RSC Advances

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DOI: 10.1039/C5RA10753A

Coordinating Effect in Ring-opening Polymerization of ε-Caprolactone Using Aluminum Complexes Bearing Bisphenolate as Catalysts

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Abstract

A series of Al complexes bearing diphenolate ligands were synthesized and their application for the ring-opening polymerization of *ε*-caprolactone was studied. Positional variation of the substituent on the aryl ring of RC*H(4,6-di-*t*-butylphenol)$_2$ ligand was shown to have a considerable influence on the catalysis result. Complexes with *ortho*-substituent showed greater catalytic activity than those with *para*-substituent. Substitutions of aryl moiety by H or methyl groups resulted in a catalytic activity falling between that of the *ortho*-substitution Al complexes and that of the *para* ones. Our results demonstrate that the coordinated functional group in the *ortho*-position of the phenyl ring could increase the catalytic activity. Moreover, X-rays of the structure and DFT analysis revealed that the coordinated functional group in the *ortho*-position could bridge two Al centers resulting in the transformation of a dinuclear Al complex with bridging benzyl alkoxide into a complex with terminal benzyl alkoxide, further promoting the efficacy of the initiator.

Keywords: Aluminum complex, *ε*-Caprolactone, Ring-opening polymerization

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Introduction

Poly(*ε*-caprolactone) (PCL) has established its practicability in a diversity of fields due to its biodegradability, biocompatibility, and permeability[1]. The common method of synthesizing PCL is

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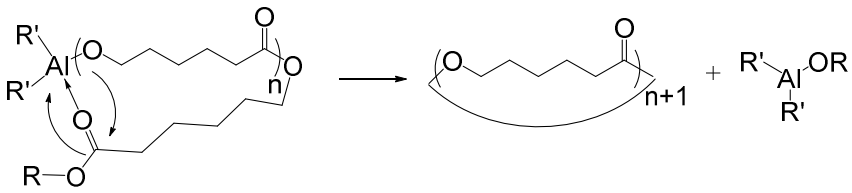
using metal complexes as catalysts for ring-opening polymerization (ROP) of ε-caprolactone (CL) [2]. Aluminum complexes are commonly used as catalysts for ROP due to their ease of synthesis and the low cost of precursor materials.[3-4] However, when metal alkoxides were used as initiators for ROP, macrocycles from backbiting reactions always occur as side reactions commonly referred to as "transesterification" shown in **Scheme 1**. The undesired backbiting reactions can be reduced by using a suitable sterically bulky ligand to coordinate with the active center and therefore provide a steric barrier to prevent larger polymer from coordination to minimize the side reactions but smaller monomers still could interact coordinatively with metal center and further be activated. It was also mentioned in the literature[4i,4o] that diphenol ligands can be useful in protecting the metal center against transesterification, thereby maintaining well controlled polymer weight and narrow polydispersity. Example like $[(EDBP)Al(\mu\text{-}OBn)]_2$[4l] was used by Lin et al. as successful catalyst to carry out "living" or "immortal" ROP of lactones (EDBP = 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol)). Further research revealed that even higher catalytic activity was found when the ligand was changed form EDBP to 2,2'-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP).[4o] It was reported that the steric effect of ligands dictated the catalytic efficiency of the aluminum complexes. This appears to be a reasonable explanation noting that the hydrogen on the tertiary carbon (C* in **Figure 1**) was close to the Al atom as revealed in the crystal structure of the MEBBP aluminum complex (**Figure 1**). [4l,4o,5] This means the methoxy group of MEBBP is unable to coordinate with Al atom and therefore had no coordinating effect on catalytic activity. However, 2-methoxyphenyl group is far from Al center and cannot hinder the monomers. To prove that steric effect is the actual reason for the superior performance of MEBBP in the catalysis of diphenolate Al complexes compared with EDBP, a series of diphenolate Al complexes were synthesized and subjected to kinetic analysis in order to examine the catalytic role of MEBBP moiety in polymerization of ε-caprolactone.



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Scheme 1. Transesterification

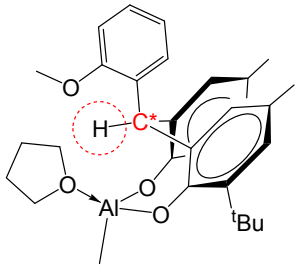

Figure 1. the structure of MEBBP Al complex

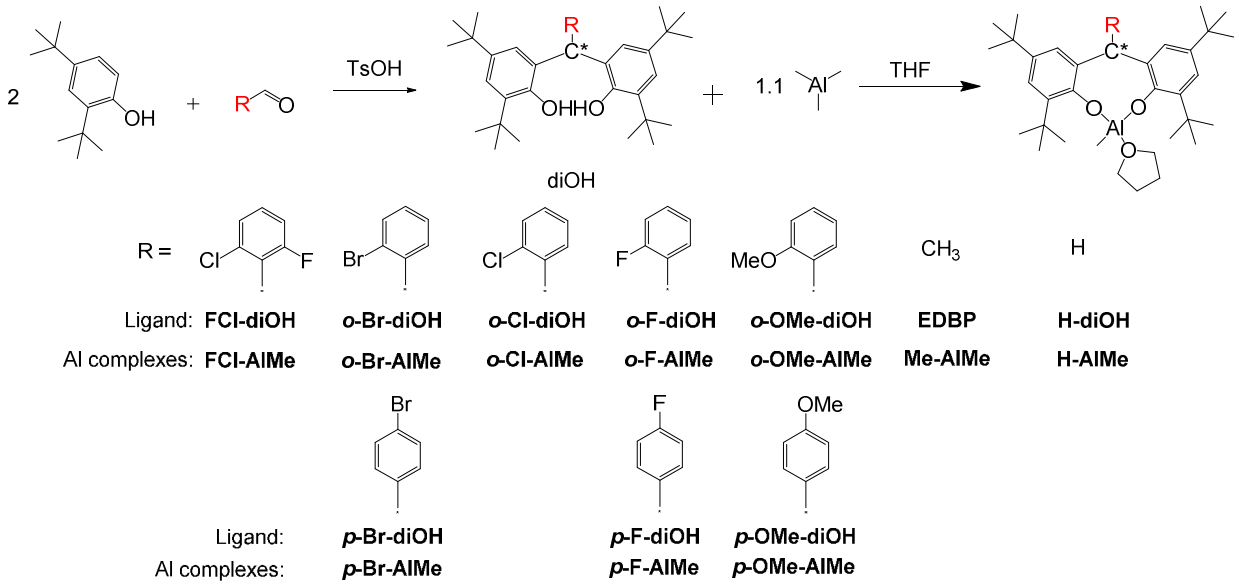

Figure 2. Synthesis of various Al complexes bearing diphenolate ligands

Results and Discussion

Synthesis and Characterization of Al Complexes.

