Salicylaldimine−Aluminum Complexes for the Facile and Efficient Ring-Opening Polymerization of ϵ-Caprolactone

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Polyesters have provided significant benefits to our daily life, and some aliphatic ones are particularly receiving attention due to their practical biodegradability via our recent concerns with the environment as well as their biocompatibility for medical and pharmaceutical applications.[1] If certain criteria for a living/controlled polymerization are met, the ring-opening polymerization (ROP) of lactones is a powerful tool for synthesizing polyesters with the desired molecular weights and narrow polydispersities, both of which are important factors for controlling the polymer properties. Therefore, a number of initiators/catalysts have been developed using various combinations of ligands and metals,[2−7] and aluminum is one of the most studied metals among them. The initiators/catalysts in the living polymerization systems are isolated before use in most cases, while the isolation of metal complexes is often a time-consuming process in order to find a new well-defined molecular catalysis,[8,9] especially when screening various ligands to create the most appropriate environment around the metal center.[10] We examined the ROP of ϵ-caprolactone (CL) using a diphenyl-substituted homosalen complex,[11] which could be prepared in situ and was the most reactive catalyst for the polymerization of racemic lactide at 70 °C in our previous studies.[12] The initiation reaction immediately took place at 25 °C, while the propagation required 70 °C. These results prompted us to study the polymerization of CL using the Al−salicylaldimine ligand complexes without the linking of two salicylaldimines. Although isolation of some salicylaldimine−Al complexes[13] and their applications in the polymerization[14] have been reported, systematic investigations of ligand substituents for the polymerizations have been rarely reported.[14b,c] We now report a facile and efficient system of the ROP of CL at room temperature using the salicylaldimine−Al complex.

The polymerization of CL was examined at 25 °C in the presence of 1 mol % of benzyl alcohol (BnOH) using the complex prepared from 1 mol % of $AlEt_3$ and 2 mol % of the ligand in situ (70 °C for 1 h). In each case, the number-average degree of polymerization (DP_n) by ^1H NMR was quite consistent with the calculated one on the basis of the amount of BnOH, and the number-average molecular weight (M_n) by size exclusion chromatography (SEC) was estimated to be greater than those by ^1H NMR. The ^1H NMR spectra of all the PCLs indicated the presence of a benzyl ester group at 5.11 ppm (singlet, CH_2Ph) as the initiating terminus. The ligands with a sterically demanding imine moiety enhanced the polymerization (entries 1−5, Table 1), and 2,4,6-tri-*tert*-butylphenylimine gave the best result (entry 5). The electron-withdrawing substituents also somewhat enhanced the polymerizations in combination with steric effects (entries 6−9), and these results are in contrast to the bis(phenolato)bis(amine)−Al system reported by Hillmyer and Tolman,[4i] where the unprecedented electronic effects of the substituents were reported. The steric effects of the salicylidene moiety appeared sensitive. The methyl substituent at the 5-position of the salicylidene moiety (entry 10) had only a little effect on the reactivity compared to that of the nonsubstituted ligand (entry 5). On the other hand, the introduction of methyl or isopropyl substituents at the 3-position of the salicylidene moiety led to a high activity of the catalyst (entries 11−13). These results were in sharp contrast with those of the lactide polymerization using the salen− and homosalen−Al complexes,[12] in which bulky substituents hindered the polymerization. In the presence of sterically demanding substituents, more than a methyl group broadened the polydispersities (entries 13 and 14) or hindered the polymerization (entry 15). The Br substituent in the 3-position presumably might have shown steric effects (entry 16) like a methyl substituent rather than electronic effects. The most reactive and efficient catalyst was obtained by the ligand with the sterically demanding 2,4,6-tri-*tert*-butylphenylimine moiety[15] and a methyl substituent at the 3-position of the salicylidene moiety. Since the preparative ortho-formylation of 2,4-dimethylphenol for the synthesis of 3,5-dimethylsalicylaldehyde was more practical than that of 2-methylphenol,[16] we used the complex in entry 12 (complex **1**) in additional experiments.

