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Organometallic calcium and strontium borohydrides as initiators for the polymerization of ε-caprolactone and L-lactide: combined experimental and computational investigations†

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$[Ca(BH_4)_2(THF)_2]$ (**1a**), a known compound, was easily prepared following a convenient new procedure from $[Ca(OMe)_2]$ and $BH_3{\cdot}THF$ in THF. Reaction of **1a** with KCp* (Cp* = (η^5-C_5Me_5)) and $K\{(Me_3SiNPPh_2)_2CH\}$ in a 1 : 1 ratio in THF resulted in the corresponding dimeric heteroleptic mono-borohydride derivatives $[Cp^*Ca(BH_4)(THF)_n]_2$ (**2a**) and $[\{(Me_3SiNPPh_2)_2CH\}Ca(BH_4)(THF)_2]$ (**3a**), respectively. Both compounds were fully characterized and the solid-state structure of **3a** was established by single crystal X-ray diffraction. Compounds **1a**, **2a**, and **3a**, together with the earlier reported compounds $[Sr(BH_4)_2(THF)_2]$ (**1b**), $[Cp^*Sr(BH_4)(THF)_2]_2$ (**2b**), and $[\{(Me_3SiNPPh_2)_2CH\}Sr(BH_4)(THF)_2]$ (**3b**), were used as initiators for the ROP of polar monomers. The general performances of the complexes in the ROP of ε-caprolactone and L-lactide demonstrate a relatively good control of the polymerization under the operating conditions established. α,ω-Dihydroxytelechelic poly(ε-caprolactone)s (PCLs) and poly(lactide)s (PLAs) were thus synthesized. DFT calculations on the initiation step of the ROP of ε-CL were carried out. Gibbs free energy profiles were determined for the three calcium complexes highlighting slightly more active calcium complexes as compared to strontium analogues, in agreement with experimental findings.

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Introduction

There is significant increasing interest in the coordination and organometallic chemistry of the heavier alkaline earth metals (Ca, Sr, Ba).[1–6] Within these series, calcium compounds remain the most largely investigated.[4,5,7] Although calcium is an inexpensive and non-toxic element present in significant amount in the human body, access to its organometallic and coordination compounds is often limited by their kinetic lability with detrimental Schlenk-type equilibria.[8,9] Modern research of organometallic and coordination compounds of the heavier alkaline earth metals essentially deals with the synthesis of new compounds,[10–12] their reactivity,[13–16] and some catalytic applications.[17–20]

Among others, the ring-opening polymerization (ROP) of cyclic esters such as ε-caprolactone (ε-CL) and lactide (LA) using well-characterized calcium, and some strontium and barium compounds, has been reported lately.[21–31] By using well-defined alkaline earth metal compounds as initiators, the access to polymers with controlled molecular features – in particular molar mass and dispersity ($Đ_M = M_w/M_n$) – end-group fidelity and, in some cases, controlled stereochemistry, is possible.[4,32,33]

Mainly alkoxides/phenoxide[26–30,34] and amido complexes[22,25,35] of the alkaline earth metals have been reported as initiators for the ROP of cyclic esters. However, these remain underdeveloped in comparison to the related rare-earth metal analogues. On the other hand, borohydride derivatives, which nowadays are well-established ROP initiators in rare earth chemistry,[36] have been so far nearly neglected in the polymerization chemistry of alkaline earth elements. The first reports in this area were only published recently by Mountford *et al.* on calcium,[31,37] followed by a report from our groups on strontium.[24] This is rather surprising given that $[Ca(BH_4)_2(THF)_2]$ (**1a**) is commercially available for applications in material

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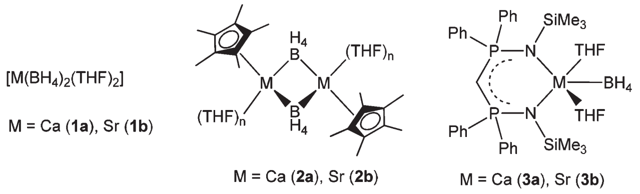
† Electronic supplementary information (ESI) available: CIF file of **3a**. CCDC 915058. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00037k



Scheme 1 Investigated alkaline earth metal borohydride compounds.

science[38] and that $[Sr(BH_4)_2(THF)_2]$ (**1b**) was reported as early as in the mid-nineties.[39]

As part of our ongoing efforts aimed both at implementing alkaline earth complexes in fine organic catalysis[40–45] and at valorizing original organometallic borohydride complexes in polymerization catalysis,[46–48] we communicated in our previous study the application of **1b** in the ROP of ε-CL as well as the synthesis and structural characterization of the borohydride half-sandwich $[Cp^*Sr(BH_4)(THF)_2]_2$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$) (**2b**) and the borohydride bis(phosphinimino)methanide $[\{(Me_3SiNPPh_2)_2CH\}Sr(BH_4)(THF)_2]$ (**3b**) complexes (Scheme 1).[24] These compounds **1b**, **2b**, and **3b** subsequently proved successful in the ROP of ε-CL.[24] Noteworthy, the strontocene borohydride complex **2b** afforded the highest molar mass poly(ε-caprolactone) (PCL) prepared from a molecular alkaline earth metal initiator in a quite controlled ROP approach. α,ω-Dihydroxytelechelic PCLs were thus obtained under mild operating conditions (23 °C, THF) as evidenced from NMR analyses, and the mechanism was investigated by DFT calculations.[24] Whereas the computed initiation step was found to be kinetically and thermodynamically possible for all three derivatives **1b**, **2b** and **3b**, the reaction appeared more kinetically facile with the more electron-enriched Cp* species **2b**, while it was calculated to be almost athermic in the case of the homoleptic bisborohydride compound **1b**.

With the aim to evaluate the potentially different polymerization abilities of strontium and calcium analogues, we then investigated, both experimentally and computationally, the ROP of ε-CL promoted by the corresponding calcium complexes $[Ca(BH_4)_2(THF)_2]$ (**1a**), $[Cp^*Ca(BH_4)(THF)_n]_2$ (**2a**) and $[\{(Me_3SiNPPh_2)_2CH\}Ca(BH_4)(THF)_2]$ (**3a**) (Scheme 1), and also extended the work to the ROP of L-lactide (LLA). Thus, we now report herein the synthesis and the structural studies of the analogous calcium borohydride complexes **2a** and **3a** (Scheme 1). We also present a full account of the experimental and computational evaluation of the catalytic efficiency of **1a, b**, **2a,b**, and **3a,b** as initiators for the ROP of ε-CL and LLA, including DFT calculations on the mechanism of the ROP of ε-CL.

