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Catalytic Behaviour in the Ring-Opening Polymerisation of Organoaluminium Supported by Bulky Heteroscorpionate Ligands


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A series of alkyl organoaluminium complexes based on bulky heteroscorpionate ligands were designed as catalysts for the ring-opening polymerisation of cyclic esters. Thus, treatment of AlX₃ (X = Me, Et) with bulky acetamide or thioacetamide heteroscorpionate ligands nbptamH (1), [nbptamH = N-naphthyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide], fbpamH (2) [fbpamH = N-fluorenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide], ptbptamH (3) [ptbptamH = N-phenyl-2,2-bis(3,5-di-tert-butyl)pyrazol-1-yl)thioacetamide], nbtptamH (4) [nbtptamH = N-naphthyl-2,2-bis(3,5-di-tert-butyl)pyrazol-1-yl)thioacetamide], ptbptamH (5) [ptbptamH = N-phenyl-2,2-bis(3,5-di-tert-butyl)pyrazol-1-yl)acetamide] and (S)-mtbpamH (6) [(S)-mtbpamH = (S)-(−)-N-(α-keto(pyrazol-1-yl)methane system and incorporating several pendant donor arms bearing an anionic functional donor group to prepare metal-based initiators for the ROP of cyclic esters.

In this context, to the best of our knowledge very few alkyl complexes without a cocatalyst are redox-inactive in nature. In fact, these entities already play a key role in catalysis for the transformation of small organic molecules, as co-catalysts in the polymerisation of olefins, and for the synthesis of cyclic carbonates. A good initiator for the ROP of cyclic esters requires a redox-inactive metal, an inert inorganic template LnM, and a polar metal-ligand bond that can undergo an insertion reaction with C–X multiple bonds. Taking all these considerations into account, we have contributed widely to this field in recent years by designing new heteroscorpionate ligands related to the bis(pyrazol-1-yl)methane system and incorporating several pendant donor arms bearing an anionic functional donor group to prepare metal-based initiators for the ROP of cyclic esters.

Some years ago, we focused on the design of alkyl organoaluminium entities based on acetamidate and organic molecules, as co-catalysts in the polymerisation of olefins, and for the synthesis of cyclic carbonates. A good initiator for the ROP of cyclic esters requires a redox-inactive metal, an inert inorganic template LnM, and a polar metal-ligand bond that can undergo an insertion reaction with C–X multiple bonds. Taking all these considerations into account, we have contributed widely to this field in recent years by designing new heteroscorpionate ligands related to the bis(pyrazol-1-yl)methane system and incorporating several pendant donor arms bearing an anionic functional donor group to prepare metal-based initiators for the ROP of cyclic esters.

In a previous study we carried out the facile synthesis and full characterisation of several organoaluminium entities based on acetamidate and...
thioacetamidate ancillary ligands in \(\kappa^2\)NO and \(\kappa^2\)NN coordination modes, respectively. \(\varepsilon\)-CL and LA were polymerised by these entities to give linear medium molecular weight polymers with moderate-to-broad polydispersities. Unfortunately, appreciable levels of selectivity were not obtained in the polymerisation of rac-LA. During our studies we realised that a dynamic exchange process in which an intramolecular associative displacement of one pyrazolyl group for another was taking place in the organoaluminium initiators, and this ‘swinging event’ could interfere with biopolymer productivities. In fact, a relevant interdependency between activities in the ROP of \(\varepsilon\)-CL and estimated exchange constants (\(k_{ex}\)) was observed; a decrease of \(k_{ex}\) was shown to correlate with increasing productivity in the ROP.

The aim of the work described here was to prepare efficient organoaluminium initiators based on bulky heteroscorpionate ligands in an effort to achieve increased activity in ROP and, assuming chain-end control, to exert better control of the polymer microstructure than their previously reported counterparts. The use of these new entities as good single-component living initiators for the polymerisation of \(\varepsilon\)-CL and rac-LA under well-controlled conditions is discussed in detail and an analysis of the polymer microstructures is provided.

**Results and Discussion**

**Synthesis and structural characterisation**

The performance of initiators in terms of activity, productivity, degree of control and stereoselectivity depends crucially on the ancillary ligands, which define the steric and electronic environment around the active metal centre. In an effort to increase the steric hindrance around the metal centre of the organoaluminium initiators, six new heteroscorpionate ligand precursors bearing more sterically encumbered substituents were designed and synthesised according to literature procedures.\(^{6,15}\) The bulkiness was imposed either in the pyrazole groups or in the acetamide/thioacetamide moiety. Thus, the one-pot reaction of bis(3,5-diisopropylpyrazol-1-yl)methane (bdmpz)\(^{16}\) or bis(3,5-di-tert-butylpyrazol-1-yl)methane (bdtbpzm)\(^{16}\) with \(\text{Bu}^\text{Li}\), followed by the addition of a series of isocyancates [fluoren-2-yl, phenyl or (\(S\)-(--)\(\alpha\)-methylbenzyl isocyanates] and isothiocyanates (phenyl and naphthyl isothiocyanates) and then saturated aqueous ammonium chloride solution, afforded the desired compounds nbptamH (1), pbpmH (2), pbptamH (3), nbptamH (4), pbpmH (5) and (S)-ntbptamH (6), which were isolated in good yields (ca. 80%) after the appropriate workup (Scheme 1). Compound 6 was isolated as an enantiopure ligand precursor. For compounds 1–6 there are three possible tautomers (see Fig. S1 in ESI†). The \(^1\)H NMR spectra of these compounds all contain a broad singlet between \(\delta\) 6.00 and 13.00 ppm (see Fig. S2 in ESI†), which corresponds to the N–H group of the acetamide or thioacetamide moieties and indicates the presence of only one tautomer in solution (depicted in Scheme 1). The different acetamide or thioacetamide compounds were characterised spectroscopically (see Experimental Section).

