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COMMUNICATION

Highly active zinc alkyl cations for the controlled and immortal ring-opening polymerization of ϵ -caprolactone[†]

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Zinc alkyl cations supported by N₂N-BIAN-type bidentate ligands were found to be highly active in the immortal ROP of ε -caprolactone to yield narrowly disperse and chain length-controlled poly(ε -caprolactone), whether in solution or bulk polymerization conditions.

Biodegradable polyesters, such as polylactide (PLA) and poly(Ecaprolactone) (E-PCL), have received considerable interest in recent years due to their important biomedical and pharmaceutical applications and as a viable alternative to petrochemicalbased plastics.¹ In this area, the ring-opening polymerization (ROP) of cyclic esters (lactide, ε -caprolactone for example) by discrete metal-based initiators [metal = Al(III), Zn(II), Sn(II), Mg(II), Ca(II) and rare earths(III)] has undoubtedly established itself as a method of choice to access well-defined and narrowly disperse polyesters through precise chain length control.² Yet, the production of such well-defined biodegradable polymers at low economical and environmental cost remains an ongoing challenge from an applied point of view. Among ROP initiators of cyclic esters, zinc alkoxide complexes supported by various multidentate chelating ligands have attracted considerable attention over the past few years, as zinc is a cheap and biocompatible metal source.² Despite these interesting features, zinc derivatives typically show a moderate catalytic activity in the ROP of ε -caprolactone, lower than that of their alkali and rare earth metal analogues.^{2g} Recently, well-defined cationic metal derivatives [metal = Al(III), Zn(II), Mg(II), Ca(II)], which exhibit an enhanced Lewis acidity (vs. that of their neutral analogues) thought to be beneficial to ROP activity, have been studied as ROP initiators of cyclic esters.³ Among them, cationic zinc derivatives of the type $(L_2)Zn(X)(L')^+$ (X = alkyl, alkoxide) and $(L_2)Zn(X)^+$ were found to polymerize *rac*-lactide and ε -caprolactone under mild conditions with, at best, a catalytic activity

^bREQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal. E-mail: tap@dq.fct.unl.pt; Fax: +351 212 948 550

[†]Electronic supplementary information (ESI) available: Experimental procedures, selected MALDI-TOF and GPC data and crystallographic information for complex **4a**. CCDC 856121. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c2dt12336c comparable to that of the most active neutral Zn initiators studied thus far. ${}^{3a,b,i-k}$

We became interested in the synthesis of cationic zinc alkyl complexes of the type $(L_2)Zn(R)(L')^+$ (R = alkyl) bearing bisaryl/alkyl-acenaphthenequinonediimines (BIANs) as chelating bidentate L₂ ligands for subsequent use in cyclic esters polymerization. These α -diimines ligands were picked since they are well-known for their electronic versatility, their easy steric tunability (via the nitrogen substituents) as well as their straightforward synthesis.⁴ Accordingly, BIANs have been widely used as ligands for coordination to various metal centres and we anticipated that such potentially bidentate ligands may be suitable for the stabilization of cationic zinc alkyls.⁵ Here we report on the synthesis of (BIAN-Ar)Zn(Me)(THF)⁺ cations and their subsequent use in the living, immortal and highly controlled ringopening polymerization of ε -CL.⁶ As shown below, when compared to the related oxophilic metal cations studied so far,³ the described Zn cationic systems first combine a high ROP activity along with an excellent molecular weight control of the resulting ε-PCL.

