行政院國家科學委員會專題研究計畫　期中進度報告

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定含反應及應用(2/3)

計畫類別：個別型計畫
計畫編號：NSC94-2113-M-018-002-
執行期間：94 年 08 月 01 日至 95 年 07 月 31 日
執行單含：國立彰化師範大學化學系暨研究所

計畫主持人：黃瑞賢

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 95 年 3 月 14 日

行政院國家科學委員會補助專題研究計畫 □ 成 果 報 告
□期中進度報告

含雙陰離子仳咯與酮胺配位基之有機金屬錯合物的合成、鑑定、反應及應用(2/3)

計畫類別：■ 個別型計畫　□ 整合型計畫

計畫編號：NSC94－2113－M－018－002－

執行期間： 94 年 8 月 1 日至 95 年 7 月 31 日

計畫主持人：黃瑞賢

共同主持人：

計畫參與人員：

成果報告類型(依經費核定清單規定繳交)：■精簡報告 □完整報告

本成果報告包括以下應繳交之附件：

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□出席國際學術會議心得報告及發表之論文各一份

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執行單位：國立彰化師範大學化學系暨研究所

中　華　民　國　95 年　　月　　日

Synthesis and Characterization of Zirconium and Hafnium Aryloxide Compounds and Their Reactivity Toward Lactide and ε-Caprolactone Polymerization

Keyword: hafnium aryloxide, zirconium aryloxide, lactide, caprolactone
關鍵字：烷氧鉿、烷氧鋯、乳酸、環己內酯

Abstract

Reactions of 2 equiv pyrrole with $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$ in toluene generated tetra-pyrrolyl metal compounds $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(C_4H_4N)_2$ (**3**, M = Zr; **4**, M = Hf) in moderate yields. Similarly, treatment of metal amides $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$ with 2,6-dimethylphenol or 2,6-diisopropylphenol in heptane resulted in the elimination of diethylamine along with the formation of the corresponding metal alkoxides $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(OR)_2$ (**5**, M = Zr, R = C_6H_3-2,6-Me_2; **6**, M = Hf, R = C_6H_3-2,6-Me_2; **7**, M = Zr, R = C_6H_3-2,6-$^i Pr_2$; **8**, M = Hf, R = C_6H_3-2,6-$^i Pr_2$) in moderate yields. All the new compounds were characterized by ^1H and ^{13}C NMR spectroscopy and the structures of **3**, **4**, **6**, **7**, and **8** have also been determined by X-ray crystallographic studies. The aryloxides and the substituted pyrrolyl ligands in both compounds **5** and **6** show fluxionality as observed by ^1H NMR signals. A kinetic study on the ring-opening polymerization of lactide exhibits a first order reaction of lactide monomer *vs* compound **8**. The catalytic properties of all the metal complexes have been studied for the ring-opening polymerization of ε-caprolactone.

中文摘要

兩當量的此各衍生物與$[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$於甲苯中反應可以得到四此各之$[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(C_4H_4N)_2$ (**3**, M = Zr; **4**, M = Hf)。相同的情形下，將$[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$與 2, 6-二甲基苯酚或 2, 6-異丙基苯酚在庚烷中反應可經由移除二甲基胺而得到金屬烷氧化合物$[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(OR)_2$ (**5**, M = Zr, R = C_6H_3-2,6-Me_2; **6**, M = Hf, R = C_6H_3-2,6-Me_2; **7**, M = Zr, R = C_6H_3-2,6-$^i Pr_2$; **8**, M = Hf, R = C_6H_3-2, 6-$^i Pr_2$)。所有化合物均經^1H and ^{13}C NMR光譜鑑定。化合物 3, 4, 6, 7, 8 亦經X-光單晶繞射鑑定。環酯類的開環聚合反應也加以研究。

Introduction

Poly-ε-caprolactone (PCL) and polylactide (PLA) are considered as biodegradable polyesters for medical and ecological applications.[1-4] PCL and PLA are mainly synthesized by ring opening polymerization using $Sn(OR)_2$ as catalysts.[5-8] However, the study of polyester generated from ring opening polymerization using non-tin metal alkoxides as catalysts have just started to attract researcher's attentions. Among those metal alkoxides, aluminum,[9-15] lithium,[16, 17] titanium[18-21] and some lanthanide metals[22-27] have been studied by different groups. We have previously examined the ring opening polymerization of ε-caprolactone and lactide with aluminum alkoxides supported by monoanionic bidentate ketiminate ligands.[28] Herein we report the synthesis and characterization of zirconium and hafnium metal complexes containing substituted pyrrolyl ligands and their applications as catalysts on the ring-opening polymerization of ε-caprolactone and lactide.

