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# 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

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ABSTRACT

Ring-opening polymerizations (ROPs) of various cyclic esters [ε-caprolactone (CL), δ-valerolactone (VL), *rac*-lactide (LC)] using a series of 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 substituents (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 the 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.



## 1. 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], reports concerning ligand effect toward the catalytic activity in the ROP of cyclic esters using a series of 'isolated' Al complexes were rare.

We recently reported a study for ring-opening polymerization (ROP) of ε-caprolactone (CL) using various Al complexes containing a series of 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, $^t$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.) [7,8]. We demonstrated 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: $R^2 = C_6F_5 \gg$ 2,6-$Me_2C_6H_3$ > 2,6-$^i Pr_2C_6H_3$ > $C_6H_5$ > cyclohexyl > $^t$Bu ≫ adamantyl, and the ROP using the $C_6F_5$ analogue proceeded in a living manner with high initiation efficiency [8]. This 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 [9,10].

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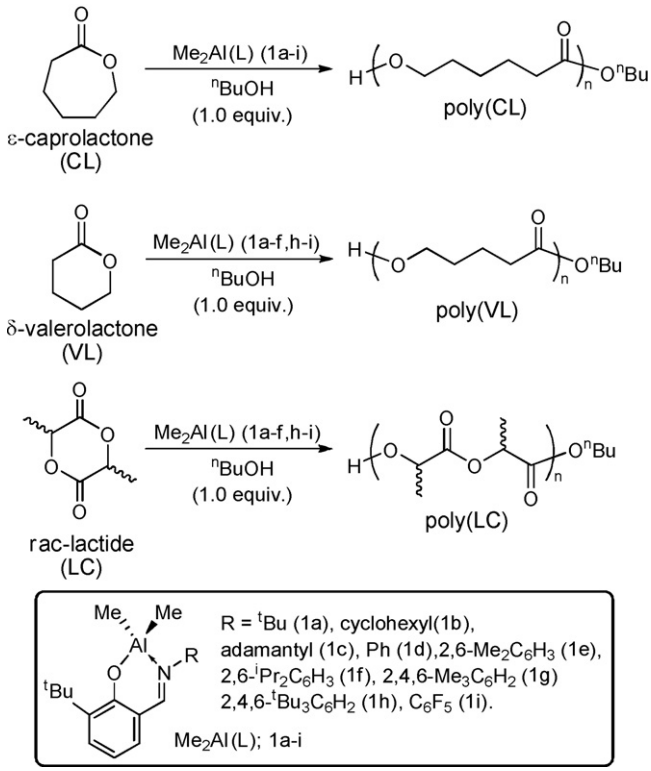



**Scheme 1.**

In this paper, we thus conducted 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, we prepared and identified the 2,4,6-$Me_3C_6H_2$ analogue (**1g**) and the 2,4,6-$^t Bu_3C_6H_2$ analogue (**1h**) in the present study including the structure analysis for **1g** by X-ray crystallography. Through these experiments, we tried to explore the ligand effect, especially effect of the aromatic substituent in the imino ligand, as well as monomers toward the catalytic activity in the ROP of various cyclic esters (Scheme 1).

## 2. Results and discussion

### 2.1. Synthesis of $Me_2Al[\text{-}2\text{-}^tBu\text{-}\{(2,4,6\text{-}R'_3C_6H_2)N{=}CH\}C_6H_3]$ ($R'$ = Me, $^t$Bu)

