DOI: 10.1002/chem.200800679

Aluminum Compounds Containing η^1- and/or η^5-Bidentate Dianionic Pyrrolyl–Methylamide Ligands

Ya-Chi Chen,[a] Che-Yu Lin,[a] Chun-Yin Li,[a] Jui-Hsien Huang,*[a] Ling-Chueh Chang,[b] and Ting-Yu Lee[b]

Abstract: A series of dialuminum compounds have been synthesized and their reactivity and application for lactide polymerization have been studied. The reaction of $AlH_3{\cdot}NMe_3$ with $[C_4H_3NH(2\text{-}CH_2NH\mathit{t}Bu)]$ in diethyl ether generated a dimeric aluminum hydride compound, $[\{[C_4H_3N(2\text{-}CH_2N\mathit{t}Bu)]AlH\}_2]$ (**1**). The structure of **1** was confirmed by spectroscopy of a deuterated analogue of **1** with an Al−D function. Direct treatment of $[C_4H_3NH(2\text{-}CH_2NH\mathit{t}Bu)]$ with $LiAlH_4$ in diethyl ether resulted in colorless crystals of $[\{Li[\mu\text{-}\eta^1{:}\eta^5\text{-}C_4H_3N(2\text{-}CH_2N\mathit{t}Bu)]_2Al\}_2]$ (**2**) in 80 % yield after recrystallization from a toluene solution. The μ-η^1:η^5-pyrrolyl protons exhibit high-field shifts at $\delta = 5.73$, 6.15, and 6.72 comparable to a similar η^5-bonding mode in the literature. Treatment of **1** with 1 equiv acetone oxime or acetone in dichloromethane gave $[\{[C_4H_3N(2\text{-}CH_2N\mathit{t}Bu)]Al\text{-}[\kappa O,\kappa N\text{-}(ON{=}CMe_2)]\}_2]$ (**3**) and $[\{[C_4H_3N(2\text{-}CH_2N\mathit{t}Bu)]Al(O{-}CHMe_2)\}_2]$ (**4**) in 67 % and 60 % yield, respectively. Compounds **1**–**4** have been characterized by X-ray diffractometry and were used as catalysts for ε-caprolactone polymerization.

Keywords: aluminum · caprolactone · lithium · ring-opening polymerization · sandwich complexes

Introduction

Aluminum hydrides are widely used as reducing agents.[1] They also have various applications, such as alkyne and olefin hydroalumination[2] and hydrogen storage.[3] Hydridoaluminates are usually soluble in most ethereal solvents but only marginally soluble in less polar organic solvents. This has limited their application in organic synthesis.[4] Therefore, discovery of new organoaluminum hydride compounds with high solubility in common organic solvents is important for organic synthesis and related applications.[5] One way to increase the solubility of aluminum hydride is to add an organic substrate to the aluminum atom, forming organoaluminum compounds. Various methods have been used to synthesize organoaluminum hydrides, which exist as monomeric,[6] dimeric,[7] or oligomeric[8] molecular structures; $LiAlH_4$ and $H_3Al{\cdot}NMe_3$[9] are two important starting materials for these syntheses. Aluminum hydrides react readily with a variety of organometallic molecules such as zirconocenes,[10] $R_2SbSiMe_3$,[11] and organic molecules such as 1-octyne and bipyridine.[12,13] We have been interested in finding new organoaluminum hydrides with ketiminate or donor-substituted pyrrole ligands, and have studied their reactions with PhNCO, CO_2, H_2O, and tertiary alcohols.[14] Donor-substituted pyrrolyl ligands can bind to the metal atoms in either a η^1 or a η^5 fashion,[15,16] but only a few examples exist in which the pyrrolyl units bind to metal atoms in both ways simultaneously.[17] Herein we report the synthesis, characterization, and reactions of donor-substituted pyrrolyl aluminum compounds with such η^1 and/or η^5 bonding modes. We also studied their applicability to ring-opening polymerizations of ε-caprolactone.

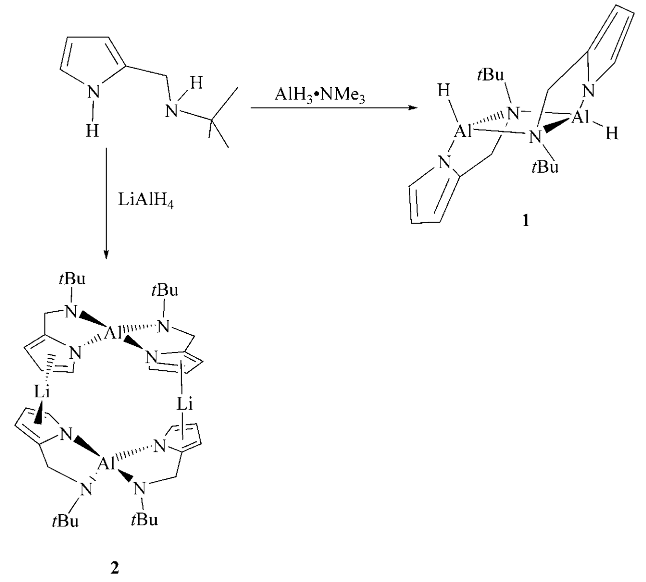
Results and Discussion

Synthesis and characterization of 1–4: The reaction of $AlH_3{\cdot}NMe_3$, generated in situ from the reaction of $LiAlH_4$ and $Me_3N{\cdot}HCl$, with $[C_4H_3NH(2\text{-}CH_2NH\mathit{t}Bu)]$ in diethyl ether afforded the dimeric aluminum hydride $[\{[C_4H_3N(2\text{-}CH_2N\mathit{t}Bu)]AlH_2\}]$ (**1**) in 69 % yield (Scheme 1). The ^{1}H NMR spectrum of **1** shows one set of resonances for the

