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Poly(trimethylene carbonate) from Biometals-Based Initiators/Catalysts: Highly Efficient Immortal Ring-Opening Polymerization Processes

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Abstract: The ring-opening polymerization (ROP) of trimethylene carbonate (TMC) was evaluated in bulk at 60–110 °C using various catalyst systems based on bio-friendly metals, including the metal bis(trimethylsilylamides) $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$, $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$, $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$, $(\text{BDI})\text{Fe}[\text{N}(\text{SiMe}_3)_2]$ [$\text{BDI} = \text{CH}(\text{CMeNC}_6\text{H}_3-2,6-i\text{-Pr}_2)_2$], $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$, $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$, $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$, $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ and ZnEt_2 , associated with an alcohol such as isopropyl or benzyl alcohol. The actual metal alkoxide initiating species has been formed *in situ* prior to the addition of TMC. Introduction of the alcohol component in excess leads to the “immortal” ring-opening polymerization (ROP) of TMC. According to such an “immortal” ROP process of TMC, whichever the metal species, as many as 200 polycarbonate chains could be successfully grown from a unique metal center in a well controlled ROP process. The best performances were obtained using the discrete $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ precursor. Under optimized conditions, as many as 50,000 equivalents of TMC could be fully converted from as little as 20 ppm of this metallic precursor, allowing the preparation of a poly(trimethylene carbon-

ate (PTMC) with a molar mass as high as $185,200 \text{ g mol}^{-1}$ with a relatively narrow molar mass distribution ($M_w/M_n = 1.68$). A double monomer feed experiment carried out with the $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{BnOH}$ initiating system proved the “living” character of the polymerization. Characterization of the PTMCs by NMR and size exclusion chromatography (SEC) showed well-defined α -hydroxy- ω -alkoxycarbonate telechelic polymers, highlighting the controlled character of this “living and immortal” ROP process. Using the $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ precursor, varying the alcohol (ROH) to 2-butanol, 3-buten-2-ol or 4-(trifluoromethyl)benzyl alcohol, revealed the versatility of this approach, allowing the preparation of accordingly end-functionalized HO-PTMC-OR polymers. The very low initial loading of metal catalyst considerably limits the potential toxicity and thus allows such polycarbonates to be used in the biomedical field.

Keywords: biometals; catalysis; living and immortal ring-opening polymerization; polycarbonates; transfer agents; trimethylene carbonate

Introduction

Biomass-derived polymers have nowadays become, from a mere curiosity a decade ago, a crucial necessity. Facing the general problems of oil prices and overall depleting fossil feedstocks, of global warming and of resulting environmental concerns, developing biocompatible polymers from monomers issued from renewable natural resources within green and sustainable chemistry has emerged as a research priority.^[1] Polymers derived from plant-based raw materials are

of increasing interest as alternatives/substitutes to more traditional commodity thermoplastics such as polystyrene, polypropylene or polyethylene, as well as for their applications in the biomedical field including tissue and bone engineering and controlled drug delivery systems.^[2]

Within these challenging contexts, we have focused our attention on establishing highly effective catalytic systems for the ring-opening polymerization (ROP) of cyclic carbonates derived from biomass, to access polycarbonates containing as little as possible of toxic

residues. Of special consideration is glycerol, which originates from the biomass *via* hydrolysis or methanolysis of triglycerides. Indeed, cheap glycerol can be converted into value-added chemicals among which is 1,3-propanediol that readily affords the six-membered trimethylene carbonate monomer (TMC, 1,3-dioxane-2-one) upon transesterification with urea.^[3] The resulting poly(trimethylene carbonate) (PTMC) is a valuable candidate for biomedical applications in light of its biodegradability, biocompatibility and low toxicity. Due to its excellent flexibility and poor mechanical strength, this elastomeric aliphatic polyester is being used as implant material for soft tissue regeneration or as drug delivery vehicle.^[2,4,5] It is also a valuable candidate for more generic industrial applications.^[5c]

Preparation of polycarbonates by polycondensation of a diol and a carbonate reagent or phosgene presents limitations intrinsic to step-growth techniques, especially rather low molar mass polymers displaying somewhat large molar mass distributions; also, when using carbonate reagents, high operating temperatures and removal of the leaving group are mandatory. ROP of cyclic carbonates offers a valuable alternative, leading to better controlled reactions and well-defined polymers. Pathways including cationic, anionic and coordination-insertion ones, revolving around non-toxic initiating systems, have been investigated.^[5] Among these, zinc-based initiators are particularly attractive given that zinc participates to the human metabolism.^[6] However, the use of zinc(II) complexes in the ROP of carbonates remains limited^[7,8] compared to that of other cyclic esters.^[2b,4b,9] Notably, Gross et al. reported the bulk polymerization of 2,2-(2-pentene-1,5-diyl)TMC at 90 °C using $\text{ZnEt}_2\text{-H}_2\text{O}$.^[7a] Regarding the homopolymerization of TMC, some of us reported recently a zinc alkoxide species, prepared *in situ* from ZnEt_2 and an amino-protected alcohol, that eventually allowed the successful controlled synthesis of PTMC at room temperature.^[7b]

Discrete zinc complexes supported by versatile β -diketiminato ligands, $[(\text{BDI})\text{Zn}(\text{X})]$ [$\text{BDI} = \text{CH}(\text{CMeNC}_6\text{H}_{5-x}\text{R}_x)_2$, $x = 1, 2$; $\text{X} = \text{alkyl, amido, alkoxide}$], as originally introduced by Coates et al., have emerged as efficient initiators for the ROP of cyclic esters, especially of lactides along with a few other lactones such as β -butyrolactone and β -valerolactone, with an overall behaviour depending on both the initiating group X and the β -diketiminato R substituents.^[10,11,12,13] Kinetic studies revealed that the zinc isopropoxide complex supported by the *i*-Pr-substituted BDI ligand exhibited the fastest rate in the ROP of *rac*-lactide, with a good overall control over the polymerization. Later on, Chisholm and Lin independently developed β -diiminato-calcium and -magnesium amide and alkoxide initiators for the successful preparation of polylactide.^[11,12] In their studies on some Schiff base derivatives of the Zn, Mg and Ca biomet-

als, Darensbourg et al. showed that, in the ROP of TMC, the order of the catalytic activity of the metal(II)-salen initiators in the presence of added external nucleophiles such as the anions derived from PPN^+ or $n\text{-Bu}_4\text{N}^+$ salts, was $\text{Ca} \gg \text{Mg} > \text{Zn}$.^[7c] A bis-(trimethylsilyl)amido-calcium complex based on a tridentate Schiff base ligand was also shown to be more active than its zinc counterpart.^[14] Other reports, yet scarce, relate to the use of group III metals for the ROP of TMC; while most of these initiators are discrete alkoxide complexes, some guanidinate derivatives have also shown high activity.^[15]

The activities ($\text{TOF} = \text{mol}_{\text{monomer}} \cdot \text{mol}_{\text{initiator}}^{-1} \cdot \text{h}^{-1}$) reported for the ROP of TMC with the above-mentioned systems remain, however, in general quite low ($\text{TOF} \leq 1790$).^[7,15] To achieve conversion of very large amounts of cyclic monomer using as little as possible of the metal component, i.e., to improve on the catalytic activity and productivity and to minimize as well the residual metal content in the final polymers while maintaining a good control over the polymerization, the concept of “immortal” polymerization is very appealing. In such an approach, the presence within the catalytic system of added protic sources such as alcohols that act as chain transfer agents (CTAs) enables the growth of several polymer chains per metal center. Immortal polymerizations are originally known from the work of Inoue on the cationic ROP of epoxides using an Al-porphyrin/alcohol catalytic system.^[16,17] It has since then been rarely applied to the ROP (*via* cationic or coordination-insertion pathways) of other heterocyclic monomers^[18] such as ϵ -caprolactone, lactide or, much more seldom, β -butyrolactone^[18b] and δ -valerolactone,^[18c] with overall performances that yet remain limited. However, no obvious example of an “immortal” ROP process applied to a cyclic carbonate that allows the effective production of polymers with high and controlled molar mass has been reported to date.

