



# Synthesis, structures and $\epsilon$ -caprolactone polymerization activity of aluminum $N,N'$ -dimethyloxalamidates

Wanda Ziemkowska<sup>a,\*</sup>, Jakub Kochanowski<sup>a</sup>, Michał K. Cyrański<sup>b</sup>

<sup>a</sup>Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland

<sup>b</sup>Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

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## ABSTRACT

Alkyl aluminum  $N,N'$ -dimethyloxalamidates  $R_4Al_2(\text{dmoa})$  (**1**,  $R = \text{Me}$ ; **2**,  $R = \text{Et}$ ; **3**,  $R = {}^i\text{Bu}$ ; **4**,  $R = {}^t\text{Bu}$ ) ( $\text{dmoa-H}_2 = N,N'$ -dimethyloxalamide) have been prepared and characterized. Molecular structures of the compounds **1** and **4** have been determined by X-ray crystallography. The centrosymmetric molecules of the compounds consist of one  $N,N'$ -dimethyloxalamidate unit bonded to two four-coordinated aluminum atoms. Each of the aluminum atoms is bonded to two alkyl groups, and oxygen and nitrogen atoms originating from two different amidate groups. A skeleton framework of the molecules of **1** and **4** consists of two fused  $\text{AlNOC}_2$  heterocyclic rings, which are flat and positioned in one plane. It was shown that compounds **1–3** were initiators in a process of ring opening polymerization (ROP) of  $\epsilon$ -caprolactone. The compound **4** exhibited low activity in ROP.

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## 1. Introduction

Transition metal amidates are ubiquitous in chemistry as important catalysts and reagents in chemical transformations [1]. Although aluminum amidates are less useful in an organic synthesis, there are reports on their application in polymerizations of acetaldehyde and phthalaldehyde [2]. Recently tris-amidate aluminum complex was proposed as the catalyst resting state in a transamidation reaction between simple secondary carboxamides and primary amines [3]. According to literature data, the structure of alkyl aluminum amidates and coordination mode of amidate ligands on aluminum depend strongly on bulkiness of amidate units and alkyl groups bonded to aluminum atoms [4–8]. Electronic effects originating from aromatic substituents are also important.

Known complexes of diamidate dianions with organoaluminum compounds are limited to a few examples [9]. We report herein the synthesis and structural characterization of aluminum  $N,N'$ -dimethyloxalamidates as an extension of the previously described organoaluminum oxalamidates [9]. Preliminary studies of the catalytic performances of the compounds in the ring opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) are also reported.

## 2. Results and discussion

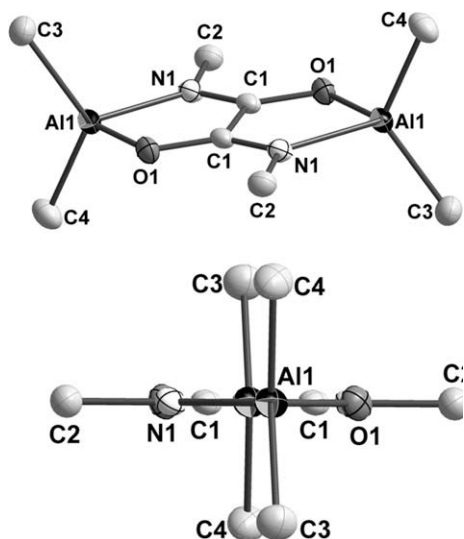
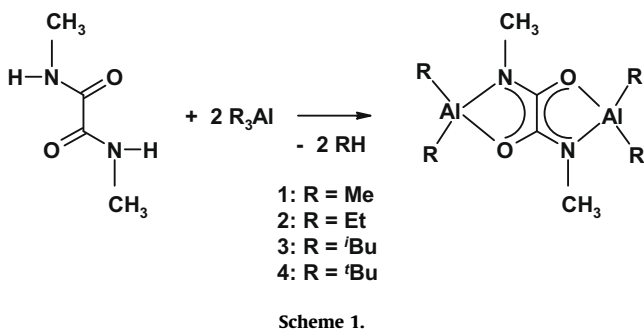
$N,N'$ -dimethyloxalamide ( $\text{dmoa-H}_2$ ) reacted with  $R_3\text{Al}$  ( $R = \text{Me}$ ,  $\text{Et}$ ,  ${}^i\text{Bu}$ ,  ${}^t\text{Bu}$ ) in a 1:2 M ratio or with an excess of  $R_3\text{Al}$ , to produce the dialkylaluminum  $N,N'$ -dimethyloxalamidates  $R_4Al_2(\text{dmoa})$  (**1**,  $R = \text{Me}$ ; **2**,  $R = \text{Et}$ ; **3**,  $R = {}^i\text{Bu}$ ; **4**,  $R = {}^t\text{Bu}$ ) (Scheme 1). Compounds **2** and **3** were isolated as liquids in 81% and 75% yield, respectively. Solid compounds **1** and **4** were obtained in 100% and 45% yield respectively.