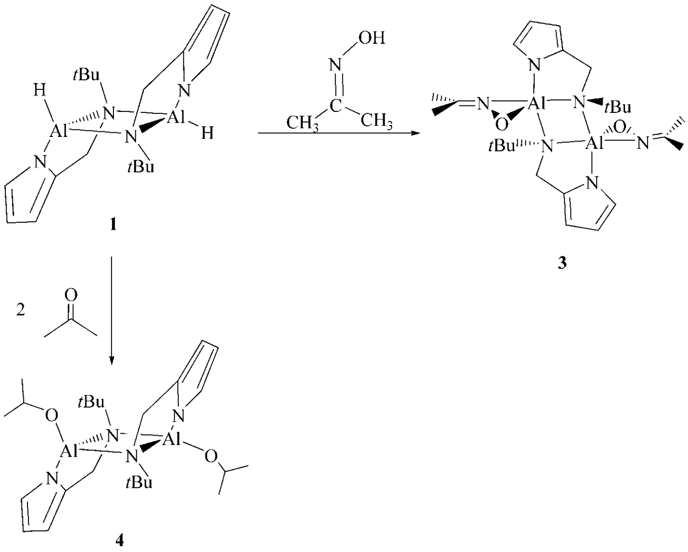
---

[a] Y.-C. Chen, C.-Y. Lin, C.-Y. Li, J.-H. Huang
Department of Chemistry
National Changhua University of Education
Changhua 50058, Taiwan
Fax:(+886) 4-7211190
E-mail: juhuang@cc.ncue.edu.tw

[b] L.-C. Chang, T.-Y. Lee
Department of Applied Chemistry
National University of Kaohsiung,
Kaohsiung 811, Taiwan



Scheme 1.



Scheme 2.

substituted pyrrolyl ligands with the methylene protons of CH_2NtBu appearing as an AB system with two doublets at $\delta = 4.43$ and 3.90 ppm. The pyrrolyl protons are in the normal η^1 model range ($\delta = 6.22$, 6.67, and 6.88 ppm). The terminal hydride was not observed in the ^1H NMR spectrum, presumably due to the quadrupole interaction with the aluminum nucleus ($I = 5/2$).[19] However, the solid-state IR spectrum supports the existence of a terminal Al–H in **1** as evidenced by the absorption at $\tilde{\nu} = 1912\ cm^{-1}$. To confirm the structure of **1**, $LiAlD_4$ was used to prepare **1-D**, in which an Al–D function is present. The ^1H and ^{13}C NMR spectra of **1** and **1-D** exhibit the same resonance pattern with very similar chemical shifts. The Al–D stretching frequency of **1-D** is shifted to $\tilde{\nu} = 1388\ cm^{-1}$ owing to the isotopic effect, which predicts it to be at $\tilde{\nu} = 1376\ cm^{-1}$.

Direct treatment of [$C_4H_3NH(2\text{-}CH_2NHtBu)$] with 1 equiv or an excess of $LiAlH_4$ in diethyl ether (Scheme 1) resulted in an off-white residue after the solution had been filtered through Celite and the solvent had been removed. The residue was recrystallized from a toluene solution to afford colorless crystals of [{Li[μ-η^1:η^5-$C_4H_3N(2\text{-}CH_2NtBu)]_2Al\}_2$] (**2**) in 80% yield. The ^1H and ^{13}C NMR spectra of **2** exhibit a symmetrical pattern with only one set of [$C_4H_3N(2\text{-}CH_2NtBu)$] signals. The μ-$\eta^1$:$\eta^5$-pyrrolyl protons exhibit high-field shifts at $\delta = 5.73$, 6.15, and 6.72 ppm, comparable to a similar η^5-bonding mode in the literature.[20] Again, the methylene protons of the CH_2NtBu gave a pseudo-AB spin system showing two very close doublets at $\delta = 3.99$ and 4.03 ppm.

Compounds **1** and **2** are highly air- and moisture-sensitive. Treatment of **1** with 1 equiv acetone oxime or acetone in dichloromethane gave [{[$C_4H_3N(2\text{-}CH_2NtBu)$]Al[κ*O*,κ*N*-(ON=$CMe_2$)]}$_2$] (**3**) and [{[$C_4H_3N(2\text{-}CH_2NtBu)$]Al(O–$CHMe_2$)}$_2$] (**4**) in 67% and 60% yield, respectively (Scheme 2). Compound **3** is highly thermolabile and decomposes at room temperature in solution within hours, forming unidentified aluminum compounds. The ^1H NMR spectra showed a *t*-butyl resonance at $\delta = 1.13$ and 0.91 ppm for **3** and **4**, respectively, and two doublets for the methylene protons of CH_2NtBu at $\delta = 4.53$ and 4.07 ppm for **3** and $\delta = 4.90$ and 3.94 ppm for **4**. The ^{13}C NMR spectrum of **3** also showed a singlet at $\delta = 157.07$ ppm corresponding to the carbon atom bound to the oximate group. Further study of the reactivity of **3** is ongoing.[21]

Crystal structures of 1–4: Compounds **1**–**4** have been characterized by X-ray crystallography. A summary of the data collection and selected bond lengths and angles are given in Tables 1 and 2. The **1** molecule (Figure 1) contains a center of symmetry and contains an almost regular Al_2N_2 square, in which two *t*-butylamino groups bridge the two aluminum atoms. The Al(1A)-N(2)-Al(1) and N(2A)-Al(1)-N(2) angles are 90.4(1) and 89.6(1)°, respectively, and the Al(1)–N(2) and Al(1)–N(2A) bond lengths are very similar (1.963(1) and 1.957(1) Å, respectively). The two aluminum atoms adopt tetrahedral structures with the dianionic substituted pyrrolyl ligand bound to the aluminum atom at an angle (91.4(1)°) that is much smaller than the tetrahedral angle. The Al–N(pyrrolyl) bond (1.834(1) Å) is much shorter than the bridging Al–N(amide) bonds (1.963(1) Å).

Crystals of **2** were obtained from a saturated toluene solution at −20°C. Its molecule (Figure 2) contains two toluene molecules in the unit cell. Compound **2** contains two bis(pyrrolylmethylamide)aluminate units linked by two lithium cations bonded to the pyrrolyl ligand $C_4H_3N(2\text{-}CH_2NtBu)$ in a η^1:η^5 manner. Although pyrrolyl ligands can coordinate to metals in a η^1 or η^5 fashion, only a few limited examples of pyrrolyl ligands bound to two metals with η^1:η^5 modes have been structurally characterized.[20,22] The dihedral angle between the two AlN_2C_2 five-membered rings is 97.1°. The lithium ions are coordinated to pyrrole rings in η^5 modes in

Table 1. Summary of crystallographic data for **1**–**4**.

