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RAPID COMMUNICATION

A synergic catalysis of (salicylaldiminate)$_2$AlEt and (BnO)$_2$AlEt in the ring-opening polymerization of ε-caprolactone

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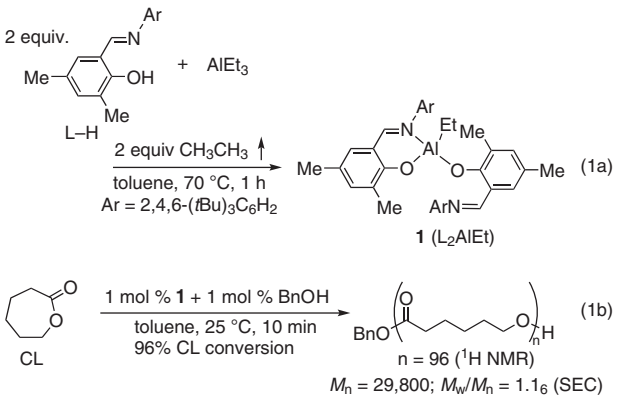
The aliphatic polyesters obtained via the ring-opening polymerization (ROP) of lactones, such as ε-caprolactone (CL), δ-valerolactone, and lactide, have attracted significant attention because of their biodegradability and biocompatibility [1]. Among the various metal catalysts that have been successfully developed for the controlled/living ROP of lactones [2, 3], metal alkoxide complexes bearing designed ancillary ligands play a pivotal role, and a coordinated anionic mechanism has been proposed in many cases. Many of the reports have dealt with well-defined single-site catalysts. However, the advantages of a mixture of two metal complexes [4, 5] or of a bi-/multi-metal complex [6–9] in a system have also been documented, and the number of such studies is rapidly increasing. We previously reported that (salicylaldiminate)$_2$AlEt **1** (L$_2$AlEt) prepared from AlEt$_3$ and 2 equiv. of a substituted salicylaldimine (L–H) in situ (Eq. 1a) efficiently catalyzed the ROP of CL at ambient temperature in the presence of benzyl alcohol (BnOH) (Eq. 1b) [10]. However, the precise structure of **1**, the active species of the catalyst(s) in the presence of BnOH, and therefore the polymerization mechanism have not been clarified. In this paper, we report the solid-state structure of **1** by X-ray diffraction. We also document that BnOH (1 equiv. to complex **1**) selectively reacts with ~0.5 equiv. of complex **1** to afford ~1 equiv. of free L–H while maintaining ~0.5 equiv. of complex **1**. The stoichiometric balance suggests the formation of 0.5 equiv. of (BnO)$_2$AlEt. On the basis of experiments on each compound and their combinations, the ROP of CL via the synergic catalysis of the two Al-complexes, remaining complex **1** (0.50 mol%) as a Lewis acid activator of CL and (RO)$_2$AlEt (0.50 mol%) as a nucleophile, is proposed.



It is often important to determine the stable conformation of a catalyst for the elucidation of the reaction mechanism. Although NMR studies of complex **1** suggested that one of the two salicylaldiminate ligands was a bidentate and the other was a monodentate because of the significantly different chemical shifts of the two imine protons (ArC*H*=NAr′, 8.02 and 9.14 ppm), the precise structure of **1** remains unclear. We obtained single crystals suitable for X-ray diffraction studies as well as elemental analysis (CCDC 724752 contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk. Anal. calcd for $C_{56}H_{81}AlN_2O_2$: C, 79.95; H, 9.71; N, 3.33. Found: C, 80.12; H, 10.07; N, 3.30) and revealed the monomeric structure of complex **1** (Fig. 1 and Supporting Information). One of the salicylaldiminate ligands of **1** is bidentate and forms a nearly planar six-membered ring (Al1–O1–C3–C4– C9–N1–), with Al1–O1 and Al1–N1 bond lengths of 1.753(3) and 1.972(4) Å, respectively. These bond lengths are close to those of the

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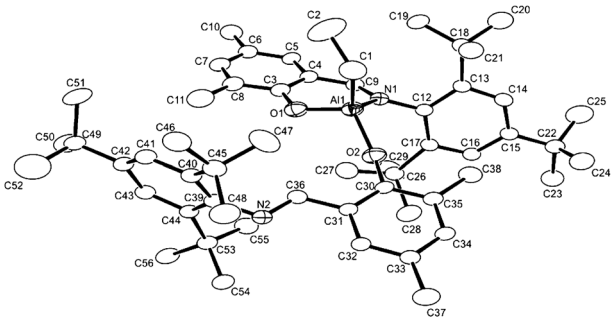


