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Improvement in Aluminum Complexes Bearing Schiff Bases in Ring-Opening Polymerization of ε-Caprolactone: A Five-Membered-Ring System

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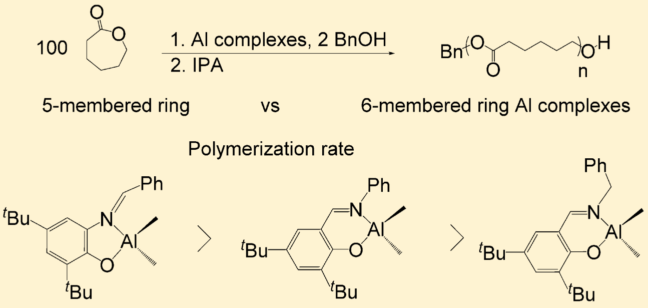
Supporting Information

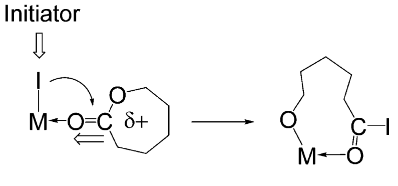
ABSTRACT: A series of five- and six-membered-ring Al complexes bearing Schiff bases was synthesized and their application to the ring-opening polymerization of ε-caprolactone (CL) was studied. The five-membered-ring Al complexes have been shown to have a significantly higher polymerization rate than six-membered-ring Al complexes (2−3 fold for CL polymerization). The X-ray data revealed that the Al center of a five-membered-ring Al complex is farther from the Schiff base ligand than is that of a six-membered-ring Al complex. The results of density functional theory calculations also suggest that more space around the Al center of five-membered-ring Al complexes may reduce the steric repulsion in CL polymerization and increase the catalytic activity of five-membered-ring Al complexes.



■ INTRODUCTION

Poly-ε-caprolactones (PCLs) are commercially available biomaterials and are extensively used in assorted fields because of their biodegradability, biocompatibility, and permeability.[1] PCL is typically synthesized through ring-opening polymerization (ROP), as ROP can offer greater molecular weight control of polymers than traditional polycondensation.[2] Many metal complexes[3] have been used as Lewis acids to increase the positive charge of carbonyl groups for easy access to the ROP of cyclic esters (Scheme 1). Among them, Al complexes[4−10] are suitable catalysts for ROP because of their strong Lewis acidity, ease of synthesis, and low-cost precursors. There have been several reports for the catalytic activity of cyclic ester ROP by utilizing Al complexes[4] bearing Schiff base ligands as catalysts because of the ease of synthesis of diverse substituents of Schiff base ligands. The results showed that the polymerization rate of cyclic ester ROP could be influenced through the steric and electronic effects of a phenolate or phenylimino group on these Al complexes bearing Schiff base ligands. In general, Al complexes bearing sterically bulky[4b,l,o,q,u] or electron-withdrawing[4b−d,k−n,p] substituents displayed higher catalytic activity. However, no study has reported the influence of the geometric structure of Al catalysts bearing Schiff base ligands on the catalytic activity of cyclic ester ROP.

Scheme 1. Role of a Metal Catalyst in the ROP of Cyclic Esters



Our group studied Ti complexes[11] with various Schiff base ligands and found that the different steric effects of these ligands altered the coordinated form and further influenced the monomer coordination and hence the catalytic activities of L-lactide (LA) and ε-caprolactone (CL) polymerizations. In continuing our research, we extend our work to Al complexes and found that Al complexes with Schiff base ligands are mostly six-membered-ring structures (Figure 1a). We wonder if the catalytic behavior of CL polymerization should be influenced by switching to five-membered-ring Al complexes bearing Schiff base ligands (Figure 1b). Herein, we report the synthesis of

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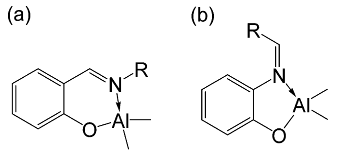

Figure 1. (a) Six-membered-ring and (b) five-membered-ring structures of Al complexes bearing Schiff base ligands.

various Al complexes with Schiff base ligands in both five- and six-membered-ring structures and the study of their structure−function relationship in catalytic ROP.

RESULTS AND DISCUSSION

Synthesis and Characterization of Al Complexes. 2-Amino-4,6-di-*tert*-butylphenol[12] was prepared through the reduction of 2,4-di-*tert*-butyl-6-nitrophenol, which was synthesized through the nitration of 2,4-di-*tert*-butylphenol (Figure 2). The five-membered-ring Schiff base ligands were formed after condensation reactions of 2-amino-4,6-di-*tert*-butylphenol with various aldehydes. All ligands reacted with a stoichiometric amount of trimethylaluminum in toluene to produce Al compounds (Figure 2). The Al complexes of six-membered-ring form were also synthesized through the aforementioned method for comparison. **L$^{6\text{-Thio}}$AlMe$_2$** could not be isolated as pure product because precipitation was hard due to its high solubility in hexane. However, we were lucky to get crystals from NMR tube by simple evaporation. Its formula and structure were confirmed through ^{1}H and ^{13}C NMR spectra, elemental analysis, and X-ray crystal analysis. The X-ray structure of **L$^{5\text{-Ph}}$AlMe$_2$** (Figure 3, CCDC 1487513) illustrated the distorted-tetrahedral geometry of the Al complex with two methyl groups. The Al atom sits 0.443 Å above the phenyl ring plane, which falls in the range of that of the six-membered-ring Schiff base Al complexes[4] (0.00−0.927 Å). The distances between the Al atom and N, O, C(22), and C(23) are 2.024(2), 1.783(2), 1.961(2), and 1.958(2) Å, respectively. The N−Al−O and C(22)−Al−C(23) angles are 85.39(7) and 122.17(10)°,

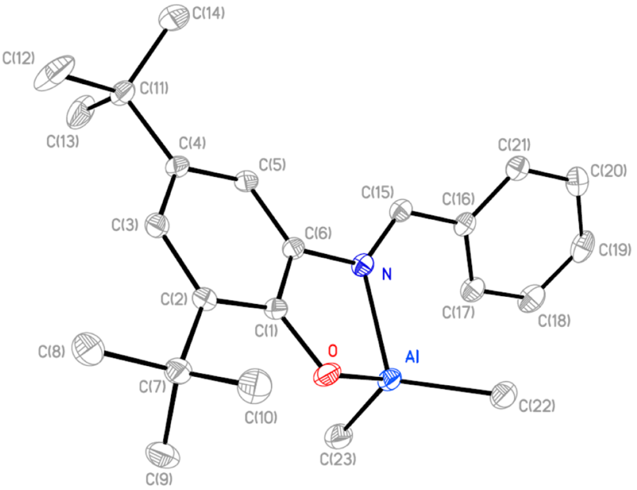

Figure 3. Molecular plot of **L$^{5\text{-Ph}}$AlMe$_2$** with 30% probability ellipsoids (all of the hydrogen atoms are omitted for clarity). Selected distances and angles: d(Al−O) = 1.7833(15) Å, d(Al−N) = 2.0240(17) Å, d(Al−C22) = 1.961(2) Å, d(Al−C23) = 1.958(2) Å; ∠O−Al−N = 85.39(7)°, ∠C22−Al−C23 = 122.17(10)°].

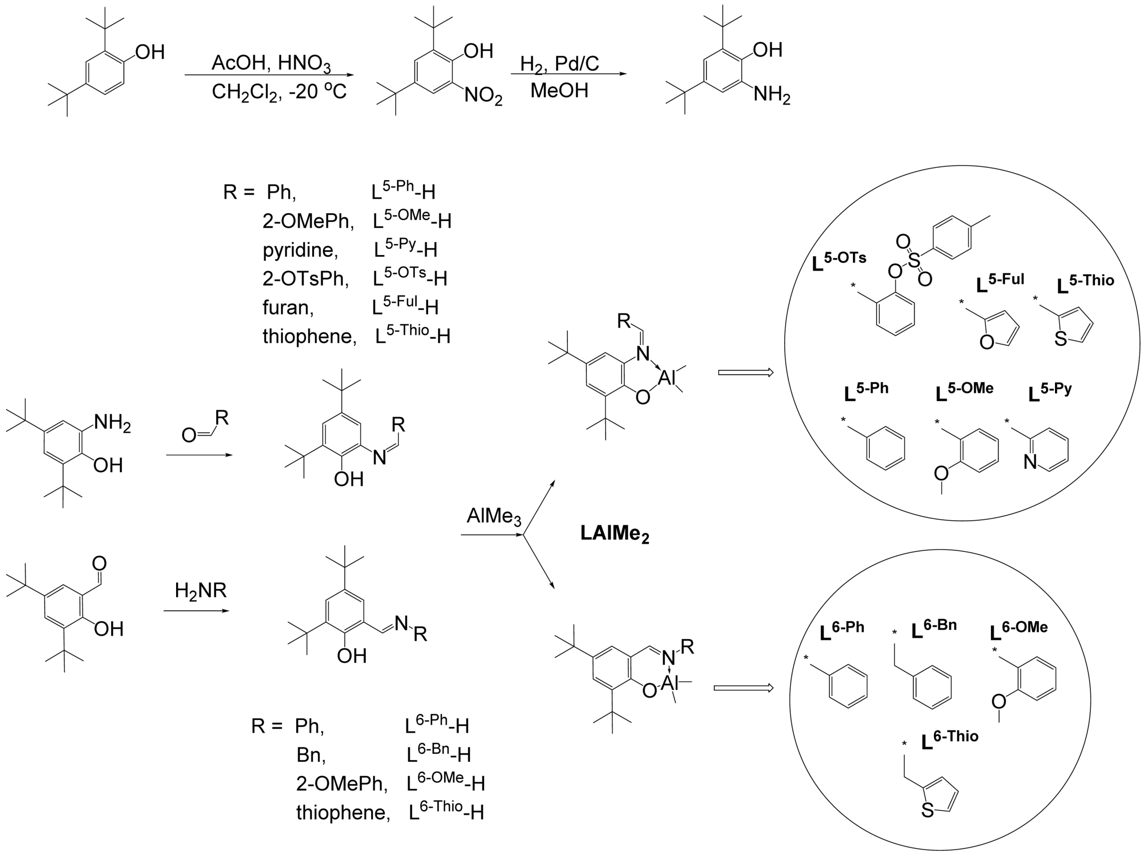

Figure 2. Synthesis of ligands and their Al complexes.