	1	**2**·2 toluene	**3**	**4**
formula	$C_{18}H_{30}Al_2N_4$	$C_{50}H_{72}Al_2Li_2N_8$	$C_{24}H_{40}Al_2N_6O_2$	$C_{24}H_{42}Al_2N_4O_2$
FW	356.42	853.00	498.58	472.58
T [K]	150(2)	150(2)	150(2)	150(2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*	*P*$\bar{1}$
a [Å]	17.4235(7)	19.015(4)	9.9108(11)	9.938(7)
b [Å]	6.5794(3)	14.690(3)	13.1651(15)	9.957(7)
c [Å]	17.2047(7)	18.149(4)	10.3241(12)	16.532(12)
α [°]	90	90	90	88.939(15)
β [°]	95.751(2)	90.672(13)	98.393(2)	73.097(13)
γ [°]	90	90	90	60.083(13)
V [Å^3]	1962.35(14)	5069.3(17)	1332.6(3)	1340.7(17)
Z	4	4	2	2
ρ_c [Mg m^{-3}]	1.206	1.118	1.243	1.171
μ [mm^{-1}]	0.155	0.098	0.141	0.135
F(000)	768	1840	536	512
crystal size [mm]	0.35 × 0.32 × 0.28	0.35 × 0.2 × 0.28	0.33 × 0.28 × 0.22	0.20 × 0.19 × 0.16
λ [Å]	0.71073	0.71073	0.71073	0.71073
rflns collected	11028	45312	27924	17351
independent rflns	2607	9913	3564	5762
	(R_{int} = 0.0147)	(R_{int} = 0.1447)	(R_{int} = 0.1044)	(R_{int} = 0.0764)
data/restraints/parameters	2607/0/116	9913/0/573	3564/0/159	5762/0/299
goodness-of-fit on F^2	1.051	1.001	0.941	0.973
R_1, wR_2 ($I > 2\sigma(I)$)	0.0293, 0.0836	0.0653, 0.1836	0.0364, 0.0963	0.0505, 0.1372
R_1, wR_2 (all data)	0.0313, 0.0850	0.1370, 0.2151	0.0569, 0.1012	0.0939, 0.1781
largest diff. peak, hole [e Å^{-3}]	0.302, −0.251	0.335, −0.363	0.452, −0.234	0.538, −0.716

Table 2. Selected bond lengths [Å] and angles [°] for compounds **1**–**4**.

1			
Al(1)–N(2A)	1.957(1)	Al(1)–N(2)	1.963(1)
Al(1)–N(1)	1.834(1)		
Al(1A)-N(2)-Al(1)	90.4(1)	N(2)-Al(1)-N(2A)	89.6(1)
N(2)-Al(1)-N(1)	91.4(1)	N(1)-Al(1)-N(2A)	117.1(1)
2			
Al(1)–N(1)	1.891(3)	Al(1)–N(2)	1.804(3)
Al(1)–N(3)	1.881(3)	Al(1)–N(4)	1.790(3)
Al(2)–N(5)	1.883(3)	Al(2)–N(6)	1.803(3)
Al(2)–N(7)	1.878(3)	Al(2)–N(8)	1.797(3)
Li(1)–N(3)$_{cent}$	1.955	Li(1)–N(7)$_{cent}$	1.949
Li(2)–N(1)$_{cent}$	1.932	Li(2)–N(5)$_{cent}$	1.918
N(3)-Al(1)-N(4)	88.7(1)	N(1)-Al(1)-N(2)	89.3(1)
N(7)-Al(2)-N(8)	88.5(1)	N(5)-Al(2)-N(6)	89.6(1)
N(7)$_{cent}$-Li(1)-N(3)$_{cent}$	152.7	N(1)$_{cent}$-Li(1)-N(5)$_{cent}$	144.1
3			
Al(1)–N(1)	1.830(1)	Al(1)–N(2)	2.002(1)
Al(1)–N(3)	2.035(1)	Al(1)–N(2A)	1.942(1)
Al(1)–O(1)	1.772(1)	O(1)–N(3)	1.440(1)
N(3)–C(11)	1.278(2)		
Al(1A)-N(2)-Al(1)	91.7(1)	N(2A)-Al(1)-N(2)	88.8(1)
O(1)-Al(1)-N(1)	120.6(1)	N(2)-Al(1)-N(1)	89.8(1)
N(2)-Al(1)-O(1)	113.7(1)	O(1)-N(3)-C(11)	117.2(1)
4			
Al(1)–O(1)	1.701(2)	Al(1)–N(1)	1.855(2)
Al(1)–N(2)	1.956(3)	Al(1)–N(2A)	1.956(3)
Al(2)–O(2)	1.696(2)	Al(1)–N(3)	1.842(2)
Al(2)–N(4)	1.969(2)	Al(2)–N(4A)	1.974(3)
Al(1A)-N(2)-Al(1)	90.9(1)	N(2A)-Al(1)-N(2)	89.1(1)
O(1)-Al(1)-N(1)	118.3(1)	N(2)-Al(1)-N(1)	118.5(1)
N(2)-Al(1)-O(1)	108.6(1)	N(2A)-Al(1)-N(1)	91.9(1)
N(2A)-Al(1)-O(1)	127.5(1)	Al(2A)-N(4)-Al(2)	90.5(1)
O(2)-Al(2)-N(3)	118.4(1)	N(4A)-Al(2)-O(2)	127.6(1)
N(4)-Al(2)-O(2)	108.7(1)	N(4)-Al(2)-N(3)	118.3(1)
N(4A)-Al(2)-N(3)	91.5(1)	N(4A)-Al(2)-N(4)	89.5(1)

a staggered sandwich geometry. The pyrrolyl ligands are bound to the hard lithium atoms similarly to a π-fashion, quite differently from other η^1-pyrrolyl lithium compounds recorded in the literature.[23] The measured centroid distances between the η^5-pyrrolyl moiety and the lithium atoms are around 2.22 Å, which is quite similar to the values reported for other heterocyclic lithium sandwich geometries.[22b]