In this contribution, the bulk “immortal” polymerization of TMC has been evaluated using several alkoxide catalytic systems based on non-toxic metals such as magnesium, calcium, yttrium, iron, and zinc.^[19] These initiators/catalysts are conveniently generated *in situ* from amido or alkyl precursors and an alcohol. The performances of these catalytic systems in terms of activity, productivity and control over the polymerization are compared. All polymers were characterized using NMR as well as size exclusion chromatography (SEC) analyses to determine their molecular structure and molar features.

Results and Discussion

The ROP of TMC was first evaluated through the screening of various catalyst systems based on non-

Table 1. Bulk polymerization of TMC initiated by amido- or alkyl-metal/benzyl alcohol systems.^[a]

Entry	Catalyst precursor	Temp. [°C]	Reaction time [min]	Conv. ^[b] [%]	$M_{n,theo}$ ^[c] [g mol ⁻¹]	$M_{n,SEC}$ ^[d] [g mol ⁻¹]	M_wM_n ^[e]	TOF ^[f] [mol-(TMC)·mol(Zn) ⁻¹ ·h ⁻¹]
1	Mg[N(SiMe ₃) ₂] ₂	60	30	74	7,650	9,490	1.47	2,960
2	Ca[N(SiMe ₃) ₂] ₂ (THF) ₂	60	30	99	10,200	9,710	1.61	3,960
3	Y[N(SiMe ₃) ₂] ₃	60	30	93	9,600	13,870	1.83	3,720
4	Fe[N(SiMe ₃) ₂] ₃	60	900	64	6,650	7,750	1.25	85
5	Fe[N(SiMe ₃) ₂] ₃	110	180	66	6,850	9,680	1.47	440
6	Fe[N(SiMe ₃) ₂] ₃	150	90	88	9,100	12,300	1.65	1,173
7	Fe[N(SiMe ₃) ₂] ₂	60	90	75	7,750	9,125	1.59	1,000
8	Fe[N(SiMe ₃) ₂] ₂	110	20	97	10,000	13,270	1.64	5,820
9	(BDI)Fe[N(SiMe ₃) ₂]	60	240	< 5	nd ^[g]	nd ^[g]	nd ^[g]	25
10	(BDI)Fe[N(SiMe ₃) ₂]	110	30	93	9,600	11,680	1.66	3,720
11	Zn[N(SiMe ₃) ₂] ₂	60	30	88	9,100	10,950	1.70	3,520
12	(BDI)Zn[N(SiMe ₃) ₂]	60	30	95	9,800	13,100	1.38	3,800
13	ZnEt ₂	60	30	94	9,700	12,000	1.49	3,760

^[a] General conditions: [TMC]₀/[M]₀/[BnOH]₀ = 2 000/1/20.

^[b] Monomer conversion determined by ¹H NMR.

^[c] Calculated from [TMC]₀/[BnOH]₀ × monomer conversion × M_{TMC} + M_{BnOH}, with M_{TMC} = 102 g·mol⁻¹ and M_{BnOH} = 108 g·mol⁻¹.

^[d] Determined by SEC vs. polystyrene standards and corrected by 0.73.^[15a]

^[e] Molar mass distribution calculated from SEC traces.

^[f] Turnover frequency determined at 60–90% conversion.

^[g] Not determined.

toxic metallic derivatives. In contrast to earlier solution studies,^[7,8] the polymerizations in the present work were preferably carried out in bulk to get closer to “green” operating conditions, as well as to establish an industrially-valuable solvent-free procedure; this shall avoid toxicity issues related to the use of an organic solvent as well as reduce the overall cost of the process. A comparative evaluation of the “immortal” ROP of TMC in bulk initiated by amido or alkyl precursors based on biometals such as [M] = Mg[N-

(SiMe₃)₂]₂, Ca[N(SiMe₃)₂]₂(THF)₂, Y[N(SiMe₃)₂]₃, (BDI)Fe[N(SiMe₃)₂]₂ [BDI = CH(CMeNC₆H₃-2,6-*i*-Pr₂)₂], Fe[N(SiMe₃)₂]₂, Fe[N(SiMe₃)₂]₃, Zn[N(SiMe₃)₂]₂, (BDI)Zn[N(SiMe₃)₂] and ZnEt₂ was performed at a typical ratio of [TMC]₀/[M]₀/[BnOH]₀ = 2,000/1/20 (Table 1). As depicted in Figure 1, at 60 °C, among amido species, the calcium precursor Ca[N(SiMe₃)₂]₂(THF)₂ exhibited the highest TOF value (3,960 h⁻¹, entry 2), closely followed by the zinc ((BDI)Zn[N(SiMe₃)₂] = 3,800 h⁻¹ (entry 12); Zn[N-

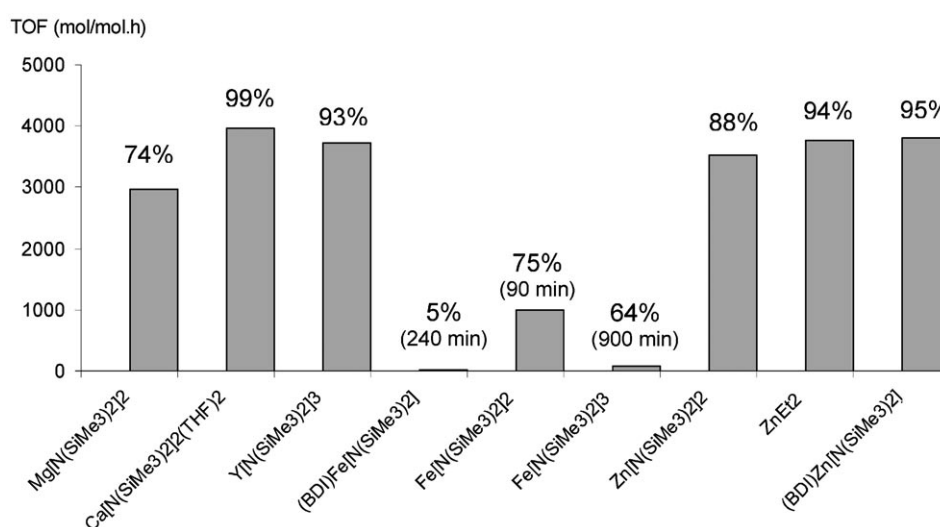


Figure 1. TOF and conversion values (for 30 min reaction time, unless otherwise stated into brackets) for the bulk ROP of TMC promoted by amido or alkyl metal/BnOH systems ([TMC]₀/[M]₀/[BnOH]₀ = 2 000:1:20 at 60 °C; see Table 1)

Table 2. Bulk polymerization of TMC initiated by the ZnEt₂/ROH (1:2) system at 60 °C.

Entry	ROH	[TMC] ₀ /[ROH] ₀ ^[a]	Reaction time [min]	Conv. ^[b] [%]	<i>M</i> _{n,theo} ^[c] [g mol ⁻¹]	<i>M</i> _{n,SEC} ^[d] [g mol ⁻¹]	<i>M</i> _w / <i>M</i> _n ^[e]
1	<i>i</i> -PrOH	200/2	15	78	8,000	7,800	1.22
2	<i>i</i> -PrOH	200/2	30	98	10,050	11,000	1.40
3	<i>i</i> -PrOH	200/2	120	100	10,250	13,400	1.55
4	<i>i</i> -PrOH	400/2	30	46	9,450	nd ^[f]	nd ^[f]
5	<i>i</i> -PrOH	400/2	60	98	20,050	30,100	1.54
6	<i>i</i> -PrOH	600/2	30	20	6,200	nd ^[f]	nd ^[f]
7	<i>i</i> -PrOH	600/2	60	99	30,350	37,300	1.48
8	<i>i</i> -PrOH	1,000/2	90	78	39,850	46,600	1.67
9	<i>i</i> -PrOH	1,000/2	120	99	50,550	64,400	1.65
10	BnOH	1,000/2	15	25	12,850	11,200	1.29
11	BnOH	1,000/2	30	60	30,700	29,900	1.58
12	BnOH	1,000/2	45	96	49,100	43,500	1.65
13	BnOH	1,000/2	60	99	50,650	64,900	1.68
14	BnOH	1,000/2	120	100	51,100	47,800	1.94

^[a] Monomer and alcohol equivalents relative to [ZnEt₂]₀.^[b] Monomer conversion determined by ¹H NMR.^[c] Calculated from [TMC]₀/[ROH]₀ × monomer conversion × *M*_{TMC} + *M*_{ROH}, with *M*_{TMC} = 102 g mol⁻¹, *M*_{*i*-PrOH} = 60 g mol⁻¹ and *M*_{BnOH} = 108 g mol⁻¹.^[d] Determined by SEC vs. polystyrene standards and corrected by 0.73.^[15a]^[e] Molar mass distribution calculated from SEC traces.^[f] Not determined.**Table 3.** Bulk “immortal” polymerization of TMC initiated by ZnEt₂ using ROH as transfer agent at 60 °C.