respectively. The X-ray structure of $\mathbf{L}^{5\text{-OMe}}\mathbf{AlMe}_2$ (Figure 4, CCDC 1487514) showed bond angles and bond lengths similar to those of $\mathbf{L}^{5\text{-Ph}}\mathbf{AlMe}_2$ (d(Al−N) = 2.007(2) Å, d(Al−O(1)) = 1.793(2) Å, d(Al−C23) = 1.952(3) Å, d(Al−C24) = 1.958(3) Å, ∠O(1)−Al−N = 85.92(8)°, ∠C(23)−Al−C(24) = 120.70(13)°). In addition, there is no interaction between the Al atom and the methoxy group (d(Al−O(2)) = 4.947 Å). For the six-membered-ring $\mathbf{L}^{6\text{-Thio}}\mathbf{AlMe}_2$ (Figure 5, CCDC 1487512), the distances between the Al atom and N, O, C(21), and C(22) are 1.971(2), 1.782(2), 1.956(2), and 1.960(2) Å, respectively. The N−Al−O and C(21)−Al−C(22) angles are 93.96(7) and 119.06(11)°, respectively. These values are comparable to the reported values in the literature for six-membered-ring Al complexes bearing Schiff base ligands: bond lengths range from 1.934[4q] to 1.983 Å[4s] for the Al−CH_3 bond, from 1.756[13] to 1.796 Å[4r] for the Al−O bond, and from 1.954[4s] to 2.027 Å[4q] for the Al−N bond. The angles are from 112.94[4o] to 123.25°[4r] for ∠C−Al−C and from 91.89[4r] to 95.74°[4r] for ∠O−Al−N. A significant difference between five- and six-membered-ring dimethyl Al complexes bearing Schiff base ligands is that the ∠O−Al−N angle of five-membered-ring Al complexes was smaller than that of six-membered-ring Al complexes by approximately 6°. This implies that there is more vacant space around the Al center of five-membered-ring Al complexes for potential substrate binding. This might contribute to the enhanced catalytic activity for five-membered-ring Al complexes (vide infra).

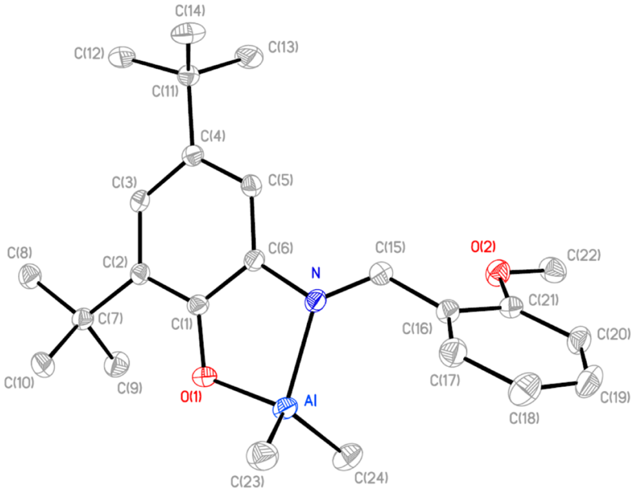

Figure 4. Molecular plot of $\mathbf{L}^{5\text{-OMe}}\mathbf{AlMe}_2$ with 30% probability ellipsoids (all of the hydrogen atoms are omitted for clarity). Selected distances and angles: d(Al−O) = 1.7932(19) Å, d(Al−N) = 2.007(2) Å, d(Al−C23) = 1.952(3) Å, d(Al−C24) = 1.958(3) Å; ∠O−Al−N = 85.92(8)°, ∠C23−Al−C24 = 120.70(13)°.

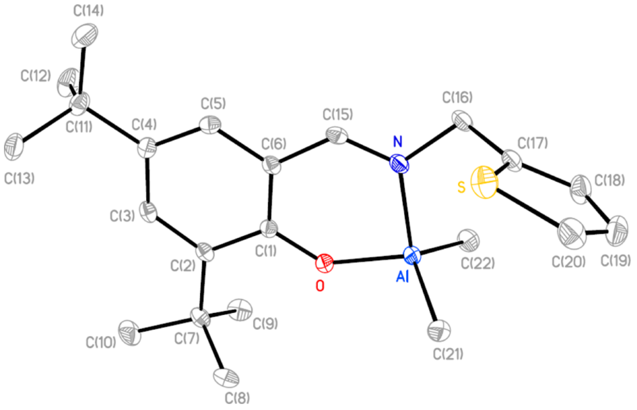

Figure 5. Molecular plot of $\mathbf{L}^{6\text{-Thio}}\mathbf{AlMe}_2$ with 30% probability ellipsoids (all of the hydrogen atoms are omitted for clarity), Selected distances and angles: d(Al−O) = 1.7815(15) Å, d(Al−N) = 1.9714(19) Å, d(Al−C21) = 1.956(2) Å, d(Al−C22) = 1.960(2) Å; ∠O−Al−N = 93.96(7)°, ∠C21−Al−C22 = 119.06(11)°.

Polymerization of ε-Caprolactone. Polymerizations of CL were studied by using all Al complexes except $\mathbf{L}^{6\text{-Thio}}\mathbf{AlMe}_2$ because of its low purity. Two equivalents of BnOH in toluene was used as an initiator (Table 1). As shown in entries 1−3 of Table 1, the positive effect of $\mathbf{L}^{5\text{-Ph}}\mathbf{AlMe}_2$ over $\mathbf{L}^{6\text{-Ph}}\mathbf{AlMe}_2$ and $\mathbf{L}^{6\text{-Bn}}\mathbf{AlMe}_2$ is evident, as only 2.5 h was required to reach 89% conversion of PCL for catalyst $\mathbf{L}^{5\text{-Ph}}\mathbf{AlMe}_2$, whereas times of 7 and 9 h were required for $\mathbf{L}^{6\text{-Ph}}\mathbf{AlMe}_2$ and $\mathbf{L}^{6\text{-Bn}}\mathbf{AlMe}_2$, respectively. In addition, $\mathbf{L}^{5\text{-Ph}}\mathbf{AlMe}_2$ afforded greater control of polymer molecular weight at levels comparable with M_n(calcd), M_n(NMR), and M_n(GPC) and narrow polydispersity indexes (PDI) (M_n(NMR) = 5000, M_n(GPC) = 4000, PDI = 1.17). Moreover, the PCL of entry 1 synthesized by $\mathbf{L}^{6\text{-Ph}}\mathbf{AlMe}_2$ gave a larger M_n(GPC) in comparison to M_n(NMR) and a broad PDI (1.73). Although $\mathbf{L}^{6\text{-Ph}}\mathbf{AlMe}_2$ had higher catalytic activity than $\mathbf{L}^{6\text{-Bn}}\mathbf{AlMe}_2$, the controllability of $\mathbf{L}^{6\text{-Ph}}\mathbf{AlMe}_2$ was lower than that of $\mathbf{L}^{6\text{-Bn}}\mathbf{AlMe}_2$. This also showed that the catalytic activity of six-membered Al complexes could be influenced greatly through different N substituents of Schiff base ligands. On the basis of these results, we decided to choose $\mathbf{L}^{5\text{-Ph}}\mathbf{AlMe}_2$ for catalytic PCL studies and scrutinized it with various substituted anilines such as Me, pyridine, OTs, benzyl, furan, and thiophene. A comparison of five-membered-ring Al complexes bearing Schiff base ligands with various substituents on an N-aromatic ring revealed that $\mathbf{L}^{5\text{-OTs}}\mathbf{AlMe}_2$ is the most effective catalyst. We compared one of the anilines substituted with a methoxy group with six-membered $\mathbf{L}^{6\text{-OMe}}\mathbf{AlMe}_2$ (entry 4, Table 1), and it also showed lower efficiency in comparison with five-membered $\mathbf{L}^{5\text{-OMe}}\mathbf{AlMe}_2$ (entry 5, Table 1). These results strongly suggest that the five-membered-ring complexes are favored for PCL.

The satisfactory results of CL polymerization using $\mathbf{L}^{5\text{-Ph}}\mathbf{AlMe}_2$ are evident from the linear relationship between M_n(GPC) and $[\text{monomer}]_0 \times \text{conversn}/[\text{BnOH}]_0$ (entries 3 and 10−13 in Table 1 and Figure 6), as well as from the low PDIs (1.12−1.27). The ^{1}H NMR spectrum of PCL (entry 9, Table 1) confirmed one benzyl group (phenyl group for peak a and methylene group for peak b) and hydroxyl chain ends (peak c) with an integral ratio of 5:2:2, suggesting that initiation occurred through BnOH insertion into CL (Figure 7).

