic activity in the ROP of LC, but the resultant polymer had no stereo-regularity. Although the Al complexes containing alkyl substituents (**1a-c**) exhibited low or negligible catalytic activities in the ROPs of CL and VL, the cyclohexyl analogue (**1b**) showed moderate catalytic activity for the ROP of LC. Attempts for the ROP of β-butyrolactone (β-BL) and γ-butyrolactone (γ-BL) using **1e,h**,**i**-^{n}BuOH catalyst systems afforded negligible amount of polymers under the similar conditions.

Introduction

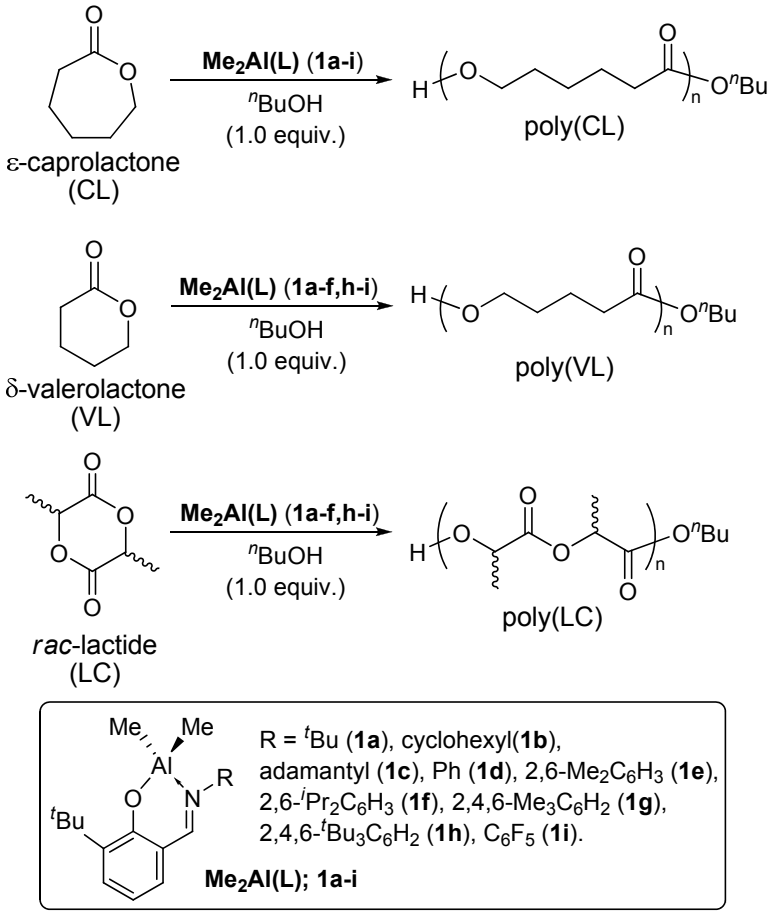
Organoaluminum compounds, especially Al alkoxides have been known to be initiators for ring-opening polymerization (ROP) of cyclic esters[1] such as lactides,[2] lactones.[2j,n,3] These aliphatic polyesters possess promising characteristics as biodegradable and bioassimilable materials not only due to their practical biodegradability, but also due to their biocompatibility for medical and pharmaceutical applications.[4] Design of monomeric or dimeric Al complex catalysts for the efficient polymerization thus attracts considerable attention.[5] Although it is known that an introduction of extremely bulky aryloxide ligands to aluminum generates monomeric Lewis acid catalysts that can be used in various organic reactions,[6] however, reports concerning ligand effect toward the catalytic activity in the ROP of cyclic esters using a series of 'isolated' Al complexes were rare.

In the previous chapter, it was described that ring-opening polyerization (ROP) of ε–caprolactone (CL) using various isolated Al complexes containing phenoxy-imine ligand of type, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}R^2N{=}CH\}C_6H_3]$ [R^1 = Me, ^{t}Bu; R^2 = ^{t}Bu, cyclohexyl, adamantyl, C_6H_5, 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$, C_6F_5], in the presence of ^{n}BuOH (1.0 equiv.). It was found that the imino substituent (R^2) rather than the aryloxo substituent (R^1) strongly affected the catalytic activity (turnover number, TON) in the ROP. The activity increased in the order: $R^2 = C_6F_5 >> 2,6\text{-}Me_2C_6H_3 > 2,6\text{-}^i Pr_2C_6H_3 > C_6H_5 >$ cyclohexyl > ^{t}Bu >> adamantyl, and the ROP using the C_6F_5 analogue proceeded in a living manner with high initiation efficiency. The fact is an interesting contrast to a previous assumption that the electrophilicity of the metal center in the ROP of lactones is much less important.[3g,i] In contrast, the observed facts are analogous to the facts that the catalytic activity, molecular weight for the resultant polymers, and the polymerization behavior for ethylene (and/or propylene) polymerization using various zirconium

complexes containing a series of bis(phenoxy)imine ligands were highly affected by the substituents on both the phenoxy and the imino groups.[7,8]

This chapter deals with ROP of various cyclic esters [ε-caprolactone (CL), δ-valerolactone (VL), *rac*-lactide (LC), β-butyrolactone (β-BL) and γ-butyrolactone (γ-BL)] using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ [**1**, R = ^{t}Bu (**a**), cyclohexyl (**b**), adamantyl (**c**), C_6H_5 (**d**), 2,6-$Me_2C_6H_3$ (**e**), 2,6-$^i Pr_2C_6H_3$ (**f**), 2,4,6-$Me_3C_6H_2$ (**g**), 2,4,6-$^t BuC_6H_2$ (**h**), C_6F_5 (**i**)] upon the presence of ^{n}BuOH (1.0 equiv.). In order to explore effect of the aromatic substituents in the imino group, preparation and identification of the 2,4,6-$Me_3C_6H_2$ analogue (**1g**) and the 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**) were examined including the structure analysis for **1g** by X-ray crystallography.

Scheme 3-1



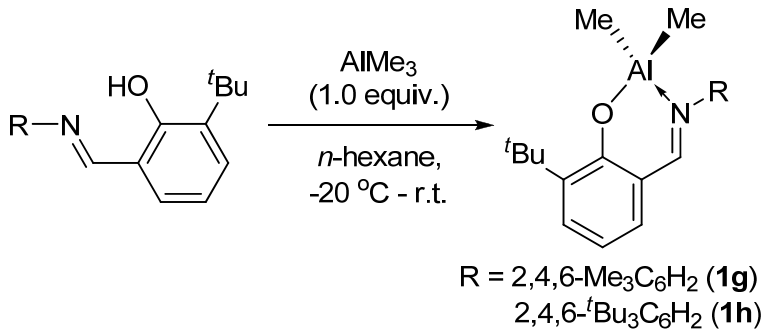
Through these experiments, I tried to explore the ligand effect, especially effect of aromotic substituent in the imino ligand, as well as monomers toward the catalytic activity in the ROP of various cyclic esters (Scheme 3-1).

Results and Discussion

1. Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,4,6\text{-}R'_3N{=}CH)C_6H_3]$ (R' = Me, ^{t}Bu).

Various Al complexes containing a series of phenoxy-imine ligands of the type, $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ [**1**, R = ^{t}Bu (**a**), cyclohexyl (**b**), adamantyl (**c**), C_6H_5 (**d**), 2,6-$Me_2C_6H_3$ (**e**), 2,6-$^i Pr_2C_6H_3$ (**f**), C_6F_5 (**i**)], were prepared according to previous chapter 2. In order to explore effect of the aromatic substituents in the imino group toward the catalytic activity, as described above, the 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**) has been chosen because a mixed catalyst system consiting of $AlEt_3$, 2-{(2,4,6-$^t Bu_3C_6H_2$)N=CH}C_6H_4OH (2 equiv. to Al), and $PhCH_2OH$ (1 equiv. to Al) was known to exhibit high catalytic activity for ROP of CL.[3j] The 2,4,6-$Me_3C_6H_2$ analogue (**1g**) and the 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**) were prepared by the analogous procedures (Scheme 3-2) and were identified based on ^1H, ^{13}C NMR spectra and elemental analysis.

Scheme 3-2



The structure of **1g** was determined by X-ray crystallography (Figure 3-1), and the structure showed that **1g** folds a distorted tetrahedral geometry around the Al metal center. This can be seen from the bond angles for C(1)-Al-C(2) [117.58(12)º], O(1)-Al-C(1)

[111.75(10)º], O(1)-Al-C(2) [110.76(11)º], although the O(1)-Al-N(1) bond angle is somewhat small [93.78(8)º]. The Al-N bond distance [1.965(2) Å] is somewhat short but within the range of those in the series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$[**1a-d**,**f-g**,**i**;1.965-1.9896 Å]. The Al-O bond distance [1.7748(19) Å] is also close to those in the other Al complexes [**1a-d**,**f-g**,**i**;1.7592-1.7792 Å].

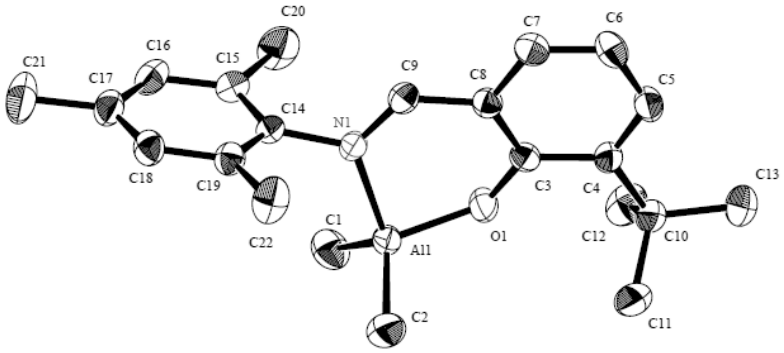


Figure 3-1. ORTEP drawing for $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,4,6\text{-}Me_3C_6H_2)N{=}CH\}C_6H_3]$ (**1g**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond distance (Å): Al(1)-O(1) 1.7748(19), Al(1)-N(1) 1.965(2), Al(1)-C(1) 1.953(2), Al(1)-C(2) 1.956(2), N(1)-C(9) 1.296(2), N(1)-C(14) 1.452(2). Selected bond angles (º): O(1)-Al(1)-N(1) 93.37(8), C(1)-Al(1)-C(2) 117.58(12), Al(1)-O(1)-C(3) 129.37(16), Al(1)-N(1)-C(9) 121.45(16), Al(1)-N(1)-C(14) 119.84(13), O(1)-Al(1)-C(1) 111.75(10), O(1)-Al(1)-C(2) 110.76(11), N(1)-Al(1)-C(1) 110.45(10), N(1)-Al(1)-C(2) 110.30(11).

2. Ring-opening polymerization of ε–caprolactone.

Ring-opening polymerizations (ROP) of ε-caprolactone (CL) were conducted at 60 ºC in the presence of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (**1a-i**) upon the addition of ^{n}BuOH (1.0 equiv. to Al), and the results are summarized in Table 3-1. The results in previous chapter by **1a-f**,**i** conducted under the same conditions are also placed for comparison. As demonstrated previously, presence of ^{n}BuOH (1.0 equiv. to Al) was prerequisite and the polymerization did not take place in the absence of ^{n}BuOH.

Table 3-1. Ring-opening polymerization of ε-caprolactone (CL) by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (**1a-i**) [R = ^{t}Bu (**1a**), cyclohexyl (**1b**), adamantyl (**1c**), C_6H_5 (**1d**), 2,6-$Me_2C_6H_3$ (**1e**), 2,6-$^i Pr_2C_6H_3$ (**1f**), 2,4,6-$Me_3C_6H_2$ (**1g**), 2,4,6-$^t Bu_3C_6H_2$ (**1h**), C_6F_5 (**1i**)].[a]

run	complex (R)	Al / μmol	time / min	yield / mg (%)	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	N[d] / μmol
1	**1a** (^{t}Bu)	20	60	46 (8)	20	1.64	1.10	5.0
2	**1b** (cyclohexyl)	20	60	156 (28)	70	2.07	1.19	13.5
3	**1c** (adamantyl)	20	60	trace	--	--	--	--
4	**1d** (C_6H_5)	20	60	258 (45)	113	2.83	1.38	16.3
5	**1e** (2,6-$Me_2C_6H_3$)	20	30	413 (74)	185	4.84	1.64	15.2
6	**1f** (2,6-$^i Pr_2C_6H_3$)	20	60	472 (84)	209	4.35	1.61	19.4
7	**1f** (2,6-$^i Pr_2C_6H_3$)	20	30	192 (34)	85	2.87	1.24	11.9
8	**1g** (2,4,6-$Me_3C_6H_2$)	20	60	499 (89)	223	4.92	1.93	18.1
9	**1g** (2,4,6-$Me_3C_6H_2$)	20	30	171 (31)	78	2.03	1.35	15.0
10	**1h** (2,4,6-$^t Bu_3C_6H_2$)	20	30	524 (94)	235	7.66	1.58	12.2
11	**1h** (2,4,6-$^t Bu_3C_6H_2$)	10	30	375(66)	330	10.6	1.68	5.9
12	**1i** (C_6F_5)	20	30	551 (99)	248	5.60	1.64	17.6
13[e]	**1i** (C_6F_5)	20	30	550 (98)	245	7.56	1.66	13.0
14	**1i** (C_6F_5)	10	30	481 (86)	430	9.34	1.64	9.2

[a]Conditions: Al 10, 20 μmol, ^{n}BuOH 1.0 equiv. to Al (in toluene 50 μL), CL 5.0 mmol. 60 ºC. [b]TON = (molar amount of CL reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standards. [d]Estimated number of polymer chain (mmol) = polymer yield (mg)/{0.56 × $M_{n(GPC)}$}.[9] [e]$PhCH_2OH$ was used in place of ^{n}BuOH [$M_n = 4.42\times10^4$ estimated by ^{1}H NMR spectrum].

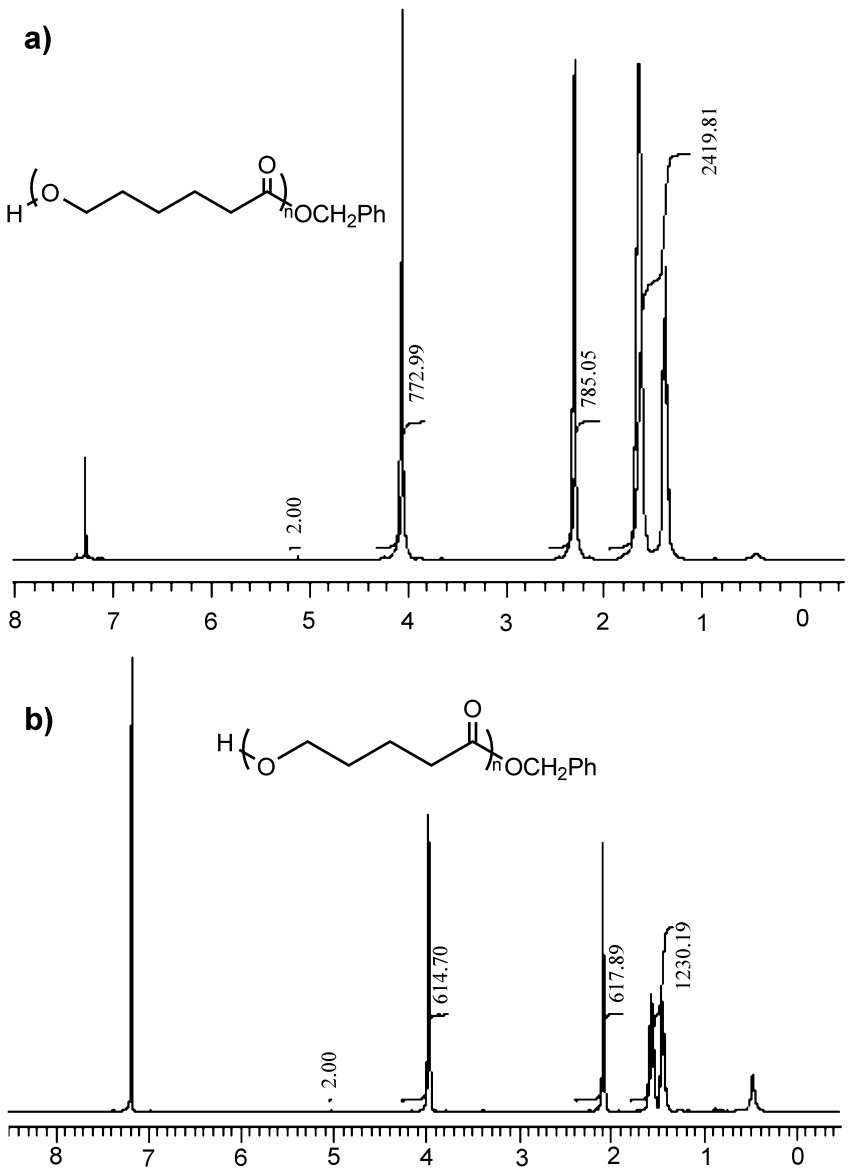
The catalytic activity [TON values, TON = CL consumed, reacted (μmol)/Al (μmol)] (TON after 60 min at 60 °C) in the ROP of CL with a series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ increased in the order: R = C_6F_5 [**1i**, TON > 248 (430) after 30 min, run 12 (run 14)] > 2,4,6-$^t Bu_3C_6H_2$ [**1h**, TON > 235 (330) after 30 min, run 10 (run 11)] >> 2,6-$Me_2C_6H_3$ (**1e**, 185 after 30 min, run 5) > 2,4,6-$Me_3C_6H_2$ (**1i**, 223, run 8) > 2,6-$^i Pr_2C_6H_3$ (**1f**, 209, run 6) > C_6H_5 (**1d**, 113, run 4). The Al complexes containing alkyl substituents in the imino group showed low catalytic activities (runs 1-3), as described chapter 2. The ROP by both the C_6F_5 analogue (**1i**) and the 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**) completed even after 30 min (Al 20 μmol, 60 ºC, runs 10,12), and the C_6F_5 analogue (**1i**) showed the

higher activity than the 2,4,6-$^{t}Bu_3C_6H_2$ analogue (**1h**) when the ROP was conducted under low Al concentration conditions (Al 10 μmol, run 14).

The ROP by **1i** in the presence of $PhCH_2OH$ in place of ^{n}BuOH was also conducted and the resultant ring-opened polymer contained polymer chain end derived from $PhCH_2OH$ (Figure 3-2a). The M_n value (4.42×10^4) estimated by ^{1}H NMR spectrum was very close to the exact value (4.23×10^4, run 13) calculated, corrected based on the M_n values by the GPC measurement *versus* polystyrene standards.[12] The result thus suggests that the ROP was initiated with Al-OR *via* coordination insertion mechanism as proposed.[1,10] Moreover, the catalyst efficiency for the ROP by **1i** in the presence of $PhCH_2OH$ was estimated based on both the exact M_n value corrected by the value measured by GPC[9] and the polymer yields. The calculated value of 65% (run 13) was lower than that by the **1i**-^{n}BuOH system (88%, run 12), and the results thus clearly explain the fact that the M_n value in the resultant ring-opened polymer by **1i**-$PhCH_2OH$ system was higher than that by **1i**-^{n}BuOH system due to the difference in the catalyst efficiency.

The catalyst efficiencies were thus estimated [based on N values (in μmol) *vs*. Al used (μmol)] in all polymerization runs at 60 ºC according to the above procedure (Table 3-1, runs 1-10,12), and the Al complexes containing alkyl substituents and 2,4,6-$^{t}Bu_3C_6H_2$ in the imino group were found to be low (runs 1-3,10). Note that the observed activity (TON value) by the 2,4,6-$^{t}Bu_3C_6H_2$ analogue (**1h**) estimated based on the polymer yield was almost equal to the C_6F_5 analogue (**1i**, run 12, 88%), whereas **1h** showed the low efficiency (run 10, 61%). The results thus suggest that the actual propagation rate by **1h** should be higher than that by **1i**.