![Scheme 1. Synthesis of compounds 1–6.](image)

Protonolysis reactions of heteroscorpionate protio-precurors 1–6 with one equivalent of AlX\(_3\) in a 1:1 molar ratio in toluene at 0 °C gave the mononuclear dialkyl aluminium complexes [AlX\(_2\)\(\{\alpha^2\text{-nbptam}\}\)] (X = Me 7, Et 8), [AlX\(_2\)\(\{\alpha^2\text{-fbpm}\}\)] (X = Me 9, Et 10), [AlX\(_2\)\(\{\alpha^2\text{-ptbam}\}\)] (X = Me 11, Et 12), [AlX\(_2\)\(\{\alpha^2\text{-ntbptam}\}\)] (X = Me 13, Et 14), [AlX\(_2\)\(\{\sigma^2\text{-ntbptam}\}\)] (X = Me 15, Et 16) and [AlX\(_2\)\(\{\alpha^2\text{-ntbptam}\}\)] (X = Me 17, Et 18), with elimination of the corresponding alkane (see Scheme 2).\(^{13,14}\) Compounds 7–18 were isolated as white or yellow solids in good yields after the appropriate workup procedure (see Experimental Section). Complexes 17 and 18 were isolated as mixtures of two diastereoisomers in similar proportions.
Scheme 2. Synthetic route to compounds 7–18.

The different acetamidate and thioacetamidate compounds were characterised spectroscopically (see Experimental Section). The $^{13}$C NMR signals of the carbonyl or thiocarbonyl groups in these complexes are good indicators of the bonding mode of the acetamidate or thioacetamidate moieties of the ligands.\(^{13a,c}\) The acetamidate carbon resonances, RNCO, were shifted to higher field with respect to those of the neutral ligands, indicating that the acetamidate moieties were coordinated to the aluminium centre through the O atom (see Scheme 2). In contrast, the corresponding signal for the thioacetamidate carbon resonance, RNCS, is shifted to lower field with respect to that in the neutral ligand (see Experimental Section), indicating that the thioacetamidate moiety is coordinated to the metal centre through the N atom. However, a small amount of delocalised E–C–N bond probably exists in the acetamidate or thioacetamidate moieties of the heteroscorpionate ligands. The $^1$H and $^{13}$C-$^1$H NMR spectra for compounds 7–14 at room temperature show broad resonances for some of the protons and carbons (see Fig. 2a), indicating the existence of fluxional behaviour (see Fig. S3, variable temperature $^1$H NMR spectra for compound 14 in toluene-$d_8$), which is thought to be due to exchange processes between coordinated and noncoordinated pyrazole rings (‘swinging events’). This type of fluxional process was observed in the aluminium counterparts.\(^{13c}\) The bulkiness imposed in the new organoaluminium derivatives bearing $^2$Bu$_2$-pyrazole seems to slow, at room temperature, the ‘swinging event’ previously observed for the Me$_2$-pyrazole counterparts\(^{13c}\) (see Fig. S3) and for complexes 15–18 the exchange process between coordinated and noncoordinated pyrazole rings does not take place at all. Thus, for complexes 17 and 18, which bear a chiral heteroscorpionate ligand, the $^1$H NMR spectra at room temperature show double signals due to the two diastereoisomers present (see Fig. 2b). It is worth noting that, given the coordination mode of the ligands, all of the complexes are chiral regardless of the existence of a chiral centre in the heteroscorpionate ligand used as the scaffold.

NOESY-1D NMR experiments were carried out in order to confirm the assignment of most $^1$H NMR resonances and $^1$H-$^{13}$C heteronuclear correlation ($^g$HSQC) experiments allowed the resonances corresponding to some carbons of the pyrazole rings and alkyl groups to be assigned. The spectroscopic data support a tetrahedral disposition for the aluminium atom with a $\kappa^2$NN coordination mode of the thioacetamidate heteroscorpionate ligand, whereas the acetamidate derivatives have a $\kappa^2$NO coordination mode, as depicted in Scheme 2.

The molecular structure of complex 14 was determined by X-ray diffraction. The ORTEP drawing is depicted in Fig. 3. The crystallographic data and selected interatomic distances and angles are given in Tables S1 and S3 in ESI.\(^{1}\) In this complex the heteroscorpionate ligand is $\kappa^2$NN coordinated to the aluminium centre, thus forming a pseudotetrahedral complex with $C_1$ symmetry. In addition, the aluminium centre is coordinated to two alkyl ligands.
The solid-state structure is consistent with those proposed in Scheme 2 on the basis of NMR data in solution and other analytical data. Given the coordination mode of the heteroscorpionate ligand, complex 14 is a chiral compound. This complex crystallises as a racemic mixture with both enantiomers included in the unit cell, which belongs to the centrosymmetric space group. The geometry around the aluminium centre can be described as distorted tetrahedral, with the dihedral angle between the N(2)–Al(1)–N(5) and C(37)–Al(1)–C(35) planes (84.25°) consistent with a distorted tetrahedral geometry. Furthermore, the angles around the aluminium atom show considerable deviation from ideal values, in the range 91.5(3)°–119.0(17)°, and the most acute angle of 91.5(3)° is observed for N(2)–Al(1)–N(5), which is constrained by the bite of the heteroscorpionate ligand. The distance between N(3) and Al(1) (3.578 Å) is too long to be considered as bonding or as an interaction between N(3) and the Al(1) atom, and it is longer than the distance observed in similar complexes with Me2-pyrazole rings, probably due to the steric hindrance caused by the tert-butyl moieties in the pyrazole rings. This steric demand of the tert-butyl groups accounts for the Al(1)–N(2) bond distance of 2.015(7) Å is longer than those in Al/Me2-pyrazolyl complexes.