MEBBP-like diphenolate ligands, RC*H(4,6-*t*-butylphenol)$_2$ (shown in **Figure 2**), were synthesized following the literature report[4o]. The varying R groups on the diphenolate ligands were designed to probe their different electronic or steric influence on catalytic behavior. All ligands reacted with a stoichiometric quantity of trimethylaluminum in THF to produce a moderate yield of Al compounds (**Figure 2**). The formula and structure were confirmed by ^{1}H and ^{13}C NMR spectra, elemental analysis, and X-ray crystal analysis. The X-ray structure of **FCl-AlMe** (**Figure 3**) illustrates the distorted tetrahedral geometry of the Al complex with THF and methyl group. The angles of O(1)-Al-O(2) and O(3)-Al-C(36) are 115.35(9), and 103.87(12)°, respectively. The distances between the Al atom and O(1), O(2), O(3), and C(36) are 1.7174(19), 1.7188(19), 1.886(2), and

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1.939(3) Å, respectively. Crystal-related data indicated the same situation that the hydrogen in C(7) was close to Al atom. The distance between Al and H in C(7) atom is 2.466 Å.

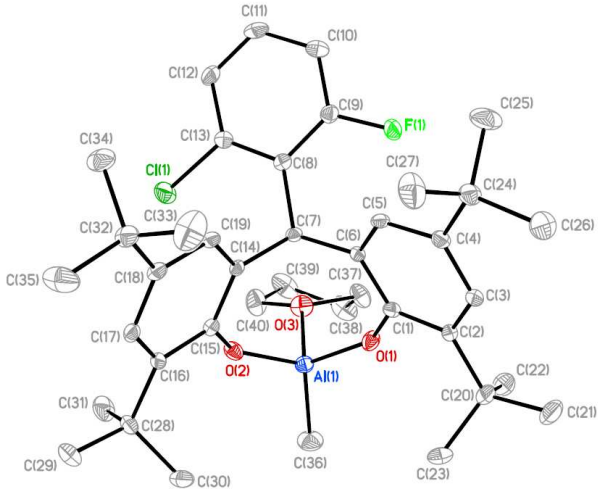

Figure 3. Molecular structures of **FCl-AlMe** as 30% probability ellipsoids. CCDC number: 1032158 (hydrogen atoms were omitted for clarity)

Polymerization of *ε*-caprolactone.

Polymerization of *ε*-caprolactone using Al complexes was investigated using one equivalent BnOH as an initiator (**Table 1**). All aluminum complexes exhibited catalytic activity in polymerization of *ε*-caprolactone and the substituent R in the bridging carbon (**C*** in **Figure 2**) highly influenced the catalytic activity. As shown in entries 1, 2, 4, 5, and 7 of **Table 1**, the coordinating groups in the *ortho*-position of the phenyl ring in the bridging carbon **C*** presented more pronounced catalytic activity than the coordinating groups in the *para*-position (entries 3, 6, and 8). The polymerization result using [Al(MEBBP)(μ-OBn)]$_2$[4o] a catalyst was listed in entry 11 of **Table 1** and it revealed the greater polymerization control with accurate molecular weight of PCL and narrow PDI but lower polymerization rate. The possible reason may be that [Al(MEBBP)(μ-OBn)]$_2$ is pure Al alkoxide but the mixture of Al alkyl complex and BnOH produces a few side product influenced the polymerization result. In addition, higher concentration of [CL] and Al complex also increase the

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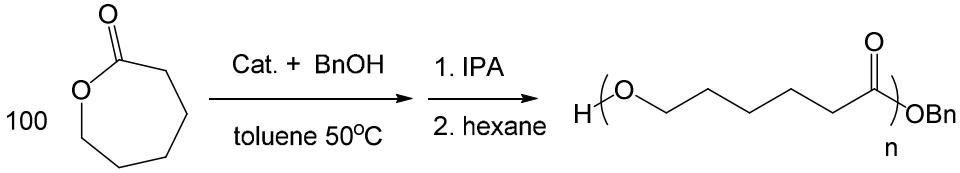
polymerization rate. A kinetic analysis was conducted to accurately compare the details of catalytic activities exerted by these Al complexes, as shown in **Table 2** and **Figure 4**.

Table 1. Results on polymerization of ε-caprolactone catalyzed by different Al complexes at 50 °C



Entry	Cat.	Time (min)	Conv.[a] (%)	Mn_{Cal}[b]	Mn_{NMR}[a]	Mn_{GPC}[c]	PDI[c]
1	FCl-AlMe	30	96	11100	15200	15600	1.43
2	*o*-BrAlMe	60	97	11200	15300	9500	1.27
3	*p*-BrAlMe	170	93	10700	17800	9300	1.30
4	*o*-Cl-AlMe	80	95	11000	19500	5900	1.33
5	*o*-F-AlMe	80	90	10400	18900	6300	1.24
6	*p*-F-AlMe	130	92	10600	10600	8000	1.63
7	*o*-OMe-AlMe	70	96	11000	14100	10500	1.28
8	*p*-OMe-AlMe	130	77	8900	15300	9200	1.30
9	Me-AlMe	90	90	10400	10800	7400	1.27
10	H-AlMe	90	88	10100	10700	10300	1.61
11[d]	[Al(MEBBP)(μ-OBn)]$_2$	180	98	11300	10800	11100	1.09

Reaction condition: toluene (5 mL), $[M]_0/[Cat.]_0/[BnOH]_0$ = 100:1:1, [CL] = 2.0 M, at 50 °C. [a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of monomer x $[monomer]_0/[Cat]_0$ x conversion yield + *M*w(BnOH). [c] Obtained from GPC analysis and calibration based on the polystyrene standard. Values in Mn_{GPC} column are the values obtained from GPC times 0.56. [d] Reaction condition: toluene (30 mL), $[M]_0/[Cat.]_0/[BnOH]_0$ = 100:1:0, [CL] = 0.67 M, at 50 °C.[4o]

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Table 2. Kinetic study of polymerization of CL using each of the Al complexes as the catalysts with 1 equivalent of BnOH in toluene

Entry	Catalyst	k_{obs} (error)
1	FCl-AlMe	0.1298 (49)
2	*o*-Br-AlMe	0.0659 (3)
3	*o*-Cl-AlMe	0.0319 (15)
4	*o*-OMe-AlMe	0.0304 (12)
5	*o*-F-AlMe	0.0279 (23)
6	Me-AlMe	0.0270 (5)
7	H-AlMe	0.0245 (4)
8	*p*-F-AlMe	0.0197 (5)
9	*p*-OMe-AlMe	0.0114 (2)
10	*p*-Br-AlMe	0.0109 (2)

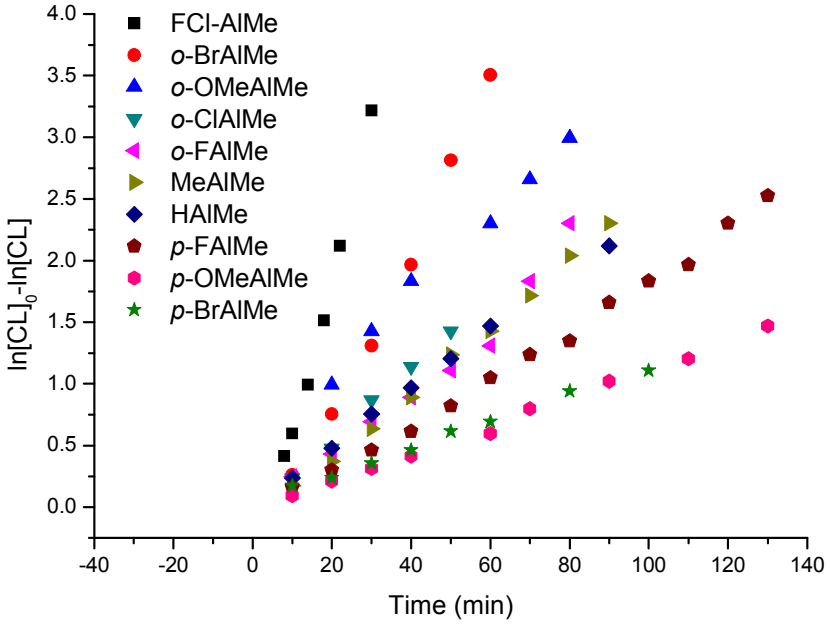

Figure 4. First-order kinetic plots of CL polymerizations with various Al complexes plotted against time (■ FCl-AlMe, ● *o*-Br-AlMe, ▲ *o*-OMe-AlMe, ▼ *o*-Cl-AlMe, ◀ *o*-F-AlMe, ▶ Me-AlMe, ◆ H-AlMe, ⬟ *p*-F-AlMe, ⬢ *p*-OMe-AlMe, ★ *p*-Br-AlMe,)

