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# Metal-catalyzed immortal ring-opening polymerization of lactones, lactides and cyclic carbonates

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This Perspective article summarizes efforts paid in our group to develop efficient metal-based catalysts for the immortal ring-opening polymerization (iROP) of cyclic esters in the presence of large amounts of alcohols (ROH) as chain transfer agents. The catalyst systems reviewed include discrete organometallic complexes based on rare earths, magnesium, calcium and more specifically zinc, as well as simple systems employing metal triflate salts, notably Al(OTf)<sub>3</sub>, for the (stereo)controlled iROP of lactide (LA),  $\beta$ -butyrolactone (BBL) and trimethylenecarbonate (TMC). Special emphasis is given to systems that allow the use of minute amounts of metal catalysts and large loadings of both monomer and alcohol for the rapid and productive formation of functional polyesters (H–Pol–OR) with controlled molecular features.

## 1. Introduction

Linear aliphatic polyesters such as poly(hydroxyalkanoate)s (PHAs), poly(L-lactic acid) (PLLA) or poly(trimethylenecarbonate) (PTMC) have attracted the most attention over the past two decades as a class of materials with huge potential.<sup>1</sup> PLLA is notably produced as a commodity thermoplastic for the packaging industries and as biomaterial for pharmaceutical and medical uses,<sup>1,2</sup> via the ring-opening polymerization (ROP)

of L-lactide (L-LA, the cyclic dimer of lactic acid), a 100% bioresourced monomer produced by fermentation of sugars from various sources. In a context of recurring economical and societal issues associated with depletion of fossil feedstocks and severe accumulation in the environment of traditional polyolefinic plastics, the use of such renewable resources and the degradability of these polyester materials are of major interest.<sup>1d</sup>

ROP of lactones and related monomers is arguably the most efficient method to prepare such aliphatic polyester materials; it allows indeed a much higher degree of control in terms of molar weight and molar weight distribution ( $M_w/M_n$ ) than step-growth processes (*i.e.*, polycondensations).<sup>3,4</sup> Also, original polymer topologies are accessible, notably via stereocontrolled ROP of monomers that contain (pro)chiral centers.<sup>3</sup> This fine tailoring is essentially achievable with suitable initiators/catalysts that control the course of the ROP processes. The latter

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His current research interests lie in the organometallic chemistry of oxophilic elements and their use in catalysis for polymer materials and fine chemicals synthesis.

Jean-François Carpentier graduated from the Chemical Engineering School of Lille in 1989 and received his PhD in molecular catalysis from University of Lille in 1992. After a post-doctoral internship in CEA, Tours, he returned to Lille in 1993 to take up a CNRS position. In 1997, he spent one year as a research associate with Prof. Richard F. Jordan at the University of Iowa, Iowa City. In 2001, he moved to University of Rennes, promoted to full Profes-



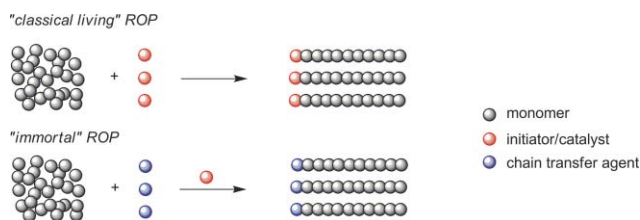
Sophie M. Guillaume

After a postdoctoral research on bimetallic uranium–rhenium hydride complexes with Dr M. Ephritikhine at the CEA-Saclay, France, Sophie then joined the CNRS in 1994 working on uranium and lanthanides chemistry centered on borohydride and cationic derivatives. In 2000, she became interested in polymer chemistry, joining the LCPO in Bordeaux, and recently the SCR in Rennes, developing new catalytic systems for the synthesis of biocompatible polymers from the ring-opening polymerization of bioresourced monomers.

Sophie M. Guillaume completed her PhD with Prof. J. T. Spencer at Syracuse University, N.Y., USA in 1992, in which she described the interactions of lanthanides with (car)boranes. After a postdoctoral research on bimetallic uranium–rhenium hydride complexes with Dr M. Ephritikhine at the CEA-Saclay, France, Sophie then joined the CNRS in 1994 working on uranium and lanthanides chemistry centered on borohydride and cationic derivatives. In 2000, she became interested in polymer chemistry, joining the LCPO in Bordeaux, and recently the SCR in Rennes, developing new catalytic systems for the synthesis of biocompatible polymers from the ring-opening polymerization of bioresourced monomers.

initiators/catalysts are also of primary importance to promote these reactions, that is, to activate the monomer. The driving force for polymerization in these processes lies in the relief of ring-strain and, accordingly, noticeable differences in reactivity are noted among this type of monomers depending on the nature of the cyclic ester. The development of highly active initiators/catalysts for more reluctant (stable) lactones is therefore mandatory.

ROP reactions promoted by organometallic complexes often proceed in a “living controlled” fashion.<sup>3a-g,4</sup> As depicted in Scheme 1, in such “classical living” ROP, there are (ideally) as many growing macromolecules as the total amount of active sites available from the catalyst molecule (therefore named “initiator”); that is, most usually only one time the amount of metallic equiv. introduced, and at most four times (*i.e.*, the largest oxidation state of the metals usually considered for such processes). This approach has inherent limitations and pitfalls: low catalytic productivity and potentially large contamination of the polymer with catalyst residues.



**Scheme 1** Illustration of the distinction between “classical living” and “immortal” ROP processes.<sup>5g</sup>

The so-called “immortal” ROP (hereafter referred to as “iROP”), initially named as such by Inoue,<sup>5</sup> provides an efficient alternative to “classical living” ROP. This process involves a bi-component system made of (i) a catalyst and (ii) an external nucleophile that acts simultaneously as the initiator and chain transfer agent (CTA) (*vide infra*). As shown in Scheme 1, the

number of growing polymer chains in an iROP exceeds the number of catalyst molecules (*e.g.*, a metallic species) used and is equal to the initial amount of CTA introduced. Hence, the process becomes “truly catalytic” with respect to both the monomer (as in a “classical living” ROP) and the polymer chains. In a general context of green and sustainable chemistry, the “catalytic” iROP strategy thus appears highly attractive, especially if performed in solvent-free conditions (bulk process).

iROP was pioneered with an Al-porphyrin alkoxide and an alcohol in the case of epoxides.<sup>5d</sup> With an excess of methanol, the authors observed the formation of polymers where the number of macromolecules coincided with the sum of the number of molecules of the metallic initiator plus those of methanol. Thereafter, other (pre)catalysts based on various metals (*e.g.*, Mg, Ca, Fe, Zn, Sn and rare earths, mainly Y) have been investigated for this process.<sup>6</sup> Organocatalysts as well have been shown to successfully fulfil such a function,<sup>3c,h,i</sup> but the current examples cannot achieve all performances of metal-based systems, in particular when stereocontrol is considered. As developed in more details in the subsequent sections, several key features are compulsory to achieve a successful controlled iROP: first, as for “classical living” ROP, initiation (*i.e.*, ring-opening of the first monomer unit) must proceed faster than propagation ( $k_i \gg k_p$ ) and irreversible termination reactions must be absent or very minimal; in addition, reversible transfer reactions must proceed faster than propagation ( $k_{tr} \gg k_p$ ), thereby offering narrow molar weight distributions.

Two mechanisms are involved in iROP promoted by metal catalyst systems. A system based on an organometallic catalyst of the type  $\{L\}M-Nu$ , in which Nu is a nucleophilic group capable to ring-open the heterocyclic monomer ( $Nu = \text{alkoxide, amido, borohydrido} \dots$ ), most usually involves a coordination-insertion mechanism (CIM). Such a mechanism is depicted Scheme 2. When using an alcohol in combination with a non-alkoxide pre-catalyst, a preliminary step consists in the *in situ* formation of the initiating alkoxide species upon alcoholysis of the  $\{L\}M-Nu$  bond. This newly formed  $\{L\}M-OR$  species undergoes coordination-insertion of the first monomer molecule leading to the propagating



**Yann Sarazin**

Research Fellow in the group of Prof. J.-F. Carpentier. His research interests include the preparation of neutral and cationic main-group complexes for catalytic applications.

Yann Sarazin gained his PhD in 2004 in the group of Prof. M. Bochmann, at the University of East Anglia (U.K.), in the field of polymerization catalysis. After a three-year post-doctoral fellowship in the same group where he studied the preparation of “naked” main-group metal cations, he returned to France in 2007 to join the team of Prof. Carpentier as a post-doctoral research fellow, and then entered the CNRS in late 2008 as a

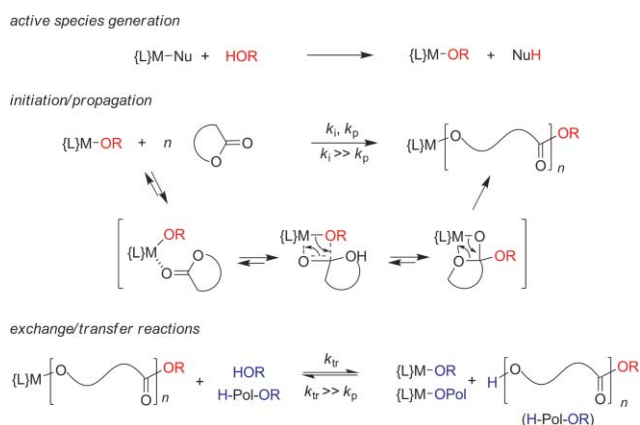


**Alexander Trifonov**

His research interests lie in the area of synthesis of organometallic and coordination compounds of rare earth metals and their application in homogeneous catalysis and material chemistry.