Results and Discussion

Synthesis of compounds 1-8. The zirconium and hafnium amide complexes

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$ (**1**, M = Zr; **2**, M = Hf) were prepared following the published procedures (see experimental section) by treatment of $M(NEt_2)_4$ with two equivalent of substituted pyrrolyl ligands (Scheme 1). Reactions of 2 equiv pyrrole with **1** and **2** in toluene generated tetra-pyrrolyl metal compounds $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(C_4H_4N)_2$ (**3**, M = Zr; **4**, M = Hf) in moderate yields. Similarly, treatment of metal amides **1** and **2** with stoichiometric amount of 2,6-dimethylphenol or 2,6-diisopropylphenol in heptane resulted in the elimination of diethylamine with the formation of the corresponding metal alkoxides $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(OR)_2$ (**5**, M = Zr, R = C_6H_3-2,6-Me_2; **6**, M = Hf, R = C_6H_3-2,6-Me_2; **7**, M = Zr, R = C_6H_3-2,6-$^i Pr_2$; **8**, M = Hf, R = C_6H_3-2,6-$^i Pr_2$) in moderate yields (Scheme 1). The resulting metal alkoxide compounds **3**-**8** were characterized by ^1H and ^{13}C NMR spectroscopy.

Scheme 1 here

Molecular structures for compounds 3, **4**, **6**, **7**, **and 8.** Compounds **3**, **4**, **6**, **7**, and **8** have been structurally characterized and selected bond lengths and angles were listed in Table 1. The molecular geometries were shown in Figure 1-5 where the molecular geometries are highly dependant on the steric hindrance of the ligands. Compounds **3**, **4**, **6**, and **8** all contain solvent molecules in their unit cells. For compound **4**, there are two independent molecules in the asymmetrical unit. However, the bond lengths and angles of the two molecules are very similar; therefore, only one molecule is discussed here. The structures for compounds **3**, **4** and **6**, with less sterically congestion, are quite similar and show highly distorted octahedral geometry, which can also be described as anti-trigonal prism. The two nitrogen atoms of the dimethylamino fragments in compounds **4** and **6** are taking trans positions with the bond angles of 162.1(2)° and 159.24(19)°, respectively. The sterically congested compounds **7** and **8** exhibit regular octahedral geometries. For the sterically congested compound **8**, the aryloxide ligands are trans to the dimethylamino fragments and the two pyrrolyl fragments are trans to each other; where the bond angles of the three axes for the octahedral geometry are 170.47(7)°, 170.47(7)°, and 140.28(11)°, respectively. The bond lengths of metal to pyrrolyl nitrogen atoms and metal to dimethylamino nitrogen atoms are very similar despite the differences in steric effect for compounds **4**, **6**, and **8**.[29-34]

Figure 1-5 here

Table 1 here

NMR study of the structures in solution. For compounds **3** and **4**, the ^1H NMR spectra of the 2-dimethylaminomethyl fragments at room temperature exhibit sharp singlets for the methylene and methyl protons at δ 3.60 and 2.43 for **3** and δ 3.18 and 1.87 for **4**. The proton-coupled ^{13}C NMR spectra of the methylene fragments for compounds **3** and **4** both show a triplet resonance at δ 62.6 and 62.5 with $^1J_{CH}$ coupling constant of 136 Hz and 139 Hz, respectively. In the solid state structures of **3** and **4**, the structures exist non-symmetrical geometry and the NMe_2, the NCH_2 of the substituted pyrrolyl ligands and the NCH and CCHC of the pyrrolide anion should have different resonance signals. However, the room temperature NMR data for **3** and **4** indicate either the solution structures are different from the solid ones; and /or equilibria are occurring. In order to elucidate eventual dynamic phenomena (rotation of the pyrrolide anions) and/or the cis/trans isomerization of the complex, a variable temperature NMR investigation and ^1H-^1H NOESY spectra were carried out. The results show the resonance signals for the substituted pyrrolyl ligands and pyrrolides remain unchanged at 250 K, which indicate a fast

rotation of the pyrrolide anions and a fast equilibrium of the cis/trans isomerization must exit at the same time.