Fig. 1 Crystal structure of complex **1**. Thermal ellipsoids are drawn at a 30% probability level, and H atoms are omitted for clarity

reported (salicylaldiminate)$AlMe_2$ complex [11, 12]. The other monodentate ligand suggested by a previous ^{1}H NMR study [10] is confirmed, and the bond length of Al1–O2 (1.706(3) Å) is significantly shorter than that of the bidentate ligand (Al1–O1, 1.753 Å). The 2,4,6-tri(*t*-butyl)phenyl group of the monodentate ligand is located on the other side of the bidentate one. The coordination of the nitrogen center of the salicylaldiminate is sterically demanding due to the two *t*-Bu groups in the *ortho*-positions of the aniline moiety, and thus only one of the two N atoms can coordinate the Al center. As a result, the coordinatively unsaturated Al center in a distorted tetrahedral structure secures a good coordination site and space for an approaching monomer.

Although Normand et al. reported no reaction between (salicylaldiminate)$AlMe_2$ and 2 equiv. of *i*-PrOH in toluene at 70 °C for 6 h [13], complex **1** immediately reacted with 1 equiv. of BnOH in C_6D_6–toluene at 25 °C. The ^{1}H NMR spectra of the reaction between **1** and BnOH (0–2 equiv.) in C_6D_6–toluene at 25 °C are shown in Fig. 2 (Supporting Information), and some of the characteristic peaks (H^a–H^d) are indicated. As the amount of BnOH increased, the integration ratio of $(H^b = H^c)/(H^a = H^d)$ decreased (Fig. 2a–e). By the addition of 0.5 equiv. of BnOH to complex **1** (Fig. 2a), 33% of the **1** was consumed on the basis of the ^{1}H NMR analysis, and the formation of free L–H^a was observed (**1**/L–$H^a = H^b/H^a$ ~ 1/1, Fig. 2b). One equiv. of BnOH was consumed by 56% of the complex **1** (Fig. 2c). In addition to the free L–H^a peaks, new broad peaks appeared around 4.5–6.0 ppm (Fig. 2b–e). From the stoichiometric balance of the reaction, a new compound can be described by $(BnO)_2AlEt$ [14]. In contrast to (R′O)AlR_2 [15] and (R′O)$_3$Al [16], the structural studies of (R′O)$_2$AlR on the simplistic compound such as $(MeO)_2AlMe$ have not been successfully reported probably due to their unorganized oligo-/polymeric structures. Therefore, the complex is described by $(BnO)_2AlEt$ on the basis of the stoichiometric balance such as RMgX under the Schlenk equilibrium. When 2.0 equiv. of BnOH was added, the H^b and H^c peaks of complex **1** finally became undetectable (Fig. 2e). Note that all the peaks of ligand

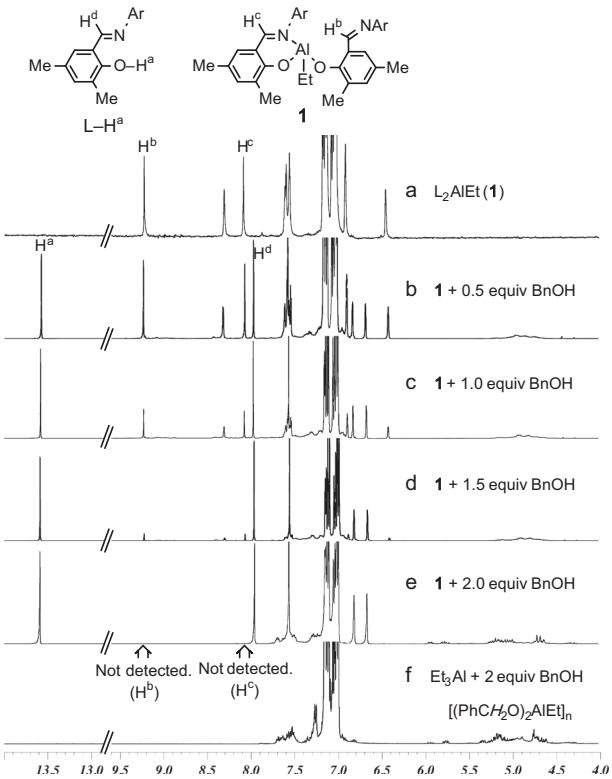
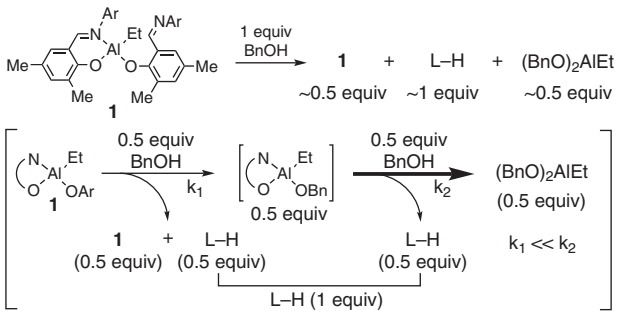