The envisioned zinc cations (BIAN-Ar)Zn(Me)(THF)⁺ ($3a^+$, Ar = mesityl; $3b^+$, Ar = 2,6-ⁱPr₂Ph; Scheme 1) were prepared *via*





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ionization of the corresponding neutral precursors (BIAN-Ar) ZnMe₂ (**2a/2b**),⁷ the latter being readily accessible by reaction of BIAN-Ar (**1a/1b**) with one equiv. of ZnMe₂ (see ESI†). Thus, reaction of the dimethyl zinc complexes (**2a/2b**)⁷ with B(C₆F₅)₃ in the presence of THF (2 equiv.) allowed the quantitative formation of cations **3a**⁺ and **3b**⁺ (as MeB(C₆F₅)₃⁻ salts), respectively, as deduced from NMR data. The salt species [**3a/3b**][MeB (C₆F₅)₃] were obtained as orange-red solids stable for months under inert atmosphere.

In the case of complex **2a**, carrying out the ionization reaction in the absence of an external base such as THF yielded an intractable mixture of products, thus reflecting the instability of the presumably formed base-free (BIAN-Mes)ZnMe⁺ cation (as MeB(C₆F₅)₃⁻ salt). The ¹¹B, ¹⁹F and ¹H NMR data (CD₂Cl₂, room temp.) for [**3a**/**3b**][MeB(C₆F₅)₃] are consistent with no cation/anion interactions under the studied conditions and thus with a non-coordinated MeB(C₆F₅)₃⁻ anion in solution.⁸ Regarding the NMR data for **3a**⁺ and **3b**⁺, these agree with an effective C_{2v} -symmetric structure for both cations, the presence of a Zn–Me⁺ moiety and the coordination of a THF molecule onto the cationic Zn centre.

Species [3a/3b][MeB(C₆F₅)₃] were then tested as ROP initiators of ε -CL and representative results are summarized in Table 1. Initial ROP experiments (100 equiv. of ε -CL vs. Zn initiator, 80 °C, toluene) carried out in the absence of an alcohol source yielded poorly defined ε -PCL (PDI > 1.5) along with a low catalytic activity. In contrast, in the presence of BnOH, cations 3a⁺ and 3b⁺ were found to be highly active catalysts for the controlled and immortal ROP of ε -CL (Scheme 2). The ROP activity of cations 3a⁺ and 3b⁺ was first tested in solution (THF). These were both found to readily polymerize ε -CL (up to 1000 equiv.) within a few hours in the presence of BnOH and in THF (60 °C) to afford narrowly dispersed ε -PCL (PDI < 1.15) with an excellent chain length control of the resulting polymers: the $M_{n(corr)}$ values match well with those predicted from the initial



Scheme 2

monomer/alcohol ratios (entries 1–3, Table 1). The controlled character of these ROPs is further substantiated by an observed linear correlation between the $M_{n(corr)}$ values of the formed ε -PCL and monomer conversion (Fig. 1). Also, as expected, the formed ε -PCL contains a BnO group at the ester end, as deduced from MALDI-TOF data (see ESI[†]).

Additional polymerization studies in bulk conditions were then performed using the more active zinc cation $3a^+$ in the presence of BnOH. This cation proved to be highly active under the studied conditions (neat ϵ -CL, 60 °C) with the complete conversion to ϵ -PCL within 2 h of up to 5000 equiv. ϵ -CL (entry 5, Table 1). Remarkably, the poly(ε -caprolactone) produced under these conditions is narrowly disperse and with $M_{n(corr)}$ values in agreement with the calculated ones. On that matter, performing the ROP of cyclic esters/carbonates in bulk (vs. solution polymerization) typically results in a significant broadening of the produced materials due to detrimental chain transfer reactions taking place under such reaction conditions. In the present case, the presence of a substantial amount of an alcohol source, acting as a chain transfer agent, appears to be beneficial to the welldefined nature of the resulting ε -PCLs. Also, as shown in entry 6 of Table 1, a natural alcohol source such as (-)-menthol may well be used in these immortal ROP reactions with comparable catalytic activity, albeit with an increase of ε -PCL's PDI.