Figure 3-2. (a) ^{1}H NMR spectrum (in C_6D_6 at 25 °C) for poly(CL) (run 13 in Table 3-1), $M_{n(NMR)}$ = 4.42 × 10^4. (b) ^{1}H NMR spectrum (in C_6D_6 at 25 °C) for poly(VL) (run 33 in Table 3-3), $M_{n(NMR)}$ = 3.10 × 10^4.



As shown in Table 3-2, the observed activities by **1e,f,h,i** decreased upon decreasing the polymerization temperature (from 60 to 50, 40 ºC), and no significant differences in the order toward the activity in the ROP using Al complexes with a series of the aromatic substituent in the imino group were seen. The C_6F_5 analogue (**1i**, run 19, 86%) thus showed the highest activity (TON values) among these Al complexes when the ROPs were conducted at 50 ºC.

Table 3-2. Ring-opening polymerization of ε-caprolactone (CL) by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ [R = 2,6-$Me_2C_6H_3$ (**1e**), 2,6-$^i Pr_2C_6H_3$ (**1f**), 2,4,6-$^t Bu_3C_6H_2$ (**1h**), C_6F_5 (**1i**)].[a]

run	complex (R)	Al / μmol	Temp. /ºC	Time / min	yield / mg (%)	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	N[d] / μmol
6	**1f** (2,6-$^i Pr_2C_6H_3$)	20	60	60	472 (84)	209	4.35	1.61	19.4
15	**1f** (2,6-$^i Pr_2C_6H_3$)	20	50	60	198(35)	88	2.58	1.27	13.7
5	**1e** (2,6-$Me_2C_6H_3$)	20	60	30	413 (74)	185	4.84	1.64	15.2
16	**1e** (2,6-$Me_2C_6H_3$)	20	50	60	449(80)	200	5.39	1.74	14.9
10	**1h** (2,4,6-$^t Bu_3C_6H_2$)	20	60	30	524 (94)	235	7.66	1.58	12.2
17	**1h** (2,4,6-$^t Bu_3C_6H_2$)	20	50	30	457 (82)	205	7.15	1.57	11.4
18	**1h** (2,4,6-$^t Bu_3C_6H_2$)	20	40	30	274 (50)	125	4.86	1.46	10.1
12	**1i** (C_6F_5)	20	60	30	551 (99)	248	5.60	1.64	17.6
19	**1i** (C_6F_5)	20	50	30	480 (86)	215	5.27	1.40	16.3
20	**1i** (C_6F_5)	20	40	30	331 (59)	148	4.33	1.28	13.7
11	**1h** (2,4,6-$^t Bu_3C_6H_2$)	10	60	30	375 (66)	330	10.6	1.68	5.9
21	**1h** (2,4,6-$^t Bu_3C_6H_2$)	10	50	30	179 (32)	160	5.79	1.47	5.5
22	**1h** (2,4,6-$^t Bu_3C_6H_2$)	10	40	30	trace	--	--	--	--
14[e]	**1i** (C_6F_5)	20	60	30	481 (86)	430	9.34	1.64	9.2
23	**1i** (C_6F_5)	20	50	30	228 (41)	205	5.58	1.39	7.3
24	**1i** (C_6F_5)	10	40	30	45 (8)	40	1.62	1.10	5.0

[a]Conditions: Al 10, 20 μmol, ^{n}BuOH 1.0 equiv. to Al (in toluene 50 μL), CL 5.0 mmol. [b]TON = (molar amount of CL reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standards. [d]Estimated number of polymer chain (μmol) = polymer yield (mg)/{0.56 × $M_{n(GPC)}$}.[9] [e]$PhCH_2OH$ was used in place of ^{n}BuOH [$M_n = 4.42\times10^4$ estimated by ^{1}H NMR spectrum].

Rather notable differences in the TON values were seen between the C_6F_5 analogue (**1i**) and the 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**), when the ROPs were performed under low Al concentration conditions (10 μmol, runs 11,14,21-24); the polymerization by **1h** did not proceed or exhibited negligible activity at 40 ºC. The observed differences, especially the tendency in the ROPs using **1h** is due to the low catalyst efficiency under these conditions. Therefore, the C_6F_5 analogue is concluded to be suited as the catalyst precursor in term of both the catalytic activity and the catalyst efficiency. As described previously, the ROP of CL by **1i** proceeded in a living manner with high initiation efficiency under optimized conditions, affording the ring-opened polymer with narrow molecular weight distributions.

3. Ring-opening polymerization (ROP) of δ-valerolactone and *rac*-lactide.

ROP of δ-valerolactone (VL) using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (**1a-i**)-^{n}BuOH (1.0 equiv. to Al) catalyst systems were performed under the similar conditions for those of CL, and the results are summarized in Table 3-3

Table 3-3. Ring-opening polymerization of δ-valerolactone (VL) by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (**1a-f**,**h-i**) [R = ^{t}Bu (**1a**), cyclohexyl (**1b**), adamantyl (**1c**), C_6H_5 (**1d**), 2,6-$Me_2C_6H_3$ (**1e**), 2,6-$^i Pr_2C_6H_3$ (**1f**), 2,4,6-$^t Bu_3C_6H_2$ (**1h**), C_6F_5 (**1i**)].

run	complex (R)	Al / μmol	time / min	yield / mg (%)	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]
25	**1a** (^{t}Bu)	20	60	trace	--	--	--
26	**1b** (cyclohexyl)	20	60	trace	--	--	--
27	**1c** (adamantyl)	20	60	trace	--	--	--
28	**1d** (C_6H_5)	20	30	264 (53)	133	1.30	1.21
29	**1e** (2,6-$Me_2C_6H_3$)	20	30	430 (86)	215	1.95	1.37
30	**1f** (2,6-$^i Pr_2C_6H_3$)	20	30	355 (71)	178	1.61	1.33
31	**1h** (2,4,6-$^t Bu_3C_6H_2$)	20	30	411 (82)	205	1.72	1.30
32	**1i** (C_6F_5)	20	30	462 (92)	230	1.94	1.38
33[d]	**1i** (C_6F_5)	20	30	452 (90)	225	2.01	1.32
34	**1e** (2,6-$Me_2C_6H_3$)	10	30	349 (70)	350	1.93	1.21
35	**1h** (2,4,6-$^t Bu_3C_6H_2$)	10	30	234 (47)	235	1.39	1.24
36	**1i** (C_6F_5)	10	30	453 (90)	450	2.54	1.39

[a]Conditions: Al 10, 20 μmol (in toluene 85 μmol), ^{n}BuOH 1.0 equiv. to Al, VL 5.0 mmol, 60 ºC. [b]TON = (molar amount of VL reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standards. [d]$PhCH_2OH$ was used in place of ^{n}BuOH [$M_n = 3.10\times10^4$ estimated by ^{1}H NMR spectrum].

The polymerization did not proceed or exhibited negligible catalytic activities, when Al complexes containing alkyl substituents in the imino group [R = ^{t}Bu, cyclohexyl, adamantly (**1a-c**)] were employed. In contrast, as seen in the ROPs of CL, the ROPs proceeded with high catalytic activities, when the Al complexes containing aromatic substituent in the imino group (**1d-f**,**h**,**i**) were employed as the catalyst precursors. The activity [TON values, TON after 60 min at 60 ºC, Al 20 μmol, initial molar ratio of [VL]/[Al]

= 250] using a series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ increased in the order: R = C_6F_5 [**1i**, TON = 230, (or 450, Al 10 μmol), run 32, (run 36)] > 2,6-$Me_2C_6H_3$ [**1e**, 215, (or 350, Al 10 μmol), run 29, (run 34)] > 2,4,6-$^tBu_3C_6H_2$ [**1h**, 205, (or 235, Al 10 μmol) run 31, (run 35)] > 2,6-$^iPr_2C_6H_3$ (**1f**, 178, run 30) > C_6H_5 (**1d**, 133, run 28). The observed trend concerning effect of aromatic substituent toward the activity in the ROP of VL was similar to that in the ROP of CL, except that the 2,6-$Me_2C_6H_3$ (**1e**) showed higher activity than 2,4,6-$^tBu_3C_6H_2$ (**1h**); the C_6F_5 analogue (**1i**) showed the highest activity and the ROP reached to completion even if the polymerization was performed with low Al concentration (Al 10 μmol, run 36).

The ROP using **1i** was conducted upon $PhCH_2OH$ instead of ^{n}BuOH and the resultant ring-opened polymer possessed polymer chain end derived from $PhCH_2OH$ confirmed by ^{1}H NMR spectrum (Figure 3-2b). Moreover, the M_n value [$M_{n(NMR)} = 3.10\times10^4$], which was estimated by ^{1}H NMR spectrum based on methylene protons at the polymer chain end derived from $PhCH_2OH$, was relatively close to theoretical [$M_{n(calc)} = 2.26\times10^4$] calculated based on VL/AL molar ratio (and 90% yield). The catalyst efficiency (73%, run 33) for the ROP by **1i**-$PhCH_2OH$ catalyst system was estimated based on these M_n values [$M_{n(calcd)}/M_{n(NMR)}$], and the result would suggest that the present ROP was initiated with Al-OR *via* coordination insertion mechanism as proposed.[1,10]

The ROP of VL using the C_6F_5 analogue (**1i**)-^{n}BuOH catalyst system was conducted in toluene at 50 ºC, and the results are summarized in Table 3-4. The ROP proceed at significant rate at the beginning and the rate gradually decreased upon consumption of VL. As shown in Figure 3-3, the rates were first order dependent upon the VL concentration, suggesting that polymerization proceeded without deactivation. The M_n values in the resultant polymer increased linearly upon increasing the TON values (polymer yields) consistently with low M_w/M_n values (M_w/M_n = 1.13-1.17, Figure 3-4). These results clearly indicate that the ROP by C_6F_5 analogue (**1i**) proceeds in a living manner, as seen in the ROP of CL. Taking into account these results, I would also conclude that the ROP of VL by

1i-^{n}BuOH (and $PhCH_2OH$) catalysts system proceeded without side reaction like transesterification.[11]

Table 3-4. Ring-opening polymerization of δ-valerolactone (VL) by $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1i**) in toluene.[a]

run	time / min	yield / mg (%)	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]
37	30	199 (40)	100	0.77	1.14
38	45	309 (62)	155	1.06	1.13
39	60	367 (73)	183	1.16	1.15
40	75	417 (83)	208	1.33	1.17

[a]Conditions: Al 20 μmol (in toluene 100 μL), *n*-butanol 1.0 equiv. to Al (in toluene 85 μL), VL 5.0 mmol, toluene 4.35 mL, initial conc. VL = 1.0 mmol/mL, 50 ºC. [b]TON=(molar amount of VL reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standard.

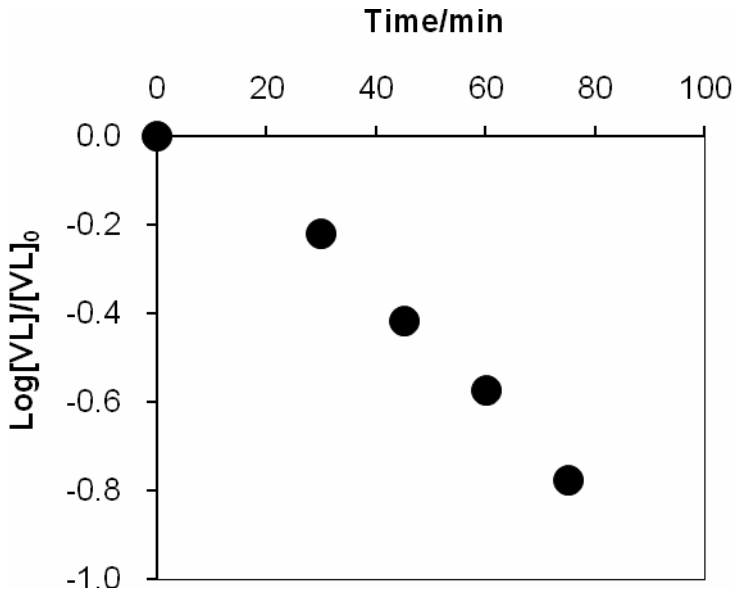


Figure 3-3. Time course plots of $\log[VL]/[VL]_0$. [VL] = concentration of VL in mmol/mL. Conditions are described in Table 3-4.

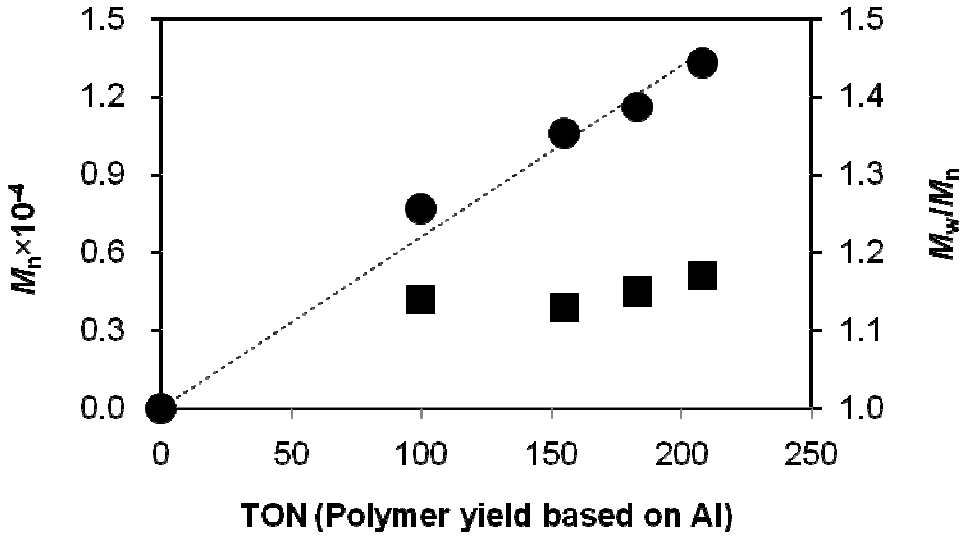


Figure 3-4. Plots of M_n and M_w/M_n values for poly(CL) *vs.* TON for ring-opening polymerization of δ-valerolactone (VL) catalyzed by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1i**) in toluene. Conditions are described in Table 3-4.

Ring-opening polymerization (ROP) of *rac*-lactide (LC) using the **1a-f**,**h-i** were conducted at 80 ºC in the presence of ^{n}BuOH, and the results are summarized in Table 3-5. The catalytic activity [TON values, TON after 24 h at 80 ºC, Al 50 μmol, initial molar ratio of [LC]/[Al] = 100] in the ROP of LC using a series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ increased in the order: R = C_6F_5 [**1i**, TON = 94, (36 after 8 h), run 49, (run 50)] > 2,4,6-^{t}Bu$_3$C$_6$H$_2$ [**1h**, 91, (24) run 47, (run 48)] > cyclohexyl (**1b**, 72, run 43) > 2,6-Me$_2$C$_6$H$_3$ (**1e**, 46, run 45) > 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1f**, 23, run 46) > C$_6$H$_5$ (**1d**, 19, run 44) >> adamantyl (**1c**, 5, run 42), ^{t}Bu (**1b**, 4, run 41). The ROPs using 2,4,6-^{t}Bu$_3$C$_6$H$_2$ analogue (**1h**), the C_6F_5 analogue (**1i**) were also conducted at 70 °C in the presence of ^{n}BuOH, but the observed activities (runs 51-52) were significantly lower than those performed at 80 °C (runs 47,49). Both the activity and the catalyst efficiency by **1i** seemed to be more sensitive to temperature than those by **1h**.

Table 3-5. Ring-opening polymerization of *rac*-lactide (LC) using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (**1a-f**,**h-i**) [R = ^{t}Bu (**1a**), cyclohexyl (**1b**), adamantyl (**1c**), C_6H_5 (**1d**), 2,6-$Me_2C_6H_3$ (**1e**), 2,6-$^i Pr_2C_6H_3$ (**1f**), 2,4,6-$^t Bu_3C_6H_2$ (**1h**), C_6F_5 (**1i**)].

run	complex (R)	temp. / ºC	time / h	yield / mg (%)	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	N[d] / μmol
41	**1a** (^{t}Bu)	80	24	27 (4)	4	--[e]	--[e]	--
42	**1c** (adamantyl)	80	24	36 (5)	5	--[e]	--[e]	--
43	**1b** (cyclohexyl)	80	24	517 (72)	72	1.71	1.22	52.1
44	**1d** (C_6H_5)	80	24	140 (19)	19	1.08	1.11	22.3
45	**1e** (2,6-$Me_2C_6H_3$)	80	24	333 (46)	46	1.69	1.15	34.0
46	**1f** (2,6-$^i Pr_2C_6H_3$)	80	24	168 (23)	23	1.35	1.10	21.5
47	**1h** (2,4,6-$^t Bu_3C_6H_2$)	80	24	657 (91)	91	2.37	1.18	47.8
48	**1h** (2,4,6-$^t Bu_3C_6H_2$)	80	8	164 (24)	24	1.43	1.08	19.8
49	**1i** (C_6F_5)	80	24	668 (94)	94	2.13	1.30	54.1
50	**1i** (C_6F_5)	80	8	264 (36)	36	1.30	1.09	35.0
51	**1h** (2,4,6-$^t Bu_3C_6H_2$)	70	24	77 (11)	11	1.09	1.14	12.2
52	**1i** (C_6F_5)	70	24	33 (5)	5	0.70	1.20	8.1

[a]Conditions: Al 50 μmol (in toluene 85 μL), ^{n}BuOH 1.0 equiv. to Al, LC 5.0 mmol, initial conc. of LC = 1.0 mmol/mL, toluene. [b]TON = (molar amount of LC reacted)/(molar amount of Al). [c]GPC data in THF vs polystyrene standards. [d]Estimated number of polymer chain (μmol) = polymer yield (mg)/{0.58 × $M_{n(GPC)}$}.[9] [e]Resultant polymer was insoluble in THF.

Although Al complexes containing alkyl substituent in the imino group were not efficient for the ROP of both CL and VL, the cyclohexyl analogue (**1b**) was found to be effective for the ROP of LC (run 43). The activity of both the *tert*-butyl analogue (**1a**) and the adamantyl analogue (**1c**) were significantly lower than **1b** probably due to the steric bulk. The moderate catalytic activity by **1b** would be caused by electronic effect of alkyl substituent, because the catalytic activity by the phenyl analogue (**1d**) possessing the same steric bulk was about quarter of that by **1b** (run 44). The results thus suggest that the nucleophilicity of ^{n}BuO would be enhanced by placing electron-releasing group as the imino substituent.

^{1}H NMR spectra of methine region of the resultant poly(LC) indicated that the resultant polymers prepared by the Al complexes (**1a-f**,**h-i**)-^{n}BuOH catalyst systems had no tacticity, and atactic polymers were thus collected (Figure 3-5).