The molecular structures of the compounds **1** and **4** were determined on the basis of an X-ray diffraction study and are shown in Figs. 1 and 2. Data collection and structure analysis are listed in Table 1 [10].

The centrosymmetric molecules of **1** and **4** consist of one  $N,N'$ -dimethyloxalamidate unit bonded to two four-coordinated aluminum atoms. Similarly to the dimeric and trimeric aluminum monoamidates  $\{R_2\text{Al}[\mu, \eta^2\text{-R}'\text{NC}(\text{R}'')\text{O}]\}_n$  ( $n = 2, 3$ ) [7,8], each of the aluminum atoms is bonded to two alkyl groups, and oxygen and nitrogen atoms originating from two different amidate groups which are a part of the same  $N,N'$ -dimethyloxalamidate unit. The geometry around the aluminum atoms is a distorted tetrahedron. A skeleton framework of the molecules of **1** and **4** consists of two fused  $\text{AlNOC}_2$  heterocyclic rings which are flat and positioned in one plane. The sums of the angles about the nitrogen atoms [ $\Sigma(\text{N}) = 360.0$ ] in the both compounds show that N(1), C(1), C(2) and Al(1) atoms are situated in one plane and C(2) atom is located in the plane of the skeleton framework. It is interesting to note that the bond lengths for C(1)–N(1) of 1.289(2) Å and C(1)–O(1) of

\* Corresponding author. Tel.: +48 22 2347316.

E-mail address: [ziemk@ch.pw.edu.pl](mailto:ziemk@ch.pw.edu.pl) (W. Ziemkowska).