Entry	ROH	[TMC] ₀ /[ROH] ₀ ^[a]	Reaction time [min]	Conv. ^[b] [%]	<i>M</i> _{n,theo} ^[c] [g mol ⁻¹]	<i>M</i> _{n,SEC} ^[d] [g mol ⁻¹]	<i>M</i> _w / <i>M</i> _n ^[e]
1	<i>i</i> -PrOH	1,000/2	90	78	39,850	46,600	1.67
2	<i>i</i> -PrOH	1,000/2	120	95	48,500	64,400	1.65
3	<i>i</i> -PrOH	1,000/5	120	96	19,650	33,800	1.66
4	<i>i</i> -PrOH	1,000/5	150	100	20,450	28,500	1.75
5	<i>i</i> -PrOH	1,000/10	150	100	10,250	21,000	1.56
6	BnOH	1,000/2	60	99	50,600	65,200	1.68
7	BnOH	1,000/5	60	100	20,500	21,100	1.74
8	BnOH	1,000/10	60	100	10,300	12,140	1.41
9	BnOH	1,000/20	45	100	5,200	6,500	1.28
10	BnOH	1,000/50	20	99	1,950	2,600	1.15
11	BnOH	2,000/20	30	94	9,700	12,000	1.49

^[a] Monomer and alcohol equivalents relative to [ZnEt₂]₀.^[b] Monomer conversion determined by ¹H NMR.^[c] Calculated from [TMC]₀/[ROH]₀ × monomer conversion × *M*_{TMC} + *M*_{ROH}, with *M*_{TMC} = 102 g mol⁻¹, *M*_{*i*-PrOH} = 60 g mol⁻¹ and *M*_{BnOH} = 108 g mol⁻¹.^[d] Determined by SEC vs. polystyrene standards and corrected by 0.73.^[15a]^[e] Molar mass distribution calculated from SEC traces.

(SiMe₃)₂]₂ = 3,520 h⁻¹, entry 11) and yttrium (Y[N(SiMe₃)₂]₃ = 3,720 h⁻¹, entry 3) systems, while the iron complexes remained less active (TOF < 1,000 h⁻¹, entries 4–10). In comparison, ZnEt₂ – a commercially available precursor as opposed to all the other ones –, proved to be a similarly active initiating system (TOF = 3,760 h⁻¹, entry 13) as the other zinc precursors investigated (entries 11 and 12). The overall order of activity under such conditions is thus Ca[N(SiMe₃)₂]₂(THF)₂ ≈ (BDI)Zn[N(SiMe₃)₂] ≈ ZnEt₂ ≈ Y[N(SiMe₃)₂]₃ ≈ Zn[N(SiMe₃)₂]₂ ≫ Mg[N-

(SiMe₃)₂]₂ ≫ Fe[N(SiMe₃)₂]₂ > Fe[N(SiMe₃)₂]₃ > (BDI)Fe[N(SiMe₃)₂]. Expectedly, the catalytic activity of these systems could be readily manipulated with the temperature. For instance, the iron systems displayed much higher TOF values upon raising the temperature to 110–150 °C (entries 4–10). The system based on (BDI)Fe[N(SiMe₃)₂], which was the less active at 60 °C (TOF = 25 h⁻¹, entry 9), gave a TOF value of 3,720 h⁻¹ at 110 °C (entry 10), similar to that of the best systems operating at 60 °C (entries 2, 3, and 12). Similarly, the system based on homoleptic

Table 4. Bulk polymerization of TMC initiated by the [(BDI)Zn(N(SiMe₃)₂)]/ROH system.

Entry	ROH	[TMC] ₀ /[ROH] ₀ ^[a]	Temp. [°C]	Reaction time [min]	Conv. ^[b] [%]	<i>M</i> _{n,theo} ^[c] [g mol ⁻¹]	<i>M</i> _{n,SEC} ^[d] [g mol ⁻¹]	<i>M</i> _w / <i>M</i> _n ^[e]
1	<i>i</i> -PrOH	200/1	60	5	87	17,800	34,700	1.98
2	<i>i</i> -PrOH	200/1	60	15	100	20,500	24,200	2.70
3	<i>i</i> -PrOH	200/5	60	5	98	4,050	11,500	1.64
4	<i>i</i> -PrOH	500/1	60	150	100	51,050	48,100	3.5
5	<i>i</i> -PrOH	500/5	60	150	100	10,250	18,000	3.8
6	BnOH	500/0	60	8	34	17,450	102,600	1.91
7	BnOH	500/1	60	8	95	48,600	42,000	1.70
8	BnOH	500/2	60	8	100	25,600	27,700	1.65
9	BnOH	500/5	60	7	99	10,200	12,400	1.55
10	BnOH	500/10	60	30	100	5,200	7,300	1.38
11	BnOH	500/20	60	60	99	2,600	3,500	1.35
12	BnOH	500/50	60	120	100	1,150	1,600	1.10
13	BnOH	1,000/5	60	10	100	20,500	25,900	1.60
14	BnOH	1,000/50	60	20	89	1,900	2,200	1.17
15	BnOH	2,000/5	60	15	79	32,350	35,700	1.90
16	BnOH	2,000/20	60	30	95	9,800	13,100	1.38
17	BnOH	5,000/20	60	75	90	23,100	28,760	1.70
18	BnOH	5,000/200	60	180	100	2,660	1,490	1.23
19	BnOH	10,000/20	60	180	89	45,500	43,290	1.90
20	BnOH	25,000/10	110	40	83	211,750	185,200	1.68
21	BnOH	25,000/20	110	50	96	122,500	110,230	1.84
22	BnOH	25,000/50	110	40	80	40,900	49,300	1.90
23	BnOH	50,000/20	110	120	93	237,250	160,600	1.68

^[a] Monomer and alcohol equivalents relative to [(BDI)Zn(N(SiMe₃)₂)]₀.

^[b] Monomer conversion determined by ¹H NMR.

^[c] Calculated from [TMC]₀/[ROH]₀ × monomer conversion × *M*_{TMC} + *M*_{ROH}, with *M*_{TMC} = 102 g·mol⁻¹, *M*_{*i*-PrOH} = 60 g·mol⁻¹ and *M*_{BnOH} = 108 g·mol⁻¹.

^[d] Determined by SEC vs. polystyrene standards and corrected by 0.73.^[15a]

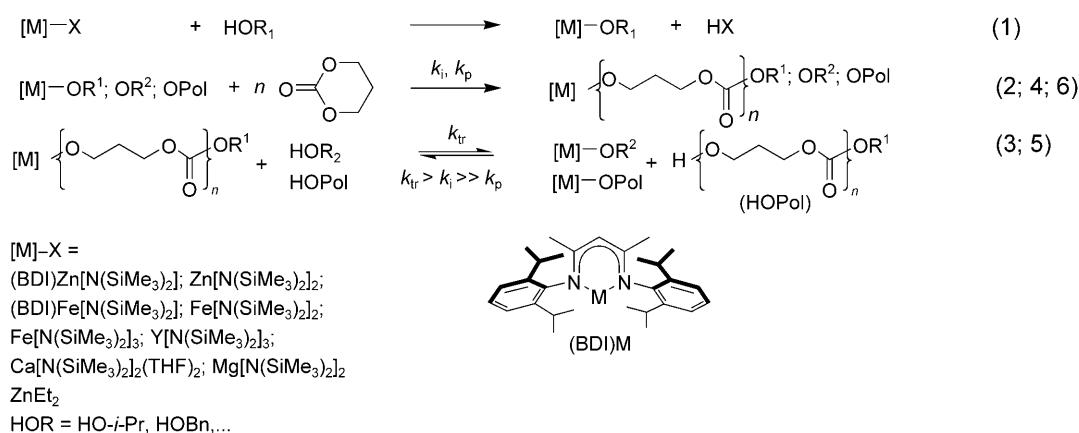
^[e] Molar mass distribution calculated from SEC traces.

bis(amido)-iron improved its TOF value from 1,000 to 5,820 h⁻¹ upon increasing the temperature from 60 to 110 °C (entries 7 and 8).

