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Calcium complexes containing oxalamidinate ligands as catalysts for ε-caprolactone polymerization†

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A series of calcium complexes containing oxalamidinate ligands is described. Reactions of oxalamidinate ligand precursors, [PhN=C{NH(CH$_2$)$_2$OMe}–C{NH(CH$_2$)$_2$OMe}=NPh] (**1**), [PhN=C{NH(CH$_2$)$_2$NMe$_2$}–C{NH(CH$_2$)$_2$NMe$_2$}=NPh] (**2**), [Ph^{TriMe}N=C{NH(CH$_2$)$_2$OMe}–C{NH(CH$_2$)$_2$OMe}=NPh^{TriMe}] (**3**), [Ph^{TriMe}N=C{NH(CH$_2$)$_2$SMe}–C{NH(CH$_2$)$_2$SMe}=NPh^{TriMe}] (**4**), [Ph^{TriMe}N=C{NHCH$_2$Py}–C{NHCH$_2$Py}=NPh^{TriMe}] (**5**), with two molar equivalents of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ gave calcium oxalamidinate complexes, [Ca{N(SiMe$_3$)$_2$}(THF)(PhN)C{N(CH$_2$)$_2$OMe}–]$_2$ (**6**), [Ca{N(SiMe$_3$)$_2$}(THF)(PhN)C{N(CH$_2$)$_2$NMe$_2$}–]$_2$ (**7**), [Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{N(CH$_2$)$_2$OMe}–]$_2$ (**8**), [Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{N(CH$_2$)$_2$SMe}–]$_2$ (**9**), [Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{NCH$_2$Py}–]$_2$ (**10**), respectively. The molecular structure of complex **7** was further characterized by the single crystal X-ray diffraction technique. The catalytic activities of complexes **6–10** toward the ring opening polymerization of ε-caprolactone were studied. Complex **8** exhibited excellent activity for the polymerization of ε-caprolactone with controlled molecular weights and polydispersities.

Introduction

Interest in producing environmentally friendly polymers which can be widely used in various applications has been attractive mainly due to their biocompatible and biodegradable properties.[1] One route for synthesizing biodegradable polymers using metal-based initiators/catalysts for ring opening polymerization has proven to be an effective pathway.[2] Although biodegradable polymers can easily be produced by using tin(II) octanoate as catalyst,[3] however, the toxicity of the metal center and the poor control of the molecular weight of the polymers produced resulting from side reactions such as *trans*-esterification encouraged researchers to develop new human-friendly metal catalysts with a growing interest. Various metal complexes have been applied in polymerizing cyclic esters and these containing Zn,[4] Mg,[5] Ca,[6] Na[7] or Fe[8] metal centers are more attractive due to their participation in the human metabolism. Among these, calcium metal is hard, inexpensive, biocompatible, and kinetically labile ion with a larger ionic radius and Lewis acidity than Mg^{2+} or Zn^{2+} ions,[9] some highly reactive calcium complexes containing nitrogen-based auxiliary ligands have received increasing attention recently for their successful application in ring opening polymerization reactions.[2] For example, Chisholm and co-workers reported a series of calcium complexes that show excellent polymerization rates and very good stereocontrol.[6e] Darensbourg also reported calcium complexes with tridentate Schiff base ligands that show excellent catalytic activity for ring opening polymerization of trimethylene carbonate or lactide to produce high molecular weight polymers with narrow polydispersities.[6g]

Amidinate ligands, which have been reported for several decades and widely applied in the coordination chemistry of a diversity of metal complexes, can be easily tuned by variation of the substituents on either or both the N and C atoms. Many amidinate ligands with various substituents have been synthesized and some of them have been applied in catalytic reactions.[10] Oxalamidinate ligands, which have similar coordination type to amidinate ligands, have been attractive owing to the discovery of their versatile bonding modes and their application in catalytic reactions for some metal complexes. They show the potential to work as diimine,[11] diimine–diamide,[12] or amidinate[13] ligands. Once the pendant functionality has been introduced, the oxalamidinate ligands can act as ligands up to three-coordinate; six-electron-donor on each side. Following our previous studies on the aluminium and magnesium oxalamidinate complexes,[12e] we report here some calcium complexes containing oxalamidinate ligands which can work as catalysts in catalyzing ring opening polymerization of ε-caprolactone.

Results and discussion

Synthesis and characterization

Preparations of ligand precursors [PhN=C{NH(CH$_2$)$_2$OMe}–C{NH(CH$_2$)$_2$OMe}=NPh] (**1**), [PhN=C{NH(CH$_2$)$_2$NMe$_2$}–C{NH-

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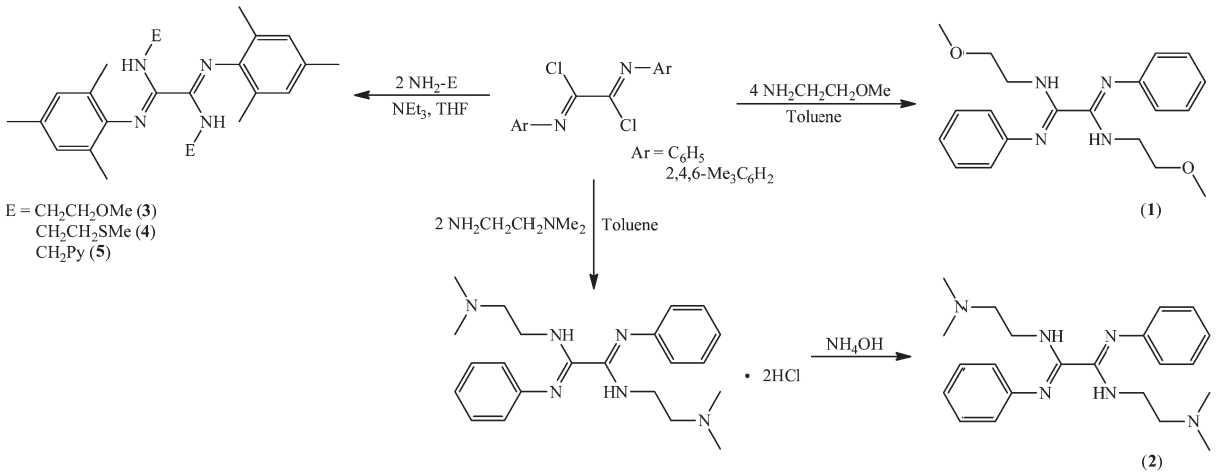
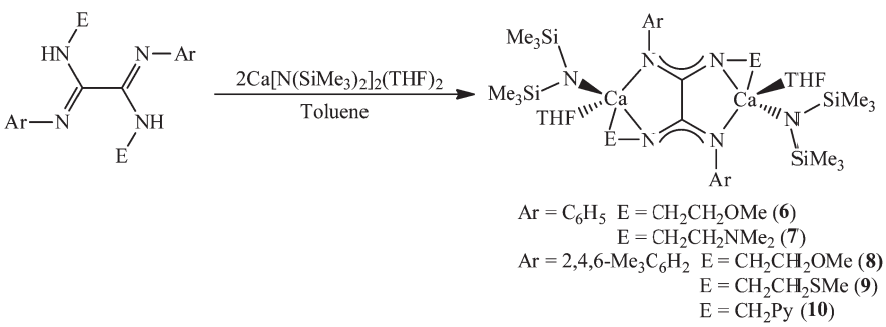