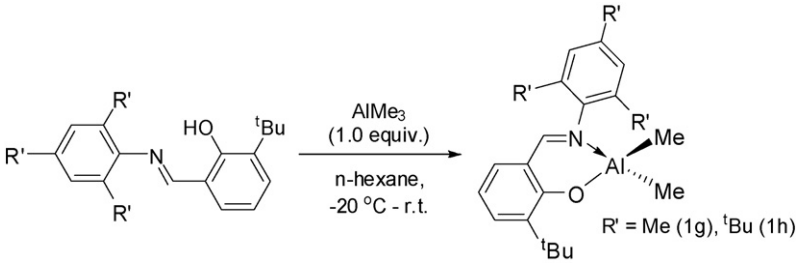
Various Al complexes containing a series of phenoxy-imine ligands of the type, $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ [**1**, R = $^t$Bu (**a**), cyclohexyl (**b**), adamantyl (**c**), $C_6H_5$ (**d**), 2,6-$Me_2C_6H_3$ (**e**), 2,6-$^i Pr_2C_6H_3$ (**f**), $C_6F_5$ (**i**)], were prepared according to our previous reports [7,8]. 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 consisting 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 2) and were identified based on $^1$H, $^{13}$C NMR spectra and elemental analysis. The structure of **1g** was determined by X-ray crystallography (Fig. 1) [11], 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(1)–Al–C(1) [111.75(10)°], O(1)–Al–C(2) [110.76(11)°], although the O(1)–Al–N(1) bond angle is somewhat small [93.37(8)°]. 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] [7,8]. 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].

### 2.2. Ring-opening polymerization of ε-caprolactone

Ring-opening polymerizations (ROPs) of ε-caprolactone (CL) were conducted at 60 °C 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 1. The results in our previous report by **1a–f,i** [8] 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 [7,8].

The catalytic activity [TON values, TON = CL consumed (μmol)/Al (μmol), TON after 60 min at 60 °C, Al 20 μmol, initial molar ratio of [CL]/[Al] = 250] 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 (or 430, Al 10 μmol) after 30 min, run 12 (run 14)] > 2,4,6-$^t Bu_3C_6H_2$ [**1h**, TON > 235 (or 330, Al 10 μmol) after 30 min, run 10 (run 11)] ≫ 2,6-$Me_2C_6H_3$ (**1e**, 185 after 30 min, run 5) > 2,4,6-$Me_3C_6H_2$ (**1g**, 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 reported previously [7,8]. 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 °C, runs 10 and 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 $PhCH_2OH$ (Fig. 2a). The $M_n$ value ($4.42 \times 10^4$) estimated by the $^1$H NMR spectrum was




**Scheme 2.**

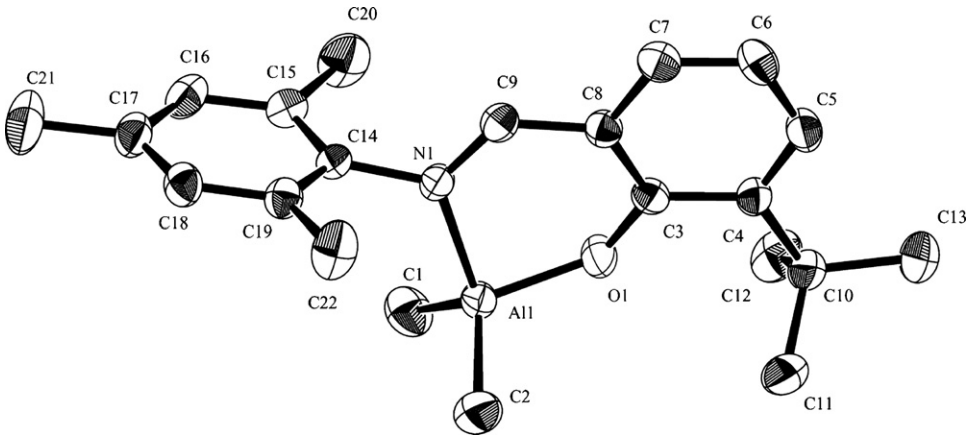



**Fig. 1.** ORTEP drawing for $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,4,6\text{-}Me_3C_6H_2)N{=}CH\}C_6H_3]$ (**1g**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond distance (Å): Al(1)–O(1) 1.7748(19), Al(1)–N(1) 1.965(2), Al(1)–C(1) 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(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).

very close to the exact value ($4.23 \times 10^4$, 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 [1,13]. 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 [12] 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 the **1i**-$PhCH_2OH$ system was higher than that by the **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 °C according to the above procedure (Table 1, runs 1–10, 12), and the Al complexes containing alkyl substituents and 2,4,6-$^t$Bu$_3$C$_6$H$_2$ in the imino group were found to be low (runs 1–3, 10, rather low $N$ values). Note that the observed activity (TON value) by the 2,4,6-$^t$Bu$_3$C$_6$H$_2$ 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**.