Alexander Trifonov received his PhD in 1989 from the Institute of Organometallic Chemistry of Russian Academy of Sciences in Nizhny Novgorod (with Prof. M. N. Bochkaev). He did postdoctoral studies in Berlin (Prof. H. Schumann, 1991), Orsay (Prof. H. Kagan, 1993–1995), and Mainz (Prof. J. Okuda 1999–2000). In 2004 he became head of the Coordination chemistry lab at IOC and was appointed in 2005 professor of chemistry at Nizhny

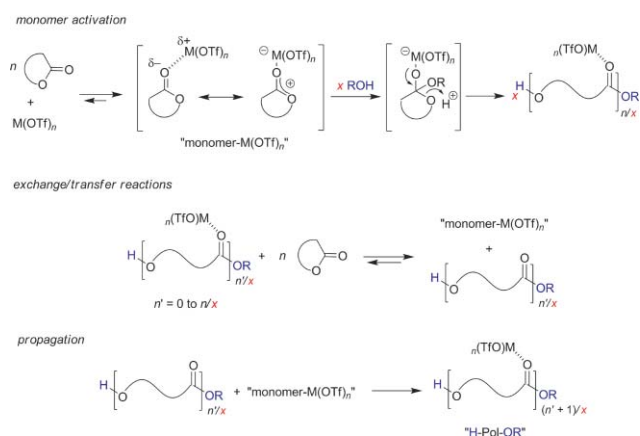




**Scheme 2** Representation of coordination-insertion mechanism (CIM) operative in the iROP of cyclic esters mediated by  $\{L\}M-Nu/ROH$  systems.

species  $\{L\}M-O-CH_2-CH_2-C(=O)OR$ . In this active species, the polymer chain undergoes rapid exchange with other protic species, initially CTA molecules introduced in excess in the reaction medium that rapidly convert to “dormant”  $\alpha$ -hydroxy,  $\omega$ -alkoxycarbonyl end-capped polyester chains (H-Pol-OR). Thus, species active for propagation for some time do reversibly convert back and forth to inactive ones. This rapid growing/dormant interconversion cycle goes on over the entire life-time of the polymerization process. Any active species bearing a  $\{L\}M-O(\text{alkoxide})$  bond can bring about the propagation and any HO-terminated (macro)molecule can behave as the CTA. While exchange between metal alkoxide species and alcohol is a usual acid-base process, its actual rapidity (as compared to propagation) is the decisive factor allowing control over the ROP. Finally, during the last termination step, deactivation of living  $\{L\}M-O-CH_2-CH_2-C(=O)OR$  species gives the H-Pol-OR macromolecules.

On the other hand, iROP systems based on simple Lewis acidic metal salts involve usually a so-called activated monomer mechanism (AMM). Such a process is depicted in Scheme 3 for a typical  $M(OTf)_n/ROH$  system (OTf = triflate). The Lewis acidic metal center first activates the monomer upon coordination to



**Scheme 3** Representation of activated monomer mechanism (AMM) operative in the iROP of cyclic esters mediated by  $M(OTf)_n/ROH$  systems.

its carbonyl oxygen. The external protic nucleophilic additive – commonly an alcohol ROH – then initiates the polymerization upon attack of the electrophilic carbon atom of the carbonyl group, which results in the ring-opening of the heterocycle *via* oxygen–acyl bond cleavage. The alcohol co-catalyst/CTA initially introduced (or any other protic source potentially present as impurity in the reagents, as for example water or triflic acid) and hydroxy end-capped macromolecules H-Pol-OR eventually produced during the process all play the role of the external nucleophile. These hydroxy end-capped (macro)molecules are involved in exchange and/or transfer reaction equilibria as “active” (*i.e.*, coordinated to the Lewis acidic metal center) and “dormant” (*i.e.*, metal-free) species. Again, as long as these transfer equilibria ( $k_{tr}$ ) are rapid enough compared to the initiation and subsequent propagation steps ( $k_{tr} \gg k_p$  and  $k_i \gg k_p$ ), the iROP remains controlled. This implies (notably but not exclusively) that all the aforementioned end-capped (macro)molecules exhibit the same reactivity, so that they are all progressively transformed into higher molar weight products by iterative incorporation of monomer units.

This AMM differs from the previous metal-based CIM in that the nucleophile is an external molecule, independent from the catalyst, while in CIM, the nucleophile is inherently included in the active catalyst as a  $\sigma$ -bonded alkoxide ligand, thus forming a two-in-one component catalyst. In both mechanisms, the alcohol ( $x$  equiv. introduced *vs.* catalyst) plays concomitantly two roles: first, one equivalent initiates the ROP, either as an external nucleophile in AMM or, if necessary (*i.e.*, when the pre-catalyst is not an alkoxide species), as an internal pro-nucleophile that transforms the catalyst precursor (an alkyl, amido, borohydride... derivative) upon alcoholysis into the  $\{L\}M-OR$  active species. Second, the remaining excess ( $x - 1$  equiv.) acts as CTA by generating  $x - 1$  polymer chains. Accordingly, in both AMM and CIM, the number-average molar weight is directly proportional to the monomer-to-alcohol (and other active chain transfer species eventually present in the reaction medium) ratio.

The main challenge in elaborating catalytic systems effective for iROP is the access to catalysts (initiators) that are inherently efficient for “classical living” ROP and that can in addition withstand large amounts of CTA, while still remaining highly active, productive and selective. When dealing with organometallic catalysis – one of the most performant to finely control ROP processes<sup>3</sup> – this often turns out to be a major problem. Indeed, these systems usually involve heteroleptic complexes based on highly acidic, oxophilic metal centers and a CTA protic reagent, typically an alcohol. Such combinations often lead to irreversible displacement of ancillaries from the metal centers (*e.g.*, *via* protonolysis/ $\sigma$ -bond metathesis pathways) and, as a consequence, to rapid loss of most/all catalytic performances (activity, control, selectivity...).

In our recent studies, we have extended the concept of “immortal” polymerization to new processes that allow ROPs to be successfully carried out with minimized amounts of a genuine catalytic system upon utilization of very large excesses of CTA. The main results achieved in the iROP of lactide (LA),  $\beta$ -butyrolactone (BBL) and trimethylenecarbonate (TMC) with a variety of metal catalysts are summarized and discussed hereafter.

## 2. Immortal stereoselective ring-opening polymerization of lactide and $\beta$ -butyrolactone promoted by group 3 metal complexes

Many group 3 metal and lanthanide-based complexes have been shown to be excellent initiators for the ROP of lactide.<sup>3,7</sup> These systems often feature living behaviors, producing PLAs with controlled molar weights and very narrow molar weight distributions. Also, some discrete heteroleptic complexes having bulky multidentate ligands have displayed excellent and often unique abilities to control the stereoselectivity for the ROP of *racemic*- and *meso*-lactide, leading to highly heterotactic and syndiotactic PLAs, respectively.

Our initial efforts in this field focused on group 3 metal complexes supported by tetradentate amino-alkoxy-bis(phenolate) ligands (Scheme 4).<sup>7,8</sup> Yttrium amido and alkoxide complexes of this class ( $\{\text{ONOO}^R\}\text{Y}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$  and  $\{\text{ONOO}^R\}\text{Y}(\text{OiPr})(\text{THF})$ , *in situ* generated) feature high activity and productivity for the classical ROP of *rac*-LA, converting thousands of monomer equiv. at room temperature within minutes. More, compounds having bulky *ortho*-substituents ( $\text{R}^1$ ) installed on the phenolate rings show very high levels of heterotacticity, as expressed by the probability of *racemic* linkage of two monomer units,  $P_r$  ( $P_r = 0.80$  for  $\text{R}^1 = t\text{Bu}$ , 0.90 for  $\text{CMe}_2\text{Ph}$ , 0.95 for  $\text{CMe}_2t\text{Bu}$ ).<sup>8</sup>



**Scheme 4** Stereospecific iROP of *rac*-lactide with  $\{\text{ONOO}^R\}\text{Y}[\text{N}(\text{SiHMe}_2)_2](\text{THF})/\text{ROH}$  systems.<sup>8,9</sup>

Remarkably, when such complexes were used with an excess of isopropanol, they featured an “immortal character”, leading to PLAs with narrow molar weight distributions and  $M_n$  values inversely proportional to the quantity of added isopropanol.<sup>9</sup> Increasing the contents of isopropanol did not affect significantly either the polymerization rate or the selectivity (Table 1). These

iROP reactions were readily achieved with up to 1000 equiv. of *rac*-LA and up to 50 equiv. of *i*PrOH resulting in a low polydispersed PLA with a  $M_n$  of only 1/50 of that with one equivalent of isopropanol. Also, the latter alcohol could be equally substituted by allylic alcohol, giving allyl end-capped heterotactic PLAs prone to subsequent functionalization (Table 1). End-group analysis of these PLA oligomers by  $^1\text{H}$  NMR and by MALDI-ToF-MS showed that the polymer chains were systematically end-capped with isopropyl ester and hydroxy groups; no cyclic oligomer was detectable. This constituted the first example of iROP of high loadings of *rac*-lactide, leading to the formation of highly heterotactic PLA. Such stereoselectivity is achieved thanks to the bulky  $\{\text{ONOO}^R\}^{2-}$  ligand which, in addition, offers unique capabilities for stabilizing the highly oxophilic and electrophilic metal center in presence of large amounts of alcohol.

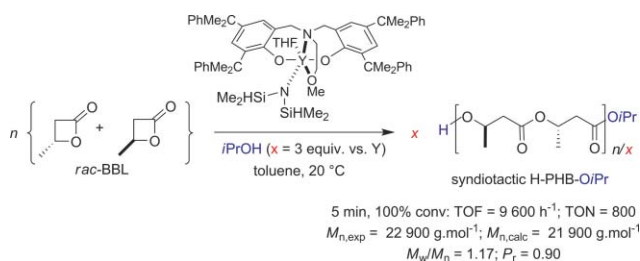
In this respect, another remarkable peculiarity of the  $\{\text{ONOO}^R\}\text{Y}$  complexes is their capability to effect highly stereoselective living ROP of *racemic*  $\beta$ -butyrolactone (*rac*-BBL) for the preparation of syndiotactic poly(3-hydroxybutyrate) (PHB).<sup>7,10</sup> One distinctive feature of the four-membered lactone BBL is its rather defiant ability to undergo ROP as compared to lactide or larger ring lactones.<sup>3</sup> Besides, efficient purification represents another difficulty associated with BBL that often prevents the achievement of high catalytic productivity in ROP reactions. Only modest success has been met when trying to expand to iROP the “classical living” ROP of *rac*-BBL with  $\{\text{ONOO}^R\}\text{Y}$  complexes. A reaction with 800 equiv. of monomer and 3 equiv. of *i*PrOH (vs. Y) was successfully conducted, offering a syndiotactic PHB with narrow molar weight distribution and an experimental molar weight close to that calculated (Scheme 5).<sup>9</sup> However, addition of more than 5 equiv. of alcohol systematically resulted in a dramatic drop of the catalytic activity, a phenomenon we could not rationalize thus far.