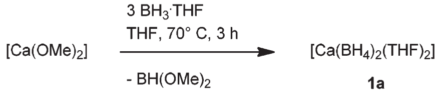
Results and discussion

Synthesis and characterization of calcium borohydride complexes 1a, 2a and 3a

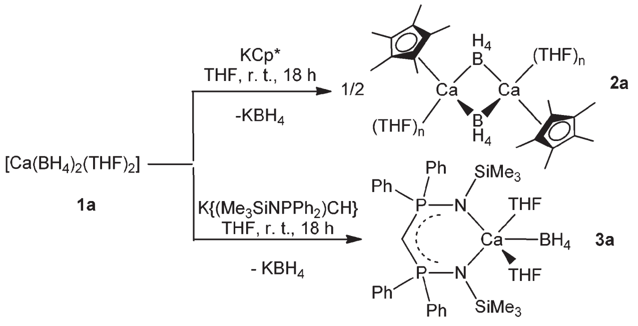
Although $[Ca(BH_4)_2(THF)_2]$ (**1a**)[49] is commercially available, we prepared it following a new procedure which is similar to the synthesis of $[Sr(BH_4)_2(THF)_2]$ (**1b**),[39] from $[Ca(OMe)_2]$[50] and $BH_3{\cdot}THF$ in THF in a 1 : 3 ratio to get a pure product (Scheme 2). In comparison to the literature,[49] no pyridine is needed for the synthesis. Reaction of **1a** with KCp* and $K\{(Me_3SiNPPh_2)_2CH\}$[51] in a 1 : 1 ratio in THF resulted in the corresponding heteroleptic mono-borohydride derivatives $[Cp^*Ca(BH_4)(THF)_n]_2$ (**2a**) and $[\{(Me_3SiNPPh_2)_2CH\}Ca(BH_4)(THF)_2]$ (**3a**), respectively (Scheme 3).

The new complexes **2a** and **3a** have been characterized by standard analytical/spectroscopic techniques. The ^1H NMR spectrum of **2a** shows the expected resonance for the Cp* ligand at δ 2.00 ppm and a broad quartet for the BH_4^- group at δ −0.44 ppm (J_{BH} = 83 Hz). For **3a** the expected signals of the bis(phosphinimino)methanide ligand were observed in the ^1H NMR spectrum. The characteristic signal of the methine group was not well resolved, resulting in a broad peak at δ 1.85 ppm, as recorded at room temperature. As for **2a**, the expected broad quartet for the BH_4^- group was observed at δ 0.10 ppm (J_{BH} = 82 Hz) for **3a**. In the ^1H NMR spectra of compounds **2a** and **3a**, the different coordination modes of the B–H protons observed in the solid state (see below) do not give rise to resolved signals. This may result from a flexible coordination mode of the BH_4^- group in solution. The ^{11}B NMR spectra of **3a** showed the awaited quintets (J_{BH} = 82 Hz) of the BH_4^- group for both compounds at δ −36.0 (**2a**) and −34.8 (**3a**) ppm, which is in the range of that recorded with **1a** (δ −36.6 ppm).

In the $^{31}P\{^1H\}$ spectrum of **3a**, a singlet was observed for the two magnetically equivalent phosphorus atoms at δ 16.4 ppm, in good agreement with the related complexes $[\{(Me_3SiNPPh_2)_2CH\}CaI(THF)_2]$ (δ 18.7 ppm)[43] and **3b** (δ 15.2 ppm).[24] Noteworthy, the NMR data did not show any sign of a ligand redistribution in solution. The IR bands of the BH_4^- group are broad precluding unambiguous identification of its coordination mode which could, however, in the case of **3a** be determined by X-ray analysis.[52,53] The poor quality of the



Scheme 2 Synthesis of $[Ca(BH_4)_2(THF)_2]$ (**1a**).



Scheme 3 Synthesis of $[Cp^*Ca(BH_4)(THF)_n]_2$ (**2a**) and $[\{(Me_3SiNPPh_2)_2CH\}Ca(BH_4)(THF)_2]$ (**3a**).

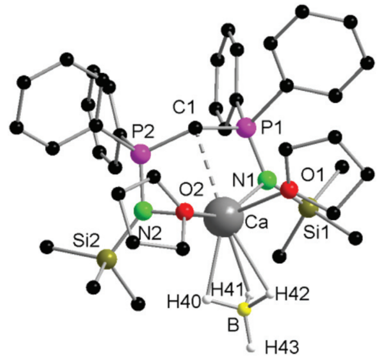
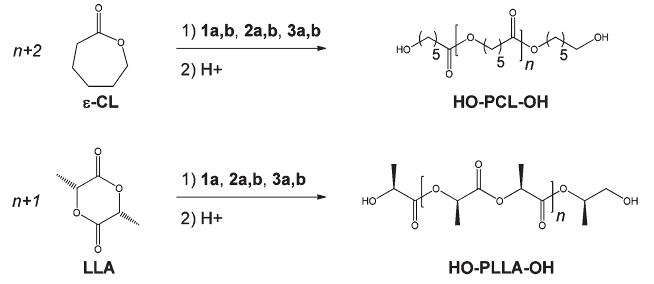


Fig. 1 Solid-state structure of **3a**, omitting some hydrogen atoms. Selected distances [Å] and angles [°]: Ca–N1 2.493(3), Ca–N2 2.488(3), Ca–O1 2.461(3), Ca–O2 2.452(3), Ca–C1 2.719(4), Ca–H40 2.37(5), Ca–H41 2.40(7), Ca–H42 2.61(6), Ca–B 2.633(5), N1–P1 1.584(4), N1–Si1 1.708(4), N2–P2 1.590(4), N2–Si2 1.706(3), C1–P1 1.726(4), C1–P2 1.741(4), B–H40 1.10(4), B–H41 1.04(7), B–H42 1.04(6), B–H43 1.09(5); N1–Ca–N2 94.09(11), N1–Ca–O1 88.36(11), N1–Ca–C1 62.88(12), N1–Ca–B 110.54(15), N2–Ca–B 107.04(14), N2–Ca–C1 63.41(11), O1–Ca–B 95.79(15), O2–Ca–B 95.24(15), P1–C1–P2 125.0(2).