Kinetic Study of ε-Caprolactone Polymerization by Five- and Six-Membered-Ring Al Complexes. The results of the kinetic study on CL polymerization at room temperature by five- and six-membered-ring Al complexes are presented in Table 2 and Figures S1 and S2 in the Supporting Information. The five-membered-ring Al catalysts showed a significantly higher polymerization rate than did the six-membered-ring Al catalysts (2−3-fold for CL polymerization). In addition, the reaction time required from BnOH and dimethyl Al complex to Al benzyl alkoxide (**induction period**)[6b] of five-membered-ring Al catalysts (1−35 min) is significantly shorter than that of six-membered-ring Al catalysts (109−227 min). The higher catalytic activity and shorter induction period when five-

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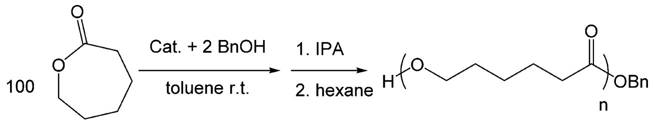
Table 1. Polymerization of CL Catalyzed by Five- and Six-Membered-Ring Al Complexes[a]



	L of $\mathbf{LAlMe_2}$	time (min)	conversn[b] (%)	M_n(calcd)[c] (g mol^{-1})	M_n(NMR)[b] (g mol^{-1})	M_n(GPC)[d] (g mol^{-1})	PDI[d]
1	$\mathbf{L}^{6\text{-Ph}}$	50/540	10/90	5200	5900	7700	1.73
2	$\mathbf{L}^{6\text{-Bn}}$	70/1500	11/94	5500	3800	3900	1.13
3	$\mathbf{L}^{5\text{-Ph}}$	60/150	50/89	5200	5000	4000	1.17
4	$\mathbf{L}^{6\text{-OMe}}$	60/500	0/95	5500	6100	7700	1.44
5	$\mathbf{L}^{5\text{-OMe}}$	60/240	32/94	5500	7600	7000	1.23
6	$\mathbf{L}^{5\text{-Py}}$	60/540	10/91	5300	11000	13700	1.41
7	$\mathbf{L}^{5\text{-OTs}}$	60/120	54/90	5200	5300	3100	1.08
8	$\mathbf{L}^{5\text{-Ful}}$	60/1640	5/75	4300	4700	3300	1.10
9	$\mathbf{L}^{5\text{-Thio}}$	50/1460	10/85	5000	3800	3500	1.21
10[e]	$\mathbf{L}^{5\text{-Ph}}$	120	>99	2900	2700	2800	1.12
11[f]	$\mathbf{L}^{5\text{-Ph}}$	200	>99	8500	9000	9700	1.20
12[g]	$\mathbf{L}^{5\text{-Ph}}$	240	87	11400	13000	13900	1.27
13[h]	$\mathbf{L}^{5\text{-Ph}}$	1520	90	25800	35800	41600	1.29

[a]Reaction conditions unless specified otherwise: toluene (5 mL), $[M]_0/[cat.]_0/[BnOH]_0 = 100/1/2$, [CL] = 2.0 M, at room temperature. [b]Obtained from ^{1}H NMR analysis. [c]Calculated from (molecular weight of monomer) × $[\text{monomer}]_0/[BnOH]_0$ × (conversion yield) + M_w(BnOH). [d]Obtained from GPC analysis and calibration based on the polystyrene standard. Values of M_n(GPC) are the values obtained from GPC times 0.56. [e]Reaction conditions: toluene (5 mL), $[M]_0/[cat.]_0/[BnOH]_0 = 50/1/2$, [CL] = 1.0 M, at room temperature. [f]Reaction conditions: toluene (5 mL), $[M]_0/[cat.]_0/[BnOH]_0 = 150/1/2$, [CL] = 3.0 M, at room temperature. [g]Reaction conditions: toluene (5 mL), $[M]_0/[cat.]_0/[BnOH]_0 = 200/1/2$, [CL] = 4.0 M, at room temperature. [h]Reaction conditions: toluene (5 mL), $[M]_0/[cat.]_0/[BnOH]_0 = 500/1/2$, [CL] = 10.0 M, at room temperature.

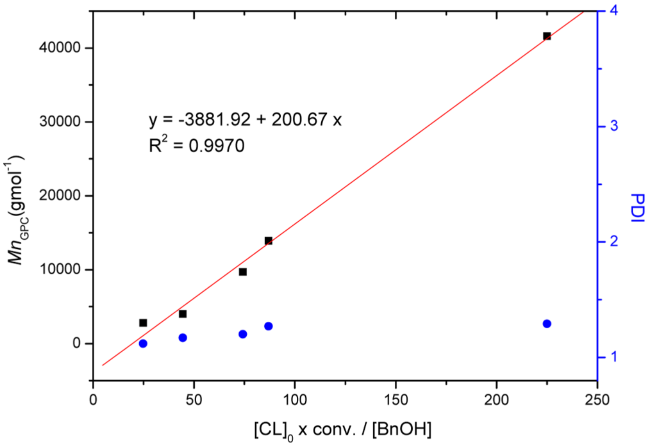


Figure 6. Linear plot of M_n(GPC) vs $[CL]_0$ × conversn/[BnOH], with PDI values indicated by blue dots (entries 3 and 10−13 in Table 1).

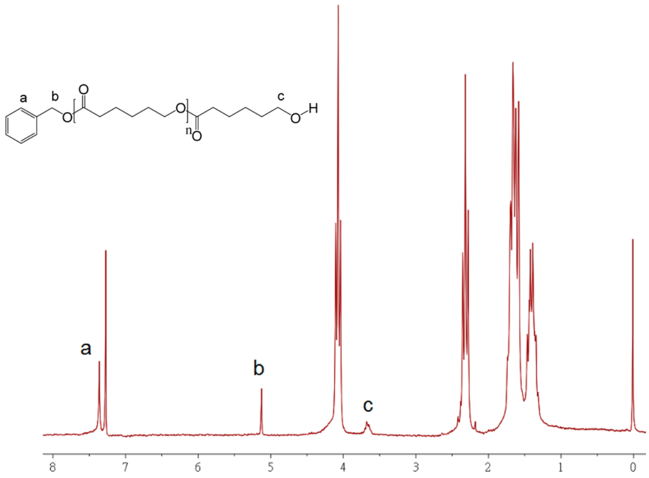


Figure 7. ^{1}H NMR spectrum of PCL (entry 9 of Table 1) with BnOH as an initiator.

membered-ring Al catalysts are used may be attributed to the larger empty space around its Al center, making coordination of CL and BnOH to the Al center much easier. This facilitates the initiation of CL and increases the rate of benzyl alkoxide formation. To prove our theory, the reactions of 2 equiv of BnOH and 1 equiv of Al complex ($\mathbf{L^{5\text{-OMe}}AlMe_2}$ and $\mathbf{L^{6\text{-OMe}}AlMe_2}$, respectively) were monitored by ^{1}H NMR (Figures S26 and S27 in the Supporting Information) to give insight into the induction period in PCL. The peak of the methyl group on Al atom (−9.23 ppm) disappeared after 30 min for $\mathbf{L^{5\text{-OMe}}AlMe_2}$ but after 240 min for $\mathbf{L^{6\text{-OMe}}AlMe_2}$. This clearly showed that five-membered-ring Al complexes could transform the dimethyl Al complex to the Al benzyl alkoxide much more quickly. It is noted, however, for five-membered-ring Al catalysts bearing N substituents with chelating properties such as $\mathbf{L^{5\text{-Ful}}AlMe_2}$, $\mathbf{L^{5\text{-Thio}}AlMe_2}$, and $\mathbf{L^{5\text{-Py}}AlMe_2}$, lower polymerization rates yet still shorter induction periods are observed. One possible reason is that the chelating groups may coordinate to an Al atom, weaken the methyl−Al bond, and facilitate benzyl alkoxide formation to give a shorter induction period. However, the same chelating feature may hinder the initial coordination of CL and hence give a lower polymerization rate in comparison to unsubstituted $\mathbf{L^{5\text{-Ph}}AlMe_2}$. In fact, such an argument on the reduction of CL coordination to the Al center by chelating groups has been reported previously.[6b] Only $\mathbf{L^{5\text{-OTs}}AlMe_2}$ has a higher catalytic activity than does $\mathbf{L^{5\text{-Ph}}AlMe_2}$ and, at this moment, the reason is unclear and further studies are in progress. In addition, the catalytic activity of $\mathbf{L^{6\text{-OMe}}AlMe_2}$ is higher than that of $\mathbf{L^{6\text{-Ph}}AlMe_2}$ and $\mathbf{L^{6\text{-Bn}}AlMe_2}$, and the induction period of $\mathbf{L^{6\text{-OMe}}AlMe_2}$ is longer than that of $\mathbf{L^{6\text{-Ph}}AlMe_2}$ and $\mathbf{L^{6\text{-Bn}}AlMe_2}$. This is totally the opposite of what is observed in five-

Table 2. Observed Rate Constants (k_{obs}) for Polymerization of CL Catalyzed by Five- and Six-Membered-Ring Al Complexes with 2 equiv of BnOH in Toluene at Room Temperature[a]

entry	L in $LAlMe_2$	k_{obs} (error), 10^{-3} min^{-1}	induction period (error), min
1	$L^{6\text{-Ph}}$	5.51(34)	129(23)
2	$L^{6\text{-Bn}}$	2.07(60)	147(27)
3	$L^{5\text{-Ph}}$	15.79(92)	12(5)
4	$L^{6\text{-OMe}}$	8.65(88)	227(37)
5	$L^{5\text{-OMe}}$	9.02(10)	13(4)
6	$L^{5\text{-Py}}$	5.95(2)	35(8)
7	$L^{5\text{-OTs}}$	19.52(130)	14(5)
8	$L^{5\text{-Ful}}$	1.30(3)	10(7)
9	$L^{5\text{-Thio}}$	1.28(2)	0

[a] The observed k_{obs} value is the slope of the first-order kinetic plot of ε-caprolactone polymerization with time. The conversion of ε-caprolactone with time was monitored by ^{1}H NMR.

membered-ring Al catalysts. This implies that substituted groups have different effects on these Al complexes with different ring sizes. A possible scenario that may explain why the catalytic activity of $\mathbf{L^{6\text{-OMe}}AlMe_2}$ is higher than that of $\mathbf{L^{6\text{-Ph}}AlMe_2}$ and $\mathbf{L^{6\text{-Bn}}AlMe_2}$ is that the extra pendant group could induce the formation of more active dinuclear Al complexes.[4i,q−s,5e] However, more work is required to verify these details.