As shown in Table 2, the observed activities (by **1e,f,h,i**) decreased upon decreasing the polymerization temperature (from 60 to 50, 40 °C), and no significant differences in the order toward the activity in the ROP using Al complexes with a series of the aromatic substituents in the imino group were seen. The $C_6F_5$ analogue (**1i**, run 19, 86%) thus showed the highest catalytic activity (TON values) among these Al complexes when the ROPs were conducted at 50 °C. Rather notable differences in the TON values were seen between the $C_6F_5$ analogue (**1i**) and the 2,4,6-$^t$Bu$_3$C$_6$H$_2$ 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 °C. 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 terms of both the catalytic activity and the catalyst efficiency. As reported previously, the ROP of CL by **1i** proceeded in a living manner with high initiation efficiency under optimized con-

**Table 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$_2$C$_6$H$_3$ (**1f**), 2,4,6-$Me_3C_6H_2$ (**1g**), 2,4,6-$^t$Bu$_3$C$_6$H$_2$ (**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[e] | **1a** ($^t$Bu) | 20 | 60 | 46 (8) | 20 | 1.64 | 1.10 | 5.0 |
| 2[e] | **1b** (cyclohexyl) | 20 | 60 | 156 (28) | 70 | 2.07 | 1.19 | 13.5 |
| 3[e] | **1c** (adamantyl) | 20 | 60 | Trace | – | – | – | – |
| 4[e] | **1d** ($C_6H_5$) | 20 | 60 | 258 (45) | 113 | 2.83 | 1.38 | 16.3 |
| 5[e] | **1e** (2,6-$Me_2C_6H_3$) | 20 | 30 | 413 (74) | 185 | 4.84 | 1.64 | 15.2 |
| 6[e] | **1f** (2,6-$^i$Pr$_2$C$_6$H$_3$) | 20 | 60 | 472 (84) | 209 | 4.35 | 1.61 | 19.4 |
| 7[e] | **1f** (2,6-$^i$Pr$_2$C$_6$H$_3$) | 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$_3$C$_6$H$_2$) | 20 | 30 | 524 (94) | 235 | 7.66 | 1.58 | 12.2 |
| 11 | **1h** (2,4,6-$^t$Bu$_3$C$_6$H$_2$) | 10 | 30 | 375 (66) | 330 | 10.6 | 1.68 | 5.9 |
| 12[e] | **1i** ($C_6F_5$) | 20 | 30 | 551 (99) | 248 | 5.60 | 1.64 | 17.6 |
| 13[e,f] | **1i** ($C_6F_5$) | 20 | 30 | 550 (98) | 245 | 7.56 | 1.66 | 13.0 |
| 14[e] | **1i** ($C_6F_5$) | 10 | 30 | 481 (86) | 430 | 9.34 | 1.64 | 9.2 |

[a] Conditions: Al 10 or 20 μmol, $^n$BuOH 1.0 equiv. to Al (in toluene 50 μL), CL 5.0 mmol, 60 °C.
[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)/{$0.56 \times M_{n(GPC)}$} [12].
[e] Cited from our preliminary article [8].
[f] $PhCH_2OH$ was used in place of $^n$BuOH [$M_n = 4.42 \times 10^4$ estimated by $^1$H NMR spectrum].

