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Metal- and Organo-Catalyzed Ring-Opening Polymerization of α-Methyl-Trimethylene Carbonate: Insights into the Microstructure of the Polycarbonate

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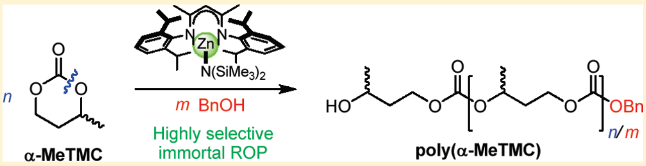
S Supporting Information



ABSTRACT: "Immortal" ring-opening polymerization (iROP) of *rac*-4-methyl-1,3-dioxan-2-one (α-methyl trimethylene carbonate, α-MeTMC) has been carried out using various catalysts combined with an alcohol acting as a co-initiator and a chain transfer agent. The Lewis acid $Al(OTf)_3$, the metallo-organic β-diiminate $[(BDI)Zn(N(SiMe_3)_2)]$ (BDI^{iPr} = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene) complex, or the organic bases, 2-*tert*-butylimino-2-diethylamino-1,3dimethylperhydro-1,3,2diazaphosphorine (BEMP), 1.5.7-triazabicyclo-[4.4.0]dec-5-ene (TBD) and 4-*N*,*N*-dimethylaminopyridine (DMAP), successfully afforded the corresponding poly(α-MeTMC)s with quite good control and activities. In comparison, at 110 °C, these same catalytic systems were more active toward the iROP of native TMC, whereas the iROP of the seven-membered analogue α-Me7CC generally featured a poorer control. The dissymmetry of α-MeTMC raises the question of catalyst selectivity in the ROP process. Detailed microstructural analyses of the poly(α-MeTMC)s using ^{1}H and ^{13}C NMR revealed (1) the preferential ring-opening at the most hindered oxygen−acyl O−C(O)O bond, i.e., closest to the α-Me substituent of the zinc-based system, in the iROP of α-MeTMC, possibly as a result of the favorable steric hindrance; (2) the absence of regioselectivity of the aluminum or guanidine catalyst systems. In addition, MALDI−ToF−MS analyses confirmed the expected α-hydroxy,ω-alkoxyester chain-ends in these polymers. DSC analyses revealed a glass transition temperature of the poly(α-MeTMC)s ($T_g \approx -17$ °C) similar to that of poly(TMC)s.

INTRODUCTION

Aliphatic polycarbonates are synthetic biodegradable polymers that are attracting increasing attention as potentially valuable "green plastics". Indeed, some aliphatic carbonate monomers can be derived from renewable bioresources, as in the case of trimethylene carbonate (TMC)—the most common cyclic carbonate— that can be derived from glycerol. In addition, these polymers can be easily eco-conceived thanks to sustainable polymerization approaches such as bulk "immortal" ring-opening polymerization. Furthermore, when their biocompatibility and low toxicity are taken into consideration, polycarbonates then become important biomaterials as drug/gene delivery systems or tissue/bone engineering (repair and regeneration) substrates.[1,2]

Our ongoing efforts aim at developing tailor-made aliphatic polycarbonates, from TMC as well as from more original cyclic carbonate monomers based on renewable resources.[3,4] We have recently reported the synthesis and ring-opening polymerization (ROP) of some seven-membered cyclic carbonates (7CCs) derived either from levulinic or itaconic green acids, namely α- and β-methyltetramethylene carbonates, respectively (α-Me7CC and β-Me7CC).[4] These studies revealed the great ability of such larger monomers to undergo quite well controlled "immortal" ring-opening polymerization (iROP) in the presence of a system composed of a catalyst (either a metallic Lewis acid, a discrete metallo-organic complex or an organic base) and a protic source (most commonly an alcohol) acting as a co-initiator and a chain transfer agent.[3,4] Detailed investigations on the microstructure of the poly(α/β-Me7CC)s highlighted a higher regioselectivity with the cleavage of the most hindered O−C(O)O bound in α-Me7CC, whereas the further remote methyl-substitution in β-Me7CC resulted in a lack of regioselectivity.[4] In light of the relatively better controlled ROP of six-membered cyclic carbonate congeners,[2,3] we next investigated the (i)ROP of *racemic*-4-methyl-1,3-dioxan-2-one (α-MeTMC) to evaluate the extent of regioselectivity as a function the catalytic systems.

The homo- and copolymerizations of α-MeTMC have scarcely been explored.[2a] The lipase-catalyzed ROP of α-MeTMC (bulk, 100 °C, 5 days) afforded poly(α-MeTMC) with a poor degree of control ($\overline{M}_w$ = 10 400 g·mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 3.7).[5] Rare earth alkoxide ("Ln(O*i*Pr)$_3$", Ln(OAr)$_3$, Ar = 2,6-di-*tert*-butyl-4-methylphenolate), Ln = La, Dy, Y) or alkyl initiators ($(C_5Me_5)_2SmMe(THF)$, $(C_5Me_5)_2Sm(THF)_2$), as well as $AlEt_3 \cdot H_2O$ or $Sn(Oct)_2$ with adventitious water were recently revisited (toluene, 0−100 °C, 6−48 h);[6,7] high molar mass ($\overline{M}_n$ up to 65 000 g·mol^{-1}) and

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Table 1. Bulk iROP of α-MeTMC Initiated by Various Catalytic Systems at $[\alpha\text{-MeTMC}]_0/[\text{catalyst}]_0/[\text{BnOH}]_0$ = 500:1:5

entry	[catalyst]	temp (°C)	reaction time[a] (min)	convn[b] (%)	$\overline{M}_{n,theo}$[c] (g mol^{-1})	$\overline{M}_{n,NMR}$[d] (g mol^{-1})	$\overline{M}_{n,SEC}$[e] (g mol^{-1})	$\overline{M}_w/\overline{M}_n$[f]	TOF[g] (h^{-1})
1	$Al(OTf)_3$	60	120	0	-	-	-	-	0
2	$Al(OTf)_3$	110	150	81	9500	9300	9300	1.18	162
3	$Al(OTf)_3$	150	15	77	9100	9200	5700	1.18	1540
4	$[(BDI^{iPr})Zn(N(SiMe_3)_2)]$	23	90	72	8450	10300	10000	1.12	240
5	$[(BDI^{iPr})Zn(N(SiMe_3)_2)]$	60	7	94	11000	10900	12600	1.28	4028
6	$[(BDI^{iPr})Zn(N(SiMe_3)_2)]$	110	120	91	10700	14100	15960	1.42	228
7[h]	$[(BDI^{iPr})Zn(N(SiMe_3)_2)]$	60	75	100	29 100	-	28300	1.56	4000
8	BEMP	60	180	72	8450	4100	6000	1.19	120
9	TBD	60	10	93	10900	9600	10000	1.19	2790
10	TBD	110	5	99	11600	12650	8500	1.55	5940
11	DMAP	60	180	30	3600	2300	2500	1.25	50