Colorless crystals of **3** were obtained from a saturated toluene solution at −20 °C. The **3** molecule (Figure 3) can be regarded as an aluminum oximate. Oximates have several possible bonding modes with metals such as group 13,[24] Zn,[25] and others,[26] as shown (**a**–**d**). Some metal oximates have been reported and structurally characterized.[21,27] The structure of **3** retains an Al_2N_2 core as in **1**, the Al(1A)-N(2)-Al(1) and N(2A)-Al(1)-N(2) angles being 91.7(1)° and 88.3(1)°, respectively. The aluminum centers have tetrahedral geometries with the oximate fragments (O–N=CMe$_2$) bound to the aluminum centers in a η^2-fashion through the N and O atoms. This is the first observation of a η^2 binding mode of an oximate in group 13 chemistry. In all other known cases, the oximate bridges two metal ions, but is always η^1-bonded to one atom. The O(1)-N(3)-C(11) bond angle (117.2(1)°) and N(3)–C(11) bond length (1.278(2) Å) are in the normal range compared to those in the literature.[28]

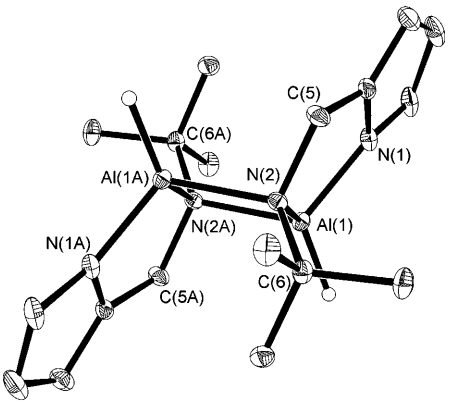
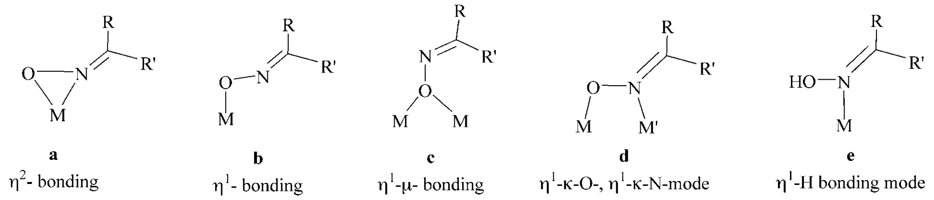


Figure 1. Molecular structure of **1**. The thermal ellipsoids are drawn at the 30 % probability level and all hydrogen atoms except those directly bonded to aluminum are omitted for clarity.



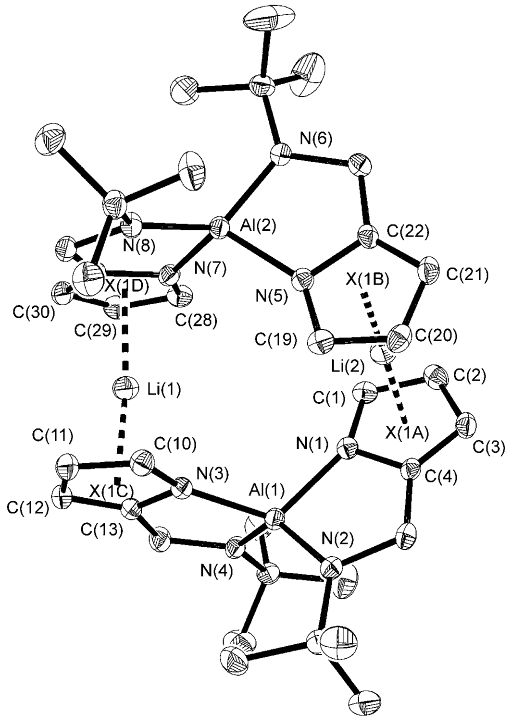


Figure 2. Molecular structure of **2**. The thermal ellipsoids are drawn at the 30 % probability level and all hydrogen atoms are omitted for clarity.

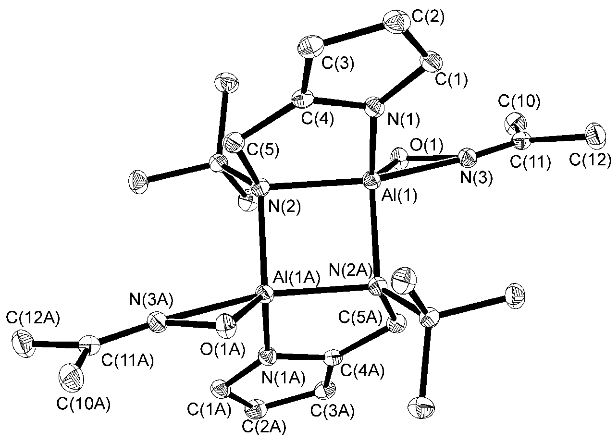


Figure 3. Molecular structure of **3**. The thermal ellipsoids are drawn at the 30 % probability level and all hydrogen atoms are omitted for clarity.

Pale pink crystals of **4** were obtained from a toluene/pentane mixed solution at −20 °C. There are two independent molecules in a unit cell. However, their bond lengths and angles are relatively similar and only one of them is described and shown here (Figure 4). The **4** structure also contains an Al_2N_2 core with angles and lengths close to a perfect square. The bite angles of $[C_4H_3N(2\text{-}CH_2N\mathit{t}Bu)]$ with aluminum atoms for **1** and **4** (91.4(1) and 91.9(1)°) are smaller than those for **2** and **3** ((89.3(1) and 89.8(1)°), presumably because the ions in **2** and **3** have higher steric-congestion.

