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# Polycarbonates Derived from Green Acids: Ring-Opening Polymerization of Seven-Membered Cyclic Carbonates

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**ABSTRACT:** Methyl substituted seven-membered ring carbonates (7CCs), namely, 4-methyl- and 5-methyl-1,3-dioxepan-2-one ( $\alpha$ -Me7CC and  $\beta$ -Me7CC), have been synthesized in high yields (up to 70%) upon cyclization of the corresponding  $\alpha,\omega$ -diols issued from green renewable acids. ("Immortal") ring-opening polymerization of these monomers has been carried out using various catalysts combined with an alcohol acting as a co-initiator and a chain transfer agent. The Lewis acid  $\text{Al}(\text{OTf})_3$ , the organometallic complexes  $[(\text{BDI}^{\text{Pr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$  ( $(\text{BDI}^{\text{Pr}}) = 2-((2,6\text{-diisopropylphenyl})\text{amido})-4-((2,6\text{-diisopropylphenyl})\text{-imino})-2\text{-pentene}$ ) and  $[(\text{ONOO}^{\text{tBu}})\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})]$  ( $\text{ONOO}^{\text{tBu}} = \text{amino-alkoxy-bis(phenolate)}$ ) or the organic 4-*N,N*-dimethylaminopyridine (DMAP), 1.5.7-triazabicyclo-[4.4.0]dec-5-ene (TBD) or 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) successfully afforded the corresponding poly( $\alpha$ - and  $\beta$ -Me7CC)s with quite good control and activities. The dissymmetry of the monomers raises the question of catalyst selectivity in the ring-opening of the 7CCs. Detailed microstructural analyses of the poly(7CC)s using  $^1\text{H}$  and  $^{13}\text{C}$  NMR and MALDI-ToF-MS techniques revealed (1) the higher regioselectivity — with preferential ring-opening at the most hindered oxygen-acyl  $\text{O}-\text{C}(\text{O})\text{O}$  bond, that is, closest to the  $\alpha$ -Me substituent — of the zinc-based system followed by the yttrium, as compared to the lack of selectivity of the aluminum one, in the ring-opening polymerization (ROP) of  $\alpha$ -Me7CC; (2) the absence of regioselectivity in the ROP of  $\beta$ -Me7CC, whichever the catalyst system used, most likely as a result of the  $\text{OC}(\text{O})\text{O}$  further remote substitution site; (3) the expected  $\alpha$ -hydroxy, $\omega$ -alkoxyester chain ends. Differential scanning calorimetry (DSC) analyses of these polymers underlined the influence of the position of the methyl substituent on the glass transition temperature. Noteworthy, this study represents the first synthesis of the  $\beta$ -Me7CC monomer and of the resulting polycarbonates.

## Introduction

The current increasing interest in polymers issued from renewable resources stems from the alternatives they provide to petroleum-based polymers issued from depleting fossil fuels. Most of the attention has long been devoted to polymers made from cyclic diesters or lactones such as lactide or  $\epsilon$ -caprolactone. Yet, rising awareness toward polycarbonates has recently emerged because of the renewed attention for green and sustainable development in polymer science. Indeed, such carbonate monomers can be derived from biomass as exemplified by trimethylene carbonate (TMC) that can be prepared from glycerol.<sup>1</sup> In line with such concerns, we investigated the ring-opening polymerization (ROP) of some seven-membered cyclic carbonates (1,3-dioxepan-2-one derivatives, hereafter referred to as 7CCs), namely, 4-methyl-1,3-dioxepan-2-one or  $\alpha$ -methyl-tetramethylene carbonate ( $\alpha$ -Me7CC) and 5-methyl-1,3-dioxepan-2-one or  $\beta$ -methyl-tetramethylene carbonate ( $\beta$ -Me7CC). Both of these methyl-substituted carbonates can be synthesized from the corresponding diol derived from either levulinic or itaconic acids, respectively, which both belong to the DOE "top 10" value chemical opportunities from carbohydrates (Scheme 1).<sup>2</sup> These latter two acids are presently industrially produced from sugars by acid-catalyzed dehydration and decomposition of celluloses, glucose, or fructose for the former, and via

fungal fermentation of glucose, xylose, or arabinose for the latter. They have the potential to be key building blocks for deriving both commodity and specialty chemicals among the corresponding  $\alpha,\omega$ -diols 1,4-pentanediol and 2-methyl-1,4-butanediol (Scheme 1). Although their overall production cost still remains to be reduced in order to be competitive with petrochemical-derived chemicals, their potential as monomer — and therefore as polymer — precursors is a major challenge that deserves to be investigated.