The bulkiness of the aryloxide groups indeed affects the M-O bond rotation rate and the fluxionality of the substituted pyrrolyl ligands. The methyl fragments of the aryloxides and the dimethylaminomethyl groups in compounds **5** and **6** show broad ^{1}H NMR signals at room temperature. Use of bulkier 2,6-diisopropylphenyl groups in compounds **7** and **8** results in greater stereo-rigidity of the molecular structures in which the methyl groups of the isopropyl fragments were split into four doublet signals, whereas the methyl groups of the dimethylamino fragments were split into two singlets. For compound **6**, ^{1}H, ^{13}C and ^{1}H-^{13}C HSQC NMR spectra have been recorded in the range of 320 to 250 K in $CDCl_3$ at a 300 MHz NMR spectrometer in order to resolve its structure in solution at various temperatures. Variable temperature ^{1}H NMR spectra of compound **6** were showed in Figure 6. The ^{1}H and ^{1}H-^{13}C HSQC NMR spectra clearly identified that the methyl groups of aryloxides and dimethylamino fragments appeared as sharp singlets at δ 2.22 and 2.46, respectively at 320 K. The methylene protons of the CH_2NM_2 fragments also show a sharp singlet at 320 K. The methyl groups of the aryloxides and dimethylamino fragments were split into complicated singlets at δ 2.45, 2.58, 2.51, 2.30, 2.02, 1.40 when temperature is lowered down to 250 K. Similarly, the methylene protons of the CH_2NM_2 fragments show splitting of signal from a sharp singlet at δ 3.87 to a complicated overlapping of two doublets and a broad singlet while the temperatures lowered from 320 K to 250 K. The observed patterns at 250 K are indicative of complex solution dynamics. As the NCH_2 signal is concerned, the splitting of the singlet at room temperature into two doublets and a singlet at low temperature could indicate that two isomers, namely *cis* and *trans* one, may presents in solution at low temperature. The two doublet may result from a solution structure similar to the solid state one (the *cis* form) and the singlet may result from a more symmetrical solution structure such as a more symmetrical pseudo-C_2 symmetry of trans geometry one (the *trans* form with the phenoxide anions in an axial arrangement and the bidentate ligands in the equatorial plane with an unpredictable mutual arrangement). Interestingly, on accordance to this, six methyl resonances are observed and assignable to i) the two non-equivalent methyls of the phenoxide anions and ii) the two non-equivalent NMe_2 methyls of the *cis* isomers; and iii) the NMe_2 moiety and of the two equivalent methyls of the reasonably freely-rotating phenoxide of the trans isomer. A ^{1}H NOESY experiment of **6** was performed at 250 K; however, due to the complication of methyl resonances we are unable to determine the *cis* and *trans* forms of **6**.[35]

Figure 6 here

Kinetic study of lactide polymerization initiated by 8. The reactions of **8** with *rac*-lactides are preceded in $CDCl_3$ at 70°C and monitored with ^{1}H NMR spectrometer. The consumptions of lactide are measured from the integration of the ^{1}H NMR signals. Plots of $\ln([\text{lactide}]_0/[\text{lactide}])$ versus time give straight lines (Figure 7), indicating the lactide polymerization to be first-order with respect to the monomer.[36]

Figure 7 here

Polymerization of ε-caprolactone. Polymerizations of ε-caprolactone by using zirconium or hafnium complexes as catalysts have been seen in the literature.[37-39] Here we use the synthesized metal complexes as catalysts to study their reactivity toward ε-caprolactone. All the compounds have been studied as catalysts for the ring opening polymerization of ε-caprolactone.

The results of polymerization studies of ε-caprolactone initiated by compounds **3-8** are shown in Table 2. It is found that compounds **3-8** catalyzed the ring-opening polymerization of ε-caprolactone to give moderate molecular weight of PCL (range 11 000 to 53 000) with a rather broad molecular weight distribution (PDI = 1.38-2.63). There are no noticeable differences toward the ring-opening polymerization relating to metals (Zr or Hf) or bulkiness of the substituted aryloxides and pyrrolyl ligands of compounds **3-8**.