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Results of the kinetic study revealed a first-order dependency on [CL] and a descending order of catalytic activity for different Al complexes as follows: FCl-AlMe > *o*-Br-AlMe > *o*-Cl-AlMe ≧ *o*-OMe-AlMe > *o*-F-AlMe ≧ Me-AlMe ≧ H-AlMe > *p*-F-AlMe > *p*-OMe-AlMe ≧ *p*-Br-AlMe. These results indicated that the coordinating group in the *ortho*-position of the phenyl ring in bridging carbon **C*** indeed increased the catalytic activity. The tendency was discovered that increasing the size of the coordinating group in the *ortho*-position of the phenyl ring in bridging carbon **C*** also increased the catalytic activity (*o*-Br-AlMe > *o*-Cl-AlMe ≧ *o*-OMe-AlMe > *o*-F-AlMe). In addition, it can be deduced that the steric effect was not a major factor because H-AlMe was not the weakest catalyst. The above results strongly implied there was another effect such as coordinating effect influenced the catalytic activity of Al complexes except steric effect. However, the crystal structures of these Al complexes presented no indication of coordination between Al and the coordinating group in the *ortho*-position of phenyl ring in bridging carbon **C***. To confirm the possibility of coordinating effect between the coordinating group and Al atom, DFT calculation of mononuclear form of *o*-OMeAlOMe and dinuclear form of (*o*-OMeAl-μ-OMe)$_2$ (**Figure 5**) was studied and the benzyl oxide and *tert*-butyl groups were replaced by methoxide and hydrogen atoms, respectively, in order to reduce computational costs. The results revealed that (*o*-OMeAl-μ-OMe)$_2$, was more stable than the *o*-OMeAlOMe about 41.3 kcal/mol in energy, indicating that the coordinating group in the *ortho*-position of phenyl ring should not be possible to coordinate Al atom.

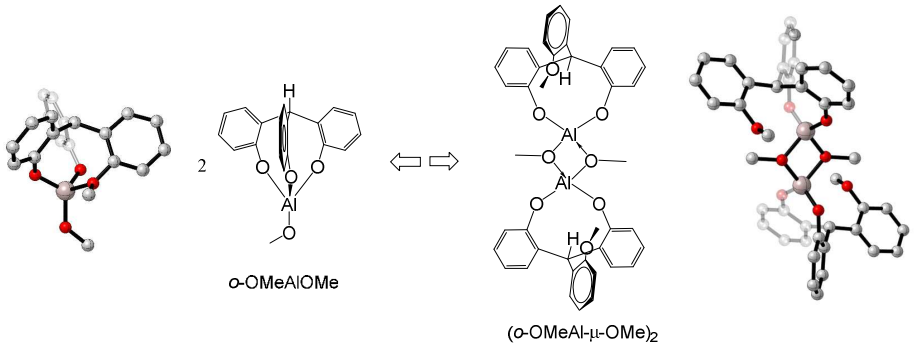

Figure 5. Models of mononuclear form of *o*-OMeAlOMe and dinuclear form of (*o*-OMeAl-μ-OMe)$_2$ for DFT calculation

To elucidate the relationship between polymerization activity and the coordinating group in the

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ortho-position, a triphenol ligand (**TriO-H**) and its Al complex were synthesized (**Figure 6**) to determine how the coordinated functional group influenced the catalytic center. The crystal data of **$TriO_2Al_2$** showed the unidentified solvent which should be THF observed from ^{1}NMR spectrum (**Figure S1**) of **$TriO_2Al_2$** and ignored by using SQUEEZE. Our results revealed the formation of an unexpected dinuclear Al complex (**$TriO_2Al_2$**) comprising two triphenolate ligands, two Al atoms, and two terminal THFs (**Figure 7**). The two Al atoms were bridged by two phenolate groups from two different triphenolate ligands. This indicates that the coordinating group in the *ortho*-position of the phenyl ring in bridging carbon **C*** could very likely coordinate with Al atom to form dinuclear complex. Compared with Al complex with MEBBP in **Figure 1**, the coordinating group in the *ortho*-position could not coordinate Al atom in monomeric form because of far distance between the coordinating group and Al atom. A survey of the structures of diphenolate Al alkoxide[4l,4m~4o,6] revealed that they prefer dinuclear form (**A** in **Figure 8**) with bridging alkoxides and terminal donor solvent molecule (benzyl aldehyde or THF). It is a clear indication that the dinuclear form would not decompose during CL coordination or alkoxide initiation **(B** in **Figure 8)**. However, bridging alkoxides were weaker initiators than terminal alkoxides because bridging alkoxides are unable to rotate freely to initiate CL attack and the volume of the lone pair electrons is less than that of the terminal alkoxide (**Figure 8**, left reaction). The coordinating functional group (X in **Figure 8**) could allow bridging alkoxides (A in **Figure 8**) to transform into terminal alkoxides (C in **Figure 8**, right reaction) and thus increase the initiating rate.

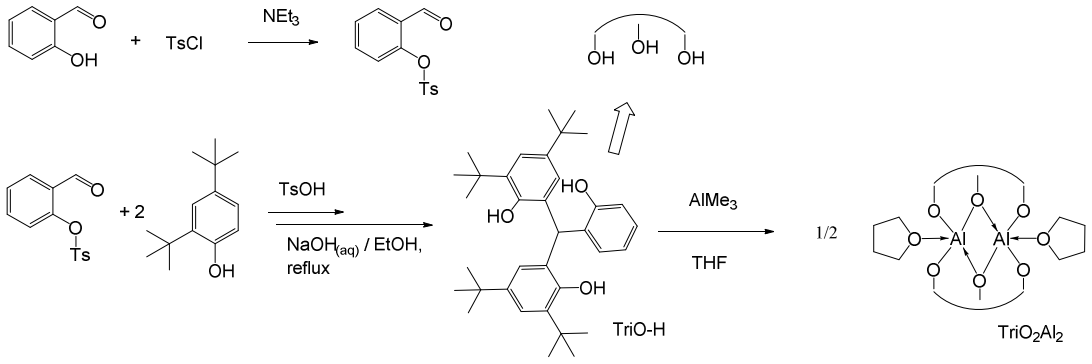

Figure 6. Synthesis of TriO-H and **$TriO_2Al_2$**

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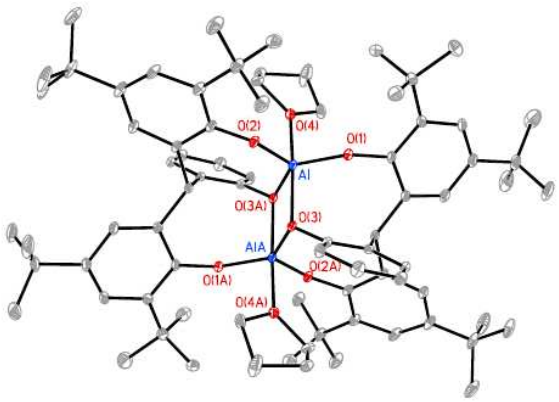