Fig. 2 400 MHz ^{1}H NMR spectra of reaction between complex **1** and BnOH (C_6D_6–toluene)

L–H and complex **1** in the mixture showed chemical shifts identical to those of the spectra of free L–H and complex **1**. This indicates no equilibrium between the remaining **1** and L–H and also none between $(BnO)_2AlEt$ and L–H on the NMR time scale. Although methylene protons of free benzyl alcohol appeared at 4.7 ppm, those of the aluminum complex appeared around 4.5–6.0 ppm as complex broad peaks, which are similar to those of $(BnO)_2AlEt$ obtained by the reaction of Et_3Al with 2 equiv. of BnOH [14] (Fig. 2f). Some difference might come from the slow formation toward the stable oligo-/polymeric structure of $(BnO)_2AlEt$. In NMR experiments, no new imine peaks derived from LAl(Et)OBn and L_2AlOBn were detected. These experiments showed that the Et–Al bond, which is often reactive under protic conditions [17], remained stable [13], and the bidentate ligand as well as the monodentate one of complex **1** was successively dissociated by the addition of BnOH. The reaction of complex **1** with 1 equiv. of BnOH is summarized in Scheme 1. The consumption of complex **1** by BnOH in our NMR experiments (33% by 0.5 equiv. BnOH; 56% by 1.0 equiv. BnOH) was slightly higher (6–8%) than the theoretical consumption (25% by 0.5 equiv. BnOH; 50% by 1.0 equiv. BnOH), probably due to the contamination with H_2O of solvents such as C_6D_6 (5–10 ppm H_2O by Karl Fischer titration).



Scheme 1 Reaction of complex **1** with 1 equiv. of BnOH

To elucidate the role of each of the compounds afforded in the reaction between **1** and BnOH, the experiments in Table 1 were conducted. Complex **1** (0.5 mol%), ligand L–H (1 mol %), and their mixture did not catalyze the ROP of CL at all (entries 1–3). We then examined the ROP of CL using (BnO)AlEt$_2$ [14, 15], (BnO)$_2$AlEt [14, 18], and (BnO)$_3$Al [14, 16], (entries 4–6, respectively). To compare the initiation efficiencies on the basis of the M_n–CL conversion, 1 mol% of benzyloxide was applied in entries 4–6. Each of them slowly polymerized CL, but their efficiencies were much lower than that of Eq. 1b. In the presence of 0.50 mol% of **1**, (BnO)AlEt$_2$ uncontrollably polymerized CL (entry 7), and a bimodal SEC trace of the polymer was obtained. One of the M_n values was extremely high ($M_n = 409{,}000$) after 10 min at 25 °C even at a low monomer conversion (27%). On the other hand, both entries 8 and 9 were monomodal by the SEC analysis. The ROP of CL of entry 8 gave a result comparable to that of Eq. 1b. The initiation efficiency of the benzyloxide group seemed to be high (~80%), and both BnO groups of (BnO)$_2$AlEt initiated the polymerization. In entry 9, 30–40% of the benzyloxide of (BnO)$_3$Al were utilized. Trimer and/or tetramer structures of (BnO)$_3$Al and (*i*PrO)$_3$Al are known [16, 19], and the organized rigid and stable structures may have led to the lower initiation efficiency. Supposing that a disproportionation reaction of (BnO)$_2$AlEt occurs, in other words, supposing that both (BnO)AlEt$_2$ and (BnO)$_3$Al form and work as the major active species in Eq. 1b, a controlled ROP of CL cannot be achieved, judging from the results of entries 7 and 9.

The mechanistic rationale is illustrated in Scheme 2. (RO)$_2$AlEt and complex **1**, coexist as documented in Fig. 2, and CL is activated by the coordination of the Lewis acid **1**. In the ^{13}C NMR spectra (150 MHz), the carbonyl carbon (C = O) of free CL appeared at 174.5 ppm (C_6D_6), and it was highfield shifted (172.8 ppm, C_6D_6–toluene) by the addition of complex **1** (1.3 equiv. to CL). Although (RO)$_2$AlEt (RO = BnO/oligo- or polymeric alkoxide) by itself only slowly polymerizes CL [18], it becomes an excellent nucleophile when the CL is appropriately activated. After the ring opening of one CL, another CL coordinated by complex **1** is repeatedly attacked by RO$^-$/R′O$^-$ from the Al center. A similar synergic mechanism in the highly efficient ROPs of δ-valerolactone and β-butyrolactone was originally reported by Aida and Inoue, who called it the Lewis acid-assisted polymerization using bulky Lewis acids and porphyrin–AlOMe [4]. The ROP of CL, however, via this mechanism is rather rare to the best of our knowledge.