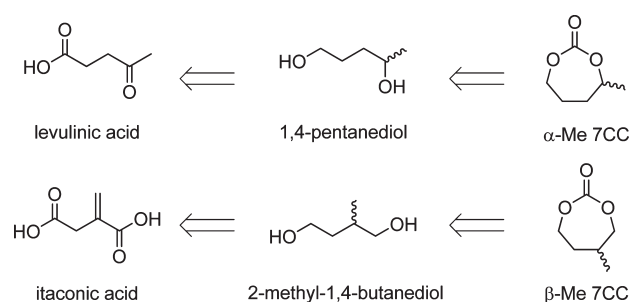
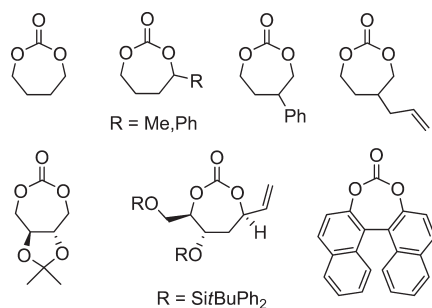
Larger ring-strained carbonates such as 7CCs are more prone to ROP as compared to five- or six-membered ones.<sup>3</sup> Nonetheless, the homopolymerization of 7CCs has remained more rarely investigated than that of their smaller congeners. This most likely results from their picky synthesis and purification that require a good control of the operating parameters, especially of temperature since these monomers are rather thermally unstable. To date, the only few reported seven-membered ring monomers include the unsubstituted 7CC and the  $\alpha$ -methyl,  $\alpha$ -phenyl,  $\beta$ -phenyl,  $\beta$ -allyl, dimethyl isopropylidene, *tert*-butyldiphenylsilyloxy, or bis(napto) functionalized congeners (Scheme 2).<sup>4–9</sup> These monomers have been polymerized through either cationic or anionic procedures using enzymes,  $\text{CF}_3\text{COOH}$ ,  $\text{TfOH}$  ( $\text{Tf} = \text{CF}_3\text{SO}_2$ ),  $\text{MeOTf}$ ,  $\text{HCl}$ ,  $\text{BCl}_3$ ,  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $[\text{Ph}_3\text{C}]^+[\text{BF}_4]^-$ ,  $\text{HSbF}_6$ , or metallic initiators/catalysts such as alkyl alkaline metals, tin derivatives ( $\text{SnCl}_4$ ,  $\text{Sn}(\text{2-ethylhexanoate})_2$ ),  $\text{Al}(\text{O}i\text{Pr})_3$ ,  $\text{ZnEt}_2 \cdot \text{H}_2\text{O}$ ,  $\{\text{bis(phenolate)}\}\text{TiX}_2$  ( $\text{X} = \text{Cl}, \text{O}i\text{Pr}$ ), or  $[\text{Cp}_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . However, most of the investigations on the ROP of these 7CCs revolved around the unsubstituted monomer.

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**Table 1.** Bulk iROP of  $\alpha$ -Me7CC Initiated by Various Metallic Catalyst/BnOH Systems