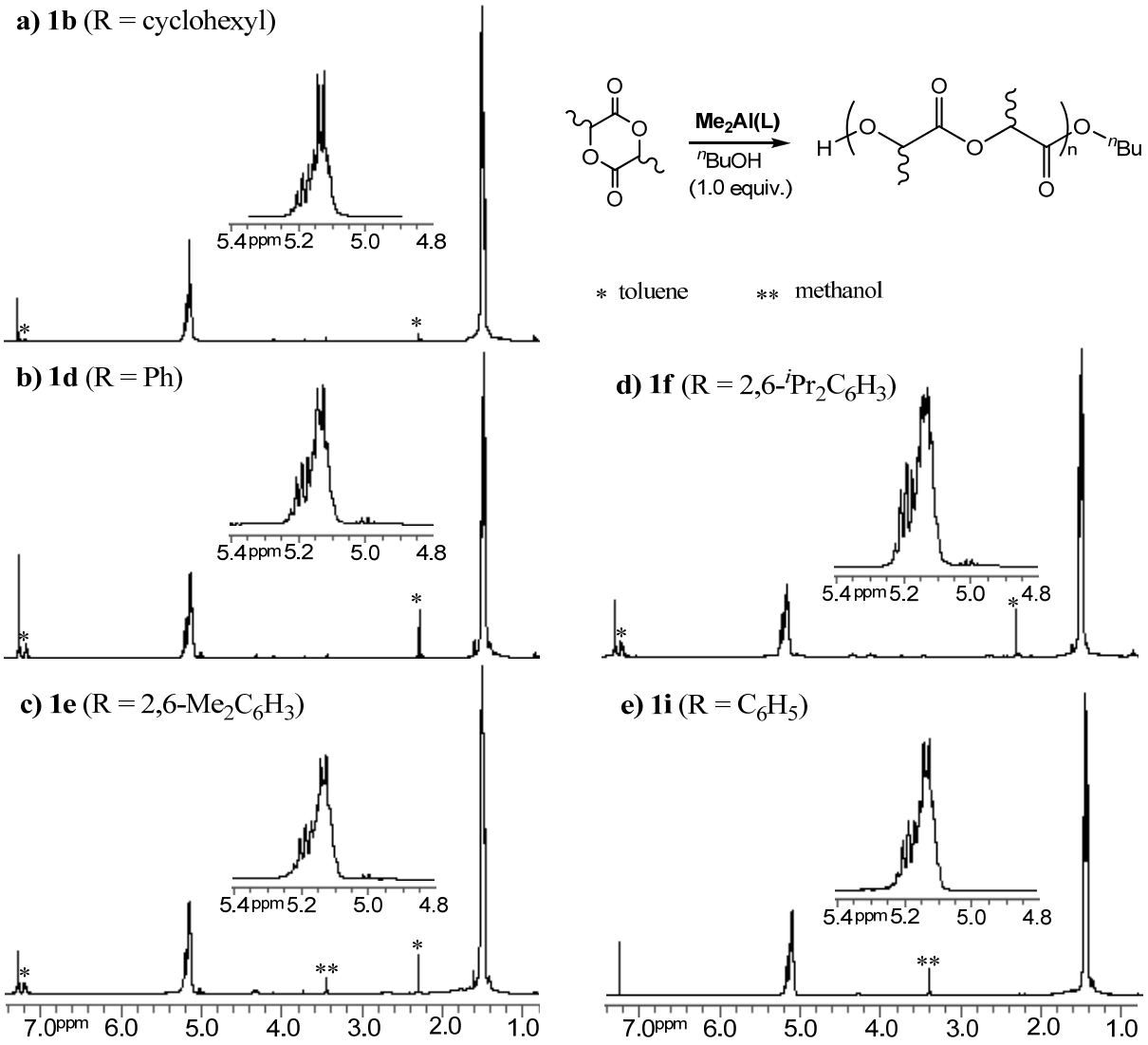


Figure 3-5. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of the methine region of the resultant poly(LC) using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{RN{=}CH\}C_6H_3]$ [R = cyclohexyl (**1b**, top left, run 43), phenyl (**1d**, center left, run 44), 2,6-$Me_2C_6H_3$ (**1e**, bottom left, run 45), 2,6-$^i Pr_2C_6H_3$ (**1f**, center right, run 46), C_6F_5 (**1i**, bottom right, run 49)]. Peak marked with * is due to resonance ascribed to impurities.

- Attempted ring-opening polymerization (ROP) of β-butyrolactone and γ-butyrolactone using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (1e,h-i) -

Ring-opening polymerization (ROP) of various cyclic esters such as β-butyrolactone and γ-butyrolactone using the $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (**1e,h,i**)-^{n}BuOH catalyst systems were attempted under bulk (neat) conditions at 80 ºC for 24 h (Al 50 μmol,

monomer/Al molar ratio = 100). However, the attempted ROPs gave negligible amount of polymers under these conditions. These results thus suggest that the present catalytic systems are limited to be effective for cyclic esters consisting of six or seven membered ring.

Concluding remarks

Ring-opening polymerization of ε-caprolactone (CL), δ-valerolactone (VL), *rac*-lactide (LC) were conducted using a series of Al complexes containing phenoxy-imine ligands of type, $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}(RN{=}CH)C_6H_3]$[**1**, R = ^{t}Bu (**a**), cyclohexyl (**b**), adamantly (**c**), C_6H_5 (**d**), 2,6-$Me_2C_6H_3$ (**e**), 2,6-$^{i}Pr_2C_6H_3$ (**f**), 2,4,6-$Me_3C_6H_2$ (**g**), 2,4,6-$^{t}Bu_3C_6H_2$ (**h**), C_6F_5 (**i**)] upon the presence of ^{n}BuOH (1.0 equiv.). It turned out that the imino substituent strongly affect toward both the catalytic activity and the catalyst efficiency, and the C_6F_5 analogue (**1i**) is a suitable catalyst precursor for the ROPs. The polymerization of CL and VL by **1i** proceeded in a living manner. The 2,4,6-$^{t}Bu_3C_6H_2$ analogue (**1h**) also exhibited remarkable catalytic activities for ROPs of CL and VL, but the catalyst efficiency of **1h** was apparently lower than **1i**. Both the C_6F_5 analogue (**1i**) and the 2,4,6-$^{t}Bu_3C_6H_2$ analogue (**1h**) also showed moderate catalyst activity in the ROP of LC, but the resultant polymer possessed no stereo regularity (atactic). The attempts for polymerization of β–butylolactone and γ–butyrolactone afforded negligible amount of polymers, suggesting that the present catalyst systems are limited to be effective for cyclic esters consisting of six or seven membered ring.

Next chapter focuses on more details for the ROPs using the C_6F_5 analogue, $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(C_6F_5)N{=}CH)\}C_6H_3]$ (**1i**), including synthesis of various Al complexes containing a series of fluorinated aromatic substituents as the imino substituent.

Experimental Section

General procedures.

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade *n*-hexane, toluene (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 stream, and were passed through a short alumina column under N_2 stream before use. All chemicals used were of reagent grade and were purified by the standard purification procedures. Reagent-grade $AlMe_3$ in *n*-hexane (Kanto Kagaku Co. Ltd.) were stored in the drybox and were used as received. Various salicylaldimines (imino-phenols) containing different substituent on the imino groups, 2-^{t}Bu-6-(RN=CH)C_6H_3OH [R = ^{t}Bu, cyclohexyl, adamantyl, Ph, 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$, 2,4,6-$^t Bu_3C_6H_2$, C_6F_5] were prepared according to the reported procedures.[7] Syntheses of Al complexes (**1a-f**,**i**) were referred to our previous report. Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). All ^{1}H, and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted, and chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^{1}H, ^{13}C). Molecular weights and the molecular weight distributions of resultant polymers were measured by gel-permeation chromatography (GPC). GPC were performed at 40 ºC on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mmϕ, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from < 10^2 to 2×10^7 MW) were calibrated versus polystyrene standard samples.

Synthesis of Me_2Al[O-2-^{t}Bu-6-{(2,4,6-$Me_3C_6H_2$)N=CH}C_6H_3] (1g).

Into a stirred solution containing 2-^{t}Bu-6-{(2,4,6-$Me_3C_6H_2$)N=CH}C_6H_3OH (1.41 g,

4.00 mmol) in *n*-hexane (10.0 mL), $AlMe_3$ (1.1 M *n*-hexane solution, 4.67 mL, 4.20 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 3-2). Removal of the solvent from the mixture by using a rotary evaporator *in vacuo* gave complex **1g** (1.39 g, 99 % yield) as yellow powder. ^{1}H NMR (C_6D_6): δ -0.28 (s, 6H, Al*Me*$_2$), 1.56 (s, 9H, ^{t}Bu), 1.98 (s, 6H, Me), 2.05 (s, 3H, Me), 6.59-6.67 (m, 4H, aromatic), 7.31 (s, 1H, C*H*=N), 7.42 (d, *J* = 7 Hz, 1H, aromatic). ^{13}C NMR (C_6D_6): δ -8.6, 18.4, 20.7, 29.5, 35.4, 117.3, 119.8, 129.7, 131.4, 133.7, 135.0, 136.8, 141.8, 142.7, 164.8, 174.8. Anal. Calcd for $C_{22}H_{31}AlNO$: C, 75.18; H, 8.60; N, 3.99. Found: C, 75.34; H, 8.76; N, 3.97. The structure was determined by X-ray crystallography. The measurement was made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation.

Synthesis of Me_2Al[O-2-^{t}Bu-6-{(2,4,6-^{t}Bu$_3C_6H_2$)N=CH}C_6H_3] (1h).

Into a stirred solution containing 2-^{t}Bu-6-{(2,4,6-^{t}Bu$_3C_6H_2$)N=CH}C_6H_3OH (0.905 g, 2.15 mmol) in *n*-hexane (3.0 mL), $AlMe_3$ (1.1 M *n*-hexane solution, 1.62 g, 2.37 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 3-2). Removal of the solvent from the mixture by using a rotary evaporator *in vacuo* gave complex **1h** (0.88 g, 85.8 % yield) as yellow powder. ^{1}H NMR (C_6D_6): δ -0.18 (s, 6H, Al*Me*$_2$), 1.26 (s, 9H, ^{t}Bu), 1.42 (s, 18H, ^{t}Bu), 1.55 (s, 9H, ^{t}Bu), 6.59 (t, *J* = 7.72 Hz, 1H, aromatic), 6.72 (d, *J* = 8.08 Hz, 1H, aromatic), 7.39 (d, *J* = 7.32 Hz, 1H, aromatic), 7.59 (s, 1H, aromatic), 7.90 (s, 1H, C*H*=N). ^{13}C NMR (C_6D_6): δ -6.7, 29.6, 31.3, 34.4, 34.8, 35.4, 37.6, 117.8, 120.2, 125.1, 133.0, 134.8, 142.3, 143.5, 143.7, 148.5, 164.7, 177.1. Anal. Calcd for $C_{31}H_{48}AlNO$: C, 77.94; H, 10.13; N, 2.93. Found: C, 77.60; H, 10.27; N, 3.02.

Ring opening polymerization (ROP) of ε-caprolactone (CL).

Typical polymerization procedures (Table 3-1, run 11) are as follows. Into a sealed Schlenk tube containing a toluene solution containing **1i** (0.010 mmol/0.085 mL of toluene),

^{n}BuOH (0.010 mmol) was added in the drybox at room temperature. The solution was stirred for 10 minutes, and the solution was then added ε-caprolactone (5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 60 ºC, and the solution was stirred for the prescribed time (30 min). The polymerization mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into methanol (400 mL). The ring-opened polymer was then collected as the methanol insoluble white precipitates; the resultant polymer was then collected onto a filter paper and was dried *in vacuo*. ^{1}H NMR ($CDCl_3$): δ 1.33 (m, 2H), 1.51-1.63 (m, 4H), 2.25 (t, 2H), 4.00 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 24.5, 25.5, 28.3, 34.1, 64.1, 173.5 (C=O).

Ring opening polymerization (ROP) of δ-valerolactone (VL).

Typical polymerization procedures (Table 3-3, run 32) are as described. Into a sealed Schlenk tube containing a toluene solution containing **1i** (0.020 mmol/0.085 mL of toluene), ^{n}BuOH (0.020 mmol) was added in the drybox at room temperature. The solution was stirred for 10 minutes, and the solution was then added δ-valerolactone (5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 60 ºC, and the solution was stirred for the prescribed time (30 min). The polymerization mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into methanol (400 mL). The ring-opened polymer was then collected as the methanol insoluble white precipitates; the resultant polymer was then collected onto a filter paper and was dried *in vacuo*. ^{1}H NMR (C_6D_6): δ 1.39-1.59 (m, 4H), 2.07 (t, 2H), 3.95 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 21.7, 28.4, 33.7, 63.8, 64.1, 172.6 (C=O).

Ring opening polymerization (ROP) of *rac*-lactide (LC).

Typical polymerization procedures (Table 3-5, run 43) are as described. Into a sealed Schlenk tube containing a toluene solution containing **1b** (0.050 mmol/0.085 mL of toluene), ^{n}BuOH (0.050 mmol) was added in the drybox at room temperature. The solution was stirred for 10 minutes, and the solution was then added toluene (4.9 mL), δ-valerolactone

(5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 60 ºC, and the solution was stirred for the prescribed time (24 h). The polymerization mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into cold methanol (300 mL). The ring-opened polymer was then collected as the methanol insoluble white precipitates; the resultant polymer was then collected onto a filter paper and was dried *in vacuo*. ^{1}H NMR ($CDCl_3$): δ 1.54-1.58 (m, 6H), 5.13-5.24 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 16.6-16.7 (m, *CH*$_3$), 69.0-69.2 (m, *C*CH_3), 169.1-169.6 (m, C=O).

Crystallographic Analysis.

The crystallographic analysis for $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(2,4,6\text{-}Me_3C_6H_2)N{=}CH\}C_6H_3]$ (**1g**) was made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo-Kα radiation. All structures were solved by direct methods and expanded using Fourier techniques.[12] All calculations were performed using the crystal structure crystallographic software package.[13] The selected crystal collection parameters: crystal color, habit = colorless, block; formula = $C_{22}H_{30}AlNO$; crystal system, space group = triclinic, $Pna2_1$ (#33); a = 8.8176(4) Å; b = 25.7758(9) Å; c = 9.3767(3) Å; V = 2131.15(14) Å^3; Z = 4; D_{calcd} = 1.095 g/cm^3; F_{000} = 760.00; no. of reflections measured = 20121; no. of observations (I > 2.00σ (I)) = 2213; R_1 = 0.0342; wR_2 = 0.0956; goodness of fit = 1.000. The crystallographic data (including CIF files) for **1g** was also deposited in Cambridge Crystallographic Data Centre as CCDC 687433. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or e-mail deposit@ccdc.cam.ac.uk.

References and Notes

1. For recent reviewing article: (a) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1. (b) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc. Dalton Trans.* **2001**, 2215. (c) Stridsberg, K. M.; Ryner, M.; Albertsson, A. C. *Adv. Polym. Sci.* **2002**, *157*, 41. (d) Albertsson, A.-C.; Varma, I. *Biomacromolecules* **2003**, *4*, 1466. (e) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, 104, 6147.
2. Examples for polymerization of lactide by Al: (a) Trofim;off, L.; Aida, T.; Inoue, S. *Chem. Lett*. **1987**, 991. (b) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627. (c) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461. (d) Wisniewski, M.; LeBorgne, A.; Spassky, N. *Macromol. Chem. Phys*. **1997**, *198*, 1227. (e) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (f) Cameron, P. A.; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S. *Macromol. Rapid Commun.* **1999**, *20*, 616. (g) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (h) Bhaw-Luximon, A.; Jhurry, D.; Spassky, N. *Polym. Bull.* **2000**, *44*, 31. (i) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552. (j) Ovitt, T. M. ; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 4686. (k) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. *Macromolecules* **2001**, *34*, 356. (l) Chisholm, M. H.; Navarro-Llobet, D.; Simonsick, W. J. Jr. *Macromolecules* **2001**, *34*, 885. (m) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (n) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. (o) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2003**, 22, 769.
3. Examples for ROP of lactones etc.: (a) Ko, B.-T.; Lin, C.-C. *Macromolecules* **1999**, *32*, 8296. (b) Taden, I.; Kang, H.-C.; Massa, W.; Spaniol, T. P.; Okuda, J.; *Eur. J. Inorg. Chem.* **2000**, 441. (c) Chakraborty, D.; Chen, E.Y.-X. *Organometallics* **2002**, *21*, 1438. (d) Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2002**, *35*, 5763. (e) Yu, R.-C.;

Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 6450. (f) Zheng, G.; Stöver, H. D. H. *Macromolecules* **2003**, *36*, 7439. (g) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2003**, 3082. (h) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* **2004**, *37*, 7968. (i) Lewinsky, J.; Horeglad, P.; Tratkiewicz, E.; Grzenda, W.; Lipkowski, J.; Kolodziejczyk, E.; *Macromol. Rapid Commun.* **2004**, *25*, 1939. (j) Nomura, N.; Aoyama, T.; Ishii, R.; Kondo, T. *Macromolecules* **2005**, *38*, 5363. (k) Amgoune, A.; Lavanant, L.; Thomas, C. M.; Chi, Y.; Welter, R.; Dagorne, S.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 6279. (l) Majoumo-Mbe, F.; Smolensky, E.; Lönnecke, P.; Shpasser, S.; Eisen, M. S.; Hey-Hawkins, E. *J. Mol. Catal. A* **2005**, *240*, 91.

4. (a) Vert, M.; Albertsson, A.; Scott, G.; Chiellini, E. Eds. *Biodegradable Polymers and Plastics;* The Royal Society of Chemistry: Cambridge, UK, 1992; p 95. (b) Vert, M.; Feijen, J.; Albertsson, A.; Scott, G.; Chiellini, E. eds. *Biodegradable Polymers and Plastics*; The Royal Society of Chemistry: Cambridge, UK, 1992; p 139. (c) Okada, M. *Prog. Polym. Sci*. **2002**, *27*, 87.
5. (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem*. **1996**, *35*, 63. (b) Qian, B.; Ward, D. L.; Smith III., M. R. *Organometallics* **1998**, *17*, 3070. (c) Rad zewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (d) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883. (e) Muñoz-Hernández, M.-A.; Keiser, T. S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416. (f) Liu, S.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Organomet. Chem.* **2000**, *596*, 109. (g) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A. *J. Chem. Soc., Dalton Trans.* **2001**, 1472. (h) Hill, M. S.; Hutchison, A. R.; Keiser, T. S.; Parkin, S.; VanAelstyn, M. A.; Atwood, D. A. *J. Organomet. Chem.* **2001**, *628*, 71. (i) Redshaw, C.; Elsegood, M. R. J. *Chem. Commun.* **2001**, 2016. (j) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; White, A. J. P.;

Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 415. (k) Chakraborty, D.; Chen, E. Y.-X. *Macromolecules* **2002**, *35*, 13. (l) Lewiński, J.; Zachara, J.; Starowieyski, K. B.; Ochal, Z.; Justyniak, I.; Kopec, T.; Stolarzewicz, P.; Dranka, M. *Organometallics* **2003**, *22*, 3773. (m) Lewinski, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (n) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P. ; Jaouen, G. *Organometallics* **2003**, *22*, 3732. (o) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64. (p) Zhu, H.; Chen, E. Y.-X. *Inorg. Chem*. **2007**, *46*, 1481. (q) Yao, W.; Mu, Y.; Gao, A.; Su, Q.; Liu, Y.; Zhang, Y. *Polymer* **2008**, *49*, 2486.

6. (a) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc*. **1988**, *110*, 3588. (b) Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc*. **1989**, *111*, 6431. (c) Maruoka, K.; Conception, A. B.; Murase, N.; Oishi, M.; Hirayame, N.; Yamamoto, H. *J. Am. Chem. Soc*. **1993**, *115*, 3943. (d) Maruoka, K.; Imoto, H.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc*. **1994**, *116*, 4131. (e) Saito, S.; Yamamoto, H. *J. Chem. Soc*., *Chem. Commun*. **1997**, 1585.
7. Syntheses of various salicylaldimines, and Ti, Zr, V complexes containing bis(phenoxy-imine) ligands: Fujita, T.; Tohi, Y.; Mitani, M. European patent EP 0874005A1, 1998.
8. (a) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847, (b) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc*. **2002**, *124*, 3327. (c) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc*. **2003**, *125*, 4293. (d) Terao, H.; Ishii, S.; Saito, J.; Matsuura, S.; Mitani, M.; Nagai, N.; Tanaka, H.; Fujita, T. *Macromolecules* **2006**, *39*, 8584.
9. Reports concerning comparison between exact number average molecular weights and M_n

values by GPC *vs*. polystyrene standards: (a) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczel, S. *Macromolecules* **1990**, *23*, 1640. (b) McLain, S. J.; Drysdale, N. E. *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) **1992**, *33*, 174. (c) Pasch, H.; Rhode, K. *J. Chromatogr., A* **1995**, *699*, 24. (d) Kricheldorf, H. R.; Eggerstedt, S. *Macromol. Chem. Phys.* **1998**, *199*, 283. (e) Duda, A.; Kowalski, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (f) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 1964. (g) Chen, H.-L.; Ko, B.-T.; Huang, B.-H.; Lin, C.-C. *Organometallics* **2001**, *20*, 5076. (h) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889. (i) Kricheldorf, H. R.; Rost, S. *Polymer* **2005**, *46*, 3248. In this chapter, the exact M_n values by GPC vs. polystyrene standards according to the following equation: $M_{n(PCL)} = 0.56 \times M_{n(GPC\ vs.\ polystyrene\ standards)}$.[9e,h]

10. Dittrich, W.; Shultz, R. C. *Angew. Macromol. Chem.* **1971**, *15*, 109.

11. Selected reports concerning transesterification in the ROP of CL and DL-lactide: (a) Duda, A.; Penczek, S. *Macromolecules* **1995**, *28*, 5981. (b) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; Le Borgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461. (c) Spassky, N.; Simic, V.; Montaudo, M. S.; Hubert-Pfalzgraf, L. G. *Macromol. Chem. Phys.* **2000**, *201*, 2432. (d) Jhurry, D.; Bhaw-Luximon, A.; Spassky, N. *Macromol. Symp.* **2001**, *175*, 67. (e) Cayuela, J.; Bounor-Legaré, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338.

12. Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, Jan M. M. *The DIRDIF-94 program system,* Crystallography Laboratory, University of Nijmegen, The Netherlands, 1998.

13. (a) Crystal Structure 3.6.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2004) 9009 New Trails Dr. The Woodlands TX 77381 USA. (b) CRYSTALS Issue 10: Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; & Betteridge, P. W. Chemical Crystallography Laboratory, Oxford, UK, 1996

Chapter 4

Ring-opening polymerization of ε-caprolactone by Al complexes containing phenoxyimine ligands: Notable effect of fluoro substituents in the imino group

Abstract

A series of Al complexes containing phenoxyimine ligands of the type, $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ [R^1;R^2 = Et;Et (**1b**); Me;Cl (**1c**)] and $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**)], have been prepared and identified on the basis of NMR spectra and elemental analyses. Their structures were determined by X-ray crystallography and these complexes fold a distorted tetrahedral geometry around Al. The ring-opening polymerizations (ROPs) of ε-caprolactone (CL) using **1a-c** in the presence of $PhCH_2OH$ proceeded efficiently in a living manner, and the propagation rates were somewhat influenced by the anionic donor employed (Me, Et or Cl). The catalytic activity using **1-6a** [Ar = C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**)]-$PhCH_2OH$ catalyst systems was strongly affected by the aromatic substituent (Ar) in the imino group, and placement of fluorine substituents especially in the *ortho*-position strongly affected the catalytic activity. The ROPs by **2-6a** accompanied certain degree of side reactions (transesterification), whereas the living polymerization systems can be accomplished using the C_6F_5 analogues (**1a-c**). Therefore, the C_6F_5 substituent in the imino group plays an essential key role in the ROP of CL in terms of both the catalytic activity and for the ROP to proceed in a living manner.

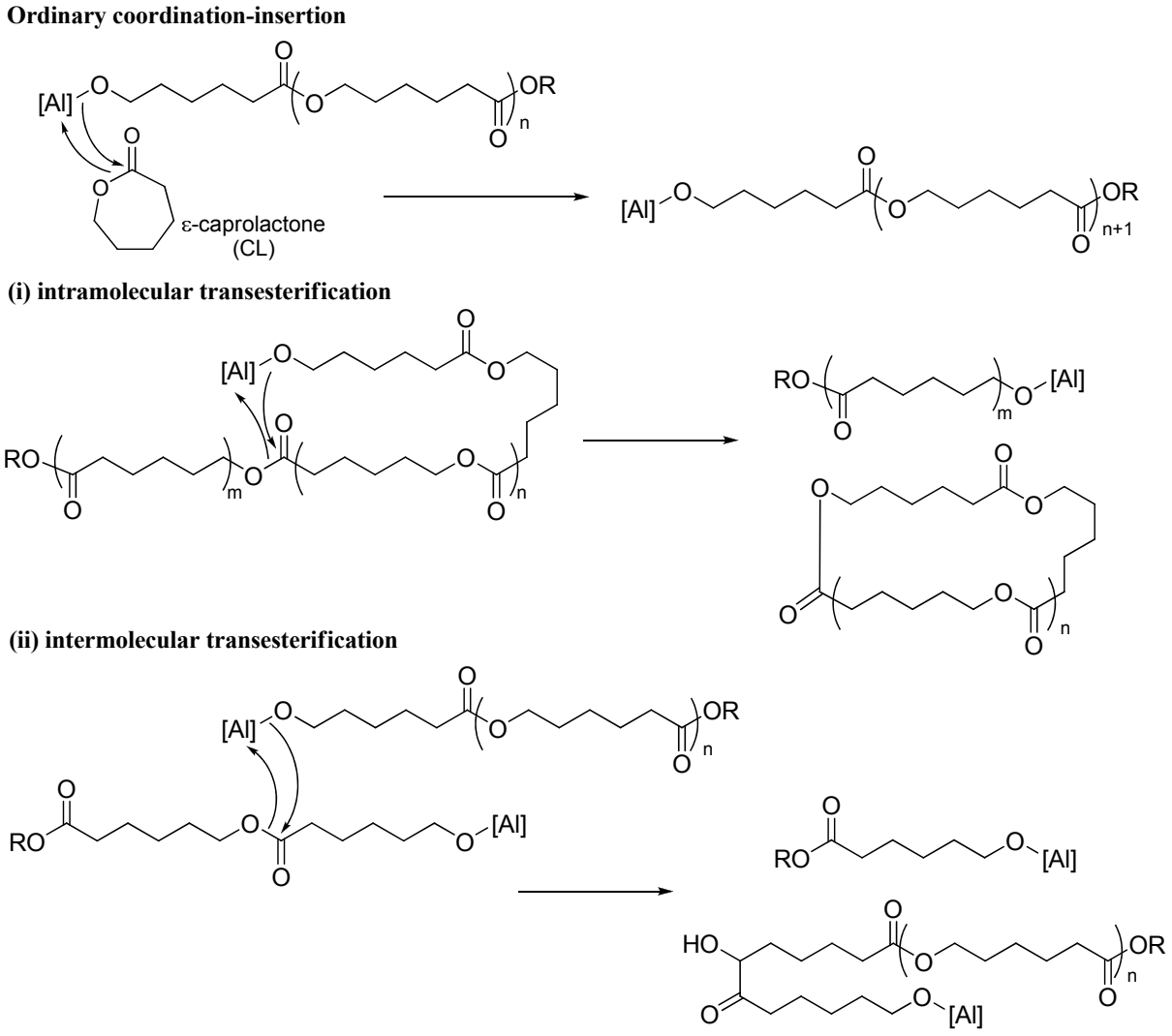
Introduction

Certain aliphatic polyesters are known to possess promising characteristics as biodegradable and bioassimilable materials not only due to their practical biodegradability, but also due to their biocompatibility for medical and pharmaceutical applications.[1] Al alkoxides are one of the important reagents employed as initiators for ring-opening polymerization (ROP) of cyclic esters[2] such as lactides,[3,4c] lactones,[3j,n,4,5] and considerable attention has thus been paid to the synthesis, structural determinations for monomeric/dimeric Al complexes.[6]

In the previous chapter, It was demonstrated that $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1a**) exhibits unique characteristics for a rapid living ring-opening polymerization (ROP) of ε-caprolactone (CL) as well as δ-valerolactone (VL) in the presence of ^{n}BuOH (1.0 equiv).[4] I also demonstrated that the imino substituent (R) in $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ plays a crucial role for the efficient ROP; the catalytic activity (turnover number, TON) in the ROP increased in the order: R = C_6F_5 >> 2,6-$Me_2C_6H_3$ > 2,6-$^iPr_2C_6H_3$ > C_6H_5 > cyclohexyl > ^{t}Bu > adamantyl (negligible activity). Moreover, the PDI value (M_w/M_n) increased without notable increase in the M_n values at high CL conversion (ca. 80%) in the ROP by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(cyclohexyl)N{=}CH\}C_6H_3]$-^{n}BuOH catalyst, whereas the M_w/M_n values kept constant (M_w/M_n = 1.17-1.19) in the ROP by the C_6F_5 analogue – ^{n}BuOH catalyst under the same conditions (at 60 ºC).[4b]

It has been generally proposed that the ROP proceeds *via* coordination and insertion of CL,[7] and presence of two types of side reactions, the intra- and the inter-molecular transesterifications, has also been known (Scheme 4-1).[8] Therefore, the fact (broadening of the M_w/M_n values in the ROP by the cyclohexyl analogue) would suggest a possibility of (probably intramolecular) transesterification accompanied in the catalytic polymerization as the side reaction.[4b]

Scheme 4-1



In this chapter, I thus investigated synthesis and structural analysis of a series of four coordinate $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ [$R^1;R^2$ = Et;Et (**1b**), Me;Cl (**1c**)], and conducted the ROPs of CL by **1a-c** in the presence of 1 equiv. of $PhCH_2OH$. This research explored effect of the anionic (alkyl or chloro) ligand ($R^1;R^2$) toward both the catalytic activity (propagation rate) and the polymerization behavior. I also investigated synthesis and structural analysis of a series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**)], and explored effect of the imino substituent toward both the activity and the polymerization behavior in the ROPs of CL by

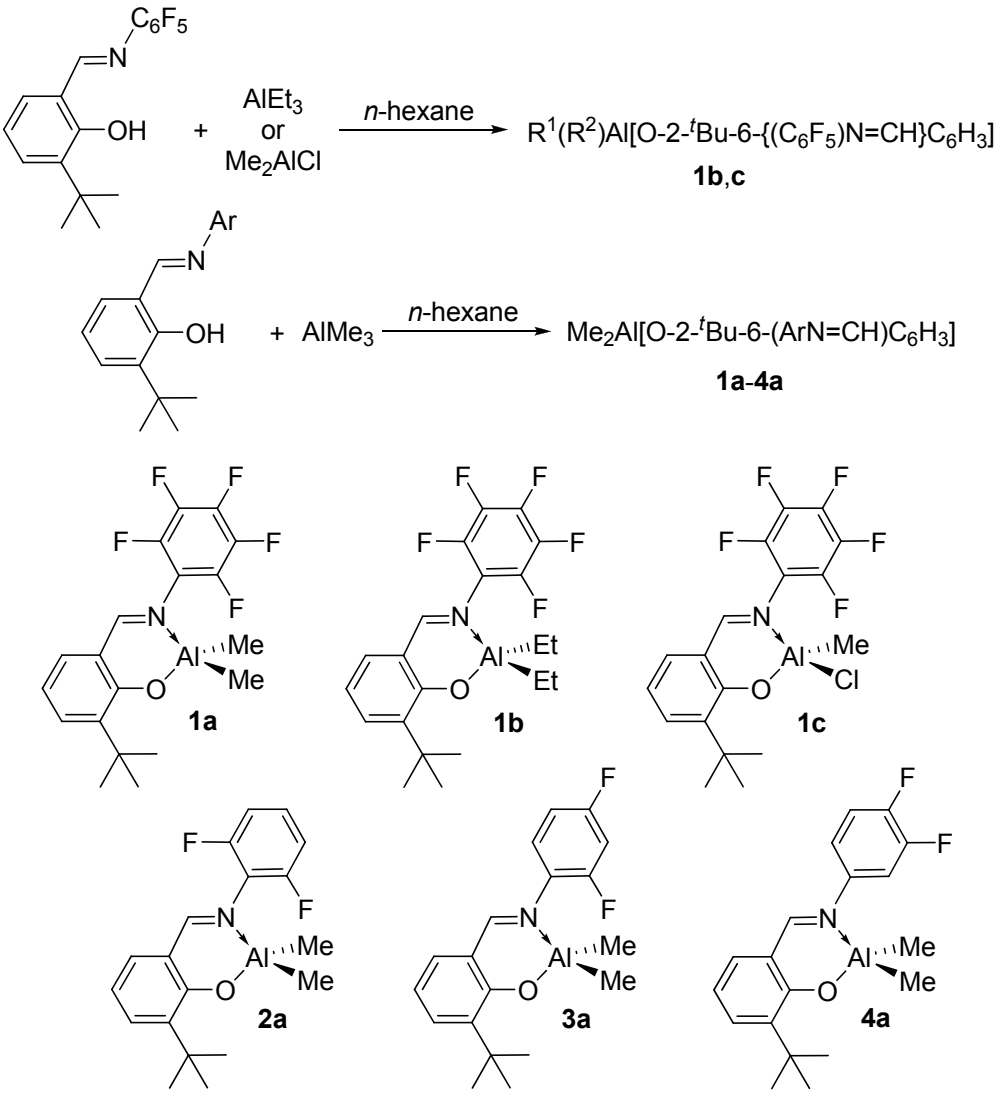
$Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = C_6F_5 (**1a**), 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**), C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**)]-$PhCH_2OH$ catalyst systems. Through this project, I wish to present important factors to establish the fast, controlled ring-opening polymerization of the cyclic esters exemplified as CL.

Results and Discussion

1. Synthesis of structural analysis of $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$, ($R^1$;$R^2$ = Et;Et; Me;Cl), and $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$, (Ar = 2,6-$F_2C_6H_3$, 2,4-$F_2C_6H_3$, 3,4-$F_2C_6H_3$).

Various Al complexes containing different anionic ligand, $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ [R^1;R^2 = Et;Et (**1b**), Me;Cl (**1c**)], have been prepared $AlEt_3$, or Me_2AlCl was treated with 1 equiv. of $2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3OH$ in *n*-hexane (Scheme 4-2). The procedure is analogous to that for synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1a**), and the complexes were identified based on ^1H and ^{13}C spectra, and elemental analyses. The structure of **1b** and **1c** were also determined by X-ray crystallography (Figure 4-1), and the selected bond distances and the angles are summarized in Table 4-1.[7]

Scheme 4-2



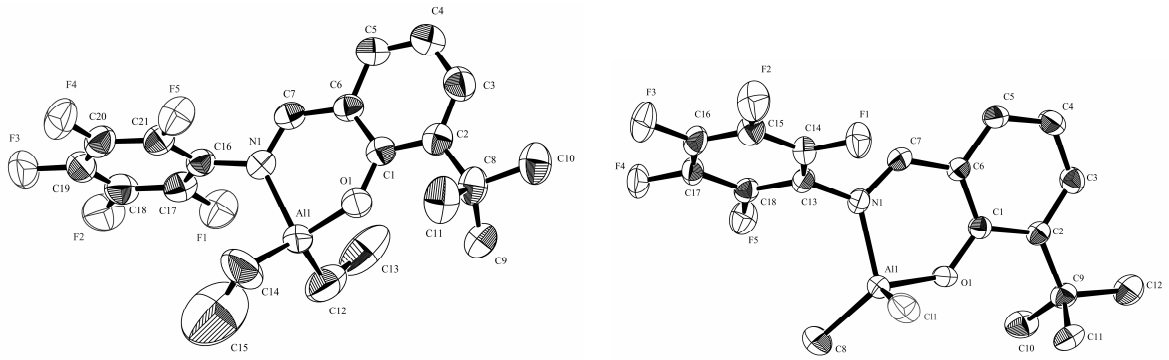


Figure 4-1. ORTEP drawings of $Et_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1b**, left), and $Me(Cl)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1c**, right). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.[7]

Table 4-1. Selected bond distances (Å) and angles (º) for $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1a**), $Et_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1b**), and $Me(Cl)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1c**).

1a		**1b**		**1c**	
Bond Distances (Å)					
Al(1)-O(1)	1.7737(16)	Al(1)-O(1)	1.753(2)	Al(1)-O(1)	1.7479(11)
Al(1)-N(1)	1.9780(19)	Al(1)-N(1)	1.986(2)	Al(1)-N(1)	1.9429(12)
Al(1)-C(1)	1.951(2)	Al(1)-C(12)	1.920(4)	Al(1)-C(8)	1.9304(17)
Al(1)-C(2)	1.941(2)	Al(1)-C(14)	2.127(10)	Al(1)-Cl(1)	2.1547(6)
N(1)-C(3)	1.300(2)	N(1)-C(7)	1.308(4)	N(1)-C(7)	1.3104(19)
N(1)-C(10)	1.436(2)	N(1)-C(16)	1.423(3)	N(1)-C(13)	1.4344(19)
Bond Angles (º)					
O(1)-Al(1)-N(1)	93.17(7)	O(1)-Al(1)-N(1)	93.26(10)	O(1)-Al(1)-N(1)	95.45(5)
C(1)-Al(1)-C(2)	118.12(12)	C(12)-Al(1)-C(14)	127.0(2)	Cl(1)-Al(1)-C(8)	113.88(6)
Al(1)-O(1)-C(9)	133.89(14)	Al(1)-O(1)-C(1)	132.06(15)	Al(1)-O(1)-C(1)	131.10(9)
Al(1)-N(1)-C(3)	122.97(14)	Al(1)-N(1)-C(7)	121.32(18)	Al(1)-N(1)-C(7)	120.78(10)
Al(1)-N(1)-C(10)	120.55(14)	Al(1)-N(1)-C(16)	120.8(2)	Al(1)-N(1)-C(13)	121.82(9)
O(1)-Al(1)-C(1)	113.73(10)	O(1)-Al(1)-C(12)	109.72(18)	O(1)-Al(1)-C(8)	116.16(7)
O(1)-Al(1)-C(2)	113.71(10)	O(1)-Al(1)-C(14)	106.67(16)	Cl(1)-Al(1)-O(1)	110.01(3)
N(1)-Al(1)-C(1)	105.34(9)	N(1)-Al(1)-C(12)	110.75(16)	N(1)-Al(1)-C(8)	117.86(7)
N(1)-Al(1)-C(2)	109.26(10)	N(1)-Al(1)-C(14)	104.2(2)	Cl(1)-Al(1)-N(1)	101.22(4)

Complexes **1b** and **1c** have a distorted tetrahedral geometry around the Al. The Al-O bond distances in **1b**,**c** [1.753(2), 1.7479(11) Å, respectively] are shorter than that in **1a** [1.7737(16) Å], and the Al-N bond distance in **1c** [1.9429(12) Å] is shorter than those in **1a**,**b** [1.9780(19), 1.986(2) Å, respectively]. One Al-carbon bond distance in **1b** [2.127 Å] is apparently longer than those in the other Al-C bond distances in **1a-c** [1.9304(17)-1.951(2) Å], this would be due to the steric bulk of two ethyl groups in **1b**. The Al-Cl bond distance [2.1547(6) Å] in **1c** seems similar to that in the reported values [ca. 2.1238-2.1239 Å in $(TTP)AlCl_2$, TTPH = 2-(*p*-tolylamino)-4-(*p*-tolylimino)-2-pentene]. The bond angle of C(in Me or Et)-Al-C(Me, Et) or C-Al-Cl is influenced by the anionic ligand (Me, Et or Cl), and the angle increased in the order: C(12)-Al-C(14) [127.0(2)º] > C(1)-Al-C(2) [118.12(12)º] > Cl(1)-Al-C(8) [113.88(6)º]. The O-Al-N angle in **1c** [95.45(5)º] is somewhat larger than

those in **1a**,**b** [93.17(7), 93.26(10), respectively], and the other angles are also influenced by the anionic donor ligands employed (Me, Et or Cl). These results would be important to consider influences of the anionic donor ligands.