Catalytic behaviour in the ROP of bulky heteroscorpionate organoaluminiums

Organoauminiums 7–18 were tested as initiators for the ROP of cyclic esters. For this purpose ε-CL and rac-LA were chosen as monomers for polymerisations. In the first screening, compounds 7–18 were tested against ε-CL in toluene at 70 °C. It can be seen from the results in Table 1 that organoaaniums 7–18 are effective initiators for the ROP of ε-CL. The activity data compare favourably with those of most discrete aluminium initiators, particularly those related to scorpionate compounds. Initiators 7–18 proved to be very productive systems and enabled the quantitative conversion of 500 equiv. of ε-CL within minutes at 70 °C (see entries 1–12 in Table 1). Moreover, all of the experimental molecular weights are in good agreement with calculated values and the molecular weight distributions are narrow, both features that are characteristic of a controlled polymerisation. The productivity of these entities and the controlled character of the polymerisation were further evidenced by the sequential polymerisation of 500 + 200 equiv. of ε-CL (entry 13), for which complete conversion was observed along with a slight broadening of the molecular weight distribution between the two stages. It is worth noting that an increase in the activity in the ROP of ε-CL is produced by the steric hindrance from the tert-butyl groups on the bulky heterscorpionate ligands (see Entries 1 and 2 versus Entries 7 and 8, respectively).

On the basis of the data in Table 1, compound 14 was chosen as the most effective initiator to carry out a more in-depth study of the catalytic behaviour of these systems in ROP (see Entries 14–19 in Table 1). A faster conversion of monomer occurred on increasing the temperature (entries 14 and 15) although an increase in the molecular weight distribution was also observed, probably due to the occurrence of transesterification reactions. The possible competition with monomer molecules during polymerisation could mean that a polar solvent, such as THF, is not appropriate for use in catalytic procedures (see Entry 16 in Table 1). Moreover, a decrease in the loading of initiator from 90 to 70 µmol, under identical conditions, seems to have a detrimental effect on the productivities in ROP (see Entry 17). Remarkably, significant levels of transfer reactions were not observed when higher [Al]:[CL] ratios were chosen (see Entries 18 and 19). In fact, compound 14 is capable of converting 1000 equiv. of ε-CL in a very controlled manner to give high molecular weight polymers with narrow molecular weight distributions (see entry 19 in Table 1).

In order to determine reaction rate constants for the best initiators, solution kinetics studies were carried out on the ROP of ε-CL for the thioacetamidate derivatives 12 and 14 and the acetamidate derivatives 16 and 18. Polymerisations were monitored over time by regular manual sampling followed by 1H NMR analysis to determine the degree of monomer conversion. The semi-logarithmic plots of \( \ln([CL]_0/[CL]) \) versus reaction time for initiators 12, 14, 16 and 18 are depicted in Figure 4, where \([CL]_0\) is the initial ε-CL monomer concentration and \([CL]\) is the ε-CL concentration at a given reaction time \( t \). In all cases the linearity of the plots shows a first order with respect to ε-CL monomer for polymerisations at 70 °C. An induction period was not observed and this indicates that initiator aggregates were not required to produce active species. The linearity of the plots also shows that termination reactions did not occur during polymerisation. The \( k_{app} \) values for these derivatives are of the same order of magnitude and are roughly one order higher than the \( k_{app} \) values found for the Me2-pyrazole derivatives.
Table 2. Polymisation of rac-LA by initiators 14 and 18.

| entry | Temp (°C) | time (h) | Conv (%)
|-------|-----------|----------|----------
| 1     | 110      | 7.5      | 87       |
| 2     | 110      | 8        | 91       |
| 3     | 110      | 9        | 84       |
| 4     | 110      | 7.5      | 56       |
| 5     | 90       | 20       | 78       |
| 6     | 90       | 20       | 78       |

Table 1. Screening for the polymerisation of ω-CL by initiators 7–18.

| entry | Init [CL]/[Al]₀ time (min) | Conv (%)
|-------|---------------------------|----------
| 1     | 7 500 75 94 53645 60400 1.28 |
| 2     | 8 500 70 94 53645 59320 1.31 |
| 3     | 9 500 180 93 53075 59300 1.29 |
| 4     | 10 500 160 95 54217 58130 1.25 |
| 5     | 11 500 60 93 53075 54910 1.13 |
| 6     | 12 500 60 98 55929 56010 1.14 |
| 7     | 13 500 50 93 53075 53850 1.11 |
| 8     | 14 500 45 93 53075 53560 1.13 |
| 9     | 15 500 95 98 55929 56650 1.12 |
| 10    | 16 500 80 94 53645 55870 1.15 |
| 11    | 17 500 65 94 53645 54980 1.14 |
| 12    | 18 500 55 93 53075 55180 1.11 |
| 13    | 14 500 + 200 60 94 75104 81520 1.19 |

Fig. 4. First-order kinetic plots for ω-CL polymerisations in toluene at 70 °C with [CL]/[Al] = 200 and [Al] = 4.5 × 10⁻⁵ mol L⁻¹. 12, kₑקרי = 5.32 × 10⁻⁴ s⁻¹ (linear fit, R² = 0.988); 14, kₑקרי = 6.03 × 10⁻⁴ s⁻¹ (linear fit, R² = 0.990); 18, kₑקרי = 2.58 × 10⁻⁴ s⁻¹ (linear fit, R² = 0.978).