Scheme 4 ROP of ε-CL and LLA in THF with calcium and strontium borohydride complexes **1a,b**, **2a,b**, **3a,b**.

crystals grown from **2a** precluded its characterization by X-ray diffraction. Therefore, in order to establish the dimeric structure of **2a**, both compounds **2a** and **3a** were analyzed by EI-MS. For **2a**, the molecular peak fitted with the formulation of **2a** as a dimeric compound. This formulation is also consistent with the analogous dimeric strontium compound **2b**.[24] Also, the molecular peak observed in the EI-MS of **3a** supported the data acquired by other methods allowing the formulation of **3a** as a monomeric species. Based on the analytical data the number of coordinated THF molecules in **2a** cannot be exactly determined. In analogy to **2b** we suggest that two molecules of THF are coordinated to the Ca atom in **2a**. This analogy is justified because **1a** and **1b** as well as **3a** and **3b** have the same amount of THF molecules coordinated to the center metal.

The solid-state structure of **3a** was established by single crystal X-ray diffraction (Fig. 1). Complex **3a** crystallizes in the triclinic space group $P\bar{1}$ as a monomeric compound. The hydrogen atoms of the BH_4^- group were localized in the difference Fourier map and refined isotropically showing that the BH_4^- group is κ^3(H)-coordinated to the calcium atom. The Ca–B distance is 2.633(5) Å and the Ca–H distances range from 2.37(5) Å to 2.61(6) Å. As expected, the bis(phosphinimino)methanide ligand forms a six-membered metallacycle (N1–P1–C1–P2–N2–Ca) upon chelation of the two trimethylsilylimine groups to the metal atom. The Ca–N distances (Ca–N1 2.493(3) Å and Ca–N2 2.488(3) Å) show an almost symmetric bonding of the ligand onto the metal center. As usually observed for bis(phosphinimino)methanide complexes,[43,54] the metallacycle adopts a twist boat conformation in which both the central carbon (C1) and calcium atoms are displaced from the N_2P_2 least-squares plane. The interaction between the methine carbon atom (C1) and the calcium atom (2.719(4) Å), which is longer than common Ca–C distances, is in the range of the related bonds in $[\{(Me_3SiNPPh_2)_2CH\}_2Ca]$ (2.765(1) Å)[55] and $[\{(Me_3SiNPPh_2)_2CH\}CaI(THF)_2]$ (2.735(6) Å).[43] Upon considering the $\{(Me_3SiNPPh_2)_2CH\}^-$ ligand as tridentate and the BH_4^- group as monodentate, the calcium atom is six-fold coordinated. The coordination polyhedron can be considered as a distorted octahedron. Compound **3a** has a non-crystallographic mirror plane through B–Ca–C1.

Ring-opening polymerization studies

The catalytic activities of the calcium and strontium series of borohydride complexes **1a,b**, **2a,b**, and **3a,b** were then assessed (Scheme 4). Polymerization studies were typically conducted in THF, with an initial monomer concentration of 1.0 M at either 23 °C or 50 °C. Selected data obtained with complexes **1a,b**, **2a,b**, and **3a,b** are collected in Tables 1 and 2.

The ability of the newly synthesized homoleptic bisborohydride calcium complex **1a** to promote the ROP of ε-CL and LLA was first evaluated (Table 1, entries 1–4, 13–16). Indeed, although some previously reported studies using the commercially available compound **1a** gave "disappointing performances",[37] our preliminary investigations[24] with the strontium analogue **1b** showed that it was active in the ROP of ε-CL at 23 °C in THF (Table 2, entries 1–4).

Even though the larger strontium derivatives have been reported to be more active than the calcium congeners in ROP,[26,30] we anticipated that **1a** would, at least to some reasonable extent and possibly under more severe operating conditions than those used with **1b**, allow the controlled synthesis of PCL. Rewardingly, under similar working conditions as those used with **1b**, up to 500 ε-CL units were successfully converted in high yields (80–99%) within two hours at 23 °C (Table 1, entries 1–4).

The control over the ROP process was rather good, affording PCLs featuring a good match between the observed (as determined by NMR and SEC) and calculated (based on two active BH_4^- functions) molar mass values, as well as moderate dispersity data ($Đ_M = M_w/M_n < 1.40$). The overall efficiency of the calcium initiator **1a** toward the ROP of ε-CL was thus similar to that of the strontium analogue **1b** (Table 1, entries 1–4 *vs.* Table 2, entries 1–2). The bisborohydride calcium complex **1a** was also found to be active in the ROP of LLA (Table 1, entries 13–16). However, rather prolonged reaction times were required with this monomer as compared to those typically used for the ROP of ε-CL, reaching only quite low LLA conversions and thus affording oligomers with, correspondingly, a rather good control (M_{nSEC} up to 6400 g mol^{-1};

Table 1 ROP of ε-CL and LLA initiated by $[Ca(BH_4)(THF)_2]$, **1a**, $[Cp^*Ca(BH_4)(THF)_n]_2$, **2a**, and $[\{(Me_3SiNPPh_2)_2CH\}Ca(BH_4)(THF)_2]$, **3a**