Table 2 here

Experimental section $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(NEt_2)_2$, $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NEt_2)_2$,[40, 41] $C_4H_3NH(CH_2NMe_2)$-2,[42, 43] $M(NEt_2)_4$ (M = Zr, Hf),[44] were prepared according to previously reported procedures.

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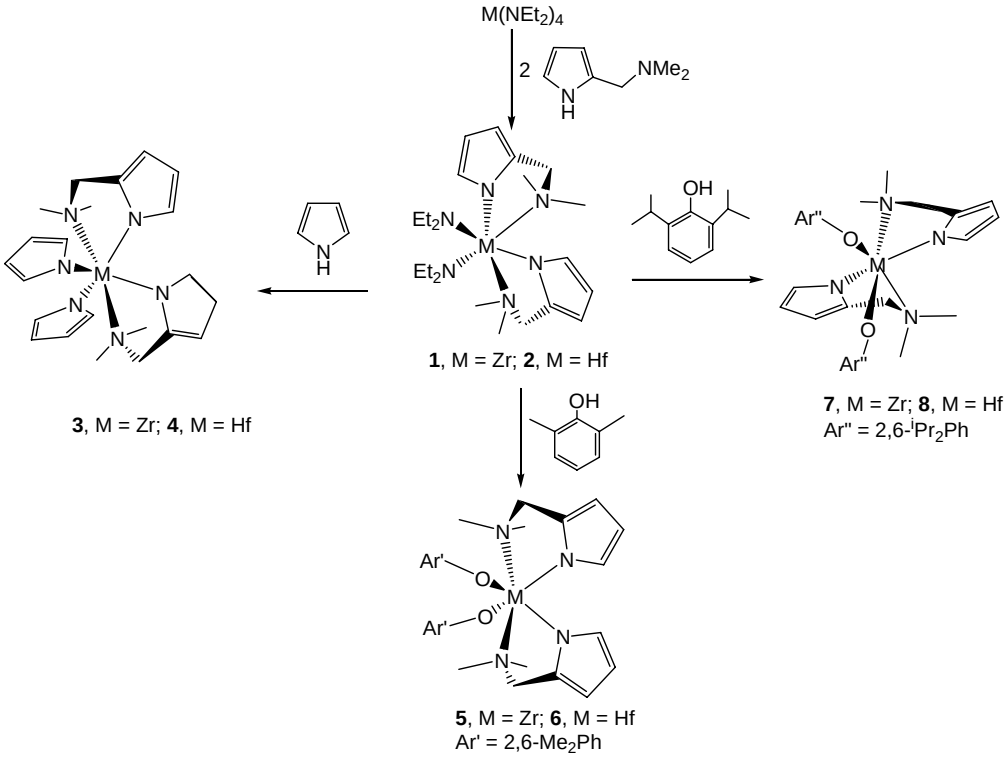
Scheme 1



Caption to Figures

Figure 1. The molecular structure for compound **3**; thermal ellipsoids were drawn at 50 % probability level. Toluene and hydrogen atoms were omitted for clarity.

Figure 2. One of two independent molecular structures of compound **4**; thermal ellipsoids were drawn at 50 % probability level. Toluene and hydrogen atoms were omitted for clarity.

Figure 3. The molecular structure for compound **6**; thermal ellipsoids were drawn at 50 % probability level. Methylene chloride molecule and hydrogen atoms were omitted for clarity.

Figure 4. The molecular structure for compound **7**; thermal ellipsoids were drawn at 30 % probability level. Hydrogen atoms were omitted for clarity.

Figure 5. The molecular structure for compound **8**; thermal ellipsoids were drawn at 50 % probability level. Methylene chloride and hydrogen atoms were omitted for clarity.

Figure 6. Variable ^{1}H NMR spectra of compound **6** in $CDCl_3$ using a 300 MHz NMR spectrometer. Spectra ranges are drawn in the range of δ 1.0-4.2.