entry	[catalyst]	$[\alpha\text{-Me7CC}]_0/$ $[\text{catalyst}]_0/$ $[\text{BnOH}]_0$	$[\alpha\text{-Me7CC}]_0$	temp (°C)	reaction time (min) <sup>a</sup>	conv <sup>b</sup> (%)	$\overline{M}_{n\text{theo}}^c$ (g mol <sup>-1</sup> )	$\overline{M}_{n\text{NMR}}^d$ (g mol <sup>-1</sup> )	$\overline{M}_{n\text{SEC}}^e$ (g mol <sup>-1</sup> )	$\overline{M}_w/\overline{M}_n^f$	TOF <sup>g</sup> (h <sup>-1</sup> )
1	Al(OTf) <sub>3</sub>	500:1:5	2.0	90	240	100	13100	14500	1550	1.51	
2	Al(OTf) <sub>3</sub>	500:1:5	bulk	40	85	84	11050	11550	5950	1.43	296
3	Al(OTf) <sub>3</sub>	500:1:5	bulk	110	15	100	13100	13900	4900	1.15	2000
4	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	100:1:1	2.0	20	30	98	12850	12500	11200	1.65	196
5	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	100:1:1	bulk	20	5	100	13100	17300	12900	1.18	1200
6	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	2.0	60	20	87	22750	21800	8850	1.33	522
7	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	2.0	60	30	93	24300	25450	10750	1.33	372
8	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	2.0	20	60	98	26000		15066	1.58	196
9	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	bulk	20	10	100	26100		8600	1.68	1200
10	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:5	2.0	60	30	100	5300	7600	7300	1.17	400
11	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:10	2.0	60	30	87	2350	2150	1400	1.36	348
12	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	300:1:5	3.0	60	30	94	7450	11900	7000	1.27	564
13	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:1	2.0	20	120	54	35200		6100	1.13	135
14	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:1	bulk	60	180	93	60550		12400	1.27	155
15	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:5	bulk	60	30	94	12300	12600	8050	1.27	940
16	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:10	bulk	60	30	93	6150	6750	5700	1.25	930
17	(ONOO <sup>tBu</sup> )Y(N(SiHMe <sub>2</sub> ) <sub>2</sub> )(THF)	50:1:0	2.4	23	1	86	5700		14500	1.56	2580
18	(ONOO <sup>tBu</sup> )Y(N(SiHMe <sub>2</sub> ) <sub>2</sub> )(THF)	50:1:1	2.4	23	1.5	81	5350	4400	5000	1.51	1620
19	(ONOO <sup>tBu</sup> )Y(N(SiHMe <sub>2</sub> ) <sub>2</sub> )(THF)	200:1:0	2.4	23	60	97	25350		13700	1.73	194
20	(ONOO <sup>tBu</sup> )Y(N(SiHMe <sub>2</sub> ) <sub>2</sub> )(THF)	200:1:1	2.4	23	3	95	24800	18650	3950	1.55	3800

<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  $[\alpha\text{-Me7CC}]_0/[\text{BnOH}]_0 \times$  monomer conversion  $\times M_{\alpha\text{-Me7CC}} + M_{\text{BnOH}}$ , with  $M_{\alpha\text{-Me7CC}} = 130 \text{ g} \cdot \text{mol}^{-1}$ ,  $M_{\text{BnOH}} = 108 \text{ g} \cdot \text{mol}^{-1}$ . <sup>d</sup> Determined by NMR taking into account the monomer conversion. <sup>e</sup> Determined by SEC vs polystyrene standards (uncorrected raw data). <sup>f</sup> Molar mass distribution calculated from SEC traces. <sup>g</sup> Turnover frequency expressed in  $\text{mol}_{\text{TMC}} \text{mol}_{\text{Catalyst}}^{-1} \text{h}^{-1}$ .

**Scheme 1.**  $\alpha$ - and  $\beta$ -Methyl Tetramethylene Carbonates Derived from Levulinic and Itaconic Acids**Scheme 2.** Seven-Membered Cyclic Carbonates Reported in the Literature and Used in ROP

In line with our studies on the “immortal” ROP of the six-membered carbonate TMC using various metallic or organic catalytic systems,<sup>10</sup> we have investigated the behavior of the one-carbon larger carbonates  $\alpha$ - and  $\beta$ -Me7CC. One important issue we aim to address is the efficiency of catalyst systems to promote the regioselective, and possibly stereocontrolled, ROP of such dissymmetric monomers. Herein we report on preliminary investigations using a series of metallic and organic catalyst systems that proved efficient for selective ROP of cyclic esters, in association or not with alcohols as external nucleophiles.

## Experimental Section

**Materials.** All manipulations involving air-sensitive compounds were performed under inert atmosphere (argon, < 3 ppm of O<sub>2</sub>) using standard Schlenk, vacuum line, and glovebox techniques. Solvents were thoroughly dried and deoxygenated by standard methods and distilled before use. CDCl<sub>3</sub> was dried over a mixture of 3 and 4 Å molecular sieves. Benzyl alcohol and isopropyl alcohol (Acros) were distilled over Mg turnings under argon atmosphere and kept over activated 4 Å molecular sieves. [(BDI<sup>iPr</sup>)Zn(N(SiMe<sub>3</sub>)<sub>2</sub>)],<sup>12</sup> [(ONOO<sup>tBu</sup>)Y(N(SiHMe<sub>2</sub>)<sub>2</sub>)(THF)],<sup>13</sup> and 1,4-pentanediol (prepared by reduction of  $\gamma$ -valerolactone)<sup>4</sup> were synthesized following literature procedures.  $\gamma$ -Valerolactone, methyl-succinic acid, triphosgene, pyridine, antipyrine, and Al(OTf)<sub>3</sub> were used as received (Aldrich).

