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A well-defined magnesium enolate initiator for the living and highly syndioselective polymerisation of methylmethacrylate†

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The reaction of (BDI)Mg^{i}Pr [BDI = HC(C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$] with 2′,4′,6′-trimethylacetophenone in toluene affords the enolate complex [(BDI)Mg(μ-OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$)]$_2$ which is found to be an excellent initiator for the living, syndioselective (σ_r > 0.95) polymerisation of methyl methacrylate.

Poly(methylmethacrylate), PMMA, is a commodity polymer which forms the basis of the Perspex® or Plexiglass® families of materials. These have a wide range of applications many of which exploit the high optical clarity of PMMA. The softening temperature (T_g) is technologically one of the most important properties of PMMA and this is strongly influenced by the tacticity of the polymer, *i.e.* the placements of the ester and methyl groups along the polymer backbone. For example, free radical-generated PMMA is biased towards the syndiotactic form (*rr* ~ 67%) affording a T_g of *ca.* 105 °C. However, as the syndiotacticity is increased, the T_g also rises (to *ca.* 135 °C for *rr* > 90%), and this holds clear advantages for applications where PMMA materials are exposed to higher temperature environments.

The synthesis of highly syndiotactic PMMA, at temperatures convenient for its industrial production, has to date proved elusive, and remains an important technological objective. Although a small number of syndiospecific initiator systems have been described,[1] they invariably require very low reaction temperatures and therefore are not commercially attractive. Most of these systems are based on relatively ill-defined organometallic derivatives of Li, Mg and Al where insight into the origin of the stereoselectivity is complicated by issues such as aggregation and ligand exchange. Moreover, control over the polymerisation is often compromised by intramolecular back-biting processes.[2] Some single-site, living systems capable of giving highly syndiotactic PMMA have been reported, most notably based on rare earth metallocenes,[1e] but these too only deliver high levels of syndiotacticity at extremely low temperatures.

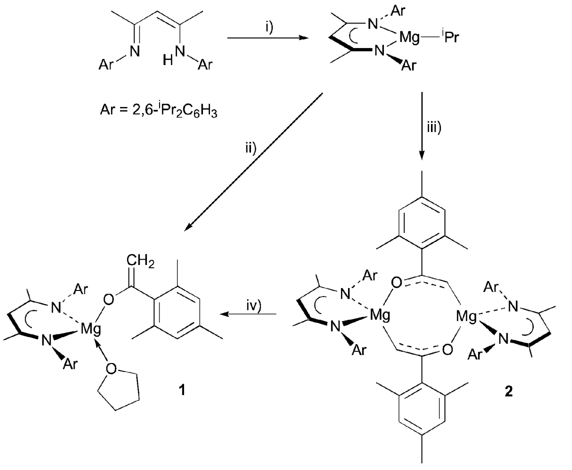
Recently we described some low-coordinate alkyl complexes of magnesium stabilised by sterically hindered β-diketiminate ligands[3] and became interested in exploring their potential for the controlled polymerisation of MMA. Here, we report the synthesis of a well-defined β-diketiminate magnesium enolate initiator, and its use for the living, highly syndioselective polymerisation of MMA under relatively mild conditions.

The coordination polymerisation of MMA is widely believed to proceed *via* an oxygen-bound metal enolate.[1e,4] Magnesium enolates are most commonly prepared *via* nucleophilic attack of an amide at the carbonyl atom of a ketone.[5] However, precedent exists for magnesium alkyl-mediated deprotonation,[6] although attack of the metal alkyl at the carbonyl carbon atom must be suppressed. We therefore selected to study the moderately acidic 2′,4′,6′-trimethylacetophenone, anticipating the mesityl group to be large enough to inhibit alkoxide formation.[7]

Addition of 2′,4′,6′-trimethylacetophenone to a thf suspension of (BDI)Mg^{i}Pr resulted in the isolation of (BDI)Mg(OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$)(thf),‡ **1** according to Scheme 1. DEPT ^{13}C NMR experiments confirm the presence of a non-metallated olefinic methylene group (δ 84.97), and finely-coupled ^{1}H NMR methylenic resonances at δ 3.58 and 2.98 ($^2J_{HH}$ 1.4 Hz) compare favourably with data for a structurally characterised oxygen-bound titanocene enolate.[7b] Performing the reaction in toluene affords the solvent-free, enolate-bridged binuclear species, **2**. The ^{1}H NMR resonances of **2** are broad in benzene-d$_6$, although in thf-d$_8$ **2** converts cleanly into the monomeric base adduct **1**.