Furthermore, kinetic studies were performed at room temperature to examine the effect of the $[CL]_0/[\mathbf{L^{5\text{-OMe}}AlMe_2} + 2\ BnOH]$ ratio ([CL] = 2.0 M in 5 mL of toluene), as described in Table S2 in the Supporting Information and Figure 8. The preliminary results indicated a first-order dependence on [CL] (Figure 8). When k_{obs} was plotted against $[\mathbf{L^{5\text{-OMe}}AlMe_2} + 2\ BnOH]$, a k_{prop} value of 0.296 M^{-1} min^{-1} was obtained (Figure 9). Polymerizing CL using $\mathbf{L^{5\text{-OMe}}AlMe_2}$ at room temperature demonstrated the following rate law:

$$d[CL]/dt = 0.296 \times [CL][\mathbf{L^{5\text{-OMe}}AlMe_2} + 2BnOH]$$

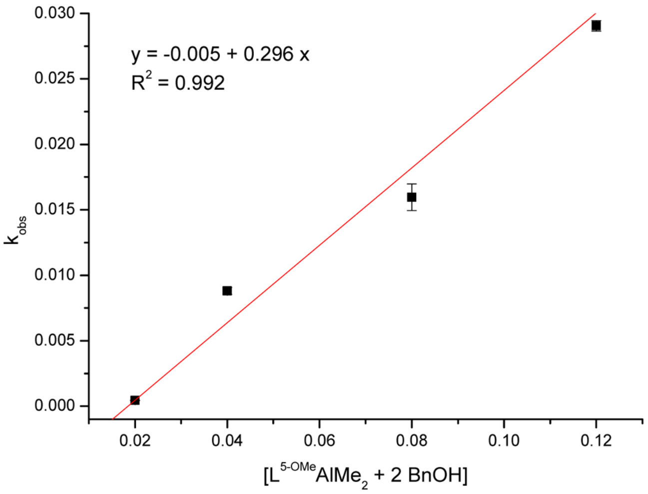


Figure 9. Linear plot of k_{obs} against $[\mathbf{L^{5\text{-OMe}}AlMe_2} + 2\ BnOH]$ for CL polymerization with [CL] = 2.0 M in toluene (5 mL).

Mechanistic Study of ε-Caprolactone Polymerization by Five- and Six-Membered-Ring Al Complexes.

According to the literature,[14] a possible mechanism is proposed in Figure 10. Formation of the benzyl alkoxide by attack of the methyl groups on the Al center by BnOH is believed to be what happened in the induction period. Monitoring the disappearance of ^{1}H NMR signals on the methyl group (Figure S26 in the Supporting Information) of $\mathbf{L^{5\text{-OMe}}AlMe_2}$ on reaction with BnOH (1:2) suggests that methyl groups of $\mathbf{L^{5\text{-OMe}}AlMe_2}$ are replaced by benzyl alcohols to form the real catalysts, $\mathbf{L^{5\text{-Ph}}Al(OBn)_2}$, before polymerization starts.[4l,t,6b,14] The lactone can coordinate to Al via carbonyl oxygen, resulting in the formation of the trigonal-bipyramidal five-coordinated Al complex **Al-CL**. One of the benzyl alkoxides undertakes a nucleophilic attack on a carbonyl carbon to form the intermediate **Al-CL-OBn**. This species then rotates to form **Al-CL-OBn′** and further chelates to the Al center in the bidentate mode, forming $\mathbf{Al_{C\text{-}O\text{-}Al\text{-}O}}$. This is immediately

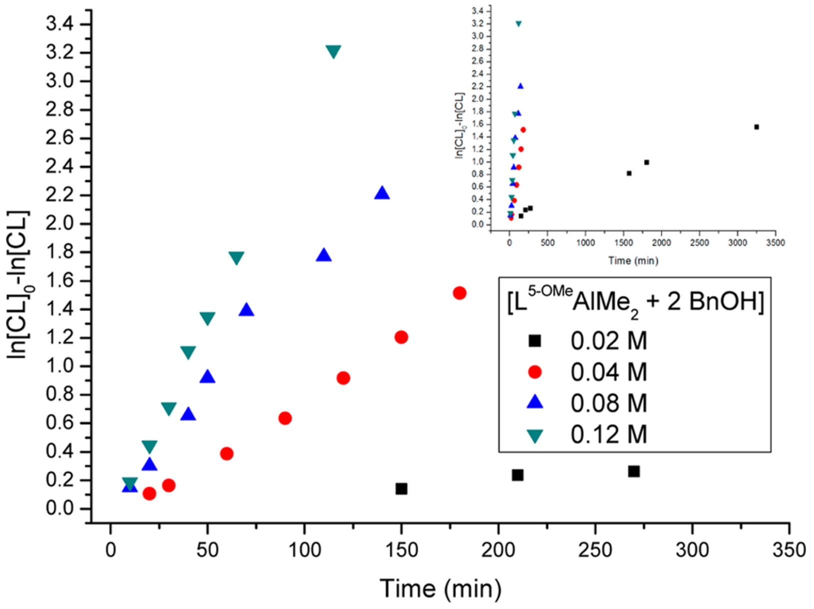


Figure 8. First-order kinetic plots of CL polymerization with various concentrations of $[\mathbf{L^{5\text{-OMe}}AlMe_2} + 2\ BnOH]$ plotted against time with [CL] = 2.0 M in toluene (5 mL).

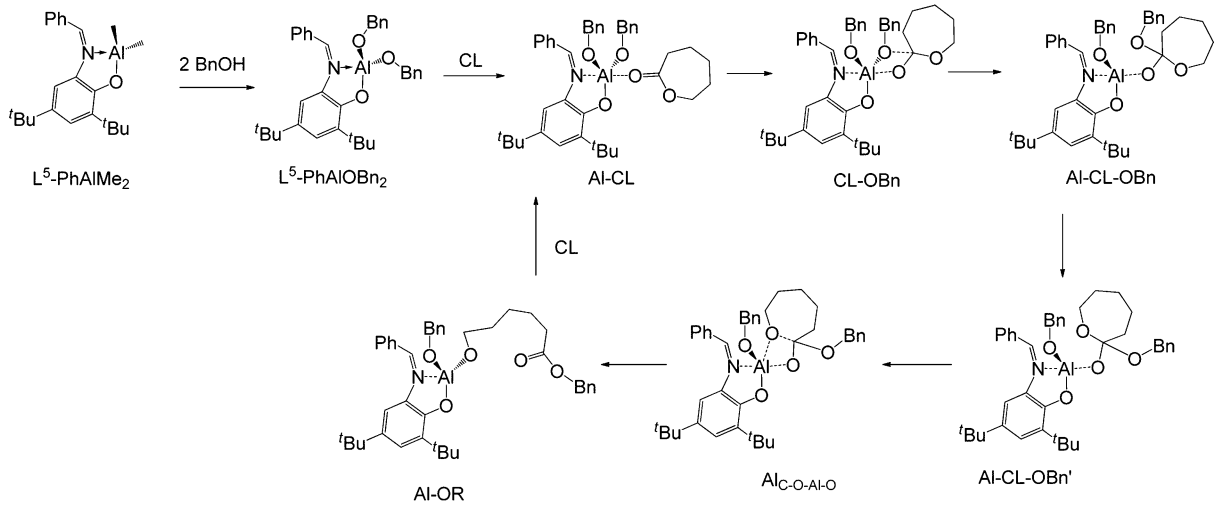


Figure 10. Mechanistic study on CL polymerization by using **L$^{5\text{-Ph}}$AlMe$_2$** as a catalyst.