**Instrumentation and Measurements.** <sup>1</sup>H (500, 300, and 200 MHz) and <sup>13</sup>C (125 and 50 MHz) NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Avance AM 500, AM 300, and DPX 200 spectrometers at 20 °C. Chemical shifts ( $\delta$ ) are reported in ppm and were referenced internally relative to tetramethylsilane ( $\delta$  0 ppm) using the residual <sup>1</sup>H and <sup>13</sup>C solvent resonance.

Average molar mass ( $\overline{M}_n$ ) 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<sup>-1</sup>) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a ResiPore 300  $\times$  7.5 mm column. The polymer samples were dissolved in THF (2 mg mL<sup>-1</sup>). All elution curves were calibrated with polystyrene (PS) standards ( $\overline{M}_{n\text{SEC}}$  values are uncorrected for possible difference in hydrodynamic volume of the polycarbonates vs PS). The SEC traces of the polymers all exhibited a unimodal and symmetrical peak.

The molar mass values of short-chain H-[poly( $\alpha$ -Me7CC)] or poly( $\beta$ -Me7CC)-OBn samples were determined by <sup>1</sup>H NMR analysis, from the relative intensity of the signals of the methine hydrogens of the poly( $\beta$ -Me7CC) chains (CH<sub>2</sub>CH(CH<sub>3</sub>)(O),  $\delta$  = 5.17 ppm) or of the methyl hydrogens of the poly( $\alpha$ -Me7CC) chains (CH<sub>2</sub>CH(CH<sub>3</sub>)(O),  $\delta$  = 1.31 ppm) to the aromatic hydrogens of the chain-end ((CO)OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>,  $\delta$  = 7.34 ppm). The number-average molar mass values thus obtained by <sup>1</sup>H NMR,  $\overline{M}_{n\text{NMR}}$ , were in close agreement with the ones calculated, as reported in Tables 1–3.

Monomer conversions were calculated from <sup>1</sup>H NMR spectra of the crude polymer sample, from the integration (Int) ratio

Table 2. Bulk iROP of  $\beta$ -Me7CC Initiated by Various Metallic Catalyst/BnOH Systems

entry	[catalyst]	$[\beta\text{-Me7CC}]_0/[\text{BnOH}]_0$	$[\beta\text{-Me7CC}]_0$	temp (°C)	reaction time (min) <sup>a</sup>	conv <sup>b</sup> (%)	$\overline{M}_{n\text{theo}}^c$ (g mol <sup>-1</sup> )	$\overline{M}_{n\text{NMR}}^d$ (g mol <sup>-1</sup> )	$\overline{M}_{n\text{SEC}}^e$ (g mol <sup>-1</sup> )	$\overline{M}_w/\overline{M}_n^f$	TOF <sup>g</sup> (h <sup>-1</sup> )
1		100/0:0	bulk	110	120	0					
2	Al(OTf) <sub>3</sub>	500:1:5	bulk	110	60	100	13100	11500	9065	1.44	500
3	Al(OTf) <sub>3</sub>	500:1:5	bulk	110	15	100	13100	22700	6200	1.18	2 000
4	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	100:1:1	2M	20	5	100	13100	15500	5700	1.11	1 200
5	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	100:1:1	bulk	20	5	100	13100	15700	6600	1.23	1 200
6	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	100:1:1	bulk	80	15	100	13100	26000	15700	1.36	400
7	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	100:1:1	bulk	80	24 × 60	100	13100	9200	9000	1.68	4
8	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	2M	20	5	20	5300	7800			480
9	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	bulk	0	25	38	10000	2300	2700	1.17	182
10	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:1	bulk	20	10	100	26100	34200	6200	1.23	1 200
11	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:5	bulk	20	10	79	4200	5100	2800	1.32	948
12	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	200:1:10	bulk	20	10	100	2700	2100	1900	1.23	1 200
13	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	300:1:1	bulk	20	15	100	39100		16930	1.48	1 200
14	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:1	2M	20	50	100	65100		4500	1.13	600
15	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:1	bulk	20	15	87	56650		4700	1.11	1 740
16	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:5	bulk	20	15	17	2300	6100			340
17	(BDI <sup>iPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	500:1:10	bulk	20	15	22	1550	3600			440