At 110 °C, the ROP of TMC carried out with the (BDI)Fe[N(SiMe₃)₂]/BnOH system at the high [TMC]₀/[(BDI)Fe[N(SiMe₃)₂]]₀/[BnOH]₀ ratio of 50,000/1/20 gave over 14 h (reaction time non-optimized) a high molar mass polymer (*M*_{n,theo} = 245,130 g·mol⁻¹, *M*_{n,SEC} = 110,300 g·mol⁻¹, *M*_w/*M*_n = 1.81). However, although almost complete conversion was achieved, the control over the molar mass and molar mass distribution was modest.^[20] A similar observation was also made for the ROP initiated by the analogous (BDI)Zn[N(SiMe₃)₂]/BnOH catalyst system (Table 4, entry 22, *vide infra*).

The ROP of TMC in bulk using simple, readily available diethylzinc in association with an alcohol (*i*-PrOH, BnOH) was next evaluated in more detail, in the light of our previous work on the preparation of amino end-functionalized PTMCs from ZnEt₂/3-(*N*-Boc-amino)-1-propanol.^[7b] Indeed, as initially established by Höcker et al., the *in situ* reaction of diethylzinc reagent with an alcohol (2 equiv. vs. Zn) in toluene solution generates the corresponding zinc(II) alk-

oxide species “Zn(OR)₂”, which subsequently initiates the controlled (but not immortal) ROP of a cyclic ester such as lactide, ε-caprolactone or trimethylene carbonate.^[7b,21] Representative results for the bulk ROP of TMC at 60 °C, gathered in Table 2, clearly illustrate the feasibility of ZnEt₂/ROH (1:2) initiating systems upon varying the alcohol component from *i*-PrOH to BnOH. Whichever the alcohol, the polymerization proceeded with as much as 1,000 TMC equiv. (vs. Zn) successfully polymerized within 2 h. The best control over the polymerization, as judged by the close agreement of the molar mass determined from SEC with that calculated based on two initiating zinc-alkoxide bonds and by the molar mass distribution which remained well below 1.94 (*M*_w/*M*_n average value = 1.55), was obtained with BnOH.^[20] The ROP appeared faster with BnOH with which 96% conversion was reached within 45 min (TOF = 1,280 h⁻¹; entry 12), as compared to 78% of monomer consumed in 90 min when using *i*-PrOH (TOF = 520 h⁻¹; entry 8). For [TMC]₀/[ZnEt₂]₀/[ROH]₀ = 1,000/1/2, productivities and especially activities were higher with benzyl alcohol (TOFs = 100–1,280 h⁻¹; TONs = 250–1,000) than with isopropyl alcohol (TOF = 495–



Scheme 1. Mechanistic representation of the [Zn/alcohol]-mediated “immortal” ROP of TMC.

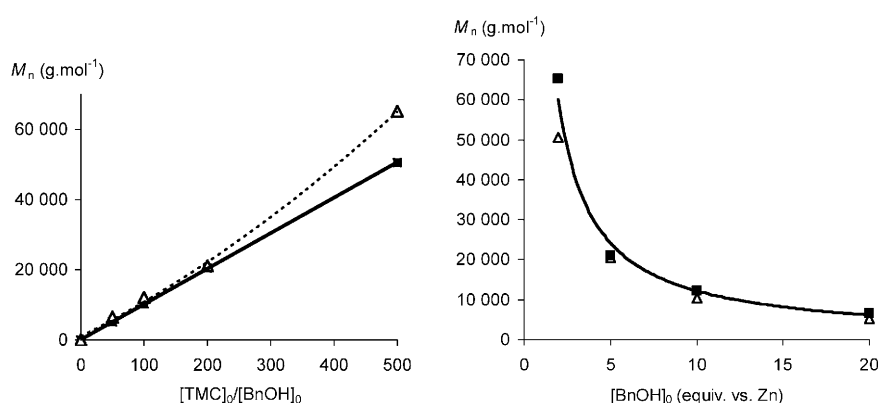


Figure 2. Dependence of the experimental molar mass $M_{n,SEC}$ on the $[TMC]_0/[BnOH]_0$ ratio for the bulk ROP of TMC promoted by (left) $[ZnEt_2]_0/[BnOH]_0 = 1\,000:1$; (right) $[TMC]_0/[ZnEt_2]_0 = 1\,000:1$ (see Table 2 and Table 3). Δ experimental values determined by SEC; \blacksquare theoretical values.

520; TON = 780–990). Considering that the alcohol is essentially involved in the initiation process [Scheme 1, Eq.(1)], the observation of different apparent reaction rates (overall activities) with BnOH and *i*-PrOH can be tentatively accounted for by the generation of different amounts of active Zn alkoxide species, especially when using such small loadings of alcohol (2 equiv. vs. Zn) [note that this amount of active Zn alkoxide species is anticipated to affect only the activity/productivity data, as the molar mass is controlled by the monomer-to-alcohol ratio].

As reported in Table 3, when using the added alcohol as a chain transfer agent (CTA), i.e., when using an excess of alcohol, the reaction time required to reach completion was again found to be higher with isopropyl alcohol as compared to benzyl alcohol. Remarkably, the “immortal” ROP with BnOH remained fairly well controlled in terms of similar $M_{n,SEC}$ and $M_{n,theo}$ values (Figure 2, left, for $[TMC]_0/[BnOH]_0 = 1,000/1$) and relatively narrow molar mass distributions. Note that in the case of “immortal” polymerization process, the expected molar mass value $M_{n,theo}$

is calculated from the initial concentration in CTA, that is, in $[ROH]_0$, rather than from that of the zinc diethyl complex. Therefore, as the concentration in CTA increases, the molar mass of the resulting PTMC decreases as illustrated in Figure 2, right, for $[TMC]_0/[ZnEt_2]_0 = 1,000/1$. However, as already observed in the absence of CTA (Table 2), the agreement between calculated and experimental molar masses was significantly lower with *i*-PrOH than with BnOH (compare entries 3–5 vs. 7 and 8, Table 3). As much as 50 macromolecular chains could thus be grown from a single zinc center by the $ZnEt_2/BnOH$ system in the presence of up to 1,000 TMC equivalents (entry 10) while as much as 2,000 TMC equivalents could be fully converted upon growing up to 20 macromolecular chains on the zinc metal (entry 11). Thus far, successful conversion of such large amounts of TMC in a controlled manner using a simple dialkylzinc precursor was unprecedented.^[7b,15]

The potentially favourable influence of ancillary ligands present in the zinc coordination sphere on the control over the polymerization was evaluated using

the amido complex $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ [$\text{BDI} = \text{CH}(\text{CMeNC}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2)_2$] in association with an alcohol.^[22] Use of such a β -diiminate ligand easily provides well-defined single-site metallic complexes, which have been fully characterized in the solid state and in solution.^[10,11a-c,e,12] The active species formed during the polymerization are thus more easily identified and the whole mechanism can be better understood.^[10,11,12] Besides, use of an initiator bearing such a BDI ligand can provide a better control over the degree of polymerization and, when a chiral monomer such as lactide is used, over the degree of stereoselectivity.^[10,11,12] Zinc as well as calcium and magnesium amido or alkoxide complexes supported by BDI ligands have been successfully applied to the ROP of various cyclic esters including essentially lactide, and to a much lesser extent β -butyrolactone or δ -valerolactone, yet excluding carbonate monomers.^[10,11,12]

The results for the ROP of TMC initiated by the $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{ROH}$ systems using *i*-PrOH or BnOH as CTA at 60°C are summarized in Table 4. With *i*-PrOH, at $[\text{TMC}]_0/[(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]]_0 = 200$ and 500, the absence of control over the degree of polymerization and the occurrence of significant side reactions are evidenced by the poor agreement of the molar mass determined by SEC with the ones calculated and by the significantly broadened molar mass distribution values (entries 1–5). The loss of control is already evidenced from the polymerization achieved with a TMC-to-*i*-PrOH ratio of 200, which led to 87% conversion within 5 min and a PTMC with a molar mass twice as high as the expected value with an M_w/M_n value close to 2 (entry 1). These results confirmed the difference in reactivity and in degree of control between *i*-PrOH and BnOH, as pointed out above with the ZnEt_2/ROH system. We assume that this difference in reactivity arises from the lower bulkiness of the primary vs. secondary alcohol. Based on these observations, subsequent ROPs of TMC

using an alcohol as CTA were then performed with BnOH.