We then examined the role of BnOH in the ROP of CL using the most efficient complex **1**. No reaction took place in the absence of BnOH (entry 17). In the case of a half amount of BnOH (0.50 mol %) to **1** (1.0 mol %), the DP_n value of the polymer gave a 2-fold number of the DP_n in entry 12 although the polydispersity index number (PDI) of PCL increased (entry 18). The polymerization with 2 equiv of BnOH (2.0 mol %) to **1** (1.0 mol %) afforded PCL of nearly half the DP_n (∼50) with a narrow polydispersity (entry 19) as does the immortal polymerization.[17] The results in entries 12, 18, and 19 suggested two mechanistic insights: (1) BnOH reacted with **1** to afford $L_nAl-OBn$, and the broad PDI in entry 18 was due to coexistence of ∼0.50 mol % of **1** (entries 12 and 18); (2) the alkoxide (−OR) exchanges between L_nAl-OR and H−OR should be faster than the propagation rate (entries 12 and 19). The opposite design of the ligand, which was prepared from aniline and bulky 3,5-di-*tert*-butylsalicylaldehyde, was not promising (entry 20). It is surprising that the salicylaldimine ligands derived from 2,4,6-tri-*tert*-butylaniline have been previously hardly utilized as ligands.[18,19]

PCL with a higher M_n (DP_n ∼ 300) was synthesized by the polymerization of 0.33 mol % of **1**−BnOH at 25 °C, and an almost quantitative conversion of CL was observed after 60 min (entry 1, Table 2).[20] The linear relationship between the monomer conversion and M_n with a narrow polydispersity indicated that the polymerization proceeded in a living/controlled manner. To obtain PCL in a short time, the reaction temperature

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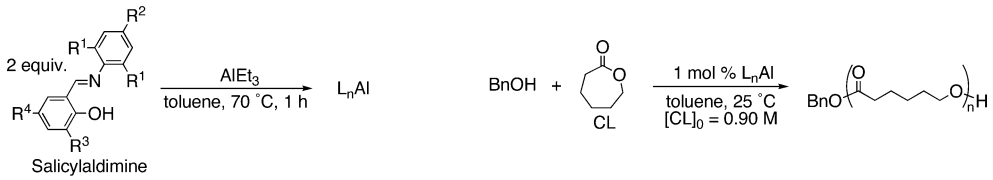
Table 1. Substituent Effects of Ligands[a]



entry	R^1	R^2	R^3	R^4	BnOH, mol %	time	conv,[b] %	DP_n by NMR	M_n,[c] $\times 10^3$	PDI[c,d]
1	H	H	H	H	1.0	24 h	31	34	8.9	1.0_6
2	Me	H				3 h	19	18	4.5	1.0_7
						24 h	80	81	19.6	1.2_7[e]
3	iPr	H				3 h	34	33	9.2	1.0_7
						24 h	97	97	26.6	1.1_9[e]
4	Ph	Ph				1 h	69	71	22.4	1.1_7
						2 h	92	91	30.5	1.1_6
5	tBu	tBu				1 h	86	92	26.1	1.1_8
6	F	F				3 h	25	25	6.5	1.0_8
						24 h	99	104	29.6	1.2_2[e]
7	H	Cl				24 h	31	30	6.7	1.0_5
8	Cl	H				3 h	28	27	8.5	1.0_8
						24 h	94	97	25.8	1.1_7
9	Cl	Cl				3 h	38	37	10.4	1.0_9
						24 h	98	97	27.4	1.1_4
10	tBu	tBu	H	Me		1 h	94	96	30.8	1.1_6
11			Me	H		10 min	95	96	29.2	1.1_6
12			Me	Me		10 min	96	96	29.8	1.1_6
13			iPr	H		10 min	94	97	29.7	1.2_8
14			Ph	H		10 min	89	104	33.1	1.2_6
15			tBu	tBu		10 min	47	47	18.1	1.1_6
16			Br	Br		10 min	72	80	27.3	1.1_4
17			Me	Me	0	10 min	0			
18					0.5	30 min	97	210	56.1	1.3_6
19					2.0	10 min	98	53	13.5	1.1_1
20	H	H	tBu	tBu	1.0	4 h	<1			