<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  $[\beta\text{-Me7CC}]_0/[\text{BnOH}]_0 \times$  monomer conversion  $\times M_{\beta\text{-Me7CC}} + M_{\text{BnOH}}$ , with  $M_{\beta\text{-Me7CC}} = 130 \text{ g} \cdot \text{mol}^{-1}$ ,  $M_{\text{BnOH}} = 108 \text{ g} \cdot \text{mol}^{-1}$ . <sup>d</sup> Determined by NMR taking into account the monomer conversion. <sup>e</sup> Determined by SEC vs polystyrene standards (uncorrected raw data). <sup>f</sup> Molar mass distribution calculated from SEC traces. <sup>g</sup> Turnover frequency expressed in  $\text{mol}_{\text{TMC}} \text{mol}_{\text{Catalyst}}^{-1} \text{h}^{-1}$ .

Table 3. Bulk iROP of  $\beta$ -Me7CC with Various Organocatalyst/BnOH Catalytic Systems;  $[\beta\text{-Me7CC}]_0/[\text{catalyst}]_0/[\text{BnOH}]_0 = 100:1:1$ 

entry	[catalyst]	$[\beta\text{-Me7CC}]_0$	temp (°C)	reaction time <sup>a</sup> (min)	conv <sup>b</sup> (%)	$\overline{M}_{n\text{theo}}^c$ (g mol <sup>-1</sup> )	$\overline{M}_{n\text{SEC}}^d$ (g mol <sup>-1</sup> )	$\overline{M}_w/\overline{M}_n^e$	TOF (mol <sub>TMC</sub> · mol <sub>Catalyst</sub> <sup>-1</sup> h <sup>-1</sup> )
1	TBD	bulk	20	60		13100			
2	TBD	bulk	60	60		13100			
3	TBD	bulk	110	60	100	13100	10 350	1.40	100
4	TBD	2M	110	75	100	13100	7 150	1.23	80
5	BEMP	bulk	20	60		13100			
6	BEMP	bulk	60	60		13100			
7	BEMP	bulk	110	60	100	13100	7 800	1.20	100
8	DMAP	bulk	20	60		13100			
9	DMAP	bulk	60	60		13100			
10	DMAP	bulk	110	60	87	11400	8 500	1.21	87

<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  $[\text{TMC}]_0/[\text{BnOH}]_0 \times$  monomer conversion  $\times M_{\text{TMC}} + M_{\text{BnOH}}$ , with  $M_{\beta\text{-Me7CC}} = 130 \text{ g} \cdot \text{mol}^{-1}$ ,  $M_{\text{BnOH}} = 108 \text{ g} \cdot \text{mol}^{-1}$ . <sup>d</sup> Determined by SEC vs polystyrene standards (uncorrected raw data). <sup>e</sup> Molar mass distribution calculated from SEC traces.

$\text{Int}_{\text{polymer}}/[\text{Int}_{\text{polymer}} + \text{Int}_{\text{monomer}}]$ , using the methyl hydrogens ( $\text{CH}_2\text{CH}(\text{CH}_3)(\text{O})$ ) of poly( $\alpha$ -Me7CC) at  $\delta = 1.31$  ppm and of  $\alpha$ -Me7CC at  $\delta = 1.41$  ppm, and the methylene hydrogens ( $\text{CH}_2\text{CH}(\text{CH}_3)(\text{O})$ ) of the poly( $\alpha$ -Me7CC) at  $\delta = 4.20$  ppm and of  $\beta$ -Me7CC at  $\delta = 3.70$  ppm, respectively.

MALDI-ToF mass spectra were recorded with an AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N<sub>2</sub> 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<sup>-1</sup>) and a solution (2:1 v:v) of  $\alpha$ -cyano-4-hydroxycinnamic acid (10 mg mL<sup>-1</sup>) 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.

