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Synthesis and Characterization of Dialkylaluminum Amidates and Their Ring-Opening Polymerization of ε-Caprolactone

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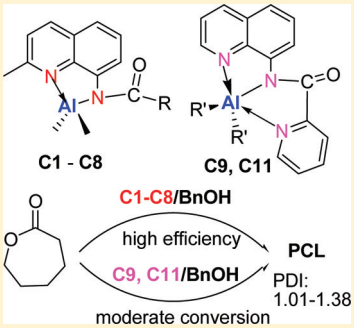
Supporting Information

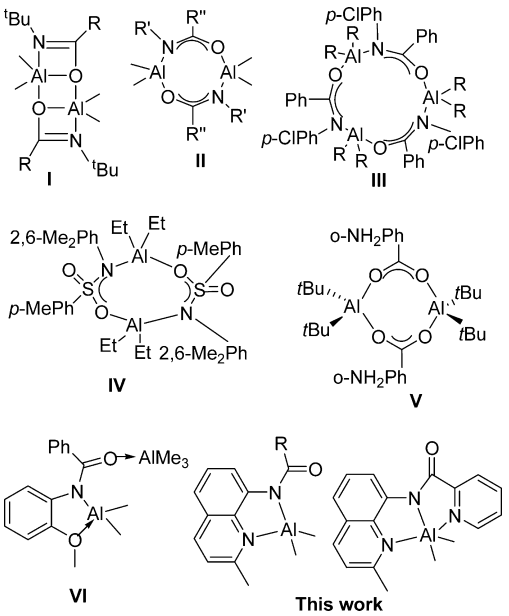
ABSTRACT: The stoichiometric reactions of *N*-(2-methylquinolin-8-yl) (R)amides (**L1**−**L8**; **L1**, R = Ph; **L2**, R = *p*-FPh; **L3**, R = *p*-ClPh; **L4**, R = *p*-(MeO)Ph; **L5**, R = *o*-MePh; **L6**, R = *p*-MePh; **L7**, R = Me; **L8**, R = CF_3) with Me_3Al afforded the corresponding dimethylaluminum amidate complexes [Me_2AlL] (**C1**−**C8**). The treatment of *N*-(2-methylquinolin-8-yl)picolinamide (**L9**) with 1 or 2 equiv of Me_3Al formed Me_2Al**L9** (**C9**) or Me_2Al**L9**·Me_3Al (**C10**), respectively; meanwhile, the stoichiometric reaction of **L9** with iBu_3Al gave iBu_2Al**L9** (**C11**). All organoaluminum amidate complexes were fully characterized by $^1H/^{13}C$ NMR spectroscopy and elemental analysis, and the unambiguous structures of complexes **C2**, **C4**, **C9**, and **C11** were further determined by single-crystal X-ray diffraction. With the assistance of 1 equiv of BnOH, all dialkylaluminum amidate complexes showed appreciable activities toward the ring-opening polymerization of ε-caprolactone and produced polycaprolactones with narrow polydispersity; the nature of the active species was also investigated.



INTRODUCTION

Alkylaluminum compounds, which tend to be highly air sensitive, are very important reagents widely employed in organic synthesis,[1] as cocatalysts in olefin polymerization,[2] and as initiators in the ring-opening polymerization (ROP) of cyclic esters[3] or copolymerization of CO_2 and epoxides.[4] Recently, the reactivity and catalytic behavior of alkylaluminum complexes have been extensively reported.[5] Using the multicoordination features of amide compounds, we have synthesized several series of titanium amidates, which act as effective precatalysts in ethylene (co)polymerization,[6] and now we consider the aluminum compounds derived from this ligand set. Indeed, there are only a few reports of alkylaluminum amidates: for example, the first aluminum amidates of the type [$Me_2Al(RNC(O)R)]_2$ possessing eight-membered cyclic structures on the basis of spectroscopic studies were reported by Wade[7] and Lappert.[8] Furthermore, alkylaluminum amidates as the dimeric compounds {$Me_2Al[\eta^2$-^{t}BuNC(R)(μ_2-O)]}$_2$ (**I**; Chart 1) or 8-membered (**II**; Chart 1) or trimeric 12-membered cyclic aluminum compounds (**III**; Chart 1) have been reported.[9] Interestingly, an aluminum amidate complex was proposed as an intermediate for transamidations.[10] With regard to the reactivity of common trialkylaluminums, the stoichiometric reaction of $AlEt_3$ with the sulfonyl amine ArNH(SO_2-*p*-Tol) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Tol = 4-MeC$_6$H$_4$) yielded the dimeric aluminum species [ArN(SO_2-*p*-Tol)$AlEt_2$]$_2$ (**IV**), possessing an 8-membered cyclic compound structurally similar to that of **II**.[11] The varied coordination modes available provided different compounds: for example, the stoichiometric

Chart 1. Different Coordination Models for Amidate Aluminum Complexes



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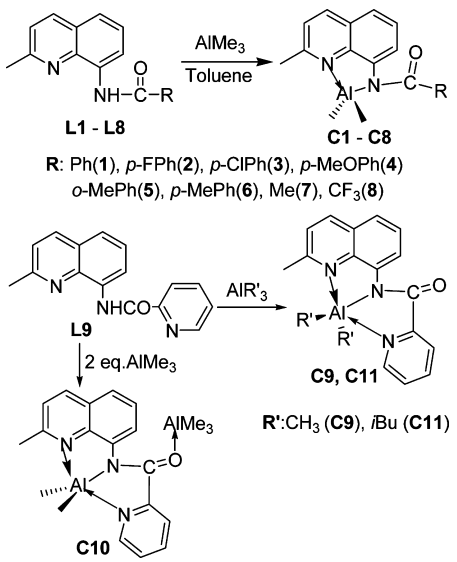
reaction of Me_3Al with 2-methoxybenzanilide in *n*-hexane gave a dinuclear aluminum complex (**VI**; Chart 1),[9] and the reaction of AlR_3 with anthranilic acid produced the dimeric carboxylates **V**,[12a−c] which were used to explain the reaction mechanism of amino acids with aluminum.[12d]

In the case of titanium amidate compounds,[6] such amidates have adopted monodentate features[6a−c] and η,μ_2-OCN coordination,[6d] in which the different coordination features affected the structure and catalytic behavior of their complexes.[6] Given our previous success in using aluminum precatalysts in the ring-opening polymerization of ε-caprolactone,[13] we explore herein the reaction of alkylaluminum with quinoline amides and isolated the highly sensitive alkylaluminum amidates in high yields, which serve as precatalysts for the ring-opening polymerization of ε-caprolactone. To the best of our knowledge, this is the first time such alkylaluminum amidates have been reported as precatalysts in the ring-opening polymerization of ε-caprolactone. In the presence of benzyl alcohol, the alkylaluminum amidates exhibited high efficiency and produced polymers with narrow polydispersity, indicating their adaptability for controlling polycaprolactones in terms of both molecular weight and polydispersity.

