Nacnac^{Bn}MgO*t*Bu: a diketiminate-based catalyst for the polymerisation of *rac*-lactide with slight isotactic preference

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Polymerisation results

Lactide polymerisations with 4 in CH_2Cl_2.

Temperature	[**4**]	[lactide]	ratio	P_m	M_w	M_n	M_w/M_n	P_n [a]
23 °C	1.60 mM	480 mM	1 : 300	0.48				
0 °C	1.96 mM	588 mM	1 : 300	0.49	162619	100551	1.62	700
0 °C	1.96 mM	588 mM	1 : 300	0.48	163013	97020	1.68	670
0 °C	1.99 mM	199 mM	1 : 100	0.49				
0 °C [b]	1.96 mM	588 mM	1 : 300		55023 [b]	44030 [b]	1.25 [b]	300 [b]
–17 °C	2.0 mM	400 mM	1 : 200	0.52				
–17 °C	2.0 mM	600 mM	1 : 300	0.52	196252	109273	1.80	760
–17 °C	1.97 mM	591 mM	1 : 300	0.52				
–17 °C	1.96 mM	980 mM	1 : 500	0.52				
–26 °C	1.93 mM	97 mM	1 : 50	0.54				
–26 °C	1.96 mM	196 mM	1 : 100	0.55				
–26 °C	1.97 mM	394 mM	1 : 200	0.54	161026	95197	1.69	660
–26 °C	1.94 mM	388 mM	1 : 200	0.55				
–26 °C	1.97 mM	394 mM	1 : 200	0.54				

Reaction times were chosen conservatively to assure complete monomer conversion: 0 °C: 2 h, –17 °C: 4 h, –26 °C: 6 – 8 h. [a] Polymerisation degree, i. e. number of monomer units per polymer chain (determined from M_n). [b] 1 equiv benzyl alcohol added.

Polymerisation kinetics

Polymerisation kinetics have not been investigated in detail. Preliminary investigations by following by NMR the reaction of 20 or 200 equiv *rac*-lactide with **4** in CD_2Cl_2 at ambient temperature indicated that, unlike the analogous *nacnac*^{Bn}ZnO*i*Pr complex,[1] polymerisations with **4** did not follow first-order kinetics (Fig. S1), most likely due to slow initiation. The latter was confirmed by the slow decay in the concentration of **4** (Fig. S2): 40% of the initial concentration was still observed after all monomer was consumed. No signals of the propagating species *nacnac*^{Bn}Mg{OC(H)(Me)C(O)}$_n$O*t*Bu could be assigned. The slow increase of the apparent first-order rate constant, indicated by the negative curvature of ln(c/c^0) in Fig. S1, would be in agreement with a slight increase in active catalytic species. Indeed, a plot of apparent first-order rate constants determined as tangents at 10, 20 and 30 min correlate with the estimated concentration of active species (Fig. S3).

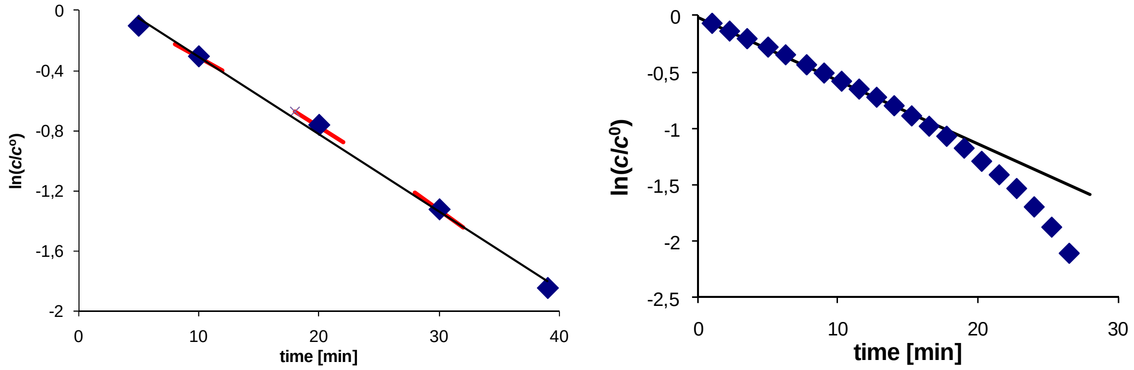

Fig. S1. Logarithmic plot of relative *rac*-lactide concentration versus time. Left: [lactide]/[Mg] = 20; [Mg] = 3 mM. Red line segments indicate tangents at the respective data points. Right: [lactide]/[Mg] = 200; [Mg] = 2 mM