Al complexes containing phenoxyimine ligands with a series of fluorinated imino groups, $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**)], were prepared by treating $AlMe_3$ with the corresponding iminophenol in *n*-hexane, and the procedure is analogous to that for **1a**. The resultant complexes were identified based on ^{1}H and ^{13}C NMR spectra, and elemental analyses. The structure of **2a**, **3a** and **4a** were also determined by X-ray crystallography (Figure 4-2), and the selected bond distances and the angles are summarized in Table 4-2.[7]

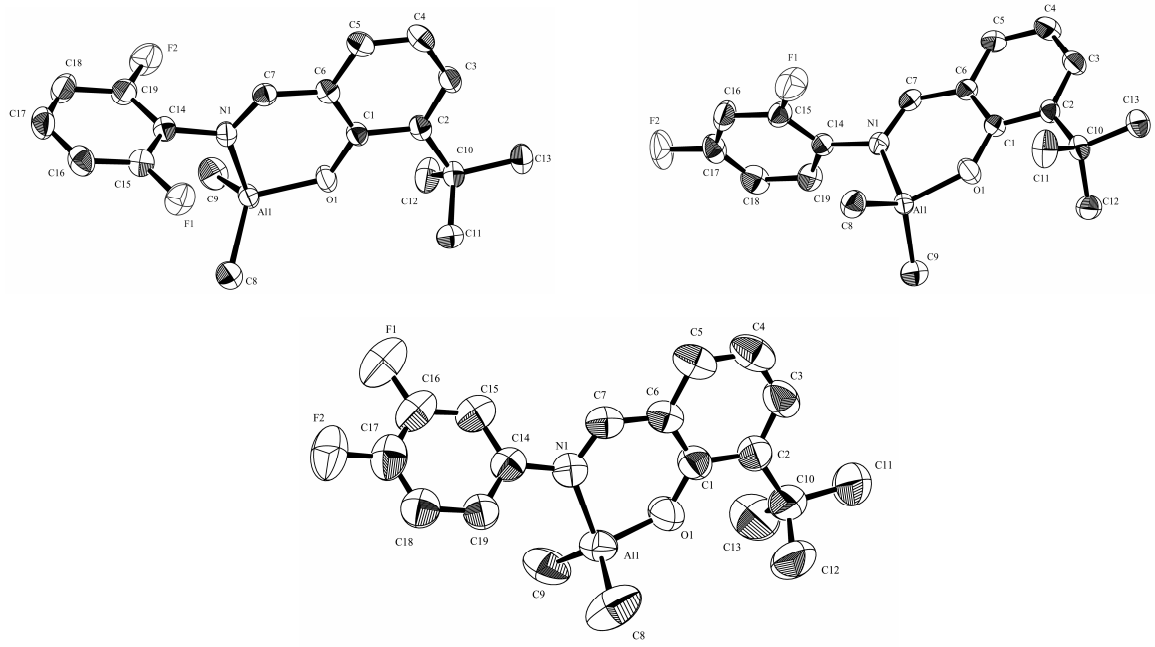


Figure 4-2. ORTEP drawings of $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(2,6\text{-}F_2C_6H_3)N{=}CH\}C_6H_3]$ (**2a**, up left), $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(2,4\text{-}F_2C_6H_3)N{=}CH\}C_6H_3]$ (**3a**, up right), and $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(3,4\text{-}F_2C_6H_3)N{=}CH\}C_6H_3]$ (**4a**, bottom center). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.[10]

Table 4-2. Selected bond distances (Å) and angles (º) for Me_2Al[O-2-^{t}Bu-6-{(2,6-$F_2C_6F_3$)N=CH}C_6H_3] (**2a**), Me_2Al[O-2-^{t}Bu-6-{(2,4-$F_2C_6H_3$)N=CH}C_6H_3] (**3a**), and Me_2Al[O-2-^{t}Bu-6-{(3,4-$F_2C_6H_3$)N=CH}C_6H_3] (**4a**).

2a		**3a**		**4a**	
Bond Distances (Å)					
Al(1)-O(1)	1.7680(15)	Al(1)-O(1)	1.7713(19)	Al(1)-O(1)	1.759(2)
Al(1)-N(1)	1.9692(14)	Al(1)-N(1)	1.9692(16)	Al(1)-N(1)	1.968(3)
Al(1)-C(8)	1.963(2)	Al(1)-C(8)	1.956(2)	Al(1)-C(8)	1.930 (4)
Al(1)-C(9)	1.973(2)	Al(1)-C(9)	1.954(3)	Al(1)-C(9)	1.921(4)
N(1)-C(7)	1.300(2)	N(1)-C(7)	1.302(2)	N(1)-C(7)	1.312(5)
N(1)-C(14)	1.435(2)	N(1)-C(14)	1.436(2)	N(1)-C(14)	1.427(4)
Bond Angles (º)					
O(1)-Al(1)-N(1)	93.15(6)	O(1)-Al(1)-N(1)	93.01(7)	O(1)-Al(1)-N(1)	93.28(13)
C(8)-Al(1)-C(9)	118.00(10)	C(8)-Al(1)-C(9)	119.29(11)	C(8)-Al(1)-C(9)	117.51(19)
Al(1)-O(1)-C(1)	133.60(11)	Al(1)-O(1)-C(1)	134.54(14)	Al(1)-O(1)-C(1)	133.4(2)
Al(1)-N(1)-C(7)	122.84(12)	Al(1)-N(1)-C(7)	123.09(14)	Al(1)-N(1)-C(7)	122.0(2)
Al(1)-N(1)-C(14)	119.56(11)	Al(1)-N(1)-C(14)	119.52(12)	Al(1)-N(1)-C(14)	120.0(2)
O(1)-Al(1)-C(8)	112.97(8)	O(1)-Al(1)-C(8)	113.02(10)	O(1)-Al(1)-C(8)	111.57(17)
O(1)-Al(1)-C(9)	112.13(9)	O(1)-Al(1)-C(9)	110.79(10)	O(1)-Al(1)-C(9)	110.47(16)
N(1)-Al(1)-C(8)	109.06(8)	N(1)-Al(1)-C(8)	107.91(9)	N(1)-Al(1)-C(8)	112.64(16)
N(1)-Al(1)-C(9)	108.54(8)	N(1)-Al(1)-C(9)	109.52(9)	N(1)-Al(1)-C(9)	108.74(15)

The structures of **2-4a** indicate that these complexes fold a distorted tetrahedral geometry around Al. The Al-N bond distances are not strongly influenced by the imino substituent [1.968(3)-1.9780(19) Å], and the Al-O bond distance in **4a** [1.759(2) Å] was somewhat shorter than those in **1-3a** [1.7680(15)-1.7737(16) Å]. The Al-C(in Me) bond distances in **4a** [1.921(4), 1.930(4) Å] were shorter than those in **1a** and **3a** [1.941(2)-1.956(2) Å], and are apparently shorter than those in **2a** [1.963(2), 1.973(2) Å]. The C-Al-C bond angles increased in the order: **3a** [119.29(11)º] > **1a**, **2a** [118.12(12)º, 118.00(10)º, respectively], **4a** [117.51º], and some bond angles are also influenced by the imino substituent.

2. Effect of ligand in the ring-opening polymerization of ε-caprolactone using $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ – $PhCH_2OH$ catalyst systems.

It was demonstrated that rapid living ring-opening polymerizations (ROPs) of both ε-caprolactone (CL) and δ-valerolactone (VL) have been achieved with high catalyst (initiation) efficiency by using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1a**) in the presence of ^{n}BuOH (1.0 equiv) in the previous chapter.[4] I also reported that the imino substituent strongly affects toward both the catalytic activity and the catalyst efficiency. As described above, in order to explore the details concerning major roles of the anionic donor ligand (Me, Et, Cl) and the imino substituents (Ar) toward both the catalytic activity and the polymerization behavior (including a possibility of accompanied side reactions like transesterification), I conducted the ROPs of CL using a series of $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ [R^1;R^2 = Me;Me (**1a**), Et;Et (**1b**), Me;Cl (**1c**)] in the presence of $PhCH_2OH$. I also conducted the ROPs of CL using a series of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = C_6F_5 (**1a**), 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**), C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**)] in the presence of $PhCH_2OH$, especially to explore role of the fluorinated substituent in the imino group. The polymerization results are summarized in Tables 4-3 to 4-5.[11]

It turned out that the ROPs of CL using pentafluorophenyl (C_6F_5) derivatives (**1a-c**) almost completed after 45 min (conv. 91-94%, Table 4-3), indicating that **1b**,**c** are also effective for the ROP of CL in terms of the activity as seen in the ROP by **1a** reported previously.[4] As shown in Figure 4-3, linear relationships between the monomer conversions and M_n values were observed in these ROPs consistently with narrow molecular weight distributions, and no significant differences were observed in the N values [number of polymer chains estimated by the $M_{n(GPC)}$ values and the conversions] during the time course.[12] These results thus clearly indicate that these ROPs proceeded in a living manner as demonstrated by **1a**.[4]

Table 4-3. Living ring opening polymerization of ε-caprolactone(CL) initiated by $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_4]$ [R^1;R^2 = Me;Me (**1a**), Et;Et (**1b**), Me;Cl (**1c**)] – $PhCH_2OH$ catalyst systems.[a]

complex (R^1;R^2)	time/min	conv.[b]/ %	$M_{n(GPC)}$[c]×10^{-4}	M_w/M_n[c]	N[d]/ μmol
1a (Me;Me)	15	48	3.15	1.19	31
1a (Me;Me)	30	81	4.87	1.21	33
1a (Me;Me)	45	94	5.53	1.22	34
1b (Et;Et)	15	48	2.32	1.24	41
1b (Et;Et)	30	78	3.50	1.23	45
1b (Et;Et)	45	91	4.12	1.21	44
1c (Me;Cl)	15	53	2.46	1.12	43
1c (Me;Cl)	30	83	3.57	1.14	47
1c (Me;Cl)	45	93	3.96	1.12	47

[a]Conditions: Al 40 μmol, $PhCH_2OH$ 40 μmol, CL 10.0 mmol (CL/Al = 250), toluene, $[CL]_0$ = 1.0 mmol/mL, 50 ºC. [b]Estimated by ^1H NMR spectra. [c]By GPC in THF *vs* polystyrene standards. [d]Estimated number of polymer chain (μmol) = initial amount of monomer (mg) ×conversion / $\{M_{n(GPC)}\times 0.56\}$.[11]

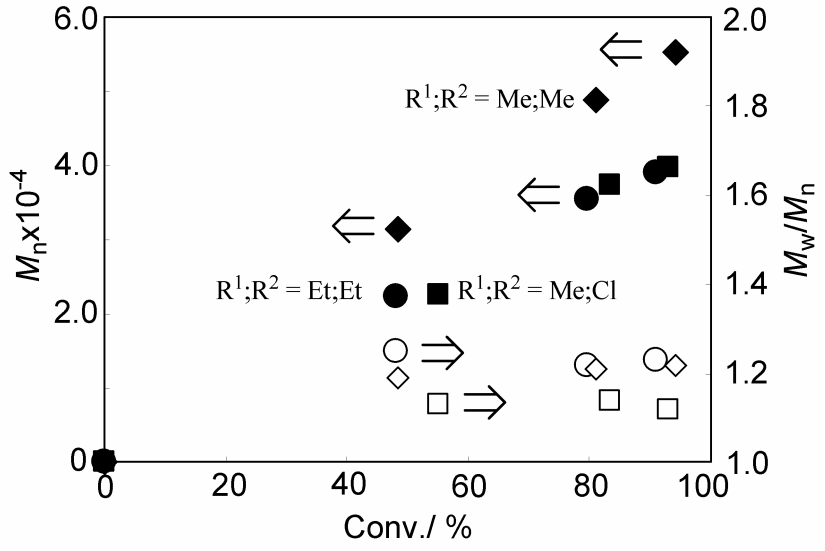


Figure 4-3. Plots of M_n and M_w/M_n *vs.* monomer conversion in the ring opening polymerization of ε-caprolactone initiated by $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_4]$ [R^1;R^2 = Me;Me (**1a**, ◆, ◇), Et;Et (**1b**, ●, ○), Me;Cl (**1c**, ■, □)] – $PhCH_2OH$ catalyst systems. The detailed conditions are summarized in Table 4-3.

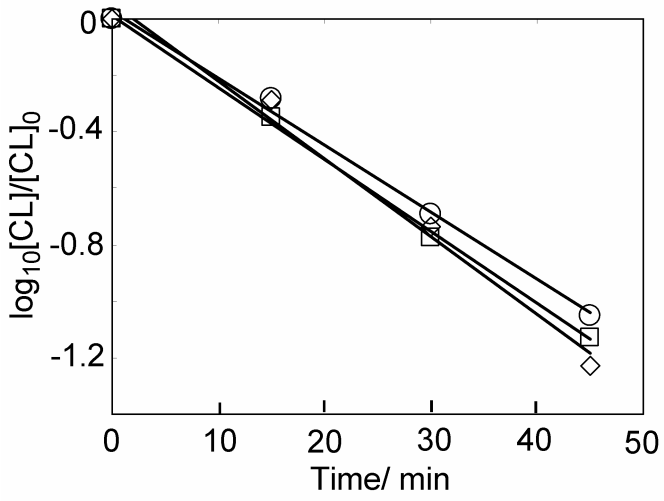


Figure 4-4. Plots of $\log_{10}[CL]/[CL]_0$ *vs.* time in the ring opening polymerization of ε-caprolactone initiated by $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_4]$ [R^1;R^2 = Me;Me (**1a**, ◇), Et;Et (**1b**, □), Me;Cl (**1c**, ○)]-$PhCH_2OH$ catalyst systems.

As shown in Figure 4-4, the propagation rates in the ROPs by **1a-c** were first order dependent upon the monomer concentration, suggesting that the ROPs proceeded without catalyst deactivation. The observed rates (k_{obs}) by **1a-c** seemed to be close (k_{obs} = 2.4-2.8×10^{-2} min^{-1}, Table 4-4), however, the estimated *N* value by **1a** was lower than those by **1b**,**c**, due to the different catalyst efficiency.[12] Therefore, the actual *k* value (propagation rate constant) by **1a** should be higher than those by **1b**,**c**. I assume that the observed difference between **1a** and **1c** would probably be due to a different electronic nature of the propagating Al species between Me and Cl, and the methyl group in **1c** would be reacted with $PhCH_2OH$ to generate the initiating species. I also speculate that the observed difference between the methyl (**1a**) and ethyl (**1b**) analogues would be due to the steric bulk around the propagating Al center (as seen in the unique Al-C bond angle, as described above), although I do not have any clear evidence to explain this speculation.

Table 4-4. Summary of the rate constants in living ring opening polymerization of ε-caprolactone (CL) initiated by $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_4]$ [$R^1;R^2$ = Me;Me (**1a**), Et;Et (**1b**), Me;Cl (**1c**)]-$PhCH_2OH$ catalyst systems.[a]

complex ($R^1;R^2$)	k_{obs}[b]$\times10^{-2}$ min^{-1}	efficiency[c] / %	$k_{cor.}$[d]$\times10^{-2}$ min^{-1}
1a (Me;Me)	2.8	85	3.3
1b (Et;Et)	2.4	>99	2.4
1c (Me;Cl)	2.6	>99	2.6

[a]Polymerization conditions are shown in Table 4-3. [b]Estimated based on Figure 4-4 (slope). [c]Estimated value described in Table 4-3, *N* (μmol)/ Al charged (μmol). [d]Corrected *k* value based on k_{obs} and the efficiency.

It also turned out that the catalytic activity in the ROPs of CL using a series of Al complexes containing phenoxyimine ligands (with different fluorinated aromatic substituents in the imino group), $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$, increased in the order: Ar = C_6F_5 (**1a**) >> 2,6-$F_2C_6H_3$ (**2a**) > 2,4-$F_2C_6H_3$ (**3a**) > 3,4-$F_2C_6H_3$ (**4a**) > 2,6-$Me_2C_6H_3$ (**6a**) > C_6H_5 (**5a**) (Table 4-5).

Table 4-5. Ring opening polymerization of ε-caprolactone (CL) initiated by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_4]$ [Ar = C_6F_5 (**1a**), 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**), C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**)]-$PhCH_2OH$ catalyst systems.[a]

complex Ar	time / min	conv.[b] / %	$M_{n(GPC)}$[c] $\times 10^{-4}$	M_w/M_n[c]	N[d] / μmol
C_6F_5 (**1a**)	15	48	3.15	1.19	31
C_6F_5 (**1a**)	30	81	4.87	1.21	33
C_6F_5 (**1a**)	45	94	5.53	1.22	34.
2,6-$F_2C_6H_3$ (**2a**)	30	21	1.06	1.12	39
2,6-$F_2C_6H_3$ (**2a**)	60	49	2.16	1.24	46
2,6-$F_2C_6H_3$ (**2a**)	90	73	2.99	1.42	49
2,6-$F_2C_6H_3$ (**2a**)	120	89	3.35	1.50	51
2,4-$F_2C_6H_3$ (**3a**)	60	25	1.20	1.11	41
2,4-$F_2C_6H_3$ (**3a**)	120	59	2.45	1.18	48
2,4-$F_2C_6H_3$ (**3a**)	180	87	3.47	1.32	50
2,4-$F_2C_6H_3$ (**3a**)	240	97	3.94	1.48	49
3,4-$F_2C_6H_3$ (**4a**)	60	19	0.95	1.13	40
3,4-$F_2C_6H_3$ (**4a**)	120	46	1.92	1.17	47
3,4-$F_2C_6H_3$ (**4a**)	180	73	2.82	1.41	51
3,4-$F_2C_6H_3$ (**4a**)	240	89	3.24	1.58	55
C_6H_5 (**5a**)	60	14	0.67	1.11	40
C_6H_5 (**5a**)	120	31	1.37	1.16	45
C_6H_5 (**5a**)	180	50	1.93	1.28	52
C_6H_5 (**5a**)	240	69	2.55	1.43	54
C_6H_5 (**5a**)	300	82	2.79	1.78	59
C_6H_5 (**5a**)	360	91	2.99	1.98	61
2,6-$Me_2C_6H_3$ (**6a**)	30	14	0.79	1.11	36
2,6-$Me_2C_6H_3$ (**6a**)	60	35	1.74	1.14	41
2,6-$Me_2C_6H_3$ (**6a**)	90	55	2.61	1.14	42
2,6-$Me_2C_6H_3$ (**6a**)	120	72	3.19	1.21	45
2,6-$Me_2C_6H_3$ (**6a**)	150	83	3.53	1.31	47
2,6-$Me_2C_6H_3$ (**6a**)	180	90	3.74	1.42	48

[a]Conditions: Al 40 μmol, $PhCH_2OH$ 40 μmol, CL 10.0 mmol (CL/Al = 250), toluene, $[CL]_0$ = 1.0 mmol/mL, 50 ºC. [b]Estimated by ^1H NMR spectra. [c]By GPC in THF *vs* polystyrene standards. [d]Estimated number of polymer chain (μmol) = CL reacted (mg) based on conversion/$\{M_{n(GPC)}\times 0.56\}$.[11]

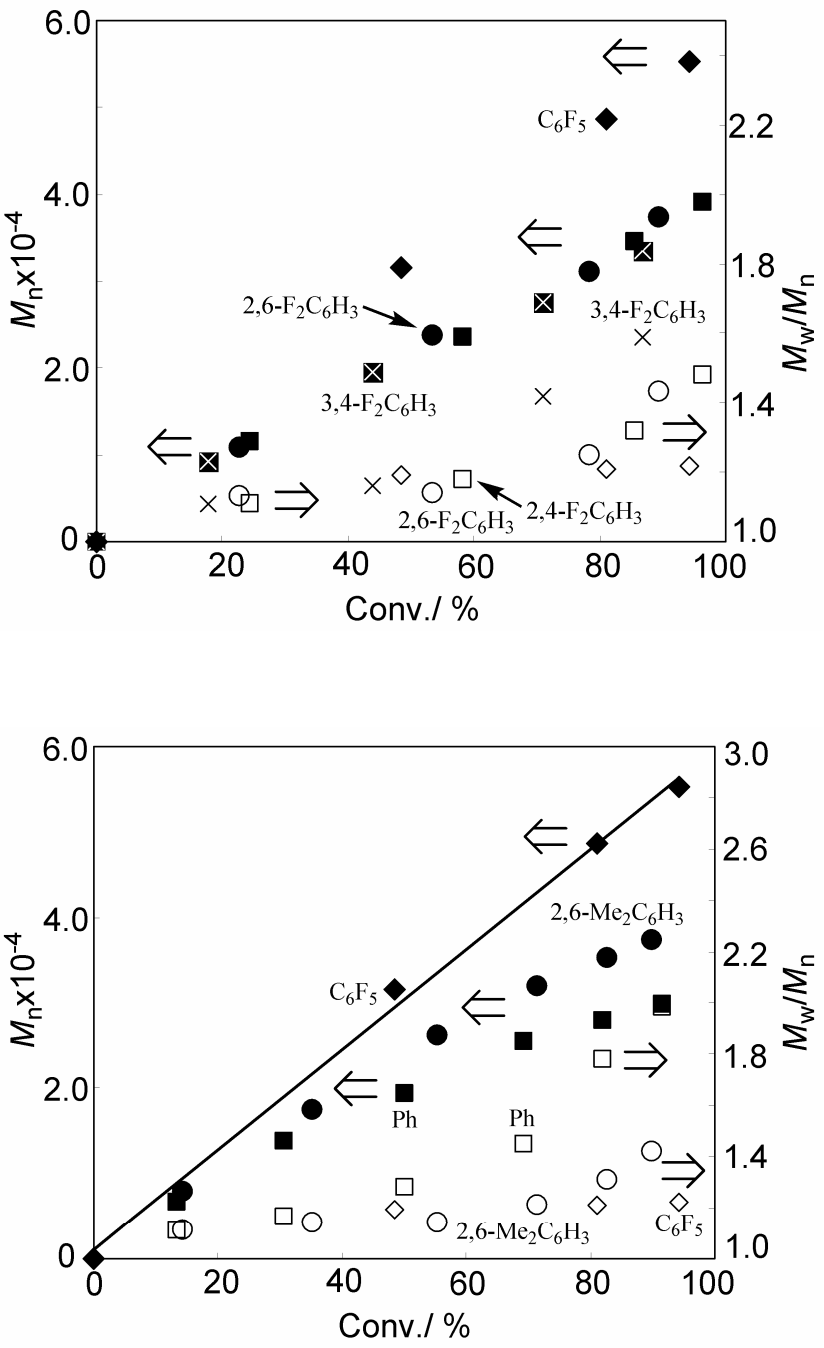


Figure 4-5. Plots of M_n and M_w/M_n vs monomer conversion in the ring opening polymerization of ε-caprolactone initiated by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_4]$ – $PhCH_2OH$ catalyst systems. Top: Ar = C_6F_5 (**1a**), 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**). Bottom: Ar = C_6F_5 (**1a**), C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**). The detailed conditions are summarized in Table 4-5.