Entry	Complex	Monomer[a]	$[Monomer]_0/[BH_4]_0$[a]	Temp. (°C)	Reaction time[b]	Conv.[c] (%)	M_{ntheo}[d] ($g\ mol^{-1}$)	M_{nNMR}[e] ($g\ mol^{-1}$)	M_{nSEC}[f] ($g\ mol^{-1}$)	$Đ_M$[g]
1	**1a**	ε-CL	50/1	23	10 min	99	5600	4300	5100	1.38
2	**1a**	ε-CL	100/1	23	20 min	99	11 300	8100	9900	1.35
3	**1a**	ε-CL	300/1	23	60 min	96	32 800	22 100	24 800	1.38
4	**1a**	ε-CL	500/1	23	110 min	80	45 600	—	39 800	1.40
5	**2a**	ε-CL	100/1	23	10 min	99	11 300	14 800	16 100	1.41
6	**2a**	ε-CL	300/1	23	15 min	100	34 200	33 000	26 900	1.49
7	**2a**	ε-CL	500/1	23	20 min	100	57 000	41 400	33 200	1.47
8	**3a**	ε-CL	100/1	23	20 min	100	11 400	9300	11 200	1.48
9	**3a**	ε-CL	300/1	23	60 min	98	33 500	20 700	28 500	1.31
10	**3a**	ε-CL	500/1	23	180 min	75	42 750	33 400	35 150	1.28
11	**3a**	ε-CL	1000/1	23	360 min	45	51 300	38 000	43 600	1.35
12	**3a**	ε-CL	1000/1	50	360 min	60	68 400	—	57 600	1.33
13	**1a**	LLA	50/1	23	65 h	53	3800	3900	4100	1.27
14	**1a**	LLA	100/1	23	65 h	42	6000	2800	3920	1.22
15	**1a**	LLA	250/1	23	66 h	24	8600	6200	6400	1.25
16	**1a**	LLA	500/1	23	67 h	6	4300	4700	5500	1.12
17	**2a**	LLA	100/1	23	20 min	50	7200	4250	5900	1.25
18	**2a**	LLA	300/1	23	40 min	31	13 400	6800	7600	1.22
19	**2a**	LLA	500/1	23	60 min	26	18 700	9500	10 100	1.19
20	**3a**	LLA	100/1	23	15 h	80	11 500	10 200	13 800	1.35
21	**3a**	LLA	300/1	23	18 h	67	28 950	24 600	25 300	1.25
22	**3a**	LLA	500/1	23	24 h	33	23 800	20 800	21 900	1.30
23	**3a**	LLA	500/1	50	18 h	48	34 600	27 800	26 900	1.36
24	**3a**	LLA	1000/1	23	24 h	0	—	—	—	—

[a] All reactions were performed in THF with $[monomer]_0 = 1.0$ M; results are representative of at least duplicated experiments. The molar mass of **2b** was calculated with two molecules of THF. [b] Reaction times were not necessarily optimized. [c] Monomer conversion determined by ^1H NMR of the crude reaction mixture. [d] Theoretical molar mass values calculated from the relation: $[monomer]_0/[BH_4]_0 \times$ monomer conversion $\times M_{Monomer}$, with $[BH_4]_0 = 2\ [Ca(BH_4)_2(THF)_2]_0$, $[[Cp^*Ca(BH_4)(THF)_2]_2]_0$ or $[\{(Me_3SiNPPh_2)_2CH\}Ca(BH_4)(THF)_2]_0$, $M_{ε\text{-}CL} = 114\ g\ mol^{-1}$, and $M_{LLA} = 144\ g\ mol^{-1}$. [e] Molar mass values determined by NMR analysis of the isolated polymer (refer to the Experimental section). [f] Number of average molar mass values determined by SEC in THF at 20 °C *vs.* polystyrene standards and corrected (refer to the Experimental section). [g] Dispersity calculated from SEC traces.

$Đ_M \leq 1.27$). Comparatively, the strontium analogue **1b** failed to polymerize LLA even at 50 °C (Table 2, entries 14–15). Our results on the successful behavior of our home-made discrete sample of **1a** – which was fully characterized as a pure sample, as discussed above – in the ROP of ε-CL and LLA are in contrast to the previous literature claims mentioned above from the commercial **1a** sample.[37] Besides, in comparison to the calcium amide $[Ca\{N(SiMe_3)_2\}(THF)_2]$ or alkoxide initiating systems derived from either binary catalytic systems $[Ca\{N(SiMe_3)_2\}(THF)_2]$/ROH (R = Me, iPr) or discrete $[\{Ca(OR)_2\}_n]$ compounds,[21,22,56,57] the bisborohydride complex **1a** thus represents, to our knowledge, the homoleptic calcium initiator providing the highest molar mass polyester ($M_{nPCL} \leq$ 39 800 $g\ mol^{-1}$).

By analogy with the strontium analogues **1b**, **2b**, and **3b**, for which the experimental and DFT investigations showed a favorable activity for **2b**, we next considered the ROP of ε-CL and LLA initiated by the calcium congener **2a** (Table 1, entries 5–7 and 17–19).[58] In THF solution at 23 °C, the activity of **2a** was about one half order of magnitude higher than that observed with **1a**, suggesting a clear beneficial effect of the ancillary Cp* ligand. Indeed, whereas only 20 min were required to quantitatively convert 500 equiv. of ε-CL from **2a**, only 80% were consumed in 110 min using **1a** (Table 1, entry 7 *vs.* 4). The same favorable influence of the Cp* surroundings was gained in the ROP of LLA, to an even larger extent. Indeed, the activity of **2a** was dramatically higher than that reached with the homoleptic bisborohydride congener **1a** (Table 1, entry 19 *vs.* 16). The recovered PCLs and PLLAs were all monodispersed with relatively narrow dispersity values ($Đ_M$ = 1.19–1.49), and the experimental molar mass values matched well the ones calculated on the basis of monomer-to-BH_4 ratios.

Our preliminary investigations on the ROP of ε-CL promoted by **2b** showed a quite good activity at 50 °C.[24] Closer examination of the behavior of **2b** at ambient temperature revealed some activity, although lower than at higher temperature (Table 2, entries 3–11). In $[ε\text{-}CL]_0/[BH_4]_0 = 300:1$ experiments, the strontium complex **2b** led to 86% conversion of the monomer at 23 °C within 120 min, while the full conversion was achieved within 90 min at 50 °C (Table 2, entries 5 and 6). As many as 560 ε-CL units were successfully converted within 480 min at 50 °C. These polymerizations showed good control in terms of theoretical/experimental molar mass agreement as well as dispersity values below 1.38, allowing the preparation of a PCL with a molar mass up to M_{nSEC} = 59 200 $g\ mol^{-1}$. Also, **2b** was less efficient in the ROP of LLA than compared to that of ε-CL with at best 140 turnovers in 48 h at 23 °C (Table 2, entries 17–20). PLLAs of a molar mass up to M_{nSEC} = 20 500 $g\ mol^{-1}$, corresponding to 140 LLA units being converted, were thus formed. Overall, complex **2b** displayed better activity compared to the homoleptic analogue **1b**. Also,

Table 2 ROP of ε-CL and LLA initiated by $[Sr(BH_4)(THF)_2]$, **1b**, $[Cp^*Sr(BH_4)(THF)_2]_2$, **2b**, and $[\{(Me_3SiNPPh_2)_2CH\}Sr(BH_4)(THF)_2]$, **3b**