[a] Polymerization conditions: $AlEt_3$, 0.020 mmol; ligand, 0.040 mmol; toluene, 2.0 mL; CL, 2.0 mmol; temp, 25 °C; a N_2 atmosphere. [b] The crude samples were analyzed by 400 MHz ^1H NMR every 0.5−6 h (entries 1−9) or 10−30 min (entries 10−20). [c] The crude samples were analyzed by SEC (polystyrene standards in $CHCl_3$) without purification. [d] Polydispersity index number (M_w/M_n) of the crude samples. [e] The SEC traces had small shoulders in the higher molecular elution volume.

Table 2. Effects of Polymerization Temperature and Initial Concentration of CL[a]

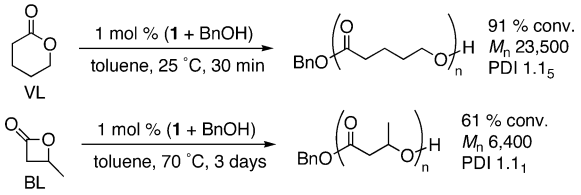
entry	temp, °C	$[CL]_0$[b]	time, min	conv,[c] %	M_n,[d] $\times 10^3$	PDI[d]
1	25	0.90	30	85	$62._9$	1.1_4
			60	98	$77._1$	1.1_6
2	50	0.90	10	98	$72._4$	1.2_5
3	50	4.7	2	81	$61._4$	1.1_8
4	70	0.90	2.5	83	$68._9$	1.1_6
5	70	4.7	1	91	$73._5$	1.1_9

[a] **1** (prepared in situ), 0.020 mol (0.33 mol %); BnOH, 0.020 mmol (0.33 mol %); CL, 5.9_6 mmol; toluene, 6.0 mL (entries 1, 2, and 4) or 0.60 mL (entries 3 and 5); a N_2 atmosphere. After the indicated reaction time, the reaction mixture was cooled at 0 °C and then immediately exposed to air to decompose the Al complex. [b] The initial concentration of CL. [c] Conversion of CL by ^1H NMR (400 MHz) of the crude samples. [d] The crude samples were analyzed by SEC ($CHCl_3$, polystyrene standards).

was elevated. At 50 °C, the monomer conversion reached 98% after 10 min at the same initial concentration of CL ($[CL]_0$) with a larger PDI (entry 2), probably due to the transesterification after the high conversion of CL. For the higher $[CL]_0$, a shorter polymerization time was sufficient (entry 3). The same tendency was observed at 70 °C (entries 4 and 5). Notably, PCL with $DP_n \sim 300$ could be synthesized in a few minutes at 50−70 °C in the present system.

Complex **1** was also effective for the polymerization of δ-valerolactone (VL) as shown in Scheme 1. Although the polymerization of β-butyrolactone (BL) was much slower even at 70 °C, poly(BL) with a narrow polydispersity was obtained until the monomer conversion

Scheme 1. Ring-Opening Polymerization of VL and BL



reached 60%. The PDI value became higher at the higher conversions; 6 days, 82% conversion, M_n 8600, PDI 1.2_0; 9 days, 88% conversion, M_n 9000, PDI 1.2_5.