RESULTS AND DISCUSSION

1. Synthesis and Characterization of Dialkylaluminum Quinolylamidates (C1−C11). The ligands **L1−L9** were prepared according to the method given in our previous work.[6d] The stoichiometric reactions of **L1−L9** with 1 equiv of $AlMe_3$ in toluene at −30 °C formed the corresponding mononuclear dialkylaluminum quinoline amidates **C1−C9**, while the treatment of **L9** with 2 equiv of $AlMe_3$ gave the dinuclear methylaluminum *N*-(2-methylquinolin-8-yl)-picolinamidate (**C10**) (Scheme 1). Reaction of **L9** with 1 equiv of iBu_3Al afforded [iBu_2Al**L9**] (**C11**). All aluminum complexes were characterized by $^1H/^{13}C$ NMR spectroscopy and elemental analysis. Comparison of the ^1H NMR spectra of **C1−C10** with those of the corresponding ligands **L1−L9** revealed that additional resonances appeared in the high-field region (δ −0.50 to −0.90 ppm), which are attributed to the methyl groups attached to the aluminum centers, while the N−*H* signals (single peak around 10.4−10.9 ppm) of the free ligands disappeared. Furthermore, the resonances from −6.0 to −9.6 ppm in the ^{13}C NMR spectra of **C1−C10** confirmed the formation of the Al−CH_3 bond.

Scheme 1. Synthesis of the Dialkylaluminum Complexes C1−C11



Single crystals of complexes **C2**, **C4**, **C9**, and **C11** were obtained from their toluene/*n*-heptane solutions at −30 °C. The molecular structure of dimethylaluminum 4-fluoro-*N*-(2-methylquinolin-8-yl)benzamidate (**C2**) is illustrated in Figure 1, and selected bond lengths and bond angles are given in Table 1. The Al center is coordinated to two N atoms, and the NCO group does not adopt the η^2 coordination model as observed in their titanium analogues.[6d] The geometry at aluminum is best described as distorted tetrahedral, as evidenced in the bond angles N(2)−Al(1)−C(19) = 115.13(10)° and C(18)−Al(1)−N(1) = 104.98(9)°. The Al−C bond distances in **C2** (Al(1)−C(19) = 1.958(2) Å, Al(1)−C(18) = 1.973(2) Å) and the Al(1)−N(1) bond (1.9808(19) Å) are typical, while the Al(1)−N(2) bond length (1.924(2) Å) is much shorter than 1.9808(19) Å (Al(1)−N(1)), indicating the typical characteristics of a σ bond. The dihedral angle between the quinoline plane and aryl plane is 60.83°.

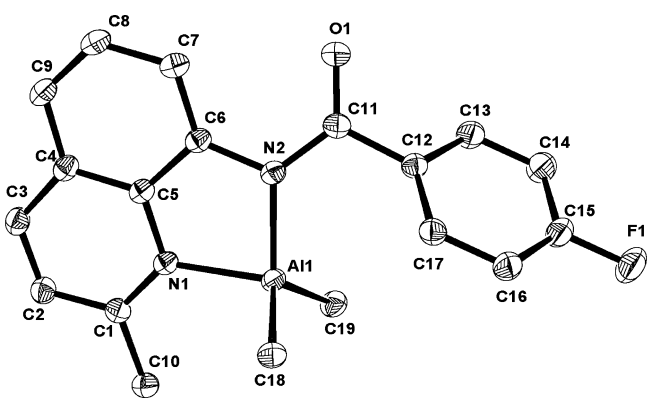


Figure 1. ORTEP drawing of **C2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

The molecular structure of dimethylaluminum 4-methoxy-*N*-(2-methylquinolin-8-yl)benzamide (**C4**; Figure 2) possesses a geometry very similar to that of **C2**, and selected bond lengths and bond angles are collected in Table 1. Small differences are observed between the Al−C bond lengths of **C4** (1.962(3), 1.968(2) Å) and those of **C2** (1.958(2), 1.978(2) Å), and also in the bond lengths Al−$N2_{imide}$ = 1.920(2) Å and Al−$N1_{quin}$ = 1.982(2) Å in **C4** versus those of **C2** (1.924(2), 1.9808(19) Å). Due to the stronger donor ability of the −OMe group on the benzene ring, the bond distances of C11−$C12_{aryl}$ and C11−$C12_{aryl}$ are shorter than those of **C2** possessing the F substituent, while the bond distance of N2−$C11_{imide}$ was elongated. The dihedral angle between the quinoline plane and the aryl plane was larger in **C4** (68.71°) versus that observed for **C2** (60.83°).

By introducing a pyridine group at the amidate, a coordination model similar to that of the N−C═O group was obtained, featuring an Al−N σ-bond in **C9**. However, there was a substantial change in the coordination geometry, and Figure 3 reveals that Al is now, in addition to the methyl groups, coordinated by three nitrogen atoms such that the geometry can be best described as distorted trigonal bipyramidal. Selected bond lengths and angles are also collected

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Table 1. Selected Bond Lengths and Bond Angles

	C2	C4	C9	C11
		Bond Lengths (Å)		
Al−N2$_{imide}$	1.924(2)	1.920(2)	1.952(2)	1.940(2)
Al−N1$_{quin}$	1.9808(19)	1.982(2)	2.134(2)	2.135(2)
Al−N1$_{Py}$			2.121(3)	2.112(3)
Al−C$_{Me}$	1.958(2)	1.962(3)	1.987(3)	1.992(2)
Al−C$_{Me}$	1.973(2)	1.968(2)	1.989(3)	1.994(3)
N2−C11$_{imide}$	1.367(3)	1.375(3)	1.356(4)	1.353(3)
C11−C12$_{aryl}$	1.502(3)	1.494(3)	1.506(4)	1.513(3)
C11−O1$_{imide}$	1.234(3)	1.232(3)	1.226(3)	1.232(3)
		Bond Angles (deg)		
C−Al−C	118.73	119.68	121.27(13)	123.82(11)
N$_{im}$−C$_{im}$−C$_{Ar}$	116.19	115.18	111.7(2)	111.2(2)
N$_{im}$−Al−N$_{Quin}$	84.75	84.61	79.02(9), 79.72(10)	78.25(9)
∠mean(quin, aryl)	60.83	68.71	13.25	22.47

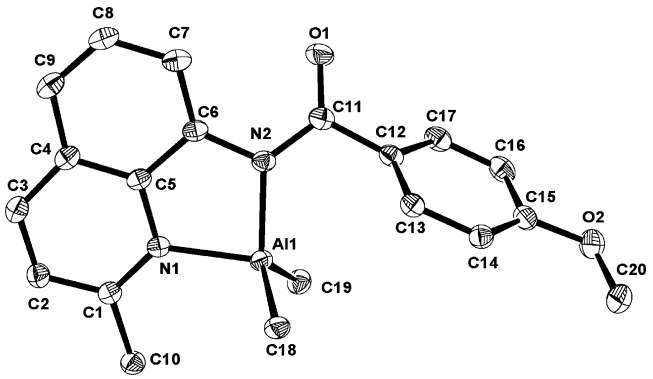

Figure 2. ORTEP drawing of **C4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