[a] Reaction times were not necessarily optimized. [b] Monomer conversion determined by ^{1}H NMR. [c] Calculated from $[\alpha\text{-MeTMC}]_0/[\text{BnOH}]_0$ × monomer conversion × $M_{\alpha\text{-MeTMC}} + M_{\text{BnOH}}$, with $M_{\alpha\text{-MeTMC}} = 116$ g mol^{-1}, $M_{\text{BnOH}} = 108$ g mol^{-1}. [d] Determined by ^{1}H NMR taking into account the monomer conversion. [e] Determined by SEC vs polystyrene standards (uncorrected raw data). [f] Molar mass distribution calculated from SEC traces. [g] Turnover frequency expressed in $\text{mol}_{\text{TMC}}\cdot\text{mol}_{\text{Catalyst}}^{-1}\cdot\text{h}^{-1}$; these values are lower estimates as they are derived from reaction times that were not necessarily optimized. [h] $[\alpha\text{-MeTMC}]_0/[\text{catalyst}]_0/[\text{BnOH}]_0$ = 5000:1:20.

relatively narrow molar mass distribution values ($1.21 < \overline{M}_w/\overline{M}_n < 1.86$) were obtained in, at the best, 86% yield. Copolymerization of α-MeTMC with either ε-caprolactone,[8a] lactide[7,9] or butylene succinate,[10] from these same initiators in addition to Ti(O*i*Pr)$_4$, then gave the corresponding block or random copolymers. These works essentially aimed at determining the thermal properties and especially the biodegradation behavior of such copolymers. The homopolymerization of α-MeTMC along with the determination of the macromolecular features of the resulting poly(α-MeTMC) thus remain to be investigated more intensely.

Herein, we describe the "immortal" ROP of *racemic* α-MeTMC using several metallic, organometallic or organic catalysts combined with an alcohol as co-initiator and chain transfer agent. Detailed characterization of the polycarbonates, especially including in-depth examination of the microstructure of the poly(α-MeTMC)s along with the evaluation of the regioselectivity in the initial opening of the cyclic carbonate, are reported in relation to the catalytic system involved. It is noteworthy that this study represents the first comprehensive investigations of polycarbonates derived from α-MeTMC.

■ EXPERIMENTAL SECTION

Materials. All manipulations involving air-sensitive compounds were performed under inert atmosphere (argon, < 3 ppm of O$_2$) using standard Schlenk, vacuum line and glovebox techniques. Solvents were thoroughly dried and deoxygenated by standard methods and distilled before use. CDCl$_3$ was dried over a mixture of 3 and 4 Å molecular sieves. Benzyl alcohol (Acros) and was distilled over Mg turnings under argon atmosphere and kept over activated 4 Å molecular sieves. Racemic-4-methyl-1,3-dioxan-2-one (α-MeTMC) (Figure S1, Supporting Information)[8a] and $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$[11] were synthesized following literature procedures. Note that the α-MeTMC has to be carefully purified when used with the zinc complexes since these latter are sensitive to impurity traces, to an extent much larger than the other (organic) catalysts.[3] All other reagents were used as received (Aldrich).

Instrumentation and Measurements. ^{1}H (400 and 200 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in CDCl$_3$ on Bruker Avance AM 400 and DPX 200 spectrometers at 20 °C. Chemical shifts (δ) are reported in ppm and were referenced internally relative to tetramethylsilane (δ 0 ppm) using the residual ^{1}H and ^{13}C solvent resonance.

Average molar mass ($\overline{M}_{n,SEC}$) and molar mass distribution ($\overline{M}_w/\overline{M}_n$) values were determined by SEC in THF at 30 °C (flow rate =1.0 mL·min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a ResiPore 300 × 7.5 mm column. The polymer samples were dissolved in THF (2 mg mL^{-1}). All elution curves were calibrated with polystyrene (PS) standards ($\overline{M}_{n,SEC}$ values are uncorrected for possible difference in hydrodynamic volume of the polycarbonates vs PS). Reported experimental SEC molar mass values for PTMC samples were corrected by a factor of 0.73.[3,12] The SEC traces of the polymers all exhibited a unimodal and symmetrical peak.

The molar mass values of short-chain H−[poly(α-MeTMC)]−OBn samples were determined by ^{1}H NMR analysis, from the relative intensity of the signals of methine hydrogens of the poly(α-MeTMC) chains ($CH_2CH(CH_3)(O)$, δ = 4.90 ppm) to the methylene hydrogens of the chain-end ($(CO)OCH_2C_6H_5$, δ = 5.12 ppm). The number-average molar mass values thus obtained by ^{1}H NMR ($\overline{M}_{n,NMR}$) were in close agreement with the ones calculated, as reported in Table 1.

Monomer conversions were calculated from ^{1}H NMR spectra of the crude reaction mixtures, from the integration (Int.) ratio $\text{Int.}_{\text{poly}(\alpha\text{-MeTMC})}/[\text{Int.}_{\text{poly}(\alpha\text{-MeTMC})}+\text{Int.}_{\alpha\text{-MeTMC}}]$, using the methine hydrogens ($CH_2CH(CH_3)(O)C(O)$) of poly(α-MeTMC) at δ = 4.90 ppm and of α-MeTMC at δ = 4.60 ppm.

MALDI−ToF mass spectra were recorded with an AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N$_2$ laser source (337 nm, 4 ns pulse width) and time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and an accelerating voltage of 20 kV. The polymer sample was dissolved in THF (HPLC grade, 10 mg·mL^{-1}) and a solution (2:1 *v*:*v*) of α-cyano-4-hydroxycinnamic acid (10 mg·mL^{-1}) in acetonitrile (HPLC grade) /0.1% TFA was prepared. Both solutions were then mixed in a 1:1 volume ratio respectively, deposited sequentially on the sample target and then air-dried. Bruker Care Peptide Calibration and Protein Calibration 1 Standards were used for external calibration.

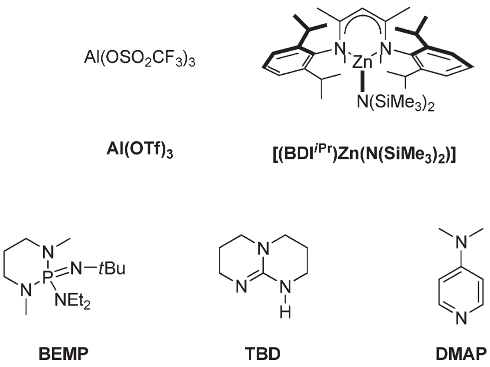
Differential scanning calorimetry (DSC) analyses were performed on a Setaram DSC 131 apparatus calibrated with indium at a rate of 10 °C·min^{-1}, under continuous flow of helium (25 mL/min), using aluminum capsules. The thermograms were recorded according to the following cycles: −40 °C to +180 at 10 °C/min; +180 to −40 °C at 10 °C/min; −40 °C to +180 °C.

Typical Polymerization Procedure. In a typical experiment (Table 1, entry 6), $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$ (5.6 mg, 8.6 μmol), a solution of BnOH (5 equiv. vs Zn, 4.7 μL, 43 μmol) in toluene (0.1 mL) and α-MeTMC (500 equiv. vs Zn, 0.500 g, 4.3 mmol) were charged in a Schlenk flask in the glovebox. The flask was then immerged in an oil bath preset at the desired temperature (110 °C) and the reaction mixture was stirred over the appropriate time (120 min; note that reaction times have not been systematically optimized). The reaction was quenched by adding an excess of an acetic acid solution (ca. 0.1 mL of a 16.5 $mmol \cdot L^{-1}$ solution in toluene). The resulting mixture was concentrated under vacuum and the conversion determined by ^{1}H NMR analysis of the residue. The crude polymer was then dissolved in CH_2Cl_2 and purified upon precipitation in cold methanol, filtered, and dried under vacuum. The final polymer was then analyzed by NMR and SEC.