The polymerisation of rac-LA was monitored over time by manual sampling followed by ¹H-NMR analysis to determine the degree of monomer conversion. The polymerisation kinetics were studied for complexes 14 and 18 with [LA]/[Al] = 200 and [Al] = 4.5 × 10⁻³ M at 110 °C, 100 °C, 90 °C, 80 °C and 70 °C, using toluene as solvent. The semi-logarithmic plots of ln([LA]/[LA]₀) versus reaction time for both initiators are shown in Figure 5, where [LA]₀ is the initial lactide monomer concentration and [LA] is the lactide concentration at a given reaction time t. Once again, the linearity of the plot indicates that the propagation was first order with respect to lactide monomer when polymerised in toluene. Furthermore, an induction period was not observed. The fastest polymerisation for rac-LA was observed for 14 at 110 °C, which gave a pseudo-first-order rate constant of 2.14 × 10⁻⁴ s⁻¹. Finally, the influence of the temperature on the polymerisation rate of rac-LA using 14 and 18 was also investigated. It can be seen from Figure 5 that the polymerisation rate increased with increasing temperature. From the five kₑקרי values determined at different temperatures, the activation energies of the polymerisations using 14 and 18 were deduced by fitting.
polymers exhibited a monomodal and narrow molecular polymerisation using 14 and 18 were 6.46 and 6.87 kJ mol\(^{-1}\), respectively. The activation energy for these initiators was much lower when compared to the \(E_a\) data for tin(II) ethylhexanoate (70.9 kJ mol\(^{-1}\)).

Microstructural analysis of the polyesters was carried out by \(^1\)H NMR spectroscopy, Size Exclusion Chromatography and MALDI-TOF MS. All of the polymers exhibited a monomodal and narrow molecular weight distribution (see Fig. S4, as an example, in ESI†).

The low molecular weight PLA sample obtained with initiator 14 was characterised in order to ascertain the nature of the initiator. It was established by MALDI-TOF (see Fig. S5 in ESI†) and \(^1\)H NMR (see Fig. S6 in ESI†) data that the polymer chains are selectively capped by –COCH\(_2\)CH\(_3\) and –OH end groups. This provides evidence that the polymerisation follows a nucleophilic route and is initiated by the transfer of an alkyl ligand to the monomer, with cleavage of the acyl-oxygen bond and formation of a metal alkoxide propagating species. The homonuclear decoupled \(^1\)H NMR spectrum of the methine region of the PLA samples derived from compounds 14 and 18 in toluene is consistent with the formation of chains that are essentially atactic (see Fig. S7 in in ESI† and P\(_{at\_}\) in Table 2).

\[
\ln k_{app} \text{ versus } T^{-1} \text{ according to the Arrhenius equation (see Fig. 6). The activation energy } E_a \text{ values for the rac-LA polymerisation using 14 and 18 were 6.46 and 6.87 kJ mol}^{-1} \text{, respectively. The activation energy for these initiators was much lower when compared to the } E_a \text{ data for tin(II) ethylhexanoate (70.9 kJ mol}^{-1}\).^{19}

![First-order kinetic plots for initiators 14 and 18 for rac-LA polymerisations in toluene with [LA]/[Al] = 200 and [Al] = 4.5 \times 10^{-3} \text{ mol L}^{-1}. (a) 14, ● at 110 °C, } k_{app} = 2.15 \times 10^{-1} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.973); \blacktriangle at 100 °C, } k_{app} = 1.07 \times 10^{-2} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.999); \blacklozenge at 90 °C, } k_{app} = 5.03 \times 10^{-3} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.997); \blacktriangle at 80 °C, } k_{app} = 1.67 \times 10^{-3} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.984); \blacklozenge at 70 °C, } k_{app} = 3.72 \times 10^{-5} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.994). (b) 18, ● at 110 °C, } k_{app} = 1.50 \times 10^{-4} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.982); \blacktriangle at 100 °C, } k_{app} = 7.10 \times 10^{-5} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.991); \blacklozenge at 90 °C, } k_{app} = 3.98 \times 10^{-5} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.993); \blacktriangle at 80 °C, } k_{app} = 1.27 \times 10^{-5} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.980); \blacklozenge at 70 °C, } k_{app} = 1.86 \times 10^{-6} \text{ s}^{-1} \text{ (linear fit, } R^2 = 0.985).\]

![First-order kinetic plots for Initiators 14 and 18 for rac-LA polymerisations in toluene with [LA]/[Al] = 200 and [Al] = 4.5 × 10^{-3} mol L^{-1}. (a) 14, ● at 110 °C, k_{app} = 2.15 × 10^{-1} s^{-1} (linear fit, R^2 = 0.973); ▲ at 100 °C, k_{app} = 1.07 × 10^{-2} s^{-1} (linear fit, R^2 = 0.999); ● at 90 °C, k_{app} = 5.03 × 10^{-3} s^{-1} (linear fit, R^2 = 0.997); ● at 80 °C, k_{app} = 1.67 × 10^{-3} s^{-1} (linear fit, R^2 = 0.984); ● at 70 °C, k_{app} = 3.72 × 10^{-5} s^{-1} (linear fit, R^2 = 0.994). (b) 18, ● at 110 °C, k_{app} = 1.50 × 10^{-4} s^{-1} (linear fit, R^2 = 0.982); ▲ at 100 °C, k_{app} = 7.10 × 10^{-5} s^{-1} (linear fit, R^2 = 0.991); ● at 90 °C, k_{app} = 3.98 × 10^{-5} s^{-1} (linear fit, R^2 = 0.993); ● at 80 °C, k_{app} = 1.27 × 10^{-5} s^{-1} (linear fit, R^2 = 0.980); ● at 70 °C, k_{app} = 1.86 × 10^{-6} s^{-1} (linear fit, R^2 = 0.985).](image1)

Comparative study between \(^1\)Bu_2-pyrazole and Me_2-pyrazole organoaluminium derivatives in ROP

We were interested in establishing an appropriate comparative discussion of the reactivity of these new initiators with those reported in a previous publication with the aim of drawing conclusions about possible improvements in ROP. For this purpose, the structures of the Me_2-pyrazole counterparts are shown in Scheme 3. The compounds previously reported are renumbered on the basis of similarities between them in order to facilitate the discussion.