Figure 7. Molecular structure of **$TriO_2Al_2$** as 30% probability ellipsoids. CCDC number: 1032157 (all of the hydrogen atoms were omitted for clarity)

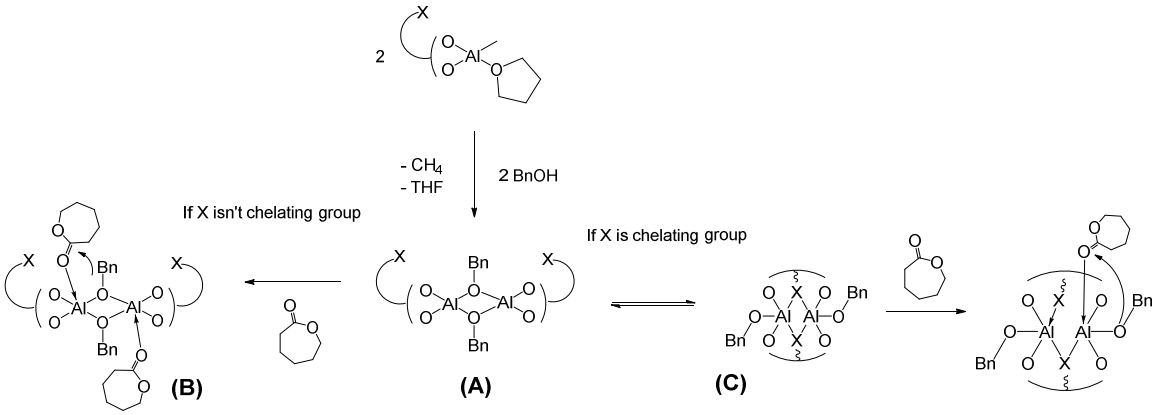

Figure 8. Possible mechanisms associated with CL polymerization between Al complexes with coordinating group X

Determining the role of coordination in polymerization using DFT calculation

To determine the likelihood of exchange between two dinuclear forms (A and C in **Figure 8**), DFT calculation of two dinuclear forms of (*o*-OMeAlOMe)$_2$ (**Figure 9**) was studied and the benzyl oxide and *tert*-butyl groups were replaced by methoxide and hydrogen atoms, respectively, in order to reduce computational costs. The results revealed that the (*o*-OMeAl-t-OMe)$_2$, in where each OMe group of the phenyl ring bridges both Al centers, is not a stable structure. Geometry optimization starting from the initial structure of (*o*-OMeAl-t-OMe)$_2$ resulted in a spontaneous collapse to a structure of (*o*-OMeAl-t-OMe)$_2$* in which each OMe group coordinates with only one

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Al atom. The conformation in which the methoxide serves as a bridging group, namely (*o*-OMeAl-μ-OMe)$_2$, was found to be slightly more stable than the (*o*-OMeAl-t-OMe)$_2$* about 2.4 kcal/mol in energy, indicating that a transformation between these two conformations should be possible. **Figure 10** illustrates a possible mechanism based on experiment data and DFT calculations. Mononuclear methyl Al complexes reacted with BnOH to form dinuclear Al benzyl alkoxide (**A**). If a third coordinating group exited in the diphenolate ligand, then **A** would transfer to **C** with the terminal benzyl alkoxide, which would initiate CL (right side of **Figure 10**). However, the dinuclear Al benzyl alkoxide (**A**) without a third coordinating group maintained the form of a bridging benzyl alkoxide throughout the process of CL coordination and benzyl alkoxide initiation. Due to its lack of free rotation and lone electron pairs, the initiating ability of briding benzyl alkoxide was weaker than that of terminal benzyl alkoxide. That explains why Al complexes with a third coordinating group in the dipheolate ligand produce greater activity than do those without a third coordinating group. This mechanism also could explain the catalytic trend of CL polymerization. FCl-AlMe presented the best catalytic activity due to the existence of two coordinated atoms in the *ortho*-position of the phenyl ring, which enhanced the likelihood of the coordination with Al. The catalytic activity increased according to an increase of the size of the halide in the *ortho*-position of the phenyl ring in bridging carbon **C*** (*o*-Br-AlMe > *o*-Cl-AlMe > *o*-F-AlMe) due to the fact that Br has the lone pairs in larger shells where they are farther from the nucleus, less tightly held, and consequently more coordinately reactive than Cl and F. In addition, it can be deduced that the steric effect was not a major factor because H-AlMe was not the weakest catalyst.

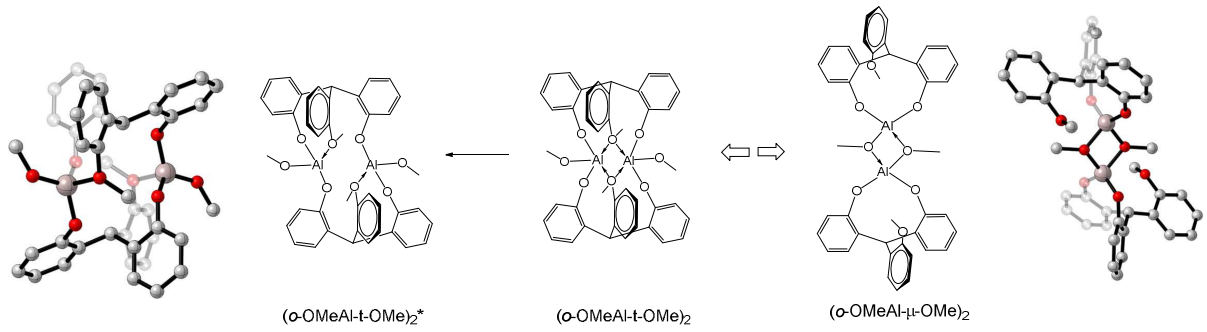

Figure 9. Models of two dinuclear forms for DFT calculation

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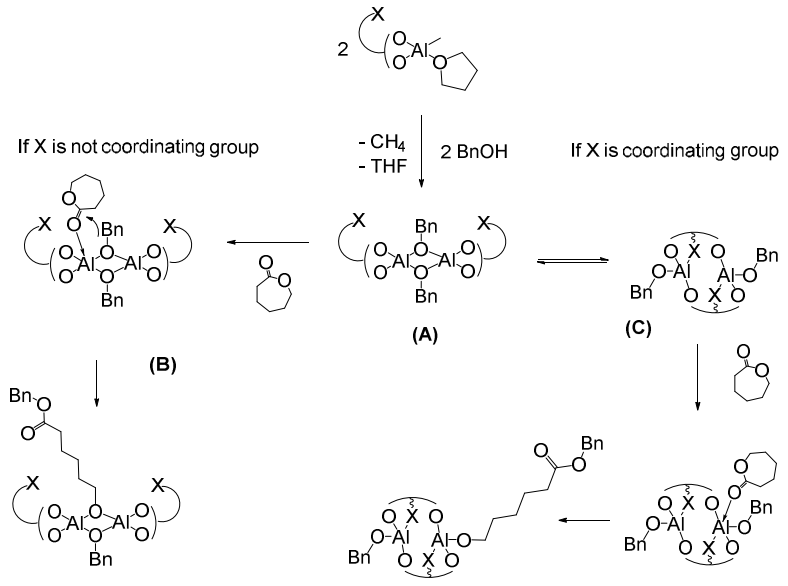