RESULTS AND DISCUSSION

Polymerization of α-MeTMC. The iROP of α-MeTMC was investigated with the catalytic systems which proved successful in the iROP of the related TMC.[3] In association with benzyl alcohol (BnOH) as co-initiator and chain transfer agent, several metallic and organic catalysts were evaluated, namely, the Lewis acid $Al(OTf)_3$, the metallo-organic β-diiminate $[(BDI)Zn(N(SiMe_3)_2)]$ (BDI^{iPr} = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene) complex, and the organic bases, 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), 1.5.7-triazabicyclo-[4.4.0]dec-5-ene (TBD) and 4-*N*,*N*-dimethylaminopyridine (DMAP) (Scheme 1). Representative results reported in Table 1 were obtained with these catalyst systems at a typical $[\alpha\text{-MeTMC}]_0/[\text{catalyst}]_0/[\text{BnOH}]_0$ ratio of 500:1:5 in bulk monomer. These investigations illustrate the first "immortal" ROP of this cyclic carbonate monomer. Taking into account the benefits from such a solvent-free iROP approach, the corresponding poly(α-MeTMC)s were thus prepared within "green" considerations.[3d]

Scheme 1. Metal-Based and Organic Catalysts Used in the ROP of α-MeTMC



The aluminum triflate system was, similarly to its behavior toward TMC (Table 2, entries 1–3),[3a–d] only active in the iROP of α-MeTMC at higher temperature (Table 1, entries 1–3). In fact, the $Al(OTf)_3$/BnOH catalyst system failed to give poly(α-MeTMC) at 60 °C, whereas it allowed the controlled iROP at temperatures above 110 °C. The unsubstituted TMC analogous monomer was more efficiently polymerized, whichever the reaction temperature (110 or 150 °C), than the present α-MeTMC (at 110/150 °C: turnover frequencies, TOF_{TMC} = 480/5880 h^{-1}, Table 2, entries 2–3;[3e] vs $TOF_{\alpha\text{-MeTMC}}$ = 162/1 540 h^{-1}, Table 1, entries 2–3). In the iROP of the one carbon larger methyl carbonate, α-Me7CC, $Al(OTf)_3$/BnOH exhibited, under similar operating conditions (bulk, 110 °C, $[\alpha\text{-Me7CC}]_0/[\text{catalyst}]_0/[\text{BnOH}]_0$ = 500:1:5) a larger activity ($TOF_{\alpha\text{-Me7CC}}$ = 2 000 h^{-1};[4] vs $TOF_{\alpha\text{-MeTMC}}$ = 162 h^{-1}; Table 1, entry 2). Indeed, only 15 min were required to fully convert 500 equiv of α-Me7CC,[4] whereas the conversion of 405 equiv of α-MeTMC required up to 150 min (Table 1, entry 2).

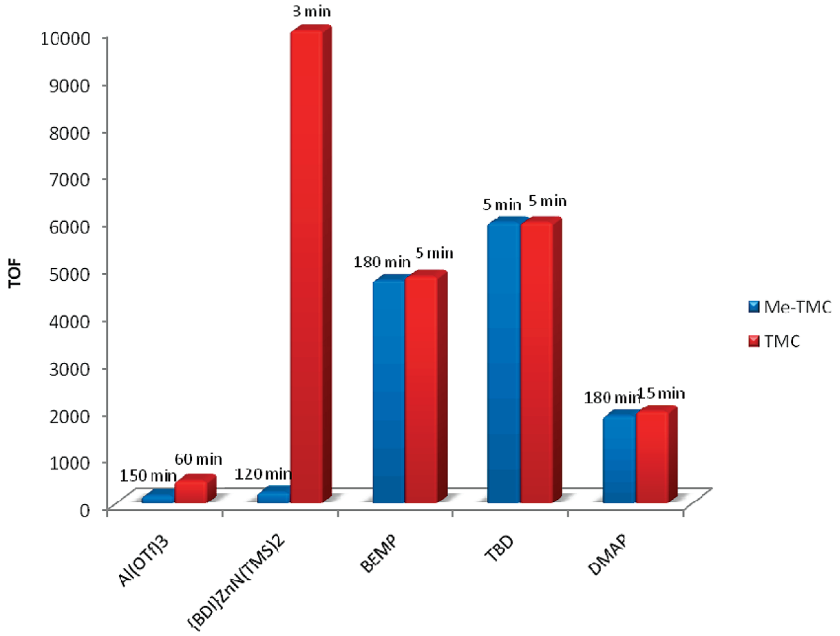
The β-diiminate-zinc based catalyst system $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$/BnOH exhibited, using the same reaction parameters ($[\text{monomer}]_0/[\text{Zn}]_0/[\text{BnOH}]_0$ = 500:1:5), a similar activity at 60 °C toward both α-MeTMC ($TOF_{\alpha\text{-MeTMC}}$ = 4 028 h^{-1}; Table 1 entry 5) and TMC (TOF_{TMC} = 4 240 h^{-1}; Table 2, entry 4).[3a,b,13] Also, under similar experimental conditions (bulk, 60 °C, $[\alpha\text{-Me7CC}]_0/[(BDI^{iPr})Zn(N(SiMe_3)_2)]_0/[\text{BnOH}]_0$ = 500:1:5), the related seven-membered ring carbonate, α-Me7CC, was less actively ring-opened then its six-membered ring analogue α-MeTMC ($TOF_{\alpha\text{-Me7CC}}$ = 940 h^{-1};[4] $TOF_{\alpha\text{-MeTMC}}$ = 4 028 h^{-1}; Table 1, entry 5). As many as 20 polymer chains could be grown per unique zinc center, itself introduced at a loading as low as 200 ppm, allowing the conversion of up to 5 000 equiv of α-MeTMC with a good activity

Table 2. Bulk iROP of TMC Initiated by Various Catalytic Systems at $[\text{TMC}]_0/[\text{catalyst}]_0/[\text{BnOH}]_0$ = 500:1:5[3]

