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A well-defined iron(II) alkoxide initiator for the controlled polymerisation of lactide

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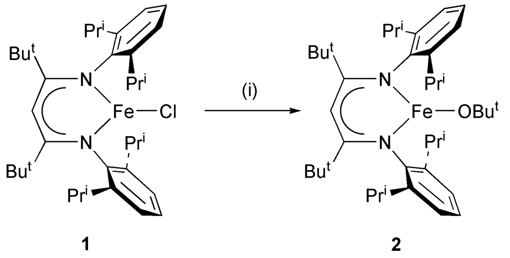
The three-coordinate iron(II) complex, (Bu^t-BDI)FeOBu^t [Bu^t-BDI = HC(C(Bu^t)N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$] is found to be a highly active initiator for the polymerisation of lactide and caprolactone at room temperature.

There is currently much interest in the development of well-defined initiators for the controlled ring-opening polymerisation (ROP) of cyclic esters due to their use in the tailored synthesis of biodegradable amd bioresorbable materials. While β-diketimate complexes[1] based on zinc,[2] magnesium[3] and tin[4] have been shown to afford living systems for the ROP of lactide, there is considerable interest in the development of iron based initiators due to their attractively low bio-toxicity. A recent report[5] described the use of iron(III) initiators for lactide and caprolactone polymerisation, including binuclear Fe$_2$(OCHPh$_2$)$_6$ and monomeric L$_2$FeOR (R = Et, CHPh$_2$; L = *N*,*N′*-bis(trimethylsilyl)benzamidinate). To our knowledge, there have been no reports to date on divalent iron initiator systems. We were attracted to a report by Holland and co-workers[6] of a remarkably robust three-coordinate iron(II) chloride complex stabilised by Bu^t-BDI (**1**, Scheme 1) which we envisaged could act as a potentially suitable precursor to a well-defined iron(II) initiator.[6] Here, we describe the synthesis of the novel three-coordinate alkoxide derivative **2** (Scheme 1) and its use to polymerise lactide with high efficiency and in a controlled manner.



Scheme 1 Reagents and conditions: (i) NaOBu^t, Et$_2$O, rt, 12 h, extraction into toluene, recrystallisation from Et$_2$O, 80% yield.

Reaction of equimolar quantities of (Bu^t-BDI)FeCl and NaOBu^t in diethyl ether at room temperature, followed by extraction with toluene, gives an orange solid in good yield. MS(CI) and elemental analyses are consistent with its formulation as a mono-alkoxide species, and a solution magnetic moment of 4.8 μ_B confirms the presence of high-spin d^6 iron(II) centres. The ^{1}H NMR spectrum of **2**† in C$_6$D$_6$ reveals eight broadened paramagnetic contact-shifted resonances. Crystals suitable for X-ray diffraction‡ were obtained by recrystallisation from diethyl ether at −10 °C. The structure (Fig. 1) is closely related to that of its chloro analogue,[6] but the preference for the oxygen atom of the *tert*-butoxide group in **2** to adopt a bent geometry precludes the presence of the crystallographic mirror plane that was observed in the chloro species. This bend [Fe–O(36)–C(37) 150.3(3)°], combined with the steric bulk of the *tert*-butyl moiety and the cavity formed by the two 2,6-diisopropylphenyl arms, causes the oxygen atom to be sited away from the exterior bisector of the N–Fe–N angle, the two N–Fe–O angles differing by *ca.* 23°. In the chloro analogue,[6] the two N–Fe–Cl angles are identical [131.83(5)°], a consequence of the mirror symmetry. The positioning of this oxygen atom closer to N(3) is reflected in the Fe–N bond distances, with that to N(3) being noticeably longer [at 1.993(3) Å] than that to N(1) [1.965(3) Å]. The geometry at iron is distorted trigonal planar, the iron atom lying 0.05 Å out of the N$_2$O plane. The six-membered chelate ring is coplanar to within 0.02 Å, but the *tert*-butoxide group is bent slightly out of this plane, the oxygen atom lying 0.13 Å out of plane. The Fe–O and C=N bond lengths are unexceptional. The electronic properties of planar three-coordinate iron(II) complexes have recently been described.[7]