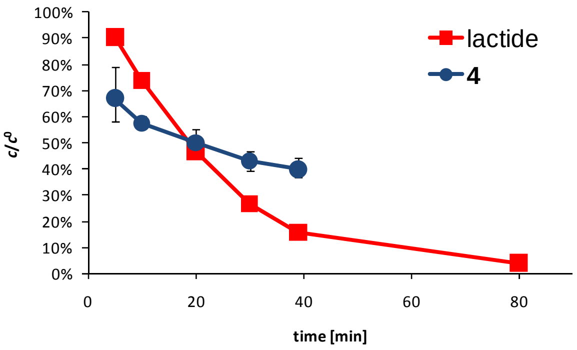

Fig. S2. Decrease of the concentration of **4** (blue circles) and *rac*-lactide (red squares) with time ([lactide]/[Mg] = 20; [Mg] = 3 mM).

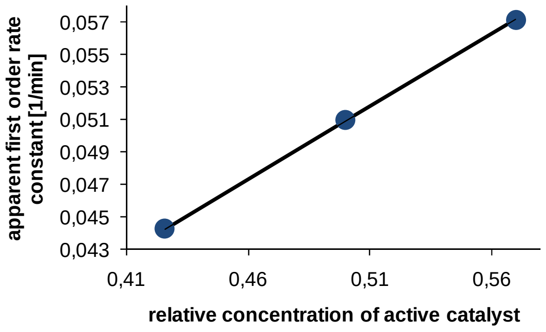

Fig. S3. Correlation between the apparent first-order rate constants at 10, 20 and 30 min (red line segments in Fig. S1, left) and the relative concentration of active catalytic species, estimated from the concentration of unreacted **4** (Fig. S2).

Time dependence of P_m

A major concern with respect to the small value of the isotactic preference was the accuracy of these values, in particular since we noticed before that unselective transesterification led to an apparent increase of P_m with time due to the formation of *rr*-triads.[1] Polymerisations with **4**, however, did not display any time dependence of P_m. Furthermore, determination of P_m from ^{13}C data yielded the same values within the margin of errors. In general, P_m values of polymers prepared at the same temperature, determined after isolation of the polymer, varied by ±0.01. Differences between P_m values determined from ^{1}H and ^{13}C data also were below 0.01. P_m values of untreated reaction samples taken during the reaction showed slightly higher variations, which however did not exceed ±0.01. Fig. S4 shows this at the example of two polymerisations at –17 °C, of which samples have been taken throughout the polymerisation.

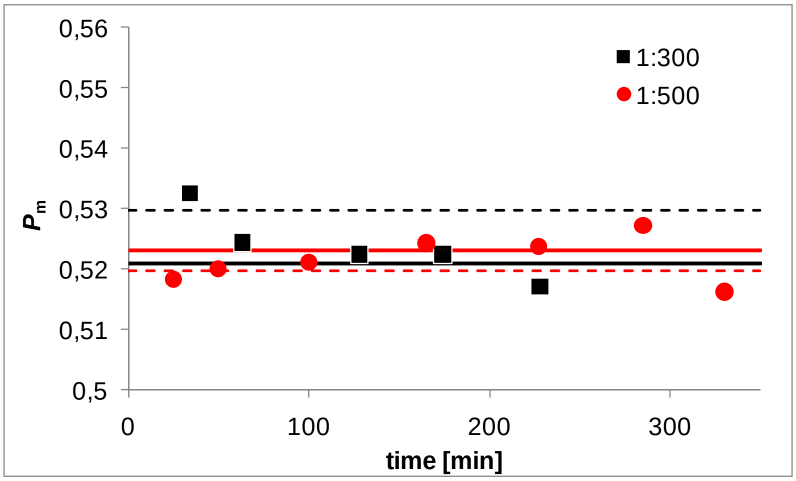

Fig. S4. Variation of P_m with time in two polymerisations at –17 °C and [Mg] to [lactide] ratios of 1:300 and 1:500. Solid lines indicate the P_m values obtained for the isolated polymer by ^{1}H NMR after 4 h of reaction time, dashed lines correspond to values determined by ^{13}C NMR for the same polymer.

1. F. Drouin, P. O. Oguadinma, T. J. J. Whitehorne, R. E. Prud'homme and F. Schaper, *Organometallics*, 2010, **29**, 2139–2147.