We also explored new bis(guanidinate) alkoxide group 3 metal complexes of the type  $[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2]_2\text{Ln}(\text{OR})$  ( $\text{OR} = \text{OtBu}$ ,  $\text{OiPr}$ ;  $\text{Ln} = \text{Y}$ ,  $\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Lu}$ ) for the “classical living” and “immortal” ROP of such cyclic esters.<sup>11</sup> A unique feature of these compounds lies in the fact that they promote the syndiospecific ROP of *rac*-BBL ( $P_r$  up to 0.84), while they are surprisingly non-stereoselective for the ROP of *rac*-LA under strictly similar conditions. Some of these compounds appeared well suited to achieve iROP of LA.<sup>11</sup>  $[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2]_2\text{Nd}(\text{OtBu})$ , which showed high initiation efficiency and good productivity for the living ROP of LA, proved able to convert quantitatively 500 equiv.

**Table 1** Selected data for the iROP of *rac*-lactide promoted by  $\{\text{ONOO}^R\}\text{Y}[\text{N}(\text{SiHMe}_2)_2](\text{THF})/\text{ROH}$  systems<sup>a,9</sup>

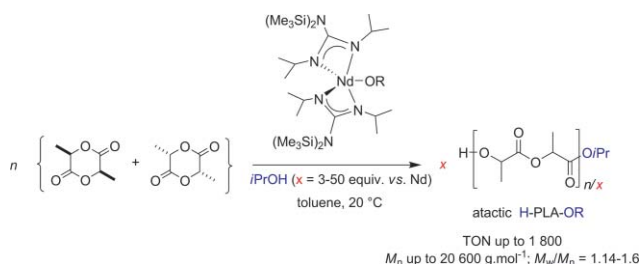
Entry	Complex (R substituent)	ROH	[LA]/[Y]/[ROH]	Time <sup>b</sup> /min	$M_{n,\text{calc}}^c/\text{g mol}^{-1}$	$M_{n,\text{SEC}}^d/\text{g mol}^{-1}$	$M_w/M_n^d$	$P_r^e$
1	<i>t</i> Bu	<i>i</i> PrOH	1000/1/4	40	36 000	37 900	1.13	0.80
2	<i>t</i> Bu	<i>i</i> PrOH	1000/1/50	40	2880	3900	1.08	0.80
3	$\text{CMe}_2\text{Ph}$	<i>i</i> PrOH	1000/1/1	360	144 000	160 000	1.13	0.90
4	$\text{CMe}_2\text{Ph}$	<i>i</i> PrOH	1000/1/2	360	72 000	71 000	1.13	0.90
5	$\text{CMe}_2\text{Ph}$	<i>i</i> PrOH	1000/1/4	360	36 000	35 000	1.08	0.90
6	$\text{CMe}_2\text{Ph}$	<i>i</i> PrOH	1000/1/10	360	14 400	20 100	1.07	0.90
7	$\text{CMe}_2\text{Ph}$	<i>i</i> PrOH	1000/1/20	360	7200	6600	1.16	0.90
8	<i>t</i> Bu	allylOH	75/1/10	15	1080	1600	1.16	0.80

<sup>a</sup> All reactions performed at 20 °C in THF with  $[\text{rac-LA}] = 0.44 \text{ M}$  until completion. <sup>b</sup> Unoptimized reaction times. <sup>c</sup> Calculated from  $[\text{LA}]_0/[\text{ROH}]_0 \times \text{monomer conversion} \times M_{\text{LA}} + M_{\text{ROH}}$ , with  $M_{\text{LA}} = 144 \text{ g mol}^{-1}$ . <sup>d</sup> Determined by SEC vs. polystyrene standards and corrected by a factor of 0.58. <sup>e</sup> Probability of *racemic* linkages between monomer units, determined by NMR.



**Scheme 5** Syndiospecific iROP of *rac*-β-butyrolactone with the  $\{ \text{ONOO}^{\text{CMe}_2\text{Ph}} \} \text{Y}[\text{N}(\text{SiHMe}_2)_2](\text{THF})/\text{iPrOH}$  system.<sup>9</sup>

of LA (vs. Nd) with up to 50 equiv. of isopropanol as CTA (Scheme 6). High productivity up to 1800 mol(LA)/mol(Nd) was achieved with a LA-to-initiator ratio up to 2000, still using 50 equiv. of CTA, to give PLAs with relatively narrow molar weight distributions and an excellent agreement between the experimental and calculated  $M_n$  values. However, poor conversion was observed when using larger amounts of LA (5000 equiv.), likely reflecting the sensitivity of the catalyst at such a high monomer loading. Nevertheless, these performances in terms of productivity and chain transfer efficiency are among the best thus far reported for the iROP of lactide with group 3 metal- and lanthanide-based initiators.



**Scheme 6** iROP of *rac*-lactide with the  $[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2]_2\text{-Nd}(\text{ORBu})/\text{iPrOH}$  system.<sup>11</sup>

As observed for systems based on bis(phenolate)  $\{ \text{ONOO}^{\text{R}} \} \text{Y}$  complexes (*vide supra*), attempts to perform iROP of *rac*-BBL with the related  $[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}i\text{Pr})_2]_2\text{Y}(\text{OiPr})/\text{iPrOH}$  (3 equiv.) system resulted in a significant decrease of activity as compared to the corresponding living ROP experiment (26% vs. 60% conv. in 8 h, respectively).<sup>11</sup>

iROP of *rac*-LA appeared feasible with other discrete group 3 metal complexes we prepared. Thus, the *tert*-butoxide yttrium complex  $\{ \text{DAB} \} \text{Y}(\text{OtBu})(\text{THF})(\text{DME})$  supported by a bulky enediamido dianionic ligand ( $\text{DAB}^{2-} = (2,6\text{-C}_6\text{H}_3i\text{Pr}_2)\text{NC}(\text{Me})=\text{C}(\text{Me})\text{N}(2,6\text{-C}_6\text{H}_3i\text{Pr}_2)^{2-}$ ) converts quantitatively 500 equiv. of *rac*-LA with up to 50 equiv. of isopropanol as CTA.<sup>12</sup> The good productivity of these catalyst systems was evidenced with experiments performed using up to 2000 equiv. of LA with 5 equiv. of *iPrOH*. High conversions and atactic PLAs with relatively narrow distributions ( $M_w/M_n < 1.5$ ) and  $M_n$  values linearly decreasing with increasing amounts of CTA were obtained. The overall chain transfer efficiency with these  $\{ \text{DAB} \} \text{Y}$  complexes was almost as good as that of the Y-alkoxide complexes supported by guanidinate ligands mentioned above. Also, the rare lactate yttrium complex supported by a tetradentate

fluorinated dialkoxy-diimino ligand,  $\{ [\text{ON}^{\text{Et}}\text{NO}^{\text{CF}_3}] \} \text{Y}((R)\text{-}t\text{Bu-lactate})_2$  readily supported the presence of 5 equiv. of *iPrOH*, allowing a controlled iROP of *rac*-LA/L-LA.<sup>13</sup> Yet, this system remains to be further investigated.

### 3. Immortal ring-opening polymerization of lactide promoted by zinc-based and related group 2 metal divalent complexes

Although intrinsically less active than the more oxophilic and electrophilic lanthanide-based complexes, zinc initiators are far more robust and therefore more likely to resist in the presence of protic impurities or the large excess of protic CTA required for any iROP process. Many Zn initiators have been successfully developed for the living ROP of LA.<sup>3a-g</sup> Two notable families of heteroleptic zinc complexes are those described by Hillmyer and Tolman where the metal is stabilized by bulky phenolate-based ancillary ligands, and by Coates who has pioneered the use of bulky β-diketiminate (BDI) bidentate ligands. While the former displayed unprecedented activities for the non-stereocontrolled living ROP of *rac*-LA,<sup>14</sup> the latter complexes not only proved remarkably active for the stereocontrolled ROP of *rac*-LA (enabling the formation of heterotactic-enriched PLA),<sup>4h,i</sup> but were also capable of promoting the ROP of *rac*-BBL to yield PHBs (albeit without control over the stereochemistry).<sup>4j</sup> However, prior to our efforts in this area, no effective system employing a well-defined zinc catalyst was known for the iROP of lactide.<sup>15</sup>

The same is equally true of the related calcium-based initiators: although a handful of ROP initiators built around this very large and oxophilic element have now been disclosed,<sup>3a,d,g,16,17</sup> the extreme sensitivity of these complexes had until very recently precluded their use for iROP of cyclic esters, most probably because they decompose in the presence of a large excess of CTA and/or monomer. The situation for Mg-based initiators is somewhat intermediary between those of Zn and Ca. Among the various Mg initiators synthesized over the past decade,<sup>3a,d,g,16a-b,18</sup> Lin *et al.* demonstrated that  $\{ [\text{phenoxy-sulfonato}] \} \text{Mg}(\text{OBn})$  compounds could withstand the addition of up to 20 equiv. of alcohol to catalyze the iROP of LA,<sup>19</sup> even if the authors seemed unable to use larger quantities of CTA.

Our interest in the use of such Zn, Mg and Ca-based catalysts was triggered by the development of systems capable of promoting iROP of large amounts of LA (L- or *rac*-isomers) with a functional CTA in styrene (S) solutions. The aim was to explore industrially viable procedures towards poly(LA-*b*-S) diblock copolymers.<sup>20</sup> To achieve this goal, a preliminary step consisted in modeling the catalytic, large-scale production of PLA chains capped by end-groups suitable for the subsequent free radical polymerization of styrene (Scheme 7).