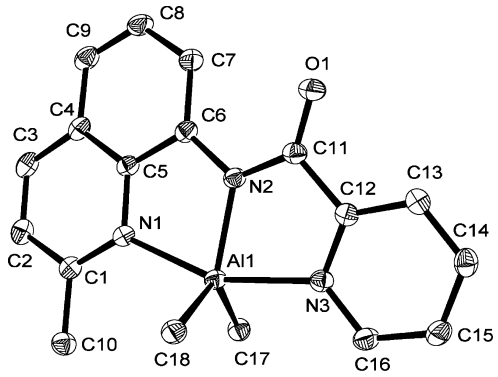

Figure 3. ORTEP drawing of **C9** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity (two independent molecules are included, only one structure is listed).

in Table 1 for comparison. It can be seen that the bond distances of Al−N2$_{imide}$, Al−N1$_{quin}$, and Al−C (1.952(2), 2.134(2), 1.987(3) and 1.989(3) Å) are much longer than those observed in **C2** and **C4**, illustrating the effect of the pyridine group on the amidate. The pyridyl plane is also almost coplanar with the quinolyl plane, with a dihedral angle of 13.25°, which is much smaller than those of **C2** (60.83°) and **C4** (68.71°). These large differences are expected to have a significant effect on the catalytic behavior of these complexes for the ROP of ε-caprolactone, and this will be discussed in the catalytic discussion (section 2).

Either treatment of **C9** with 1 equiv of $AlMe_3$ or the reaction of **L9** with 2 equiv of $AlMe_3$ in toluene produced the same binuclear aluminum complex **C10**, in which the N of the amide formed a σ-bond with one Al; meanwhile, the O atom of the amide coordinated with $AlMe_3$ via an O-donating type bond. However, recrystallization of complex **C10** failed in obtaining the dimetallic complex but instead afforded single crystals of **C9**, indicating the weak nature of the donating bonding of the O of the amide with $AlMe_3$ in **C10**. In our previous work,[13b] the molecular structure of a dinuclear aluminum compound revealed the presence of a coordinated $AlMe_3$ at the oxygen atom via dative bonding. More importantly, the compound **C10** was confirmed by $^1H/^{13}C$ NMR measurements and elemental analysis. In the ^1H NMR of **C9**, there is only one resonance attributed to the methyl group, which appeared at δ −0.70 ppm (s, 6H); in contrast, two resonances for the methyl groups were observed at δ −0.68 (s, 6H) and −0.72 ppm (s, 9H) in the spectrum of **C10**.

Figure 4 reveals that the molecular structure of diisobutylaluminum *N*-(2-methylquinolin-8-yl)picolinamide (*i*Bu$_2$Al**L9**, **C11**) possesses a geometry similar to that of **C9**, and selected bond lengths and bond angles are collected in Table 1. Small differences are observed between the Al−C bond lengths of **C11** (1.992(2), 1.994(3) Å) versus those of **C2** (1.987(3),

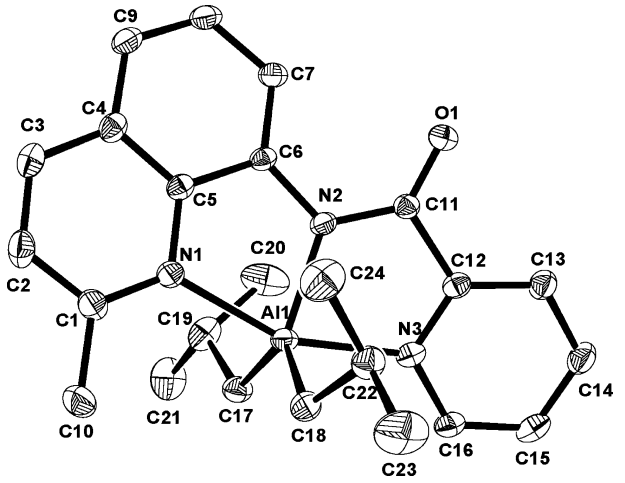

Figure 4. ORTEP drawing of **C11** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

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1.989(3) Å), also in the bond lengths Al−N2$_{imide}$ = 1.940(2) Å, Al−N1$_{quin}$ = 2.135(2) Å, and Al−N1$_{Py}$ = 2.112(3) Å in **C11** compared with those of **C9** (Al−N2$_{imide}$ = 1.952(2) Å, Al−N1$_{quin}$ = 2.134(2) Å, Al−N1$_{Py}$ = 2.121(3) Å). Due to the greater hindrance associated with the iBu group around the Al center, the Al−C bond length in **C11** is much longer than that in **C9**, whereas the Al−N2$_{imide}$ bond length in **C11** is much shorter than that of **C9**.

2. Catalytic Behavior toward Ring-Opening Polymerization (ROP) of ε-Caprolactone (ε-CL). Aluminum compounds are often reported as efficient catalysts for ring-opening polymerization (ROP) of cyclic esters.[5] The catalytic behavior of **C1**−**C11** was explored toward the ROP of ε-CL, which is the first example of the use of aluminum amidates for ring-opening polymerization. Generally these complexes exhibited good activity for the ROP of ε-CL, and the detailed investigations for the optimization of the conditions were conducted by employing **C2** as the initiator, the results for which are collected in Table 2.

Table 2. ROP of ε-CL by C2/BnOH [a]

run	complex	CL:Al:BnOH	T/°C	t/min	yield/mg (%)	$10^{-4}M_n$ [b]	M_w/M_n
1	**C2**	250:1:1	20	30	trace		
2	**C2**	250:1:1	20	60	322 (56.1)	0.75	1.05
3	**C2**	250:1:1	20	90	510 (88.9)	0.82	1.07
4	**C2**	250:1:1	20	720	574 (100)	0.94	1.21
5	**C2**	250:1:1	40	30	485 (84.5)	2.61	1.14
6	**C2**	250:1:1	40	60	515 (89.7)	2.74	1.24
7	**C2**	250:1:1	60	30	530 (92.3)	2.95	1.16
8	**C2**	250:1:1	60	60	557 (97.0)		
9	**C2**	250:1:1	80	5	430 (74.9)	2.16	1.19
10	**C2**	250:1:1	80	10	541 (92.3)	2.88	1.22
11	**C2**	250:1:1	80	20	558 (97.2)	3.19	1.28
12	**C2**	250:1:1	80	30	563 (98.1)	3.69	1.29
13	**C2**	250:1:1	80	60	574 (100)	3.97	1.30
14	**C2**	500:1:1	80	10	1058 (92.2)	2.93	1.23
15	**C2**	500:1:1	80	30	1120 (97.6)	5.32	1.29
16	**C2**	1000:1:1	80	10	1940 (84.5)	6.19	1.24
17	**C2**	1000:1:1	80	30	2220 (96.7)	8.28	1.29
18	**C2**	1000:1:1	80	60	2250 (98.0)	9.71	1.35
19	**C2**	1500:1:1	80	10	2762 (80.2)	9.61	1.28
20	**C2**	2000:1:1	80	10	3361 (73.2)	10.62	1.30
21	**C2**	2500:1:1	80	10	3510 (61.1)	11.85	1.35
22	**C2**	250:1:0	20	30	trace		
23	**C2**	250:1:0	20	90	416 (72.5)	5.18	1.19