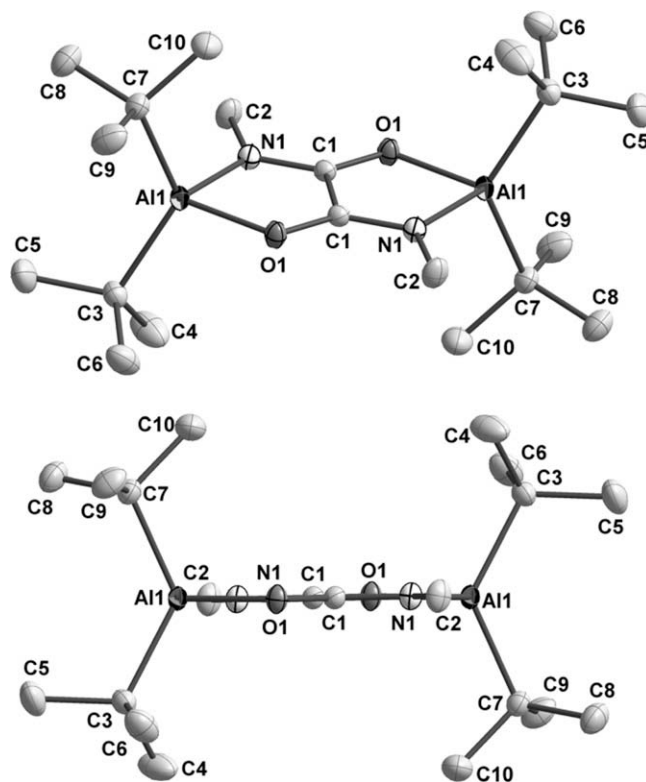


**Fig. 1.** (Top) Molecular structure of  $\text{Me}_4\text{Al}_2(\text{dmoa})$  (**1**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Al(1)–O(1) 1.859(1), Al(1)–C(3) 1.944(2), Al(1)–C(4) 1.949(2), Al(1)–N(1) 1.958(2), C(1)–N(1) 1.289(2), C(1)–O(1) 1.287(2), O(1)–Al(1)–C(3) 110.49(6), O(1)–Al(1)–C(4) 111.19(8), C(3)–Al(1)–C(4) 121.15(8), O(1)–Al(1)–N(1) 86.36(6), C(3)–Al(1)–N(1) 112.37(7), C(4)–Al(1)–N(1) 109.92(8). (Bottom) View of the molecule showing that two fused central cycles and two N(1)–C(2) bonds are situated in one plane.

1.287(2) Å in the compound **1** and the bond lengths for C(1)–N(1) of 1.294(1) Å and C(1)–O(1) of 1.280(1) Å in the compound **4** indicate a delocalized structure within the OCCN groups. The bond lengths for Al(1)–O(1) of 1.859(1) Å and 1.862(1) Å in **1** and **4** respectively are found to be similar to those in aluminum amidates [in the region of 1.806(2)–1.925(3) Å] reported by Lin and coworkers [7,8]. On the other hand, Al(1)–N(1) bond distances [1.958(2) Å in **1** and 1.957(1) Å in **4**] are similar only to those of aluminum amidates with a delocalized structure within the OCN groups in which the Al–N bond lengths are situated in the region of 1.954(3)–1.987(2) Å.

Besides molecular structure determination of the compounds **1** and **4**, all compounds were characterized by NMR spectroscopy and elemental analyses. The  $^1\text{H}$  NMR spectrum of **1** in solution revealed one singlet of  $\text{CH}_3\text{Al}$  group protons at  $-0.80$  ppm and one singlet of  $\text{NCH}_3$  group protons at 3.00 ppm in a 2:1 relative intensity ratio. In the  $^1\text{H}$  NMR spectrum of the compound **4**, protons of four  $(\text{CH}_3)_3\text{CAI}$  groups exhibited one singlet at 0.90 ppm. The singlet at 3.06 ppm was assigned to the protons of two methyl groups attached to the nitrogen atoms of the amidate moiety.  $^1\text{H}$  NMR spectra of **1** and **4** in solutions are in agreement with the solid-state structures.

Besides the signal at 3.02 ppm of  $\text{NCH}_3$  protons, the  $^1\text{H}$  NMR spectrum of **2** revealed signals of protons of ethyl group bonded



**Fig. 2.** (Top) Molecular structure of  $i\text{-Bu}_4\text{Al}_2(\text{dmoa})$  (**4**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Al(1)–O(1) 1.862(1), Al(1)–N(1) 1.957(1), C(1)–O(1) 1.280(1), C(1)–N(1) 1.294(1), Al(1)–C(3) 1.987(1), Al(1)–C(7) 1.987(1), O(1)–Al(1)–N(1) 86.47(3), O(1)–Al(1)–C(3) 108.33(4), N(1)–Al(1)–C(3) 112.24(4), O(1)–Al(1)–C(7) 107.58(4), N(1)–Al(1)–C(7) 109.91(4), C(3)–Al(1)–C(7) 125.24(4). (Bottom) View of the molecule showing that two fused  $\text{C}_2\text{NOAl}$  cycles are coplanar.