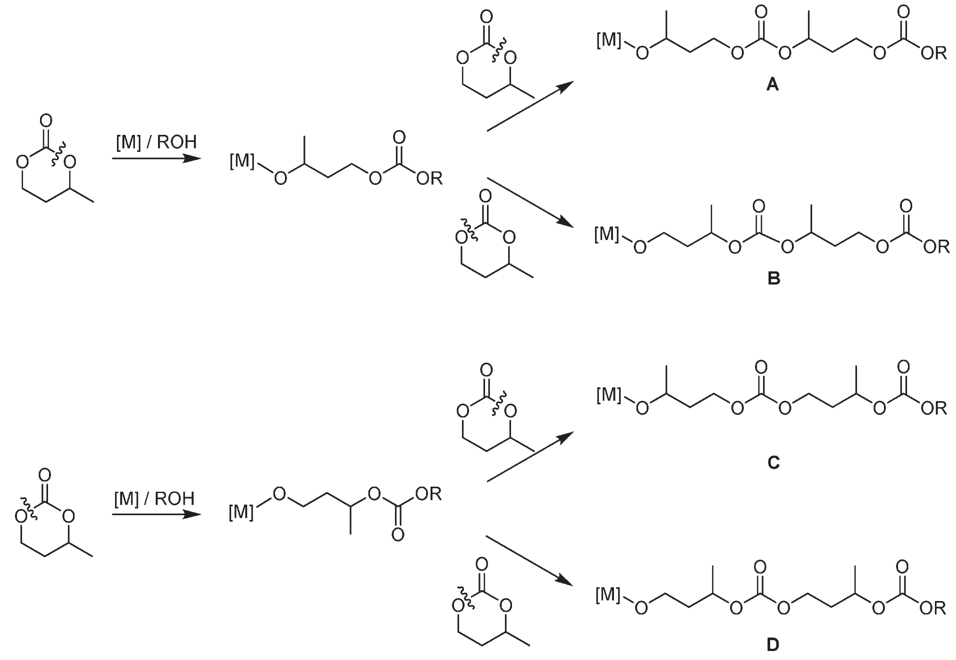
entry	[catalyst]	temp (°C)	reaction time[a] (min)	convn[b] (%)	$\overline{M}_{n,theo}$[c] (g mol^{-1})	$\overline{M}_{n,SEC}$[d] (g mol^{-1})	$\overline{M}_w/\overline{M}_n$[e]	TOF[f] (h^{-1})
1[3a–d]	$Al(OTf)_3$	60	120	0	-	-	-	-
2[3e]	$Al(OTf)_3$	110	60	96	9900	13800	1.62	480
3[3e]	$Al(OTf)_3$	150	5	98	10100	10950	1.55	5880
4[3a,b]	$[(BDI^{iPr})Zn(N(SiMe_3)_2)]$	60	7	99	10200	12400	1.55	4240
5[3e]	$[(BDI^{iPr})Zn(N(SiMe_3)_2)]$	110	3	100	10320	11750	1.77	10000
6[3f]	BEMP	60	60	85	8780	8250	1.25	425
7[3f]	BEMP	110	5	80	8270	6950	1.43	4800
8[3f]	TBD	60	30	99	10210	10900	1.85	990
9[3f]	TBD	110	5	99	10210	12700	1.52	5940
10[3f]	DMAP	60	30	50	5210	5050	1.18	500
11[3f]	DMAP	110	15	97	10000	13200	1.53	1940

[a] Reaction times were not necessarily optimized. [b] Monomer conversion determined by ^{1}H NMR. [c] Calculated from $[\text{TMC}]_0/[\text{BnOH}]_0$ × monomer conversion × $M_{TMC} + M_{BnOH}$, with M_{TMC} = 102 g mol^{-1}, M_{BnOH} = 108 g mol^{-1}. [d] Determined by SEC vs polystyrene standards and corrected by a factor of 0.73.[12] [e] Molar mass distribution calculated from SEC traces. [f] Turnover frequency expressed in $mol_{TMC} \cdot mol_{Catalyst}^{-1} \cdot h^{-1}$; these values are lower estimates as they are derived from reaction times that were not necessarily optimized.

Scheme 2. TOF (Non-Optimized Values) and Conversion Values Obtained at 110 °C (Reaction Times in Brackets) for the Bulk iROP of α-MeTMC (Blue Box) and TMC (Red Box) Using the Various Catalyst Systems at [α-MeTMC/TMC]$_0$/[Catalyst]$_0$/[BnOH]$_0$ = 500:1:5 (Tables *1* and 2)



Scheme 3. Possible Regioselectivities for the ROP of α-MeTMC



(TOF$_{\alpha\text{-MeTMC}}$ = 4 000 h^{-1}) and control over the polycarbonate molar features (Table 1, entry 7; [α-MeTMC]$_0$/[Zn]$_0$/[BnOH]$_0$ = 5 000:1:20).

The organo-basic catalysts BEMP, TBD, and DMAP all successfully promoted the polymerization of α-MeTMC with BnOH, even at 60 °C, yet with distinct activities (Table 1, entries 8–11). TBD clearly displayed a higher activity whereas both BEMP- or DMAP-based catalytic systems remained poorly active at this temperature. The better ability of the guanidine to polymerize α-MeTMC was similarly observed in the iROP of TMC at 60 °C (TBD > BEMP ≈ DMAP) or 110 °C (TBD ≈ BEMP > DMAP; Table 2, entries 6–11).[3f]

Comparison of the overall performances of the various catalytic systems toward the iROP of α-MeTMC and TMC at 110 °C revealed better efficiencies with the unsubstituted TMC (Scheme 2). The difference is more pronounced with the

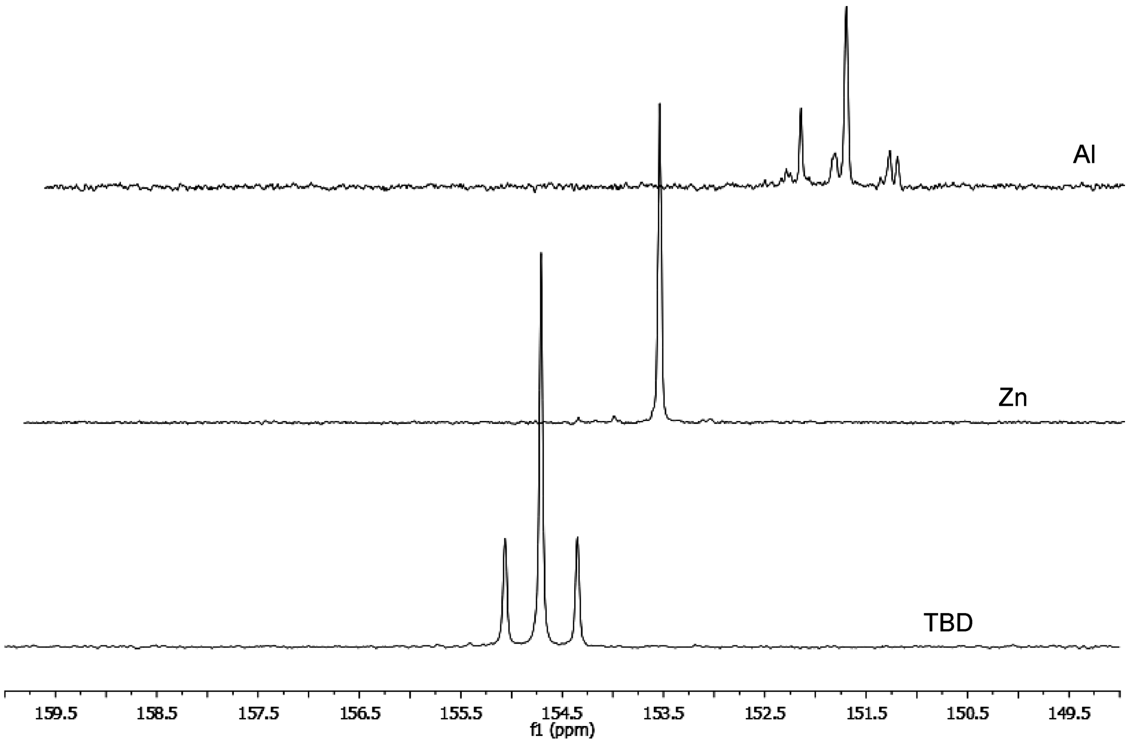


Figure 1. Details of the carbonyl region of the $^{13}C\{^1H\}$ NMR spectra (100 MHz, $CDCl_3$, 20 °C) of H-[poly(α-MeTMC)]-OBn samples prepared from catalyst/BnOH systems; bottom: TBD (Table 1, entry 8) (X_{reg} = ca. 0.39), middle: $[(BDI^{iPr})Zn(N(SiMe_3)_2]$ (Table 1, entry 4) ($X_{reg} > 0.98$), top: $Al(OTf)_3$ (Table 1, entry 3) (X_{reg} = ca. 0.62).