[a] Conditions: 20 μmol of cat.; 1.0 M ε-CL toluene solution. [b] GPC data in THF vs polystyrene standards, using a correcting factor of 0.56.[14]

The precatalyst **C2** showed efficiency in the ROP of ε-caprolactone in both the presence and absence of benzyl alcohol (BnOH) (Table 2, runs 1−4 and 23),[5n,13a] though lower activity was observed without the benzene alcohol and such conditions also produced polymers with a still narrow molecule distribution PDI value. Thus, the aluminum complex, in the presence of benzyl alcohol, exhibited better control for the ROP of ε-CL. As a consequence, detailed investigations of complex **C2** have been carried out by using BnOH as coinitiator (Table 2).

Table 2 displays results for both the elevation of the temperature (runs 1, 5, 7, and 12) and the variation of the polymerization time (runs 2−4 and 9−13), which resulted in higher molecular weight polymer and higher conversion rate. For example, only a trace of polymer was obtained at room temperature over 30 min (run 1), whereas high conversion of 92.3% was achieved at 80 °C over 10 min (run 10, Table 2). When the polymerization time was increased from 5 to 60 min (runs 9−13, Table 2), the molecular weight increased with amplified conversion rate, while the molecular weight distribution remained fairly constant (1.19−1.30), consistent with good control for this polymerization process.

As high-molecular-weight polyesters possess better mechanical properties for subsequent utilization, high-molecular-weight PCL is an attractive target.[15] An increase of the monomer/Al ratio often leads to higher molecular weights; however, this is usually to the detriment of the monomer conversion rate. Here, we also investigated the effect of the ε-CL/Al molar ratio on the catalytic behavior, and the results are given in Table 2 (runs 10, 14, 16, and 19−21). When the mole ratio CL:Al is increased from 250 to 2500, the molecular weight increased from 2.88 × 10^4 to 11.85 × 10^4 with little change of molecular weight distribution (1.22 to 1.35), but the conversion rate significantly decreased, producing polymers with lower molecular weight than the calculated M_n values. This may be due to bulky chain transfer properties that resulted in an increase of chain termination when the concentration of monomer increased.[16] It was generally observed that all PCLs obtained in the presence of benzyl alcohol possessed narrow distributions (M_w/M_n = 1.05−1.35) with unimodal characteristics (Table 2), consistent with a single-site active species.

We also investigated the behavior of the other complexes herein toward the ring-opening polymerization of ε-CL, and the results are collected in Table 3. Generally, the amidate aluminum complexes with aryl substituents showed good catalytic activity with high conversion (>90%). The substituent on the aryl ring greatly affected the catalytic activity, with more strongly electron donating substituents leading to higher conversions. Such results were similar to literature reports,[5k,l,15e] and the activity order **C4** (*p*-OMe) > **C6** (*p*-Me) > **C5** (*o*-Me) > **C1** > **C3** (*p*-Cl) > **C2** (*p*-F) was observed. The effect on the molecular weight of the polymer ((2.88−3.66) × 10^4) and on the distribution (PDI 1.22−1.38) was less pronounced. When the substituent on the amidate was changed to an alkyl group, the catalytic activity decreased substantially with lower conversion rates (<90%) and lower molecular weight (runs 6 and 7, Table 3). When the substituent on the amidate was replaced with a pyridine group, the activity decreased rapidly and the conversion decreased to 63.9%, while the molecular weight of the obtained polymer was much lower than those obtained by **C1**−**C5** (run 8), and the binuclear complex **C10** exhibited slightly higher activity than did the mononuclear aluminum complex **C9**. Diisobutylaluminum *N*-(2-methylquinolin-8-yl)picolinamide (iBu$_2$Al**L9**, **C11**) showed much higher activity toward the ring-opening polymerization of ε-CL than did **C9**, which may be attributed to the greater steric hindrance of *i*Bu, which could be beneficial for the existence of a living species. For comparison, blank experiments were also conducted, and the results showed that without benzyl alcohol trimethylaluminum showed poor activity for ring-opening polymerization of ε-CL, even at high temperature (run 13). In the presence of 1 equiv of benzyl alcohol, it can initiate the ring-opening polymerization of ε-CL with considerable activity but produced a polymer with much lower molecular weight and with rather broader distribution (run 14). When the amount of BnOH was increased to 2 or 3 equiv, only trace polymer was obtained (runs 15 and 16). The active species in the reaction of

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Table 3. ROP of ε-CL by C1, C3−C11/BnOH [a]

run	complex	CL:Al:BnOH	T/°C	t/min	yield/mg (%)	$10^{-4}M_n$ [b]	M_w/M_n [b]
1	**C1**	250:1:1	80	10	552 (96.2)	3.55	1.36
2	**C3**	250:1:1	80	10	546 (95.1)	3.66	1.38
3	**C4**	250:1:1	80	10	574 (100)	3.39	1.31
4	**C5**	250:1:1	80	10	553 (96.3)	3.49	1.38
5	**C6**	250:1:1	80	10	565 (98.4)		
6	**C7**	250:1:1	80	10	499 (86.9)	2.84	1.21
7	**C8**	250:1:1	80	10	485 (84.5)	2.54	1.20
8	**C9**	250:1:1	80	10	367 (63.9)	2.93	1.07
9	**C10**	500:2:2	80	10	802 (69.9)	1.28	1.10
10	**C10**	250:2:1	80	10	440 (76.7)	2.84	1.25
11	**C10**	500:2:1	80	10	1010 (88.0)	5.71	1.20
12	**C11**	250:1:1	80	10	466 (81.2)		
13	$AlMe_3$	250:1:0	80	10	52 (8.9)	5.60	1.41
14	$AlMe_3$	250:1:1	80	10	288 (50.2)	1.53	2.97
15	$AlMe_3$	250:1:2	80	10	trace		
16	$AlMe_3$	250:1:3	80	10	trace		
17	**C5**	250:1:2	80	10	568 (99.0)	1.65	1.61
18	**C5**	250:1:5	80	10	431 (75.1)	0.98	1.64
19	**C5**	250:1:10	80	10	trace		

[a]Conditions: 20 μmol of cat.; 1.0 M ε-CL toluene solution. [b]GPC data in THF vs polystyrene standards, using a correcting factor of 0.56.[14]

$AlMe_3$ with 1−3 equiv of BnOH, proposed as $[(BnO)_2AlMe]_n$ derivatives in the literature,[17] could explain the differing polymerization results, through the formation of other aggregated aluminum alkoxides, which are inactive for the ROP of ε-CL. Also, the polymerization behavior when **L2** was employed as the initiator was also investigated under the same conditions, and the results showed that it cannot initiate the ring-opening polymerization of ε-CL in either the absence or presence of benzyl alcohol. Use of increased amounts of BnOH gives polymers with lower molecular weights and broader distributions (runs 4 and 17−19, Table 3), suggesting that the BnOH works as the chain transfer reagent. Similar results were also observed using **C10**/BnOH (runs 9 and 11, Table 3).