The results indicate that substitution of the *ortho*-position, especially the fluorine substituent, strongly affects the catalytic activity. As described above, the ROP by the C_6F_5 analogue (**1a**) proceeded in a living manner, and this means that a linear relationship between the monomer conversions and the M_n values consistently with low M_w/M_n values was observed (Figure 4-5, plotted as ◆,◇).

In contrast, as shown in Figure 4-5 (bottom), the molecular weight distributions (M_w/M_n values) in the resultant polymers prepared by **5a** (plotted as □) became broad after certain monomer conversions [ex. M_w/M_n = 1.16 (conv. 31%), 1.78 (conv. 82%), 1.98 (conv. 91%), respectively, Table 4-5], and an increase in the *N* value (number of polymer chain) was also seen at high CL conversion. The results strongly suggest the presence of certain degree of transesterification (shown in Scheme 4-1)[8] accompanied along with the propagation in the ROP of CL. Similarly, increases in both the M_w/M_n and the *N* values at high monomer conversion, were observed in the ROPs of CL using the above Al complexes (**2**-**6a**, Figure 4-5), whereas no significant changes in both the M_w/M_n and the *N* values were seen in the ROP using the C_6F_5 analogue (**1a**). The results also suggest that certain degree of transesterification would be accompanied in the ROPs under these conditions, although degree of the transesterification seemed decreasing in presence of *ortho*-substituent [**5a** (C_6H_5) *vs.* **6a** (2,6-$Me_2C_6H_3$), **5a** (C_6H_5) *vs.* **2a** (2,6-$F_2C_6H_3$), **3a** (2,4-$F_2C_6H_3$) *vs.* **4a** (3,4-$F_2C_6H_3$), Table 4-5]. I thus assume that the presence of rather strong electron withdrawing group (C_6F_5) would be required to prohibit the transesterification accompanied with the propagation in the ROP. Taking into account these results, use of the C_6F_5 substituent in the imino group is thus essential in terms of both the catalytic activity and for the ROP to proceed in the living manner.

Concluding Remarks

A series of Al complexes containing phenoxyimine ligands of the type, $R^1(R^2)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ [R^1;R^2 = Et;Et (**1b**), Me;Cl (**1c**)] and $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**)], have been prepared and identified on the basis of NMR spectra and elemental analyses, and their structures were determined by X-ray crystallography. The ring-opening polymerizations (ROPs) of ε-caprolactone (CL) using **1a-c** in the presence of $PhCH_2OH$ proceeded efficiently in a living manner, and the propagation rates were affected by the anionic donor employed (Me, Et or Cl). The catalytic activity using **1-6a** [Ar = C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**)]-$PhCH_2OH$ catalyst systems was highly affected by the aromatic substituent in the imino group, and placement of fluorinated substituents especially in the *ortho*-position affected the catalytic activity. The ROPs using **2-6a**-$PhCH_2OH$ catalyst systems accompanied certain degree of side reactions like transesterification, whereas the living polymerization systems can be accomplished using the C_6F_5 analogues (**1a-c**). Therefore, the C_6F_5 substituent in the imino group plays an essential key role in the ROP of CL in terms of both the catalytic activity and for the ROP to proceed in a living manner. I believe that the results obtained here should be highly promising for designing more efficient catalysts of living ring opening polymerization of cyclic esters.

Experimental Section

General procedures.

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade *n*-hexane, toluene (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 stream, and were passed through a short alumina column under N_2 stream before use. All chemicals used were of

reagent grade and were purified by the standard purification procedures. Reagent-grade $AlMe_3$, $AlEt_3$, Me_2AlCl in *n*-hexane (Kanto Kagaku Co. Ltd.) were stored in the drybox and were used as received. Various salicylaldimines (imino-phenols) containing different substituent on the imino groups, 2-^{t}Bu-6-(RN=CH)C_6H_3OH [R = Ph, 2,6-$Me_2C_6H_3$, C_6F_5, 2,6-$F_2C_6H_3$, 2,4-$F_2C_6H_3$, 3,4-$F_2C_6H_3$] were prepared according to the reported procedures.[9] Syntheses of Al complexes (**1,5,6a**) were referred to our previous report.[4a,b] Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). All ^1H, and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted, and their chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C). Molecular weights and the molecular weight distributions of resultant polymers were measured by gel-permeation chromatography (GPC). GPC were performed at 40 ºC on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm□, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from < 10^2 to 2×10^7 MW) were calibrated versus polystyrene standard samples.

Synthesis of 2-^{t}Bu-6-{(2,4-$F_2C_6H_3$)N=CH}C_6H_3OH.

A mixture of 2,4-difluoroaniline (1.42 g, 11.0 mmol), 3-*tert*-butyl-2-hydroxy-benzaldehyde (1.78 g, 10.0 mmol), and *p*-toluene sulfonic acid (3 mg, 17 μmol) in toluene (25 mL) was refluxed for 17 h. Removal of the solvent from the reaction mixture by a rotary evaporator *in vacuo* gave dark yellow oil, and the purification by silica gel column chromatography using *n*-hexane afforded yellow oil (2.87 g, 99% yield). ^1H NMR (C_6D_6): δ 1.58 (s, 9H, ^{t}Bu), 6.30-6.48 (m, 3H, aromatic), 6.77 (t, 1H, J = 8 Hz, aromatic), 6.88 (d, 1H, J = 7 Hz, aromatic), 7.36 (d, 1H, J = 7 Hz, aromatic), 7.95 (s, 1H, C*H*=N), 14.01 (s, 1H, OH). ^{13}C NMR (C_6D_6): δ 29.6, 35.2, 104.8 (dd, J_1 = 3 Hz, J_2 = 2 Hz),

111.5 (dd, J_1 = 22 Hz, J_2 = 4 Hz), 118.7, 119.3, 121.9 (dd, J_1 = 10 Hz, J_2 = 2 Hz), 131.2, 132.9 (dd, J_1 = 11 Hz, J_2 = 4 Hz), 138.1, 156.0 (dd, J_1 = 252 Hz, J_2 = 12 Hz), 161.2 (dd, J_1 = 247 Hz, J_2 = 11 Hz), 161.3, 165.0. Anal. Calcd. for $C_{17}H_{17}F_2NO$: C, 70.58; H, 5.92; N, 4.84. Found: C, 70.20; H, 6.10; N, 4.80.

Synthesis of 2-^{t}Bu-6-{(3,4-$F_2C_6H_3$)N=CH}C_6H_3OH.

A mixture of 3,4-difluoroaniline (1.42 g, 11.0 mmol), 3-*tert*-butyl-2-hydroxy-benzaldehyde (1.78 g, 10.0 mmol), and *p*-toluene sulfonic acid (3 mg, 17 μmol) in toluene (25 mL) was refluxed for 18 h. The solution was then concentrated *in vacuo*, and the purification by silica gel column chromatography using *n*-hexane afforded yellow oil (2.81 g, 97% yield). ^{1}H NMR (C_6D_6): δ 1.61 (s, 9H, ^{t}Bu), 6.23-6.60 (m, 3H, aromatic), 6.79 (t, 1H, J = 8 Hz, aromatic), 6.89 (d, 1H, J = 7 Hz, aromatic), 7.37 (d, 1H, J = 7 Hz, aromatic), 7.75 (s, 1H, C*H*=N), 13.79 (s, 1H, OH). ^{13}C NMR (C_6D_6): δ 29.6, 35.2, 110.1 (d, J = 190 Hz), 117.5 (d, J = 18 Hz), 117.8 (dd, J_1 = 5 Hz, J_2 = 3 Hz), 118.8, 119.1, 131.1, 131.2, 145.0 (dd, J_1 = 6 Hz, J_2 = 3 Hz), 149.4 (dd, J_1 = 246 Hz, J_2 = 13 Hz), 150.8 (dd, J_1 = 248 Hz, J_2 = 14 Hz), 161.0, 164.0. Anal. Calcd. for $C_{17}H_{17}F_2NO$: C, 70.58; H, 5.92; N, 4.84. Found: C, 70.81.; H, 6.27; N, 4.73.

Synthesis of Et_2Al[O-2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3] (1b).

Into a stirred solution containing 2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3OH (1.37 g, 4.00 mmol) in *n*-hexane (5.0 mL), $AlEt_3$ (0.90 M *n*-hexane solution, 4.67 mL, 4.20 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature slowly and was stirred for 3 h. The mixture was then concentrated *in vacuo*, and the chilled solution (-20 ºC) afforded yellow microcrystals of **1b** (1.26 g, 74% yield). ^{1}H NMR (C_6D_6): δ 0.33 (s, 4H, Al*C*H_2CH$_3$), 1.36 (s, 6H, AlCH$_2$*C*H_3), 1.49 (s, 9H, ^{t}Bu), 6.52 (br, 1H, *Aromatic*), 6.64 (br, 1H, *Aromatic*), 7.33 (s, 1H, C*H*=N), 7.40 (br, 1H, *Aromatic*). ^{13}C NMR (C_6D_6): δ 0.3, 9.1, 29.3, 35.3, 118.0, 119.3, 121.6-121.9(m), 134.7, 136.7-137.0(m), 137.3, 138.8-139.5(m), 140.4-140.6(m), 141.4-141.7(m), 142.3, 143.0-143.1(m), 167.0, 177.3.

Anal. Calcd. for $C_{21}H_{23}F_5AlNO$: C, 59.02; H, 5.42; N, 3.28. Found: C, 58.71; H, 5.18; N, 3.12.

Synthesis of Me(Cl)Al[O-2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3] (1c).

Into a stirred solution containing 2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3OH (0.87 g, 3.00 mmol) in mixture of *n*-hexane (10.0 mL) and toluene (4 mL), Me_2AlCl (0.46 M *n*-hexane solution, 6.90 mL, 3.15 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 4-2). The mixture was then concentrated *in vacuo*, and the chilled solution (-20 ºC) afforded colorless microcrystals of **1c** (939 mg, 78% yield). ^{1}H NMR (C_6D_6): δ -0.06 (t, J = 2 Hz, 3H, *Me*), 1.44 (s, 9H, ^{t}*Bu*), 6.52 (t, J = 8 Hz, 3H, *Aromatic*), 6.60 (dd, J_1 = 8 Hz, J_2 = 2 Hz, *Aromatic*), 7.26 (s, 1H, *N=CH*), 7.39 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 1H, *Aromatic*). ^{13}C NMR (C_6D_6): δ-11.1, 29.3, 35.3, 119.2, 119.2, 120.1-120.5(m), 134.9, 136.6-137.0(m), 138.1, 139.1-139.5(m), 140.5-140.7(m), 141.9-142.1(m), 142.5, 142.9-143.2(m), 165.4, 177.91. Anal. Calcd. for $C_{18}H_{16}F_5AlClNO$: C, 51.50; H, 3.84; N, 3.34. Found: C, 51.38; H, 3.79; N, 3.23.

Synthesis of Me_2Al[O-2-^{t}Bu-6-{(2,6-$F_2C_6H_3$)N=CH}C_6H_3] (2a).

Into a stirred solution containing 2-^{t}Bu-6-{(2,6-$F_2C_6H_3$)N=CH}C_6H_3OH (0.87 g, 3.00 mmol) in *n*-hexane (7.5 mL), $AlMe_3$ (0.47 M *n*-hexane solution, 6.67 mL, 3.15 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 4-2). The mixture was then concentrated *in vacuo*, and the resultant solid was dissolved in a minimum amount of toluene. The chilled solution (-20 ºC) afforded colorless microcrystals of **2a** (878 mg, 85% yield). ^{1}H NMR (C_6D_6): δ -0.21 (t, J = 1 Hz, 6H, Al*Me*$_2$), 1.49 (s, 9H, ^{t}Bu), 6.38-6.49 (m, 3H, *Aromatic*), 6.53 (t, J = 8 Hz, 1H, *Aromatic*), 6.59 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1H, *Aromatic*), 7.37 (m, 2H, *Aromatic,* C*H*=N). ^{13}C NMR (C_6D_6): δ -10.0, 29.4, 35.3, 112.1-112.3(m), 117.5, 119.6, 124.1(t, J = 2 Hz), 134.5, 136.0, 142.0, 156.5 (dd, J_1 = 250 Hz, J_2 = 4 Hz), 165.8, 176.1-176.2(m). Anal. Calcd. for $C_{19}H_{22}AlNO$: C, 66.08; H, 6.42; N, 4.06. Found: C, 66.06;

H, 6.12; N, 4.04.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,4\text{-}F_2C_6H_3)N{=}CH\}C_6H_3]$ (3a).

Into a stirred solution containing 2-^{t}Bu-6-{(2,4-$F_2C_6H_3$)N=CH}C_6H_3OH (1.16 g, 4.00 mmol) in *n*-hexane (10.0 mL), $AlMe_3$ (0.43 M *n*-hexane solution, 9.67 mL, 4.20 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 4-2). The mixture was then concentrated *in vacuo*, and the chilled solution (-20 ºC) afforded colorless microcrystals of **3a** (1.28 g, 93% yield). ^{1}H NMR (C_6D_6): δ -0.26 (s, 6H, Al*Me*$_2$), 1.52 (s, 9H, ^{t}Bu), 6.26-6.36 (m, 2H, *Aromatic*), 6.50-6.64 (m, 3H, *Aromatic*), 7.34 (s, 1H, C*H*=N), 7.40 (d, J = 7 Hz, 1H, *Aromatic*). ^{13}C NMR (C_6D_6): δ -9.6, 29.4, 35.3, 105.3 (t, J = 25 Hz), 111.9 (dd, J_1 = 22 Hz, J_2 = 3 Hz), 117.6, 119.7, 126.0 (d, J = 10 Hz), 130.9 (dd, J_1 = 11 Hz, J_2 = 3 Hz), 134.3, 135.7, 141.9, 155.5 (dd, J_1 = 251 Hz, J_2 = 12 Hz), 161.6 (dd, J_1 = 248 Hz, J_2 = 11 Hz), 165.3, 173.5. Anal. Calcd. for $C_{19}H_{22}F_2AlNO$: C, 66.08; H, 6.42; N, 4.06. Found: C, 66.16; H, 6.54; N, 4.08.

Synthesis of $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(3,4\text{-}F_2C_6H_3)N{=}CH\}C_6H_3]$ (4a).

Into a stirred solution containing 2-^{t}Bu-6-{(3,4-$F_2C_6H_3$)N=CH}C_6H_3OH (1.16 g, 4.00 mmol) in *n*-hexane (10.0 mL), $AlMe_3$ (1.09 M *n*-hexane solution, 4.67 mL, 4.20 mmol Al) was added dropwise over 10 min period at -20 ºC. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 4-2). The mixture was then concentrated *in vacuo*, and the chilled solution (-20 ºC) afforded colorless microcrystals of **4a** (1.12 g, 87% yield). ^{1}H NMR (C_6D_6): δ -0.28 (s, 6H, Al*Me*$_2$), 1.53 (s, 9H, ^{t}Bu), 6.40-6.46 (m, 3H, *Aromatic*), 6.61 (t, J = 8 Hz, 1H, *Aromatic*), 6.66 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1H, *Aromatic*), 7.19 (s, 1H, C*H*=N), 7.42 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 1H, *Aromatic*). ^{13}C NMR (C_6D_6): δ -8.9, 29.4, 35.3, 117.59, 118.12 (dd, J_1 = 18 Hz, J_2 = 2 Hz), 118.74 (dd, J_1 = 6 Hz, J_2 = 3 Hz), 119.74, 134.24, 135.56, 141.84, 143.19 (dd, J_1 = 7 Hz, J_2 = 4 Hz), 149.90 (dd, J_1 = 249 Hz, J_2 = 13 Hz), 150.78 (dd, J_1 = 250 Hz, J_2 = 14 Hz), 164.89, 170.72. Anal. Calcd. for

$C_{19}H_{22}F_2AlNO$: C, 66.08; H, 6.42; N, 4.06. Found: C, 66.28; H, 6.59; N, 4.03.

Ring opening polymerization (ROP) of ε-caprolactone (CL).

Typical polymerization procedures (Table 4-3) are as described. Into a sealed Schlenk tube containing a toluene solution of **1a** (40 μmol/0.100 mL of toluene), $PhCH_2OH$ (0.040 mmol/0.096 mL of toluene) was added in the drybox at room temperature. The solution was stirred for 10 min, and the solution was then added toluene (8.76 mL) and ε-caprolactone (5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 50 ºC, and the solution was stirred for the prescribed time (15 min). A small amount of the reaction mixture was partly taken out from the mixture for certain period to monitor the reaction, especially to analyze the monomer conversion [by ^{1}H NMR (400 MHz)] and M_n, M_w/M_n (by GPC).

Crystallographic Analysis.

All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo Kα radiation. The selected crystal collection parameters are summarized in Table 4-6, and the detailed results are described in the Supporting Information.[10] All structures were solved by direct methods and expanded using Fourier techniques,[13] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complex **1b,c**, and **2-4a** were performed using the Crystal Structure[14] crystallographic software package.

Table 4-6. Crystal data and structure refinement parameters for $Et_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1b**), $Me(Cl)Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1c**), $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**)].