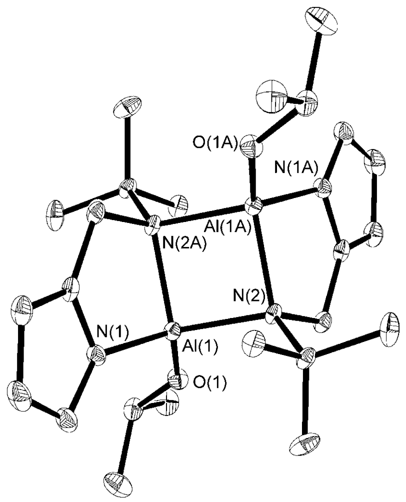


Figure 4. Molecular structure of **4**. The thermal ellipsoids are drawn at the 30 % probability level and all hydrogen atoms are omitted for clarity.

Ring-opening polymerization of ε-caprolactone catalyzed by 1, 2, 3, and 4: The conditions and results of the ring-opening polymerizations of ε-caprolactone using compounds **1**, **2**, **3**, and **4** as catalysts in dichloromethane (**1**, **3**, and **4**) or toluene (**2**) at room temperature are summarized in Table 3. The range of the polydispersity index (PDI) of the poly(ε-caprolactone) product (1.29 to 1.75) was comparable to or a little broader than that of the polymer obtained with other aluminum compounds.[29] Compounds **1**–**4** were all found to catalyze the polymerization of ε-caprolactone, but **3** and **4**

Table 3. Polymerization of ε-caprolactone using **1**, **2**, **3**, and **4** as initiators at room temperature.

Initiator[a]	Monomer [g]	Product [g]	M_n(obs)[b]	M_n/M_w[c]	Yield [%][d]	Activity[e]
1	0.97	0.2314	25 000	1.39	20.75	2.75×10^3
2	0.52	0.2951	25 900	1.29	51.23	3.51×10^3
3	0.69	0.7072	38 900	1.75	97.56	8.40×10^3
4	0.73	0.7581	48 200	1.36	99.48	9.01×10^3

[a] [Al]* = initialized catalyst with [M]/[I] = 100. [b] Obtained directly from GPC data. [c] M_n/M_w = Weight-average molecular weight/number-average molecular weight. [d] Yield [%] = (Product[g]−initiator [g])/monomer[g]. [e] Activity = product [g]/initiator [mol].

showed higher reactivities and yields than **1** and **2**. This is consistent with the results reported in the literature that a large number of metal alkoxides are active in ring-opening polymerization.[30]

Conclusion

This work provides a good method for synthesis and characterization of organoaluminum hydrides from aluminum trihydride. Compound **1** shows good reactivity toward unsaturated organofunctional groups such as C=O or C=NOH to form aluminum alkoxides or aluminum oximates. A further study of the reactivity and reaction pathways of **1** with various organic functional groups is in progress. The PDIs of the poly-ε-caprolactone polymerized using the aluminum compounds synthesized are relatively broad, but fine tuning of the steric properties of the aluminum alkoxides may make it possible to obtain to obtain a better PDI value for the polymers.

Experimental Section

General procedure: All reactions were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or in a glove box. Toluene and diethyl ether were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded by using a Bruker Avance 300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual protons of $CDCl_3$ ($\delta = 7.24$, 77.0 ppm) and C_6D_6 ($\delta =$ 7.15, 128.0 ppm). Elemental analyses were performed by using a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center of the NCHU. [C_4H_3NH(2-CH_2NH*t*Bu)] was prepared by a similar procedure to that reported in the literature.[14] $LiAlH_4$, Me_3N·HCl and acetone oxime (Aldrich) were used as received.

[{[C_4H_3N(2-CH_2N*t*Bu)]AlH}$_2$] (1): A flask was charged with Me_3N·HCl (2.00 g, 20.9 mmol) and diethyl ether (20 mL) and cooled to 0 °C. A $LiAlH_4$ (0.95 g, 25.1 mmol)/diethyl ether (20 mL) suspension was added to the solution dropwise and stirred for another 2 h after the addition was complete. The solution was then filtered through Celite to yield a Me_3N·AlH_3/diethyl ether solution, to which a [C_4H_4N(2-CH_2NH*t*Bu)] (3.19 g, 20.9 mmol)/diethyl ether (20 mL) solution was added dropwise with stirring at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 12 h. The resulting suspension was vacuum-dried, then the residue was extracted with toluene and filtered through Celite. The filtrate was concentrated to a small amount and recrystallized to generate **1** (2.56 g, 68.6 % yield). ^1H NMR (C_6D_6): $\delta = 0.74$ (s, 18 H; N*t*Bu), 3.90, 4.43 (dd, 4 H; $^2J_{HH} = 16.8$ Hz, CH_2N), 6.22, 6.67, 6.88 (m, 6 H; pyrrolyl protons); ^{13}C NMR (C_6D_6): $\delta = 28.7$ (q, $J_{CH} = 126$ Hz, NC*Me*$_3$), 45.3 (t, $J_{CH} = 138$ Hz, *C*H_2N), 56.6 (s, N*C*Me_3), 104.4 (d, $J_{CH} = 167$ Hz, pyrrole), 115.2 (d, $J_{CH} = 170$ Hz, pyrrole), 120.7 (d, $J_{CH} = 180$ Hz, pyrrole), 138.1 ppm (s, pyrrole); elemental analysis calcd (%) $C_{18}H_{30}N_4Al_2$ (356.42): C 60.66, H 8.48, N 15.72; found C 61.28, H 9.08, N 15.84.

{[C_4H_3N(2-CH_2N*t*Bu)]AlD}$_2$ (1-D): The procedure was the same as for **1**, except that the $LiAlH_4$ was substituted with $LiAlD_4$.