3. Mechanism of Ring-Opening Polymerization of ε-Caprolactone by Aluminum Amides. As reported elsewhere in the literature for numerous systems, aluminum alkoxides are assumed to be the active species in the ring-opening polymerization of ε-caprolactone.[18] In this work, some experiments were conducted to investigate the mechanism in more detail. First, the ^{1}H NMR spectra of the resultant polymer was measured to analyze the end group of the polymer, and the results showed a signal for $-OCH_2Ph$ (δ 5.10 ppm), thereby providing evidence for an active species possessing an Al−OCH_2Ph group. Attempts to isolate an intermediate such as **L**(Me)Al−OCH_2Ph by treatment of **C2** with 1 equiv of benzyl alcohol in toluene for 12 h failed, and the NMR spectra of the residue showed two kinds of resonances in the region for aryls; in particular, a broad peak appeared at δ 10.79 ppm. At the same time, the signals for the methyl group were the same as those of the free ligand. The above results were consistent with the recovery of the free ligand in this reaction. In addition, there were some broad peaks at around δ 4.93−5.04 and −1.11 to −1.29 ppm, indicative of unreacted **C2**; according to the integration of ^{1}H NMR spectra, the ratio of free ligand and unreacted **C2** was about 1.7:1. A similar reaction of **C5** with an additional 1 equiv of BnOH afforded similar results with a 1.7:1 ratio of ligand **L5** to unreacted **C5**. However, the reaction of **C5** with 2 equiv of BnOH completely formed the ligand **L5**, as confirmed by NMR spectroscopy; there were some broad peaks around δ 5.1 and −0.83 to −1.29, which were assigned to the presence of unidentified compounds $AlMe_x(OCH_2Ph)_{3-x}$, which are plausibly acting as initiators in the polymerization of ε-CL in a fashion similar to our previous results.[13b] The ligand was probably released within the reaction of the amidate alunmium complexes with BnOH, which is consistent with the observation by the Chen and Roesky groups.[17,19] In order to further investigate the mechanism, the ^{1}H NMR of **C6** with BnOH and ε-CL (the ratio is 1:1:10) after heating at 80 °C showed that there is still a peak for −NHC(O)− at δ 10.76 ppm and two kinds of resonances for $PhCH_2O$ and quin-Me, but also with strong signals for the polymer. For comparison, blank experiments with the free ligand and $AlMe_3$ were conducted for the ROP of ε-CL. Therefore, the ligand itself could not initiate the ROP of ε-CL, and $AlMe_3$ showed only very low activity in the absence of BnOH (run 13, Table 3). When 1 equiv of BnOH was employed as initiator for $AlMe_3$, considerable activity could be achieved with 50.2% conversion yield (run 14, Table 3), giving a polymer showing broad molecular distribution. However, using more BnOH (2 or 3 equiv), the catalytic systems produced only trace amounts of polymer (runs 15 and 16, Table 3). In contrast, the polymerization by complexes **C1**−**C11**/BnOH showed high activity and produced polymers with narrow molecular distributions. These results are further evidence of the advantage of using aluminum complex precatalysts in the ROP of CL, which can afford single-site active species for PCLs with narrow molecular weight distributions. Possibly, any ligands released could coordinate with the alkylaluminum to some extent and act as active species to initiate the polymerization. Though the true active species remains unknown, the ligands used herein have played an important role with regard to the formation of the active species, which efficiently initiated the ROP polymerization of ε-CL in a controlled manner. These complicated species, which underpin this catalytic process, are deserving of further detailed investigations.

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CONCLUSIONS

A series of dialkylaluminum compounds (**C1**−**C11**) containing quinoline amides were synthesized and characterized by $^1H/^{13}C$ NMR spectroscopy and elemental analysis. The molecular structures of the highly sensitive dialkylaluminum compounds **C2**, **C4**, **C9**, and **C11** were confirmed by single-crystal X-ray crystallography. This is the first time the ROP of ε-CL employing aluminum amidates has been reported. All dialkylaluminum amidates exhibited good to high activities in the ROP of ε-CL in the presence of BnOH. The substituents at the amide groups greatly affected the catalytic behavior of their aluminum complexes, and higher activity was achieved by introducing a more strongly electron donating group. With the assistance of benzyl alcohol, the alkylaluminum complexes easily decomposed to the free ligands together with observed aluminum alkoxides; the mixtures of aluminum compounds could efficiently initiate the ring-opening polymerization of ε-CL.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glovebox techniques. Toluene, *n*-heptane, and THF were dried by refluxing over sodium and benzophenone, distilled under nitrogen, and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. C_6D_6 was dried over activated 4 Å molecular sieves. CH_2Cl_2 and $CDCl_3$ were dried over CaH_2 for 48 h, distilled under nitrogen, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. $AlMe_3$ and iBu_3Al were purchased from Aldrich and used as received. The ligands *N*-(2-methylquinolin-8-yl)-benzamide (**L1**−**L6**), *N*-(2-methylquinolin-8-yl)acetamide (**L7** and **L8**), and *N*-(2-methylquinolin-8-yl)picolinamide (**L9**) were synthesized according to the literature procedures.[6d] Elemental analyses were performed using a PE2400II Series (Perkin-Elmer Co.). ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker DMX-400 (400 MHz for ^1H, 100 MHz for ^{13}C) instrument. 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 $SiMe_4$ (δ 0.00, ^1H, ^{13}C). The GPC measurements were performed on a setup consisting of a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and a combination of Styragel HT-2, HT-3, and HT-4, the effective molar mass ranges of which are 100−10 000, 500−30 000 and 5000−600 000, respectively. THF was used as the eluent (flow rate 1 mL min^{-1}, at 40 °C). Molecular weights and molecular weight distributions were calculated using polystyrene as the standard.

Synthesis of *N*-(2-Methylquinolin-8-yl)acetamide (L7). To a stirred toluene solution (50 mL) of 2-methylquinolin-8-amine (1.58 g, 10 mmol) was added 0.72 g (12 mmol) acetic acid at room temperature. The mixture was stirred for 15 min and heated to 80 °C. Trichlorophosphine (0.545 g, 4.0 mmol) was added slowly through a dropping funnel over a period of 15 min. After reflux for an additional 6 h, the solvent was removed by vacuum evaporation. *N*-(2-Methylquinolin-8-yl)acetamide (**L7**) was purified by column chromatography (silica gel, petroleum ether−ethyl acetate 5:1), and 2.16 g (8.3 mmol) of **L7** was obtained (yield 83.0%).[1] H NMR: 9.32 (d, 1H, *J* = 7.56, Qin *H*), 8.02 (d, 1H, *J* = 8.38, Qin *H*), 8.00 (s, 1H, N*H*), 7.44 (m, 2H, Qin *H*), 7.31 (d, 1H, *J* = 8.38, Qin *H*), 2.74 (s, 3H, Qin CH_3), 2.36 (s, 3H, $COCH_3$). ^{13}C NMR: 173.6, 156.5, 142.5, 138.6, 138.1, 129.9, 126.59, 123.8, 123.6, 120.5, 27.1, 25.5. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.82; H, 6.09; N, 14.12.