Figure 10. Possible mechanism of ROP using Al complexes bearing diphenolate ligand as catalysts

Conclusions

The present work describes a variety of synthetic procedures used to access Al species bearing diphenolate ligands and their application in CL polymerization. Polymerization results reveal that the coordinating functional group in the *ortho*-position of the phenyl ring in the bridging methanetriyl carbon increased the catalytic activity and proved that coordination between the third coordinating group and Al enhanced the catalytic activity of Al complexes. The crystal structure of **TriO$_2$Al$_2$** provided a possible coordination model between Al and the third coordinated group. DFT calculations resulted in a more stable dinuclear Al intermediate with terminal benzyl alkoxide in a distorted tetrahedral form. Based on experiment data and DFT calculations, a possible mechanism of CL polymerization was proposed and the coordinating effect of the third coordinated group allowed the transfer of dinuclear Al complexes with bridging benzyl alkoxide to Al complexes with terminal benzyl alkoxide, resulting in greater ability to initiate CL polymerization.

Experimental Section

Standard Schlenk techniques and a N_2-filled glovebox were used throughout the isolation and

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handling of all the compounds. Solvents, ε-caprolactone, and deuterated solvents were purified prior to use. EDBP was purchased from ALDRICH. Deuterated chloroform, paraformaldehyde, 2,4-di-*tert*-butylphenol, and ε-caprolactone were purchased from Acros. Benzyl alcohol, trimethylaluminum, 2-fluorobenzaldehyde, 2-chlorobenzaldehyde, 2-bromobenzaldehyde, 2-methoxybenzaldehyde 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, 4-bromobenzaldehyde, 2-chloro-6-fluorobenzaldehyde, 2,5-dimethoxybenzaldehyde, and *p*-toulenesulfonic acid were purchased from Alfa Aesar. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini2000-200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. GPC measurements were performed on a Jasco PU-2080 PLUS HPLC pump system equipped with a differential Jasco RI-2031 PLUS refractive index detector using THF (HPLC grade) as an eluent (flow rate 1.0 mL/min, at 40 °C). The chromatographic column was JORDI Gel DVB 103 Å, and the calibration curve was made by primary polystyrene standards to calculate Mn(GPC). Me-AlMe[4l], H-AlMe[7b], *o*-OMe-diOH[8], *p*-OMe-diOH[13], and H-diOH[7] were prepared following literature procedures.

Synthesis of FCl-diOH

A mixture of 2,4-di-*tert*-butylphenol (4.12 g, 20 mmol) and 2-chloro-6-fluorobenzaldehyde (1.58 g, 10 mmol) with catalytic amount of benzenesulfonic acid was refluxed for one day in hexane (30 mL). The solution was at -20 °C for 2 days and yellow crystalline solids were obtained. Yield : 3.92 g (63 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.33~7.19 (7H, m, *H*-Ar), 6.14 (1H, s, C*H*), 4.71 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.17 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.92 (*C*OH-Ph(^{t}Bu)$_2$), 159.91, 150.67, 142.37, 136.19, 134.97, 129.02, 127.11, 125.92, 124.22, 123.18, 115.39, 114.92 (*C*-Ar), 40.51 (*C*H), 34.83 (*o*-*C*(CH$_3$)$_3$), 34.25 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(*C*H$_3$)$_3$), 29.92 (*p*-C(*C*H$_3$)$_3$). Elemental Anal. Found (Calcd.) for **FCl-diOH**: $C_{35}H_{46}ClFO_2$: C, 75.89 (75.99) ; H, 8.02 (8.38) %.

Synthesis of *o*-Br-diOH

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Using a method is similar to that for FCl-diOH except 2-bromobenzaldehyde was used in place of 2-chloro-6-fluorobenzaldehyde. Yield : 2.21g (76 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.64 (1H, d, *J* = 7.8 Hz, 2-*H*-Ar(*o*-Br)), 7.20 (4H, s, *H*-Ph(^{t}Bu)$_2$), 6.96 (1H, d, *J* = 7.8 Hz, 5-*H*-Ar(*o*-Br)) , 6.57 (2H, m, 3,4-*H*-Ar(*o*-Br)), 6.94 (1H, s, C*H*), 4.72 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.16 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.63 (*C*OH), 142.66, 140.49, 136.56, 133.21, 130.85, 128.79, 127.71, 126.48, 126.35, 125.65, 124.16, 123.05 (*C*-Ar), 46.85 (*C*H), 34.91 (*o*-*C*(CH$_3$)$_3$), 34.22 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(*C*H$_3$)$_3$), 29.84 (*p*-C(*C*H$_3$)$_3$). Elemental Anal. Found (Calcd.) for ***o*-Br-diOH**: $C_{35}H_{47}BrO_2$: C, 72.63 (72.52) ; H, 8.05 (8.17) %.

Synthesis of *o*-Cl-diOH

Using a method is similar to that for FCl-diOH except 2-chlorobenzaldehyde was used in place of 2-chloro-6-fluorobenzaldehyde.. Yield : 1.96 g (73 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.47, 7.34, 6.98, 6.60 (8H, m, *H*-Ph), 6.00 (1H, s, C*H*), 4.67 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.16 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.56 (*C*OH-Ph(^{t}Bu)$_2$), 142.70, 138.77, 136.89, 134.75, 130.89, 124.37, 129.82, 128.55, 127.11, 126.30, 124.09, 123.11 (*C*-Ar), 44.16 (*C*H), 34.85 (*o*-*C*(CH$_3$)$_3$), 34.24 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(*C*H$_3$)$_3$), 29.85 (*p*-C(*C*H$_3$)$_3$). Elemental Anal. Found (Calcd.) for ***o*-Cl-diOH**: $C_{35}H_{47}ClO_2$: C, 78.42 (78.55) ; H, 8.95 (8.85) %.

Synthesis of *o*-F-diOH

Using a method is similar to that for FCl-diOH except 2-fluorobenzaldehyde was used in place of 2-chloro-6-fluorobenzaldehyde. Yield : 1.89 g (73 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.32~6.65 (8H, m, *H*-Ar), 5.88 (1H, s, C*H*), 4.42 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.16 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.53 (*C*OH), 142.81, 136.63, 130.60, 129.14, 128.97, 126.18, 124,39, 123.93, 123.27, 120.37, 115.76, 115.32 (*C*-Ar), 40.37 (*C*H), 34.86 (*o*-*C*(CH$_3$)$_3$), 34.29 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(*C*H$_3$)$_3$), 29.84 (*p*-C(*C*H$_3$)$_3$). Elemental Anal. Found (Calcd.) for ***o*-F-diOH**: $C_{35}H_{47}FO_2$: C, 81.25 (81.04) ; H, 8.99 (9.13) %.