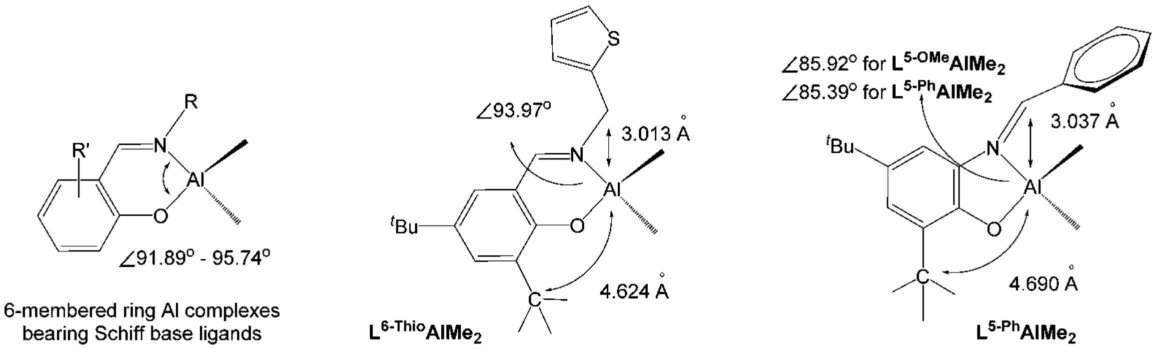


Figure 11. Geometries of five- and six-membered-ring Al complexes bearing Schiff base ligands.

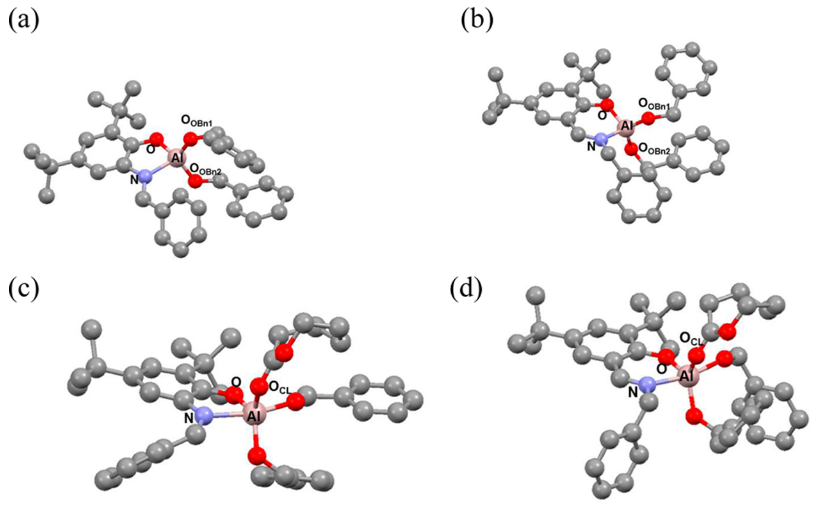


Figure 12. Optimized structures: (a) **L$^{5\text{-Ph}}$Al(OBn)$_2$**, d(Al−O) = 1.789 Å, d(Al−N) = 1.998 Å, ∠O−Al−N = 87.17°; (b) **L$^{6\text{-Ph}}$Al(OBn)$_2$**, d(Al−O) = 1.791 Å, d(Al−N) = 1.943 Å, ∠O−Al−N = 95.05°; (c) **CL-Al(L$^{5\text{-Ph}}$)(OBn)$_2$**, d(Al−O) = 1.818 Å, d(Al−N) = 2.145 Å, d(Al−O$_{\text{CL}}$) = 1.951 Å, ∠O−Al−N = 80.33°; (d) **CL-Al(L$^{6\text{-Ph}}$)(OBn)$_2$**, d(Al−O) = 1.815 Å, d(Al−N) = 2.062 Å, d(Al−O$_{\text{CL}}$) = 1.985 Å, ∠O−Al−N = 88.01°. Hydrogen atoms are omitted for clarity.

followed by a ring-opening step and recovery of the active state **Al-OR**. The tetrahedral four-coordinated complex **Al-OR** can accommodate another lactone to repeat the ring-opening polymerization. The comparison of X-ray structures between five- and six-membered-ring Al complexes revealed that the bite angles (∠O−Al−N) of six-membered-ring dimethyl Al complexes[4r] bearing Schiff base ligands are larger (91.89−95.74°) than those of five-membered-ring complexes (85.39° for **L$^{5\text{-Ph}}$AlMe$_2$** and 85.92° for **L$^{5\text{-OMe}}$AlMe$_2$**). The smaller bite angle ∠O−Al−N makes the five-membered ring significantly more puckered than the six-membered ring. The result is that the Al center of a five-membered-ring Al complex is farther from the Schiff base ligand than is that of a six-membered-ring Al complex. With **L$^{6\text{-Thio}}$AlMe$_2$** as an example, the distance between the Al atom and the quaternary carbon atom on the ortho position of the phenolate group is 4.624 Å, and the distance between the Al atom and the methylene group of the thiophen-2-ylmethyl group is 3.013 Å (Figure 11). However, the Al center of **L$^{5\text{-Ph}}$AlMe$_2$** is far from the Schiff base ligand (distance between the Al atom and the quaternary carbon atom on the ortho position of the phenolate group 4.690 Å; distance between the Al atom and the methylene group of the benzyl group 3.037 Å). It is reasonable to assume that **CL-OBn** in the CL polymerization process by using a five-membered-ring Al complex is more stable than that of a six-membered-ring Al complex because of less steric repulsion, and this stability increases the polymerization rate.

To shed light on the influence of the steric congestion, we further accessed the structural features and stabilities of five- and six-membered-ring Al complexes by means of density functional theory (DFT) calculations. ROP catalysts **L$^{5\text{-Ph}}$Al(OBn)$_2$** and **L$^{6\text{-Ph}}$Al(OBn)$_2$** were optimized at the B3LYP-D3/6-31g*/PCM(toluene) level. The calculated O−Al−N bite angles for **L$^{5\text{-Ph}}$Al(OBn)$_2$** and **L$^{6\text{-Ph}}$Al(OBn)$_2$** are respectively similar to their dimethyl analogues (Figure 12a,b). To measure the occupied space, the percent buried volume (%V_{bur})[15] was theoretically analyzed with the SambVca suite.[16] The results show that **L$^{6\text{-Ph}}$Al(OBn)$_2$** is more sterically crowded than **L$^{5\text{-Ph}}$Al(OBn)$_2$**, as their %V_{bur} values are 74.3 and 60.1, respectively. Since the CL-coordinated complex plays a crucial role in the polymerization process, the bond dissociation energies (BDEs) of corresponding **CL-Al(L)(OBn)$_2$** complexes were computed. Both optimized structures of **CL-Al(L$^{5\text{-Ph}}$)(OBn)$_2$** and **CL-Al(L$^{6\text{-Ph}}$)(OBn)$_2$** are best described as a distorted TBP with an Al−O$_{\text{CL}}$ distance of 1.951 Å in **CL-Al(L$^{5\text{-Ph}}$)(OBn)$_2$** and 1.985 Å in **CL-Al(L$^{6\text{-Ph}}$)(OBn)$_2$** (Figure 12c,d). The BDEs of Al−CL are 13.4 and 11.8 kcal/mol for **CL-Al(L$^{5\text{-Ph}}$)(OBn)$_2$** and **CL-Al(L$^{6\text{-Ph}}$)(OBn)$_2$**, respectively. The crowded environment of **CL-Al(L$^{6\text{-Ph}}$)(OBn)$_2$** situates the CL far away from the Al atom and forms a weaker Al−CL bond than that of **CL-Al(L$^{5\text{-Ph}}$)(OBn)$_2$**. In comparison with the six-membered-ring **L$^{6\text{-Ph}}$Al(OBn)$_2$**, **L$^{5\text{-Ph}}$Al(OBn)** is less bulky and hence favors the CL coordination to afford **CL-Al-(L$^{5\text{-Ph}}$)(OBn)$_2$**. Moreover, the resultant Al−CL bond is harder to break, and ROP therefore proceeds more readily. Without a doubt, five-membered-ring Al catalysts showed greater catalytic activities and shorter induction periods in comparison to those of six-membered-ring Al catalysts. However, this can be attributed to geometry, electronic effects, or both. To confirm the real effect influencing catalytic activity and induction period, the charge on the aluminum center was calculated through natural population analysis (NPA). The values of the charge on aluminum center are almost identical: 2.050 and 2.055 for **L$^{5\text{-Ph}}$Al(OBn)$_2$** (Figure 12a) and **L$^{6\text{-Ph}}$Al(OBn)$_2$** (Figure 12b), respectively. From the NPA results, we conclude that only steric effects influence the catalytic activity and induction period of five- and six-membered-ring Al catalysts in CL ROP.

■ CONCLUSIONS

A series of five- and six-membered-ring Al complexes bearing Schiff base ligands were synthesized, and their CL polymerization was studied. The five-membered-ring Al complexes revealed an appreciably higher (2−3-fold) polymerization rate than the six-membered-ring Al complexes in the CL polymerization with a shorter induction period. Geometric structure data revealed that the Al center of a five-membered-ring Al complex is farther away from the Schiff base ligand in comparison with the six-membered-ring Al complex. This phenomenon could reduce the steric repulsion of the transition state **CL-OBn** in the CL polymerization process and increase the catalytic activity of the five-membered-ring Al complex. The reported new strategy can be used to design Al complexes bearing Schiff base ligands with high catalytic activity for CL polymerization. We anticipate this work may inspire other scientists to design new Al catalysts with a five-membered-ring form for ring-opening polymerization.