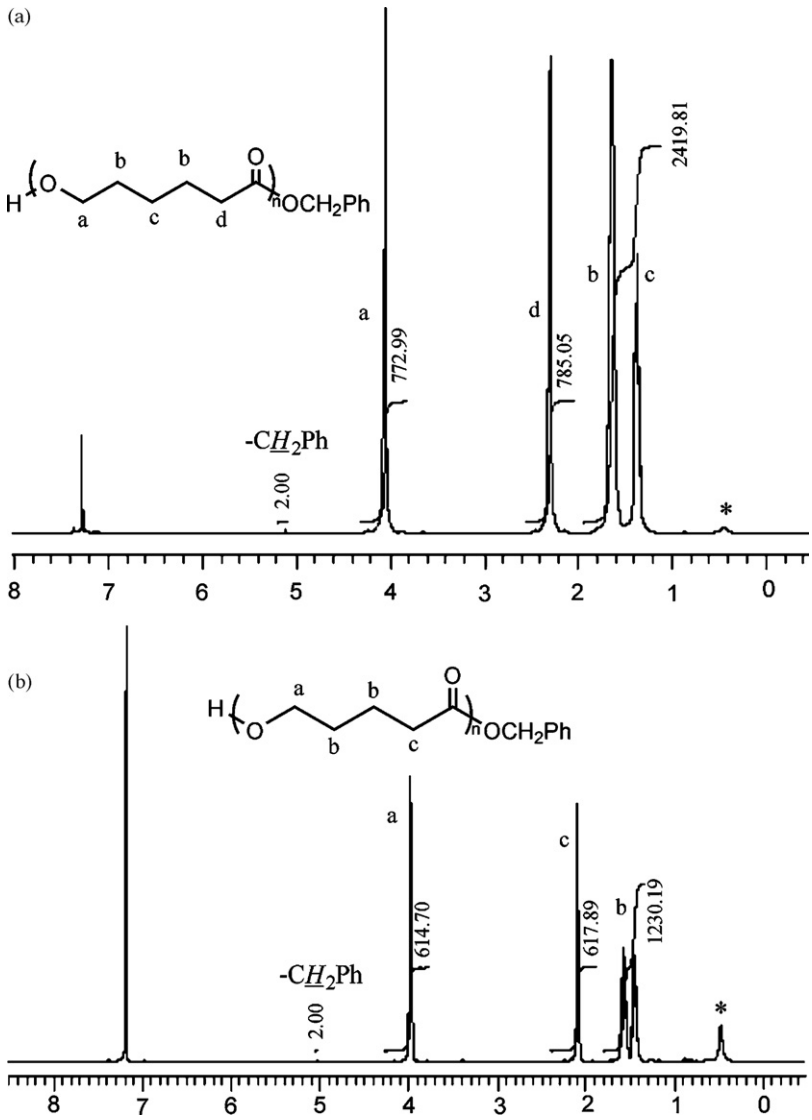



**Fig. 2.** (a) $^1$H NMR spectrum (in $C_6D_6$ at 25 °C) for poly(CL) (run 13 in Table 1, CL = ε-caprolactone), $M_{n(NMR)} = 4.42 \times 10^4$. (b) $^1$H NMR spectrum (in $C_6D_6$ at 25 °C) for poly(VL) (run 33 in Table 3), $M_{n(NMR)} = 3.10 \times 10^4$. Peak marked with * is due to a resonance ascribed to impurities.

ditions, affording the ring-opened polymer with narrow molecular weight distributions [8].

### 2.3. Ring-opening polymerization (ROP) of δ-valerolactone and rac-lactide

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

The polymerizations did not proceed or exhibited negligible catalytic activities, when the Al complexes containing alkyl substituents in the imino group [R = $^t$Bu, cyclohexyl, adamantyl (**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 substituents in the imino group (**1d**–**f**,**h**,**i**) were employed as the catalyst precursors. The activity [TON values, TON after 60 min at 60 °C, 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-$^i Pr_2C_6H_3$ (**1f**, 178, run 30) > $C_6H_5$ (**1d**, 133, run 28). The observed trend concerning effect of the aromatic substituent toward the activity in the ROP of VL was similar to that in the ROP of CL, except that the 2,6-$Me_2C_6H_3$ analogue (**1e**) showed the higher activity than the 2,4,6-$^tBu_3C_6H_2$ analogue (**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 conditions (Al 10 μmol, run 36).