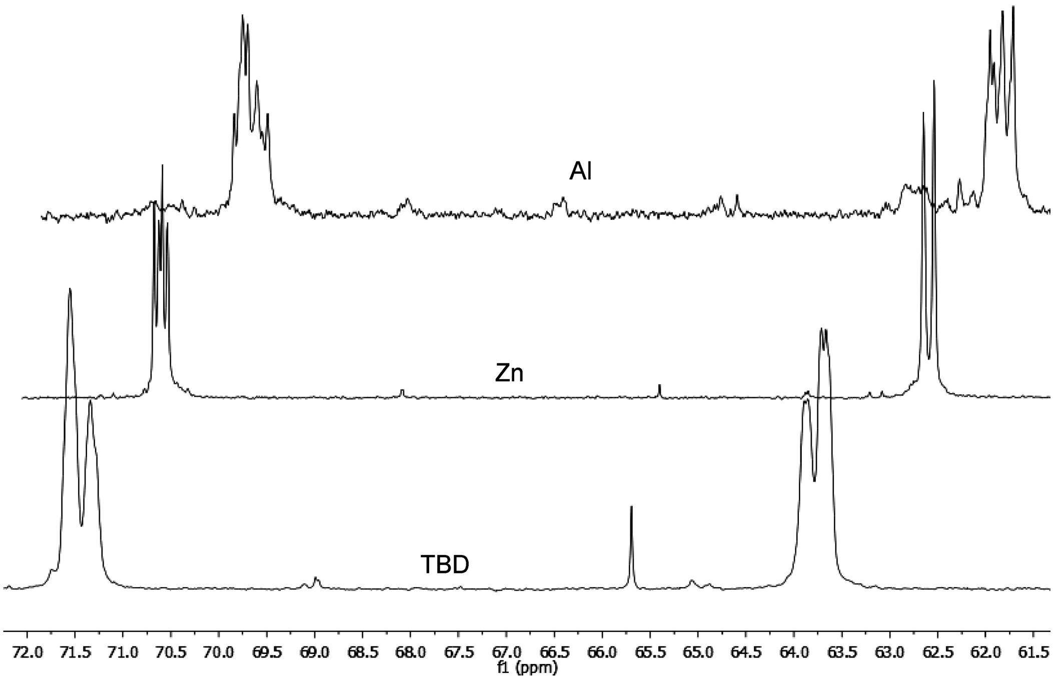


Figure 2. Details of the CH_3CHO and OCH_2 regions of the $^{13}C\{^1H\}$ NMR spectra (100 MHz, $CDCl_3$, 20 °C) of H-[poly(α-MeTMC)]-OBn samples prepared from catalyst/BnOH systems: bottom, TBD (Table 1, entry 8) (X_{reg} = ca. 0.39); middle, $[(BDI^{iPr})Zn(N(SiMe_3)_2]$ (Table 1, entry 4) ($X_{reg} >$ 0.98); top, $Al(OTf)_3$ (Table 1, entry 3) (X_{reg} = ca. 0.62).

metal-based catalyst systems [although the TOF values were not optimized and must be therefore compared with caution]. This apparent reactivity trend can be likely accounted for by the presence of the methyl substituent which may sterically disfavor monomer coordination or nucleophilic attack of the initiator, as opposed to the naked cyclic carbonate analogue.

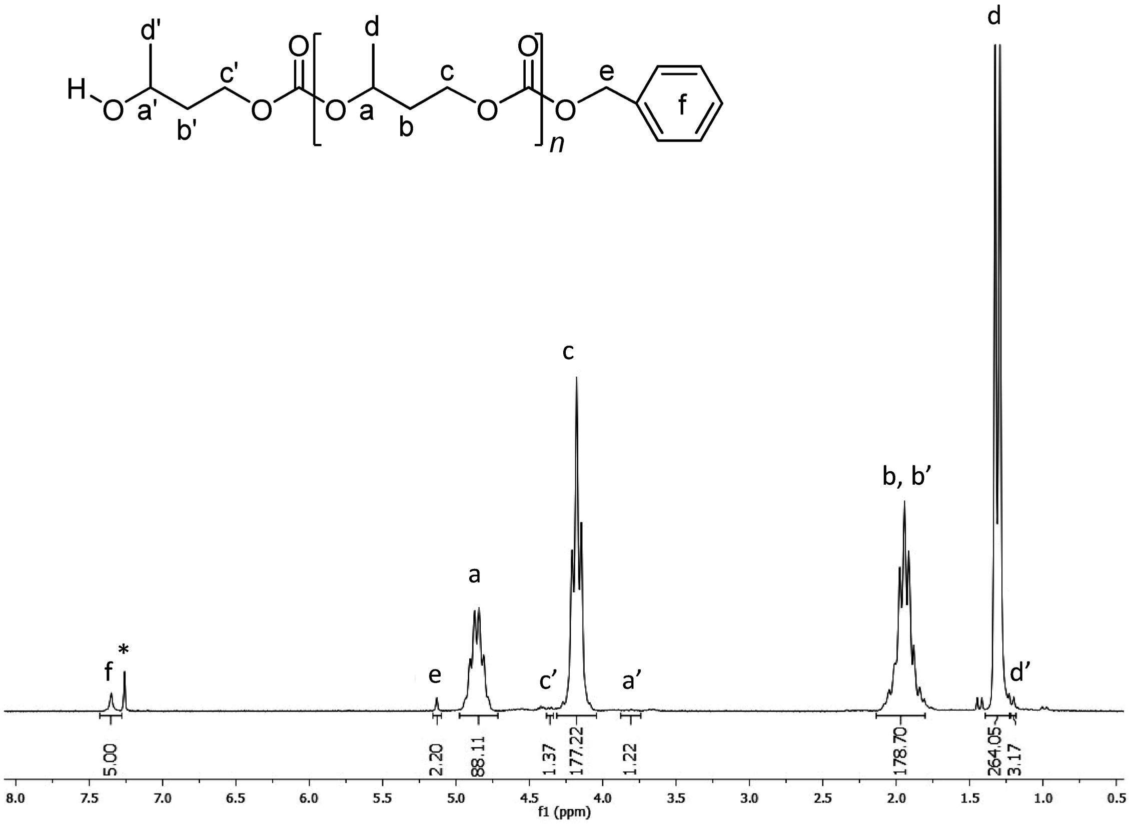


Figure 3. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 20 °C) of a H-[poly(α-MeTMC)]-OBn sample prepared from the $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$/BnOH system ($X_{reg} > 0.98$) (Table 1, entry 4) with assignments of main-chain and terminal groups (∗ refers to the residual $CDCl_3$ resonance).