to aluminum atoms (triplet at 0.93 ppm of  $\text{AlCH}_2\text{CH}_3$  and quartet at  $-0.06$  of  $\text{AlCH}_2\text{CH}_3$  protons. In the  $^1\text{H}$  NMR spectrum of **3** the following signals were present: a singlet at 3.01 ppm of  $\text{NCH}_3$ , a multiplet at 1.77 ppm of  $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , two doublets at 0.88 and 0.89 ppm of  $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , and a multiplet at 0.04 ppm of  $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$  protons, in a 3:2:6:6:4 relative intensity ratio. Each of the complexes **1–4** exhibited one signal of  $\text{C}=\text{O}$  carbons in the  $^{13}\text{C}$  NMR spectra in the region of 164.3–164.4 ppm. The NMR spectra indicated the equivalence of alkyl groups bonded to the aluminum atoms and the equivalence of  $\text{C}=\text{O}$  carbons of oxalamidate units, which is in agreement with the structures of **1–4**.

Some of organoaluminum compounds with nitrogen-containing ligands are known as good initiators in ring opening polymerization (ROP) of cyclic esters [11]. We found, that complexes **1–3** initiate ROP of  $\epsilon$ -CL. The catalytic activity of the compound **4** is much lower than that of **1–3**. The results are listed in Table 2.

The catalytic behavior of the complexes in polymerization was studied in methylene dichloride with monomer to aluminum ratios fixed at 25, 50 and 100. Compound **1** showed low catalytic activity at 25  $^\circ\text{C}$ . At a higher temperature (60  $^\circ\text{C}$ ) the reaction rate increased dramatically. For example, at 25  $^\circ\text{C}$  poly- $\epsilon$ -caprolactone (PCL) was obtained with a yield of 13% in 48 h, while at 60  $^\circ\text{C}$  the yield of the polymer was 100% in 24 h (Table 2, entries 3 and 4). On the other hand, polymers obtained at lower temperature revealed more narrow PDI values and lower molecular weights (Table 2, entries 1 and 3). Compounds **2** and **3** exhibited better reactivity towards ROP than that of the compound **1**. Independent of the temperature, the molar ratio of [Al]:monomer and the time of polymerization, PCL has been obtained quantitatively (Table 2,

**Table 1**  
Crystal data and data collection parameters for **1** and **4**.

	1	4
Empirical formula	C <sub>8</sub> H <sub>18</sub> Al <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>42</sub> Al <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	228.20	396.52
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	5.7261(7)	8.8629(4)
<i>b</i> (Å)	6.5520(5)	11.6433(6)
<i>c</i> (Å)	9.433(1)	12.5053(5)
$\alpha$ (°)	94.698(9)	90
$\beta$ (°)	101.21(1)	103.376(4)
$\gamma$ (°)	111.01(1)	90
<i>V</i> (Å <sup>3</sup> )	319.62(6)	1255.5(1)
<i>Z</i>	1	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.186	1.049
Absorption coefficient (mm <sup>-1</sup> )	0.208	0.130
<i>F</i> (0 0 0)	122	436
Crystal size (mm)	0.3 × 0.20 × 0.10	0.50 × 0.20 × 0.10
$\theta$ Range for data collection (°)	3.38–28.65	2.94–27.50
Index ranges	–7 ≤ <i>h</i> ≤ 7, –8 ≤ <i>k</i> ≤ 8, –12 ≤ <i>l</i> ≤ 12	–11 ≤ <i>h</i> ≤ 8, –15 ≤ <i>k</i> ≤ 15, –16 ≤ <i>l</i> ≤ 16
Reflections collected	6037	10 575
Independent reflections	1559 ( <i>R</i> <sub>int</sub> = 0.0375)	2842 ( <i>R</i> <sub>int</sub> = 0.0150)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1559/0/63	2842/0/125
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	0.659	0.941
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0359, <i>wR</i> <sub>2</sub> = 0.0921	<i>R</i> <sub>1</sub> = 0.0310, <i>wR</i> <sub>2</sub> = 0.1028
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0610, <i>wR</i> <sub>2</sub> = 0.0887	<i>R</i> <sub>1</sub> = 0.0354, <i>wR</i> <sub>2</sub> = 0.1090
Maximum/minimum of residual electron density	0.383 and –0.271	0.399 and –0.282