Entry	Complex	Monomer[a]	$[Monomer]_0/[BH_4]_0$[a]	Temp. (°C)	Reaction time[b]	Conv.[c] (%)	M_{ntheo}[d] ($g\ mol^{-1}$)	M_{nNMR}[e] ($g\ mol^{-1}$)	M_{nSEC}[f] ($g\ mol^{-1}$)	$Đ_M$[g]
1	**1b**	ε-CL	300/1	23	60 min	90	15 390	15 200	19 100	1.57
2	**1b**	ε-CL	500/1	23	135 min	75	21 380	27 800	35 000	1.31
3	**2b**	ε-CL	100/1	23	40 min	95	10 800	8500	9600	1.23
4	**2b**	ε-CL	100/1	50	30 min	100	11 400	7300	8100	1.38
5	**2b**	ε-CL	300/1	23	120 min	86	29 400	22 300	24 800	1.28
6	**2b**	ε-CL	300/1	50	90 min	100	34 200	20 700	18 200	1.27
7	**2b**	ε-CL	500/1	23	240 min	75	42 700	—	38 700	1.30
8	**2b**	ε-CL	500/1	50	300 min	100	57 000	—	43 500	1.29
10	**2b**	ε-CL	1000/1	23	480 min	42	47 900	—	45 100	1.40
11	**2b**	ε-CL	1000/1	50	480 min	56	63 800	—	59 200	1.38
12	**3b**	ε-CL	100/1	23	30 min	94	10 700	7600	8300	1.40
13	**3b**	ε-CL	300/1	23	80 min	97	33 170	31 700	28 400	1.31
14	**3b**	ε-CL	500/1	23	150 min	95	53 600	—	41 300	1.85
15	**1b**	LLA	100/1	23	65 h	0	—	—	—	—
16	**1b**	LLA	100/1	50	65 h	0	—	—	—	—
17	**2b**	LLA	100/1	23	18 h	60	8600	6900	7200	1.30
18	**2b**	LLA	300/1	23	29 h	35	15 100	12 800	13 600	1.27
19	**2b**	LLA	500/1	23	48 h	28	20 160	17 900	20 500	1.62
20	**2b**	LLA	1000/1	23	65 h	0	—	—	—	—
21	**3b**	LLA	100/1	23	12.5 h	100	14 400	10 200	10 600	1.64
22	**3b**	LLA	300/1	23	14 h	52	22 400	20 000	18 800	1.56
23	**3b**	LLA	500/1	23	13.5 h	54	38 900	18 300	20 700	1.60
24	**3b**	LLA	1000/1	23	14 h	22	31 680	21 000	19 800	1.38

[a] All reactions were performed in THF with $[monomer]_0 = 1.0$ M; results are representative of at least duplicated experiments. [b] Reaction times were not necessarily optimized. [c] Monomer conversion determined by ^1H NMR of the crude reaction mixture. [d] Theoretical molar mass value calculated from the relation: $[monomer]_0/[BH_4]_0 \times$ monomer conversion $\times M_{Monomer}$, with $[BH_4]_0 = 2\ [Sr(BH_4)_2(THF)_2]_0$, $[[Cp^*Sr(BH_4)(THF)_2]_2]_0$ or $[\{(Me_3SiNPPh_2)_2CH\}Sr(BH_4)(THF)_2]_0$, $M_{ε\text{-CL}} = 114\ g\ mol^{-1}$, and $M_{LLA} = 144\ g\ mol^{-1}$. [e] Molar mass values determined by NMR analysis of the isolated polymer (refer to the Experimental section). [f] Number of average molar mass values determined by SEC in THF at 20 °C *vs.* polystyrene standards and corrected (refer to the Experimental section). [g] Dispersity calculated from SEC traces.

the calcium complexes **1a** and **2a** were generally more effective in the ROP of ε-CL and LLA than the strontium analogues **1b** and **2b**.

The bis(phosphiniminomethanide) borohydride calcium complex **3a** was also found to be active in the ROP of ε-CL and LLA. At room temperature, **3a** smoothly afforded PCL with quite high molar masses ($M_{nSEC} \leq 57\,600\ g\ mol^{-1}$) (Table 1, entries 8–12). However, the complex showed lower efficiency with increased loading of ε-CL. Indeed, the calculated molar mass and the M_n values determined experimentally from NMR and SEC analyses agreed relatively well, while the dispersity remained in the range $Đ_M = 1.28–1.48$. However, when the initial monomer charge overcame 300 equiv., reaction times proportionally longer than hinted from lower ε-CL feed experiments were required to reach high ε-CL conversion. This lower activity could be compensated to some extent upon raising the temperature from 23 °C to 50 °C (Table 1, entries 11–12). As many as 600 ε-CL units were thus polymerized, yet quite slowly (within 6 h). The same behavior was observed in the ROP of LLA (Table 1, entries 20–24). However, the ROP of LLA was significantly slower than that of ε-CL, in agreement with the typical difference in both monomers' reactivity generally observed in the literature.[21] Similarly, a higher polymerization temperature favored the conversion of an initial loading of 500 equiv. of LLA, affording at best 240 turnovers in 18 h at 50 °C (Table 1, entry 23). Complex **3a** was also similarly less active in the presence of larger LLA loadings, failing to polymerize any LLA in the presence of 1000 equiv. at 23 °C within 24 h (Table 1, entry 24). Unlike in our previous attempts,[24] the strontium analogue **3b** was found to be active in the ROP of ε-CL at 23 °C. A turnover of 475 was reached within 2.5 h with a fair control of molar masses (Table 2, entries 12–14). Under the same operating conditions, the ROP of LLA promoted from **3b** did afford PLLA, yet with a lower activity as compared to the ROP of ε-CL (Table 2, entries 21–24). While 100 LLA units were successfully polymerized within 12.5 h, only 270 turnovers were reached at best within 14 h under such operating conditions (Table 2, entries 21 and 23).