Electrospray high-resolution mass spectroscopy was performed on a Bruker Micro-ToF-Q 2 instrument. IR spectra were acquired on a Shimadzu IRAffinity-1 spectrometer equipped with an ATR.

Differential scanning calorimetry (DSC) analyses were performed on a Setaram DSC 131 apparatus at a heating rate of 10 °C min<sup>-1</sup>, under a continuous flow of helium (25 mL min<sup>-1</sup>), using aluminum capsules. The thermograms were recorded according to the following cycles: -60 °C to +200 at 10 °C min<sup>-1</sup>; +200 to -60 °C at 10 °C min<sup>-1</sup>; -60 °C to +200 at 10 °C min<sup>-1</sup>.

(±)-4-Methyl-1,3-dioxepan-2-one ( $\alpha$ -Me7CC). A solution of triphosgene (20.0 g, 70 mmol) in anhydrous dichloromethane (120 mL) was added dropwise over 90 min to a stirred solution of (±)-1,4-pentanediol (14.0 g, 140 mmol) and pyridine (63.9 g, 820 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (300 mL) at -78 °C. After 30 min, the reaction mixture was quenched by addition of a saturated aqueous solution of ammonium chloride (200 mL) followed by water (100 mL). The mixture was allowed to warm to 5 °C and the organic phase was separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 × 30 mL) and the organic extracts were combined, washed with brine (100 mL), and dried over MgSO<sub>4</sub>. After removal of volatiles under a vacuum, the residue was isolated by distillation (120 °C, reduced pressure) as a colorless solid (9.0 g, 51%). The monomer was stored in the fridge. Alternatively,  $\alpha$ -Me7CC could be prepared from 1,4-pentanediol according to the procedure described below for  $\beta$ -Me7CC. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.39 (m,  $J_{\text{HH}} = 6$  Hz, 1H, CH<sub>3</sub>CHO), 4.25–4.15 (m,  $J_{\text{HH}} = 5$  Hz, 2H, CH<sub>2</sub>O), 1.93–1.78 (m,  $J_{\text{HH}} = 5$  Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH), 1.41 (d, 3H,  $J_{\text{HH}} = 6$  Hz, CH<sub>3</sub>) (Figure S1, Supporting Information). <sup>13</sup>C-{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  154.9 (C=O), 79.0 (CH<sub>3</sub>CHO), 70.4 (CH<sub>2</sub>O), 34.6 (CH<sub>2</sub>CHCH<sub>3</sub>O), 27.0 (CH<sub>2</sub>CH<sub>2</sub>O), 21.9 (CH<sub>3</sub>CHO) (Figure S2, Supporting Information). HRMS-ESI<sup>+</sup> ( $m/z$ ): 130.06 ([M]<sup>+</sup>, calc: 130.0630). IR  $\nu$ (C=O): 1750 cm<sup>-1</sup>.

(±)-2-Methyl-1,4-butanediol. A solution of (±)-methylsuccinic acid (10.0 g, 75.7 mmol) in THF (200 mL) was added dropwise onto a suspension of LiAlH<sub>4</sub> (8.9 g, 235 mmol) in THF (200 mL) and the reaction mixture was refluxed for 24 h.



After being cooled to room temperature, a saturated  $\text{Na}_2\text{SO}_4$  aqueous solution was added, the mixture was filtered, and the organic phase was separated. Removal of volatiles and distillation of the residue under a vacuum at 100 °C afforded ( $\pm$ )-2-methyl-1,4-butanediol as a colorless oil (5.8 g, 55.7 mmol, 74%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.78–3.43 (m,  $J$  = 7 Hz, 4H,  $\text{CH}_2\text{OH}$ ), 3.34 (s, 2H, OH), 1.81 (m, 1H,  $\text{CHMe}$ ), 1.60 (m,  $J$  = 6 Hz, 2n H,  $\text{CH}_2\text{CH}_2\text{CH}$ ), 0.94 (d,  $J$  = 7 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  67.8 ( $\text{CHMe}$ ), 60.6 ( $\text{CHMe}$ ), 37.2 ( $\text{CHMeCH}_2\text{OH}$ ), 33.7 ( $\text{CH}_2\text{CH}_2\text{CHMe}$ ), 17.2 ( $\text{CH}_2\text{CH}_2\text{OH}$ ).