**Table 2**  
Ring opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL).

Run	Initiator	Al/CL	Time (h)	Temp. (°C)	Yield <sup>a</sup> (%)	<i>M</i> <sub>n</sub> <sup>b</sup> × 10 <sup>-4</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>a</sup>
1	<b>1</b>	1:25	48	25	20	0.77	1.18
2	<b>1</b>	1:50	24	60	100	3.74	1.47
3	<b>1</b>	1:100	48	25	13	1.46	1.37
4	<b>1</b>	1:100	24	60	100	12.63	2.44
5	<b>2</b>	1:25	48	60	100	1.68	1.71
6	<b>2</b>	1:50	24	60	100	1.83	1.64
7	<b>2</b>	1:100	24	60	100	4.03	1.60
8	<b>3</b>	1:50	24	60	100	6.89	2.08
9	<b>3</b>	1:100	48	25	100	2.73	2.84
10	<b>3</b>	1:100	24	60	100	9.05	1.81
11	<b>4</b>	1:100	24	25	0	–	–
12	<b>4</b>	1:100	24	60	9	0.96	2.98

<sup>a</sup> Isolated yield.<sup>b</sup> GPC data in CHCl<sub>3</sub> vs. polystyrene standards.

entries 5–9). The PDI values were situated in the region of 1.60–2.84. In contrast, catalytic activity of the compound **4** is low. An attempt for the ROP of  $\epsilon$ -caprolactone at 25 °C afforded no polymer (Table 2, entry 10). At 60 °C the polymer was formed in a 9% yield (Table 2, entry 11).

The alkyl aluminum *N,N'*-dimethyloxalamidates **1–4** were the first aluminum diamidates tested for an activity in the polymerization of cyclic esters. In comparison with aluminum amine bis(phenolate)s reported by Chen and coworkers (time of polymerization 15–30 min, temperature 50 °C, yield 87–99%, PDI 1.04–1.12) [111], the compounds **1–3** exhibited lower catalytic activity. On the other hand, the catalytic activity of **1–3** was similar to that of alkylaluminum macrocyclic Schiff base complexes (time 11–24 h, temperature 25–60 °C, conversion 14–99%, PDI 1.1–2.6) [11e] and better than a catalytic activity of aluminum complexes bearing *N,O*-chelate phenolate ligands (time 680 min, temperature 60 °C, yield 19.4–29.8%, PDI 1.32–1.40) [11c].

Summarizing, we have prepared alkyl aluminum *N,N'*-dimethyloxalamidates in the reaction of *N,N'*-dimethyloxalamide with

*R*<sub>3</sub>Al (*R* = Me, Et, <sup>*i*</sup>Bu, <sup>*t*</sup>Bu). The methyl-, ethyl- and *iso*-butylaluminum derivatives feature catalytic activity in the ROP of  $\epsilon$ -CL. Though, the performance of this catalytic process was plagued by the poor degree of control expressed by high PDI values. The *tert*-butylaluminum derivative exhibited the poor catalytic activity.

### 3. Experimental

#### 3.1. Materials and instrumentation

All manipulations were carried out using standard Schlenk techniques under an inert gas atmosphere. The solvents were distilled over a blue benzophenone-K complex. *N,N'*-dimethyloxalamide,  $\epsilon$ -CL and *R*<sub>3</sub>Al (*R* = Me, Et, <sup>*i*</sup>Bu) were purchased from Aldrich. <sup>*t*</sup>Bu<sub>3</sub>Al was synthesized as described in the literature [12]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Mercury-400BB spectrometer. <sup>1</sup>H NMR spectra were recorded at 400.09 MHz. Chemical shifts were referenced to the residual proton signals of

$\text{CDCl}_3$  (7.26 ppm).  $^{13}\text{C}$  NMR spectra were acquired at 100.60 MHz (standard: chloroform  $^{13}\text{CDCl}_3$ , 77.20 ppm). IR spectra were obtained using a Nicolet 6700 FT-IR infrared spectrometer. Hydrolyzable alkyl groups and a content of aluminum for compounds **1–4** were determined according to the literature [13].