■ EXPERIMENTAL SECTION

Standard Schlenk techniques and a N$_2$-filled glovebox were used throughout the isolation and handling of all the compounds. Solvents, ε-caprolactone, and deuterated solvents were purified prior to use. Deuterated chloroform and ε-caprolactone were purchased from Acros. Benzyl alcohol, trimethylaluminum, 4,6-di-*tert*-butylphenol, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, palladium on carbon (10%), furfural, 2-pyridinecarboxaldehyde, 2-methoxybenzaldehyde, benzaldehyde, *p*-toluenesulfonyl chloride, salicyaldehyde, *o*-anisidine, aniline, and benzylamine were purchased from Alfa Aesar. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000-200 (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 M_{n}(GPC). 2-Amino-4,6-di-*tert*-butylphenol,[12] 2-formylphenyl-4-methylbenzenesulfonate,[17] **L$^{5\text{-Ph}}$-H**,[18] **L$^{5\text{-Py}}$-H**,[19] **L$^{5\text{-ful}}$-H**,[20] **L$^{5\text{-Thio}}$-H**,[20] **L$^{6\text{-Ph}}$-H**,[21] **L$^{6\text{-OMe}}$-H**,[22] and **L$^{6\text{-Bn}}$-H**[23] were prepared following literature procedures.

Synthesis of L$^{5\text{-OMe}}$-H. A mixture of 2-amino-4,6-di-*tert*-butylphenol (2.21 g, 10 mmol) and 2-methoxybenzaldehyde (1.36 g, 10 mmol) was refluxed for 1 day in ethanol (20 mL). The solution was removed under vacuum to give a yellow mud, and then cold hexane (20 mL) was transferred to the washed red powder three times to give a light yellow powder. Yield: 2.41 g (71%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 9.13 (1H, s, C*H*═N), 7.23 (1H, s, p-Ar *H*), 7.20 (1H, s, o-Ar *H*), 7.45 (1H, t, p-Ar *H*OMe, J = 8.0 Hz), 7.00 (1H, t, m-Ar *H*OMe, J = 8.0 Hz), 8.17 (1H, d, o-Ar *H*OMe, J = 8.0 Hz), 7.08 (1H, d, m-Ar *H*OMe, J = 8.0 Hz), 3.94 (3H, s, OC*H*$_3$), 1.45 (9H, s, C(C*H*$_3$)$_3$), 1.34 (9H, s, C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 159.47 (*C*═N), 151.76, 148.73, 141.23, 135.40, 134.89, 132.61, 127.29, 124.71, 122.91, 120.81, 111.17, 110.23 (Ar), 55.53 (OCH$_3$), 34.89, 34.55 (*C*(CH$_3$)$_3$), 31.67, 29.47 (C(*C*H$_3$)$_3$). Anal. Found (calcd) for **L$^{5\text{-OMe}}$-H**, C$_{22}$H$_{29}$NO$_2$: N, 4.23 (4.13); C, 77.92 (77.84); H, 8.54 (8.61).

Synthesis of L$^{5\text{-OTs}}$-H. This compound was preprared using a method similar to that for **L$^{5\text{-OMe}}$-H** except that 1-(5-bromo-2-hydroxyphenyl)ethan-1-one was used in place of 2-methoxybenzaldehyde. Yield: 3.45 g (72%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.47 (1H, s, C*H*═N), 8.06 (1H, d, Ar *H*, J = 6 Hz), 7.27−7.65 (6H, m, Ar *H*), 7.13 (2H, d, Ar*H*, J = 6 Hz), 6.96 (1H, s, Ar *H*), 2.20 (3H, s, C*H*$_3$), 1.44 (9H, s, C(C*H*$_3$)$_3$), 1.36 (9H, s, C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 149.38 (*C*═N), 149.04, 148.75, 146.08, 141.23, 135.19, 132.07, 129.89, 129.48, 128.13, 127.65, 127.43, 123.85, 109.97 (Ar), 21.45 (CH$_3$), 34.91, 34.53 (*C*(CH$_3$)$_3$), 31.62, 29.42 (C(*C*H$_3$)$_3$). Anal. Found (calcd) for **L$^{5\text{-OTs}}$-H**, C$_{28}$H$_{33}$NO$_4$S: N, 2.83 (2.92); C, 70.51 (70.12); H, 6.99 (6.94).

Synthesis of L$^{6\text{-Thio}}$-H. A mixture of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) and thiophen-2-ylmethanamine (1.13 g, 10 mmol) was refluxed for 1 day in ethanol (20 mL). **L$^{6\text{-Thio}}$-H** crystallized after the solution was kept at −20 °C for 1 day. Yield: 2.33 g (71%).^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.35 (1H, s, C*H*═N), 7.32, 7.02 (2H, s, Ar *H*), 7.19, 6.91 (3H, br, Thio*H*), 4.88 (2H, s, NC*H*$_2$), 1.38 (9H, s, C(C*H*$_3$)$_3$), 1.24 (9H, s, C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 166.77 (*C*=N), 157.97, 140.89, 140.11, 136.73, 127.16, 126.92, 126.12, 125.38, 124.91, 117.79 (Ar), 57.22 (N*C*H$_2$), 35.03, 34.10 (*C*(CH$_3$)$_3$), 31.50, 29.45 (C(*C*H$_3$)$_3$). Anal. Found (calcd) for **L$^{6\text{-Thio}}$-H**, $C_{20}H_{27}NOS$: N, 4.58 (4.25); C, 72.44 (72.90); H, 8.01 (8.26).

Synthesis of L$^{5\text{-Ph}}$AlMe$_2$. A mixture of **L$^{5\text{-Ph}}$-H** (3.08 g, 5 mmol) and AlMe$_3$ (6 mL, 2.0 M, 12 mmol) in toluene (15 mL) was stirred for 3 h at 0 °C. Volatile materials were removed under vacuum to give a yellow powder, and then hexane (30 mL) was transferred to the suspension. A yellow powder was obtained after filtering. Yield: 2.63 g (72%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.82 (1H, s, C*H*=N), 7.90 (2H, d, Ar *H*, *J* = 6 Hz), 7.53−7.62 (3H, m, Ar *H*), 7.34 (1H, s, Ar *H*), 7.24 (1H, s, Ar *H*), 1.44 (9H, s, m-C(C*H*$_3$)$_3$), 1.35 (9H, s, C(C*H*$_3$)$_3$), −0.74 (6H, s, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 170.45 (*C*=N), 162.34, 147.00, 140.71, 139.26, 132.94, 129.77, 129.20, 127.70, 122.19, 118.66 (Ar), 31.28, 29.28 (*C*(CH$_3$)$_3$), 35.31, 34.07 (C(*C*H$_3$)$_3$), −9.23 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{5\text{-Ph}}$AlMe$_2$**, $C_{23}H_{32}AlNO$: N, 3.72 (3.83); C, 75.40 (75.58); H, 8.90 (8.83). Mp: 140 °C.

Synthesis of L$^{5\text{-Py}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{5\text{-Py}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.79 g (76%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.69 (1H, d, *J* = 8.0 Hz, *o*-pyridine *H*), 8.62 (1H, s, NC*H*), 7.98 (1H, t, *J* = 8.0 Hz, pyridine *H*), 7.72 (1H, d, *J* = 8.0 Hz, pyridine *H*), 7.52 (1H, t, *J* = 8.0 Hz, pyridine *H*), 7.36−7.34 (2H, m, Ar *H*), 1.46 (s, 9H, C*H*$_3$), 1.33 (s, 9H, C*H*$_3$), −0.86 (s, 6H, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 162.45 (*C*=N), 140.68, 140.12, 138.96, 129.11, 125.35, 109.18, 147.71, 147.51, 137.23, 128.48, 124.42 (Ar), 35.31, 34.42 (*C*(CH$_3$)$_3$), 31.42, 28.96 (C(*C*H$_3$)$_3$), −9.01 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{5\text{-Py}}$AlMe$_2$**, $C_{22}H_{31}AlN_2O$: N, 7.78 (7.64); C, 72.24 (72.10); H, 8.21 (8.53). Mp: 180 °C.

Synthesis of L$^{5\text{-Ful}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{5\text{-Ful}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.06 g (58%).^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.49 (1H, s, NC*H*), 7.77, 7.30 (2H, s, Ar *H*), 7.23−7.17 (2H, m, Ful *H*), 6.70 (1H, t, *J* = 2.0 Hz, Ful *H*), 1.44 (s, 9H, C*H*$_3$), 1.33 (s, 9H, C*H*$_3$), −0.74 (s, 6H, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 157.68 (*C*=N), 147.73, 139.90, 126.18, 121.53, 113.88, 108.45, 148.76, 139.35, 138.48, 132.00 (Ar), 35.27, 34.54 (*C*(CH$_3$)$_3$), 31.61, 29.09 (C(*C*H$_3$)$_3$), −9.92 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{5\text{-Ful}}$AlMe$_2$**, $C_{21}H_{30}AlNO_2$: N, 3.79 (3.94); C, 71.12 (70.96); H, 8.46 (8.51). Mp: 144 °C.

Synthesis of L$^{5\text{-OMe}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{5\text{-OMe}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.69 g (68%).^{1}H NMR (CDCl$_3$, 200 MHz): δ 9.11 (1H, s, C*H*=N), 7.89 (1H, d, o-Ar *H*OMe, *J* = 8 Hz), 7.62 (1H, t, m-Ar *H*OMe, *J* = 8 Hz), 7.32, 7.20 (2H, s, Ar *H*), 6.99−7.13 (2H, m, Ar *H*OMe), 3.94 (3H, s, OC*H*$_3$), 1.44 (9H, s, C(C*H*$_3$)$_3$), 1.34 (9H, s, C(C*H*$_3$)$_3$), −0.80 (6H, s, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 159.84 (*C*=N), 156.48, 138.75, 138.57, 135.19, 125.69, 121.88, 157.25, 134.86, 129.66, 120.86, 111.36, 110.21 (Ar), 55.80 (O*C*H$_3$), 35.17, 34.47 (*C*(CH$_3$)$_3$), 31.65, 29.09 (C(*C*H$_3$)$_3$), −9.91 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{5\text{-OMe}}$AlMe$_2$**, $C_{24}H_{34}AlNO_2$: N, 3.36 (3.54); C, 72.66 (72.88); H, 8.68 (8.66). Mp: 160 °C.