Synthesis of *p*-Br-diOH

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Using a method is similar to that for FCl-diOH except 4-bromobenzaldehyde was used in place of 2-chloro-6-fluorobenzaldehyde.. Yield : 1.84 g (64 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48 (2H, d, J = 6.6 Hz, *o*-*H*-Ar(*p*-Br)), 7.26 (2H, s, *H*-Ph(^{t}Bu)$_2$), 7.06 (2H, d, J = 6.6 Hz, *m*-*H*-Ar(*p*-Br)), 6.65 (2H, s, *H*-Ph(^{t}Bu)$_2$), 5.62 (1H, s, C*H*), 4.75 (2H, br, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.16 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.34 (*C*OH), 142.93, 140.35, 136.70, 131.86, 131.17, 127.58, 124.31, 123.95, 123.08, 121.10, 115.86 (*C*-Ar), 46.36 (*C*H), 34.32 (*o*-*C*(CH$_3$)$_3$), 34.22 (*p*-*C*(CH$_3$)$_3$), 31.48 (*o*-C(*C*H$_3$)$_3$), 29.92 (*p*-C(*C*H$_3$)$_3$). Elemental Anal. Found (Calcd.) for ***p*-Br-diOH**: $C_{35}H_{47}BrO_2$: C, 72.53 (72.52) ; H, 8.12 (8.17) %.

Synthesis of TriO-H

A mixture 2-(bis(3,5-di-tert-butyl-2-hydroxyphenyl)methyl)phenyl 4-methylbenzenesulfonate[8] (6.7 g, 10 mmol) and NaOH (0.4 g, 10 mmol) in ethanol (50 mL) was refluxed for one day and the solvent was removed from the mixture under vacuum. The residue was extracted with hexane (3 × 100 mL). The organic layer was dried over MgSO4, filtered, and concentrated to 20 mL. The solution was at -20 ℃ for 2 days and white powder was obtained. Yield : 2.73g (53 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.25-6.99, 6.94-6.82 (4H, m, ArOH) 7.28, 6.74 (4H, s, Bu$^t_2$ArOH), 5.79 (1H, s, C*H*), 5.00 (1H, s, O*H*) 4.83 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.67 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.92 (*C*OH-Ph(^{t}Bu)$_2$), 159.91, 150.67, 142.37, 136.19, 134.97, 129.02, 127.11, 125.92, 124.22, 123.18, 115.39, 114.92 (*C*-Ar), 40.51 (*C*H), 34.83 (*o*-*C*(CH$_3$)$_3$), 34.25 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(*C*H$_3$)$_3$), 29.92 (*p*-C(*C*H$_3$)$_3$). Elemental Anal. Found (Calcd.) for **TriO-H**: $C_{35}H_{48}O_3$: C, 81.51 (81.35) ; H, 9.19 (9.36) %.

Synthesis of FCl-AlMe

A mixture of FCl-diOH (3.11 g, 5 mmol) and $AlMe_3$ (3 mL, 2.0 M, 5.5 mmol) in THF (20 mL), was stirred for 3 hr at 0 ^{o}C. Volatile materials were removed under vacuum to give light yellow powder and then hexane (30 mL) was transferred to be the suspension. The white powder was obtained after filtering. Yield: 2.1 g (63 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.52~6.92 (7H, m, *H*-Ar), 6.79 (1H, s,

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C*H*), 4.08 (2H, br, OC*H*$_2$CH$_2$), 1.99 (2H, br, OCH$_2$C*H*$_2$), 1.41 (18H, s, *o*-C(C*H*$_3$)$_3$), 1.23 (18H, s, *p*-C(C*H*$_3$)$_3$), -0.57 (3H, s, AlCH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz) δ 152.90 (*C*OCH$_3$-Ar(*p*-OMe)), 139.00, 136.41, 130.85, 127.53, 127.32, 126.01, 124.94, 124.71, 121.22, 116.20, 115.65 (*C*-Ar), 71.11 (O*C*H$_2$CH$_2$), 25.26 (OCH$_2$*C*H$_2$), 39.44 (*C*H), 35.23 (*o*-*C*(CH$_3$)$_3$), 34.16 (*p*-*C*(CH$_3$)$_3$), 31.63 (*o*-C(*C*H$_3$)$_3$), 30.26 (*p*-C(*C*H$_3$)$_3$), -13.36 (Al*C*H$_3$). Elemental Anal. Found (Calcd.) for **FCl-AlMe**: C$_{40}$H$_{55}$AlClFO$_3$: C, 71.89 (71.67) ; H, 7.96 (8.61) %. Mp：184 ^{o}C.

Synthesis of *o*-Br-AlMe

Using a method is similar to that for FCl-AlMe except ***o*-Br-diOH** was used in place of **FCl-diOH**. Yield: 2.7 g (77 %). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.70~6.98 (8H, m, *H*-Ph), 6.02 (1H, s, C*H*), 4.21 (4H, br, OC*H*$_2$CH$_2$), 2.05 (4H, br, OCH$_2$C*H*$_2$), 1.39 (18H, s, *o*-C(C*H*$_3$)$_3$), 1.21 (18H, s, *p*-C(C*H*$_3$)$_3$), -0.60 (3H, s, AlC*H*$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz) δ 153.10 (*C*OAl), 143.99, 139.12, 136.77, 133.71, 131.35, 130.78, 127.20, 125.97, 124.15, 120.66, 120.35 (*C*-Ar), 71.49 (O*C*H$_2$CH$_2$), 25.29 (OCH$_2$*C*H$_2$), 42.83 (*C*H), 35.12 (*o*-*C*(CH$_3$)$_3$), 34.09 (*p*-*C*(CH$_3$)$_3$), 31.63 (*o*-C(*C*H$_3$)$_3$), 30.14 (*p*-C(*C*H$_3$)$_3$), -13.56 (Al*C*H$_3$). Elemental Anal. Found (Calcd.) for ***o*-Br-AlMe**: C$_{40}$H$_{56}$AlBrO$_3$: C, 69.40 (69.45) ; H, 8.39 (8.16) %. Mp：208 ^{o}C.

Synthesis of *o*-Cl-AlMe

Using a method is similar to that for FCl-AlMe except ***o*-Cl-diOH** was used in place of **FCl-diOH**. Yield: 2.0 g (62 %). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.67~7.00 (8H, m, *H*-Ph), 6.16 (1H, s, C*H*), 4.32 (4H, br, OC*H*$_2$CH$_2$), 2.08 (4H, br, OCH$_2$C*H*$_2$), 1.39 (18H, s, *o*-C(C*H*$_3$)$_3$), 1.23 (18H, s, *p*-C(C*H*$_3$)$_3$), -0.59 (3H, s, AlC*H*$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz) δ 152.95 (*C*OAl), 142.42, 139.05, 136.79, 135.09, 130.23, 134.28, 131.31, 130.40, 130.09, 126.98, 125.82, 120.70 (*C*-Ar), 71.36 (O*C*H$_2$CH$_2$), 25.26 (OCH$_2$*C*H$_2$), 40.57 (*C*H), 35.12 (*o*-*C*(CH$_3$)$_3$), 34.10 (*p*-*C*(CH$_3$)$_3$), 31.64 (*o*-C(*C*H$_3$)$_3$), 29.87 (*p*-C(*C*H$_3$)$_3$), -13.64 (Al*C*H$_3$). Elemental Anal. Found (Calcd.) for ***o*-Cl-AlMe**: C$_{40}$H$_{56}$AlClO$_3$: C, 73.92 (74.22) ; H, 8.99 (8.72) %. Mp：216 ^{o}C.