Table 1 Roles of complex **1**, L–H, and/or (BnO)$_n$AlEt$_{3-n}$[a]

Entry	Complex **1**, mol%	(BnO)$_n$AlEt$_{3-n}$,[b] (mol%)	Conv. of CL,[c] %	$M_n \times 10^{-3}$ (M_w/M_n)[d]
1	0.5	NA[e]	0	NM[f]
2[g]	0	NA[e]	0	NM[f]
3[g]	0.5	NA[e]	0	NM[f]
4	0	$n = 1$ (1.0)	20	NM[f]
5	0	$n = 2$ (0.50)	8	NM[f]
6	0	$n = 3$ (0.33)	6	NM[f]
7	0.5	$n = 1$ (0.25)	27	39.0 (6.0)[h]
8	0.5	$n = 2$ (0.50)	91	28.7 (1.1_9)[i]
9	0.5	$n = 3$ (0.25)	85	83.7 (1.4_2)

[a]Polymerization conditions: complex **1** prepared in situ, 0.010 mmol (Entries 1, 3, and 7–9); BnOAlEt$_2$, 0.020 mmol (Entry 4) or 0.005 mmol (Entry 7); (BnO)$_2$AlEt, 0.010 mmol (Entries 5 and 8); (BnO)$_3$Al, 0.007 mmol (Entry 6) or 0.005 mmol (Entry 9); CL, 0.220 mL (2.00 mmol); toluene, 2.0 mL; temp., 25 °C; time, 10 min.

[b]Each complex was prepared according to ref. [14].

[c]The conversion of CL was determined by 300 MHz ^{1}H NMR.

[d]M_n and M_w/M_n were determined by SEC (polystyrene standards, $CHCl_3$, 40 °C).

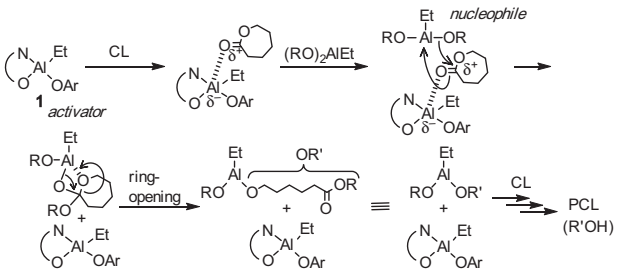
[e]Not added.

[f]Not measured.

[g]The salicylaldimine ligand (L–H, 0.020 mmol, 1 mol%) was added.

[h]The SEC trace was bimodal, with peaks of $M_n = 409{,}000$ ($M_w/M_n = 1.2_3$) and 19,000 ($M_w/M_n = 1.1_8$).

[i]The expected M_n in this entry was 23,300. $M_{n(\mathrm{SEC})} = M_{n(\mathrm{theo})}/0.45$ (correlation factor for PSt standards, THF). $M_{n(\mathrm{theo})} = 108.14$ (BnOH) + 114.14 (CL) × 91 (CL conv. %)/1 (BnOH, mol%) ~ 10,500. Since the correlation factor in $CHCl_3$ that we used for the SEC analysis is not known, we applied the value of THF (0.45) for convenience. The calculated efficiency of BnOH was ~80% (23,300/28,700 = 0.81).



Scheme 2 Mechanistic rationale of synergic catalysis

In conclusion, the single-crystal X-ray diffraction of **1** shows that one of the ligands of **1** is bidentate and the other monodentate. BnOH (1 equiv. to complex **1**) is consumed by ~0.5 equiv. of **1**, and the bidentate ligand of **1** as well as the monodentate one is successively dissociated to afford the free ligand L–H (~1 equiv.) and $(BnO)_2AlEt$ (~0.5 equiv.). Although complex **1** does not polymerize CL at all and $(BnO)_2AlEt$ does but only slowly, the coexistent combination of these two complexes is found to be highly efficient in the ROP of CL. The remaining complex **1** (~0.5 equiv.) coordinates CL, and $(BnO)_2AlEt$ acts as an excellent nucleophile toward the CL activated by complex **1**. Since the Lewis acidity and nucleophilicity of the two metal complexes can be independently designed and tuned, it may be possible to develop a more efficient synergic catalysis than a single-site one in which the Lewis acidity and nucleophilicity of the metal center are inevitably correlated. Further studies of such synergic catalysis systems are now in progress in our laboratory.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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