The ROP using the $C_6F_5$ analogue (**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 (Fig. 2b). Moreover, the $M_n$ value [$M_{n(NMR)} = 3.10 \times 10^4$], which was estimated by the $^1$H NMR spectrum based on methylene protons at the polymer chain end derived from $PhCH_2OH$, was relatively close to the theoretical value [$M_{n(calcd)} = 2.26 \times 10^4$] 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

**Table 2**
Effect of temperature in 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-$^iPr_2C_6H_3$ (**1f**), 2,4,6-$^tBu_3C_6H_2$ (**1h**), $C_6F_5$ (**1i**)][a]

| Run | Complex (R) | Al (μmol) | Temperature (°C) | Time (min) | Yield (mg(%)) | TON[b] | $M_n$[c] × $10^{-4}$ | $M_w/M_n$[c] | $N$[d] (μmol) |
|---|---|---|---|---|---|---|---|---|---|
| 6[e] | **1f** (2,6-$^iPr_2C_6H_3$) | 20 | 60 | 60 | 472 (84) | 209 | 4.35 | 1.61 | 19.4 |
| 15[e] | **1f** (2,6-$^iPr_2C_6H_3$) | 20 | 50 | 60 | 198 (35) | 88 | 2.58 | 1.27 | 13.7 |
| 5[e] | **1e** (2,6-$Me_2C_6H_3$) | 20 | 60 | 30 | 413 (74) | 185 | 4.84 | 1.64 | 15.2 |
| 16[e] | **1e** (2,6-$Me_2C_6H_3$) | 20 | 50 | 60 | 449 (80) | 200 | 5.39 | 1.74 | 14.9 |
| 10 | **1h** (2,4,6-$^tBu_3C_6H_2$) | 20 | 60 | 30 | 524 (94) | 235 | 7.66 | 1.58 | 12.2 |
| 17 | **1h** (2,4,6-$^tBu_3C_6H_2$) | 20 | 50 | 30 | 457 (82) | 205 | 7.15 | 1.57 | 11.4 |
| 18 | **1h** (2,4,6-$^tBu_3C_6H_2$) | 20 | 40 | 30 | 274 (50) | 125 | 4.86 | 1.46 | 10.1 |
| 12[e] | **1i** ($C_6F_5$) | 20 | 60 | 30 | 551 (99) | 248 | 5.60 | 1.64 | 17.6 |
| 19[e] | **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-$^tBu_3C_6H_2$) | 10 | 60 | 30 | 375 (66) | 330 | 10.6 | 1.68 | 5.9 |
| 21 | **1h** (2,4,6-$^tBu_3C_6H_2$) | 10 | 50 | 30 | 179 (32) | 160 | 5.79 | 1.47 | 5.5 |
| 22 | **1h** (2,4,6-$^tBu_3C_6H_2$) | 10 | 40 | 30 | Trace | – | – | – | – |
| 14[e] | **1i** ($C_6F_5$) | 10 | 60 | 30 | 481 (86) | 430 | 9.34 | 1.64 | 9.2 |
| 23 | **1i** ($C_6F_5$) | 10 | 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 × $M_{n(GPC)}$} [12].
[e] Cited from our preliminary article [8].

**Table 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-$^iPr_2C_6H_3$ (**1f**), 2,4,6-$^tBu_3C_6H_2$ (**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] |
|---|---|---|---|---|---|---|---|
| 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-$^iPr_2C_6H_3$) | 20 | 30 | 355 (71) | 178 | 1.61 | 1.33 |
| 31 | **1h** (2,4,6-$^tBu_3C_6H_2$) | 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-$^tBu_3C_6H_2$) | 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 °C.
[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 × $10^4$ estimated by $^1$H NMR spectrum].

[$M_{n(calcd)}/M_{n(NMR)}$], and the result would suggest that the present ROP was initiated with Al-OR via coordination insertion mechanism as proposed [1,13].

The ROPs of VL using the $C_6F_5$ analogue (**1i**)-$^n$BuOH catalyst system were conducted in toluene at 50 °C, and the results are summarized in Table 4. The ROP proceeded at significant rate at beginning and the rate gradually decreased upon consumption of VL. As shown in Fig. 3, the rates were first order dependent upon the VL concentration, suggesting that the ROP 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, Fig. 4). These results clearly indicate that the ROP by the $C_6F_5$ analogue (**1i**) proceeds in

**Table 4**
Ring-opening polymerization of δ-valerolactone (VL) by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**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 °C.
[b] TON = (molar amount of VL reacted)/(molar amount of Al).
[c] GPC data in THF vs. polystyrene standard.