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Synthesis of *o*-F-AlMe

Using a method is similar to that for FCl-AlMe except ***o*-F-diOH** was used in place of **FCl-diOH**. Yield: 1.7 g (53 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.64 (1H, t, *J* = 8.4 Hz, 2-*H*-Ar(*o*-F)), 7.19~7.07 (7H, m, *H*-Ar), 6.17 (1H, s, C*H*), 4.33 (4H, br, OCH_2CH$_2$), 2.07 (4H, br, OCH$_2$CH_2), 1.39 (18H, s, *o*-C(CH_3)$_3$), 1.22 (18H, s, *p*-C(CH_3)$_3$), -0.60 (3H, s, AlCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.57 (*C*OCH$_3$-Ar(*o*-F)), 139.08, 136.97, 132.31, 131.29, 130.34, 127.42, 123.74, 121.01, 120.35, 115.28, 114.84 (*C*-Ar), 71.30 (O*C*H$_2$CH$_2$), 20.93 (OCH$_2$*C*H$_2$), 36.17 (*C*H), 35.15 (*o*-*C*(CH$_3$)$_3$), 34.12 (*p*-*C*(CH$_3$)$_3$), 31.63 (*o*-C(*C*H$_3$)$_3$), 30.07 (*p*-C(*C*H$_3$)$_3$), -14.04 (Al*C*H$_3$). Elemental Anal. Found (Calcd.) for ***o*-F-AlMe**: $C_{40}H_{56}AlFO_3$: C, 75.89 (76.16) ; H, 8.65 (8.95) %. Mp：226 ^{o}C.

Synthesis of *o*-OMe-AlMe

Using a method is similar to that for FCl-AlMe except ***o*-OMe-diOH** was used in place of **FCl-diOH**. Yield: 2.1 g (64 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.78~7.59 (8H, m, *H*-Ar), 6.01 (1H, s, C*H*), 4.31 (4H, br, OCH_2CH$_2$), 3.15 (3H, s, OCH_3), 2.00 (4H, br, OCH$_2$CH_2, THF), 1.39 (18H, s, *o*-C(CH_3)$_3$), 1.20 (18H, s, *p*-C(CH_3)$_3$), -0.60 (3H, s, AlCH$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.11 (*C*OCH$_3$), 158.44 (*C*OAl), 152.81, 138.74, 136.60, 135.25, 132.58, 129.31, 126.79,123.77, 120.31, 114.12 (*C*-Ar), 70.92 (O*C*H$_2$CH$_2$,THF), 25.27 (OCH$_2$*C*H$_2$,THF), 56.39 (O*C*H$_3$), 37.27 (*C*H), 35.15 (*o*-*C*(CH$_3$)$_3$), 34.10 (*p*-*C*(CH$_3$)$_3$), 31.67 (*o*-C(*C*H$_3$)$_3$), 30.10 (*p*-C(*C*H$_3$)$_3$), -13.87(Al*C*H$_3$). Elemental Anal. Found (Calcd.) for ***o*-OMe-AlMe**: $C_{41}H_{59}AlO_4$: C, 76.99 (76.60) ; H, 8.98 (9.25) %. Mp：202 ^{o}C.

Synthesis of *p*-Br-AlMe

Using a method is similar to that for FCl-AlMe except ***p*-Br-diOH** was used in place of **FCl-diOH**. Yield: 2.8 g (82 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ7.32 (2H, m, *o*-*H*-Ar(*p*-Br)), 7.08 (2H, m, *m*-*H*-Ar(*p*-Br)), 5.85 (1H, s, C*H*), 4.12 (4H, br, OCH_2CH$_2$), 1.88 (4H, br, OCH$_2$CH_2), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.21 (18H, s, *p*-C(CH_3)$_3$), -0.60 (3H, s, AlCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.39 (*C*OAl), 145.24, 139.82, 137.09, 132.02, 131.09, 130.49, 124.13, 121.28, 119.06 (*C*-Ar), 71.34

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(OCH_2CH_2), 25.09 (OCH_2CH_2), 41.11 (*C*H), 35.18 (*o*-*C*(CH_3)$_3$), 34.21 (*p*-*C*(CH_3)$_3$), 31.66 (*o*-C(*C*H_3)$_3$), 30.04 (*p*-C(*C*H_3)$_3$), -14.05 (Al*C*H_3). Elemental Anal. Found (Calcd.) for ***p*-Br-AlMe**: $C_{40}H_{56}AlBrO_3$: C, 69.48 (69.45) ; H, 8.51 (8.16) %. Mp: 228 ^oC.

Synthesis of *p*-F-AlMe

p-F-diOH was synthesized using a method is similar to that for FCl-diOH; however, it is brown oil and it could not be crystallized in hexane. *p*-F-AlMe was synthesized using a method is similar to that for FCl-AlMe with impure *p*-F-diOH. Yield: 1.9 g (61 %). ^1H NMR ($CDCl_3$, 200 MHz) δ 7.12~6.85 (8H, *H*-Ar), 5.88 (1H, s, C*H*), 4.12 (4H, br, OCH_2CH_2), 1.88 (4H, br, OCH_2CH_2), 1.40 (18H, s, *o*-C(CH_3)$_3$), 1.21 (18H, s, *p*-C(CH_3)$_3$), -0.60 (3H, s, AlCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.37 (*C*OAl), 141.52, 139.75, 137.03, 132.36, 130.79, 130.64, 124.22, 121.17, 120.94, 114.31, 113.90 (*C*-Ar), 66.50 (OCH_2CH_2), 25.14 (OCH_2CH_2), 41.78 (*C*H), 35.18 (*o*-*C*(CH_3)$_3$), 34.19 (*p*-*C*(CH_3)$_3$), 31.66 (*o*-C(*C*H_3)$_3$), 30.04 (*p*-C(*C*H_3)$_3$), -14.09 (Al*C*H_3). Elemental Anal. Found (Calcd.) for ***p*-F-AlMe**: $C_{40}H_{56}AlFO_3$: C, 76.60 (76.16) ; H, 9.45 (8.95) %. Mp：226 ^oC.