The general comparison of the data for the ROP of 300 equivalents of monomer per borohydride group initiated by complexes **1a,b**, **2a,b**, and **3a,b** is informative. It shows that, among all evaluated complexes, calcium borohydride **2a** provides the best compromise in terms of activity and control. However, the activity as well as the control imparted by these large calcium and strontium borohydride series of complexes in the ROP of ε-CL or LLA, remained – similarly to literature data on related alkaline earth metal borohydride initiating complexes[31,37] – lower compared to those achieved with related rare earth element borohydride complexes or with other post-metallocene non-borohydride alkaline earth metal precursors used in an "immortal" ROP procedure.[21]

The nature of the end-groups capping the PCL or PLLA chains was examined by NMR analyses of the polymer samples recovered after precipitation. In particular, ^1H NMR spectroscopy attested the presence of –C*H*$_2$OH or –OC*H*(Me)-C*H*$_2$OH and –C(O)C*H*(Me)OH termini on PCL or PLLA, respectively. Such α,ω-dihydroxytelechelic polymers were expected based on previous literature reports on the ROP of such lactone or diesters initiated by rare earth element borohydride derivatives.[46–48,59–65] Indeed, detailed insights, especially based on NMR, IR, MALDI-ToF and DFT investigations, have established that the reduction of the oxygen of the carbonyl adjacent to the borohydride group in the first inserted monomer unit occurred, thereby inducing the formation of a second hydroxyl end-function in place of the usual C(O)X terminus generally generated upon ROP forming a non-borohydride precursor [LMX] with L = ancillary ligand(s), M = metal center and X = nucleophile such as OR$^-$ or NR$_2$$^-$. Note that the other hydroxyl end-capping group is formed upon deactivation of the active metal–oxygen bond.[45–48,58–63]

In light of our already published studies on strontium analogues,[24] DFT calculations on the initiation step of the ROP of ε-CL were carried out. Gibbs free energy profiles were determined for the three calcium complexes **1a**, **2a**, and **3a** (Fig. 2). The computed reaction profiles are very similar to those obtained for the parent strontium compounds, as it proceeds in two steps. Indeed, the first B–H activation is concomitant with the BH$_3$ trapping by the endocyclic oxygen of the ε-CL. Moreover, the ring-opening is determined as the rate determining step of the reaction, as the barrier is the highest of the two. The relative instability of the ε-CL adduct of complex **3a** is due to the fact that this is not a simple adduct. Indeed, this complex was obtained by following the intrinsic reaction coordinate from the nucleophilic attack TS. The intermediate obtained for **3a** is distorted with a short B–H⋯C distance of 1.27 Å.

Detailed analysis of the energetics of the reaction profiles showed that although the three complexes are quite similar within the precision of the computational method, complex **2a** leads to the best compromise since both barriers are equivalent, around 32–36 kcal mol^{-1}. Indeed, for complexes **1a** and **3a**, the second barrier is around 36–38 kcal mol^{-1} whereas the first one is lower than 30 kcal mol^{-1}. This is in harmony with the above experimental observations. Moreover, comparing the calcium complexes activities with those of their strontium analogues revealed that the calcium complexes lead to energetic parameters slightly lower than those calculated for the related strontium complexes.[24] Therefore, the calcium complexes are slightly more active than their strontium analogues. These conclusions are in good agreement with the experimental remarks.

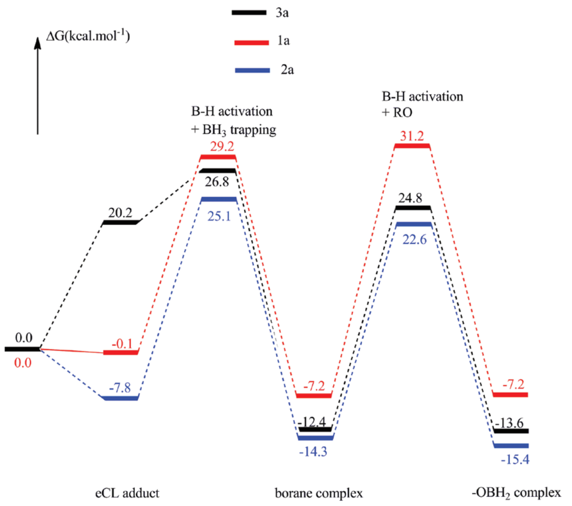


Fig. 2 Gibbs free energy profiles computed at room temperature for the initiation step of the ROP of ε-CL initiated by calcium borohydride complexes **1a**, **2a**, and **3a**. The energies are given in kcal mol^{-1}.

Summary

[Ca(BH$_4$)$_2$(THF)$_2$] (**1a**), which is also commercially available, was prepared following a new procedure from [Ca(OMe)$_2$] and BH$_3$·THF in THF. Reaction of **1a** with KCp* and K{(Me$_3$SiNPPh$_2$)$_2$CH} in a 1 : 1 ratio in THF resulted in the corresponding heteroleptic mono-borohydride derivatives [Cp*Ca(BH$_4$)(THF)$_n$]$_2$ (**2a**) and [{(Me$_3$SiNPPh$_2$)$_2$CH}Ca(BH$_4$)(THF)$_2$] (**3a**), respectively. Compounds **1a**, **2a**, and **3a** were together with the earlier reported compounds [Sr(BH$_4$)$_2$(THF)$_2$] (**1b**), [Cp*Sr(BH$_4$)(THF)$_2$]$_2$ (**2b**), and [{(Me$_3$SiNPPh$_2$)$_2$CH}Sr(BH$_4$)(THF)$_2$] (**3b**) used as initiators for the ROP of polar monomers.

The general performances of the complexes **1a**,**b**, **2a**,**b**, and **3a**,**b** in the ROP of ε-CL and LLA demonstrate relatively good control of the polymerization under the operating conditions described, in terms of both theoretical *vs.* experimental molar mass values agreement and of moderate dispersity data. Overall, significantly lower catalytic activity and control were observed with these alkaline earth metal complexes in comparison to the corresponding rare earth element catalysts. Although active, these calcium and strontium catalytic systems may exhibit a somewhat limited scope regarding the living ROP of larger monomer loadings, especially in the case of the larger strontium complexes. Interestingly, the calcium and strontium borohydride complexes afford α,ω-dihydroxytelechelic polymers, with the former being slightly more efficient than the latter ones, as further supported by DFT insights.

Experimental

General considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high vacuum (10^{-3} Torr) line, or in an argon-filled MBraun or Jacomex glovebox. Hydrocarbon solvents (*n*-pentane) were dried using an MBraun solvent purification system (SPS-800). Tetrahydrofuran was distilled under nitrogen from K benzophenone ketyl prior to use. All solvents were stored *in vacuo* over LiAlH$_4$ in a re-sealable flask. Deuterated tetrahydrofuran was obtained from Aldrich Inc.