( $\pm$ )-5-Methyl-1,3-dioxepan-2-one ( $\beta$ -Me7CC). Pyridine (40.0 mL, 400 mmol, 6.0 equiv) was added dropwise over 1 h to a solution of ( $\pm$ )-2-methyl-1,4-butanediol (7.0 g, 67 mmol, 1.0 equiv) and triphosgene (10.0 g, 34 mmol, 0.5 equiv) in  $\text{CH}_2\text{Cl}_2$  (500 mL) at –90 °C. After the mixture was stirred at –78 °C over 2 h, a saturated  $\text{NH}_4\text{Cl}$  aqueous solution (200 mL) was added quickly (the desired product is soluble in water) to extract the product. The organic phase was dried over  $\text{MgSO}_4$ , volatiles were removed under a vacuum, and the resulting residue was distilled quickly (to avoid polymerization by residual basic impurities) under a vacuum (reduced pressure) at 100 °C, to give  $\beta$ -Me7CC as a colorless oil (4.9 g, 57%). The carbonate was stored under inert atmosphere at –30 °C. Lowering the amount of pyridine (3 equiv) added over 30 min to a THF solution of the diol, and reacting over 6 h from 0 to 23 °C gave a comparable yield (57%). Attempts to exchange pyridine by antipyrine (2 equiv) with its addition carried out at 45–50 °C, as initially reported for the synthesis of  $\alpha$ -substituted 7CCs,<sup>4</sup> led in our hands to maximal yields of 30%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.30 (m,  $J$  = 7 Hz, 1H,  $\text{CH}_2\text{CHHO}$ ), 4.16 (m,  $J$  = 7 Hz, 2H,  $\text{CH}_2\text{CHHO}$ ,  $\text{CHCHHO}$ ), 3.86 (m,  $J$  = 7 Hz, 1H,  $\text{CHCHHO}$ ), 2.13 (m,  $J$  = 7 Hz, 1H,  $\text{CH}$ ), 2.00 (m,  $J$  = 7 Hz, 1H,  $\text{CH}_2\text{CHHCH}$ ), 1.66 (m,  $J$  = 7 Hz, 1H,  $\text{CH}_2\text{CHHCH}$ ), 1.01 (d,  $J$  = 7 Hz, 3H,  $\text{CH}_3$ ) (Figure S3, Supporting Information).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.0 ( $\text{C}=\text{O}$ ), 75.1 ( $\text{CHCH}_2\text{O}$ ), 69.0 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 34.9 ( $\text{CH}_2\text{CH}_2\text{CHMe}$ ), 32.1 ( $\text{CHMe}$ ), 15.6 ( $\text{CH}_3$ ) (Figure S4, Supporting Information). HRMS-ESI<sup>+</sup> ( $m/z$ ): 130.063 ( $[\text{M}]^+$ , calc: 130.0630). IR  $\nu(\text{C}=\text{O})$ : 1750  $\text{cm}^{-1}$ .