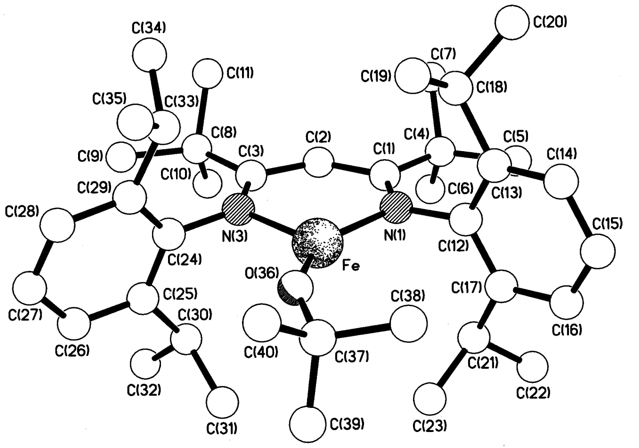


Fig. 1 The molecular structure of **2**. Selected bond lengths (Å) and angles (°): Fe–N(1) 1.965(3), Fe–N(3) 1.993(3), Fe–O(36) 1.786(3), N(1)–C(1) 1.340(5), N(3)–C(3) 1.330(5); N(1)–Fe–N(3) 95.79(13), N(1)–Fe–O(36) 143.8(2), N(3)–Fe–O(36) 120.2(2), Fe–O(36)–C(37) 150.3(3).

2 has been investigated as an initiator for the polymerisation of the cyclic esters *rac*-lactide (LA) and ε-caprolactone (CL). It is found to be highly active for both monomers at room temperature. Polymerisation of 100 equivalents of *rac*-LA in toluene gives 94% conversion within 20 min.§ The resultant PLA has a polydispersity (PDI) of 1.12 and M_n 37500 Da (based on polystyrene standards). NMR analyses (^{1}H homodecoupled and ^{13}C{^{1}H} experiments) show that atactic PLA is formed.

The linear relationship between the number average molecular weight (M_n) and [M]$_o$/[I]$_o$ (Fig. 2), and M_n *versus* conversion (Fig. 3) for the polymerisation of *rac*-LA are indicative of a well-controlled polymerisation. The slightly broadened PDI's evident in Fig. 2, where conversions are typically >95%, are attributable to transesterification side reactions (evident by ^{13}C NMR) which become more prevalent as the monomer concentration falls.

The activity of this iron(II) system for lactide polymerisation is comparable to its zinc(II) relative, and occupies a position

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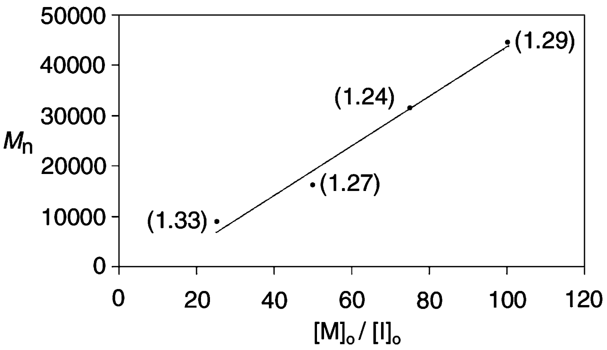

Fig. 2 Plot of M_n (determined by GPC) *versus* the number of equivalents of LA; rt, toluene.

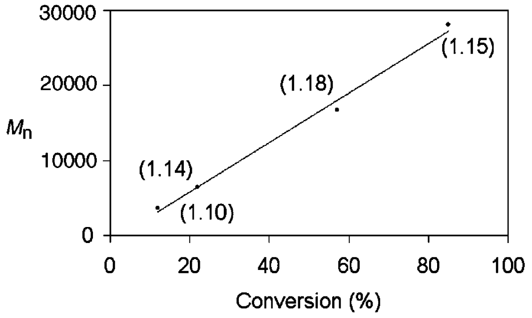

Fig. 3 Relationship between M_n (determined by GPC) and monomer conversion (determined by ^{1}H NMR); LA : **2** = 100 : 1, rt, toluene.

amongst the most active systems for controlled lactide polymerisation. For divalent centres stabilised by β-diketiminate ligands, activities follow the trend Mg > Zn ≈ Fe > Sn and correlate reasonably well with the electrophilicities of the metal centres,¶ although the Sn derivative is undoubtedly also strongly influenced by the presence of its stereochemically active lone pair of electrons.