Preliminary experiments using the $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{BnOH}$ system under “immortal” conditions quickly revealed the superiority of this discrete system over the more rustic $\text{ZnEt}_2/\text{BnOH}$ combination. In fact, controlled ROP of 1,000 TMC equivalents in the presence of 5 equivalents of alcohol could be efficiently achieved with both zinc precursors; however, the activity of the Zn-BDI system was 6 times higher than that of the ZnEt_2 system ($\text{TOF} = 6,000$ vs. $1,000 \text{ h}^{-1}$, respectively, Table 4, entry 13 vs. Table 3, entry 7). We assume that this enhanced performance most likely arises from the bulky ancillary BDI ligand, which is not active during the ROP of TMC but provides a greater stability to the oxophilic zinc center in the presence of large amounts of surrounding alcohol molecules, thus preventing catalyst deactivation (e.g., *via* aggregation).^[23] From this encouraging result, we verified that “immortal” polymerization could also be carried out over a wide range of $[\text{TMC}]_0/[\text{BnOH}]_0$ ratios. Using 500 TMC equivalents, up to 50 polymer chains were successfully grown from a unique zinc center within less than 2 h at 60°C (entries 6–12). Assuming that all the added alcohol molecules contribute to the “immortal” polymerization, the calculated M_n values matched well the experimental ones while the M_w/M_n ratio remained quite narrow, highlighting the well controlled character of the polymerization. The decrease of the experimental molar mass ($M_{n,\text{SEC}}$) of the PTMC with increasing amount of added BnOH, as depicted in Figure 3, evidences that the $[(\text{BDI})\text{Zn}(\text{OR})]/\text{ROH}$ ($\text{R} = \text{Bn}$, and then growing PTMC chain) transfer efficiently takes place (Scheme 1). Similarly, as many as 50–200 chains were successfully grown from a unique $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]$ precursor, upon raising the monomer content to as much as 50,000 units (entries 13–23). With such tens of thousands of TMC equivalents,

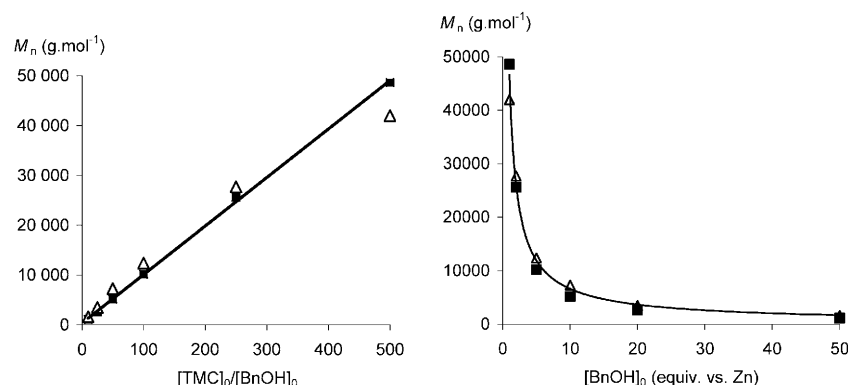


Figure 3. Dependence of the experimental molar mass $M_{n,\text{SEC}}$ on the $[\text{TMC}]_0/[\text{BnOH}]_0$ ratio for the bulk ROP of TMC promoted by (left) $[(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]]_0/[\text{BnOH}]_0 = 1:20$; (right) $[\text{TMC}]_0/[(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]]_0 = 500:1$ (see Table 4). Δ experimental values determined by SEC; \blacksquare theoretical values.

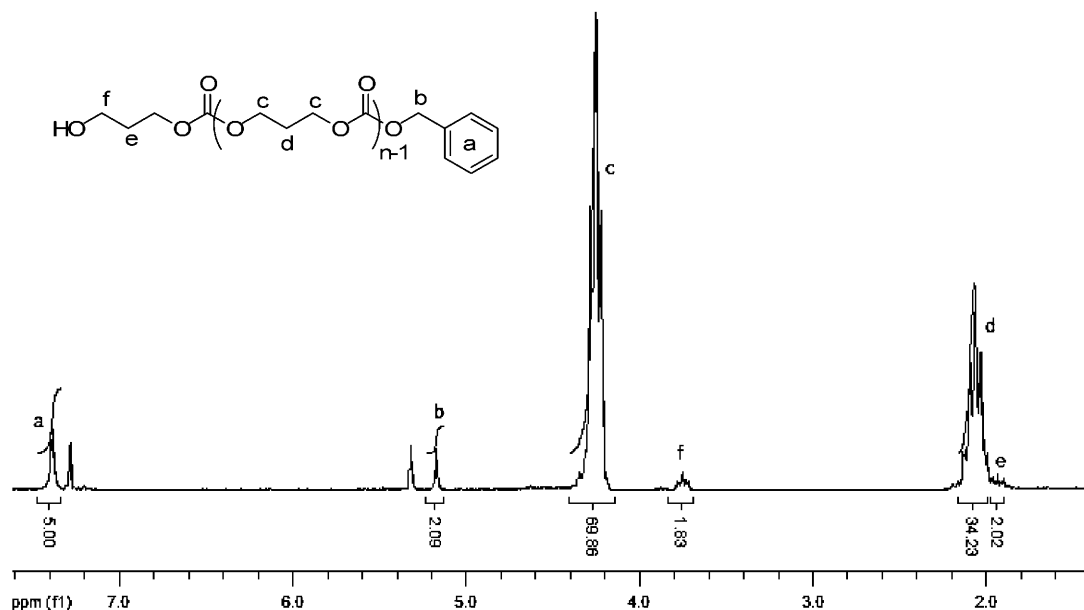


Figure 4. ^1H NMR (200 MHz, CDCl_3 , 23°C) spectrum of a PTMC synthesized from the $(\text{BDI})\text{Zn}(\text{N}(\text{SiMe}_3)_2)/\text{BnOH}$ system (Table 3, entry 13).

almost quantitative conversions (83–96%) could still be reached at 60 – 110°C within 2 h (entries 19–23). Up to a $[\text{TMC}]_0/[\text{Zn}]_0$ ratio of 25,000, the control of the molar mass is quite well maintained [as judged by the good agreement between experimental and calculated M_n values] and slightly decreases when doubling-up the monomer content up to 50,000 (entries 20–23). We assume that the latter slight discrepancy most likely results from the increasing amount of impurities present in such a large quantity of monomer. These impurities (possibly protic) compete with the zinc alkoxide initiating species (or the CTA, BnOH) for the ROP of TMC, thereby proportionally decreasing the experimental molar mass value below that anticipated from initiation by only the zinc alkoxide active species and the $[\text{TMC}]_0/[\text{BnOH}]_0$ ratio. Also, there does not seem to be an increase of the molar mass distribution upon increasing the alcohol content (entries 20–23), suggesting that side reactions such as inter-molecular transesterification reactions (bimolecular reshuffling) do not occur at higher extent under these conditions.^[24,25] Remarkably, under such operating conditions, turnover numbers and turnover frequencies reach the previously unmatched values for the ROP of TMC of $\text{TON}=46,500\text{ mol}(\text{TMC})\cdot\text{mol}(\text{Zn})^{-1}$ (entry 23) and $\text{TOF}=31,125\text{ mol}(\text{TMC})\cdot\text{mol}(\text{Zn})^{-1}\cdot\text{h}^{-1}$ (entry 20).^[19] The increase in these activity and productivity data are tremendous in light of the available record reported for the TMC/ $\text{Zn}(\text{acac})_2$ system ($\text{TON}=1,293$ in 1 h; $\text{TOF}=970$ – $1,290\text{ h}^{-1}$ at 110°C).^[7d]

The “controlled-living” character of the ROP of TMC was evidenced by a double monomer feed ex-

periment.^[24] A PTMC of $M_{n,\text{SEC}}=12\,200\text{ g}\cdot\text{mol}^{-1}$ and $M_w/M_n=1.58$ was first synthesized from the complete polymerization of 500 TMC equivalents using the $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{BnOH}$ (1/5) catalyst system. Subsequent to a second addition of 500 TMC equivalents, the polymerization resumed up to full conversion to afford a PTMC with an $M_{n,\text{SEC}}=21\,900\text{ g}\cdot\text{mol}^{-1}$ and $M_w/M_n=1.63$. As confirmed by the shift of the symmetrical SEC elution peak toward a lower retention time and by the corresponding increase of the molar mass, the molar mass increased proportionally to the molar amount of TMC added in the second step while keeping the molar mass distribution narrow. This “living” character of the polymerization opens valuable opportunities for the synthesis of block copolymers.