[{Li[μ-η^1:η^5-C_4H_3N(2-CH_2N*t*Bu)]$_2$Al}$_2$](2): A [C_4H_4N(2-CH_2NH*t*Bu)] (3.19 g, 20.9 mmol)/diethyl ether (25 mL) solution was added dropwise at 0 °C to a 100 mL Schlenk flask charged with $LiAlH_4$ (1.25 g, 33 mmol) and diethyl ether (25 mL). The mixture was stirred for another 8 h and filtered through Celite. The volatiles were removed under vacuum and the residue was recrystallized from a toluene solution to yield the final product (8.78 g, 80 % yield). ^1H NMR (C_6D_6): $\delta = 1.16$ (s, 26 H; N*tBu*), 3.99, 4.03 (dd, 4 H; C*H*$_2$N), 5.73, 6.15, 6.72 ppm (m, 6 H; pyrrolyl protons); ^{13}C NMR (C_6D_6): $\delta = 30.2$ (q, $J_{CH} = 124$ Hz, NC*Me*$_3$), 42.9 (t, $J_{CH} =$ 134 Hz, *C*H_2N), 50.7 (s, N*C*Me_3), 102.2 (d, $J_{CH} = 169$ Hz, pyrrole), 111.3 (d, $J_{CH} = 169$ Hz, pyrrole), 119.6 (d, $J_{CH} = 182$ Hz, pyrrole), 145.5 ppm (s, pyrrole).

[{[C_4H_3N(2-CH_2N*t*Bu)]Al[κ*O*,κ*N*-(O−N=CMe_2)]}$_2$] (3): Acetone oxime (0.2 g, 2.8 mmol)/CH_2Cl_2 solution (20 mL) was added dropwise at −78 °C to a CH_2Cl_2 (20 mL) solution of **1** (0.5 g, 1.4 mmol) in a 100 mL Schlenk flask . The solution was stirred at room temperature for 1 h and volatiles were removed under vacuum. The resulting solid was recrystallized from a saturated toluene solution to generate final product (0.47 g, 67.2 % yield). ^1H NMR (C_6D_6): $\delta = 1.13$ (s, 18 H; N*tBu*), 1.57 (s, 6 H; ON=C*Me*), 1.69 (s, 6 H; ON=C*Me*), 4.07, 4.53 (dd, 4 H; $^2J_{HH} = 16.7$ Hz, C*H*$_2$N), 6.29, 6.80, 6.99 ppm (m, 6 H; pyrrolyl protons); ^{13}C NMR (C_6D_6): $\delta =$ 15.4 (q, $J_{CH} = 130$ Hz, ON=C*Me*), 21.0 (q, $J_{CH} = 128$ Hz, ON=C*Me*), 28.7 (q, $J_{CH} =$ 126 Hz, NC*Me*$_3$), 44.2 (t, $J_{CH} = 138$ Hz, *C*H_2N), 57.1 (s, N*C*Me_3), 103.4 (d, $J_{CH} = 165$ Hz, pyrrole), 114.1 (d, $J_{CH} = 169$ Hz, pyrrole), 120.9 (d, $J_{CH} =$ 180 Hz, pyrrole), 137.8 (s, pyrrole), 157.1 ppm (s, ON=C); elemental analysis calcd (%) $C_{24}H_{40}N_6O_2Al_2$ (498.28): C 57.82, H 8.09, N 16.86; found C 67.19, H 7.62, N 17.09.

[{[C_4H_3N(2-CH_2N*t*Bu)]Al(O-$CHMe_2$)]}$_2$] (4): Acetone (0.2 mL, 2.8 mmol)/CH_2Cl_2 solution (20 mL) was added dropwise at 0 °C to a CH_2Cl_2 (20 mL) solution of **1** (0.5 g, 1.4 mmol) in a 100 mL Schlenk flask . The solution was stirred at room temperature for 0.5 h and volatiles were removed under vacuum. The resulting pale pink powder was recrystallized from a saturated toluene/pentane mixed solution to generate final product (0.40 g, 59.7 % yield). ^1H NMR (C_6D_6): $\delta = 0.91$ (s, 18 H; N*tBu*), 1.19 (d, 6 H; $^3J_{HH} = 6.0$ Hz, OCH*Me*$_2$), 1.25 (d, 6 H; $^3J_{HH} = 6.0$ Hz, OCH*Me*$_2$), 3.94, 4.90 (dd, 4 H; $^2J_{HH} = 16.7$ Hz, C*H*$_2$N), 4.27 (m, 2 H; OC*H*Me_2), 6.22, 6.71, 6.92 ppm (m, 6 H; pyrrolyl protons); ^{13}C NMR (C_6D_6): $\delta = 27.4$ (q, $J_{CH} = 125$ Hz, OCH*Me*$_2$), 28.1 (q, $J_{CH} = 128$ Hz, OCH*Me*$_2$), 28.5 (q, $J_{CH} = 126$ Hz, NC*Me*$_3$), 44.2 (t, $J_{CH} = 140$ Hz, *C*H_2N), 56.6 (s, N*C*Me_3), 64.9 (d, $J_{CH} = 140$ Hz, O*C*HMe_2), 104.0 (d, $J_{CH} = 166$ Hz, pyrrole), 115.0 (d, $J_{CH} = 171$ Hz, pyrrole), 120.4 (d, $J_{CH} = 180$ Hz, pyrrole), 137.2 ppm (s, pyrrole); elemental analysis calcd (%) $C_{24}H_{42}Al_2N_4O_2$ (472.58): C 61.00 ,H 8.96, N 11.86; found: C 60.66, H 9.03, N 11.66.

Polymerization: Polymerizations of ε-caprolactone were carried out in toluene solutions under a nitrogen-filled Schlenk line. In a typical reaction, catalyst was first dissolved in CH_2Cl_2 or toluene (2.5 mL) and ε-caprolactone monomer was added ($[M]/[I] = 100$). The reaction mixture was stirred to produce a gel- or solid-like polymer. The reaction was quenched with acidified water (3 % CH_3COOH) and the resulting solid was washed with hexane, dried and weighed for yield.

The molecular weight of the polymers was determined on gel permeation chromatography (GPC) instruments (Waters, RI 2414 and pump 1515). M_n and M_w values were determined from calibration plots established with polystyrene standards.

Crystallographic structural determination of 1, 2, 3, and 4: Crystal data collection, refinement parameters, and bond lengths and angles are listed in Tables 1 and 2, respectively. The crystals were mounted in capillaries, transferred to a goniostat and then observations were made at 150 K. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. Structure determinations were performed by using the SHELXTL package of programs. All refinements were carried out by full-matrix least-squares methods using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were included in calculated positions in the refinements.