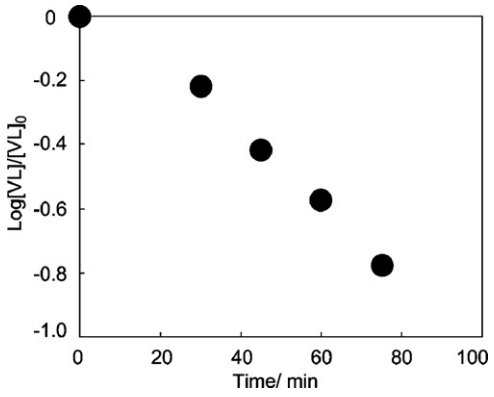



**Fig. 3.** Time course plots of log[VL]/[VL]$_0$. [VL] = concentration of δ-valerolactone (VL) in mmol/mL. Detailed conditions are described in Table 4.

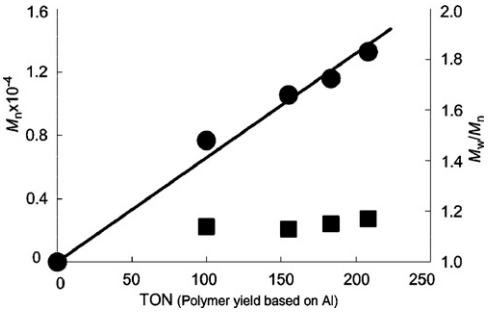



**Fig. 4.** Plots of $M_n$ and $M_w/M_n$ values for poly(CL) vs. TON for ring-opening polymerization of δ-valerolactone (VL) catalyzed by $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1i**) in toluene. Detailed conditions are described in Table 4.

a living manner, as seen in the ROP of CL. Taking into account these results, we would also conclude that the ROP of VL by **1i**-$^n$BuOH (and $PhCH_2OH$) catalysts system proceeded without side reaction like transesterification [14].

Ring-opening polymerizations (ROPs) of *rac*-lactide (LC) using **1a**–**f**,**h**,**i** were conducted at 80 °C in the presence of $^n$BuOH, and the results are summarized in Table 5. The catalytic activity [TON values, TON after 24 h at 80 °C, 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 after 8 h), run 47 (run 48)] > cyclohexyl (**1b**, 72, run 43) > 2,6-$Me_2C_6H_3$ (**1e**, 46, run 45) > 2,6-$^i$Pr$_2$C$_6$H$_3$ (**1f**, 23, run 46) > $C_6H_5$ (**1d**, 19, run 44) ≫ adamantyl (**1c**, 5, run 42), $^t$Bu (**1b**, 4, run 41). The ROPs using the 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**.

Although the Al complexes containing alkyl substituent in the imino group (**1a**–**c**) 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 that by **1b** probably due to the steric bulk. The moderate catalytic activity by **1b** would be caused by an 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 O$^n$Bu 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 (stereo regularity), and atactic polymers were thus collected (Fig. 5).

### 2.4. Attempted ring-opening polymerizations of β-butyrolactone and γ-butyrolactone

Ring-opening polymerizations (ROPs) of 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 °C 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.

### 2.5. Concluding remarks

We have conducted ring-opening polymerization of ε-caprolactone (CL), δ-valerolactone (VL), and *rac*-lactide (LC) using a series of Al complexes containing phenoxy-imine ligands of 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$_2$C$_6$H$_3$ (**f**), 2,4,6-$Me_3C_6H_2$ (**g**), 2,4,6-$^t$Bu$C_6H_2$ (**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$_3$C$_6$H$_2$ 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$_3$C$_6$H$_2$ 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-butyrolactone 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.