### 3.2. Complex syntheses

#### 3.2.1. Synthesis of $\text{Me}_4\text{Al}_2(\text{dmoa})$ (**1**)

Trimethyl aluminum (1.584 g, 22 mmol) was injected to a stirred solution of *N,N'*-dimethylloxalamide (1.140 g, 10 mmol) in  $\text{Et}_2\text{O}$  (50  $\text{cm}^3$ ) at  $-76^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature. A light yellow solution of the post-reaction mixture was obtained. The solvent and the excess of  $\text{Me}_3\text{Al}$  were removed *in vacuo* from the post-reaction mixture, and a white solid of the compound **1** was obtained quantitatively (yield 2.26 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.00 ( $\text{NCH}_3$ , s, 6H),  $-0.80$  ( $\text{AlCH}_3$ , s, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 164.29 ( $\text{C}=\text{O}$ ), 24.74 ( $\text{NCH}_3$ ),  $-13.43$  ( $\text{AlCH}_3$ ) ppm.

X-ray quality crystals were grown by sublimation *in vacuo* from the post-reaction solid. Mp. (sublimed crystals):  $117\text{--}120^\circ\text{C}$ . IR ( $1500\text{--}1700\text{ cm}^{-1}$ , Nujol):  $\nu = 1662.3$  (s).

Elemental anal.: Al, 23.85; hydrolyzable methyl groups, 26.05; Calc. for  $\text{Me}_4\text{Al}_2(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)$ : Al, 23.68; Me, 26.32 wt.%.

#### 3.2.2. Synthesis of $\text{Et}_4\text{Al}_2(\text{dmoa})$ (**2**)

Compound **2** was synthesized as described for compound **1**, using 2.508 g (22 mmol) of  $\text{Et}_3\text{Al}$  and a solution of *N,N'*-dimethylloxalamide (1.140 g, 10 mmol) in  $\text{Et}_2\text{O}$  (50  $\text{cm}^3$ ). Volatiles were removed from the post-reaction mixture. A pure compound **2** was distilled off *in vacuo* as a thick liquid (yield 2.284 g, 8.1 mmol, 81%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.02 ( $\text{NCH}_3$ , s, 6H), 0.93 ( $\text{AlCH}_2\text{CH}_3$ , t,  $^3J_{\text{H-H}} = 8.1$  Hz, 12H),  $-0.06$  ( $\text{AlCH}_2\text{CH}_3$ , q,  $^3J_{\text{H-H}} = 8.1$  Hz, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 164.42 ( $\text{C}=\text{O}$ ), 29.47 ( $\text{NCH}_3$ ), 8.18 ( $\text{AlCH}_2\text{CH}_3$ ),  $-2.09$  ( $\text{AlCH}_2\text{CH}_3$ , broad) ppm.

Elemental anal.: Al, 18.88; hydrolyzable ethyl groups, 41.24; Calc. for  $\text{Et}_4\text{Al}_2(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)$ : Al, 19.01; Et, 40.85 wt.%.

#### 3.2.3. Synthesis of $^i\text{Bu}_4\text{Al}_2(\text{dmoa})$ (**3**)

Compound **3** was synthesized as described for compound **1**, using 4.356 g (22 mmol) of  $^i\text{Bu}_3\text{Al}$  and a solution of *N,N'*-dimethylloxalamide (1.140 g, 10 mmol) in  $\text{Et}_2\text{O}$  (50  $\text{cm}^3$ ). Volatiles were removed from the post-reaction mixture. A pure compound **3** was distilled off *in vacuo* as a thick liquid (yield 2.955 g, 7.5 mmol, 75%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.01 ( $\text{NCH}_3$ , s, 6H), 1.77 ( $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , m, 4H), 0.88 ( $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , d,  $^3J_{\text{H-H}} = 6.3$  Hz, 12H), 0.89 ( $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , d,  $^3J_{\text{H-H}} = 6.3$  Hz, 12H), 0.04 ( $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , m, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 164.30 ( $\text{C}=\text{O}$ ), 29.40 ( $\text{NCH}_3$ ), 27.85, 27.80 [ $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ ], 25.69 [ $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ ], 20.43 [ $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$ , broad] ppm.