Synthesis of 2,2,2-Trifluoro-*N*-(2-methylquinolin-8-yl)-acetamide (L8). By using the same procedure as **L7**, 2,2,2-trifluoro-*N*-(2-methylquinolin-8-yl)acetamide (**L8**) was isolated as a yellow solid. Yield: 2.03 g (80.1%). ^1H NMR: 9.45 (d, 1H, *J* = 7.38, Qin *H*), 8.36 (d, 1H, *J* = 7.45, Qin *H*), 8.02 (s, 1H, N*H*), 7.65 (m, 1H, Qin *H*), 7.25(s, 1H, Qin *H*), 7.12 (m, 1H, Qin *H*), 2.38 (s, 3H, Qin CH_3). ^{13}C NMR: 172.3, 156.2, 141.3, 140.5, 138.9, 129.0, 126.1, 122.3, 120.0, 118.5, 26.2, 23.5. Anal. Calcd for $C_{12}H_9F_3N_2O$: C, 56.70; H, 3.57; N, 11.02. Found: C, 56.61; H, 3.59; N, 11.15.

Synthesis of Complexes C1−C11. *Synthesis of Dimethylaluminum N-(2-Methylquinolin-8-yl)benzamidate, [Me_2Al**L1**] (**C1**).* To a stirred solution of *N*-(2-methylquinolin-8-yl)benzamide (0.262 g, 1.0 mmol) in toluene (15.0 mL) was added 1.0 mL (1.0 mmol) of $AlMe_3$ solution (1.0 M solution in toluene) dropwise at −30 °C. The slurry was warmed slowly to room temperature and was stirred for 3 h, and the solution became clear. Following concentration to 5 mL in vacuo, 10 mL of *n*-heptane was added, and the solution was placed in the freezer (−30 °C) to afford **C1** as a yellow powder. Yield: 0.261 g (82.1%). ^1H NMR ($CDCl_3$): δ 8.95 (d, 1H, *J* = 7.82, Qin *H*), 8.36 (d, 1H, *J* = 8.41, Qin *H*), 7.76 (d, 2H, *J* = 7.11, Qin *H*), 7.67 (t, 1H, *J* = 8.02, Qin *H*), 7.45 (m, 5H, Ar *H*), 2.81 (s, 3H, Py CH_3), −0.87 (s, 6H, $Al(CH_3)_2$).^{13}C NMR ($CDCl_3$): δ 174.6, 156.5, 141.2, 140.8, 140.6, 138.8, 130.2, 128.8, 128.4, 127.2, 126.5, 123.1, 122.1, 119.3, 22.8, −8.9. Anal. Calcd for $C_{19}H_{19}AlN_2O$: C, 71.68; H, 6.02; N, 8.80; Found: C, 71.22; H, 6.13; N, 8.73.

*Synthesis of Dimethylaluminum 4-Fluoro-N-(2-methylquinolin-8-yl)benzamidate, [Me_2Al**L2**] (**C2**).* The synthesis of **C2** was carried out by the same procedure as for **C1**, except 4-fluoro-*N*-(2-methylquinolin-8-yl)benzamide was used. Yield: 0.293 g (87.1%). ^1H NMR ($CDCl_3$): δ 8.89 (d, 1H, *J* = 7.88, Qin *H*), 8.38 (d, 1H, *J* = 8.44, Qin *H*), 7.77 (m, 2H, Qin *H*), 7.69 (t, 1H, *J* = 8.04, Qin *H*), 7.52 (s, 1H, *J* = 8.08, Ar *H*), 7.45 (d, 1H, *J* = 8.44, Ar *H*), 7.15 (t, 2H, *J* = 8.68, Ar *H*), 2.83 (s, 3H, Qin CH_3), −0.84 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR ($CDCl_3$): 174.2, 165.5, 163.0, 157.0, 141.7, 139.2, 130.0, 129.9, 129.3, 126.9, 123.4, 123.1, 115.8, 115.6, 23.3, −8.6. Anal. Calcd for $C_{19}H_{18}AlFN_2O$: C, 67.85; H, 5.39; N, 8.33. Found: C, 67.56; H, 5.61; N, 8.24.

*Synthesis of Dimethylaluminum 4-Chloro-N-(2-methylquinolin-8-yl)benzamidate, [Me_2Al**L3**] (**C3**).* Using the same procedure as for **C1**, dimethylaluminum 4-chloro-*N*-(2-methylquinolin-8-yl)-benzamidate, [Me_2Al**L3**] (**C3**), was isolated as a yellow solid. Yield: 0.286 g (81.2%). ^1H NMR ($CDCl_3$): δ 8.90 (d, 1H, *J* = 7.32, Qin *H*), 8.38 (d, 1H, *J* = 7.56, Qin *H*), 7.69 (m, 3H, Qin *H*), 7.51 (m, 2H, Ar *H*), 7.44 (m, 2H, Ar *H*), 2.83 (s, 3H, Qin CH_3), −0.84 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 173.9, 165.3, 163.1, 157.2, 141.3, 139.5, 130.0, 129.8, 129.3, 127.2, 123.9, 123.0, 115.2, 115.3, 23.3, −8.6. Anal. Calcd for $C_{19}H_{18}AlClN_2O$: C, 64.68; H, 5.14; N, 7.94. Found: C, 64.81; H, 5.17; N, 7.79.

*Synthesis of Dimethylaluminum 4-Methoxy-N-(2-methylquinolin-8-yl)benzamidate, [Me_2Al**L4**] (**C4**).* Using the same procedure as for **C1**, dimethylaluminum 4-methoxy-*N*-(2-methylquinolin-8-yl)-benzamidate, [Me_2Al**L4**] (**C4**), was isolated as a yellow solid. Yield: 0.255 g (73.2%). ^1H NMR ($CDCl_3$): δ 8.84 (d, 1H, *J* = 7.92, Qin *H*), 8.36 (d, 1H, *J* = 8.40, Qin *H*), 7.76 (d, 2H, *J* = 8.12, Qin *H*), 7.67 (t, 1H, *J* = 8.04, Qin *H*), 7.47 (d, 1H, *J* = 8.18, Ar *H*), 7.43 (d, 1H, *J* = 8.45, Ar *H*), 6.97 (d, 2H, *J* = 8.13, Ar *H*), 3.88 (s, 3H, OCH_3), 2.82 (s, 3H, Qin CH_3), −0.83 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 175.2, 156.8, 141,4, 140.9, 139.1, 129.3, 129.1, 129.0, 128.2, 127.5, 126.8, 125.3, 123.3, 113.8, 55.4, 23.1, −8.6. Anal. Calcd for $C_{20}H_{21}AlN_2O_2$: C, 68.95; H, 6.08; N, 8.04. Found: C, 68.72; H, 6.11; N, 8.15.