X-Ray analysis§ of crystals of **2** (grown from heptane) revealed the structure shown in Fig. 1. The complex has a central eight-membered MgOCCMgOCC ring, the like of which has not previously been structurally characterised.¶ This eight-membered ring adopts a ‘boat-like’ conformation with C(30)/O(30)/C(30′)/O(30′) coplanar to within 0.03 Å and the two metal atoms 0.45 [Mg′] and 0.57 Å [Mg] ‘above’ this plane. The geometry at each Mg centre is distorted tetrahedral with angles in the range 91.5(1)–124.4(1)° and the two Mg–C bonds are both long [Mg–C(31′) 2.318(3), Mg′–C(31) 2.317(3) Å]. Combined with the intra-ring C–O and C–C bond lengths of *ca.* 1.29 and 1.37 Å, respectively, these lengths indicate a degree of delocalisation across the O–C–C unit but with a distinct bias towards an oxygen-metallated enolate. Related oxo-allyl bridged binuclear complexes of zinc and palladium have been reported previously, but neither shows the core bond order observed for **2**. As would be expected for a late transition metal, the palladium cation [{(PPh$_3$)$_2$Pd}$_2$(μ-CH$_2$COPh)$_2$]$^{2+}$ contains carbon-metallated bonds,[8] whereas Boersma concluded that in [(BrZn(μ-CH$_2$COO^{t}Bu)·THF)$_2$] the enolate cannot realistically be described as either C- or O-metallated.[9]

Addition of MMA to toluene or chloroform solutions of **2** at −30 °C leads to rapid polymerisation. Using 400 equivalents of monomer, for example, > 95% conversion is attained within 10 min. The resultant PMMA exhibits narrow molecular weight distributions (≈ 1.1) and measured molecular weights are in



Scheme 1 *Reagents and conditions*: (i) ^{n}BuLi, toluene, −78 °C; ^{i}PrMgCl; (ii) 2,4,6-Me$_3$C$_6$H$_2$C(=O)CH$_3$, thf; (iii) 2,4,6-Me$_3$C$_6$H$_2$C(=O)CH$_3$, toluene; (iv) thf.

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† Electronic supplementary information (ESI) available: synthetic and polymerisation details. See http://www.rsc.org/suppdata/cc/b2/b201896a/

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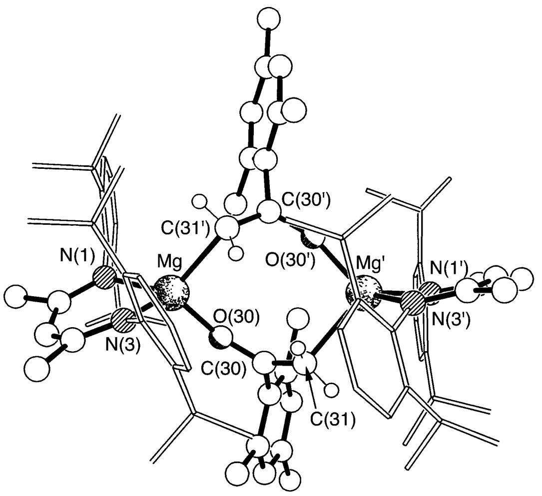

Fig. 1 The molecular structure of **2**. Selected bond lengths (Å) and angles (°); Mg–O(30) 1.908(2), Mg′–O(30′) 1.921(2), Mg–C(31′) 2.318(3), Mg′–C(31) 2.317(3), Mg–N(1) 2.067(2), Mg′–N(1′) 2.082(2), Mg–N(3) 2.085(2), Mg′–N(3′) 2.085(2), O(30)–C(30) 1.294(3), O(30′)–C(30′) 1.287(3), C(30)–C(31) 1.366(4), C(30′)–C(31′) 1.373(4); N(1)–Mg–N(3) 92.78(8), N(1′)–Mg′–N(3′) 91.52(8), O(30)–Mg–C(31′) 101.39(9), O(30′)–Mg′–C(31) 98.67(9), Mg–O(30)–C(30) 153.5(2), Mg′–O(30′)–C(30′) 157.3, O(30)–C(30)–C(31) 124.6(2), O(30′)–C(30′)–C(31′) 124.8(2), C(30)–C(31)–Mg′ 120.4(2), C(30′)–C(31′)–Mg 118.6(2).

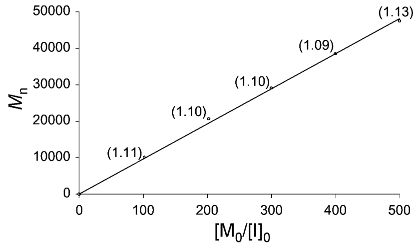

Fig. 2 A graph of M_n (determined by GPC, *vs.* PMMA standards) *vs.* the number of equivalents MMA (−30 °C; $CDCl_3$).

good agreement with theoretical values calculated from the molar ratio of monomer:initiator (Fig. 2). Analysis of the product by ^1H NMR spectroscopy shows that the polymer is highly syndiotactic with an *rr*:*rm*:*mm* triad ratio of 92:8:0 (σ_r = 0.96). In accord with the high degree of syndiotacticity, the material was found to display a T_g of 135 °C (by thermal mechanical analysis).