Scheme 1 Preparation of ligand precursors.

$(CH_2)_2NMe_2\}$═NPh] (**2**) have been reported by the reactions of bis(imidoyl)chloride with the relevant amines.[12e] Following the previous established procedures, similar ligand precursors [Ph^{TriMe}N═C{NH$(CH_2)_2$OMe}–C{NH$(CH_2)_2$OMe}═NPh^{TriMe}] (**3**), [Ph^{TriMe}N═C{NH$(CH_2)_2$SMe}–C{NH$(CH_2)_2$SMe}═NPh^{TriMe}] (**4**), [Ph^{TriMe}N═C{NHCH$_2$Py}–C{NHCH$_2$Py}═NPh^{TriMe}] (**5**) were prepared straightforwardly by treatment of N^1,N^2-bis(2,4,6-trimethylphenyl) oxaldiimidoyl dichloride with suitable amine or hydrochloride salts of amine in the presence of triethylamine in refluxed THF, in high yield.[14] All of these ligand precursors are characterized by NMR spectroscopy as well as elemental analyses. Syntheses and the proposed structures are summarized in Scheme 1. Treatment of these ligand precursors with two molar equivalents of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ in THF affords calcium complexes, [Ca{N(SiMe$_3$)$_2$}(THF)(PhN)C{N$(CH_2)_2$OMe}–]$_2$ (**6**), [Ca{N(SiMe$_3$)$_2$}(THF)(PhN)C{N$(CH_2)_2$NMe$_2$}–]$_2$ (**7**), [Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{N$(CH_2)_2$OMe}–]$_2$ (**8**), [Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{N$(CH_2)_2$SMe}–]$_2$ (**9**), [Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{NCH$_2$Py}–]$_2$ (**10**), as shown in Scheme 2. The NMR spectroscopy showed one singlet corresponding to the SiMe$_3$ group (δ 0.33 ppm for **6**; δ 0.41 ppm for **7**; δ 0.31 ppm for **8**; δ 0.38 ppm for **9**; δ 0.33 ppm for **10**) and two multiplets corresponding to the coordinated THF (δ 1.07 and 3.25 ppm for **6**; δ 1.14 and 3.28 ppm for **7**; δ 1.25 and 3.35 ppm for **8**; δ 1.16 and 3.27 ppm for **9**; δ 1.10 and 3.28 ppm for **10**) in each case at room temperature. This indicates complexes are highly symmetric species in solution. The elemental analysis data are also consistent with a complex containing one coordinated THF on each side.[6c–e,k] Suitable crystals for the structural determination of **7** were obtained from concentrated hexane solution. The molecular structure is depicted in Fig. 1. The structure also confirmed a symmetric penta-coordinated calcium center with a planar amidinate moiety on each side. Similar to the magnesium complexes discussed previously,[12e] deprotonated ligand precursor **2** acts as a tridentate ligand. Each metal center is coordinated with two nitrogen atoms from different amidinate units, one nitrogen atom from pendant arm and one oxygen atom from coordinated THF. The geometry around the calcium center of **7** can be described as distorted trigonal bipyramid with O and N(4) occupying the axial positions (O–Ca–N(4) 143.94(6)°). The N(1), N(2) and N(3) atoms reside equatorially, however with different angles (67.95(5)°, 90.66(5)°, 138.27(5)°) subtended by calcium.[15] The bond lengths of CNN units (N(1)–C(7A) = 1.342(2) Å) and N(2)–C(7) = 1.315(2) Å) are similar, which might result from the delocalization of π-electrons within the amidinate moiety.[12e,13] The bond lengths between calcium and nitrogen atoms of the oxalamidinate ligand are relatively similar (2.3620(16) and 2.3736(16) Å). The bond lengths of calcium amide (Ca–N(4) = 2.3358(16) Å) are close to those (2.512(2)–2.2863(12) Å) found in the literature.[6a,c,d,i–k,n] Moreover, this bond length is significantly shorter



Scheme 2 Preparation of calcium complexes.

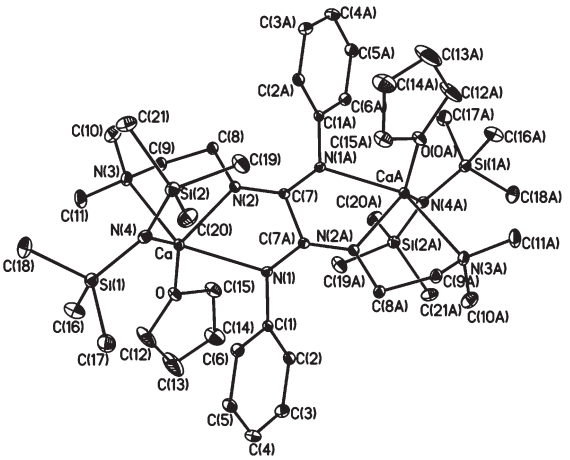


Fig. 1 Molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): Ca–N(1) 2.3620(16), Ca–N(2) 2.3736(16), Ca–N(3) 2.5565(17), Ca–O 2.4348(14), Ca–N(4) 2.3358(16), C(7)–C(7A) 1.540(14), N(1)–C(7A) 1.342(2), N(1)–C(1) 1.398(2), N(2)–C(7) 1.315(2), N(2)–C(8) 1.452(2); O–Ca–N(2) 90.66(5), N(2)–Ca–N(4) 125.34(6), O–Ca–N(4) 143.94(6), N(2)–Ca–N(1) 67.95(5), N(1)–Ca–N(3) 138.27(5), N(2)–C(7)–N(1A) 130.68(17), N(2)–C(7)–C(7A) 115.1(2), N(1A)–C(7)–C(7A) 114.1(2). Hydrogen atoms on carbon atoms omitted for clarity.