Detailed studies for the iROP of both *rac*- and L-LA in styrene were performed with catalyst/TEMPO-OH systems, based on simple homoleptic precursors  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ ,  $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ ,  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$  and the discrete complex  $\{ \text{BDI}^{\text{iPr}} \} \text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>4h,i</sup> As indicated by selected data gathered in Table 2, all constituted selective catalysts; *i.e.*, they were fully inert towards styrene but efficiently promoted the iROP of LA. While all were effective at low monomer loadings (< 500 equiv. vs. metal), it quickly became apparent that the sensitivity of

**Table 2** Selected data for the iROP of LA in styrene using different amido complex/TEMPO-OH systems<sup>20</sup>

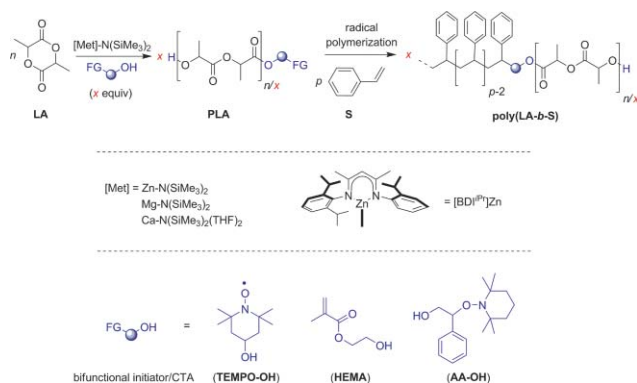
Entry	Complex	LA	[LA] <sub>0</sub> /[Met] <sub>0</sub> /[TEMPO-OH] <sub>0</sub>	Temp. <sup>a</sup> /°C	Time <sup>a</sup> /min	Yield <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> /g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> /g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>	TOF <sup>e</sup> /h <sup>-1</sup>
1	Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	<i>rac</i>	2000/1/20	50	90	100	14 570	12 800	1.21	1 333
2	Mg[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	<i>rac</i>	2000/1/20	50	90	20	3 050	2 900	1.17	267
3	Ca[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (THF) <sub>2</sub>	<i>rac</i>	2000/1/20	50	90	59	8 670	8 100	1.13	787
4	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	<i>rac</i>	2000/1/20	50	90	100	14 570	12 200	1.09	1 333
5	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	<i>rac</i>	5000/1/10	80	90	100	72 170	40 700	1.40	3 333
6	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	L-	500/1/10	100	3	100	7 370	5 900	1.07	10 000
7	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	L-	20 000/1/100	100	900	91	26 380	36 800	1.27	1 213

<sup>a</sup> Reaction times not necessarily optimized. <sup>b</sup> Isolated yield following re-precipitation. <sup>c</sup> Calculated from [LA]<sub>0</sub>/[TEMPO-OH]<sub>0</sub> × monomer conversion × *M*<sub>LA</sub> + *M*<sub>TEMPO-OH</sub>, with *M*<sub>LA</sub> = 144 g mol<sup>-1</sup> and *M*<sub>TEMPO-OH</sub> = 172 g mol<sup>-1</sup>. <sup>d</sup> Determined by SEC vs. polystyrene standards and corrected by a factor of 0.58. <sup>e</sup> Non-optimized turnover frequency expressed in mol(LA) mol(Zn)<sup>-1</sup> h<sup>-1</sup>.

**Table 3** Selected data for the iROP of L-LA in styrene promoted with {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/ROH<sup>a,20</sup>

Entry	ROH	Yield <sup>b</sup> (%)	<i>M</i> <sub>n,theo</sub> <sup>c</sup> /g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> /g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>
1	TEMPO-OH	97	28 110	25 900	1.20
2	HEMA	99	28 640	27 500	1.20
3	AA-OH	99	28 790	27 200	1.19

<sup>a</sup> Polymerizations carried out in styrene with [L-LA]<sub>0</sub> = 4.0 M, [Zn]<sub>0</sub> = 0.8 mM, [L-LA]<sub>0</sub>/[Zn]<sub>0</sub>/[ROH]<sub>0</sub> = 5000/1/25, *T* = 100 °C, *t* = 90 min. <sup>b</sup> See Table 2. <sup>c</sup> See Table 2. <sup>d</sup> See Table 2.

**Scheme 7** iROP of lactides with metal-amide/ROH systems.

Mg- and Ca-based complexes impeded their use for the catalytic conversion of large quantities of monomer (2000 equiv., entries 2 and 3). The limitations of Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> were only evident at higher monomer loadings (5000 equiv.), where, as anticipated, only the sterically shielded {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>] was truly effective (entry 5). Besides, it is worth mentioning that the results obtained with {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/TEMPO-OH represented the first occurrence of a catalyst for the stereocontrolled iROP of *rac*-LA to give heterotactic-enriched PLA. This particular catalyst system proved truly remarkable, allowing the near-quantitative conversion of up to 20 000 equiv. of L-LA in the presence of as many as 100 equiv. of CTA (entry 7). Kinetic investigations revealed an activation energy of 33.1 kJ mol<sup>-1</sup>,<sup>20</sup> comparable to that reported by Coates *et al.* for the living ROP of *rac*-LA in CH<sub>2</sub>Cl<sub>2</sub> initiated by {BDI<sup>IPr</sup>}Zn(OiPr).<sup>4h,i</sup>

TEMPO-OH was used as the prototypical bi-functional CTA, owing to its commercial availability and ease of purification. The

catalytic approach was next extended to 2-hydroxyethyl methacrylate (HEMA) and 1-hydroxy-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane<sup>21</sup> (AA-OH) (Scheme 7), which equally showed excellent abilities as CTA for the iROP of 5000 equiv. of L-LA in styrene (Table 3). The controlled and immortal nature of these catalytic processes was systematically confirmed by good agreement between theoretical and experimental molar weights, narrow polydispersity indexes and end-group analyses (NMR, MALDI-ToF-MS) of these functionalized PLAs.

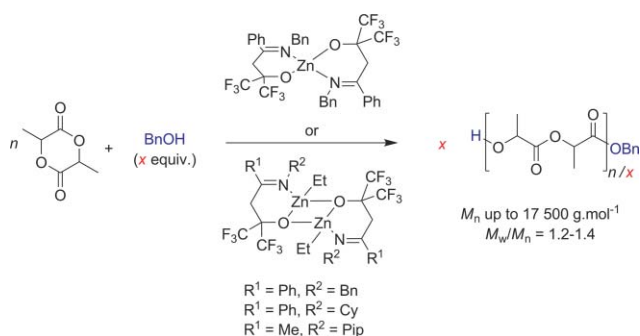
Parallel to this work, we set out on the development of a broader range of complexes of divalent main-group metals that we could use for the above and related purposes. We developed new ligands based on oxygen-containing alkoxides and phenoxides, with the rationale that they would constitute better candidates for the stabilization of Zn- or alkaline earth (Ae)-based initiators. While phenoxides often lead to mononuclear compounds, alkoxides often produce highly aggregated polynuclear species, due to the high bridging tendency of the relatively more basic alkoxide ligands. The use of fluorinated tertiary alkoxide ligands has proven to be a valuable strategy to overcome this drawback.<sup>22</sup> Electron-withdrawing CF<sub>3</sub> groups α- to the alkoxide generate intra- and inter-molecular repulsions, as well as a less basic alkoxide O-atom; as a result, a generally reduced bridging tendency is observed. Following this line, we have described some new bi- and tetradentate fluorinated dialkoxide-diamino, fluorinated (di)alkoxide-(di)imino that are effective for the preparation of discrete complexes of Y, La, Zr, and Al, and in turn developing valuable applications in the field of polymerization catalysis.<sup>22,23</sup>

We have recently extended this work to the preparation of a broad range of homo- and heteroleptic complexes of zinc stabilized by fluorinated imino-alkoxide {ON<sup>R1,R2</sup>}<sup>-</sup> ligands.<sup>24</sup> Heteroleptic complexes of the type {ON<sup>R1,R2</sup>}ZnEt were prepared, although the stability of such species towards detrimental ligand



redistribution reactions appeared to be strongly governed by the nature of the ligand around the metal center. For instance, while  $\{\text{ON}^{\text{Ph,Bn}}\}\text{ZnEt}$ ,  $\{\text{ON}^{\text{Ph,Cy}}\}\text{ZnEt}$  and  $\{\text{ON}^{\text{Mc,Pip}}\}\text{ZnEt}$  (Bn = benzyl; Cy = cyclohexyl; Pip = *N*-benzylpiperidinyl) were all kinetically stable,  $\{\text{ON}^{\text{Mc,Ph}}\}\text{ZnEt}$  (with a less electron-donating group on the imino N atom) could not be isolated. Also, all attempts to isolate alkoxide derivatives of the type  $\{\text{ON}^{\text{R}1,\text{R}2}\}\text{Zn}(\text{OiPr})$  were thwarted by disproportionation reactions, even if it was possible to visualize spectroscopically by NMR in  $\text{C}_6\text{D}_6$  these transient species.

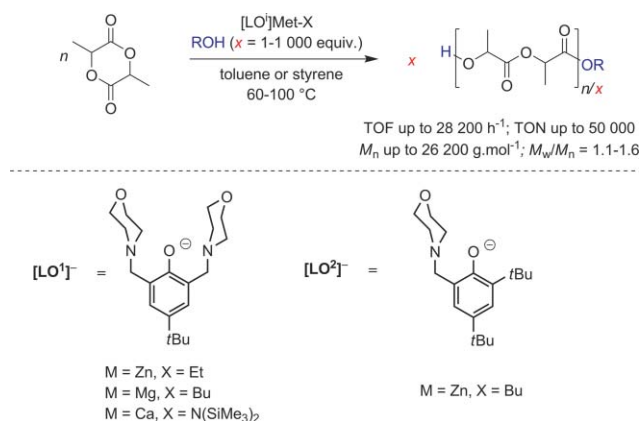
Compounds  $\{\text{ON}^{\text{R}1,\text{R}2}\}\text{ZnEt}$  and  $\{\text{ON}^{\text{Ph,Bn}}\}_2\text{Zn}$  were used in combination with BnOH for the (i)ROP of *rac*-LA (Scheme 8).<sup>24</sup> Although slow at 50 °C when used with 1 equiv. of alcohol, they all converted 100–250 equiv. of monomer in a controlled, albeit non-stereoselective, fashion. Analyses were consistent with a CIM in the cases of the heteroleptic complexes  $\{\text{ON}^{\text{R}1,\text{R}2}\}\text{ZnEt}$ , although obviously in the case of the homoleptic  $\{\text{ON}^{\text{Ph,Bn}}\}_2\text{Zn}$ , its inertness towards BnOH (as monitored by NMR spectroscopy) and its lower activity were consistent with an AMM. Addition of excess BnOH (2.5–5 equiv.) to  $\{\text{ON}^{\text{Ph,Bn}}\}\text{ZnEt}$  yielded a system still capable of promoting the controlled iROP of *rac*-LA, highlighting the suitability of the fluorinated alkoxide  $\{\text{ON}^{\text{R}1,\text{R}2}\}^-$  ligands to generate Zn-based catalysts capable of coping with the presence of excess alcohol CTA.