Our present study in this project focuses on more details for the ROPs using the $C_6F_5$ analogue, $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(C_6F_5)N{=}CH\}C_6H_3]$ (**1i**), including not only synthesis of various Al

**Table 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$_2$C$_6$H$_3$ (**1f**), 2,4,6-$^t$Bu$_3$C$_6$H$_2$ (**1h**), $C_6F_5$ (**1i**)][a]

| Run | Complex (R) | Temperature (°C) | Time (min) | 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$_2$C$_6$H$_3$) | 80 | 24 | 168 (23) | 23 | 1.35 | 1.10 | 21.5 |
| 47 | **1h** (2,4,6-$^t$Bu$_3$C$_6$H$_2$) | 80 | 24 | 657 (91) | 91 | 2.37 | 1.18 | 47.8 |
| 48 | **1h** (2,4,6-$^t$Bu$_3$C$_6$H$_2$) | 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 | 1.3 | 1.09 | 35.0 |
| 51 | **1h** (2,4,6-$^t$Bu$_3$C$_6$H$_2$) | 70 | 24 | 77 (11) | 11 | 1.09 | 1.14 | 12.2 |
| 52 | **1i** ($C_6F_5$) | 70 | 24 | 33 (5) | 5 | 0.7 | 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 4.9 mL.
[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 × $M_{n(GPC)}$} [12].
[e] Resultant polymer was insoluble in THF.

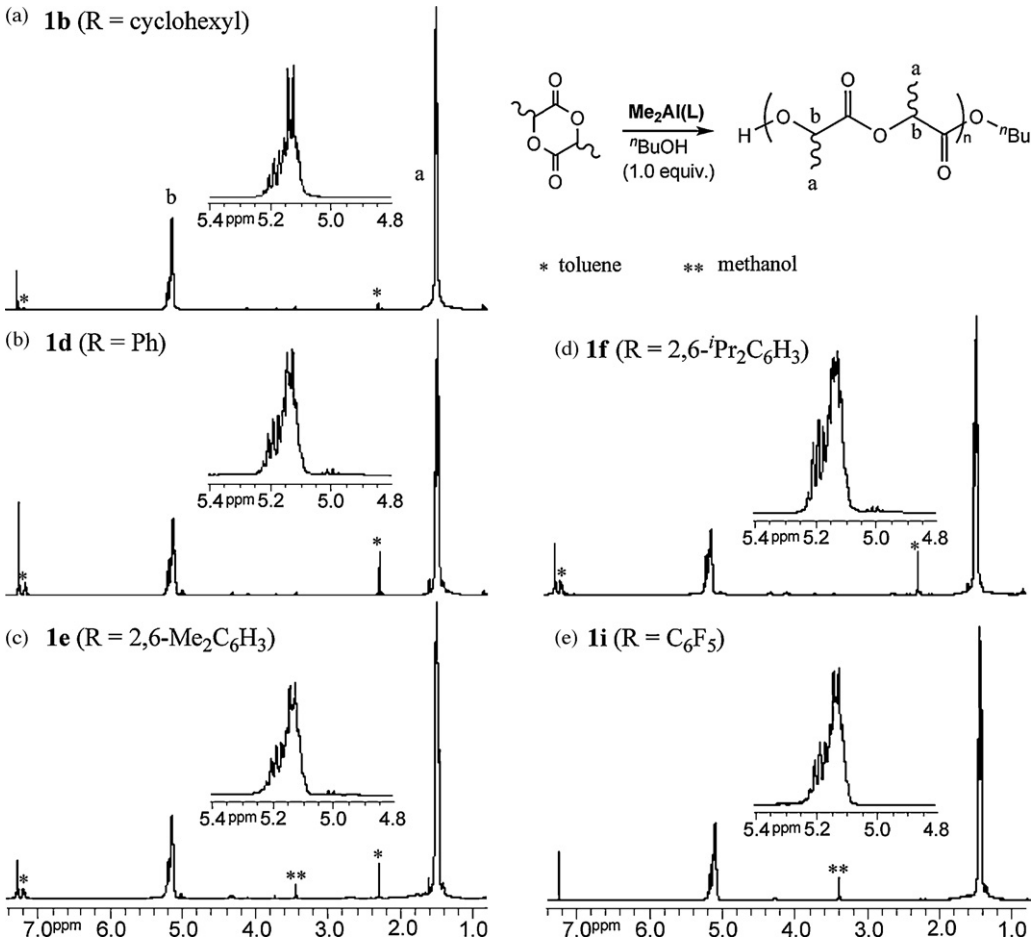



**Fig. 5.** $^1$H NMR spectra (in $CDCl_3$ at 25 °C) of the methine region of the resultant poly(LC) using $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{RN{=}CH\}C_6H_3]$ [R = cyclohexyl (**1b**, top left, run 43), phenyl (**1d**, center left, run 44), 2,6-$Me_2C_6H_3$ (**1e**, bottom left, run 45), 2,6-$^iPr_2C_6H_3$ (**1f**, center right, run 46 in Table 4), $C_6F_5$ (**1i**, bottom right, run 49)].

complexes containing a series of fluorinated aromatic substituents as the imino substituent, but also isolation of the initiating species for the ROP. These results will be introduced in the near future.