than that of calcium amine (Ca–N(3) = 2.5565(17) Å) due to different electronic donating properties between the nitrogen atom of the amidinate group and the nitrogen atom of the pendant arm. The Ca–O bond length of coordinated THF (Ca–O = 2.4348(14) Å) is longer than those found in the lierature.[6c,d,i,k]

Polymerization studies

Several calcium complexes are known as efficient catalysts/initiators in the ring opening polymerization of cyclic esters,[6] complexes **6–10** were introduced to examine the catalytic activities toward the ROP of ε-caprolactone. Representative results are collected in Table 1. As usual polymerization of ε-caprolactone was examined in toluene at 0 °C in the absence of benzyl alcohol for 1 min using **8** as catalyst (entry 1). Although the isolated polycaprolactone demonstrated a narrow weight distribution, however, the molecular weight determined by GPC deviated largely from the theoretical value. A similar observation was also reported by Feijen,[6a,b] indicating the amide group was not a good initiator for the propagation step. Optimized conditions were found to be toluene at 0 °C in the presence of benzyl alcohol after several trials on running polymerization of ε-caprolactone in dichloromethane, tetrahydrofuran and toluene using **8** as catalyst (entries 2, 4–5). We also used 9-anthracenemethanol (9-AnOH) as an initiator (entry 3), however, with poor controlled behaviour. The same conditions were applied to examine the catalytic activities of the other four catalysts. Based on the experimental results, complex **9** demonstrated similar activity to **8** within the same period, whereas complexes **6**, **7** and **10** exhibited poor conversion within 1 min at 0 °C (entries 6–9). Based on the good conversions demonstrated by **8** and **9**, ligands with chalcogenide pendant functionalities could enhance the catalytic activities of ROP in this system. This might result from the interaction between the calcium metal and dative atoms. We also examined the catalytic activity of $Ca\{N(SiMe_3)_2\}_2(THF)_2$ as catalyst in the presence of benzyl alcohol (entry 10). It is worth noting that introduction of oxalamidinate ligands could efficiently enhance the catalytic activity. Complex **8** in the presence of alcohol even demonstrates better activities than the [tmhd]/^{i}PrOH system[6d] and other calcium alkoxide systems.[6a] The poor conversions demonstrated by **6** and **7** might result from the solubility caused by the less bulky phenyl group. Therefore the catalytic activities of complex **6** in the presence of benzyl alcohol were examined in toluene, CH_2Cl_2 or THF within 1 min at 30 °C (entries 11–13). The conversion enhanced up to 99% in toluene whereas poor conversions were observed upon using CH_2Cl_2 or THF as solvents. Due to the ease of preparation and better controlled character, complex **8** was introduced to examine the living and immortal characters under optimized conditions. Experimental results exhibited that complex **8** can work as a catalyst to initiate high monomer-to-initiator ratios in the presence of benzyl alcohol accompanied by increasing temperature and volume, with high conversions of CL even up to $[CL]_0/[Ca]_0$ ratios of 1000, yielding PCLs with a molecular weight as large as 114 000 in 240 min (entries 14–18). The linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) demonstrated in Fig. 2 (entries 2, 14–18) implies the "living" character of the polymerization process. In order to examine the 'immortal' character, an increasing amount of benzyl alcohol up to 40 equivalents has been investigated. The produced polymers still exhibited good control of the polymerization in terms of the agreement with experimental molecular weights (M_n) and the ratio of monomer to alcohol (entries 19–22). The dependence of the experimental molecular weights (M_n) on the amount of added benzyl alcohol, for a given $[CL]_0/[Ca]_0$ ratio of 600 (Fig. 3), evidences that $[Ca]_0$/[BnOH] transfer takes place efficiently, since the molecular weights of resulting polymers decrease with increasing quantities of alcohol, assuming that all the added alcohol molecules contribute to the "immortal" polymerization.[16]

The end group analysis is demonstrated by the ^{1}H NMR spectrum of the polymer produced from ε-caprolactone and **8** with the ratio of $[M]_0$:[BnOH] = 30 (Table 1, entry 21), as shown in Fig. 4. Peaks are assignable to the corresponding protons in the proposed structure, indicating the ROP might be initiated with metal benzyl oxide complex first, followed by the ring cleavage of the acyl-oxygen bond to form a metal alkoxide intermediate, which further reacts with excess lactones to yield polyesters. The MALDI-TOF-MS analysis of a low molecular weights PCLs (M_n(obsd) = 2200, Table 1, entry 22) clearly revealed a major population of PCLs unequivocally confirmed as $Na^+{\cdot}H\{O(CH_2)_5C(O)\}_nOBn$ (Fig. 5). The degree of polymerization indicated by this spectrum (n = 16, M_n(ms) = 1958 g mol^{-1}) is in good agreement with the experimental value and the mass spectrum shows a cluster of homologous peaks separated by a molecular mass of ~114 Da corresponding to one ε-caprolactone repeating unit. No evidence for cyclic

Table 1 Polymerization of ε-caprolactone using complexes **6–10** as catalysts in toluene if not otherwise stated[a]