**Scheme 8** iROP of *rac*-lactide with  $\{\text{ON}^{\text{R}1,\text{R}2}\}\text{-Zn/ROH}$  systems.<sup>24</sup>

In our recent investigations on mono-anionic multidentate phenoxide-based  $\{\text{LO}\}^-$  ligands for the stabilization of  $\{\text{LO}\}\text{M-X}$  complexes ( $\text{M} = \text{Zn}, \text{Mg}, \text{Ca}$ ), we have just shown that the 4-*tert*-butyl-2,6-*bis*(morpholinomethyl)phenoxy pro-ligand ( $\{\text{LO}^1\}^-$ ) enabled the isolation of the stable heteroleptic  $\{\text{LO}^1\}\text{ZnEt}$ ,  $\{\text{LO}^1\}\text{Mg}(\text{nBu})$  and  $\{\text{LO}^1\}\text{Ca}[\text{N}(\text{SiMe}_3)_2]$  (Scheme 9).<sup>17</sup> Upon treatment with 10 equiv. of *i*PrOH, the Ca derivative yielded cleanly  $\{\text{LO}^1\}\text{Ca}(\text{OiPr})$ , and no sign of decomposition could be detected; identical observations were made by NMR monitoring of  $\{\text{LO}^1\}\text{ZnEt}/i\text{PrOH}$ . The related complex  $\{\text{LO}^2\}\text{ZnEt}$  ( $\{\text{LO}^2\}^- = 2,4\text{-di-tert-butyl-6-(morpholinomethyl)phenoxy}$ ) was also readily prepared, although attempts to isolate  $\{\text{LO}^2\}\text{MgX}$  and  $\{\text{LO}^2\}\text{CaX}$  derivatives have so far been unsuccessful.

Comprehensive studies of the iROP of *L*-LA in toluene at 60 °C catalyzed by these complexes in association with *i*PrOH were conducted (Table 4).<sup>17</sup> For all these binary systems, the excellent agreement between experimental and theoretical molar weights and narrow polydispersities indicated that the iROP proceeded in a well-controlled fashion. The Mg and Ca complexes provided highly active catalysts upon addition of up to 10–50 equiv. of CTA, converting 500–2 500 equiv. of monomer within minutes (entries



**Scheme 9** iROP of lactide with phenoxide complexes/ROH systems.<sup>17,26</sup>

1–2). These binary systems exhibited unprecedented activities; in particular, the calcium derivative allowed the nearly complete conversion of 500 equiv. in as little as 1 min, with a corresponding TOF value over 28 000  $\text{h}^{-1}$ . Despite this catalytic efficacy, these two systems showed their limitations at higher alcohol and/or monomer loadings, as their TOFs dropped severely in the presence of 100 (or more) equiv. of *i*PrOH and/or 5 000 equiv. of *L*-LA.

Expectedly,  $\{\text{LO}^1\}\text{ZnEt}$  and  $\{\text{LO}^2\}\text{ZnEt}$  were less active (as compared to their Ca and Mg congeners) by *ca.* one order of magnitude, but proved truly unique in their ability to convert in a controlled fashion very large amounts of monomer (up to 50 000 equiv., *i.e.*, as low as 20 ppm of Zn, entry 10) in the presence of as much as 1 000 equiv. of CTA (entry 9). The presence of alcohol (1 or more equiv.) was mandatory to generate an efficient catalytic system (entries 3 vs. 4) for a rapid and *controlled* polymerization. Comparative experiments (entries 5–8) deliberately run to limited conversion with  $\text{ZnEt}_2$ ,  $\{\text{BDI}^{\text{iPr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ ,  $\{\text{LO}^1\}\text{ZnEt}$  and  $\{\text{LO}^2\}\text{ZnEt}$  showed that  $\{\text{LO}^1\}\text{ZnEt}$ , where the metal center is surrounded by two morpholine side-arms, was the most active of its class,<sup>25</sup> while  $\{\text{LO}^2\}\text{ZnEt}$  was noticeably less active. Slower kinetics in this latter case most probably resulted from catalyst decomposition under such extreme monomer and CTA loadings, highlighting the importance of the presence of two protecting arms in  $\{\text{LO}^1\}\text{ZnEt}$  as opposed to a single one as in the more sensitive  $\{\text{LO}^2\}\text{ZnEt}$ . In relation to the aforementioned studies regarding the iROP of LA in styrene, the potential of these binary catalysts was illustrated by the suitability of the  $\{\text{LO}^1\}\text{ZnEt}/\text{TEMPO-OH}$  system to promote in a controlled fashion the iROP of 1000 equiv. of *L*-LA in styrene upon addition of 10 equiv. of CTA (Table 4, entry 11).<sup>26</sup>

#### 4. Immortal ring-opening polymerization of $\beta$ -butyrolactone promoted by zinc-based and related group 2 metal divalent complexes

Simple alkyl- and amido- homoleptic zinc derivatives have been evaluated in association with an alcohol for the ROP of *rac*-BBL.<sup>27</sup> In the presence of BnOH, we found that  $\text{ZnEt}_2$  gives atactic PHBs, however with poor reproducibility and low conversion (Table 5, entry 1).<sup>28</sup> Similar atactic PHBs oligomers were prepared with limited success *via* iROP of *rac*-BBL from  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]$  (entries 2, 3).

**Table 4** Selected data for the iROP of L-LA using various metal complex/*i*PrOH systems<sup>a, 17,26</sup>

Entry	Complex	[L-LA] <sub>0</sub> /[Met] <sub>0</sub> / [ <i>i</i> PrOH] <sub>0</sub>	[L-LA] <sub>0</sub> / mol L <sup>-1</sup>	Time/min	Yield <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>	TOF <sup>e</sup> /h <sup>-1</sup>
1	{LO <sup>1</sup> }Mg( <i>n</i> Bu)	1000/1/10	2.0	6	96	13 900	13 100	1.14	9 600
2	{LO <sup>1</sup> }Ca[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	500/1/10	2.0	1	94	6 800	6 500	1.27	28 200
3	{LO <sup>1</sup> }ZnEt	1000/1/-	2.0	60	18	26 000	10 300	2.2	180
4	{LO <sup>1</sup> }ZnEt	1000/1/10	2.0	60	97	14 000	15 100	1.10	970
5	ZnEt <sub>2</sub>	20 000/1/250	6.0	80	11	1 300	1 600	1.09	1 650
6	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	20 000/1/250	6.0	80	65	7 500	6 700	1.10	9 770
7	{LO <sup>2</sup> }ZnEt	20 000/1/250	6.0	80	47	5 500	4 700	1.08	7 070
8	{LO <sup>1</sup> }ZnEt	20 000/1/250	6.0	80	74	8 600	8 900	1.16	11 130
9	{LO <sup>1</sup> }ZnEt	20 000/1/1000	6.0	180	99	2 900	2 400	1.33	6 600
10	{LO <sup>1</sup> }ZnEt	50 000/1/500	6.0	16 × 60	100	14 500	13 500	1.60	3 125
11 <sup>f</sup>	{LO <sup>1</sup> }ZnEt	1000/1/10	2.0	15	97	14 140	13 700	1.30	3 880

<sup>a</sup> Polymerizations performed in toluene at 60 °C. <sup>b</sup> See Table 2. <sup>c</sup> See Table 2. <sup>d</sup> See Table 2. <sup>e</sup> See Table 2. <sup>f</sup> Polymerization run in styrene at 100 °C using TEMPO-OH as CTA.

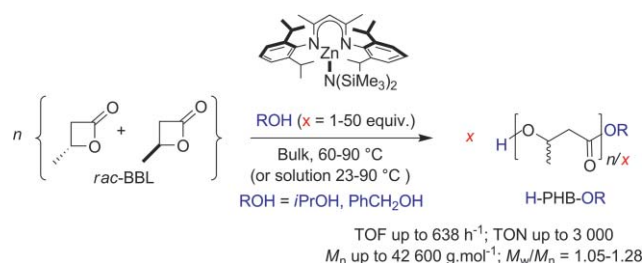
**Table 5** Selected data for the bulk iROP of BBL using zinc complex/BnOH systems<sup>27,28</sup>

Entry	Complex	[BBL] <sub>0</sub> /[Met] <sub>0</sub> / [ <i>i</i> PrOH] <sub>0</sub>	Solvent	Temp./ °C	Time <sup>a</sup> / min	Conv. <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>	TOF <sup>e</sup> /h <sup>-1</sup>
1	ZnEt <sub>2</sub>	100/1/2	Toluene	60	120	50	2260	3000	1.14	25
2	Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	100/1/2	Toluene	60	120	75	3330	3700	1.30	38
3	Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	100/1/5	Toluene	60	120	79	1470	1800	1.27	40
4	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	500/1/5	Bulk	60	40	85	7420	7900	1.06	638
5	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	500/1/10	Bulk	60	60	73	3300	4800	1.05	368
6	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	1000/1/50	Bulk	90	180	97	1800	1500	1.12	323
7	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	2000/1/200	Bulk	90	360	19	200	—	—	63
8	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	5000/1/50	Bulk	90	900	60	5200	5700	1.04	20
9	{BDI <sup>IPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	10 000/1/10	Bulk	90	4620	21	18 200	21 000	1.10	27
10	{LO <sup>1</sup> }ZnEt/ <i>i</i> PrOH	500/1/10	Bulk	60	180	95	4140	4300	1.07	158

<sup>a</sup> Reaction times not necessarily optimized. <sup>b</sup> Monomer conversion determined by <sup>1</sup>H NMR. <sup>c</sup> Calculated from [BBL]<sub>0</sub>/[BnOH]<sub>0</sub> × monomer conversion × *M*<sub>BBL</sub> + *M*<sub>BnOH</sub>, with *M*<sub>BBL</sub> = 86 g mol<sup>-1</sup> and *M*<sub>BnOH</sub> = 108 g mol<sup>-1</sup>. <sup>d</sup> Determined by SEC vs. polystyrene standards (uncorrected value). <sup>e</sup> Non-optimized turnover frequency expressed in mol(BBL).mol(Metal)<sup>-1</sup>.h<sup>-1</sup>.