(all 99 atom% D) and was degassed, dried, and stored *in vacuo* over Na/K alloy in a re-sealable flask. [$Ca(OMe)_2$],[50] [$Sr(BH_4)_2(THF)_2$] (**1b**),[39] [$Cp^*Sr(BH_4)(THF)_2$]$_2$ (**2b**),[24] [{$(Me_3SiNPPh_2)_2CH$}$Sr(BH_4)(THF)_2$] (**3b**),[24] KCp*,[66] and K{$(Me_3SiNPPh_2)_2CH$}[51] were prepared according to literature procedures.

NMR spectra were recorded on a Bruker Avance 400 MHz, Avance II NMR 300 MHz or Bruker AC-500 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and were reported relative to tetramethylsilane (^{1}H and ^{13}C NMR), 15% $BF_3{\cdot}Et_2O$ (^{11}B NMR), and 85% phosphoric acid (^{31}P NMR), respectively. IR spectra were obtained on an FTIR spectrometer Bruker Tensor 37. Mass spectra were recorded at 70 eV on a DFS Thermo Scientific. Elemental analyses were carried out with an Elementar vario Micro Cube.

Monomer conversions were determined from ^{1}H NMR spectra of the crude polymer sample, from the integration (Int.) ratio $\mathrm{Int.}_{PCL}/[\mathrm{Int.}_{PCL} + \mathrm{Int.}_{\varepsilon\text{-}CL}]$ or $\mathrm{Int.}_{PLLA}/[\mathrm{Int.}_{PLLA} + \mathrm{Int.}_{LLA}]$, using the $-CH_2OC(O)$ methylene triplet (δ_{PCL} 4.04 ppm, $\delta_{\varepsilon\text{-}CL}$ 4.19 ppm for) for ε-CL, or the methine hydrogen in $-OCHCH_3C(O)$ (δ_{LLA} 5.05 ppm, δ_{PLLA} 5.18 ppm) for LLA. The number of average molar mass (M_{nSEC}) and dispersity ($Đ_M = M_w/M_n$) values were determined by size exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore 300 × 7.5 mm columns. The recovered polymer samples were dissolved in THF (2 mg mL^{-1}) and filtered; only the soluble fraction was analyzed. All elution curves were calibrated with polystyrene standards. M_{nSEC} values of PCLs and PLLAs were calculated using the correcting factors previously reported (PCL: $M_{nSEC} = M_{nSEC}$ raw data × 0.56; PLLA: $M_{nSEC} = M_{nSEC}$ raw data × 0.58),[59,67,68] thus taking into account the difference in hydrodynamic radii of PCL and PLLA *vs.* polystyrene. SEC traces of the polymers all exhibited a unimodal and symmetrical peak. The molar masses of short-chain polymer samples were determined by ^{1}H NMR analysis in $CDCl_3$ from the relative intensities of the signals of the PCL or PLLA main-chain methylene protons for PCL ($-CH_2OC(O)$, δ 4.04 ppm) or methine protons for PLLA ($-CHCH_3C(O)$, δ 5.15 ppm), and those of the chain-end methylene protons ($-CH_2OH$, δ 3.65 ppm).

[$Ca(BH_4)_2(THF)_2$] (1a). To a suspension of [$Ca(OMe)_2$] (511 mg, 5.0 mmol) in 25 mL of THF was added 15 mL of 1.0 M $BH_3{\cdot}THF$ in THF (15.0 mmol). The mixture was heated to reflux for 3 h to obtain an almost clear solution. The solution was allowed to cool to ambient temperature and filtrated. The volatile components were evaporated in vacuum and the product was obtained as a colorless powder. Yield: 1.03 g (96%).

^{1}H NMR (d_8-THF, 300.13 MHz): δ 0.41 (q, br, 8 H, BH_4, $^1J_{H\text{-}B}$ = 82 Hz) ppm. ^{11}B NMR (d_8-THF, 96.29 MHz): δ −36.6 (qt, $^1J_{H\text{-}B}$ = 82 Hz) ppm.

[$Cp^*Ca(BH_4)(THF)_n$]$_2$ (2a). THF (15 mL) was condensed onto a mixture of [$Ca(BH_4)_2(THF)_2$] (290 mg, 1.1 mmol) and KCp* (193 mg, 1.1 mmol) at −78 °C. The colorless suspension was stirred for 18 h at ambient temperature. The mixture was filtrated and the solvent was evaporated in vacuum. The residue was washed with 15 mL of *n*-pentane and dried in vacuum to obtain a pale yellow solid. Yield: 188 mg (56%).

^{1}H NMR (d_8-THF, 300.13 MHz): δ 2.00 (s, 15 H, CH_3), −0.44 (q, 4 H, BH_4, $^1J_{H\text{-}B}$ = 83 Hz) ppm. ^{1}H{^{11}B} NMR (d_8-THF, 300.13 MHz): δ 2.00 (s, 15 H, CH_3), −0.44 (s, 4 H, BH_4) ppm. ^{11}B NMR (d_8-THF, 96.29 MHz): δ −36.0 (qt, $^1J_{H\text{-}B}$ = 83 Hz) ppm. ^{13}C{^{1}H} NMR (d_8-THF, 75.47 MHz): δ 111.4 (*C*-CH$_3$), 10.5 (C-*C*H$_3$) ppm. IR (ATR, cm^{-1}): 2962 (w), 2913 (w), 2870 (w), 2279 (m, B-H), 1627 (w), 1439 (m), 1378 (m), 1259 (s), 1226 (s), 1084 (vs), 1034 (vs), 956 (s), 914 (s), 779 (vs), 759 (m), 722 (m), 668 (m), 523 (s). EI-MS (70 eV, 170 °C): *m*/*z* (%) = 380 ([*M* − (4THF)]$^+$, <1), 365 ([*M* − (4THF, BH$_4$)]$^+$, <1), 310 ([Cp*$_2$Ca]$^+$, 1), 245 ([*M* − (4THF, Cp*)]$^+$, 1), 190 ([*M* − (4THF)/2]$^+$, 1), 175 ([Cp*Ca]$^+$, 3), 136 ([Cp*]$^+$, 95), 110 ([*M* − (4THF, 2Cp*)]$^+$, 29), 70 ([$Ca(BH_4)_2$]$^+$, 23), 55 ([$Ca(BH_4)$]$^+$, 60). $C_{18}H_{35}BO_2Ca$ (334.36): calc. C 64.66, H 10.55; found C 59.92, H 10.28 (despite several attempts, the carbon value of **2a** remains constantly low, maybe due to carbide formation).