	1b	**1c**	**2a**	**3a**	**4a**
formula	$C_{21}H_{23}AlF_5NO$	$C_{18}H_{16}AlClF_5NO$	$C_{19}H_{22}AlF_2NO$	$C_{19}H_{22}AlF_2NO$	$C_{19}H_{22}AlF_2NO$
fw	427.39	419.76	345.37	345.37	345.37
cryst color, habit	yellow, block	colorless, block	colorless, block	colorless, block	yellow, block
cryst size (mm)	0.62 × 0.44 × 0.24	0.32 × 0.20 × 0.15	0.22 × 0.20 × 0.18	0.54 × 0.42 × 0.35	0.30 × 0.18 × 0.15
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	*C*2/*c* (#15)	$P2_1/a$ (#14)	*P*-1 (#2)	*P*-1 (#2)	$P2_1/c$ (#14)
a (Å)	32.263(3)	12.4278(6)	7.5473(4)	7.7061(4)	7.0439(3)
b (Å)	7.9795(5)	12.3734(6)	9.8452(7)	9.7853(6)	20.8564(11)
c (Å)	20.2578(16)	12.7793(7)	12.7096(7)	12.7343(8)	26.5114(13)
β (º)	124.982(2)	91.7271(17)	74.8131(14)	105.4480(18)	93.2474(13)
V ($Å^3$)	4272.9(6)	1964.24(17)	906.84(9)	915.65(10)	3888.5(3)
Z value	8	4	2	2	8
D_{calcd} (g/cm^3)	1.329	1.419	1.265	1.253	1.180
F_{000}	1776.00	856.00	364.00	364.00	1456.00
no. of reflns measd	19796	19089	9121	9074	31362
no. of observations	2862	3467	3214	3460	3306
no. of variables	285	260	239	239	485
R_1	0.0554	0.0319	0.0433	0.0681	0.0456
wR_2	0.0921	0.0948	0.1619	0.2190	0.1167
goodness of fit	1.004	1.007	1.000	1.000	1.006

References and Notes

1. For example, see: (a) Cox, M. K. In *Biodegradable Polymers and Plastics*; Vert, M.; Feijen, J.; Albertsson, A.; Scott, G.; Chiellini, E. Eds.; The Royal Society of Chemistry: Cambridge, UK, 1992; p. 95. (b) Doi, Y.; Kumagai, Y.; Tanahashi, N.; Mukai, K. In *Biodegradable Polymers and Plastics*; Vert, M.; Feijen, J.; Albertsson, A.; Scott, G.; Chiellini, E. Eds.; The Royal Society of Chemistry: Cambridge, UK, 1992; p.139. (c) Okada, M. *Prog. Polym. Sci*. **2002**, *27*, 87.
2. For recent reviewing article, see: (a) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci*. **1999**, *147*, 1. (b) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc*. *Dalton Trans*. **2001**, 2215. (c) Stridsberg, K. M.; Ryner, M.; Albertsson, A. C. *Adv. Polym. Sci*. **2002**, *157*, 41. (d) Albertsson, A.-C.; Varma, I. *Biomacromolecules* **2003**, *4*, 1466. (e) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147.
3. Examples for polymerization of lactide by Al, see: (a) Trofimoff, L.; Aida, T.; Inoue, S. *Chem. Lett*. **1987**, 991. (b) Spassky, N.; Wisniewski, M.; Pluta, C.; LeBorgne, A. *Macromol. Chem. Phys*. **1996**, *197*, 2627. (c) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461. (d) Wisniewski, M.; LeBorgne, A.; Spassky, N. *Macromol*. *Chem. Phys*. **1997**, *198*, 1227. (e) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (f) Cameron, P. A.; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S. *Macromol. Rapid Commun.* **1999**, *20*, 616. (g) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (h) Bhaw-Luximon, A.; Jhurry, D.; Spassky, N. *Polym. Bull.* **2000**, *44*, 31. (i) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc*. **2000**, *122*, 1552. (j) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci.*, *Part A: Polym. Chem*. **2000**, *38*, 4686. (k) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. *Macromolecules* **2001**, *34*, 356. (l) Chisholm, M. H.; Navarro-Llobet, D.; Simonsick,

Jr., W. J. *Macromolecules* **2001**, *34*, 885. (m) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (n) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc*. **2002**, *124*, 1316. (o) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2003**, *22*, 769.

4. (a) Iwasa, N.; Liu, J.; Nomura, K. *Catal. Commun.* **2008**, *9*, 1148. (b) Liu, J.; Iwasa, N.; Nomura, K. *Dalton Trans.* **2008**, 3978. (c) Iwasa, N.; Fujiki, M.; Nomura, K. *J. Mol. Catal. A* accepted (accepted manuscript, web released on June 27, 2008).
5. Examples for ROP of lactones etc., see: (a) Ko, B.-T.; Lin, C.-C. *Macromolecules* **1999**, *32*, 8296. (b) Taden, I.; Kang, H.-C.; Massa, W.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem*. **2000**, 441. (c) Chakraborty, D.; Chen, E.Y.-X. *Organometallics* **2002**, *21*, 1438. (d) Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2002**, *35*, 5763. (e) Yu, R.-C.; Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 645. (f) Zheng, G.; Stöver, H. D. H. *Macromolecules* **2003**, *36*, 7439. (g) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2003**, 3082. (h) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* **2004**, *37*, 7968. (i) Lewinsky, J.; Horeglad, P.; Tratkiewicz, E.; Grzenda, W.; Lipkowski, J.; Kolodziejczyk, E. *Macromol. Rapid Commun.* **2004**, *25*, 1939. (j) Nomura, N.; Aoyama, T.; Ishii, R.; Kondo, T. *Macromolecules* **2005**, *38*, 5363. (k) Amgoune, A.; Lavanant, L.; Thomas, C. M.; Chi, Y.; Welter, R.; Dagorne, S.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 6279. (l) Majoumo-Mbe, F.; Smolensky, E.; Lönnecke, P.; Shpasser, S.; Eisen, M. S.; Hey-Hawkins, E. *J. Mol. Catal*. *A* **2005**, *240*, 91. (m) Yao, W.; Mu, Y.; Gao, A.; Su, Q.; Liu, Y.; Zhang, Y. *Polymer* **2008**, *49*, 2486.
6. Selected examples, for synthesis, structural determinations for monomeric/dimeric Al complexes, see: (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem*. **1996**, *35*, 63. (b) Qian, B.; Ward, D. L.; Smith III., M. R. *Organometallics* **1998**, *17*, 3070. (c) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (d)

Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883. (e) Muñoz-Hernández, M.-A.; Keiser, T. S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416. (f) Liu, S.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Organomet. Chem.* **2000**, *596*, 109. (g) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan G. A., *J. Chem. Soc., Dalton Trans.* **2001**, 1472. (h) Hill, M. S.; Hutchison, A. R.; Keiser, T. S.; Parkin, S.; VanAelstyn, M. A.; Atwood, D. A. *J. Organomet. Chem.* **2001**, *628*, 71. (i) Redshaw, C.; Elsegood, M. R. J. *Chem. Commun.* **2001**, 2016. (j) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 415. (k) Chakraborty, D.; Chen, E. Y.-X. *Macromolecules* **2002**, *35*, 13. (l) Lewiński, J.; Zachara, J.; Starowieyski, K. B.; Ochal, Z.; Justyniak, I.; Kopec, T; Stolarzewicz, P.; Dranka, M. *Organometallics* **2003**, *22*, 3773. (m) Lewinski, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (n) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P.; Jaouen, G. *Organometallics* **2003**, *22*, 3732. (o) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64. (p) Zhu, H.; Chen, E. Y.-X. *Inorg. Chem*. **2007**, *46*, 1481.

7. Dittrich, W.; Shultz, R. C. *Angew. Macromol. Chem.* **1971**, *15*, 109.
8. Selected reports concerning transesterification in the ROP of CL, DL-lactide, (a) Duda, A.; Penczek, S. *Macromolecules* **1995**, *28*, 5981. (b) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461. (c) Spassky, N.; Simic, V.; Montaudo, M. S.; Hubert-Pfalzgraf, L. G. *Macromol. Chem. Phys.* **2000**, *201*, 2432. (d) Jhurry, D.; Bhaw-Luximon, A.; Spassky, N. *Macromol. Symp.* **2001**, *175*, 67. (e) Cayuela, J.; Bounor-Legaré, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338.
9. Syntheses of various salicylaldimine ligands: Fujita, T.; Tohi, Y.; Mitani, M. European patent EP 0874005A1 (1998).

10. The detailed structural results including CIF file are shown in the Supporting Information.
11. I estimated conversions of CL by ^{1}H NMR spectra, and most of the spectra were shown in the Supporting Information. Moreover, the exact M_n values for ring-opened poly(CL)s were corrected from the M_n values by GPC *vs.* polystyrene standards according to the following equation: $M_{n(PCL)} = 0.56 \times M_{n(GPC\ vs.\ polystyrene\ standards)}$ according to the following reference: (a) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889. (b) Duda, A.; Kowalski, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. I did not estimate the M_n values from the $_{1}$H NMR spectra, because the spectra were a mixture of the reaction products [CL, poly(CL), toluene etc.] and seemed lacking the accuracy.
12. Based on the results for estimation of number of the polymer chains (*N* value), *N* values by **1b**,**c** were slightly larger than the Al complex charged. I assume that these would be due to the accuracy of the M_n values corrected, because the corrected M_n values used for the estimation were based on the M_n value measured by GPC in THF *vs.* polystyrene standards. Since number of polymer chain (*N* values) did not change during the time course, I assume that the ROPs by **1b**,**c** proceeded with quantitative initiation efficiencies. The catalyst efficiency by **1a** estimated based on *N* value is 85%, and the value is somewhat higher than that estimated previously by ^{1}H NMR spectra (68%).[4b,c] I believe that this would also be due to the reason described above (accuracy of estimation of *N* value).
13. DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Delder, R.; Israel, R.; Smits, J. M. M. (1994). The DIRDIF94 program system, Technical report of crystallography laboratory, University of Nijmegen, The Netherlands.
14. (a) CrystalStructure 3.6.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2004). 9009 New Trails Dr. The Woodlands TX 77381 USA. (b) CRYSTALS

Issue 10: Watkin, D.J.; Prout, C.K.; Carruthers, J.R.; Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK. (1996).

Consideration

As described above, the propagation rate in the ring-opening polymerization (ROP) of ε-caprolactone (CL) using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1a**) depended upon the first order of the CL concentration. The fact thus clearly suggests that the rate determining step in the ROP is the coordination and insertion step. Moreover, the fluorine substituents especially in the *ortho*-position in the aromatic imino group strongly affects the catalytic activity, and certain degree of side reaction (trans esterification) was accompanied in the ROPs using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3]$ [Ar = 2,6-$F_2C_6H_3$ (**2a**), 2,4-$F_2C_6H_3$ (**3a**), 3,4-$F_2C_6H_3$ (**4a**), C_6H_5 (**5a**), 2,6-$Me_2C_6H_3$ (**6a**)] as the initiation precursors. Therefore, geometry optimization of the assumed propagating species (after first insertion), $MeAl[O\text{-}2\text{-}^tBu\text{-}6\text{-}(ArN{=}CH)C_6H_3][O(CH_2)_5C(O)OMe]$ (**1a'-6a'**), were explored to compare their optimized structures and energies in the stabilized structures by the semiempirical molecular orbital method (semi-empirical PM3). The results are summarized in Table 4-7.

Table 4-7. Relative stabilization energies and Al-O bond distances of $MeAl[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3][O(CH_2)_5C(O)OMe]$[R = C_6F_5 (**1a'**), 2,6-$F_2C_6H_3$ (**2a'**), 2,4-$F_2C_6H_3$ (**3a'**), 3,4-$F_2C_6H_3$ (**4a'**), Ph (**5a'**), 2,6-$Me_2C_6H_3$ (**6a'**)].[a]

R	$\Delta E_{propagating}$[b/] kJ/mol (Δ Heat of formation)	Al-O / Å
Ph	0	1.783
2,6-$Me_2C_6H_3$	-24.304	1.788
2,4-$F_2C_6H_3$	-360.924	1.780
2,6-$F_2C_6H_3$	-352.317	1.780
3,4-$F_2C_6H_3$	-352.889	1.778
C_6F_5	-865.776	1.778

[a]Equibrium geometry at ground state with semiempirical PM3, geometry optimization, RHF/PM3D Spartan '06 for Windows (Wavefunction Inc.). [b]$\Delta E_{propagating}$ = (estimated heat of formation in the proposed propagating species of corresponding Al complex) – (estimated heat of formation in the proposed propagating species of Al complex containing Ph substituent, **5a'**, $MeAl[O\text{-}2\text{-}^tBu\text{-}6\text{-}(PhN{=}CH)C_6H_3][O(CH_2)_5C(O)OMe]$).

The calculated energies in the optimized structures with a series of aromatic imino group (Ar) increased in the order: C_6F_5 (**1a'**) >> 2,6-$F_2C_6H_3$ (**2a'**), 2,4-$F_2C_6H_3$ (**3a'**), 3,4-$F_2C_6H_3$ (**4a'**) > 2,6-$Me_2C_6H_3$ (**6a'**) > C_6H_5 (**5a'**). The results thus suggest that placement of the fluorine substituents stabilizes the propagating species, especially the stabilization of the C_6F_5 analogue should be remarkable. In contrast, no significant differences in the Al-O bond distances were observed in all Al complexes employed, suggesting that there are no distinct difference in their nucleophilicity (ability of the alkoxide to attack the CL).

Figure 4-6 shows optimized structures for the selected assumed propagating species in the ROP of CL. Note that structures of both the C_6F_5 analogue (**1a'**) and 2,6-$F_2C_6H_3$ analogue (**2a'**) fold distorted triangular-pyramidal geometry around the Al center with the Me ligand in the apical site, thus forming rather open coordination site in the *trans* position of the Me ligand, which would facilitate the coordination of CL and the subsequent insertion (Figure 4-6a,b). A driving force to fold these geometries would be a rather short distance [2.5 Å in **1a'**] between H (β-H in the alkoxide) and F (*ortho* position in the C_6F_5). In contrast, assumed structures in the **4-6a'** (without *ortho* fluorine substituent) fold geometries having a rather open coordination site in the *trans* position of the propagating polymer chain (alkoxy group), which would not be favored for the subsequent insertion of CL after coordination (Figure 4-6c,d). The observed differences should be noteworthy and would be helpful for explanation of the observed difference in both the activity and the polymerization behaviors.

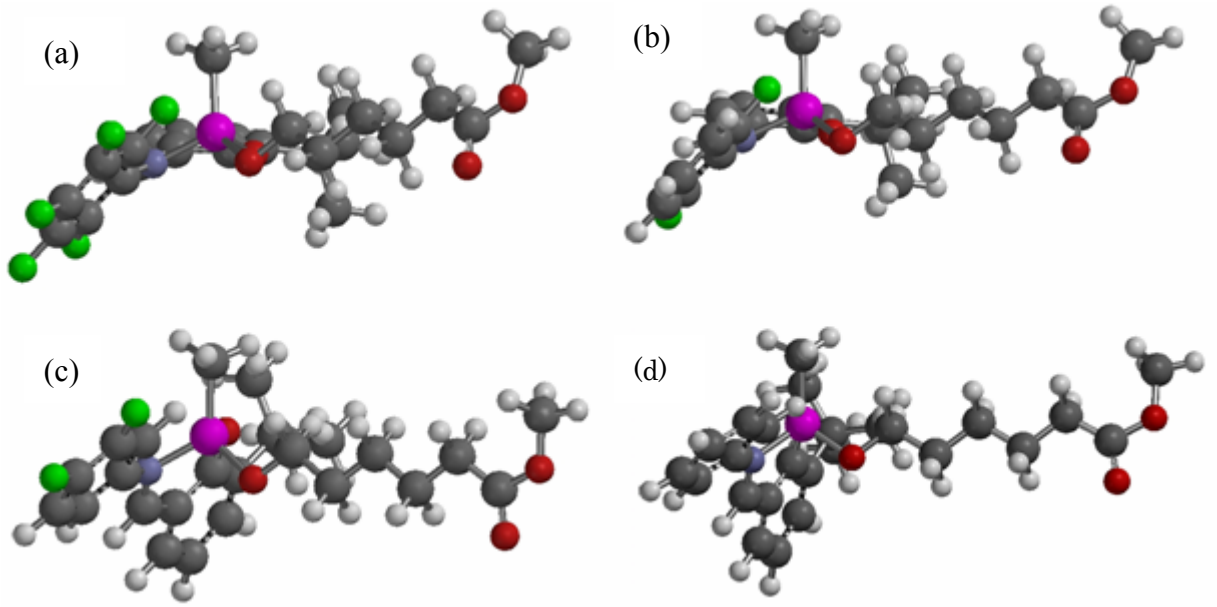


Figure 4-6. Optimized structures for proposed propagating species, MeAl[O-2-^{t}Bu-6-(RN=CH)C_6H_3][O$(CH_2)_5$C(O)OMe] [R = (a) C_6F_5 (**1a'**, up left), (b) 2,6-$F_2C_6H_3$ (**2a'**, up right), (c) 3,4-$F_2C_6H_3$ (**4a'**, bottom left), (d) Ph (**5a'**, bottom right)], in the ring-opening polymerization of ε-caprolactone.

In particular, the structures in **1a'** should have a significant advantage for subsequent insertion as well as for insertion of CL efficiently. This is because the geometry, especially the polymer chain end (alkoxy group) is positioned close to the carbonyl carbon of the coordinated CL (Figure 4-7), which should facilitate coordination/insertion in an efficient manner.

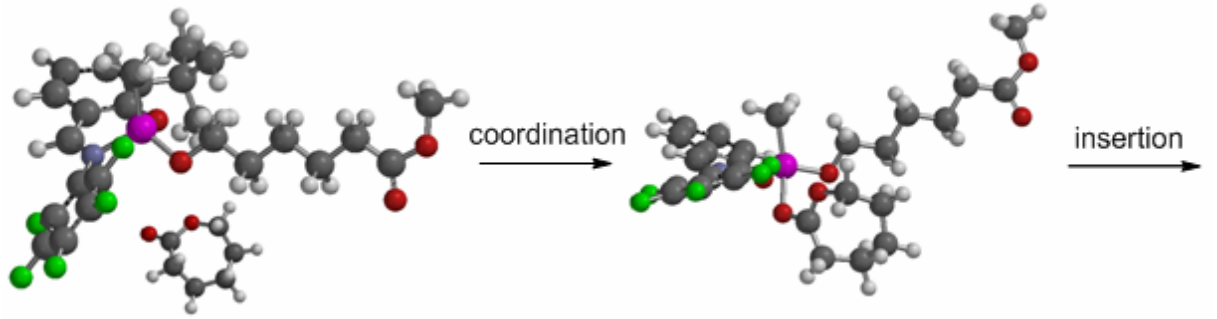


Figure 4-7. The expectation of MeAl[O-2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3][O$(CH_2)_5$C(O)OMe] coordinated by CL (coordinated species to **1a'**).

In contrast, the geometry in **4a'** should not be suited for the subsequent insertion of CL, because the coordination of CL into the position (*trans* to the propagating polymer chain) would afford a dormant species (Figure 4-8); propagation would proceed if CL is coordinated to the site positioned trans to the Me ligand (rather unfavorable insertion compared to the former site).