All these catalytic systems remained much less efficient than those based on {BDI<sup>IPr</sup>}Zn complexes, and they were definitively less active towards the iROP of BBL in comparison with that of TMC (Table 6, *vide infra*).<sup>29</sup>

As demonstrated by Coates, the alkoxide complex {BDI<sup>IPr</sup>}Zn(O*i*Pr) efficiently enables the controlled living classical ROP of *rac*-BBL, affording high molar weight atactic PHBs (*M*<sub>n</sub> up to 28 000 g mol<sup>-1</sup>; *M*<sub>w</sub>/*M*<sub>n</sub> = 1.14–1.20) with high reaction rates,<sup>4j</sup> and with high efficiencies similar to those observed for the living heterospecific ROP of *rac*-LA.<sup>4h,i</sup> Our evaluation of the binary catalytic systems composed of the corresponding amido precursor, {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>], combined to an alcohol (typically BnOH) as CTA, revealed a rather high efficiency for both the solution and bulk iROP of *rac*-BBL (Scheme 10) (Table 5, entries 4–9).<sup>27</sup> These polymerizations proceeded smoothly under mild operating conditions (60–90 °C) to produce atactic PHBs with controlled, moderate to high molar weights (*M*<sub>n</sub> up to *ca.* 21 000 g mol<sup>-1</sup>). The highest productivity (TON<sub>max</sub> = 3 000 within 15 h) was achieved at 90 °C (entry 9). In comparison to {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/BnOH, the {LO<sup>1</sup>}ZnEt/*i*PrOH system proved somewhat less active for the bulk iROP of BBL performed at 60 °C, but afforded a similarly good control over the polymerization (entry 10).<sup>17</sup> Following such “immortal” procedures, PHBs could be prepared for the first time from low loadings of a metallic catalyst (down to 100 ppm), allowing the



**Scheme 10** iROP of *rac*-β-butyrolactone with {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/ROH system.<sup>27</sup>

growth of as many as 50–200 PHB chains per metal center. Other significant advantages over previous procedures include a lower reaction times and solvent-free processes.

## 5. Immortal ring-opening polymerization of trimethylene carbonate promoted by zinc-based and related group 2, 3 and 8 metal complexes

Using the simple, readily available ZnEt<sub>2</sub> with BnOH as co-activator and CTA, the bulk iROP of TMC proceeds under mild conditions in a fairly well controlled manner (Table 6, entries 1–4).<sup>29a</sup> As much as 50 macromolecular chains could be grown from a single zinc center by the ZnEt<sub>2</sub>/BnOH system in the presence of up

**Table 6** Selected data for the bulk iROP of TMC using metal complex/BnOH systems<sup>29</sup>

Entry	Complex	[TMC] <sub>0</sub> /[Met] <sub>0</sub> /[ROH] <sub>0</sub>	Temp./°C	Time <sup>a</sup> /min	Conv. <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> /g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> /g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>	TOF <sup>e</sup> /h <sup>-1</sup>
1	ZnEt <sub>2</sub>	1000/1/2	60	60	99	50 600	65 200	1.68	990
2	ZnEt <sub>2</sub>	1000/1/5	60	60	100	20 500	21 100	1.74	1000
3	ZnEt <sub>2</sub>	1000/1/50	60	20	99	1950	2600	1.15	2970
4	ZnEt <sub>2</sub>	2000/1/20	60	30	94	9700	12 000	1.49	3760
5	Mg[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	2000/1/20	60	30	74	7650	9490	1.47	2960
6	Ca[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (THF) <sub>2</sub>	2000/1/20	60	30	99	10 200	9710	1.61	3960
7	Y[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	2000/1/20	60	30	93	9600	13 870	1.83	3720
8	Fe[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	2000/1/20	60	15 × 60	64	6650	7750	1.25	85
9	Fe[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	2000/1/20	60	90	75	7750	9125	1.59	1000
10	{BDI <sup>iPr</sup> }Fe[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	2000/1/20	60	4 × 60	< 5	nd <sup>f</sup>	nd <sup>f</sup>	nd <sup>f</sup>	25
11	Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	2000/1/20	60	30	88	9100	10 950	1.70	3520
12	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	2000/1/20	60	30	95	9800	13 100	1.38	3800
13	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	500/1/0	60	8	34	17 450	102 600	1.91	1275
14	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	500/1/5	60	7	99	10 200	12 400	1.55	4245
15	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	1000/1/5	60	10	100	20 500	25 900	1.60	6000
16	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	1000/1/50	60	20	89	1900	2200	1.17	2670
17	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	5000/1/200	60	3 × 60	100	2660	1490	1.23	1665
18	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	25 000/1/20	60	15 × 60	75	95 800	93 400	1.65	1250
19	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	25 000/1/50	110	40	80	40 900	49 300	1.90	30 000
20	{BDI <sup>iPr</sup> }Zn[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	50 000/1/20	110	2 × 60	93	237 250	160 600	1.68	23 250
21	{LO <sup>i</sup> }ZnEt/ <i>i</i> PrOH	500/1/5	60	7	98	10 100	12 100	1.52	4200
22	{LO <sup>i</sup> }ZnEt/ <i>i</i> PrOH	25 000/1/20	60	15 × 60	97	123 900	117 200	1.62	1620
23	{LO <sup>i</sup> }ZnEt/ <i>i</i> PrOH	100 000/1/100	110	8 × 60	96	98 000	94 400	1.51	12 000

<sup>a</sup> Reaction times were not necessarily optimized. <sup>b</sup> Monomer conversion determined by <sup>1</sup>H NMR. <sup>c</sup> Calculated from [TMC]<sub>0</sub>/[BnOH]<sub>0</sub> × monomer conversion × *M*<sub>TMC</sub> + *M*<sub>BnOH</sub>, with *M*<sub>TMC</sub> = 102 g mol<sup>-1</sup> and *M*<sub>BnOH</sub> = 108 g mol<sup>-1</sup>. <sup>d</sup> Determined by SEC vs. polystyrene standards. <sup>e</sup> Non-optimized turnover frequency expressed in mol(TMC).mol(Metal)<sup>-1</sup>.h<sup>-1</sup>. <sup>f</sup> Not determined.

to 1000 TMC equiv., while as much as 2000 TMC equiv. could be fully converted to give up to 20 macromolecular chains *per* metal. Similar *M*<sub>n,SEC</sub> and *M*<sub>n,calc</sub> values and monomodal molar weight distributions were observed in all cases. Successful conversions of such large amounts of TMC in a relatively controlled manner using a simple ZnEt<sub>2</sub> precursor were unprecedented.<sup>30</sup>

Still revolving around the use of biofriendly metals, the range of metallic derivatives was enlarged to other homoleptic species such as amides {Mg[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}, Ca[N(SiMe<sub>3</sub>)<sub>2</sub>](THF)<sub>2</sub>, Y[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, and to discrete heteroleptic precursors such as {BDI<sup>iPr</sup>}Fe[N(SiMe<sub>3</sub>)<sub>2</sub>], {BDI<sup>iPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>] and {LO<sup>i</sup>}ZnEt, associated with an alcohol (*i*PrOH or BnOH). These investigations further confirmed that both the β-diiminate amido and the phenoxy alkyl zinc complexes provided the overall best performances in iROP of TMC, combining high activity, productivity, degree of control and a relatively good stability.<sup>29</sup> At 60 °C, the magnesium (TOF = 2960 h<sup>-1</sup>) and even more so the three iron amido systems (TOF ≤ 1000 h<sup>-1</sup>) were clearly less active than {BDI<sup>iPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>] (TOF = 3800 h<sup>-1</sup>), while the calcium and yttrium amido derivatives were more active (TOF, Ca = 3960 h<sup>-1</sup>, Y = 3720 h<sup>-1</sup>) (Table 6, entries 5–12). However, these last two as well as the Mg initiators proved much more sensitive towards residual impurities (present in increasing amounts with larger loadings of monomer), undergoing fatal deactivation faster than other species.

While in classical “living” operating conditions (*i.e.*, no alcohol used as CTA), good control with {BDI<sup>iPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>] could not be achieved (entry 13), addition of an alcohol as CTA led to enhanced activities and better control (entries 14–20). With

this {BDI<sup>iPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/BnOH system, as many as 50–200 chains were successfully grown from a unique zinc precursor while maintaining almost quantitative conversions at 60–110 °C within 2 h, allowing the conversion of as much as 50 000 TMC equiv. The good control of the molar weight was maintained up to a [TMC]<sub>0</sub>/[Zn]<sub>0</sub> ratio of 25 000 and slightly decreased when the monomer content was doubled to 50 000 equiv., most likely resulting from greater contamination by impurities (*vide infra*). The loading of metallic species was lowered to as little as 20 ppm while maintaining high activity (TOF = 23 250 h<sup>-1</sup> and up to 31 125 h<sup>-1</sup>,<sup>29a-c</sup>) and productivity (TON = 46 500). These performances largely surpassed the corresponding achievements reported with the TMC/Zn(acac)<sub>2</sub> system (TON = 1293; TOF up to 1290 h<sup>-1</sup> at 110 °C),<sup>31</sup> while maintaining the control and living nature of the polymerization (a successful double monomer feed experiment showed the expected increase in the polymer molar weight based on the sequential monomer input).<sup>29</sup>

{LO<sup>i</sup>}ZnEt/*i*PrOH proved to be a similarly performing catalytic system (entries 21–23).<sup>32</sup> While {BDI<sup>iPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/ROH systems are able to withstand both large amounts of alcohol as CTA (up to 200 equiv.) and large monomer loadings (up to 50 000 equiv., TON = 46 500 in 2 h), the catalytic system based on the phenoxy ligand enables even heavier monomer inputs (up to 100 000 equiv., TON = 96 000 in 8 h) with as much as 100 PTMC chains simultaneously growing *per* zinc center.<sup>32</sup> In this latter case, the control over the polymerization was relatively better than with the {BDI<sup>iPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>], although the PTMC molar weights were somewhat different.