2 is also highly active, though less controlled, for the ring-opening polymerisation of ε-caprolactone. The polymerization of 100 equivalents of ε-CL in toluene yielded 95% conversion within 5 min, affording polycaprolactone with M_n = 86,200 Da and PDI = 1.38.

In summary, (Bu^t-BDI)Fe(OBu^t) is amongst the most active initiators for the ROP of cyclic ester monomers such as *rac*-LA and CL. For *rac*-LA, the system is well controlled though transesterification side reactions become competitive at low monomer concentrations.

Notes and references

† Selected spectroscopic data for **2**: δ_H (250 MHz, C_6D_6, 25 °C): 44.0, 8.5, 3.2, 1.3, −0.5, −13.7, −32.1, −98.0, μ_{eff}(Evans) = 4.8 μ_B. Anal.Calcd for $FeN_2OC_{39}H_{62}$: C, 74.26; H, 9.91; N, 4.44. Found: C, 74.34; H, 10.01; N, 4.38%. MS (CI): m/z = 631 (M + H).

‡ Crystal data for **2**: $C_{39}H_{62}N_2OFe$, M = 630.8, monoclinic, $P2_1/n$ (no. 14), a = 9.783(1), b = 17.927(2), c = 21.781(2) Å, β = 96.91(1)°, V = 3792.2(5) Å^3, Z = 4, D_c = 1.105 g cm^{-3}, μ(Cu-Kα) = 3.40 mm^{-1}, T = 203 K, orange plates; 5553 independent measured reflections, F^2 refinement, R_1 = 0.056, wR_2 = 0.119, 3501 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 407 parameters. One of the isopropyl groups was found to be disordered, and two 50% occupancy orientations were identified. CCDC reference number 191757. See http://www.rsc.org/suppdata/dt/b2/b209703f/ for crystallographic data in CIF or other electronic format.

§ Typical polymerisation procedure: polymerisation reactions were performed under a nitrogen atmosphere. The initiator was added to the monomer in toluene. After stirring at rt for a period of time, the solvent was evaporated under reduced pressure to give the polymer, which was analysed by NMR. Conversions were calculated by integration of the CH signals of LA relative to those of PLA and by integration of the CH_2 signals of ε-CL relative to those of PCL. GPC analyses were performed in chloroform using a Gynkotek 300 HPLC pump connected to two 5 micron mixed bed columns (Polymer Laboratories) and a Knauer differential refractometer. Columns were calibrated using polystyrene standards (10^3–10^6 Da) and the chromatograms were analysed using Viscotek Trisec software (conventional calibration).

¶ Zn and Fe have similar electronegativities on the Allred–Rochow scale: 1.66 and 1.64, respectively. Mg = 1.23, Sn = 1.72.[8]

1 For a review of metal β-diketiminate complexes, see: L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.
2 M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583.
3 M. H. Chisholm, J. C. Huffman and K. Phomphrai, *J. Chem. Soc., Dalton Trans.*, 2001, 222.
4 A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2001, 283.
5 B. J. O'Keefe, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 4384.
6 J. M. Smith, R. J. Lachicotte and P. L. Holland, *Chem. Commun.*, 2001, 1542.
7 H. Andres, E. L. Bominaar, J. M. Smith, N. A. Eckert, P. L. Holland and E. Munck, *J. Am. Chem. Soc.*, 2002, **124**, 3012–3025.
8 (*a*) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, 1958, **5**, 264; (*b*) E. J. Little and M. M. Jones, *J. Chem. Educ.*, 1960, **37**, 231.