In preliminary studies intending to compare the catalytic performance of the present cationic zinc systems to that of related neutral analogues, the neutral Zn ethyl complex 4a, which is



Fig. 1 Dependence of M_n (•) and polydispersity index $[M_w/M_n$ (•)] of PCL on monomer (M) conversion for ε -CL polymerization using $3a^+$ in THF at 60 °C in the presence of BnOH: $3a^+/BnOH/[M]_0 = 1/3/300$ (M_n and PDI determined by GPC).

Table 1 Ring-opening polymerization of ε -CL by zinc cations $3a^+$, $3b^+$ and species $4a^a$

Entry	Initiator	Init./BnOH/ε-CL	Time (h)	Conv. ^b (%)	$M_{n(corr.)}^{c}$ (g mol ⁻¹)	$M_{\rm n(theo.)}^{d} ({\rm g \ mol}^{-1})$	PDI ^c
1	3a ⁺	1/3/300	2	90	11 500	11 400	1.08
2	3a ⁺	1/3/1000	6	91	35 250	34 580	1.13
3	$3b^+$	1/3/300	6	95	12 320	10 840	1.07
4	3a ⁺	$1/3/1500^{e}$	2	67	37 950	34 360	1.12
5	$3a^+$	$1/50/5000^{e}$	2	100	13 600	11 400	1.14
6	3a ⁺	$1/3/1500^{f}$	2	84	42 440	47 490	1.26
7	4a	$1/3/1500^{e}$	2	49	27 960	29 990	1.27

^{*a*} Conditions (unless specified otherwise): THF, M = monomer, $[M]_0 = 1$ M, 60 °C. ^{*b*} Determined by ¹H NMR spectroscopy. ^{*c*} Determined by gel permeation chromatography (GPC) with polystyrene standards (correcting factor = 0.56). ^{*d*} Calculated using the following formula M_n = conv. × $(M_0/I) \times (1/BnOH) \times 114.14$. ^{*e*} Bulk conditions (neat ε -CL, 60 °C). ^{*f*} (–)-Menthol was used as an alcohol source, bulk conditions (neat ε -CL, 60 °C).



Fig. 2 Molecular structure (ORTEP view) of the neutral Zn ethyl complex 4a. Selected bond distances (Å) and angles (°): Zn(1)-N(1) = 2.212(2), Zn(1)-N(2) = 1.876(2), Zn(1)-C(33) = 1.947(2), C(1)-N(1) = 1.278(2), C(12)-N(2) = 1.462(2), N(1)-Zn(1)-N(2) = 83.13(6), N(2)-Zn(1)-C(33) = 160.3(1), N(1)-Zn(1)-C(33) = 116.60(9).

supported by BIAN-derived amido-imino ligand, was prepared for subsequent use in ROP of ε -CL. Complex **4a**, readily prepared in good yield upon mixing BIAN-Mes with one equiv. of ZnEt₂ (toluene, room temp.), thus arises from the insertion of a BIAN-imine group into a Zn–Et bond (Scheme 3). Although never reported in BIAN/organozinc chemistry, a similar reactivity has been once observed with a related-diimine Zn dialkyl compound.⁹ The proposed formulation for complex **4a** was unambiguously established by single-crystal X-ray crystallography, confirming the formation of a three-coordinate Zn ethyl complex (Fig. 2). All bonding and geometrical parameters for **4a** are rather as expected, with a zinc metal centre adopting a distorted planar trigonal geometry.

Compound **4a** was found to exhibit a good activity in the bulk ROP of ε -CL, yet inferior to that of cation **3a**⁺ under identical conditions (entry 4 *vs.* entry 7, Table 1). In addition, this lower catalytic performance for **4a** comes along with a broader PDI (1.27) for the produced ε -PCL.

In conclusion, easily accessible cationic zinc alkyl species were found to be highly active in the ROP of ε -PCL in the presence of alcohol sources such as BnOH and (–)-menthol. Remarkably, these systems retain a high catalytic activity and an excellent chain length control (of the resulting material) under bulk polymerization conditions.

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