Synthesis of *p*-OMe-AlMe

Using a method is similar to that for FCl-AlMe except ***p*-OMe-diOH** was used in place of **FCl-diOH**. Yield: 2.2 g (67 %). ^1H NMR ($CDCl_3$, 200 MHz) δ 7.17 (2H, d, *J* = 8.6 Hz, *H*-Ph(*t* Bu)$_2$), 6.89 (2H, d, *J* = 8.6 Hz, *o*-*H*-Ar(*p*-OMe)), 6.89 (2H, d, *J* = 8.6 Hz, *p*-*H*-Ar(*p*-OMe)), 5.84 (1H, s, C*H*), 4.24 (4H, br, OCH_2CH_2), 1.89 (4H, br, OCH_2CH_2), 3.79 (3H, s, Ar(*p*-O*C*H_3)), 1.40 (18H, s, *o*-C(CH_3)3), 1.22 (18H, s, p-C(CH3)$_3$), -0.61 (3H, s, AlCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 157.06 (*C*OCH_3-Ar(*p*-OMe)), 153.39 (*C*OAl-Ph(*t*Bu)$_2$), 158.44 (*C*OAl), 139.50, 137.83, 136.82, 132.64, 130.23, 124.37, 120.91, 112.74 (*C*-Ar), 71.46 (OCH_2CH_2), 24.98 (OCH_2CH_2), 55.09 (Ar(*p*-O*C*H_3)), 40.54 (*C*H), 35.13 (*o*-*C*(CH_3)$_3$), 31.68 (*p*-*C*(CH_3)$_3$), 31.60 (*o*-C(*C*H_3)$_3$), 30.02 (*p*-C(*C*H_3)$_3$), -14.08 (Al*C*H_3). Elemental Anal. Found (Calcd.) for ***p*-OMe-AlMe**: $C_{41}H_{59}AlO_4$: C, 76.87 (76.60) ; H, 9.60 (9.25) %. Mp：210 ^oC.

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DOI: 10.1039/C5RA10753A

Synthesis of $TriO_2Al_2$

Using a method is similar to that for FCl-AlMe except **TriO-H** was used in place of **FCl-diOH**; however the product was not pure from the NMR spectrum. The crystal was obtained into the NMR tube 0.05 g of **$TriO_2Al_2$**in 1 mL $CDCl_3$ was set with a cover for 1 month at room temperature.

General procedures for the polymerization of ε-caprolactone

A typical polymerization procedure was exemplified by the synthesis of entry 1 (**Table** 1) using complex **FCl-AlMe** as a catalyst. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (5.0 mL) was added to a mixture of complex **FCl-AlMe** (0.1 mmol), BnOH (0.1 mmol), and *ε*-caprolactone (10 mmol) at 50 ^{o}C. At indicated time intervals, 0.05 mL aliquots were removed, trapped with $CDCl_3$ (1mL), and analyzed by ^{1}H NMR. After the solution was stirred for 30 min, the reaction was then quenched by adding a drop of *iso*-propanol, and the polymer precipitated as white solid when pouring into *n*-hexane (30.0 mL). The isolated white solid was dissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) was added to give purified crystalline solid. Yield: 1.00 g (88 %).

General procedures for the X-ray experiment

X-ray experimental procedure of **FCl-AlMe** was that 0.10 g of **FCl-AlMe** in 1 mL CH_2Cl_2 was set into the NMR tube with a cover. The colorless crystal appeared after CH_2Cl_2 in the NMR tube evaporated. X-ray experimental procedure of **$TriO_2Al_2$** was that 1.0 g of impure **$TriO_2Al_2$** in 10 mL THF was set into 20 mL vial and frozen at -10 ^{o}C. The colorless crystal of **$TriO_2Al_2$** was obtained after a week.

Computational Methods

All the DFT calculations were accomplished by the Gaussian 09 package.[9] The B3LYP hybrid functional[10,11] in combination with the 6-31G(d) basis sets was employed in the present DFT calculations. In addition, empirical correction for dispersion was taken into account by using the D3 version of Grimme's dispersion correction[12].

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DOI: 10.1039/C5RA10753A

Electronic supplementary information (ESI) available: Polymer characterization data, and details of the kinetic study.

Acknowledgment This study is supported by Kaohsiung Medical University "Aim for the top 500 universities grant" under Grant No. KMU-DT103007, NSYSU-KMU JOINT RESEARCH PROJECT (NSYSU KMU 103-I004), and the Ministry of Science and Technology (Grant NSC 101-2113-M-037 -009-MY2). We thank Center for Research Resources and Development at Kaohsiung Medical University for the instrumentation and equipment support.

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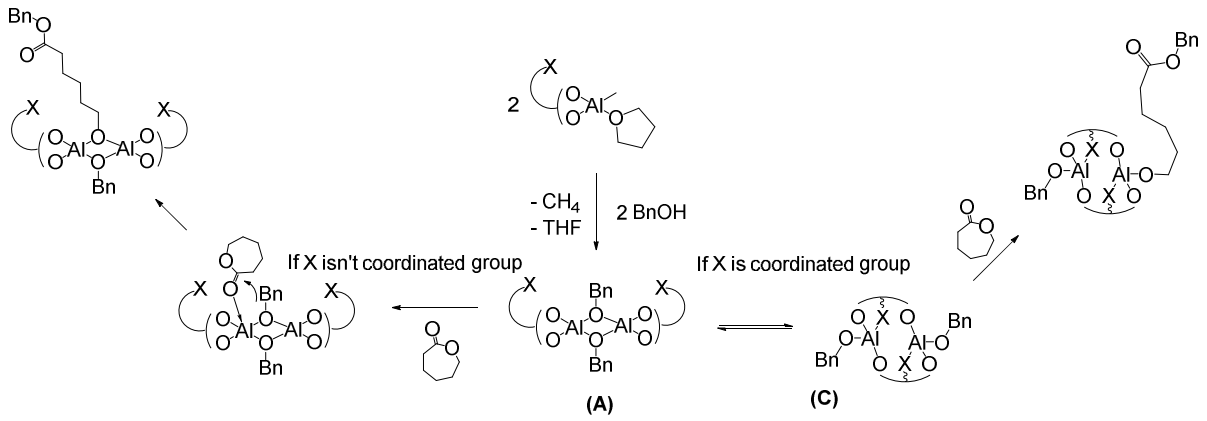
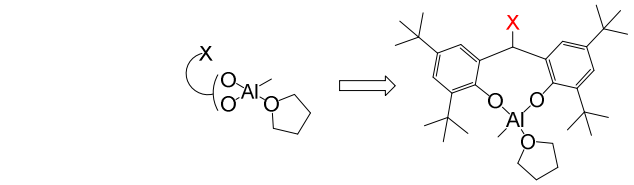
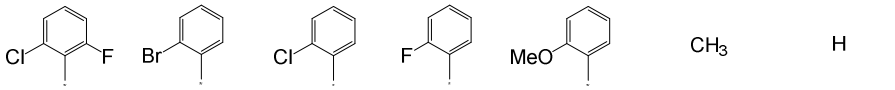
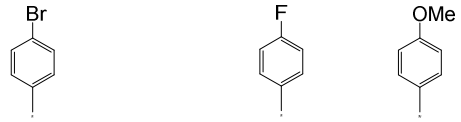






Ligand:	**FCl-diOH**	***o*-Br-diOH**	***o*-Cl-diOH**	***o*-F-diOH**	***o*-OMe-diOH**	**EDBP**	**H-diOH**
Al complexes:	**FCl-AlMe**	***o*-Br-AlMe**	***o*-Cl-AlMe**	***o*-F-AlMe**	***o*-OMe-AlMe**	**Me-AlMe**	**H-AlMe**



Ligand:	***p*-Br-diOH**	***p*-F-diOH**	***p*-OMe-diOH**
Al complexes:	***p*-Br-AlMe**	***p*-F-AlMe**	***p*-OMe-AlMe**