![Scheme 3. Non-bulky heteroscorpionate initiators reported previously.](image2)

Nature of the alkyl group

The nature of the alkyl group in both families of initiators (Me_2- and \(^1\)Bu_2-pyrazole derivatives) seems to affect the catalytic activity, which decreases in the order ED > Me – a
trend that is also consistent with the decrease in the lability of the M–C bond (see as examples entry 1 versus entry 2, and entry 3 versus entry 4 in Table 3 for \( ^{13} \)Bu$_2$-pyrazole derivatives; and also entry 5 versus 6, and entry 7 versus 8 in Table 3 for Me$_2$-pyrazole analogues).

Similar behaviour has also been observed in analogous derivatives.$^{13a,13c,20}$

**Table 3.** Polimerisation of \( \varepsilon \)-CL catalysed by alkyl aluminium compounds.

<table>
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<tr>
<th>entry</th>
<th>Init</th>
<th>[CL]$_0$</th>
<th>[Al]$_0$</th>
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<th>conv (%)</th>
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<th>$M_n$(exp.) (Da)</th>
<th>$M_w/M_n$</th>
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<td></td>
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<td>58130</td>
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</table>

$^{(a)}$Polimerisation conditions: 90 \( \mu \)mol of initiation, 20 mL of toluene as solvent at 70 °C. $^{(b)}$Percentage conversion of the monomer (weight of polymer recovered/weight monomer) \(< 100\). $^{(c)}$Theoretical $M_n = (\text{monomer/initiator}) \times (\% \text{ conversion}) \times (M_n(\varepsilon-\text{CL})).$ $^{(d)}$Determined by GPC relative to polystyrene standards in tetrahydrofuran.

### Influence of the encumbered substituents in the pyrazole moieties

The presence of encumbered substituents in the pyrazole moieties of the aluminium derivatives seems to improve catalytic performance in terms of activity and degree of control. As a first comparison, alkyl aluminium derivatives 11–18 were found to be markedly more active than the analogous Me$_2$-pyrazole derivatives 11$'$–12$'$ and 15$'$–18$'$, which were recently reported by our group. As an example, compound 12 can quantitatively polymerise, in a controlled fashion, 500 equiv. of \( \varepsilon \)-CL in only 60 minutes (see entry 6 in Table 1), whereas compound 12$'$ requires 8 hours to achieve 70% conversion.$^{13c}$ The \( ^{13} \)Bu$_2$-pyrazole initiators show reasonably well-controlled behaviour in the ROP of lactones and lactides, giving rise to polymers with excellent consistency between calculated and observed molecular weights (see Table 1 and Table 2). In contrast, derivatives 11$'$–12$'$ and 15$'$–18$'$ gave rise to polymers with substantially higher molecular weights than those predicted,$^{13c}$ a trend that is consistent with poor rates of initiation (\( \varepsilon \)-CL initiation in the Al-Et bond) compared to propagation.

The polymers obtained by both families of initiator had a monomodal weight distribution, but the $M_w/M_n$ values for Me$_2$-pyrazole derivatives are somewhat higher than those expected for a purely living polymerisation, probably due to higher levels of the transesterification side reaction, which would result in the formation of macrocycles with a wider range of molecular weight distributions. The overall results are consistent with a better controlled polymerisation model for \( ^{13} \)Bu$_2$-pyrazole derivatives, which gave rise to $M_w/M_n$ values between 1.04 and 1.15 (see Tables 1 and 2).

As far as the stereoselectivities in the ROP of \( \text{rac} \)-LA are concerned, the \( ^{13} \)Bu$_2$-pyrazole derivative 14 (see $P_m$ in entries 1–3 in Table 2) and the counterparts 11$'$–12$'$ and 15$'$–18$'$ did not have any control over the tacticity of the growing polymer chain, essentially giving rise to atactic polymers. Unexpectedly, and assuming a chain-end mechanism, the high steric demand of the \( ^{13} \)Bu substituents in the two pyrazole rings did not lead to sufficient steric congestion and, as a consequence, did not provide more selective active centres to the incoming lactide. On the other hand, the sterically hindered initiator 18, which is a mixture of two diastereoisomers, promoted an isotactic bias in the polymerisation of \( \text{rac} \)-LA in toluene at 70 °C to produce slightly enhanced degrees of isotacticity (see $P_m$ in entries 4–6 in Table 2) – albeit with a significant decrease in activity.

### Influence of the steric hindrance in the acetamidate/thioacetamidate moiety

Improvements in catalytic performance were also observed in cases where only the pendant donor arm of the heteroscorpionate ligand was chosen to increase the steric hindrance in the organoaluminium initiators. Thus, the most congested thioacetamidate derivatives 7 and 8 show better catalytic behaviour in the polymerisation of \( \varepsilon \)-CL than their analogues 11$'$ and 12$'$, as do the acetamidate derivatives 9 and 10 with respect to their analogues 15$'$ and 16$'$ (Table 3). For instance, compound 10 converts 95% of the monomer in 160 minutes in a controlled fashion, whereas compound 16$'$ requires three hours to achieve 84% conversion.

### Conclusions

Guided by the results of previous studies, in which several organoaluminums based on heteroscorpionate scaffolds were reported, we focused our efforts on improving the catalytic behaviour of these systems in the ROP of cyclic esters by the introduction of encumbered substituents in the structure. A total of twelve thioacetamidate and acetamidate organoaluminium derivatives with bulky heteroscorpionate ligands were synthesised and fully characterised. These new compounds were tested as initiators in the ROP of \( \varepsilon \)-CL and \( \text{rac} \)-LA. Improvements in productivity and in the control of the polymerisation process were observed. In fact, excellent agreement was found between calculated and observed molecular weights, and polyesters with very narrow polydispersities were obtained with these entities. Among the twelve compounds described, organoaluminium 14, with bulky substituents in the pyrazole and thioacetamidate moieties, can be highlighted as the most efficient initiator in ROP.
by the best initiators complement the catalytic study and provided values for \( k_{\text{rup}} \) and \( E_c \).