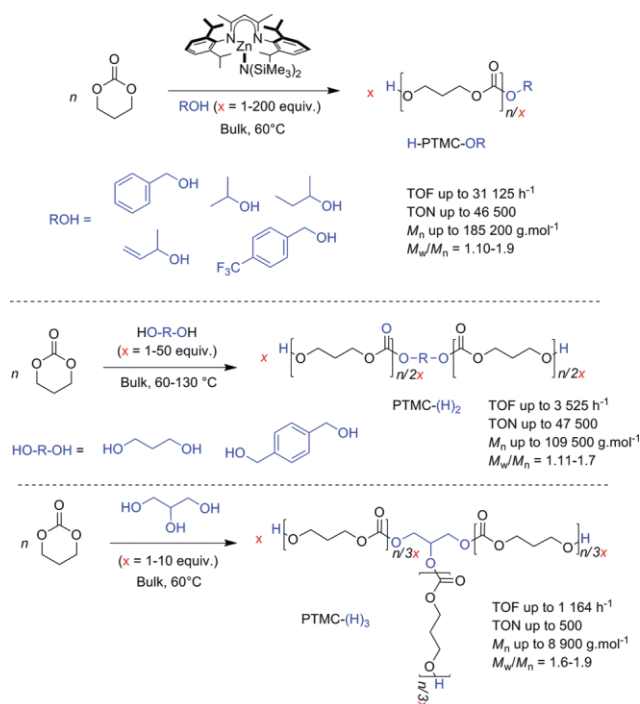
The ability of this iROP catalytic approach to provide access to end-functionalized polycarbonates was demonstrated with

**Table 7** Selected data for the bulk iROP of TMC promoted by  $\text{ZnEt}_2$  or  $\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{alcohol}$  systems at  $60^\circ\text{C}^{29\text{d}}$

Entry	Complex	Alcohol	$[\text{TMC}]_0/[\text{Metal}]_0$ $[\text{Alcohol}]_0$	Time <sup>a</sup> /min	Conv. <sup>b</sup> (%)	$M_{n,\text{calc}}^c/\text{g mol}^{-1}$	$M_{n,\text{SEC}}^d/\text{g mol}^{-1}$	$M_w/M_n^d$	TOF <sup>e</sup> /h <sup>-1</sup>
1	$\text{ZnEt}_2$	PPD	500/1/10	30	100	10 300	13 700	1.48	1 000
2	$\text{ZnEt}_2$	PPD	10 000/1/10	$3 \times 60$	84	85 830	51 400	1.64	2 800
3	$\text{ZnEt}_2$	BDM	500/1/10	50	95	9 800	8 400	1.48	570
4	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	PPD	500/1/10	45	98	5 080	6 060	1.21	653
5	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	PPD	10 000/1/10	$3 \times 60$	85	86 800	82 000	1.43	2 834
6	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	PPD	50 000/1/50	$26 \times 60$	95	97 060	88 900	1.48	1 827
7	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	BDM	500/1/10	30	100	5 250	6 080	1.54	1 000
8	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	BDM	10 000/1/10	$3 \times 60$	93	95 080	89 100	1.62	3 100
9	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	GLY	500/1/5	25	97	10 000	8 900	1.63	1 160
10	$\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$	GLY	500/1/10	30	100	5 190	3 450	1.92	1 000

<sup>a</sup> See Table 6. <sup>b</sup> See Table 6. <sup>c</sup> Calculated from  $[\text{TMC}]_0/[\text{alcohol}]_0 \times \text{monomer conversion} \times \text{MTMC} + M_{\text{alcohol}}$ , with  $M_{\text{TMC}} = 102 \text{ g mol}^{-1}$ ,  $M_{\text{PPD}} = 76 \text{ g mol}^{-1}$ ,  $M_{\text{BDM}} = 138 \text{ g mol}^{-1}$  and  $M_{\text{GLY}} = 92 \text{ g mol}^{-1}$ . <sup>d</sup> See Table 6. <sup>e</sup> See Table 6.

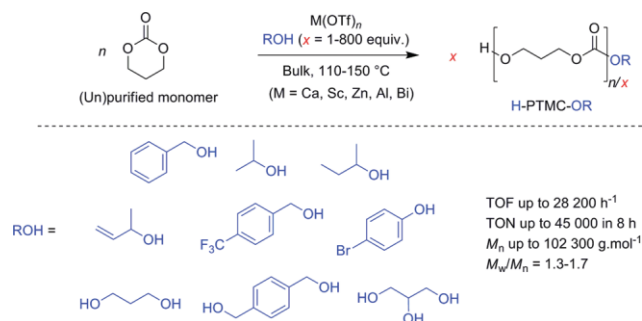
the use of various alcohols as co-initiator/CTA in combination with  $\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$  (Scheme 11, Table 7).<sup>29</sup> The related systems  $\text{ZnEt}_2/\text{ROH}$  proved again less active than that derived from  $\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ . Varying the protic ROH source allowed the easy preparation of the corresponding  $\alpha$ -hydroxy,  $\omega$ -alkoxycarbonate telechelic PTMCs with the expected end-group fidelity.<sup>29</sup> Similarly, higher polyols such as 1,3-propanediol (PPD), 1,4-benzenedimethanol (BDM) or glycerol (GLY) were successfully used for the iROP of TMC to synthesize up to 50  $\alpha,\omega$ -hydroxy end-capped linear or star telechelic PTMCs. Large amounts of TMC (up to 50 000 equiv.) were polymerized to prepare for the first time PTMCs-(H)<sub>2</sub> and PTMCs-(H)<sub>3</sub> from minute amounts of the metal catalyst (20 ppm). These PTMC-diols or PTMC-triols could be advantageously exploited as multifunctional CTAs to give access to original linear or star block copolymers *via* iROP of another comonomer.<sup>33</sup>



**Scheme 11** iROP of TMC with  $\{\text{BDI}^{\text{Pr}}\}\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{ROH}$  systems for synthesis of end-functionalized linear and star PTMCs.<sup>29</sup>

## 6. Immortal ring-opening polymerization of trimethylene carbonate and $\beta$ -butyrolactone promoted by metal triflate-based systems

Seeking for more robust and inexpensive catalytic systems, we have evaluated metal-based Lewis acids such as the metal triflates  $\text{M}(\text{OTf})_n$  ( $\text{M} = \text{Ca}, \text{Sc}, \text{Zn}, \text{Al}, \text{Bi}$ ;  $\text{OTf} = \text{CF}_3\text{SO}_3^-$ ) or the metallic salt  $\text{Fe}(\text{acac})_3$  in combination with an alcohol as co-initiator/CTA, in the iROP of TMC (Scheme 12).<sup>34,35</sup>



**Scheme 12** iROP of TMC with  $\text{M}(\text{OTf})_n/\text{ROH}$  systems.<sup>34</sup>

The major advantage of such systems over the ones described in the previous sections (based on alkyl, amido, borohydrido or alkoxide catalyst precursors) is their high tolerance towards water and other impurities, which allowed the bulk iROP to be run with technical grade monomer (*i.e.*, unpurified raw reagent used as received). In fact, these triflate metal salts along with  $\text{Fe}(\text{acac})_3$ , associated with  $\text{BnOH}$  as CTA, do efficiently polymerize both *purified* or *unpurified* TMC in bulk “immortal” operating conditions at  $110\text{--}150^\circ\text{C}$  (Table 8).

For the bulk iROP of *purified* TMC, catalyst systems based on  $\text{Ca}(\text{OTf})_2$  and  $\text{Zn}(\text{OTf})_2$  are significantly less active than those based on the corresponding homoleptic metal amido complexes, *i.e.*,  $\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ ,  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]$  previously evaluated (Table 6), while  $\text{Fe}(\text{acac})_3$  exhibited a slightly higher activity compared to  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$ .<sup>29,32</sup> Systems based on  $\text{Al}(\text{OTf})_3$  and  $\text{Bi}(\text{OTf})_3$  and, to a lesser extent  $\text{Sc}(\text{OTf})_3$ , display the best TOF values, allowing the almost quantitative conversion of TMC, whether *purified* or *not* (Table 8). Relatively high reaction



**Table 8** Selected data for the bulk iROP of TMC initiated by M(OTf)<sub>3</sub>/BnOH systems<sup>34a</sup>

Entry	Compound	TMC	[TMC] <sub>0</sub> /[Metal] <sub>0</sub> / [BnOH] <sub>0</sub>	Temp./ °C	Time/ min <sup>a</sup>	Conv. <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>	TOF <sup>e</sup> /h <sup>-1</sup>
1	Sc(OTf) <sub>3</sub>	Purified	500/1/5	150	10	73	7 550	8 250	1.69	2 190
2	Al(OTf) <sub>3</sub>	Purified	500/1/5	150	5	98	10 100	10 950	1.55	5 880
3	Bi(OTf) <sub>3</sub>	Purified	500/1/5	150	10	99	10 200	11 400	1.51	2 970
4	Sc(OTf) <sub>3</sub>	Unpurified	10 000/1/10	150	150	85	86 900	20 200	1.30	3 400
5	Al(OTf) <sub>3</sub>	Unpurified	10 000/1/10	150	20	92	94 050	61 200	1.42	27 600
6	Bi(OTf) <sub>3</sub>	Unpurified	10 000/1/10	150	20	94	96 080	34 500	1.50	28 200
7	Al(OTf) <sub>3</sub>	Unpurified	10 000/1/500	110	3.5	93	2 000	2 000	1.53	2 660
8	Al(OTf) <sub>3</sub>	Unpurified	10 000/1/800	110	5	100	1 400	1 300	1.52	2 000
9	Al(OTf) <sub>3</sub>	Unpurified	50 000/1/20	130	8	90	229 600	102 270	1.53	5 625
10	Al(OTf) <sub>3</sub>	Unpurified	50 000/1/50	130	8	75	76 600	53 730	1.59	4 690

<sup>a</sup> See Table 6. <sup>b</sup> See Table 6. <sup>c</sup> See Table 6. <sup>d</sup> See Table 6. <sup>e</sup> See Table 6.

temperatures (110–150 °C) were required to achieve such activities (TOF up to 27 600 and 28 200 h<sup>-1</sup> with Al- and Bi- triflates, respectively), which are comparable to those obtained with *e.g.* the {BDI<sup>Pr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/BnOH system (TOF up to 31 125 h<sup>-1</sup>) at 60 °C, yet with *purified* TMC.