Elemental anal.: Al, 13.90; hydrolyzable iso-butyl groups, 57.88; Calc. for  $^i\text{Bu}_4\text{Al}_2(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)$ : Al, 13.62;  $^i\text{Bu}$ , 57.50 wt.%.

#### 3.2.4. Synthesis of $^t\text{Bu}_4\text{Al}_2(\text{dmoa})$ (**4**)

Compound **4** was synthesized as described for compound **1**, using 1.360 g (5 mmol) of  $^t\text{Bu}_3\text{Al}\cdot\text{OEt}_2$  and a solution of *N,N'*-dimethylloxalamide (0.285 g, 2.5 mmol) in  $\text{Et}_2\text{O}$  (30  $\text{cm}^3$ ). Volatiles were removed from the post-reaction mixture. A pure compound **4** was crystallized from an *n*- $\text{C}_6\text{H}_{14}$  solution at  $-20^\circ\text{C}$  as colorless crystals (yield 0.443 g, 1.1 mmol, 45%). Mp.:  $171\text{--}174^\circ\text{C}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.06 ( $\text{NCH}_3$ , s, 6H), 0.90 ( $\text{AlC}(\text{CH}_3)_3$ , s, 36H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 164.30 ( $\text{C}=\text{O}$ ), 30.07 ( $\text{NCH}_3$ ), 29.36 ( $\text{AlC}(\text{CH}_3)_3$ ), 14.90 ( $\text{AlC}(\text{CH}_3)_3$ ) ppm.

IR ( $1500\text{--}1700\text{ cm}^{-1}$ , Nujol):  $\nu = 1648.8$  (s).

Elemental anal.: Al, 13.95; hydrolyzable *tert*-butyl groups, 57.20; Calc. for  $^t\text{Bu}_4\text{Al}_2(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)$ : Al, 13.62;  $^t\text{Bu}$ , 57.50 wt.%.

### 3.2.5. General procedure for $\epsilon$ -caprolactone polymerization

Polymerization reactions were carried out in closed glass ampoules. A solvent ( $\text{CH}_2\text{Cl}_2$ ), monomer and initiator solution were added into ampoules successively. The ampoules were kept in thermostat. The reactions were terminated by 5% HCl aq. solution. The resulting polymer was washed by  $\text{CH}_3\text{OH}$  for several times and dried in vacuum. In general,  $\epsilon\text{-CL}$  (2.28 g, 2 mmol) was polymerized by an initiator (for the ratios of  $\epsilon\text{-CL}/[\text{Al}]$  see Table 2) in 20  $\text{cm}^3$  of  $\text{CH}_2\text{Cl}_2$ . An approximate conversion yield was obtained as a ratio of the PLC mass to the monomer mass.

### 3.2.6. X-ray crystal structure determinations

Crystals of compounds **1** and **4** were mounted in inert oil and sealed in glass capillaries under argon. Determination of the crystal structures was performed on a KUMA CCD  $\kappa$ -axis diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation. A crystal of **1** was positioned at 62.25 mm from the KM4CCD camera and 1328 frames were measured at  $0.9^\circ$  intervals with a counting time of 20 s. A crystal of **4** was positioned at 62.25 mm from the KM4CCD camera and 856 frames were measured at  $0.7^\circ$  intervals with a counting time of 10 s. Data reduction and analysis were carried out with the Kuma Diffraction programs. The data were corrected for Lorentz and polarization effects. The multi-scan absorption correction for **4** was applied [14]. No absorption correction for **1** was applied. The structures were solved by direct methods [15] and refined using SHELXL [16]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a difference map and refined isotropically. The atomic scattering factors were taken from the International Tables [17].

The X-ray structures were measured in the Crystallography Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

### Supplementary material

CCDC 753781 and 753782 contain the supplementary crystallographic data for **1** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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