Entry	Catalyst	$[M]_0 : [Ca]_0 : [BnOH]$	T (°C)	t (min)	M_n[b] (obsd)	M_n[c] (calcd)	Conv.[d] (%)	Yield[e] (%)	M_w/M_n[b]
1	**8**	200 : 1 : 0	0	1	140 000	18 400	80	80	1.13
2	**8**	200 : 1 : 1	0	1	39 000	23 000	99	82	1.32
3[f]	**8**	200 : 1 : 1	0	1	21 500	23 000	99	95	1.92
4[g]	**8**	200 : 1 : 1	0	1	36 800	19 300	84	84	1.24
5[h]	**8**	200 : 1 : 1	0	1	—	—	30	—	—
6	**6**	200 : 1 : 1	0	1	—	—	12	—	—
7	**7**	200 : 1 : 1	0	1	—	—	Trace	—	—
8	**9**	200 : 1 : 1	0	1	37 800	23 000	99	88	1.93
9	**10**	200 : 1 : 1	0	1	—	—	56	—	—
10	$Ca\{N(SiMe_3)_2\}_2(THF)_2$	400 : 1 : 2	0	1	21 500	18 900	86	73	1.12
11	**6**	200 : 1 : 1	30	1	37 600	23 000	99	83	1.42
12[g]	**6**	200 : 1 : 1	30	1	—	—	Trace	—	—
13[h]	**6**	200 : 1 : 1	30	1	—	—	Trace	—	—
14	**8**	400 : 1 : 1	0	1	65 000	44 400	97	97	1.19
15	**8**	600 : 1 : 1	0	30	—	—	35	—	—
16	**8**	600 : 1 : 1	30	5	89 400	64 500	94	94	1.22
17[i]	**8**	800 : 1 : 1	30	180	104 000	91 500	99	99	1.16
18[i]	**8**	1000 : 1 : 1	30	240	112 000	114 000	99	99	1.20
19	**8**	600 : 1 : 5	30	5	20 000	13 800	99	99	1.56
20	**8**	600 : 1 : 10	30	15	9600	7000	99	95	1.33
21	**8**	600 : 1 : 20	30	30	5000	3500	99	88	1.49
22	**8**	600 : 1 : 40	30	40	2200	1800	99	99	1.47

[a] In 7.5 mL. [b] Obtained from GPC analysis times 0.56. [c] Calculated from $[M(\text{monomer}) \times [M]_0/[Ca]_0 \times \text{conversion yield}/([BnOH]_{eq})] + M(BnOH)$. [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield. [f] [BnOH] was replaced with [9-AnOH]. [g] In 7.5 mL CH_2Cl_2. [h] In 7.5 mL THF. [i] In 15 mL.

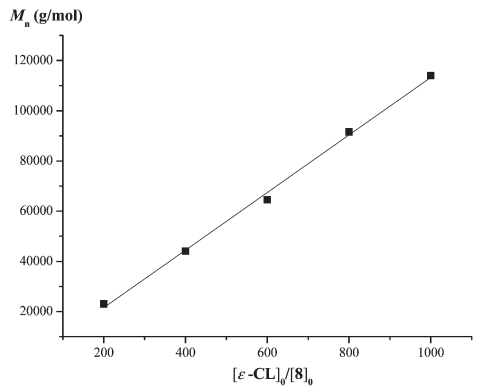


Fig. 2 Dependence of the experimental molar mass determined by M_nGPC, on the $[\varepsilon\text{-CL}]_0/[\mathbf{8}]_0$ ratio for the ROP of ε-CL with $[\mathbf{8}]_0/[BnOH]_0 = 1/1$ (Table 1).

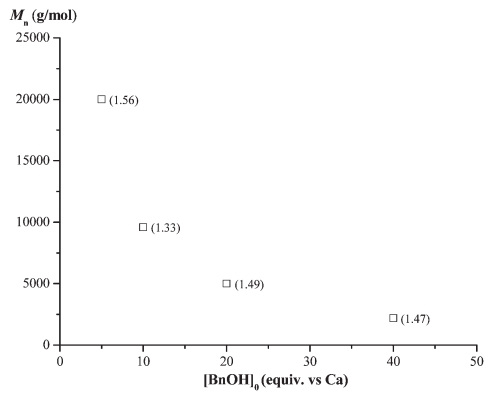


Fig. 3 Dependence of the experimental molar mass determined by GPC, M_nGPC, of PCLs on the amount of added benzyl alcohol for the ROP of ε-caprolactone initiated by the **8**/BnOH system at $[\varepsilon\text{-CL}]_0/[\mathbf{8}]_0 = 600/1$ (Table 1).

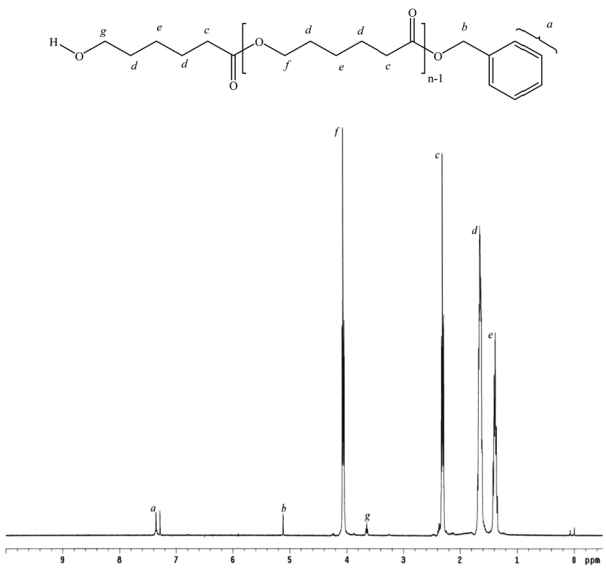


Fig. 4 ^{1}H NMR spectrum of PCL-30 initiated by **8** in toluene at 30 °C (Table 1, entry 21).

polymers was found, indicating that the side reactions did not happen during polymerization.[17]

In conclusion, a family of calcium complexes bearing oxalamidinate ligands have been prepared and fully characterized. Under optimized conditions, complexes **8** and **9** demonstrate efficient catalytic activities, and productivities for the controlled "living" and "immortal" ROP of ε-caprolactone in the presence of benzyl alcohol. The poor conversion demonstrated by **6**, **7** and **10** might result from the solubility caused by the less bulky phenyl group and the interaction between the