CCDC 659272 (**2**), 659273 (**4**) and 659994 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the National Science Council of Taiwan. We also thank the National Changhua University of Education for supporting the X-ray diffractometer and NMR spectrometer.

[1] a) N. B. Malkar, V. G. Kumar, *Synth. Commun.* **1998**, *28*, 977–993; b) C. Boga, M. Contento, F. Manescalchi, *Makromol. Chem. Rapid Commun.* **1989**, *10*, 303–306; c) H. C. Brown, N. M. Yoon, *J. Am. Chem. Soc.* **1966**, *88*, 1464–1472.

[2] a) K. Igawa, K. Tomooka, *Angew. Chem.* **2006**, *118*, 238–240; *Angew. Chem. Int. Ed.* **2006**, *45*, 232–234; b) C. Perez-Balado, F. Lucaccioni, I. E. Marko, *Tetrahedron Lett.* **2005**, *46*, 4883–4886; c) S. S. Kumar, H. W. Roesky, *Dalton Trans.* **2004**, 3927–3937; d) A. Parenty, J.-M. Campagne, *Tetrahedron Lett.* **2002**, *43*, 1231–1233.

[3] a) D. D. Graham, L. F. Culnane, M. Sulic, C. M. Jensen, I. M. Robertson, *J. Alloys Compd.* **2007**, *446–447*, 255–259; b) T. A. Johnson, D. E. Dedrick, R. D. Stephens, J. P. Chan, (General Motors, Detroit, MI), US-A 20070178042, **2007**; c) G. Sandrock, J. Reilly, J. Graetz, J. E. Wegrzyn, (Brookhaven National Laboratory, Upton, NY), US-A 20070025908, **2007**; d) S. M. Opalka, O. M. Lovvik, H. W. Brinks, P. W. Saxe, B. C. Hauback, *Inorg. Chem.* **2007**, *46*, 1401–1409.

[4] A. E. Finholt, A. C. Bond Jr, H. I. Schlesinger, *J. Am. Chem. Soc.* **1947**, *69*, 1199–1203.

[5] a) R. J. Wehmschulte, P. P. Power, *Polyhedron* **2000**, *19*, 1649–1661; b) M. Hovorka, I. Smiskova, R. Holakovsky, J. Beran, I. Stibor, *Pure Appl. Chem.* **1998**, *70*, 415–418.

[6] a) L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald, H. W. Roesky, *Angew. Chem.* **2006**, *118*, 2664–2667; *Angew. Chem. Int. Ed.* **2006**, *45*, 2602–2605; b) C.-Y. Lin, C.-F. Tsai, H.-J. Chen, C.-H. Hung, R.-C. Yu, P.-C. Kuo, H. M. Lee, J.-H. Huang, *Chem. Eur. J.* **2006**, *12*, 3067–3073; c) H. Zhu, Z. Yang, J. Magull, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Organometallics* **2005**, *24*, 6420–6425; d) L. Contreras, A. H. Cowley, F. P. Gabbaï, R. A. Jones, C. J. Carrano, M. R. Bond, *J. Organomet. Chem.* **1995**, *489*, C1–C3; e) S. Bensiek, M. Bangel, B. Neumann, H.-G. Stammler, P. Jutzi, *Organometallics* **2000**, *19*, 1292–1298; f) C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 1885–1887; *Angew. Chem. Int. Ed.* **2000**, *39*, 1815–1817.

[7] a) C. Klein, H. Nöth, M. Tacke, M. Thomann, *Angew. Chem.* **1993**, *105*, 923–926; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 886–888; b) W. Zheng, H. W. Roesky, M. Noltemeyer, *Organometallics* **2001**, *20*, 1033–1035; c) H. S. Isom, A. H. Cowley, A. Decken, F. Sissingh, S. Corbelin, R. J. Lagow, *Organometallics* **1995**, *14*, 2400–2406; d) C. Y. Tang, A. J. Downs, T. M. Greene, S. Parsons, *Dalton Trans.* **2003**, 540–543.

[8] a) H. Nöth, A. Schlegel, J. Knizek, H. Schwenk, *Angew. Chem.* **1997**, *109*, 2754–2758; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2640–2643; b) U. Fooken, M. A. Khan, R. J. Wehmschulte, *Inorg. Chem.* **2001**, *40*, 1316–1322.

[9] a) R. A. Kovar, J. O. Callaway, *Inorg. Synth.* **1976**, *22*, 37–47; b) H. W. Roesky, *Aldrichimica Acta* **2004**, *37*, 103–108; c) S. S. Kumar, H. W. Roesky, *Dalton Trans.* **2004**, 3927–3937; d) L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald, H. W. Roesky, *Angew. Chem.* **2006**, *118*, 2664–2667; *Angew. Chem. Int. Ed.* **2006**, *45*, 2602–2605.

[10] V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2006**, *25*, 519–522.

[11] S. Schulz, A. Kuczkowski, M. Nieger, *Organometallics* **2000**, *19*, 699–702.

[12] C. Granel, R. Jerome, P. Teyssie, C. B. Jasieczek, A. J. Shooter, D. M. Haddleton, J. J. Hastings, D. Gigmes, S. Grimaldi, P. Tordo, D. Greszta, K. Matyjaszewski, *Macromolecules* **1998**, *31*, 7133–7141.

[13] T. Ishikawa, A. Ogawa, T. Hirao, *J. Am. Chem. Soc.* **1998**, *120*, 5124–5125.

[14] a) P.-C. Kuo, I.-C. Chen, J.-C. Chang, M.-T. Lee, C.-H. Hu, C.-H. Hung, H. M. Lee, J.-H. Huang, *Eur. J. Inorg. Chem.* **2004**, 4898–4906; b) J.-C. Chang, C.-H. Hung, J.-H. Huang, *Organometallics* **2001**, *20*, 4445–4447; c) C.-Y. Lin, H. M. Lee, J.-H. Huang, *J. Organomet. Chem.* **2007**, *692*, 3718–3722.

[15] a) N. Al Obaidi, K. P. Brown, A. J. Edwards, S. A. Hollins, C. J. Jones, J. A. McCleverty, B. D. Neaves, *J. Chem. Soc. Chem. Commun.* **1984**, 690–692.