The molar mass values determined for the poly(α-MeTMC)s by NMR analyses ($\overline{M}_{n,NMR}$, refer to the Experimental Section) remained in rather good agreement with the ones calculated ($\overline{M}_{n,theo}$),[14] assuming that all the added alcohol molecules contribute to the "immortal" polymerization as effective chain transfer agents, with a fast and reversible exchange between the growing polycarbonates and the dormant alcohol moieties.[3d] The molar mass values determined by SEC ($\overline{M}_{n,SEC}$) were referenced to PS standards and were not corrected for possible difference in hydrodynamic radius of these poly(α-MeTMC)s. In fact, these values were within the same range as the $\overline{M}_{n,theo}$ and $\overline{M}_{n,NMR}$ values; this observation suggests that the correction factor for $\overline{M}_{n,SEC}$ values of poly(α-MeTMC)s. vs PS standards should be actually close to unity. Under similar operating conditions, given the poly(α-MeTMC) molar mass, the molar mass distribution values measured with either catalytic systems ranged from $1.12 < \overline{M}_w/\overline{M}_{n(\alpha\text{-MeTMC})} < 1.56$ (Table 1). These molar mass distribution values are, whichever the catalytic system, generally slightly lower than those obtained in similar bulk iROP of TMC ($1.18 < \overline{M}_w/\overline{M}_{n(TMC)} < 1.85$ (Table 2)[3] or α-Me7CC ($1.13 < \overline{M}_w/\overline{M}_{n(\alpha\text{-Me7CC})} < 1.73$).[4] All these data demonstrate that the iROP of α-MeTMC with either catalytic system is overall fairly well controlled, most likely thanks to the favorable contributions both of the steric hindrance provided by the methyl substituent in α-position to the carbonate and of the size of the cyclic carbonate (six-membered carbonates were less reactive than seven-membered ones).

Microstructural Analyses. Regioselectivity of the O−C(O)O Bond Cleavage in α-MeTMC. One aim of this study was to evaluate the regioselectivity of the various catalytic systems in the iROP of α-MeTMC, in comparison to their behavior with the corresponding α/β-Me7CCs. Indeed, the studies on the seven-membered cyclic carbonates suggested a better regioselectivity with the α-substituted 7CC monomer, the further remote position of the substituent on the β-Me7CC presumably disfavoring the discrimination between the two O−C(O)O bonds.[4] The regioselectivity in the iROP of α-MeTMC was anticipated to be better in the case of the zinc complex supported by the β-diiminate surrounding ligand than in the case of the aluminum triflate or organic base systems. It was thus foreseen that the ROP of the smaller α-substituted six-membered ring, α-MeTMC, might exhibit some preferential opening-selectivity thereby offering a more regular microstructure of the poly(α-MeTMC)s.

The microstructure of the prepared poly(α-MeTMC)s was investigated by ^{13}C NMR spectroscopy at 100 MHz. The carbonyl region was first carefully analyzed since these resonances are diagnostic of the diad sequences, as previously reported for seven-membered analogues.[4] As depicted Scheme 3, the indistinguishable diads **A** and **D** result from the stereoregular enchainment of the monomer units, that is from the regioregular cleavage of either of the O−C(O)O bonds in α-MeTMC. These diads **A** and **D** give a resonance which is flanked ($\Delta\delta = \pm$ ca. 0.35 ppm; see Figure 1) by two other resonances at higher and lower field, respectively. These latter two equally intense signals are representative of the two magnetically inequivalent carbonyl groups that result from the regioirregular enchainment of the monomer units, that is, from the alternated cleavage of the two O−C(O)O bonds in α-MeTMC leading to diads **B** and **C** (Scheme 3). Considering the intensity of these two smaller resonances relative to the central one thus allows evaluating the regioregularity X_{reg} in the ROP.[4,15] As evidenced hereafter, the methine and methylene

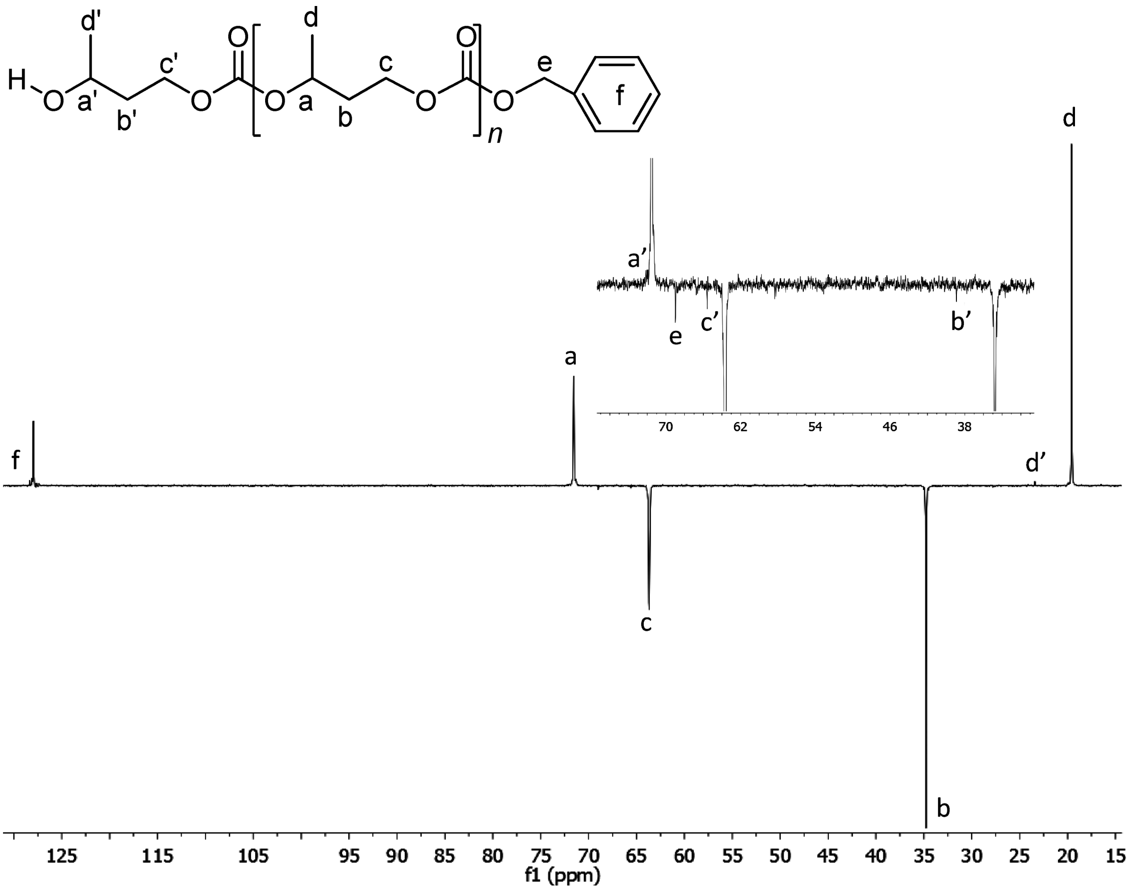


Figure 4. ^{13}C DEPT (100 MHz, C_6D_6, 20 °C) NMR spectrum of a H-[poly(α-MeTMC)]-OBn sample prepared from the $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$/BnOH system ($X_{reg} > 0.98$) (Table 1, entry 4).

regions of the $^{13}C\{^1H\}$ NMR spectrum similarly enable estimating the extent of regioregularity provided by the catalytic system.[4]