The structure of complex **1** was examined. A clean ^1H NMR spectrum of the complex prepared from 1 equiv of the ligand (L−H) to $AlEt_3$ in toluene-d_8 indicated the formation of $LAlEt_2$ in which the phenolic proton (ArO−H) was completely consumed.[21] In addition to the assigned peaks of the $LAlEt_2$ complex, some other minor peaks were also detected.[22] Free rotation of ArO−Al was restricted by coordination of the pendant Schiff base nitrogen to the Al center, which made the methylene protons of the ethyl groups diastereotopic (Figure 1a). This complex (1 mol %) in the presence of BnOH (1 mol %) needed 1 h to reach >90% conversion of CL. It suggested that complex **1** is formed by the reaction of 2 equiv of the ligand to $AlEt_3$, although it is known that the second equivalent of the analogous ketimine (L′−H) reacts very slowly with $L'AlR_2$.[23,24] Using the 2 equiv of the ligand to $AlEt_3$, the peaks of $LAlEt_2$ were not detected. To our surprise, *all ten Csp^2−H's, six tBu's, and four Csp^2−CH_3's individually appeared in ^1H NMR,*

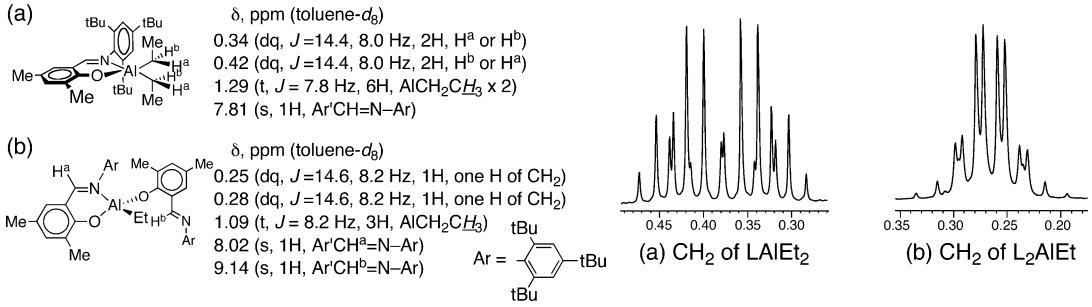


Figure 1. ^{1}H NMR assignment (400 MHz) of Et groups and imine protons: (a) $LAlEt_2$; (b) L_2AlEt.

and two imine protons are under a very different environment (8.02 and 9.14 ppm). These suggested that one ligand chelated the Al center but the other was monodentate (Figure 1b), and the conformation is highly restricted. It is known that the chemical shifts of the ^{27}Al NMR correspond to the coordination number of the Al center.[25] Unfortunately, no peak of **1** was obtained in the 350 ppm range from −70 to 280 ppm, probably due to the extremely low symmetric property around the Al center. So far we have not succeeded in obtaining single crystals of **1** for an X-ray diffraction analysis but only a powdery complex. The structure of **1** in the presence of 1 equiv of BnOH was examined, and the free ligand (L−H) and unidentified complex compounds in addition to complex **1** were detected in ^{1}H NMR (toluene-d_8). The active species of the present system is still under investigation.

In conclusion, a facile and efficient catalytic system of salicylaldimine−aluminum complexes for the ROP of CL was realized through a systematic exploration of the ligand substituents. Such studies of designing ligands will be informative for the development of finely tuned catalysts/initiators. The in-situ reaction between the ligand and $AlEt_3$ is clean enough to directly use the complex to achieve the living/controlled ROP of CL. Further details of the polymerizations of CL, the active species of the Al complex in the presence of BnOH, and applications to other monomers using **1** are now under investigation in our laboratory.

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Supporting Information Available: Experimental details, NMR data of the $LAlEt_2$ (^{1}H, ^{13}C, and ^{1}H−^{13}C (HMQC)), complex **1** (^{1}H, ^{13}C, ^{1}H−^{13}C (HMQC), and ^{27}Al), and **1** in the presence of 1 equiv of BnOH (^{1}H). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) The minor peaks detected in the synthesis of $LAlEt_2$ turned out to be those of L_2AlEt. The concentration of $AlEt_3$ that we used should have been slightly lower (~4%) than we calculated. It was consistent with 4% of L_2AlEt in the synthesis of $LAlEt_2$ and the free ligand L−H (~8%) in the synthesis of L_2AlEt.

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