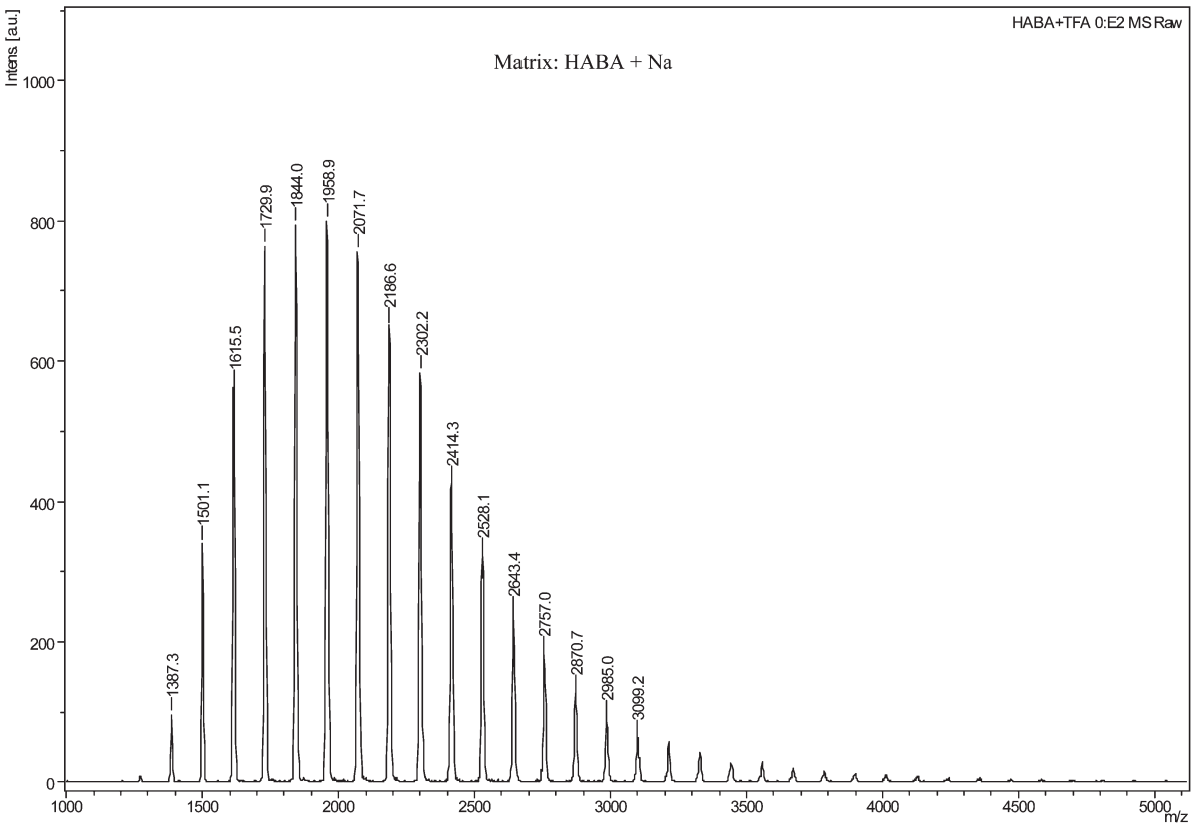


Fig. 5 MALDI-TOF mass spectrum of H-PCL-OBn (M_n = 2200 g mol^{-1}, Table 1, entry 22).

pendant functionality and the metal center. To the best of our knowledge, this is the first example of calcium complexes containing oxalamidinate ligands applied in ROP of ε-caprolactone. Preliminary studies on fine-tuning of ligand precursors and further application of metal complexes to the catalytic reactions are currently underway.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed with an Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and a Waters styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard. Matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were carried out with a Bruker Autoflex III TOF/TOF equipped with an MCP detector. The sample was dissolved in THF, and the matrix was 2,5-dihydroxybenzoic acid (HABA). Ions formed by a pulsed UV laser beam with 3 ns bandwidth (nitrogen laser λ was 337 nm) were accelerated through 20 kV, and the detection voltage was set at 1.7 kV.

PCl_5 (RDH), oxalyl chloride (Acros), 2-methoxyethylamine (Acros), unsym-dimethyl-ethylenediamine (Acros), 2,4,6-trimethylaniline (Alfa-Aesar), 2-(aminoethyl)pyridine (Acros), oxanilide (Acros), 2-aminoethanethiol hydrochloride (Alfa-Aesar), calcium iodide (Alfa-Aesar), sodium bis(trimethylsilyl)amide (Acros) and 9-anthracenemethanol (Acros) were used as supplied. Benzyl alcohol (TEDIA) and triethylamine (TEDIA) were dried over magnesium sulfate and distilled before use. ε-Caprolactone (Acros) was dried over magnesium sulfate and distilled under reduced pressure before use. HCl·H_2N-$(CH_2)_2$SMe,[18] [PhN=C{NH$(CH_2)_2$OMe}–C{NH$(CH_2)_2$OMe}=NPh] (**1**),[12e] [PhN=C{NH$(CH_2)_2$NMe$_2$}–C{NH$(CH_2)_2$NMe$_2$}=NPh] (**2**),[12e] N^1,N^2-bis(2,4,6-trimethylphenyl) oxaldiimidoyl dichloride,[14] [Ph^{TriMe}N=C{NHCH$_2$Py}–C{NHCH$_2$Py}=NPh^{TriMe}] (**5**)[14] and Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$[6f] were prepared by literature methods.

Preparations

[Ph^{TriMe}N=C{NH$(CH_2)_2$OMe}–C{NH$(CH_2)_2$OMe}=NPh^{TriMe}] (**3**). To a flask containing N^1,N^2-bis(2,4,6-trimethylphenyl) oxaldiimidoyl dichloride (2.67 g, 7.2 mmol), 2-methoxyethylamine

(1.25 mL, 4.4 mmol) and triethylamine (2.20 mL, 16.2 mmol), 30 mL THF were added. The reaction mixture was refluxed for 48 h. After cooling, the suspension was filtered and all the volatiles were removed *in vacuo*. The residue was washed with 20 mL hexane to afford a white solid. Yield, 2.60 g, 81%. ^{1}H NMR (400 MHz): δ 2.16(s, 2- and 6-CH_3, 12H), 2.24(s, 4-CH_3, 6H), 2.78(br, CH_2, 4H), 3.23(br, CH_2-O-CH_3, 10H), 6.78(s, Ar-C*H*, 4H). ^{13}C{^{1}H} NMR (100 MHz): δ 18.4(2- and 6-*C*H$_3$), 20.7(4-*C*H$_3$), 41.7(*C*H$_2$), 58.6(O-*C*H$_3$), 71.2(*C*H$_2$), 127.8(Ar-*C*H), 127.9, 130.8, 144.0(*C*). Anal. Calc. for $C_{26}H_{38}N_4O_2$: C, 71.20; H, 8.73; N, 12.77. Found: C, 70.99; H, 8.52; N, 12.90%.