*Synthesis of Dimethylaluminum 2-Methyl-N-(2-methylquinolin-8-yl)benzamidate, [Me_2Al**L5**] (**C5**).* Using the same procedure as for **C1**, dimethylaluminum 2-methyl-*N*-(2-methylquinolin-8-yl)-benzamidate, [Me_2Al**L5**] (**C5**), was isolated as a yellow solid. Yield: 0.283 g (85.2%). ^1H NMR ($CDCl_3$): δ 8.36 (d, 1H, *J* = 8.42, Qin *H*), 7.66 (t, 1H, *J* = 7.93, Qin *H*), 7.48 (d, 2H, *J* = 8.30, Qin *H*), 7.43 (d, 1H, *J* = 8.45, Qin *H*), 7.33 (d, 1H, *J* = 7.88, Ar *H*), 7.25 (m, 3H, Ar *H*), 2.81 (s, 3H, Py CH_3), 2.41 (s, 3H, Ar CH_3), −0.90 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR: 175.1, 156.7, 141.5, 141.0, 140.0, 139.1, 136.0, 130.6, 129.5, 129.4, 127.1, 126.9, 125.6, 121.6, 119.3, 23.2, 19.6, −9.2. Anal. Calcd for $C_{20}H_{21}AlN_2O$: C, 72.27; H, 6.37; N, 8.43. Found: C, 72.15; H, 6.42; N, 8.52%.

*Synthesis of Dimethylaluminum 4-Methyl-N-(2-methylquinolin-8-yl)benzamidate, [Me_2Al**L6**] (**C6**).* Using the same procedure as for **C1**, dimethylaluminum 4-methyl-*N*-(2-methylquinolin-8-yl)-benzamidate, [Me_2Al**L6**] (**C6**), was isolated as a yellow solid. Yield:

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Table 4. Crystal Data and Refinement Details for C2, C4, C9, and C11

	C2	C4	C9	C11
empirical formula	$C_{19}H_{18}AlFN_2O$	$C_{20}H_{21}AlN_2O_2$	$C_{36}H_{36}Al_2N_6O_2$	$C_{24}H_{30}AlN_3O$
formula wt	336.33	348.37	638.67	403.49
cryst color	colorless	colorless	colorless	colorless
temp (K)	173(2)	173(2)	173(2)	173(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Pna2_1$
a (Å)	7.3526(15)	8.9394(18)	13.006(3)	15.405(3)
b (Å)	8.7401(17)	26.659(5)	17.275(4)	9.907(2)
c (Å)	13.854(3)	7.5551(15)	14.339(3)	14.858(3)
α (deg)	74.85(3)	90	90	90
β (deg)	88.40(3)	94.03(3)	90.54	90
γ (deg)	79.40(3)	90	90	90
V (Å^3)	844.5(3)	1796.1(6)	3221.5(11)	2267.6(8)
Z	2	4	4	4
D_{calcd} (Mg m^{-3})	1.323	1.288	1.317	1.182
μ (mm^{-1})	0.138	0.128	0.134	0.108
$F(000)$	352	736	1344	864
cryst size (mm)	0.50 × 0.45× 0.18	0.76 × 0.47 × 0.46	0.44 × 0.38 × 0.29	0.40 × 0.25 × 0.20
θ range (deg)	2.46−27.51	2.41−26.38	1.57−27.48	2.74−27.48
limiting indices	$-7 \le h \le 9$	$-11 \le h \le 11$	$-16 \le h \le 13$	$-19 \le h \le 14$
	$-10 \le k \le 11$	$-33 \le k \le 33$	$-22 \le k \le 22$	$-5 \le k \le 12$
	$-17 \le l \le 18$	$-9 \le l \le 9$	$-17 \le l \le 18$	$-13 \le l \le 19$
no. of rflns collected	9341	18 344	28 296	6255
no. of unique rflns	3868	3667	7347	3662
R_{int}	0.0398	0.0466	0.0555	0.0298
completeness to θ (%)	99.2	99.8	99.4	99.1
goodness of fit on F^2	1.100	1.143	1.235	1.073
final R indices ($I > 2\sigma(I)$)	R1 = 0.0632, wR2 = 0.1803	R1 = 0.0638, wR2 = 0.1721	R1 = 0.0804, wR2 = 0.1758	R1 = 0.0444, wR2 = 0.1180
R indices (all data)	R1 = 0.0682, wR2 = 0.1852	R1 = 0.0656, wR2 = 0.1738	R1 = 0.0873, wR2 = 0.1801	R1 = 0.0454, wR2 = 0.1190
largest diff peak, hole (e Å^{-3})	0.363, −0.276	0.422, −0.407	0.360, −0.395	0.252, −0.264

0.283 g (85.2%). ^{1}H NMR ($CDCl_3$): δ 8.90 (d, 1H, J = 7.72, Qin H), 8.39 (d, 1H, J = 8.40, Qin H), 7.69 (m, 3H, Ar H), 7.52 (d, 1H, J = 7.56, Qin H), 7.45 (d, 1H, J = 8.40, Ar H), 7.28 (d, 2H, J = 7.80, Ar H), 2.83 (s, 3H, Qin CH_3), 2.44 (s, 3H, Ar CH_3), −0.85 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR: 175.5, 165.2, 163.5, 156.9, 141.1, 139.8, 130.0, 129.9, 129.8, 127.2, 123.6, 123.2, 115.7, 115.3, 23.3, 19.8, −8.9. Anal. Calcd for $C_{20}H_{21}AlN_2O$: C, 72.27; H, 6.37; N, 8.43. Found: C, 72.20; H, 6.30; N, 8.55.

*Synthesis of Dimethylaluminum N-(2-Methylquinolin-8-yl)-acetamidate, [Me$_2$Al**L7**] (**C7**).* Using the same procedure as for **C1**, dimethylaluminum *N*-(2-methylquinolin-8-yl)acetamide, [Me$_2$Al**L7**] (**C7**), was isolated as a yellow solid. Yield: 0.283 g (85.2%). ^{1}H NMR ($CDCl_3$): 8.49 (d, 1H, J = 7.32, Qin H), 8.38 (s, 1H, J = 7.14, Qin H), 7.52 (m, 3H, Qin H), 2.88 (s, 3H, Qin CH_3), 2.44 (s, 3H, $COCH_3$), −0.50 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR: 174.9, 157.1, 142.0, 139.5, 138.8, 129.5, 126.9, 123.3, 122.1, 120.3, 27.0, 23.3, −9.6. Anal. Calcd for $C_{14}H_{17}AlN_2O$: C, 65.61; H, 6.69; N, 10.93. Found: C, 65.55; H, 6.61; N, 10.85.