The carbonyl region of the $^{13}C\{^1H\}$ NMR spectra (Figure 1 and Figure S2, Supporting Information) of poly(α-MeTMC) samples prepared at 110 °C[16] from $[(BDI^{iPr})Zn(N(SiMe_3)_2]$/BnOH show an almost unique resonance at δ 155.11 ppm corresponding to diads A and D. This observation indicates a very high regioselectivity ($X_{reg} > 0.98$) of the zinc-based catalytic system. On the other hand, for a poly(α-MeTMC) prepared from TBD, two additional resonances of equal intensity assigned to diads B and C were observed at δ 155.45 and 154.74 ppm; their relative intensity compared to that of the central resonance was diagnostic of a significantly lower regioselectivity (X_{reg} = ca. 0.39).[17] In the case of $Al(OTf)_3$, these resonances for the carbonyl group were somewhat split and their relative intensity indicated an intermediary degree of regioselectivity (X_{reg} = ca. 0.62).[17,18]

Correspondingly, the $OCHCH_3$ and OCH_2 groups of regioregular poly(α-MeTMC) samples prepared from $[(BDI^{iPr})Zn(N(SiMe_3)_2]$/BnOH appeared each as a set of sharp resonances at δ ca. 71.7 and 63.7 ppm) (Figure 2).[19,20] For less regioregular poly(α-MeTMC) samples prepared from TBD and $Al(OTf)_3$, additional resonances appeared upfield (δ ca. 71.4 ppm) and downfield (δ *ca.* 63.85 ppm) of these signals, respectively, and the overall resolution was lower. Relative integration of these sets of resonances in the case of TBD gave X_{reg} values in the range 0.34−0.35, that is in good agreement with the one determined from the carbonyl region (X_{reg} = 0.39). The lower resolution of the spectrum in the case of the poly(α-MeTMC) sample prepared from $Al(OTf)_3$ allowed a rough estimate of X_{reg} = *ca.* 0.6, also consistent with the value determined from the carbonyl region for this catalyst system.

The X_{reg} values illustrate that the $[(BDI^{iPr})Zn(N(SiMe_3)_2]$/BnOH system achieves the best regioselectivity ($X_{reg} > 0.98$), as opposed to the $Al(OTf)_3$/BnOH and TBD/BnOH systems which are less or hardly regioselective (X_{reg} = ca. 0.62 and 0.35−0.39, respectively). These regioselectivity values follow the same trend than that observed in the iROP of α-Me7CC. With this analogous α-methyl substituted seven-membered carbonate, the $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$/BnOH allowed to achieve the most regioselective (X_{reg} = 0.71) iROP, while the $Al(OTf)_3$/BnOH system was hardly regioselective (X_{reg} = 0.27).[4] Apparently, the smaller ring size of α-MeTMCC (as compared to α-Me7CC) and the bulkier structure of the zinc (vs aluminum) catalyst are in favor of regioselective processes. The lack of regioselectivity of TBD, although inherently different in nature, is in line with the poor stereoselectivity that this and most other organocatalysts have been thus far able to achieve in ROP of cyclic esters.[21]

Nature of the Terminal Monomer Units and End-Groups. Identification of the polycarbonate chain ends was made on a low molecular mass polymer ($\overline{M}_{n,theo}$ = 4 200 $g\cdot mol^{-1}$; $\overline{M}_{n,NMR}$ = 7 400 $g\cdot mol^{-1}$) through careful ^1H and ^{13}C NMR spectroscopy and MALDI−ToF mass spectrometry investigations. A typical 200 MHz ^1H NMR spectrum of a regioregular ($X_{reg} > 0.98$) poly(α-MeTMC) prepared in the presence of $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$ combined

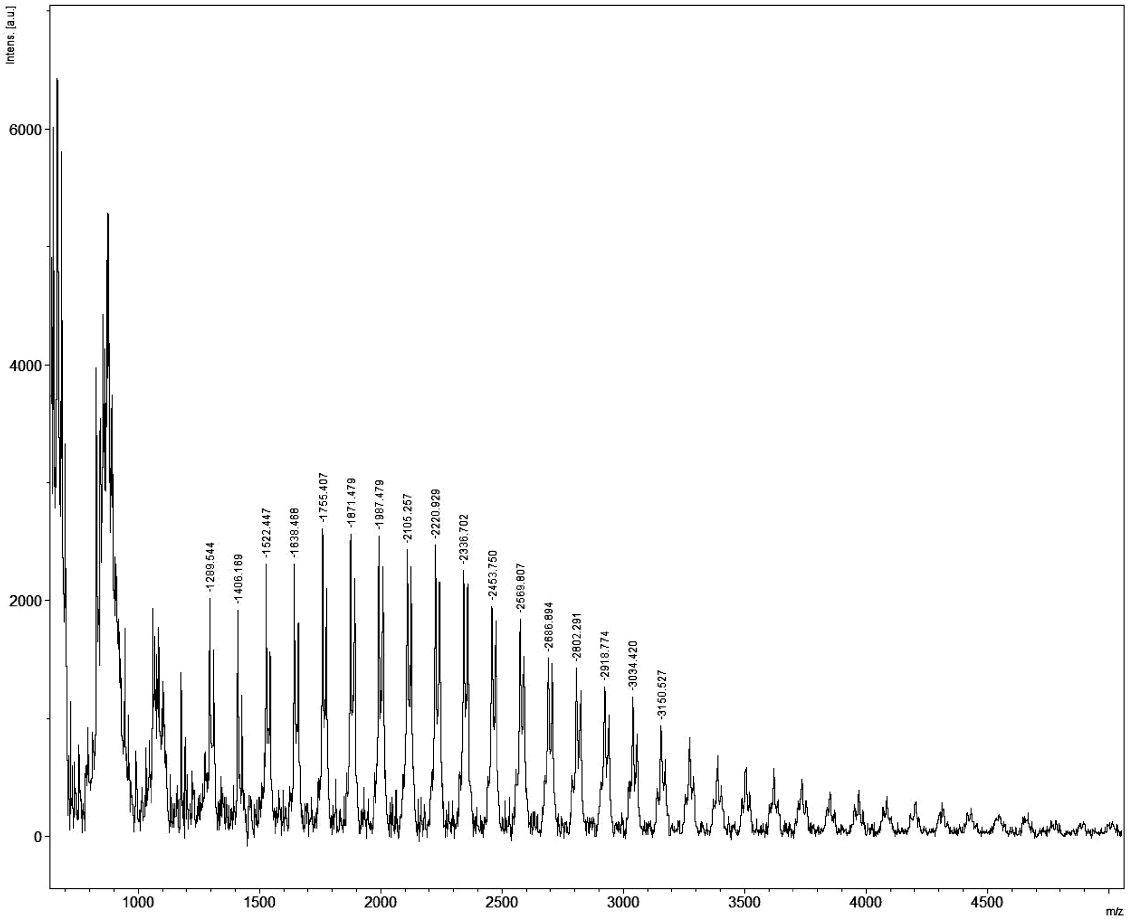


Figure 5. MALDI−ToF mass spectrum of a low molar mass H-[poly(α-MeTMC)]-OBn sample prepared from the DMAP/BnOH system (Table 1, entry 11).

with BnOH is depicted Figure 3. The terminal benzyloxy carbonate end-group was evidenced by the typical set of low intensity resonances at δ 7.35 (br s) and 5.13 (s) ppm (labeled **f** and **e**, respectively) for $C_6H_5CH_2O$. The three signals at δ 4.35, 3.72, and 1.22 ppm ((t) labeled **c**′, (m) **a**′, and (d) **d**′, respectively) were assigned respectively to the methylene, methine and methyl groups of the other chain terminus, that is $HOCH(CH_3)CH_2CH_2OC(O)$. The methylene group adjacent to the terminal methine ($HOCH(CH_3)CH_2CH_2OC(O)$, **b**′) overlaps with the main chain signal ((m), **b**) at δ 1.95 ppm. All these assignments were confirmed by $^1H-^1H$ COSY, ^{13}C DEPT and $^{13}C-^1H$ HMQC NMR experiments (Figures S3 and S4, Supporting Information).