Unexpectedly, the steric hindrance imposed on the structures of the new initiators was not sufficient to control the tacticity of the PLAs obtained by ROP of rac-lactide. However, when the polymerisations were carried out with compound 18, a slightly higher level of isotacticity was obtained and the probability value increased slightly in this case to \( P_m = 0.60 \). The behaviour observed during the propagation cannot be the result of the high steric demand of the \( \text{Bu} \) substituents in the two pyrazole rings because better control was not obtained with the other bulky heteroscorpionate initiators.

In conclusion, rational tuning of the catalyst design has enabled the preparation of the most efficient catalyst systems for the ROP of cyclic esters. However, further iterations of ligand design will be required to identify organoaluminiums that would be capable of achieving stereochemical control under solution ROP conditions.

**Experimental**

All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were pre-dried over sodium wire (toluene, n-hexane and THF) and distilled under nitrogen from sodium (toluene and THF) or sodium-potassium alloy (n-hexane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. \( ^1H \) and \( ^{13}C \) NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated systems for the ROP of cyclic esters. However, further iterations of ligand design will be required to identify organoaluminiums that would be capable of achieving stereochemical control under solution ROP conditions.

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**Synthesis of nbptamH (1)**

In a 250 mL Schlenk tube, bdmpzm (2.00 g, 9.79 mmol) was dissolved in dry THF (70 mL) and cooled to −78 °C. A 1.6 M solution of Bu\(_2\)Li (6.12 mL, 9.79 mmol) in hexane was added and the solution was stirred for 1 h. The resulting mixture was added dropwise to a cooled (−10 °C) solution of 1-naphthyl isothiocyanate (1.81 g, 9.79 mmol). The reaction mixture was allowed to warm up to ambient temperature and was stirred for 1 h. The product was hydrolyzed with saturated aqueous NH\(_4\)Cl (15 mL). The organic layer was extracted, dried over MgSO\(_4\), filtered, and the solvent was removed in vacuo to give the product as a yellow oil, which was triturated with hexane to give the pure product as a yellow solid. Yield: 3.12 g, 82%. Anal. Calcd for C\(_{32}\)H\(_{33}\)NS: C, 76.8; H, 6.0; N, 18.0. Found: C, 76.8; H, 6.2; N, 17.8. \(^1H\) NMR (C\(_{6}\)D\(_{6}\), 297 K), \( \delta \) (ppm): 12.87 (brs, 1 H, NaphNHCS), 8.52–6.93 (m, 7 H, NaphNHCOS), 8.11 (s, 1 H, CH), 6.95 (s, 2 H, H\(_2\)), 1.88 (s, 6 H, Me\(_3\)), 1.79 (s, 6 H, Me\(_3\)). \(^{13}C\)\(^1\)H\) NMR (C\(_{6}\)D\(_{6}\), 297 K), \( \delta \) (ppm): 76.7 (CH), 149.2, 140.1 (C\(_{6}\)), 106.6 (C\(_4\)), 13.4 (Me\(_3\)), 10.6 (Me\(_3\)), 189.9 (NaphNHCOS), 134.5–121.8 (NaphNHCOS).

**Synthesis of fbpmH (2)**

The synthetic procedure was the same as for compound 1, using bdtpzm (2.00 g, 9.79 mmol), a 1.6 M solution of Bu\(_2\)Li (6.12 mL, 9.79 mmol) and fluorenyl-2-y1 isocyanate (2.03 g, 9.79 mmol) to give 2 as a white solid. Yield: 3.38 g, 84%. Anal. Calcd for C\(_{32}\)H\(_{33}\)N\(_2\): C, 73.0; H, 6.2; N, 17.0. Found: C, 73.3; H, 6.2; N, 16.8. \(^1H\) NMR (C\(_{6}\)D\(_{6}\), 297 K), \( \delta \) (ppm): 10.35 (brs, 1 H, FluNHCO), 7.93–7.10 (m, 7 H, Ar−FluNHCOS), 6.84 (s, 1 H, CH), 5.90 (s, 2 H, H\(_4\)), 3.87 (s, 2 H, CH\(_2\)-FluNHCOS), 2.42 (s, 6 H, Me\(_3\)), 2.27 (s, 6 H, Me\(_3\)). \(^{13}C\)\(^1\)H\) NMR (C\(_{6}\)D\(_{6}\), 297 K), \( \delta \) (ppm): 71.3 (CH), 150.1, 141.4 (C\(_{6}\)), 107.6 (C\(_4\)), 14.0 (Me\(_3\)), 11.6 (Me\(_3\)), 162.4 (FluNHCOS), 144.0–116.0 (Ar−FluNHCOS), 37.2 (CH\(_2\)-FluNHCOS).