A further demonstration of the living nature of the polymerisation is the linear relationship between monomer conversion and number average molecular weight (Fig. 3). Throughout the reaction polydispersities are consistently low and the syndiotactic content of the polymers remains in the range 91–93% *rr*. The ability of the BDI ligand to afford high levels of tacticity control by a chain-end control mechanism is noteworthy: similarly impressive control has been seen using analogous zinc complexes in lactide polymerisation.[10]‖

In conclusion, to our knowledge, complex **2** represents the first example of a well-defined magnesium initiator for the living, highly syndioselective polymerisation of MMA under relatively mild reaction conditions. The effect of varying the ancillary ligand substituents upon operating temperature and syndiotacticity will be reported in due course.

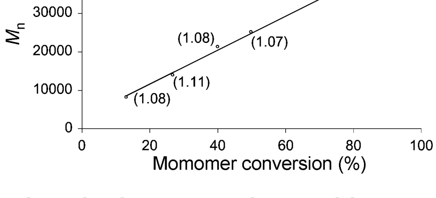

Fig. 3 The relationship between M_n (determined by GPC, *vs.* PMMA standards) and monomer conversion (determined by ^1H NMR); MMA:**2** = 400:1; −30 °C; $CDCl_3$.

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Notes and references

‡ *Selected spectroscopic data* for **1**: δ_H(250 MHz, thf-d_8, 25 °C) 1.12 (d, 12H, $^3J_{HH}$ 6.9 Hz, CH*Me*$_2$), 1.17 (d, 12H, $^3J_{HH}$ 6.9 Hz, CH*Me*$_2$), 1.66 (s, br, 6H, HC{C(*Me*)NAr}$_2$), 1.71 (s, br, 6H, mesityl *o*-Me), 2.06 (s, br, 3H, mesityl *p*-Me), 2.98 (d, 1H, $^2J_{HH}$ 1.4 Hz, OC(Ar′)=C*H*H′), 3.13 (sept, 4H, $^3J_{HH}$ 6.9 Hz, C*H*Me$_2$), 3.42 (d, 1H, $^2J_{HH}$ 1.4 Hz, OC(Ar′)=CH*H*′), 4.89 (s, 1H, *H*C{C(Me)NAr}$_2$), 6.42 (s, 2H, mesityl *m*-H), 7.10 (m, 6H, HC{C(Me-)NAr}$_2$ *m*-, *p*-H); δ_C(62.9 MHz, thf-d_8, 25 °C) 21.72 (mesityl *o*-Me), 22.94 (mesityl *p*-Me), 26.24 (HC{C(*Me*)NAr}$_2$), 26.39 (NAr CH*Me*Me′), 27.31 (NAr CHMe*Me*′), 30.61 (NAr *C*HMe$_2$), 84.97 (OC(=*C*H$_2$)), 96.88 (H*C*{C(Me)NAr}$_2$), 126.05 (NAr C_m), 127.51 (NAr C_p), 129.51 (mesityl C_m), 136.00 (mesityl C_p), 137.70 (mesityl C_o), 144.91 (NAr C_o), 145.56 (mesityl C_{ipso}), 147.74 (NAr C_{ipso}), 165.83 (O*C*(=CH$_2$)), 171.78 (HC{*C*(Me)NAr}$_2$). For **2**: δ_H(250 MHz, C_6D_6, 25 °C) 1.11 (d, br, 24H, $^3J_{HH}$ 6.8 Hz, CH*Me*$_2$), 1.57 (s, br, 6H, HC{C(*Me*)NAr}$_2$), 1.99 (s, br, 6H, mesityl *o*-Me), 2.14 (s, br, 3H, mesityl *p*-Me), 3.07 (m, br, 4H, C*H*Me$_2$), 3.72 (s, br, 1H, OC(Ar′)=CH*H*), 4.10 (s, br, 1H, OC(Ar′)=C*H*H), 4.84 (s, 1H, *H*C{C(Me)NAr}$_2$), 6.60 (s, br, 2H, mesityl *m*-H), 7.00–7.13 (m, 6H, HC{C(Me)NAr}$_2$ *m*-, *p*-H). Anal. Calc. (found) for $C_{80}H_{108}N_4O_2Mg_2$: C, 79.65 (79.63); H, 9.02 (8.84); N, 4.64 (4.55)%.

§ *Crystal data* for **2**: $C_{80}H_{108}N_4O_2Mg_2\cdot C_7H_{16}$, M = 1306.5, monoclinic, $P2_1/c$ (no. 14), a = 20.803(2), b = 15.497(1), c = 26.768(1) Å, β = 111.48(1)°, V = 8030.2(9) Å^3, Z = 4, D_c = 1.081 g cm^{-3}, μ(Cu-Kα) = 0.62 mm^{-1}, T = 183 K, colourless prisms; 11880 independent measured reflections, F^2 refinement, R_1 = 0.060, wR_2 = 0.151, 9227 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$], 901 parameters. CCDC reference number 182915. See http://www.rsc.org/suppdata/cc/b2/b201896a/ for crystallographic data in CIF or other electronic format.

¶ A search of the October 2001 release of the CCDC found no examples of a comparable eight-membered di-magnesium ring system.

‖ The analogous magnesium system, while highly active for lactide polymerisation, also gives rise to trans-esterification side reactions.[11]

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