Characterization of the PTMCs by ^1H and ^{13}C NMR analyses (in CDCl_3) revealed the presence of both a hydroxymethyl and an alkoxy carbonate ($\text{OCOO-}i\text{-Pr}/\text{OCOOBn}$) chain-end, as identified by each diagnostic resonance: $-\text{CH}_2\text{OH}$, $\delta=3.75$, triplet and $-\text{OCH}(\text{CH}_3)_2$, $\delta=4.85$, triplet or $-\text{OCH}_2\text{C}_6\text{H}_5$, $\delta=5.16$ ppm. The representative ^1H NMR spectrum of an HO-PTMC-OBn polymer is shown in Figure 4. No other signal was ever detected, even for the polymers prepared in the presence of a large excess of alcohol. Also, ^{13}C NMR data confirmed the presence of the main-chain $[-(\text{CH}_2)_3\text{OC}(\text{O})\text{O}-]$, $\delta=155.3$ ppm] and terminal $[-(\text{CH}_2)_3\text{OC}(\text{O})\text{OCH}_2\text{Ph}]$, $\delta=155.7$ and 70.1 ppm] carbonate groups. These NMR analyses clearly revealed the absence of the signals corresponding to ether units ($\delta_{\text{C}}=66.5$ – 67.7 ppm; $\delta_{\text{H}}=3.3$ – 3.1 ppm),^[26] thus highlighting the absence of decar-

boxylation of the PTMCs, a trend yet often observed in ROP of carbonates.^[5a] Use of either ^1H resonance among the $-\text{CH}_2\text{OH}$, $-\text{OCH}(\text{CH}_3)_2$ and $-\text{OCH}_2\text{C}_6\text{H}_5$ groups to evaluate the NMR molar mass of the polymer gave values in good agreement with the theoretical data established from the TMC-to-ROH ratio, as well as with those measured by SEC (refer to the Experimental Section). This good match further highlights the effective reaction between the catalyst precursor $[\text{M}]-\text{X}$ [$\text{M} = (\text{BDI})\text{Zn}/\text{Fe}$, Ca , Mg , Y ; $\text{X} = \text{Et}$ or $\text{N}(\text{SiMe}_3)_2$] and alcohol, leading quantitatively, within the operating conditions (especially, a pre-mixing time of 15 min), to the formation of the alkoxide analogue $[\text{M}]-\text{O}-i\text{-Pr}/\text{OBn}$ that subsequently propagates the ROP of TMC. Hydrolysis of the metal-alkoxide bond of the active species $[\text{M}]-[\text{O}(\text{CH}_2)_3\text{OC}(\text{O})]_n\text{O}-i\text{-Pr}/\text{OBn}$ [which occurs upon quenching the polymerization] generates the hydroxymethyl end group, whereas the other chain end functionality arises from the alcohol introduced. Establishing such a general and straightforward procedure to prepare *in situ* the real active metal alkoxide species from an easy to handle precursor and the alcohol is time-saving and thus highly valuable.

The “immortal” ROP mechanism common to all metallic precursors used in the present work and suggested from all these results and observations is depicted in Scheme 1. The first step of the polymerization of TMC, as performed in the present studies using a metal alkyl or amide precursor $[\text{M}]-\text{X}$ in the presence of an alcohol, involves the *in situ* formation of the initiating alkoxide species upon alcoholysis of the $[\text{M}]-\text{X}$ bond [Eq. (1)]. The resulting alkoxide group on this newly formed $[\text{M}]-\text{OR}^1$ then undergoes coordination-insertion of the first TMC molecule to give the active growing species $[\text{M}]-[\text{O}(\text{CH}_2)_3\text{OC}(\text{O})]\text{OR}^1$ [Eq. (2)]. This active polymer chain can then undergo a rapid exchange with another HOR^2 molecule present in excess in the reaction medium [Eq. (3)]. This thus gives a novel $[\text{M}]-\text{OR}^2$ species that can similarly behave as the first alike species according to Eq. (4), along with an α -hydroxy- ω -alkoxycarbonate end-capped polycarbonate chain (HOPol). This latter “dormant” macromolecule, which will become numerically more and more important as the whole reaction proceeds, can – because Eq. (3) is reversible – revive into a growing species upon behaving as a CTA similarly to the excess of initial ROH [Eq. (5)]. Thus, species active for some time do convert back and forth to inactive ones [Eqs. (3) and (5)]. This rapid growing/dormant interconversion cycle goes on over the entire life-time of the macromolecules. Any active species bearing a metal-oxygen bond ($[\text{M}]-\text{OR}^{1,2,\dots}$, $[\text{M}]-\text{OPol}$) can carry on the propagation [Eqs. (4) and (6)] and any HO-terminated (macro)molecule ($\text{HOR}^{1,2,\dots}$, HOPol) can behave as a CTA [Eqs. (3) and (5)]. The chain trans-

fer reaction involved here is reversible and much more rapid than the chain growth. While the exchange between the metal alkoxide species $[\text{M}]-[\text{O}(\text{CH}_2)_3\text{OC}(\text{O})]\text{OR}^1$, $[\text{M}]-\text{OR}^{2,3,\dots}$ or $[\text{M}]-\text{OPol}$ and the alcohol $\text{HOR}^{2,3,\dots}$ or HOPol [Eqs. (3) and (5)] is not unusual, its actual rapidity is the decisive factor allowing the control of the ROP, as illustrated with the molar mass distribution which remains quite low. All the experimental results gathered in Table 1, Table 2, Table 3, and Table 4 show M_w/M_n values below 1.94, a quite narrow value considering the bulk feature of the ROP process.^[20] Considering that this transfer to the intentionally added CTA is fast and reversible, this so-called “immortal” ROP process can as well be referred to as a “living ROP involving reversible transfer”^[24] (which yet does not exclude some minor transesterification side reactions^[25]). The whole number of growing polymer chains thus exceeds the number of metallic precursor molecules initially introduced – making the process catalytic *vs.* the monomer *and* the macromolecules as well – and is defined by the initial amount of CTA added. In the present study, as many as 200 PTMC chains could be grown from a unique metallic center. This is in contrast to a “classical” polymerization where the number of macromolecules is given by the number of active sites available from the initiator molecules. During the last termination step, deactivation of all living macromolecular species gives the HO-PTMCs-OR ($\text{R} = i\text{-Pr}$, Bn).