[Ph^{TriMe}N=C{NH(CH$_2$)$_2$SMe}–C{NH(CH$_2$)$_2$SMe}=NPh^{TriMe}] (**4**). The procedure for the preparation of **4** was similar to that used for **3** but with N^1,N^2-bis(2,4,6-trimethylphenyl) oxaldiimidoyl dichloride (2.00 g, 5.5 mmol), HCl·H$_2$N(CH$_2$)$_2$SMe (1.50 g, 11.6 mmol) and triethylamine (3.20 mL, 23.3 mmol). A white solid was obtained. Yield, 1.60 g, 61%. ^{1}H NMR (400 MHz): δ 1.84(s, S-CH_3, 6H), 2.13(s, 2- and 6-CH_3, 12H), 2.23(s, 4-CH_3, 6H), 2.33(br, CH_2, 4H), 2.86(br, CH_2, 4H), 6.79(s, Ar-C*H*, 4H). ^{13}C{^{1}H} NMR (100 MHz): δ 14.8(S-*C*H$_3$), 18.4(2- and 6-*C*H$_3$), 20.6(4-*C*H$_3$), 34.1(*C*H$_2$), 40.8(*C*H$_2$), 128.0(Ar-*C*H), 131.2, 143.6, 144.4(*C*). Anal. Calc. for $C_{26}H_{38}N_4S_2$: C, 66.34; H, 8.14; N, 11.90. Found: C, 65.90; H, 8.16; N, 12.08%.

[Ca{N(SiMe$_3$)$_2$}(THF)(PhN)C{N(CH$_2$)$_2$OMe}–]$_2$ (**6**). To a solution of Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (1.01 g, 2.0 mmol) in 10 mL toluene, a solution of **1** (0.35 g, 1.0 mmol) in 10 mL toluene was added over 10 min at 0 °C. The resulting colorless solution was warmed to room temperature and stirred overnight. After 12 h of stirring, all the volatiles were removed *in vacuo* and the residue was washed with hexane to afford a brown solid. Yield, 0.40 g, 44%. ^{1}H NMR (600 MHz, C_6D_6): δ 0.33(s, Si*Me*$_3$, 36H), 1.08(m, *THF*, 8H), 2.82(br, CH_2, 4H), 2.94(br, CH_2, 4H), 3.05(s, O-CH_3, 6H), 3.26(m, *THF*, 8H), 6.74(t, Ar-C*H*, 2H, J = 7.8 Hz), 7.06(br, Ar-C*H*, 4H), 7.24(t, Ar-C*H*, 4H, J = 6.0 Hz). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 5.9(Si*Me*$_3$), 25.2(*THF*), 49.7(*C*H$_2$), 59.6 (O-*C*H$_3$), 68.7(*THF*), 75.1(*C*H$_2$), 118.6, 121.6, 128.9(Ar-*C*H), 128.5, 152.1, 165.3(*C*). Anal. Calc. for $C_{40}H_{76}Ca_2N_6O_4Si_4$: C, 53.53; H, 8.53; N, 9.36. Found: C, 51.74; H, 8.92; N, 9.72%.

[Ca{N(SiMe$_3$)$_2$}(THF)(PhN)C{N(CH$_2$)$_2$NMe$_2$}–]$_2$ (**7**). The procedure for the preparation of **7** was similar to that used for **6** but with Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (1.01 g, 2.0 mmol) and **2** (0.38 g, 1.0 mmol). A brown solid was obtained. Yield, 0.45 g, 49%. ^{1}H NMR (600 MHz, C_6D_6): δ 0.42(s, Si*Me*$_3$, 36H), 1.14(m, *THF*, 8H), 1.84(br, CH_2, 4H), 2.00(br, N*Me*$_2$, 12H), 3.09(br, CH_2, 4H), 3.28(m, *THF*, 8H), 6.78(t, Ar-C*H*, 2H, J = 7.2 Hz), 7.15(br, Ar-C*H*, 4H), 7.29(t, Ar-C*H*, 4H, J = 7.8 Hz). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 6.1(Si*Me*$_3$), 25.1(*THF*), 45.0(N*Me*$_2$), 48.4 (*C*H$_2$), 61.2(*C*H$_2$), 69.2(*THF*), 118.5, 128.3, 128.7(Ar-*C*H), 121.6, 151.9, 164.8(*C*). Anal. Calc. for $C_{42}H_{82}Ca_2N_8O_2Si_4$: C, 54.61; H, 8.95; N, 12.13. Found: C, 53.99; H, 9.00; N, 12.60%.

[Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{N(CH$_2$)$_2$OMe}–]$_2$ (**8**). The procedure for the preparation of **8** was similar to that used for **6** but with Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (1.01 g, 2.0 mmol) and **3** (0.44 g, 1.0 mmol). A brown solid was obtained. Yield, 0.48 g, 40%. ^{1}H NMR (600 MHz, C_6D_6): δ 0.31(s, Si*Me*$_3$, 36H), 1.25(m, *THF*, 8H), 2.27(s, 4-CH_3, 6H), 2.46(s, 2- and 6-CH_3, 12H), 2.76 (m, CH_2, 4H), 2.87(m, CH_2, 4H), 3.06(s, O-CH_3, 6H), 3.35(m, *THF*, 8H), 6.89(s, Ar-C*H*, 4H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 5.9(Si*Me*$_3$), 20.8(2- and 6-*C*H$_3$), 20.9(4-*C*H$_3$), 25.1(*THF*), 46.8 (*C*H$_2$), 59.7(O-*C*H$_3$), 68.9(*THF*), 74.9(*C*H$_2$), 128.6(Ar-*C*H), 128.3, 129.6, 130.2, 147.4, 163.0(*C*). Anal. Calc. for $C_{46}H_{88}Ca_2N_6O_4Si_4$: C, 56.28; H, 9.03; N, 8.56. Found: C, 56.18; H, 8.83; N, 8.53%.

[Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{N(CH$_2$)$_2$SMe}–]$_2$ (**9**). The procedure for the preparation of **9** was similar to that used for **6** but with Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (1.01 g, 2.0 mmol) and **4** (0.47 g, 1.0 mmol). A brown solid was obtained. Yield, 0.46 g, 45%. ^{1}H NMR (600 MHz, C_6D_6): δ 0.38(s, Si*Me*$_3$, 36H), 1.17(m, *THF*, 8H), 1.82(s, S-CH_3, 6H), 2.21(s, 4-CH_3, 6H), 2.32(m, CH_2, 4H), 2.42(s, 2- and 6-CH_3, 12H), 2.79(m, CH_2, 4H), 3.27(m, *THF*, 8H), 6.81(s, Ar-C*H*, 4H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 6.1(Si*Me*$_3$), 15.4(S-*C*H$_3$), 20.8(4-*C*H$_3$), 21.3(2- and 6-*C*H$_3$), 25.0 (*THF*), 36.3(*C*H$_2$), 46.7(*C*H$_2$), 68.9(*THF*), 128.5(Ar-*C*H), 128.8, 129.4, 129.6, 147.6, 164.9 (*C*). Anal. Calc. for $C_{46}H_{88}Ca_2N_6O_2S_2Si_4$: C, 54.49; H, 8.75; N, 8.29. Found: C, 53.96; H, 8.55; N, 8.04%.

[Ca{N(SiMe$_3$)$_2$}(THF)(Ph^{TriMe}N)C{NCH$_2$Py}–]$_2$ (**10**). The procedure for the preparation of **10** was similar to that used for **6** but with Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (1.01 g, 2.0 mmol) and **5** (0.50 g, 1.0 mmol). A dark blue solid was obtained. A crystalline solid was recrystallized from concentrated hexane solution after a couple of hours. Yield, 0.28 g, 27%. ^{1}H NMR (600 MHz, C_6D_6): δ 0.33(s, Si*Me*$_3$, 36H), 1.10(m, *THF*, 8H), 2.34(s, 4-CH_3, 6H), 2.56(s, 2- and 6-CH_3, 12H), 3.28(m, *THF*, 8H), 4.28(s, CH_2, 4H), 6.24(d, Ar-C*H*, 2H, J = 7.8 Hz), 6.49(t, Ar-C*H*, 2H, J = 6.6 Hz), 6.68(t, Ar-C*H*, 2H, J = 7.8 Hz), 6.97(s, Ar-C*H*, 4H), 8.69(d, Ar-C*H*, 2H, J = 4.8 Hz). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 5.8 (Si*Me*$_3$), 20.9(2- and 6-*C*H$_3$) 21.0(4-*C*H$_3$), 25.0 (*THF*), 54.7(*C*H$_2$-Py), 68.8(*THF*), 121.0, 122.6, 129.7, 130.4, 137.4, 148.2(Ar-*C*H), 128.3, 128.7, 147.3, 163.5, 164.0(*C*). Anal. Calc. for $C_{52}H_{86}Ca_2N_8O_4Si_4$: C, 59.61; H, 8.27; N, 10.69. Found: C, 59.16; H, 8.26; N, 10.49%.

Polymerization procedure of ε-caprolactone. Typically, to a flask containing the prescribed amount of catalyst (0.03125 mmol) was added 7.5 mL THF (containing 0.0625 mmol benzyl alcohol). After 3 min, the ε-caprolactone was added. The reaction mixture was stirred at 0 °C or 30 °C for the prescribed time. After the reaction was quenched by the addition of acetic acid solution (5 mL, 0.35 N), the resulting mixture was poured into *n*-heptane (25 mL) to precipitate polymers. Crude products were recrystallized from THF/hexane and dried *in vacuo* to a constant weight.

Crystal structure data

Crystals **7** were grown from concentrated hexane solution and isolated by filtration. A suitable crystal of **7** was mounted onto a glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas using an Oxford Cryosystems Cryostream unit. Diffraction data were collected at 100 K using Oxford Gemini S diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program.[19] The space group determination was based on a check of the Laue symmetry and systematic absences and

Table 2 Summary of crystal data for complex **7**

	7
Formula	$C_{42}H_{82}Ca_2N_8O_2Si_4$
F_w	923.68
T (K)	100(2)
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	15.3218(2)
b (Å)	15.5131(2)
c (Å)	23.0555(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	5480.03(12)
Z	4
ρ_{calc} (Mg m^{-3})	1.120
μ(Mo K$_\alpha$) (mm^{-1})	0.334
Reflections collected	29 787
No. of parameters	262
Indep. reflns (R_{int})	6728(0.0286)
Final R indices $R_1{}^a$, $wR_2{}^a$	0.0442, 0.1353
R indices (all data)	0.0624, 0.1429
GoF^b	1.005

^{a} $R_1 = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|]$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; $w = 0.10$. ^{b} GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[20] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 2. CCDC reference number 900478 for **7**.

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References

1 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.

2 (*a*) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215; (*b*) G. W. Coates, *J. Chem. Soc., Dalton Trans.*, 2002, 467; (*c*) K. Nakano, N. Kosaka, T. Hiyama and K. Nozaki, *Dalton Trans.*, 2003, 4039; (*d*) M. H. Chisholm and Z. Zhou, *J. Mater. Chem.*, 2004, **14**, 3081; (*e*) G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618; (*f*) J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602; (*g*) C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832; (*h*) A. K. Sutar, T. Maharana, S. Dutta, C.-T. Chen and C.-C. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1724.

3 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841.

4 (*a*) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229; (*b*) M. H. Chisholm, J. C. Gallucci and H. Zhen, *Inorg. Chem.*, 2001, **40**, 5051; (*c*) M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2005, **44**, 8004; (*d*) H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Macromolecules*, 2006, **39**, 3745; (*e*) C.-T. Chen, C.-Y. Chan, C.-A. Huang, M.-T. Chen and K.-F. Peng, *Dalton Trans.*, 2007, 4073; (*f*) M.-T. Chen and C.-T. Chen, *Dalton Trans.*, 2011, **40**, 12886.

5 (*a*) M.-L. Shueh, Y.-L. Wang, B.-H. Huang, C.-Y. Kuo and C.-C. Lin, *Macromolecules*, 2004, **37**, 5155; (*b*) H.-Y. Tang, H.-Y. Chen, J.-H. Huang and C.-C. Lin, *Macromolecules*, 2007, **40**, 8855; (*c*) M.-T. Chen, P.-J. Chang, C.-A. Huang, K.-F. Peng and C.-T. Chen, *Dalton Trans.*, 2009, 9068; (*d*) C. N. Ayala, M. H. Chisholm, J. C. Gallucci and C. Krempner, *Dalton Trans.*, 2009, 9237; (*e*) F. Drouin, T. J. J. Whitehorne and F. Schaper, *Dalton Trans.*, 2011, **40**, 1396.