Similar monomer conversions were indeed achieved at lower temperatures (60 °C) with organometallic-based systems,<sup>29</sup> which appear more efficient towards the iROP of *purified* TMC than the metal salts systems. However, the outcome of the polymerization is completely different when dealing with *unpurified* batches of monomer. Indeed, the iROP of *unpurified* TMC initiated by the {BDI<sup>Pr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/BnOH system at 60 °C failed to give any polymer within 3 h, whereas the iROP initiated by Al(OTf)<sub>3</sub>/BnOH converted 90% of 50 000 equiv. of unpurified TMC over 8 h (Table 8, entries 9, 10). The Al(OTf)<sub>3</sub>/BnOH system withstands as many as 800 growing PTMC chains per metal for the iROP of unpurified TMC.<sup>34</sup>

The versatility of these systems based on such simple, air- and moisture-tolerant triflate metallic salts was demonstrated by the polymerization of unpurified TMC with Al(OTf)<sub>3</sub> in the presence of various mono- (BnOH, *i*PrOH, 2-butanol, 3-buten-2-ol, 4-bromophenol and (4-trifluoromethyl)benzyl alcohol) or difunctional (propanediol, 1,4-benzenedimethanol, glycerol) alcohols as co-initiator/CTA, affording the corresponding linear telechelic α,ω-di- or tri-hydroxy functionalized PTMCs with high conversions and activities, especially at elevated temperature (Scheme 12).

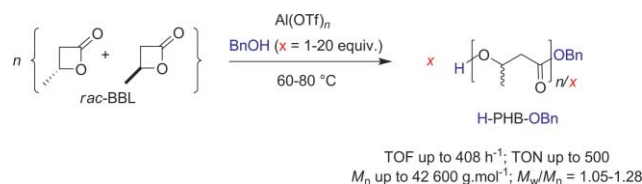
Another important feature of these polymerizations using unpurified TMC lies in the apparently poorer molar weight agreement (*M*<sub>n,SEC</sub> vs. *M*<sub>n,calc</sub> calculated from the monomer-to-alcohol ratio; the larger the initial loading of TMC, the larger the discrepancy), although the molar weight distribution values remained within the expected range (*M*<sub>w</sub>/*M*<sub>n</sub> ~1.5). This deviation arises from the presence of “transfer active” impurities (supposedly protic reagents such as water or residual alcohol/diol) present in the technical grade monomer, the quantity of which increased with monomer loadings, thus increasing the effective concentration in CTA beyond that determined by the amount of alcohol initially added. We showed that the fraction (*X* = 0.056 mol%) of such “transfer active” impurities contained in a given sample of TMC monomer can be readily determined from the experimental *M*<sub>n,SEC</sub> values following eqn (1):

$$M_n = [TMC]_0 / \{ [ROH]_0 + (X[TMC]_0) \} \text{conv.}_{(TMC)} M_{TMC} + M_{ROH} \quad (1)$$

In turn, this fraction *X* allowed to predict and tune the polymer molar weight using eqn (2)

$$M_n = [TMC]_0 / \{ [ROH]_0 + (X[TMC]_0) \} \times \text{monomer conversion} \times M_{TMC} + M_{ROH} \quad (2)$$

In comparison, the iROP of *rac*-BBL using the Al(OTf)<sub>3</sub>/BnOH system remained significantly less efficient (Scheme 13, Table 9).<sup>28</sup> When performed in toluene at 60–80 °C, full conversion of up to 500 equiv. of BBL, with as many as 20 equiv. of added BnOH, was obtained with a modest control over the polymers formed. However, only limited conversions were observed with monomer loadings of 1000 and more equiv. More, the same process when conducted in bulk monomer led to side reactions (crotonisation), whereas in absence of any added BnOH, the polymerization proceeded without significant control (*M*<sub>w</sub>/*M*<sub>n</sub> = 1.7). Overall performances (TOF up to 408 h<sup>-1</sup>; TON up to 500 in 80 min) remained well below those obtained for TMC and were also inferior to those observed with {BDI<sup>Pr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]/BnOH for the iROP of BBL (*vide supra*, Scheme 10, Table 5). All attempts with Bi(OTf)<sub>3</sub> only yielded PHB oligomers with [BBL]<sub>0</sub>/[Bi(OTf)<sub>3</sub>]<sub>0</sub> ratios lower than 200/1.<sup>28</sup>

**Scheme 13** Immortal ROP of *rac*-BBL with the Al(OTf)<sub>3</sub>/BnOH system.<sup>28</sup>

## 7. Outlook and concluding remarks

Most of the catalyst systems we investigated exhibited a good control for the “immortal” ROP of LA, BBL or TMC, as evidenced by the agreement between the theoretical and experimental molar weights, narrow molar weights distribution values and end-group fidelity (as determined by MALDI-ToF-MS, NMR and/or SEC). Although side transesterification/transcarbonation reactions

**Table 9** Selected data for the iROP of *purified* BBL initiated by the Al(OTf)<sub>3</sub>/BnOH system<sup>28</sup>

Entry	[BBL] <sub>0</sub> /[Al(OTf) <sub>3</sub> ] <sub>0</sub> / [BnOH] <sub>0</sub>	[Al(OTf) <sub>3</sub> ] <sub>0</sub> / mmol L <sup>-1</sup>	Temp./ °C	Time <sup>a</sup> / min	Conv. <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>n,SEC</sub> <sup>d</sup> / g mol <sup>-1</sup>	<i>M</i> <sub>n,NMR</sub> / g mol <sup>-1</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>	TOF <sup>e</sup> /h <sup>-1</sup>
1	100/1/0	20	60	30	35	3000	2400	nd	1.72	70
2	200/1/10	10	80	30	100	1800	1700	1200	1.16	400
3	500/1/10	4	80	80	100	4400	1700	4000	1.61	375
4	500/1/20	4	80	80	100	2200	1800	3300	1.23	375
5	1000/1/10	2	80	150	38	3400	1500	2900	1.40	152
6	1 000/1/20	2	80	150	40	1800	1300	1600	1.24	160

<sup>a</sup> Reactions performed in toluene. <sup>b</sup> See Table 5. <sup>c</sup> See Table 5. <sup>d</sup> See Table 5. <sup>e</sup> See Table 5.

could not be fully avoided, especially when operating under bulk conditions, these catalyst systems proved remarkably safe for the integrity of the macromolecule. Notably, for all the iROP reactions studied with TMC, no case of decarboxylation was noticed, whereas it is often observed with other initiating systems reported in the literature such as the tin-based ones. These results represent obvious examples that ultimately enable the preparation, almost at will, of well-defined oligomers as well as high molar weight materials. The molar weight of the PLAs, PHBs and PTMCs could be easily tuned according to the [monomer]<sub>0</sub>/[alcohol]<sub>0</sub> ratio. Besides, the living feature of these iROP was demonstrated with successful chain extension experiments.

These various catalyst systems displayed different reactivities and overall performances. Despite the unprecedented activities unveiled by systems based on calcium and magnesium organometallic precursors, especially those derived from the {LO<sup>1</sup>}<sup>-</sup> ligand, such systems showed limitations at higher alcohol and/or monomer loadings. Obviously, the same assessment stands for rare earth-based organometallic systems, although some of the latter catalysts, *i.e.*, those supported by {ONOO<sup>R</sup>}<sup>2-</sup> ligands, proved unique in combining capabilities for stereocontrolled iROP of *rac*-LA. Zinc-based organometallic systems provided the best overall compromise, affording high activities and unprecedented productivities, as long as rigorously purified monomers are used. Significant influence of ancillary ligand(s) was demonstrated by the presence of protecting arms as in the single site complexes {LO<sup>1</sup>}ZnEt or {BDI<sup>IPr</sup>}Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]. The notable performances (TOF up to 31 125 h<sup>-1</sup>) observed with these systems most likely arise from the bulky ancillary BDI or bis(morpholine)phenoxy ligands, which are inactive during the ROP but however provide a greater stability to the oxophilic zinc center in the presence of large amounts (up to 1 000 equiv.) of alcohol CTA molecules, thus preventing catalyst deactivation.<sup>36</sup> Catalyst systems based on simple M(OTf)<sub>3</sub> salts revealed highly attractive since their robustness allowed the iROP of an unpurified monomer; namely, technical grade TMC could be effectively polymerized at very high monomer (up to 100 000 equiv.) and alcohol (800 equiv.) loadings.

Operating under such immortal conditions offers clear advantages over previously known procedures, most especially as it permits the use of significantly lower metal catalyst loadings. This feature is directly relevant to the general context of “green” chemistry since truly catalytic amounts of initiating species are being employed.<sup>37</sup> This opens up opportunities for the large-scale production of these and related polyesters and polycarbonates. Besides, the use of bio-friendly metal (pre)catalyst loadings as low as 20 ppm allows to circumvent toxicity issues revolving around

the resulting polyesters or polycarbonates, and notably it renders post-polymerization chemical treatments (otherwise necessary to remove metallic residues from polymers)<sup>38</sup> superfluous. Considering the biocompatibility and (bio)degradability of these polyesters and polycarbonates, such iROP processes stand out as a most promising approach that should be generalized to the preparation of polymers with controlled architecture, *e.g.*, to those aimed at biomedical applications.

Of course many challenges remain. One can for instance cite the further development of catalytic systems efficient toward the iROP of the more reluctant monomer BBL for the preparation of poly(3-hydroxybutyrate)s, or the design of platforms of bulky multidentate ligands that could stabilize highly oxophilic group 2 and 3 metal centers towards high loadings of protic CTAs and enable them to preserve their unique and intrinsic high reactivity.

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