**Synthesis of ptbptamH (3)**

The synthetic procedure was the same as for compound 1, using bdtpbzm (3.65 g, 9.79 mmol), a 1.6 M solution of Bu\(_2\)Li (6.12 mL, 9.79 mmol) and phenyl isothiocyanate (1.32 g, 9.79 mmol) to give 3 as a yellow solid. Yield: 4.07 g, 82%. Anal. Calcd for C\(_{32}\)H\(_{34}\)NS: C, 71.0; H, 8.9; N, 13.8. Found: C, 71.1; H, 9.0; N, 13.5. \(^1H\) NMR (C\(_{6}\)D\(_{6}\), 297 K), \( \delta \) (ppm): 10.10 (brs, 1 H, PhNHCS), 8.04 (d, 2 H, \( J_{\text{HH}} = 7.3 \) Hz, \( H^6 \)), 7.07 (t, 2 H, \( J_{\text{HH}} = 7.3 \) Hz, \( H^7 \)), 6.88 (t, 1 H, \( J_{\text{HH}} = 7.3 \) Hz, \( H^6 \)), 7.97 (s, 1 H, CH), 6.08 (s, 2 H, H\(_3\)), 1.36 (s, 18 H, \( \text{Bu}^3 \)), 1.34 (s, 18 H, \( \text{Bu}^3 \)). \(^{13}C\)\(^1\)H\) NMR (C\(_{6}\)D\(_{6}\), 297 K), \( \delta \) (ppm): 82.0 (CH), 160.5, 153.2 (C\(_{6}\)), 102.5 (C\(_4\)), 32.3, 31.9 [C(CH\(_3\))], 1.3Bu\(_{10}^3\).
The synthetic procedure was the same as for compound 1, using dibdbpm (3.65 g, 9.79 mmol), a 1.6 M solution of BuLi (6.12 mL, 9.79 mmol) and 1-naphthyl isocyanate (1.81 g, 9.79 mmol) to give 6 as a yellow solid. Yield: 4.42 g, 81%. Anal. Calcld. for C_{35}H_{33}N_{5}O: C, 73.2; H, 8.5; N, 13.0. ^{1}H NMR (C_{6}D_{6}, 297 K), δ (ppm): 7.05 (brs, 1 H, NPhNHC), 7.92 (d, 2 H, J_{HH} = 7.2 Hz), 7.21 (t, 2 H, J_{HH} = 7.2 Hz, H_{A}), 7.00 (t, 1 H, J_{HH} = 7.3 Hz, H_{A}), 6.98 (s, 1 H, CH), 5.88 (s, 2 H, H_{A}), 1.24 (s, 18 H, Bu'), 1.13 (s, 18 H, Bu'). ^{13}C({^{1}H}) NMR (C_{6}D_{6}, 297 K), δ (ppm): 76.6 (CH), 160.7, 153.2 (C_{5}orf), 103.5 (C_{5}), 32.3, 31.8 [C(CH_{3})_{3}, Bu'orf], 30.4 [C(CH_{3})_{3}, Bu'], 29.6 [C(CH_{3})_{3}, Bu'], 164.9 (PhNHC), 138.5 (C_{6}, PhNHC), 130.5 (C_{6}, PhNHC), 123.4 (C_{6}, PhNHC), 119.6 (C_{6}, PhNHC).

The synthetic procedure was the same as for compound 1, using dibdbpm (3.65 g, 9.79 mmol), a 1.6 M solution of BuLi (6.12 mL, 9.79 mmol) and 1-fluorenyl isocyanate (1.17 g, 9.79 mmol) to give 7 as a white solid. Yield: 4.28 g, 89%. Anal. Calcld. for C_{35}H_{33}F_{5}O: C, 73.3; H, 9.2; N, 14.2. Found: C, 74.0; H, 8.8; N, 14.4. ^{1}H NMR (C_{6}D_{6}, 297 K), δ (ppm): 7.05 (brs, 1 H, NPhNHC), 7.92 (d, 2 H, J_{HH} = 7.2 Hz), 7.21 (t, 2 H, J_{HH} = 7.2 Hz, H_{A}), 7.00 (t, 1 H, J_{HH} = 7.3 Hz, H_{A}), 6.98 (s, 1 H, CH), 5.88 (s, 2 H, H_{A}), 1.24 (s, 18 H, Bu'), 1.13 (s, 18 H, Bu'). ^{13}C({^{1}H}) NMR (C_{6}D_{6}, 297 K), δ (ppm): 76.6 (CH), 160.7, 153.2 (C_{5}orf), 103.5 (C_{5}), 32.3, 31.8 [C(CH_{3})_{3}, Bu'orf], 30.4 [C(CH_{3})_{3}, Bu'], 29.6 [C(CH_{3})_{3}, Bu'], 164.9 (PhNHC), 138.5 (C_{6}, PhNHC), 130.5 (C_{6}, PhNHC), 123.4 (C_{6}, PhNHC), 119.6 (C_{6}, PhNHC).

The synthetic procedure of (5)-mtpbpmH (6) was carried out in an identical manner to compound 1, using dibdbpm (3.65 g, 9.79 mmol), a 1.6 M solution of BuLi (6.12 mL, 9.79 mmol) and fluoronaphthalene (1.44 g, 9.79 mmol) to give 6 as a white solid. Yield: 4.42 g, 87%. [α]_{D}^{25} = 22.9° (c = 0.1, toluene). Anal. Calcld. for C_{35}H_{33}NF_{5}O: C, 74.0; H, 9.5; N, 13.5. Found: C, 74.4; H, 9.6; N, 13.3. ^{1}H NMR (C_{6}D_{6}, 297 K), δ (ppm): 7.05 (brs, 1 H, NPhNHC), 7.92 (d, 2 H, J_{HH} = 7.2 Hz), 7.21 (t, 2 H, J_{HH} = 7.2 Hz, H_{A}), 7.00 (t, 1 H, J_{HH} = 7.3 Hz, H_{A}), 6.98 (s, 1 H, CH), 5.88 (s, 2 H, H_{A}), 1.24 (s, 18 H, Bu'), 1.13 (s, 18 H, Bu'). ^{13}C({^{1}H}) NMR (C_{6}D_{6}, 297 K), δ (ppm): 76.6 (CH), 160.7, 153.2 (C_{5}orf), 103.5 (C_{5}), 32.3, 31.8 [C(CH_{3})_{3}, Bu'orf], 30.4 [C(CH_{3})_{3}, Bu'], 29.6 [C(CH_{3})_{3}, Bu'], 164.9 (PhNHC), 138.5 (C_{6}, PhNHC), 130.5 (C_{6}, PhNHC), 123.4 (C_{6}, PhNHC), 119.6 (C_{6}, PhNHC).