## 3. Experimental

### 3.1. 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-$^iPr_2C_6H_3$, 2,4,6-$^tBu_3C_6H_2$, $C_6F_5$] were prepared according to the reported procedures [9]. Syntheses of Al complexes (**1a**–**f**,**i**) were referred to our previous report [7,8]. Elemental analyses were performed by using a PE2400II Series (PerkinElmer 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 $SiMe_4$ ($\delta$ 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 °C 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 mm $\phi$, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from $<10^2$ to $2 \times 10^7$ MW) were calibrated versus polystyrene standard samples.

### 3.2. Synthesis of *$Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}\{(2,4,6\text{-}Me_3C_6H_2)N{=}CH\}C_6H_3]$* (**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 °C. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 2). The mixture was then concentrated *in vacuo*, and the resultant solid was dissolved in a minimum amount of *n*-hexane. The chilled solution (−20 °C) afforded colorless microcrystals of **1g** (1.39 g, 99% yield). $^1$H NMR ($C_6D_6$): $\delta$ −0.28 (s, 6H, $AlMe_2$), 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, CH=N), 7.42 (d, $J$ = 7 Hz, 1H, aromatic). $^{13}$C NMR ($C_6D_6$): $\delta$ −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.

### 3.3. Synthesis of *Me$_2$Al[O-2-$^t$Bu-6-{(2,4,6-$^t$Bu$_3$C$_6$H$_2$)N=CH}C$_6$H$_3$] (**1h**)*

Into a stirred solution containing 2-$^t$Bu-6-{(2,4,6-$^t$Bu$_3$C$_6$H$_2$)N=CH}C$_6$H$_3$OH (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 °C. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 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, $AlMe_2$), 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, CH=N). $^{13}$C NMR ($C_6D_6$): $\delta$ −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.

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

Typical polymerization procedures (Table 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 min, and the solution was then added ε-caprolactone (5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 60 °C, 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 ($CDCl_3$): $\delta$ 1.33 (m, 2H), 1.51–1.63 (m, 4H), 2.25 (t, 2H), 4.00 (t, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 24.5, 25.5, 28.3, 34.1, 64.1, 173.5 (C=O).

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

Typical polymerization procedures (Table 3, run 32) are as follows. 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 min, and the solution was then added δ-valerolactone (5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 60 °C, 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 ($C_6D_6$): $\delta$ 1.39–1.59 (m, 4H), 2.07 (t, 2H), 3.95 (t, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 21.7, 28.4, 33.7, 63.8, 64.1, 172.6 (C=O).

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

Typical polymerization procedures (Table 5, run 43) are as follows. 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 min, and the solution was then added toluene (4.9 mL), *rac*-lactide (5.0 mmol). The reaction mixture was then placed into an oil bath preheated at 60 °C, 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 ($CDCl_3$): $\delta$ 1.54–1.58 (m, 6H), 5.13–5.24 (m, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 16.6–16.7 (m, $CH_3$), 69.0–69.2 (m, $CCH_3$), 169.1–169.6 (m, C=O).

### 3.7. Crystallographic analysis

The crystallographic analysis for $Me_2Al$[O-2-$^t$Bu-6-{(2,4,6-$Me_3C_6H_2$)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 [15], and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure crystallographic software package [16]. The selected crystal collection parameters: crystal color, habit = red, 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 = 20,121; no. of observations ($I > 2.00\sigma$ (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. Detailed analysis results such as CIF file, the structure report including crystal data and crystallographic parameters are shown in Supplementary Material.

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.06.009.

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