[{$(Me_3SiNPPh_2)_2CH$}$Ca(BH_4)(THF)_2$] (3a). THF (10 mL) was condensed onto a mixture of [$Ca(BH_4)_2(THF)_2$] (107 mg, 0.5 mmol) and K{$(Me_3SiNPPh_2)_2CH$} (298 mg, 0.5 mmol) at −78 °C. The colorless suspension was stirred for 18 h at ambient temperature. The mixture was filtrated and the solvent was concentrated in vacuum to 2 mL and layered with 10 mL of *n*-pentane to obtain colorless single crystals suitable for X-ray analysis. Yield: 170 mg (45%).

^{1}H NMR (d_8-THF, 300.13 MHz): δ 7.58–7.52 (m, 8 H, *m*-P*Ph*), 7.26–7.13 (m, 12 H, *o*-, *p*-P*Ph*), 1.85 (br, 1 H, P-C*H*-P), 0.10 (q, br, 4 H, BH_4, $^1J_{H\text{-}B}$ = 82.2 Hz), 0.13 (s, 18 H, SiCH_3) ppm. ^{11}B NMR (d_8-THF, 96.29 MHz): δ −34.8 (qt, $^1J_{H\text{-}B}$ = 83 Hz) ppm. ^{13}C{^{1}H} NMR (d_8-THF, 75.47 MHz): δ 140.7 (dd, $^1J_{C\text{-}P}$ = 91.0 Hz, $^3J_{C\text{-}P}$ = 4.2 Hz, i-P*Ph*), 132.3 (t, $^3J_{C\text{-}P}$ = 5.2 Hz, *m*-P*Ph*), 130.5 (t, $^4J_{C\text{-}P}$ = 1.2 Hz, *p*-P*Ph*), 128.5 (t, $^2J_{C\text{-}P}$ = 5.8 Hz, *o*-P*Ph*), 23.3 (t, $^1J_{C\text{-}P}$ = 107.1 Hz, P-*C*H-P), 5.5 (t, $^3J_{C\text{-}P}$ = 1.9 Hz, Si*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (d_8-THF, 121.49 MHz): δ 16.4 ppm. IR (ATR, cm^{-1}): 3054 (w), 2948 (w), 2886 (w), 2218 (m), 1976 (m), 1590 (w), 1483 (w), 1435 (m), 1269 (s), 1239 (s), 1166 (w), 1102 (m), 1069 (s), 1037 (w), 999 (w), 954 (w), 827 (vs), 802 (s), 777 (s), 739 (s), 708 (vs), 694 (vs), 653 (s), 634 (s), 605 (m), 587 (m), 555 (m), 532 (m). EI-MS (70 eV, 190 °C): *m*/*z* (%) = 613 ([*M*]$^+$ − (2THF), 1), 598 ([*M*]$^+$ − (2THF,BH$_4$), 6), 558 ([CH(PPh$_2$NSiMe$_3$)$_2$]$^+$, 39), 543 ([CH(PPh$_2$NSiMe$_3$)$_2$ − Me]$^+$, 100), 471 ([CH(PPh$_2$)(PPh$_2$NSiMe$_3$)]$^+$, 16), 455 ([CH(PPh$_2$)(PPh$_2$NSiMe$_2$)]$^+$, 21). $C_{39}H_{59}BN_2O_2P_2Si_2Ca$ (756.91): calc. C 61.89, H 7.86, N 3.70; found C 61.22, H 7.92, N 3.69.

Details of the X-ray diffraction measurement, structure solution and refinement

General. Data were collected on a diffractometer equipped with a STOE imaging plate detector system IPDS2 using MoKα radiation with graphite monochromatization (λ = 0.71073 Å) at 153 K. The structure solution was performed by direct methods, full-matrix-least squares refinement against F^2 using SHELXS-97 and SHELXL-97 software.[69]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the

Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 915058.

Crystal data for **3a:** $C_{39}H_{59}BN_2O_2Si_2P_2Ca$, M = 756.89, triclinic, a = 10.107(2) Å, b = 11.994(2) Å, c = 18.948(4) Å, α = 79.98(3)°, β = 89.67(3)°, γ = 70.24(3)°, V = 2125.2(7) Å^3, T = 153.15 K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 0.313 mm^{-1}, 19 390 reflections measured, 10 943 independent reflections (R_{int} = 0.1290). The final R_1 value was 0.0769 ($I > 2\sigma(I)$). The final w$R(F^2)$ value was 0.1963 (all data). The goodness of fit on F^2 was 0.860.

Typical polymerization experiment

In a typical experiment (Table 1, entry 5), compound **2a** (10 mg, 15 μmol, 1 equiv.) was dissolved in dry THF and then ε-CL (341 mg, 2.99 mmol, 200 equiv.) was added to produce an initial monomer concentration of 1.0 M. The mixture was then stirred at the desired temperature over the appropriate reaction time (reaction times were not systematically optimized). The polymerization was quenched with excess acetic acid (*ca.* 0.1 mL of a 1.6 mM solution in toluene). The resulting mixture was concentrated to dryness under vacuum and the conversion was determined from ^{1}H NMR analysis of the residue in $CDCl_3$. The crude polymer was then dissolved in CH_2Cl_2 (2 mL) and precipitated in cold pentane (10 mL), filtered and dried under vacuum. The final polymer was then analyzed by NMR and SEC (Tables 1 and 2).

Computational details

Calculations were carried out at the DFT level using the hybrid functional B3PW91[70,71] with the Gaussian 03[72] suite of programs. Calcium, phosphorus and silicon were represented by a relativistic effective-core potential (RECP)[73,74] from the Stuttgart group and their corresponding optimized basis set. Polarized all-electron double-ζ 6-31G(d,p)[75] basis sets were used for B, C, H, O and N. Geometry optimizations were carried out without any symmetry restrictions. The nature of the extrema (minimum or transition state) was verified with analytical frequency calculations.

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