Figure 7. Plot of ln([lactide]$_0$/[lactide]) versus time for the reaction of **8** with *rac*-lactide in $CDCl_3$ at 70 °C.

Figure 1 Figure 2

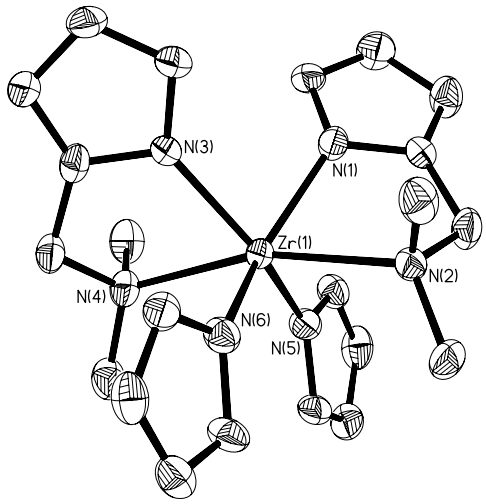


Figure 3

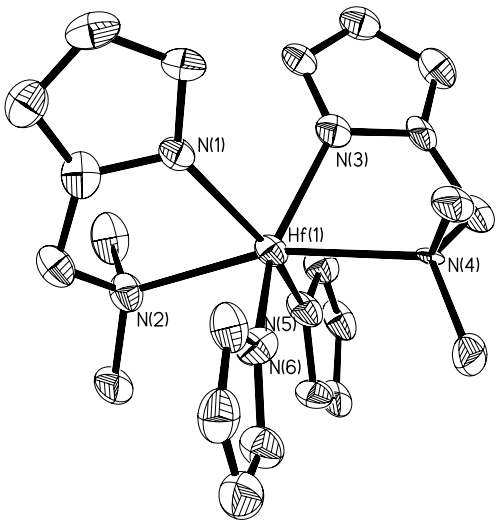
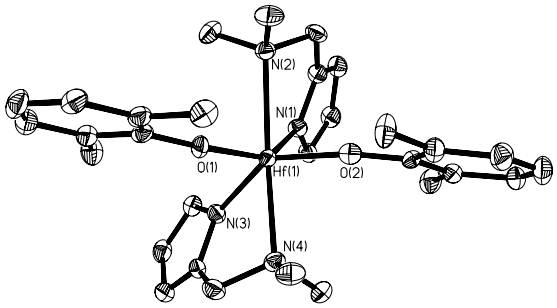