Synthesis of L$^{5\text{-Thio}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{5\text{-Thio}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.75 g (74%).^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.86 (1H, s, NC*H*), 7.82−7.80 (2H, br, Ar *H*), 7.30−7.21 (3H, m, Ar *H*), 1.44 (s, 9H, C*H*$_3$), 1.35 (s, 9H, C*H*$_3$), −0.61 (s, 6H, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 170.36 (*C*=N), 162.27, 146.90, 140.60, 139.19, 132.87, 129.68, 129.28, 128.95, 128.14, 127.64, 122.06 (Ar), 35.28, 34.00 (*C*(CH$_3$)$_3$), 31.29, 29.35 (C(*C*H$_3$)$_3$), −9.00 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{5\text{-Thio}}$AlMe$_2$**, $C_{21}H_{30}AlNOS$: N, 4.01 (3.77); C, 67.91 (67.89); H, 8.49 (8.14). Mp: 164 °C.

Synthesis of L$^{5\text{-OTs}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{5\text{-OTs}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 3.59 g (67%).^{1}H NMR (CDCl$_3$, 200 MHz) δ. ^{13}C NMR (CDCl$_3$, 50 MHz) δ152.57 (*C*=N), 151.54, 149.99, 146.68, 134.49, 133.26, 130.33, 130.12, 128.78, 128.09, 127.86, 127.47, 126.71, 124.93, 110.46, 109.87 (Ar), 35.24, 34.76 (*C*(CH$_3$)$_3$) 31.65, 29.14 (C(*C*H$_3$)$_3$), 21.62 (*C*H$_3$), −9.99 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{5\text{-OMe}}$AlMe$_2$**, $C_{24}H_{34}AlNO_2$: N, 3.22 (3.54); C, 72.53 (72.88); H, 8.51 (8.66). Mp: 170 °C.

Synthesis of L$^{6\text{-Ph}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{6\text{-Ph}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.41 g (66%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.24 (1H, s, C*H*=N), 7.54, 7.04 (2H, s, Ar *H*), 7.23−7.43 (5H, m, Ar *H*), 1.38 (9H, s, C(C*H*$_3$)$_3$), 1.25 (9H, s, C(C*H*$_3$)$_3$), −0.79 (6H, s, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 170.45 (*C*=N), 162.34, 147.00, 140.71, 139.26, 132.94, 129.77, 129.20, 127.70, 122.19, 118.66 (Ar), 31.28, 29.28 (*C*(CH$_3$)$_3$), 35.31, 34.07 (C(*C*H$_3$)$_3$), −9.23 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{6\text{-Ph}}$AlMe$_2$**, $C_{23}H_{32}AlNO$: N, 3.87 (3.83); C, 75.77 (75.58); H, 8.90 (8.83). Mp: 90 °C.

Synthesis of L$^{6\text{-Bn}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{6\text{-Bn}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.39 g (63%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.15 (1H, s, C*H*=N), 7.52, 6.97 (2H, s, Ar *H*), 7.29−7.40 (5H, m, Ar *H*), 4.71 (2H, s, NC*H*$_2$), 1.39 (9H, s, C(C*H*$_3$)$_3$), 1.28 (9H, s, C(C*H*$_3$)$_3$), −0.95 (6H, s, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 171.75 (*C*=N), 140.40, 138.77, 134.99, 131.83, 129.05, 128.97, 128.51, 120.34, 118.11 (Ar), 60.40 (*C*H$_2$), 35.25, 34.02 (*C*(CH$_3$)$_3$), 31.32, 29.25 (C(*C*H$_3$)$_3$), −10.00 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{6\text{-Ph}}$AlMe$_2$**, $C_{24}H_{34}AlNO$: N, 3.51 (3.69); C, 75.70 (75.95); H, 8.95 (9.03). Mp: 108 °C.

Synthesis of L$^{6\text{-OMe}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{6\text{-OMe}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. Yield: 2.93 g (74%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.39 (1H, s, C*H*=N), 7.55, 7.08 (2H, s, p-Ar *H*), 6.96−7.35 (4H, m, Ar *H*OMe), 3.89 (3H, s, OC*H*$_3$), 1.44 (9H, s, m−C(C*H*$_3$)$_3$), 1.31 (9H, s, C(C*H*$_3$)$_3$), −0.84 (6H, s, Al(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 169.03 (*C*=N), 163.87, 151.82, 140.80, 138.60, 135.93, 132.64, 128.73, 128.56, 121.60, 121.54, 119.11, 111.22 (Ar), 54.92 (O*C*H$_3$), 35.27, 34.03 (*C*(CH$_3$)$_3$), 31.27, 29.32 (C(*C*H$_3$)$_3$), −10.48 (Al(*C*H$_3$)$_2$). Anal. Found (calcd) for **L$^{6\text{-OMe}}$AlMe$_2$**, $C_{24}H_{34}AlNO_2$: N, 3.85 (3.54); C, 73.23 (72.88); H, 8.89 (8.66). Mp: 130 °C.

Synthesis of L$^{6\text{-Thio}}$AlMe$_2$. This compound was preprared using a method similar to that for **L$^{5\text{-Ph}}$AlMe$_2$** except that **L$^{6\text{-Thio}}$-H** was used in place of **L$^{5\text{-Ph}}$-H**. This substance could not be purified with hexane because it dissolves in hexane. The ^{1}H NMR spectrum was complex and revealed that the disproportionation product was also produced. A single crystal was obtained in an NMR tube when CDCl$_3$ was vaporized.

General Procedures for the Polymerization of ε-Caprolactone. A typical polymerization procedure is exemplified by the synthesis of entry 3 (Table 1) using complex **L$^{5\text{-Ph}}$AlMe$_2$** 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 **L$^{5\text{-Ph}}$AlMe$_2$** (0.1 mmol), BnOH (0.2 mmol), and ε-caprolactone (10 mmol) at room temperature. At indicated time intervals, 0.05 mL aliquots were removed, trapped with CDCl$_3$ (1 mL), and analyzed by ^{1}H NMR. After the solution was stirred for 150 min, the reaction was then quenched by adding a drop of isopropyl alcohol, and the polymer precipitated as a white solid when it was poured into *n*-hexane (30.0 mL). The isolated white solid was dissolved in CH$_2$Cl$_2$ (5.0 mL), and then *n*-hexane (70.0 mL) was added to give a purified crystalline solid. Yield: 0.92 g (81%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00068.

Polymer characterization data and details of the kinetic study (PDF)

Accession Codes

CCDC 1487512−1487514 contain the supplementary crystallographic data for this paper. 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, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Mattanavee, W.; Suwantong, O.; Puthong, S.; Bunaprasert, T.; Hoven, V. P.; Supaphol, P. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1076−1085. (b) Zander, N. E.; Orlicki, J. A.; Rawlett, A. M.; Beebe, T. P., Jr. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2074−2081. (c) Tarafder, S.; Bose, S. *ACS Appl. Mater. Interfaces* **2014**, *6*, 9955−9965. (d) Castaño, O.; Sachot, N.; Xuriguera, E.; Engel, E.; Planell, J. A.; Park, J.-H.; Jin, G.-Z.; Kim, T.-H.; Kim, J.-H.; Kim, H.-W. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7512−7522. (e) Rainbolt, E. A.; Washington, K. E.; Biewer, M. C.; Stefan, M. C. *Polym. Chem.* **2015**, *6*, 2369−2381. (f) Palmer, L. C.; Newcomb, C. J.; Kaltz, S. R.; Spoerke, E. D.; Stupp, S. I. *Chem. Rev.* **2008**, *108*, 4754−4783. (g) Cameron, D. J. A.; Shaver, M. P. *Chem. Soc. Rev.* **2011**, *40*, 1761−1776. (h) Nicolas, J.; Mura, S.; Brambilla, D.; Mackiewicz, N.; Couvreur, P. *Chem. Soc. Rev.* **2013**, *42*, 1147−1235. (i) Palivan, C. G.; Goers, R.; Najer, A.; Zhang, X.; Car, A.; Meier, W. *Chem. Soc. Rev.* **2016**, *45*, 377−411.

(2) (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176. (b) Jacobsen, S.; Degee, P.; Fritz, H. G.; Dubois, P.; Jerome, R. *Polym. Eng. Sci.* **1999**, *39*, 1311−1319.

(3) (a) Wheaton, C. A.; Hayes, P. G.; Ireland, B. J. *Dalton Trans.* **2009**, 4832−4846. (b) Guillaume, S. M.; Kirillov, E.; Sarazin, Y.; Carpentier, J.-F. *Chem. - Eur. J.* **2015**, *21*, 7988−8003. (c) Carpentier, J.-F. *Organometallics* **2015**, *34*, 4175−4189. (d) Bellemin-Laponnaz, S.; Dagorne, S. *Chem. Rev.* **2014**, *114*, 8747−8774. (e) Piedra-Arroni, E.; Amgoune, A.; Bourissou, D. *Dalton Trans.* **2013**, *42*, 9024−9029. (f) Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Trans.* **2010**, *39*, 8363−8376. (g) Hoskins, J. N.; Grayson, S. M. *Polym. Chem.* **2011**, *2*, 289−299. (h) Thomas, C. M. *Chem. Soc. Rev.* **2010**, *39*, 165−173. (i) Arbaoui, A.; Redshaw, C. *Polym. Chem.* **2010**, *1*, 801−826.