6 (*a*) Z. Zhong, P. J. Dijkstra, C. Birg, M. Westerhausen and J. Feijen, *Macromolecules*, 2001, **34**, 3863; (*b*) M. Westerhausen, S. Schneiderbauer, A. N. Kneifel, Y. Söltl, P. Mayer, H. Nöth, Z. Zhong, P. J. Dijkstra and J. Feijen, *Eur. J. Inorg. Chem.*, 2003, 3432; (*c*) M. H. Chisholm, J. Gallucci and K. Phomphrai, *Chem. Commun.*, 2003, 48; (*d*) Z. Zhong, S. Schneiderbauer, P. J. Dijkstra, M. Westerhausen and J. Feijen, *Polym. Bull.*, 2003, **51**, 175; (*e*) M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2004, **43**, 6717; (*f*) Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.*, 2006, 340; (*g*) D. J. Darensbourg, W. Choi and C. P. Richers, *Macromolecules*, 2007, **40**, 3521; (*h*) H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Polymer*, 2007, **48**, 2257; (*i*) D. J. Darensbourg, W. Choi, O. Karroonnirun and N. Bhuvanesh, *Macromolecules*, 2008, **41**, 3493; (*j*) V. Poirier, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.*, 2009, 9820; (*k*) S.-M. Ho, C.-S. Hsiao, A. Datta, C.-H. Hung, L.-C. Chang, T.-Y. Lee and J.-H. Huang, *Inorg. Chem.*, 2009, **48**, 8004; (*l*) M. Helou, O. Miserque, J.-M. Brusson, J.-F. Carpentier and S. M. Guillaume, *ChemCatChem*, 2010, **2**, 306; (*m*) Y. Sarazin, D. Roşca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron and J.-F. Carpentier, *Organometallics*, 2010, **29**, 6569; (*n*) X. Xu, Y. Chen, G. Zou, Z. Ma and G. Li, *J. Organomet. Chem.*, 2010, **695**, 1155; (*o*) M. G. Cushion and P. Mountford, *Chem. Commun.*, 2011, **47**, 2276; (*p*) M. L. Dias, L. C. Palermo and A. C. Silvino, *Macromol. Symp.*, 2011, **299–300**, 156.

7 (*a*) H.-Y. Chen, J. Zhang, C.-C. Lin, J. H. Reibenspies and S. A. Miller, *Green Chem.*, 2007, **9**, 1038; (*b*) H.-Y. Chen, M.-Y. Liu, A. K. Sutar and C.-C. Lin, *Inorg. Chem.*, 2010, **49**, 665; (*c*) Y. Huang, Y.-H. Tsai, W.-C. Hung, C.-S. Lin, W. Wang, J.-H. Huang, S. Dutta and C.-C. Lin, *Inorg. Chem.*, 2010, **49**, 9416; (*d*) B. Calvo, M. G. Davidson and D. García-

Vivó, *Inorg. Chem.*, 2011, **50**, 3589; (*e*) W.-Y. Lu, M.-W. Hsiao, S. C. N. Hsu, W.-T. Peng, Y.-J. Chang, Y.-C. Tsou, T.-Y. Wu, Y.-C. Lai, Y. Chen and H.-Y. Chen, *Dalton Trans.*, 2012, **41**, 3659.

8 (*a*) V. C. Gibson, E. L. Marshall, D. Navarro-Llobet, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2002, 4321; (*b*) B. J. O'Keefe, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 4384; (*c*) D. S. Mcguinness, E. L. Marshall, V. C. Gibson and J. W. Steed, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3798; (*d*) J. L. Gorczynski, J. Chen and C. L. Fraser, *J. Am. Chem. Soc.*, 2005, **127**, 14956; (*e*) X. Wang, K. Liao, D. Quan and Q. Wu, *Macromolecules*, 2005, **38**, 4611.

9 J. E. Huheey, E. A. Keiter and R. L. Keiter, in *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper Collins College Publishers, New York, 4th edn, 1993, pp. 292, 344.

10 (*a*) J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219; (*b*) F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; (*c*) M. P. Coles, *Dalton Trans.*, 2006, 985; (*d*) P. C. Junka and M. L. Cole, *Chem. Commun.*, 2007, 1579; (*e*) F. T. Edelmann, *Chem. Soc. Rev.*, 2009, **38**, 2253; (*f*) S. Collins, *Coord. Chem. Rev.*, 2011, **255**, 118.

11 (*a*) M. Döring, H. Görls and R. Beckert, *Z. Anorg. Allg. Chem.*, 1994, **620**, 551; (*b*) M. Döring, P. Fehling, H. Görls, W. Imhof, R. Beckert and D. Lindauer, *J. Prakt. Chem.*, 1999, **341**, 748.

12 (*a*) F. Gerstner, W. Schwarz, H.-D. Hausen and J. Weidlein, *J. Organomet. Chem.*, 1979, **175**, 33; (*b*) T. Döhler, H. Görls and D. Walther, *Chem. Commun.*, 2000, 945; (*c*) M. Ruben, D. Walther, R. Knake, H. Görls and R. Beckert, *Eur. J. Inorg. Chem.*, 2000, 1055; (*d*) D. Walther, T. Döhler, N. Theyssen and H. Görls, *Eur. J. Inorg. Chem.*, 2001, 2049; (*e*) C.-T. Chen, C.-A. Huang, Y.-R. Tzeng and B.-H. Huang, *Dalton Trans.*, 2003, 2585.

13 C.-T. Chen, L. H. Rees, A. R. Cowley and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 2001, 1761.

14 J. Wuckelt, M. Döring, H. Görls and P. Langer, *Eur. J. Inorg. Chem.*, 2001, 805.

15 A. W. Addison and T. N. Rao, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

16 S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2861.

17 (*a*) Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, H. Yasuda, A. Harada and J. Okuda, *Macromolecules*, 2002, **35**, 7538; (*b*) K. Phomphrai, C. Pongchan-o, W. Thumrongpatanaraks, P. Sangtrirutnugul, P. Kongsaeree and M. Pohmakotr, *Dalton Trans.*, 2011, **40**, 2157.

18 M. Fujita, M. Otsuka and Y. Sugiura, *J. Med. Chem.*, 1996, **39**, 503.

19 G. M. Sheldrick, *SADABS, Program for Area Detector Absorption Correction*. Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

20 G. M. Sheldrick, *SHELXTL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