The ^1H NMR spectra of regioirregular poly(α-MeTMC) samples prepared with TBD (X_{reg} = ca. 0.39) or $Al(OTf)_3$ (X_{reg} = ca. 0.62) combined with BnOH exhibited the same resonances for the $C_6H_5CH_2O$ chain-end group (δ 7.12 (s), **f** and 5.13 (s), **e** ppm). The signals for the opposite chain end overlap with the main chain signals and could not be unambiguously assigned to the two possible diads **B** and **C**.

The ^{13}C DEPT NMR spectra of poly(α-MeTMC) samples prepared form the regioregular $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$/BnOH system depicted Figure 4 confirmed the previous ^1H NMR assignments of the polymer chain termini. In addition to the most intense resonances observed for the polymer main chain (**a**, **b**, **c**, **d**), a series of lower intensity resonances was observed that could be assigned to the $PhCH_2O$ (δ 69.2 ppm) and $HOCH(CH_3)CH_2CH_2O$ (δ 74.2, 65.7, 38.9, 23.6 ppm; **a**′, **c**′, **b**′, and **d**′, respectively) moieties. Another characteristic trend that supports this assignment is the downfield shift between the main chain and terminal resonance for the CH_3 groups (δ(**d**) 19.6 vs δ(**d**′) 23.6 ppm) and the adjacent methylene group (δ(**b**) 34.8 vs δ(**b**′) 38.9 ppm), which reflects replacement of an ester by a hydroxyl group, respectively. A similar behavior was observed in the ^{13}C NMR spectra of regioregular polymers derived from the seven-membered ring analogue (α-Me7CC).[4]

In the ^{13}C NMR spectra of poly(α-MeTMC)s prepared from a regioirregular $Al(OTf)_3$ or TBD/BnOH system, the region at δ 60−75 ppm contains several low intensity resonances assignable [as confirmed in the ^{13}C DEPT NMR spectra] to methylene and methine carbons of $OC(O)OCH_2CH_2CH(CH_3)OH$ and $OC(O)OCH(CH_3)CH_2CH_2OH$ terminal units (Figure S5, Supporting Information). This indicates unselective cleavage of both oxygen-acyl O−C(O)O bonds.

The MALDI−ToF mass spectrum of a regioregular (X_{reg} > 0.98) poly(α-MeTMC) sample prepared from $[(BDI^{iPr})Zn(N(SiMe_3)_2)]$/BnOH is depicted Figure 5. It features one major distribution of peaks unambiguously assignable to H-[poly(α-MeTMC)]−OBn molecules cationized by Na^+ ions with a repeat unit of 116 g·mol^{-1} (i.e., the molar mass of α-MeTMC). The most intense signal detected at m/z = 1 755 g·mol^{-1} corresponds to the species H−[α-MeTMC]$_{14}$−$OCHH_2Ph$.

Na^+ (calculated isotopic mass for $^{12}C_{77}{}^{1}H_{120}{}^{23}Na_1{}^{16}O_{43}$: 1 755 g·mol^{-1}); the other minor population observed at m/z +16 corresponds to the analogous H−[α-MeTMC]$_{14}$−OCHH$_2$Ph. K^+ series.

The thermal properties of poly(α-MeTMC) samples were briefly investigated by DSC and displayed a single glass transition at low temperature and the absence of a melting temperature transition, thus highlighting their amorphous feature. The T_g values for poly(α-MeTMC)s were similar to that of PTMC samples (T_{gPTMC} = −15 °C; M_n = 10 000 g·mol^{-1}),[12] ranging around −18/−16 °C (Table 1, entries 3 and 5, respectively).

CONCLUSION

Polycarbonates have been synthesized from the "immortal" ROP of α-MeTMC using various metallic and organic catalyst systems in combination with BnOH as external nucleophile (initiator) and chain transfer agent. The systems based on the zinc β-diiminate complex [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)] and the guanidine (TBD) or phosphazene (BEMP) organocatalysts exhibited the best activities and all catalytic systems featured a quite good control over molar masses. Detailed NMR and MALDI−ToF−MS analyses revealed (*i*) the oxygen−acyl bound cleavage of the cyclic carbonate to yield α,ω-hydroxy-benzylester telechelic H−[poly(α-MeTMC)]−OBn macromolecules and (*ii*) that α-MeTMC is preferentially ring-opened at the most hindered oxygen−acyl O−C(O)O bond, with very high regioselectivity for the β-diiminate zinc-based catalyst. All poly(α-MeTMC)s were atactic and amorphous.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Additional NMR spectra of monomer and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Note that the TOF value calculated at 110 °C in the ROP of α-MeTMC is apparently lower than that obtained at 60 °C. This is likely just the result of nonoptimized reactions times. In fact, the [(BDI^{iPr})Zn(NSiMe$_3$)$_2$]/BnOH system remains stable at 110 °C, as observed for instance with TMC (Table 2, entry 4 vs 5).

(14) In an iROP process, the expected molar mass value $\overline{M}_{n,theo}$ is calculated from the initial concentration in chain transfer agent, i.e. in alcohol.

(15) The degree of regioregularity was calculated by the formula X_{reg} = 1 − (relative intensity of the related regioirregular resonances), the resonance for regioregular enchainment being set to 1. The degree of regioregularity, X_{reg}, is opposed to the degree of randomness, X_{rand} = 1 − X_{reg}). For a perfectly statistical ROP process X_{reg} = 0 (i.e., X_{rand} = 1), the probability of formation of these B and C sequences is equal and a 1:2:1 distribution for the three carbonyl resonances is expected. For a more regioregular ROP process $X_{reg} \rightarrow 1$ (i.e., $X_{rand} \rightarrow 0$), the high and low field carbonyl resonances are expected to progressively decreases such that only the central resonance should be observed for a perfectly regioregular (X_{reg} = 1) ROP.

(16) In our previous studies on the ROP of α-Me7CC, the degree of regioselectivity of the [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$]/BnOH catalyst system was shown to decrease with increasing temperature, while the Al(OTf)$_3$/BnOH system was hardly regioselective whichever the temperature.[4]

(17) Average value calculated from the relative intensities of the C(=O) resonances.

(18) Two additional weak signals are observed in the polymer prepared from the Al(OTf)$_3$/BnOH system; a duplicated NMR analysis on an independently prepared polymer with this catalyst system gave identical results. The origin/identity of these signals remains obscure thus far.

(19) No comparison of the absolute intensity of each of these individual resonances (CO, OCH, OCH$_2$) can be done due to the obviously different relaxation times of these inherently different groups.

(20) The splitting pattern of the OCHCH$_3$ and OCH$_2$ resonances in the regioregular specimens could not be clearly rationalized at this stage. Note that these resonances illustrated Figure 2 at δ ca. 71.7 and 63.7 ppm display exactly the same appearance in the ^{13}C DEPT NMR spectrum illustrated Figure 4 (upon zooming).

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