(4) (a) Lewiński, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789−5791. (b) Nomura, N.; Aoyama, T.; Ishii, R.; Kondo, T. *Macromolecules* **2005**, *38*, 5363−5366. (c) Iwasa, N.; Liu, J.; Nomura, K. *Catal. Commun.* **2008**, *9*, 1148−1152. (d) Liu, J.; Iwasa, N.; Nomura, K. *Dalton Trans.* **2008**, 3978−3988. (e) Iwasa, N.; Fujiki, M.; Nomura, K. *J. Mol. Catal. A: Chem.* **2008**, *292*, 67−75. (f) Iwasa, N.; Katao, S.; Liu, J.; Fujiki, M.; Furukawa, Y.; Nomura, K. *Organometallics* **2009**, *28*, 2179−2187. (g) Wu, J.; Pan, X.; Tang, N.; Lin, C.-C. *Eur. Polym. J.* **2007**, *43*, 5040−5046. (h) Du, Z.-X.; Xu, J.-T; Yang, Y.; Fan, Z.-Q. *J. Appl. Polym. Sci.* **2007**, *105*, 771−776. (i) Arbaoui, A.; Redshaw, C.; Hughes, D. L. *Chem. Commun.* **2008**, 4717−4719. (j) Zhang, C.; Wang, Z.-X. *J. Organomet. Chem.* **2008**, *693*, 3151−3158. (k) Darensbourg, D. J.; Karroonnirun, O. *Organometallics* **2010**, *29*, 5627−5634. (l) Pappalardo, D.; Annunziata, L.; Pellecchia, C. *Macromolecules* **2009**, *42*, 6056−6062. (m) Iwasa, N.; Katao, S.; Liu, J.; Fujiki, M.; Furukawa, Y.; Nomura, K. *Organometallics* **2009**, *28*, 2179−2187. (n) Darensbourg, D. J.; Karroonnirun, O.; Wilson, S. J. *Inorg. Chem.* **2011**, *50*, 6775−6787. (o) Zhang, W.; Wang, Y.; Sun, W.-H.; Wang, L.; Redshaw, C. *Dalton Trans.* **2012**, *41*, 11587−11596. (p) Matsubara, K.; Terata, C.; Sekine, H.; Yamatani, K.; Harada, T.; Eda, K.; Dan, M.; Koga, Y.; Yasuniwa, M. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 957−966. (q) Yu, X.-F.; Wang, Z.-X. *Dalton Trans.* **2013**, *42*, 3860−3868. (r) Han, H.-L.; Liu, Y.; Liu, J.-Y.; Nomura, K.; Li, Y.-S. *Dalton Trans.* **2013**, *42*, 12346−12353. (s) Normand, M.; Roisnel, T.; Carpentier, J.-F.; Kirillov, E. *Chem. Commun.* **2013**, *49*, 11692−11694. (t) Tabthong, S.; Nanok, T.; Kongsaeree, P.; Prabpai, S.; Hormnirun, P. *Dalton Trans.* **2014**, *43*, 1348−1359. (u) Meduri, A.; Fuoco, T.; Lamberti, M.; Pellecchia, C.; Pappalardo, D. *Macromolecules* **2014**, *47*, 534−543. (v) Qu, Z.; Duan, R.; Pang, X.; Gao, B.; Li, X.; Tang, Z.; Wang, X.; Chen, X. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 1344−1352. (w) Zaitsev, K. V.; Piskun, Y. A.; Oprunenko, Y. F.; Karlov, S. S.; Zaitseva, G. S.; Vasilenko, I. V.; Churakov, A. V.; Kostjuk, S. V. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 1237−1250. (x) Shen, M.; Zhang, W.; Nomura, K.; Sun, W.-H. *Dalton Trans.* **2009**, 9000−9009. (y) Gao, A.; Mu, Y.; Zhang, J.; Yao, W. *Eur. J. Inorg. Chem.* **2009**, *2009*, 3613−3621. (z) van der Meulen, I.; Gubbels, E.; Huijser, S.; Sablong, R.; Koning, C. E.; Heise, A.; Duchateau, R. *Macromolecules* **2011**, *44*, 4301−4305.

(5) (a) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2003**, 3082−3087. (b) Tang, Z.; Gibson, V. C. *Eur. Polym. J.* **2007**, *43*, 150−155. (c) Ding, K.; Miranda, M. O.; Moscato-Goodpaster, B.; Ajellal, N.; Breyfogle, L. E.; Hermes, E. D.; Schaller, C. P.; Roe, S. E.; Cramer, C. J.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2012**, *45*, 5387−5396. (d) Du, H.; Velders, A. H.; Dijkstra, P. J.; Sun, J.; Zhong, Z.; Chen, X.; Feijen, J. *Chem. - Eur. J.* **2009**, *15*, 9836−9845. (e) Issenhuth, J.-T.; Pluvinage, J.; Welter, R.; Bellemin-Laponnaz, S.; Dagorne, S. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4701−4709.

(6) (a) Yu, R.-C.; Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 6450−6455. (b) Tseng, H.-C.; Chiang, M. Y.; Lu, W.-Y.; Chen, Y.-J.; Lian, C.-J.; Chen, Y.-H.; Tsai, H.-Y.; Lai, Y.-C.; Chen, H.-Y. *Dalton Trans.* **2015**, *44*, 11763−11773.

(7) (a) Darensbourg, D. J.; Ganguly, P.; Billodeaux, D. *Macromolecules* **2005**, *38*, 5406−5410. (b) Bhaw-Luximon, A.; Jhurry, D.; Spassky, N. *Polym. Bull.* **2000**, *44*, 31−38. (c) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688−2689.

(8) (a) Pang, X.; Du, H.; Chen, X.; Wang, X.; Jing, X. *Chem. - Eur. J.* **2008**, *14*, 3126−3136. (b) Pang, X.; Du, H.; Chen, X.; Zhuang, X.; Cui, D.; Jing, X. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6605−6612. (c) Pang, X.; Chen, X.; Du, H.; Wang, X.; Jing, X. *J. Organomet. Chem.* **2007**, *692*, 5605−5613.

(9) (a) Sun, W.-H.; Shen, M.; Zhang, W.; Huang, W.; Liu, S.; Redshaw, C. *Dalton Trans.* **2011**, *40*, 2645−2653. (b) Bakewell, C.; Platel, R. H.; Cary, S. K.; Hubbard, S. M.; Roaf, J. M.; Levine, A. C.; White, A. J. P.; Long, N. J.; Haaf, M.; Williams, C. K. *Organometallics* **2012**, *31*, 4729−4736.

(10) (a) Gong, S.; Ma, H. *Dalton Trans.* **2008**, 3345−3357. (b) Ma, W.-A.; Wang, L.; Wang, Z.-X. *Dalton Trans.* **2011**, *40*, 4669−4677.

(11) Chen, H.-Y.; Lu, W.-Y.; Chen, Y.-J.; Hsu, S. C. N.; Ou, S.-W.; Peng, W.-T.; Jheng, N.-Y.; Lai, Y.-C.; Wu, B.-S.; Chung, H.; Chen, Y.; Huang, T.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 327−333.

(12) Evangelio, E.; Saiz-Poseu, J.; Maspoch, D.; Wurst, K.; Busque, F.; Ruiz-Molina, D. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2278−2285.

(13) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1472−1476.

(14) Chang, M.-C.; Lu, W.-Y.; Chang, H.-Y.; Lai, Y.-C.; Chiang, M.-Y.; Chen, H.-Y.; Chen, H.-Y. *Inorg. Chem.* **2015**, *54*, 11292−11298.

(15) $\%V_{bur}$ is a measurement of the volume of a ligand bonded to a transition metal. The calculation uses a compound's crystal structure

to evaluate how much space a ligand occupies. (a) Falivene, L.; Cavallo, L.; Talarico, G. *ACS Catal.* **2015**, *5*, 6815−6822. (b) Maity, A. K.; Fortier, S.; Griego, L.; Metta-Magaña, A. J. *Inorg. Chem.* **2014**, *53*, 8155−8164.

(16) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759−1766.

(17) Chen, H.-Y.; Liu, M.-Y.; Sutar, A. K.; Lin, C.-C. *Inorg. Chem.* **2010**, *49*, 665−674.

(18) Suzuki, Y.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2002**, *31*, 358−359.

(19) Li, A.; Ma, H.; Huang, J. *Organometallics* **2013**, *32*, 7460−7469.

(20) Vinsova, J.; Cermakova, K.; Tomeckova, A.; Ceckova, M.; Jampilek, J.; Cermak, P.; Kunes, J.; Dolezal, M.; Staud, F. *Bioorg. Med. Chem.* **2006**, *14*, 5850−5865.

(21) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626−3629.

(22) Gong, D.; Wang, B.; Jia, X.; Zhang, X. *Dalton Trans.* **2014**, *43*, 4169−4178.

(23) Uddin Ahmad, J.; Nieger, M.; Sundberg, M. R.; Leskelä, M.; Repo, T. *J. Mol. Struct.* **2011**, *995*, 9−19.

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