The synthetic procedure of [AlMe_{2}(x^2-nptbamH)] (7) was carried out in an identical manner to compound 1, using dibdbpm (1.27 g, 2.50 mmol) and AlMe_{2} (2M in toluene) (1.25 mL, 2.50 mmol). Yield: 1.21 g, 86%. Anal. Calcld. for C_{35}H_{33}AlN_{5}S: C, 68.2; H, 8.9; N, 12.4. Found: C, 68.7; H, 9.1; N, 12.0. ^{1}H NMR (C_{6}D_{6}, 297 K), δ (ppm): 3.10 (brs, 1 H, NPhNHC), 5.65 (s, 1 H, NPhNHC), 2.28 (s, 6H, Me), 1.15 (s, 18 H, Bu').
Synthesis of $[\text{AlEt}_2(\kappa^2-\text{ptbptam})]$ (12)

The synthesis of 12 was carried out in an identical manner to 7, using pbptamH (3) (1.27 g, 2.50 mmol) and AlEt$_3$ (1M in hexane) (2.50 mL, 250 mmol). Yield: 1.30 g, 88%.

Anal. Calcd. for C$_{29}$H$_{36}$N$_8$: C, 56.0; H, 6.5; N, 14.5. Found: C, 56.1; H, 6.3; N, 14.3.

Synthesis of $[\text{AlMe}_2(\kappa^2-\text{ntbptam})]$ (13)

The synthesis of 13 was carried out in an identical manner to 7, using ntbptamH (4) (1.39 g, 2.50 mmol) and AlMe$_3$ (2M in toluene) (1.25 mL, 250 mmol). Yield: 1.33 g, 87%.

Anal. Calcd. for C$_{29}$H$_{36}$N$_8$: C, 56.0; H, 6.5; N, 14.5. Found: C, 56.1; H, 6.3; N, 14.3.

Synthesis of $[\text{AlEt}_2(\kappa^2-\text{ptbptam})]$ (14)

The synthesis of 14 was carried out in an identical manner to 7, using pbptamH (3) (1.39 g, 2.50 mmol) and AlEt$_3$ (1M in hexane) (2.50 mL, 250 mmol). Yield: 1.30 g, 88%.

Anal. Calcd. for C$_{29}$H$_{36}$N$_8$: C, 56.0; H, 6.5; N, 14.5. Found: C, 56.1; H, 6.3; N, 14.3.

Synthesis of $[\text{AlMe}_2(\kappa^2-\text{ntbptam})]$ (15)

The synthesis of 15 was carried out in an identical manner to 7, using pbptamH (5) (1.23 g, 2.50 mmol) and AlMe$_3$ (2M in toluene) (1.25 mL, 250 mmol). Yield: 1.18 g, 86%.

Anal. Calcd. for C$_{29}$H$_{36}$N$_8$: C, 56.0; H, 6.5; N, 14.5. Found: C, 56.1; H, 6.3; N, 14.3.
Polymerisation of ε-CL were carried out on a Schlenk line in a dried Schlenk flask equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of solvent and temperature equilibration was ensured by stirring the solution for 15 min in a temperature-controlled bath. ε-CL was injected into the glovebox with the required amount of rac-LA and initiator, separately, and then attached to the vacuum line. The initiator and monomer were dissolved in methanol, filtered, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight. Polymerisations of rac-LA were performed on a Schlenk line in a flame-dried Schlenk flask equipped with a magnetic stirrer. The Schlenk tubes were charged in the glovebox with the required amount of rac-LA and initiator, separately, and then attached to the vacuum line. The initiator and monomer were dissolved in methanol, filtered, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight.

Polymerisation kinetics

Kinetic experiments were carried out in flasks at 100 °C on the Schlenk line using stock solutions of the reagents. Specifically, at appropriate time intervals a sample was removed by syringe and quickly quenched into 1 mL vials containing 0.6 mL of undried ‘wet’ CDC13. The quenched aliquots were analyzed by 1H NMR spectroscopy. For rac-LA polymerisation, the [LA]0/[LA] ratio was determined by integration of the peaks for LA (5.0 ppm for the methine proton signal) and PLA (5.2 ppm for the methine proton signal) according to the equation [LA]0/[LA] = (A3.0 + A3.5)/A0.0. Apparent rate constants (kapp) were extracted from the slopes of the best-fit lines to the plots of ln([LA]0/[LA]) versus time. For ε-CL polymerisation, the [CL]0/[CL] ratio was determined by integration of the peaks for CL (4.2 ppm for the CH2–O proton signal) and PCL (4.0 ppm for the CH2–O proton signal) according to the equation [CL]0/[CL] = (A4.2 + A4.0)/A0.2. Apparent rate constants (kapp) were extracted from the slopes of the best-fit lines to the plots of ln([CL]0/[CL]) versus time.

X-ray crystallographic structure determination

X-ray crystallography: A summary of crystal data collection and refinement parameters for all compounds is given in Table S1. The single crystals of 3, 5 and 14 were mounted on a glass fibre and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated Mo-Kα radiation source (λ = 0.71073 Å). Data were integrated using SAINT22 and an absorption correction was performed with the program SADABS.22 The software package SHELXTL version 6.1022 was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on F2. All non-hydrogen atoms were refined with anisotropic thermal parameters except those involved in the disordered groups. The three compounds show disorder for ‘Bu or Et groups. Restraints DELU and SIMU were used for to make the ADP values of the disordered atoms more reasonable but, finally, for 3 and 5 a better result was obtained when they were refined isotropically.

Hydrogen atoms were placed using a ‘riding model’ and included in the refinement at calculated positions. For compound 14, only crystals of low quality (Rint = 0.21) that were very weakly diffraacting could be grown but the data were of sufficient quality to determine the molecular and the crystal structure.

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Notes and references

1 Deparmento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071-Ciudad Real, Spain. Fax: +34 926295318. Tel: +34 926295300. Email: Antonio.Otero@uclm.es and Agustín.Lara@uclm.es
2 Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Farmacia, Universidad de Castilla-La Mancha, 02071-Albacete, Spain.
3 Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Escuela Técnica Superior de Ingenieros Industriales, 13071 Ciudad Real, Spain.
4 Electronic Supplementary Information (ESI) available: Figures and tables giving experimental details. Details of data collection and refinement for complexes 3, 5 and 14. CCDC reference numbers 1033053–1033054–1033055