Several features of this “immortal” ROP process of TMC are quite unique. First, at the operating temperature of 60 or 110 °C, the ROP proceeds quite fast, allowing completion within short reaction times (although not always optimized), especially in the case of the $(\text{BDI})\text{Zn}[\text{N}(\text{SiMe}_3)_2]/\text{BnOH}$ catalyst system (Table 4). Also outstanding is the ability to prepare well-defined high molar mass polymers. Indeed, PTMCs of M_n as high as 160,600–185,200 $\text{g}\cdot\text{mol}^{-1}$ with an M_w/M_n of 1.68 could be prepared upon growing of 10–20 macromolecules per $[(\text{BDI})\text{Zn}]$ center, involving as much as 25,000–50,000 monomer equivalents in a single experiment (Table 4, entries 20–23). For comparison, the polymerization of TMC in chlorobenzene solution promoted at 80 °C by $\text{SnOct}_2/\text{BnOH}$ ($[\text{TMC}]_0/[\text{SnOct}_2]_0 = 500$) resulted in the growth of at most 13 chains per tin center; however, under such conditions, only low molar mass PTMCs were obtained ($\text{DP}_{\text{NMR}} = 50$).^[27] Also, whereas as many as 256 poly(ϵ -caprolactone) chains were successfully grown from a bisphenolate-aluminum alkoxide ($\text{TOF} = 800 \text{ h}^{-1}$), only oligomers ($M_n = 440 \text{ g}\cdot\text{mol}^{-1}$) were recovered.^[18g] The TOF values in these latter examples remained much lower than the values unveiled in the present work which can be as large as 31,125 h^{-1} (Table 4, entry 20). This highest TOF reported to date for the ROP of TMC is also over 20 times larger than

the previously known highest value of 1,290 obtained with the TMC/Zn(acac)₂ system.^[7d] This also represents a large batch synthesis of PTMCs scaled up to 20 g of monomer, a significant laboratory scale, without any loss in the final conversion.^[6c,28]

Another important outcome of such an “immortal” ROP of carbonate monomers is the easy access to end-functionalized polycarbonates. Upon varying the added alcohol component used as co-initiator/CTA, various α -hydroxy- ω -alkoxycarbonate telechelic PTMCs have been synthesized. From the (BDI)Zn[N(SiMe₃)₂]/ROH, with ROH = isopropyl alcohol, benzyl alcohol, 2-butanol, 3-buten-2-ol, *p*-trifluoromethylbenzyl alcohol systems, the corresponding functionalized PTMCs, HO-PTMC-OR, have been successfully prepared at [TMC]₀/[(BDI)Zn[N(SiMe₃)₂]]₀/[ROH]₀ = 2,000/1/20. NMR characterization (refer to the Experimental Section) confirmed the selective hydroxy/alkoxide end-capping of the polymers.

Regarding the potential biomedical applications of PTMCs,^[2] use of as little as 20 ppm of initiating metallic precursor to synthesize the polymers (Table 4 entry 23) results in, at worse, trace amounts of metal residues in the final precipitated sample and thus precludes any reservations concerning its potential toxicity. In comparison, the limit of residual tin in commercially used medical polymers has been set by the Food and Drug Administration at 20 ppm.^[26a] In light of the greater toxicity of tin relative to the biometals selected for the present study,^[2,4b,6] the PTMCs described in the present work appear most suitable for therapeutic applications. In this context, the “immortal” ROP of carbonates as reported here further appears as a great opportunity to considerably diminish the amount of metallic species of the initiating system beyond the accessible weighing limit.^[28a] The dilemma being the smallest quantity of metallic reagent that can be reasonably weighted, one can further decrease this value upon using a large excess of a protic source as chain transfer agent for the ROP process.

Conclusions

All the investigated alkyl or amido zinc, iron, yttrium, calcium or magnesium precursors, in association with a protic source such as alcohol as chain transfer agent, form efficient initiating systems for the bulk “immortal” ROP of TMC. Polymerization proceeds first through a pre-initiation step involving the *in situ* formation of a metal alkoxide derivative, followed by the coordination-insertion of the first TMC unit leading to the active species which then further propagates the “immortal” polymerization, thanks to a swift alkoxide/alcohol exchange reaction. The whole process is reasonably well controlled over the wide

range of [TMC]₀/[[M]–X]₀/[ROH]₀ = 500–50,000/1/1–200. Unprecedented activities and productivities have been reached, in particular with (BDI)Zn[N(SiMe₃)₂] as the catalyst precursor, which allowed the growth of up to 50 polymer chains per metal center in the presence of a loading of metal as low as 20 ppm. This β -diiminate amido zinc complex provides an ideal compromise affording the overall best performances combining both a high activity and a good stability. Indeed, the magnesium, calcium and yttrium amido derivatives investigated, which are more active than (BDI)Zn[N(SiMe₃)₂], remain yet more sensitive and undergo rapid deactivation when the TMC loading is increased, while the iron amido systems are less active. This is the first obvious example of an efficient “immortal” polymerization of a carbonate monomer, which ultimately enables the preparation of oligomeric or still high molar mass materials, at will. The possibility to tune the end-functionality of the polymers upon varying the nature of the alcohol confers a great versatility to these systems. Finally, the high activity and control that can be maintained even at very high monomer/alcohol ratios allow the preparation of uncontaminated biocompatible polycarbonates that can be directly applied to the biomedical field.

Experimental Section

Materials

All manipulations were performed under an inert atmosphere (argon, <3 ppm of O₂) using standard Schlenk, vacuum line and glove-box techniques. Solvents were thoroughly dried and deoxygenated by standard methods and distilled before use. CDCl₃ was dried over a mixture of 3 and 4 Å molecular sieves. Trimethylene carbonate (TMC, 1,3-dioxane-2-one, Labso Chimie Fine, Blanquefort-France) was first dissolved in THF and stirred over CaH₂ for 2 days before being filtered and dried. TMC was finally recrystallized from cold THF. ZnEt₂ (1.1 M solution in toluene), benzyl alcohol, 2-propanol, 2-butanol, 3-buten-2-ol and 4-(trifluoromethyl)benzyl alcohol (all purchased from Aldrich) were dried before use. Mg[N(SiMe₃)₂]₂,^[29a] Ca[N(SiMe₃)₂]₂,^[29a] Y[N(SiMe₃)₂]₃,^[29b] Fe[N(SiMe₃)₂]₂,^[29c] Fe[N(SiMe₃)₂]₃,^[29d] (BDI)Fe(N(SiMe₃)₂),^[29e,f] Zn[N(SiMe₃)₂]₂,^[29g] and (BDI)Zn(N(SiMe₃)₂)^[10b] were synthesized following literature procedures.

Instrumentation and Measurements

¹H (500, 200 MHz) and ¹³C (125, 50 MHz) NMR spectra were recorded in CDCl₃ on Bruker Avance AM 500 and DPX 200 spectrometers at 23 °C and were referenced internally using the residual ¹H and ¹³C solvent resonance relative to tetramethylsilane (δ = 0).

Average molar mass (M_n) and molar mass distribution (M_w/M_n) values were determined from chromatogram traces recorded by SEC in THF at 20 °C (flow rate = 1.0 mL·min^{−1}) on a Polymer Laboratories PL50 apparatus equipped with a

refractive index detector and a PLgel 5 Å MIXED-C column. The polymer samples were dissolved in THF (2 mg·mL⁻¹). All elution curves were calibrated with polystyrene standards. $M_{n,SEC}$ values of PTMCs were calculated using the average correction coefficient previously reported ($M_{n,SEC} = M_{n,SEC,raw\ data} \times 0.73$; 0.73 = average of the coefficients determined from low molar mass PTMCs (0.57; $M_n < 5,000$) and from high molar mass PTMCs (0.88; $M_n > 10,000$) using MALDI-TOF-MS and viscosimetry analyses, respectively.^[15a] The SEC traces of the polymers all exhibited a unimodal and symmetrical peak.

Monomer conversions were calculated from ¹H NMR spectra of the crude polymer sample, from the integration (Int.) ratio Int. PTMC/[Int. PTMC + Int. TMC], using the methylene group in the α-position of the carbonate [$CH_2OC(O)$, $\delta = 4.25$ ppm].

For short-chain PTMCs, the molar mass values were determined by ¹H NMR analysis from the relative intensity of the signals of the methylene protons of the PTMC chains [$-CH_2OC(O)$] at $\delta = 4.25$ ppm to the α-hydroxymethyl (CH_2OH) at $\delta = 3.75$ ppm and, as double-checking, to the benzyloxy carbonate hydrogens (Ph CH_2O) at $\delta = 5.16$ ppm. The number-average molar mass values thus obtained by ¹H NMR were in close agreement with the ones calculated; for instance, $M_{n,NMR} = 5,750$, 2,800 and 11,000 g·mol⁻¹ for entries 10, 11 and 16 in Table 4, respectively.