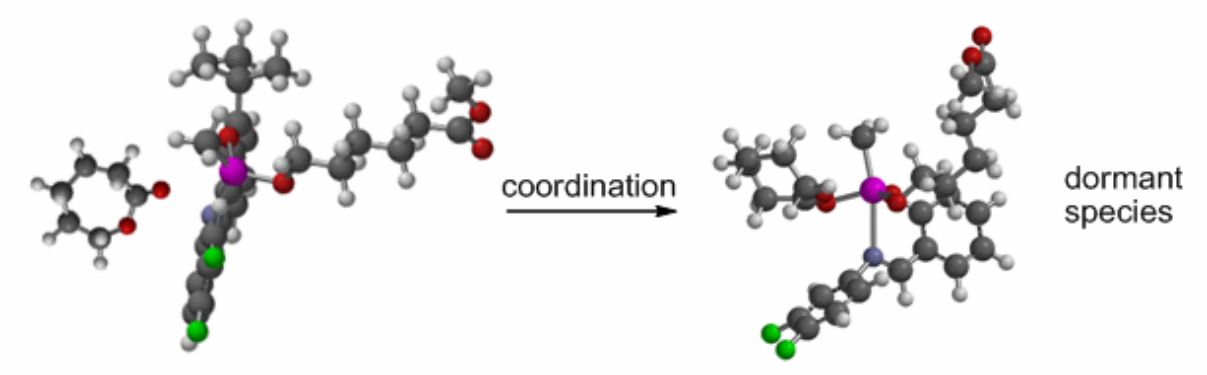


Figure 4-8. The expectation of MeAl[O-2-^{t}Bu-6-{(3,4-$F_2C_6H_3$)N=CH}C_6H_3] [$O(CH_2)_5C(O)OMe$] coordinated by CL (coordinated species to **4a'**).

Although these are results based on the calculation of the proposed propagating species, the assumption introduced here should be helpful for better explanation of the observed facts.

The probable major driving force to fold geometry in **1a'** should be an agnostic H-F interaction [2.5 Å by semi-empirical PM3] between fluorine in the C_6F_5 and the β-hydrogen in the propagating species (Figure 4-9). The distance would imply the presence of the interaction according to a previous report by Fujita *et al.*, and they proposed the interaction would inhibit β-hydrogen elimination (probable chain transfer reaction) from the titanium metal center in ethylene polymerization, thereby the polymerization proceeded in a living manner.[1] Taking into these account, I believe that I can include these calculation results, and the H-F interaction would be a driving force for the efficient coordination/insertion in the ROP in the present catalysis.

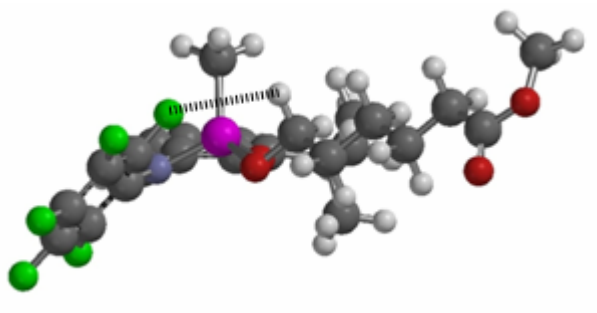


Figure 4-9. Assumed H-F interaction in MeAl[O-2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3][O$(CH_2)_5$C(O)OMe] (**1a'**).

Reference

1. Fujita *et al*. estimated H-F bond distance at 2.3 Å by DFT.

   Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327.

Chapter 5

Concluding Remarks and Future Perspectives

Concluding Remarks

In this thesis, (1) precise synthesis of new functional polyethers in the presence of conventional catalyst utilized by relative monomer reactivities in the substituted monomers, and (2) the design of efficient Al complexes for ring-opening polymerization (ROP) of cyclic esters were studied. In chapter 1, the steric effect of substituted oxirane monomers toward the reactivity in the ROP was investigated, and the precise synthesis of polyether containing oxirane ring in the side chain by the selective ROP of bifunctional epoxide was established. In chapter 2-4, both the synthesis of mononuclear Al complexes containing phenoxy-imine ligand and the ROP of cyclic esters using the complexes as the catalyst precursors were examined, and information concerning both ligand effect for the reactivity and the mechanism of the ROP were obtained. Moreover, based on the obtained knowledge, the efficient living ROPs of cyclic esters are accomplished.

In chapter 1, organotin phosphate condensate mediated the ring-opening polymerization of various cyclic ethers. The ROP of monosubstituted oxiranes reached to high conversion, whereas the conversion of the disubstituted was considerably lower. Consequently, the polymerization of glycidyl 2-methylglycidylether with both mono- and disubstituted oxirane groups was carried out resulting in the formation of polyether containing oxirane ring in the side chain.

In chapter 2, Al complexes of type, $Me_2Al[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$, have been prepared by the reaction of $AlMe_3$ with $2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3OH$ in high yield. In contrast, the reactions of $AlMe_3$ with 1.0 equiv. of $2\text{-}(R^2N{=}CH)C_6H_4OH$ yielded $Me_2Al[\mu_2\text{-}O\text{-}2\text{-}(R^2N{=}CH)C_6H_4](AlMe_3)$ with additional $AlMe_3$ coordinating to the oxygen.

Complexes were tested as catalyst precursors for ring-opening polymerisation (ROP) of ε-caprolactone (CL) in the presence of ^{n}BuOH (1.0 equiv. to Al), and their catalytic activities were strongly influenced by the imino substituent (R^2). The efficient ROP has been achieved using the C_6F_5 analogue, with the ROP taking place in a living manner.

In chapter 3, ROPs of various cyclic esters [ε-caprolactone, δ-valerolactone, *rac*-lactide] using Al complexes containing phenoxy-imine ligands have been explored in the presence of ^{n}BuOH. Both the catalytic activity and the catalyst efficiency in the ROPs were found to be highly affected by the imino substituent. The C_6F_5 analogue also showed the highest catalytic activity for ROP of δ-valerolactone, and the polymerization proceeded in a living manner.

In chapter 4, the ROPs of CL using $R^1(R^2)$Al[O-2-^{t}Bu-6-{(C_6F_5)N=CH}C_6H_3] [R^1;R^2 =Me,Me, Et;Et, Me;Cl] in the presence of $PhCH_2OH$ proceeded efficiently in a living manner, and the propagation rates were affected by the anionic donor employed. The catalytic activity using Me_2Al[O-2-^{t}Bu-6-(ArN=CH)C_6H_3] [Ar =C_6F_5, 2,6-$F_2C_6H_3$, 2,4-$F_2C_6H_3$, 3,4-$F_2C_6H_3$, C_6H_5, 2,6-$Me_2C_6H_3$]-$PhCH_2OH$ catalyst systems was highly affected by the aromatic substituent in the imino group, and placement of fluorinated substituents especially in the *ortho*-position affected the catalytic activity. The ROPs using the Al complexes except C_6F_5 analogues-$PhCH_2OH$ catalyst systems accompanied certain degree of side reactions like transesterification. Therefore, the C_6F_5 substituent in the imino group plays an essential key role in the ROP of CL in terms of both the catalytic activity and for the ROP to proceed in a living manner.

Perspective (Future research)

According to the achievements through this study, the following research plans can be considered as the future research.

Perspective of polyethers containing oxirane ring in the side chain (chapter 1).

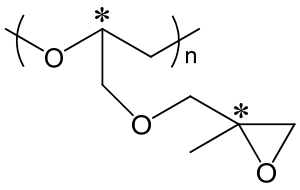
The following applications can be highly considered in the resultant polyethers containing oxirane ring in the side chain prepared in the chapter 1.

1) Elastomers needless cross-linkers

The cross-linking of elastomers is generally carried out in order to improve the durability, heat resistance, solvent resistance, and hardness. It is widely known that the condition of cross-linking is both high temperature and high pressure. However, since the resultant polyethers have the oxirane ring with high reactivity in the side chain, it is easy to proceed the cross-linking at room temperature without cross-linkers.

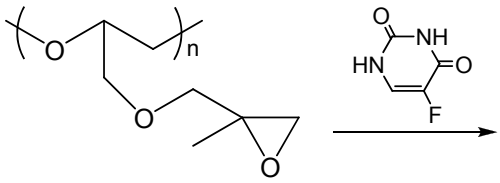
2) Column chromatography for separation of optical isomers

Resolution of enatiomers by liquid chromatography on chiral stationary phases is practically useful method not only for obtainment of optical isomers, but also for determination of their purities.[3] Polymers contain certain chirality such as phenylcarbamates have been used as the column packing reagents for better separations, and the resultant polymers obtained by ROP of single enatiomer should be thus are useful chiral packing materials for high-performance liquid chromatographic resolution of enantiomers.



3) Drug delivery systems (DDS)

For example, 5-fluoropyrimidine-2,4(1*H*,3*H*)-dione known as anticancer medicine[4] supported by the polymer is expected to keep the effective ingredient of a drug.



However, the polymer for DDS must be synthesized by low toxicity catalysts. Then, in the case of chiral packing materials for HPLC, it is also better that the polymer is prepared by low toxicity catalysts, because many optical isomers are used for pharmaceutical intermediates. Moreover, uniform polymer chain length is necessary to apply it for these uses. Therefore, it is expected that Al complex catalysts for cyclic esters in this study apply for the ROP of oxirane compounds, as described below.

Perspective of Al complex catalysts (chapter 2-4).

As above mentioned, the ROP of oxirane compounds using the Al catalysts will make it possible to create various functional polymers. Then, I consider applying the Al catalysts to the ROP of cyclic ethers by the following methods.

Ring-opening polymerization of oxirane compounds

The propagating species of Al complexes in this study seemed to be low nucleophilicity for ROP of oxirane compounds, because they indicated low activity in the ROP of β-butyrolactone and *rac*-lactide. On the other hand, Deffieux *et al*. recently achieved fast and controlled anionic polymerization of propylene oxide (PO) using catalyst systems consisting of onium salts in combination with $Al^{i}Bu_3$.[5] The formation of ate

complex consisting of onium salts and Al^{i}Bu$_3$ plays a role toward increasing the nucleophilicity of propagating species. Therefore, I think that addition of onium salts into Al complexes is efficient for increasing nucleophilicity (Figure 5-1).

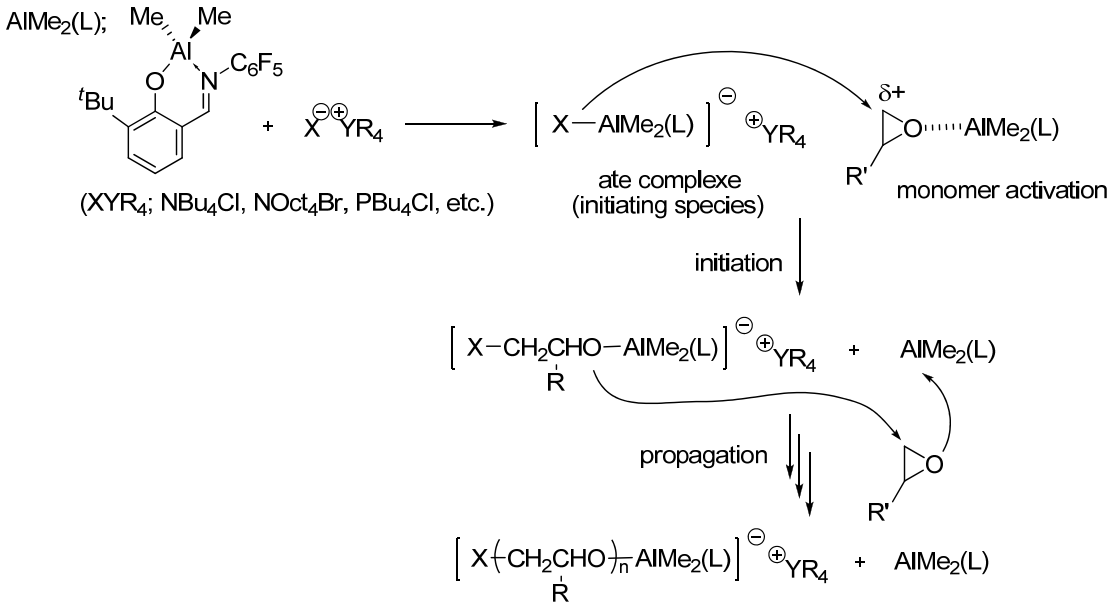


Figure 5-1. The catalyst systems consisting of Al complex and onium slats.

Moreover, Figure 5-1 described that Al complex not ate complex plays a role toward activation of oxirane monomer. It might be effective for the ROP that the activation of monomer and propagation of polymer in the ROP are performed with each chemicals, because Okuda *et al.* propose that the ROP proceeds under the synergic interaction of a neutral Al complex with the corresponding ate complex.[6]

On the other hand, Chen *et al*. reported the ROP of PO by cationic Al complex generated in the polymerization system (*in situ* system).[7] Moreover, Jordan *et al*. reported isolated cationic Al complex, and search the possibility for catalyst of ethylene polymerization.[8] However, it is difficult for cationic ROP of PO to control the polymerization due to chain transfers such as back-biting, and the cationic process is not industrialized in spite of fast polymerization. Therefore, I will study the cationic ROP using

various Al complexes, and the synergic interaction with a neutral Al complex.

The whole perspective

Since the ROP of cyclic esters using the Al catalysts take place in a living manner, it may be possible to make block copolymers and graft copolymers by copolymerization of cyclic esters and cyclic ethers, and the precise copolymerization will provide promising polymers for various purposes.

For example, artificial blood vessels are made of polyesters possessing biocompatibility. However, since the polyesters do not display elasticity, a defect such as a kink is occurred by bending or impress. Therefore, precise copolymerization with cyclic ethers is effective for giving elasticity to the polyesters. On the other hand, the resultant copolymer consisting polyester and polyether is expected to display an amphiphile, and it makes the copolymer micelle colloid in the body. Therefore, it is useful for DDS, that is, in order to carry the effective ingredients to an affected part.

Indeed, the precise ROP of cyclic monomers is one of the most powerful tools to yield novel polymers.

References

1. Pedersen, C. J. *J. Am. Chem. Soc*. **1967**, *89*, 7017.
2. Lehn, J. M.; Montavon, F. *Helv. Chim. Acta* **1978**, *61*, 67.
3. (a) Blashke, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 13. (b) Okamoto, Y.; Kawashima, M.; Hatada, K. *J.Am.Chem.Soc.* **1984**, *106*, 5357.
4. (a) Bertram, J. S.; Heidelberger, C. *Cancer Res.* **1974**, *34*, 526. (b) Benedict, W. F.; Rucker, N.; Faust, J.; Kouri, R. E. *Cancer Res.* **1975**, *35*, 857.
5. Labbé, A.; Carlotti, S.; Billouard, C.; Debois, P.; Deffieux, A. *Macromolecules* **2007**, *40*, 7842.
6. Braune, W.; Okuda, J. *Angew. Chem. Int. Ed.* **2003**, *42*, 64.
7. Chakraborty, D.; Rodriguez, A.; Chen, E. Y.-X. *Macromolecules* **2003**, *36*, 5470.
8. Jordan, R. F. *et al*. *J. Am. Chem. Soc.* **1997**, *119*, 8125; **1998**, *120*, 8277; **1998**, *120*, 9384; **1999**, *121*, 8673.

List of Publications

学位論文の主たる部分を公表した論文

1) “Notable effect of imino substituent for the efficient ring-opening polymerization of ε-caprolactone initiated by Al complexes containing phenoxy-imine ligand of type, $Me_2Al(L)$ [L:O-2-^{t}Bu-6-(RN=CH)C_6H_3; R: 2,6-^{i}Pr$_2$C$_6$H$_3$, ^{t}Bu, adamantyl, C_6F_5]”
Iwasa, N.; Liu, J.; Nomura, K.
Catal. Commun. **2008**, *9*, 1148.

2) “Synthesis of Al complexes containing phenoxy-imine ligands and their use as the catalyst precursors for efficient living ring-opening polymerization of ε-caprolactone”
Liu, J.; Iwasa, N.; Nomura, K.
Dalton Trans. **2008**, 3978.

3) “Ring-opening polymerization of various oxirane derivatives using organotin phosphate condensate; Selective synthesis of the polyether containing oxirane ring in the side chain”
Iwasa, N.; Miura, K.; Kan, S.; Furukawa, Y.
Polym. Bull. **2008**, *61*, 207.

4) “Ring-opening polymerization of various cyclic esters by Al complex catalysts containing a series of phenoxy-imine ligands: Effect of the imino substituents for the catalytic activity”
Iwasa, N.; Fujiki, M.; Nomura, K.
J. Mol. Cat. A: Chem. in press (accepted manuscript, web released on June 27, 2008).

5) “Ring-opening polymerization of ε-caprolactone by Al complexes containing phenoxy-imine ligands: Notable effect of fluoro substituents in the imino group”
Iwasa, N.; Katao, S.; Fujiki, M.; Furukawa, Y.; Nomura, K.
Submitted to Macromolecules

学位論文の主たる部分を公開した特許

1) “アルミニウム化合物、開環重合触媒、及びポリエステルの製造方法”
岩佐成人、古川喜朗、野村琴広
特許出願（奈良先端科学技術大学院大学と共同）
特願 2007-171172

学位論文の主たる部分を公表した学会発表（本人発表）

－国際会議発表－

1) “Living ring-opening polymerization of ε-caprolactone using Al complexes containing phenoxy-imine ligand: notable effect of imino substituent”
Iwasa,N.; Liu, J.; Fujiki, M.; Nomura, K.
NAIST/GIST Joint Symposium on Advanced Materials, OP7, GIST, 22th 11/’07.

2) “Living ring-opening polymerization of ε-caprolactone using Al complexes containing phenoxy-imine ligand: notable effect of imino substituent”
Iwasa, N.; Liu, J.; Fujiki, M.; Nomura, K.
The 10th Pacific Polymer Conference, 6P1S1-018b, Kobe International Conference Center, 6th 12/’07.

3) “Living ring-opening polymerization of ε-caprolactone using Al complexes containing phenoxy-imine ligands: notable effect of imino substituent”
Iwasa, N.; Liu, J.; Fujiki, M.; Nomura, K.
IUPAC 42nd World Polymer Congress (Macro 2008), 0105, Taipei international convention center, 30th 6/’08.

－国内学会発表－

1) “フェノキシーイミン配位子を有する Al 錯体の合成、構造解析、およびそれを用いたラクトンの開環重合”
岩佐成人、Liu Jingyu、野村琴広
第 54 回有機金属化学討論会, PA205, 広島大学, 2007 年 10 月 27 日

Acknowledgement

本論文は、奈良先端科学技術大学院大学　物質創成科学研究科　高分子創成科学講座における2006年11月から2008年9月までの研究成果をまとめたものである。

奈良先端科学技術大学院大学　物質創成科学研究科　高分子創成科学講座　藤木道也教授には、本研究を進めるにあたり、ご指導を仰ぎ、またご校閲を賜わりましたことを心より感謝し厚く御礼申し上げます。

本研究を進めるにあたり、常に親身になってご指導、ご鞭撻頂き、適切なご助言や有意義なご討論を賜りました野村琴広准教授に心より感謝し厚く御礼申し上げます。

本研究の機会を与えて頂き、また温かく見守りご支援くださった ダイソー株式会社　古川喜朗研究所長、菅伸治副研究所長、三浦克人主席 に心より感謝し厚く御礼申し上げます。

本研究の意義を一層深めるため、議論を重ね適切なご助言を受け賜わりました奈良先端科学技術大学院大学　物質創成科学研究科　反応制御科学講座　垣内喜代三教授、生体適合性物質科学講座　安藤剛准教授に心より感謝し厚く御礼申し上げます。

本研究を進めるうえで、数々の貴重なご助言、激励を頂きました高分子創成科学講座　内藤昌信助教、尾之内久成助教に心より御礼申し上げます。

本研究を進めるにあたり、NMR測定でお世話になりました淺野間文夫技術職員、そしてX線構造解析でお世話頂きました片尾昇平技術職員に心より感謝し厚く御礼申し上げます。

高分子創成科学講座の皆様には、本研究を進めるうえで有意義な議論ができたこと、また充実した研究室生活を伴に過ごせたことを嬉しく思い、心より感謝し厚く御礼申し上げます。

最後に、いつも温かく見守ってくれた　父　岩佐喜代一、母　房子、義父　藤田正夫、義母　恵子、そして絶えず笑顔で応援してくれた　妻　知世、娘　悠生に心より感謝します。ありがとう。

岩佐　成人

2008 年 7 月