*Synthesis of Dimethylaluminum 2,2,2-Trifluoro-N-(2-methylquinolin-8-yl)acetamidate, [Me$_2$Al**L8**] (**C8**).* Using the same procedure as for **C1**, dimethylaluminum 2,2,2-trifluoro-*N*-(2-methylquinolin-8-yl)acetamidate, [Me$_2$Al**L8**] (**C8**), was isolated as a yellow solid. Yield: 0.283 g (85.2%). ^{1}H NMR ($CDCl_3$): 9.40 (d, 1H, J = 7.28, Qin H), 8.27 (s, 1H, Qin H), 7.38 (m, 3H, Qin H), 2.34 (s, 3H, Qin CH_3), −0.56 (s, 6H, $Al(CH_3)_2$). ^{13}C NMR: 174.1, 156.4, 141.6, 140.8, 138.5, 129.4, 126.7, 122.9, 120.5, 118.5, 27.5, 23.0, −9.6. Anal. Calcd for $C_{14}H_{14}AlF_3N_2O$: C, 54.20; H, 4.55; N, 9.03. Found: C, 54.31; H, 4.50; N, 9.01.

*Synthesis of Dimethylaluminum N-(2-Methylquinolin-8-yl)-picolinamidate, [Me$_2$Al**L9**] (**C9**).* Using the same procedure as for **C1**, dimethylaluminum *N*-(2-methylquinolin-8-yl)benzamidate, [Me$_2$Al**L9**] (**C9**), was isolated as a yellow solid. Yield: 0.267 g (83.5%). ^{1}H NMR ($CDCl_3$): δ 9.40 (d, 1H, J = 7.80), 8.54 (d, 1H, J = 4.92), 8.47 (d, 1H, J = 7.84), 8.23 (d, 1H, J = 8.37), 8.10 (t, 1H, J = 7.65), 7.66 (d, 1H, J = 4.86), 7.62 (d, 1H, J = 7.89), 7.51 (d, 1H, J = 7.91), 7.41 (d, 1H, J = 8.38), 2.97 (s, 3H), −0.70 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 165.1, 156.4, 149.9, 144.2, 139.8, 139.7, 139.0, 138.7, 128.1, 126.5, 126.4, 124.0, 122.8, 120.3, 120.2, 23.1, −6.0. Anal. Calcd for $C_{18}H_{18}AlN_3O$: C, 67.70; H, 5.68; N, 13.16. Found: C, 67.82; H, 5.77; N, 13.12.

*Synthesis of Dimethylaluminum N-(2-Methylquinolin-8-yl)-picolinamidate Trimethylaluminum [AlMe$_2$**L9**·AlMe$_3$] (**C10**).* To a stirred solution of *N*-(2-methylquinolin-8-yl)picolinamide (**L9**; 0.263 g, 1.0 mmol) in toluene (15.0 mL) was added 2.0 mL (2.0 mmol) of $AlMe_3$ solution (1.0 M solution in toluene) dropwise at −30 °C. The slurry was warmed slowly to room temperature and was stirred for 3 h, and the solution became clear. Following concentration to 5 mL in vacuo, 10 mL of *n*-heptane was added, and the solution was placed in the freezer (−30 °C) to afford **C10** as a yellow powder. Yield: 0.314 g (80.1%). ^{1}H NMR ($CDCl_3$): δ 9.30 (d, 1H, J = 6.72), 8.65 (d, 1H, J = 7.94), 8.59 (d, 1H, J = 5.00), 8.30 (d, 1H, J = 8.42), 8.18 (t, 1H, J = 7.77), 7.75 (t, 1H, J = 5.26), 7.69 (m, 2H), 7.48 (d, 1H, J = 11.94), 3.00 (s, 3H), −0.68 (s, 6H), −0,72 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.3, 157.7, 147.3, 145.1, 140.5, 139.4, 139.2, 136.5, 128.1, 127.7, 126.7, 125.2, 124.7, 124.0, 123.4, 23.4, −6.0, −6.7. Anal. Calcd for $C_{21}H_{27}Al_2N_3O$: C, 64.44; H, 6.95; N, 10.74. Found: C, 64.56; H, 6.82; N, 10.52.

*Synthesis of Diisobutylaluminum N-(2-Methylquinolin-8-yl)-picolinamidate, [iBu$_2$Al**L9**] (**C11**).* To a stirred solution of *N*-(2-methylquinolin-8-yl)picolinamide (**L9**; 0.263 g, 1.0 mmol) in toluene (15.0 mL) was added 2.0 mL (2.0 mmol) of Al*i*Bu$_3$ solution (1.0 M solution in toluene) dropwise at −30 °C. The slurry was warmed slowly to room temperature and was stirred for 3 h, and the solution became clear. Following concentration to 5 mL in vacuo, 10 mL of *n*-

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heptane was added, and the solution was placed in the freezer (−30 °C) to afford **C11** as a yellow powder. Yield: 0.344 g (85.2%). ^{1}H NMR ($CDCl_3$): δ 9.49 (d, 1H, J = 7.86), 8.57 (d, 1H, J = 4.98), 8.45 (d, 1H, J = 7.79), 8.22 (d, 1H, J = 8.36), 8.10 (t, 1H, J = 7.64), 7.65 (d, 1H, J = 4.85), 7.61 (m, 1H), 7.47 (d, 1H, J = 8.07), 7.40 (d, 1H, J = 8.37), 3.00 (s, 3H), 1.07 (m, 2H), 0.55 (d, 6H, J = 6.44), 0.42 (d, 6H, J = 6.40), 0.17 (d, 2H, J = 7.16), 0.12 (d, 2H, J = 6.72). ^{13}C NMR ($CDCl_3$): δ 165.5, 156.5, 151.2, 144.6, 140.4, 139.9, 139.4, 138.9, 128.5, 126.7, 126.1, 124.0, 122.8, 120.4, 120.1, 28.4, 28.3, 27.8, 27.0, 24.0, 23.5, 19.5. Anal. Calcd for $C_{24}H_{30}AlN_3O$: C, 71.44; H, 7.49; N, 10.41. Found: C, 71.52; H, 7.40; N, 10.53.

Ring-Opening Polymerization (ROP) of ε-Caprolactone (CL). Typical polymerization procedures in the presence of benzyl alcohol (Table 2, run 10) are as follows. A toluene solution of **C2** (0.020 mmol, 1.0 mL of toluene) and BnOH (0.020 mmol) were added into a Schlenk tube in the glovebox at room temperature. The solution was stirred for 2 min, and then ε-caprolactone (5.0 mmol) along with 3.44 mL of toluene was added to the solution. The reaction mixture was then placed into an oil bath preheated to 80 °C, and the solution was stirred for the prescribed time (10 min). The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried in vacuo.

Crystal Structure Determinations. Single crystals of **C2**, **C4**, **C9**, and **C11** suitable for X-ray structural analysis were obtained from chilled toluene/*n*-heptane solution. With graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[20] Details of the X-ray structure determinations and refinements are provided in Table 4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray crystal structural data for **C2**, **C4**, **C9**, and **C11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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