Figure 4



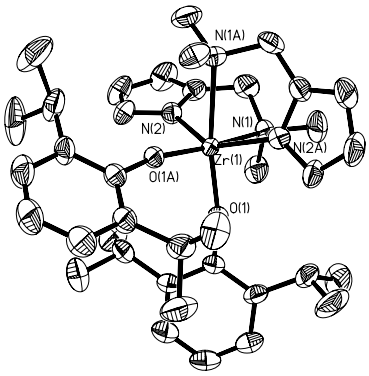


Figure 5

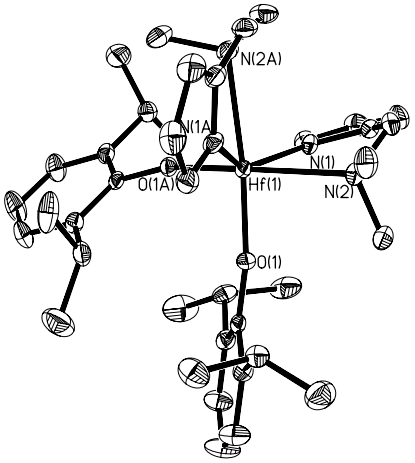


Figure 6

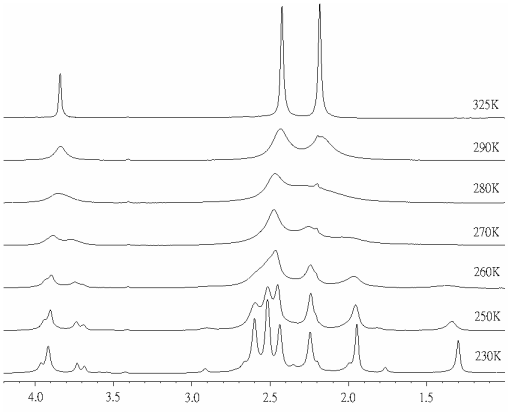


Figure 7

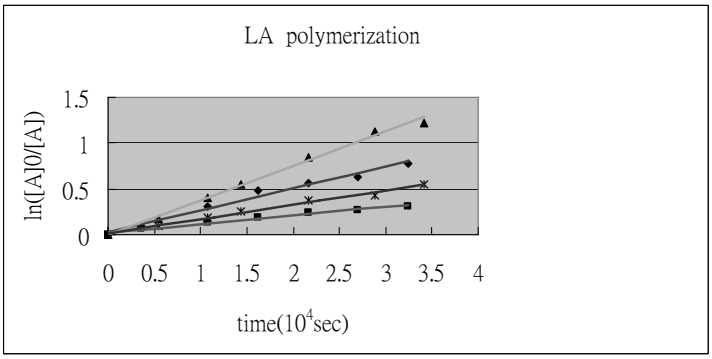


Table 1 **Selected Bond Distances (Å) and Angles (°) for Compounds 3, 4, 6, 7, 8**

		3	
Zr(1)—N(1)	2.1445(16)	Zr(1)—N(2)	2.3824(16)
Zr(1)—N(3)	2.1393(16)	Zr(1)—N(4)	2.3957(16)
Zr(1)—N(5)	2.1611(16)	Zr(1)—N(6)	2.1577(16)
N(1)—Zr(1)—N(6)	143.09(6)	N(3)—Zr(1)—N(5)	143.47(6)
N(2)—Zr(1)—N(4)	163.05(6)	N(1)—Zr(1)—N(2)	71.07(6)
N(3)—Zr(1)—N(4)	72.62(6)		
		4	
Hf(1)—N(1)	2.134(6)	Hf(1)—N(2)	2.381(6)
Hf(1)—N(3)	2.133(7)	Hf(1)—N(4)	2.359(6)
Hf(1)—N(5)	2.140(6)	Hf(1)—N(6)	2.112(7)
N(1)—Hf(1)—N(5)	143.5(2)	N(2)—Hf(1)—N(4)	162.1(2)
N(3)—Hf(1)—N(6)	143.8(2)	N(1)—Hf(1)—N(2)	73.2(2)
N(3)—Hf(1)—N(4)	70.6(2)		
		6	
Hf(1)—N(1)	2.190(5)	Hf(1)—N(2)	2.391(5)
Hf(1)—N(3)	2.182(5)	Hf(1)—N(4)	2.389(5)

Hf(1)—O(1)	1.975(4)	Hf(1)—O(2)	1.945(5)
N(1)—Hf(1)—N(2)	71.87(18)	N(3)—Hf(1)—N(4)	71.8(2)
N(4)—Hf(1)—N(2)	159.24(19)	N(1)—Hf(1)—O(1)	142.54(19)
O(2)—Hf(1)—N(3)	139.59(18)		
		7	
Zr(1)—O(1)	1.924(2)	Zr(1)—N(1)	2.535(3)
Zr(1)—N(2)	2.137(3)		
N(1)—Zr(1)—N(2)	69.68(10)	O(1)—Zr(1)—N(1A)	168.04(10)
N(2)—Zr(1)—N(2A)	141.17(15)		
		8	
Hf(1)—O(1)	1.9446(16)	Hf(1)—N(1)	2.162(2)
Hf(1)—N(2)	2.508(2)		
N(1)—Hf(1)—N(2)	70.87(7)	O(1A)—Hf(1)—N(2)	170.47(7)
N(1)—Hf(1)—N(1A)	140.28(11)		

Table 2 **Ring-opening polymerization of ε-caprolactone initiated by complexes 3-8**

Entry	Catalyst	[M]/[cata]	T(°C)	Yield (%)	Mn	PDI
1	**3**	100	25	96	18 457	2.63
2	**3**	100	65	98	15 612	2.38
3	**4**	100	25	99	52 962	1.45
4	**4**	100	65	97	26 416	2.10
5	**5**	100	50	76	21 219	1.55
6	**6**	100	50	75	17 727	1.38
7	**7**	100	50	93	14 764	1.38
8	**8**	100	50	94	10 907	1.23