[16] a) M. R. DuBois, *Coord. Chem. Rev.* **1998**, *174*, 191–205; b) J. R. Ascenso, A. R. Dias, A. P. Ferreira, A. C. Galvão, M. S. Salema, L. F. Veiros, *Inorg. Chim. Acta* **2003**, *356*, 249–258; c) H. Schumann, J. Gottfriedsen, J. Demtschuk, *Chem. Commun.* **1999**, 2091–2092.

[17] a) G. Aharonian, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 4257–4263; b) A. S. Hock, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2006**, *128*, 16373–16375; c) J. Llop, C. Vinas, F. Teixidor, L. Victori, *J. Chem. Soc. Dalton Trans.* **2002**, 1559–1565; d) M. Ganesan, C. D. Bérubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 1707–1713.

[18] For a similar procedure see: J.-H. Huang, L.-S. Chi, F.-M. Huang, P.-C. Kuo, C.-C. Zhou, G.-H. Lee, S.-M. Peng, *J. Chin. Chem. Soc.* **2000**, *47*, 895–900.

[19] M. P. Coles, D. C. Swenson, R. F. Jordan, V. G. Young Jr, *Organometallics* **1997**, *16*, 5183–5194.

[20] a) G. Aharonian, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 4257–4263; b) Y. Yang, S. Li, D. Cui, X. Chen, X. Jiang, *Organometallics* **2007**, *26*, 671–678.

[21] The reactions of **3** with various small organic molecules are still under investigation. For more information on the reactivity of coordinated oximate compounds see: A. J. L. Pombeiro, V. Y. Kukushkin, in *Comprehensive Coordination Chemistry II, Vol. 1*, (Eds: J. A. McCleverty, T. J. Meyer), Elsevier, Oxford, **2004**, pp. 631–637.

[22] a) M. Ganesan, C. D. Bérubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 1707–1713; b) H.-D. Hausen, J. Tödtmann, J. Weidlein, *J. Organomet. Chem.* **1994**, *466*, C1–C4; c) G. Gao, I. Korobkov, S. Gambarotta, *Inorg. Chem.* **2004**, *43*, 1108–1115; d) G. Nikiforov, P. Crewdson, S. Gambarotta, I. Korobkov, P. H. M. Budzelaar, *Organometallics* **2007**, *26*, 48–55; e) L. Bonomo, O. Dandin, E. Solari, C. Floriani, R. Scopelliti, *Angew. Chem.* **1999**, *111*, 963–966; *Angew. Chem. Int. Ed.* **1999**, *38*, 913–915; f) J. B. Love, A. J. Blake, C. Wilson, S. D. Reid, A. Novak, P. B. Hitchcock, *Chem. Commun.* **2003**, 1682–1683.

[23] I. Heldt, U. Behrens, *Z. Anorg. Allg. Chem.* **2005**, *631*, 749–758.

[24] a) J. R. Jennings, K. Wade, *J. Chem. Soc. A* **1967**, 1333–1338; b) I. Pattison, K. Wade, *J. Chem. Soc. A* **1968**, 2618–2622; c) N. W. Mitzel, C. Lustig, M. Woski, *Z. Naturforsch.* **2003**, *58b*, 363–368; d) M. Ullrich, R. J. F. Berger, T. Pape, N. W. Mitzel, *Dalton Trans.* **2006**, 5334–5336; e) M. Ullrich, N. W. Mitzel, K. Bergander, R. Frohlich, *Dalton Trans.* **2006**, 714–721; f) N. W. Mitzel, C. Lustig, M. Woski, *Dalton Trans.* **2004**, 397–401; g) N. W. Mitzel, C. Lustig, *Angew. Chem.* **2001**, *113*, 4521–4524; *Angew. Chem. Int. Ed.* **2001**, *40*, 4390–4392; h) H. D. Hausen, G. Schmoger, W. Schwarz, *J. Organomet. Chem.* **1978**, *153*, 271–279.

[25] N. A. Bell, H. M. M. Shearer, C. B. Spencer, *Acta. Crystallogr. Sect. C* **1984**, 40, 613–616.

[26] a) K. Wieghardt, I. Tolksdorf, J. Weiss, W. Swiridorff, *Z. Anorg. Allg. Chem.* **1982**, *490*, 182–190; b) N. W. Mitzel, A. J. Blake, S. Parsons, D. W. H. Rankin, *J. Chem. Soc. Dalton Trans.* **1996**, 2089–2093.

[27] V. Y. Kukushkin, A. J. L. Pombeiro, *Coord. Chem. Rev.* **1999**, *181*, 147–175.

[28] a) R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2001**, *20*, 2294–2302; b) L. Cuesta, M. A. Huertos, D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, A. Menéndez-Velázquez, S. Garcia-Granda, *Inorg. Chem.* **2007**, *46*, 2836–2845; c) M. Kopylovich, V. Y. Kukushkin, M. Haukka, J. J. R. Frausto da Silva, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 4798–4804.

[29] a) C.-T. Chen, C.-A. Huang, B.-H. Huang, *Macromolecules* **2004**, *37*, 7968–7973; b) A. Amgoune, L. Lavanant, C. M. Thomas, Y. Chi, R. Welter, S. Dagorne, J.-F. Carpentier, *Organometallics* **2005**, *24*, 6279–6282; c) N. Nomura, T. Aoyama, R. Ishii, T. Kondo, *Macromolecules* **2005**, *38*, 5363–5366; d) C.-H. Huang, F.-C. Wang, B.-T. Ko, T.-L. Yu, C.-C. Lin, *Macromolecules* **2001**, *34*, 356–361.

[30] a) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* **2007**, *107*, 5813–5840; b) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176; c) M. R. T. Breteler, Z. Zhong, P. J. Dijkstra, A. A. Palmans, J. Peeters, J. Feijen, *J. Polym. Sci., Part A: Polym Chem.* **2007**, *45*, 429–436; d) P. Dubois, N. Ropson, R. Jerome, P. Teyssie, *Macromolecules* **1996**, *29*, 1965–1975.

Received: April 10, 2008