Typical Polymerization Procedure

(BDI)Zn[N(SiMe₃)₂] (0.0109 g, 16.9 μmol) was added to C₆H₅CH₂OH (1 equiv., 1.75 μL, 16.9 μmol) placed in toluene (0.1 mL) and stirred over 15 min just prior to the addition of the monomer (0.862 g of TMC, 8.44 mmol). The mixture was then stirred at the required temperature over the appropriate time (reaction times have not been systematically optimized). The reaction was quenched with an excess of an acetic acid solution (ca. 2 mL of a 1.74 mol/L solution in toluene). The resulting mixture was concentrated under vacuum and the conversion determined by ¹H NMR analysis of the residue. This crude polymer was then dissolved in CH₂Cl₂ and purified upon precipitation in cold methanol, filtered and dried under vacuum. The final polymer was then analyzed by NMR and SEC.

Spectroscopic Data

HO-PTMC-OBn: ¹H NMR (200 MHz, CDCl₃) (Figure 1): $\delta = 7.29$ (m, 5H, C₆H₅), 5.16 (s, 2H, PhCH₂), 4.25 [t, $J = 6.2$ Hz, 4nH, C(O)OCH₂CH₂CH₂OC(O)], 3.75 (t, $J = 6$ Hz, 2H, HOCH₂), 2.05 [qt, $J = 6$ Hz, 2nH, C(O)OCH₂CH₂CH₂OC(O)], 1.89 (qt, $J = 5.9$ Hz, 2H, HOCH₂CH₂); ¹³C NMR (50 MHz, CDCl₃): $\delta = 155.7$ [HOCH₂CH₂CH₂OC(O)], 155.3 [C(O)OCH₂CH₂CH₂OC(O)], 135.5 (C₆H_{5ortho}), 129.0 (C₆H_{5meta}), 128.8 (C₆H_{5para}), 70.1 (CH₂C₆H₅), 65.4 [C(O)OCH₂CH₂CH₂OH], 64.7 [C(O)OCH₂CH₂CH₂OC(O)], 59.3 [C(O)OCH₂CH₂CH₂OH], 32.0 [C(O)OCH₂CH₂CH₂OH], 28.4 [C(O)OCH₂CH₂CH₂OC(O)]. Polymerization using various alcohols as CTA (ROH = 2-propanol, 2-butanol, 3-buten-2-ol, *p*-trifluoromethylbenzyl alcohol) were similarly carried out with [TMC]₀/[(BDI)Zn[N(SiMe₃)₂]]₀/[ROH]₀ = 2 000/1/20.

HO-PTMC-O-*i*-Pr: ¹H NMR (200 MHz, CDCl₃): $\delta = 4.85$ [m, 1H, CH(CH₃)₂]; 4.25 [t, $J = 6.2$ Hz, 4nH, C(O)OCH₂CH₂CH₂OC(O)], 3.75 (t, $J = 6$ Hz, 2H, HOCH₂), 2.05 [qt, $J = 6$ Hz, 2nH, C(O)OCH₂CH₂CH₂OC(O)], 1.28 [d, $J = 6.2$ Hz, 6H, CH(CH₃)₂]; ¹³C NMR (50 MHz, CDCl₃): $\delta = 155.8$ [C(O)OCH₂CH₂CH₂OC(O)], 155.1 [C(O)OCH₂CH₂CH₂OC(O)], 72.1 [CH(CH₃)₂], 65.1 [C(O)OCH₂CH₂CH₂OH], 65.0 [C(O)OCH₂CH₂CH₂OC(O)], 59.1 [C(O)OCH₂CH₂CH₂OH], 31.7 [C(O)OCH₂CH₂CH₂OH], 29.1 [C(O)OCH₂CH₂CH₂OC(O)], 22.0 [CH(CH₃)₂].

HO-PTMC-OCH(CH₃)CH₂CH₃: ¹H NMR (500 MHz, CDCl₃): $\delta = 4.86$ [m, 1H, CH(CH₃)CH₂CH₃], 4.25 [t, $J = 6.2$ Hz, 4nH, C(O)OCH₂CH₂CH₂OC(O)], 3.75 (t, $J = 6$ Hz, 2H, HOCH₂), 2.05 [qt, $J = 6$ Hz, 2nH, C(O)OCH₂CH₂CH₂OC(O)], 1.61 [m, 2H, CH(CH₃)CH₂CH₃], 1.28 [d, $J = 6.2$ Hz, 3H, CH(CH₃)CH₂CH₃], 0.98 [t, $J = 7.6$ Hz, 3H, CH(CH₃)CH₂CH₃]. ¹³C NMR (50 MHz, CDCl₃): $\delta = 155.8$ [C(O)OCH₂CH₂CH₂OC(O)], 155.4 [C(O)OCH₂CH₂CH₂OC(O)], 90.7 [OCH(CH₃)CH₂CH₃], 65.7 [C(O)OCH₂CH₂CH₂OH], 65.4 [C(O)OCH₂CH₂CH₂OC(O)], 59.4 [C(O)OCH₂CH₂CH₂OH], 32.0 [C(O)OCH₂CH₂CH₂OH], 29.4 [C(O)OCH₂CH₂CH₂OC(O)], 28.4 [OCH(CH₃)CH₂CH₃], 19.8 [OCH(CH₃)CH₂CH₃], 10.1 [OCH(CH₃)CH₂CH₃].

HO-PTMC-OCH₂(4-CF₃C₆H₄): ¹H NMR (500 MHz, CDCl₃): $\delta = 7.87$ – 7.63 (d, $J = 7.8$ Hz, 2H, aromatics), 7.53–7.49 (d, $J = 8$ Hz, 2H, aromatics), 5.22 (s, 1H, PhCH₂O), 4.25 [t, $J = 6.2$ Hz, 4nH, C(O)OCH₂CH₂CH₂OC(O)], 3.75 (t, $J = 6$ Hz, 2H, HOCH₂), 2.05 [qt, $J = 6$ Hz, 2nH, C(O)OCH₂CH₂CH₂OC(O)]; ¹³C NMR (50 MHz, CDCl₃): $\delta = 155.9$ [C(O)OCH₂CH₂CH₂OC(O)], 155.3 [C(O)OCH₂CH₂CH₂OC(O)], 139.8 (C1 arom), 128.7, 126.1 (C2, C3 arom), 68.9 [C(O)OCH₂-Ph-CF₃], 65.1 [C(O)OCH₂CH₂CH₂OH], 65.0 [C(O)OCH₂CH₂CH₂OC(O)], 59.4 [C(O)OCH₂CH₂CH₂OH], 32.0 [C(O)OCH₂CH₂CH₂OH], 28.6 [C(O)OCH₂CH₂CH₂OC(O)] [C4 and CF₃ carbons were not observed].

HO-PTMC-OCH(CH₃)CH=CH₂: ¹H NMR (200 MHz, CDCl₃): $\delta = 5.68$ [m, 1H, OCH(CH₃)CH=CH₂], 5.20 [m, 2H, OCH(CH₃)CH=CH₂], 4.83 [m, 1H, OCH(CH₃)CH=CH₂], 4.25 [t, $J = 6.2$ Hz, 4nH, C(O)OCH₂CH₂CH₂OC(O)], 3.75 (t, $J = 6$ Hz, 2H, HOCH₂), 2.05 [qt, $J = 6$ Hz, 2nH, C(O)OCH₂CH₂CH₂OC(O)], 1.22 [d, $J = 6.6$ Hz, 3H, OCH(CH₃)CH=CH₂]; ¹³C NMR (125 MHz, CDCl₃): $\delta = 155.8$ [C(O)OCH₂CH₂CH₂OC(O)], 155.1 [C(O)OCH₂CH₂CH₂OC(O)], 132.0 [OCH(CH₃)CH=CH₂], 121.1 [OCH(CH₃)CH=CH₂], 72.8 [OCH(CH₃)CH=CH₂], 65.5 [C(O)OCH₂CH₂CH₂OH], 65.1 [C(O)OCH₂CH₂CH₂OC(O)], 59.4 [C(O)OCH₂CH₂CH₂OH], 32.0 [C(O)OCH₂CH₂CH₂OH], 29.1 [C(O)OCH₂CH₂CH₂OC(O)], 19.7 [OCH(CH₃)CH=CH₂].

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