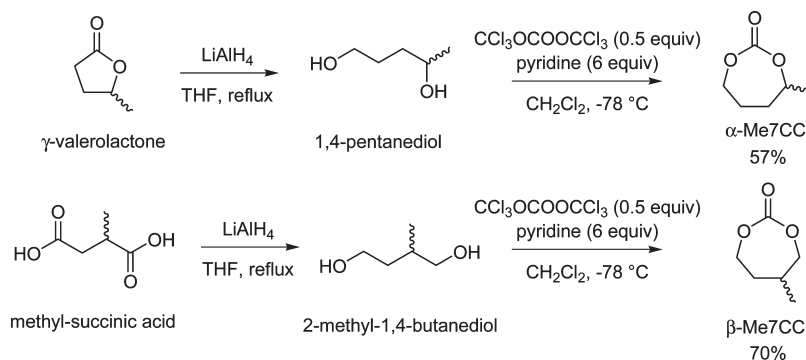
**Typical Polymerization Procedure.**  $[(\text{BDI}^{\text{IPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$  (10.0 mg, 15.5  $\mu\text{mol}$ ) was added to benzyl alcohol (1.6  $\mu\text{L}$ , 15.5  $\mu\text{mol}$ , 1 equiv) placed in toluene (0.1 mL) and stirred over 15 min just prior to the addition of the monomer via a syringe (0.60 g, 4.6 mmol). The mixture was then stirred at the required temperature over the appropriate time (reaction times were not 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 a vacuum and the conversion was determined by  $^1\text{H}$  NMR analysis of the residue. This crude polymer was then dissolved in  $\text{CH}_2\text{Cl}_2$  and purified upon precipitation in cold methanol, filtered, and dried under a vacuum. The final colorless polymer was then analyzed by NMR and SEC. **BnO-[poly( $\alpha$ -Me7CC)]-H.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (s, 10H,  $\text{C}_6\text{H}_5$ ), 5.15 (s, 4H,  $\text{CH}_2\text{Ph}$ ), 4.79 (m,  $J$  = 6 Hz, (2n+1)H,  $\text{CH}_2\text{CH}(\text{CH}_3)\text{O}$ ), 4.14 (m,  $J$  = 6 Hz, (4n+2)H,  $\text{C}(\text{O})\text{OCH}_2$ ), 3.84 (m, 1H,  $\text{CH}(\text{CH}_3)\text{OH}$ ), 3.66 (t,  $J$  = 6 Hz, 2H,  $\text{CH}_2\text{OH}$ ), 1.71 (m,  $J$  = 6 Hz, (8n+6)H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)$ ), 1.52 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ ), 1.30 (d,  $J$  = 6 Hz, (3n+3)H,  $\text{CH}_3\text{CHO}$ ), 1.23 (d,  $J$  = 6 Hz, 3H,  $\text{CH}_3\text{CHOH}$ ) (Figure 5).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  160.8 ( $\text{C}=\text{O}$ ), 128.1 ( $\text{C}_6\text{H}_5$ ), 74.4 ( $\text{OC}(\text{O})\text{OCH}(\text{CH}_3)-(\text{CH}_2)_3\text{OH}$ ), 74.0 ( $\text{CH}_2\text{CH}(\text{CH}_3)\text{OC}(\text{O})\text{O}$ ), 73.8 ( $\text{OC}(\text{O})\text{OCH}(\text{CH}_3)(\text{CH}_2)_3$ ), 68.9 ( $\text{OCH}_2\text{Ph}$ ), 67.6 ( $\text{OC}(\text{O})\text{OCH}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{OH}$ ), 67.1 ( $\text{CH}_2\text{OC}(\text{O})\text{O}$ ), 67.0 ( $\text{CH}_2\text{OH}$ ), 66.9 ( $\text{OC}(\text{O})\text{OCH}_2$ ), 66.8 ( $\text{CH}(\text{CH}_3)\text{OH}$ ), 35.1 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ ), 32.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)$ ), 25.1 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ ), 24.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)$ ), 23.4 ( $\text{CH}(\text{CH}_3)\text{OH}$ ), 19.6 ( $\text{OC}(\text{O})\text{OCH}(\text{CH}_3)$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.8 ( $\text{C}=\text{O}$ ), 128.1 ( $\text{C}_6\text{H}_5$ ), 74.4 ( $\text{OC}(\text{O})\text{OCH}(\text{CH}_3)(\text{CH}_2)_3\text{OH}$ ), 74.0 ( $\text{CH}_2\text{CH}(\text{CH}_3)\text{OC}(\text{O})\text{O}$ ), 73.8 ( $\text{O}(\text{CO})\text{OCH}(\text{CH}_3)\text{CH}_2$ ),

68.8 ( $\text{OCH}_2\text{Ph}$ ), 67.7 ( $\text{OCH}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{OH}$ ), 67.1 ( $\text{CH}_2\text{OC}(\text{O})\text{O}$ ), 67.0 ( $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 66.9 ( $\text{OC}(\text{O})\text{OCH}_2$ ), 66.8 ( $\text{O}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{OH}$ ), 35.2 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ ),  $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 32.1 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)$ ), 25.2 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ ),  $\text{CH}_2\text{CH}_2\text{OH}$ , 24.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)$ ),  $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 23.5 ( $\text{CH}(\text{CH}_3)\text{OH}$ ), 19.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}$ ) (Figure S7, Supporting Information). **BnO-[poly( $\beta$ -Me7CC)]-H.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38 (m, 5H,  $\text{C}_6\text{H}_5$ ), 5.17 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 4.19 (m,  $J$  = 6 Hz, 4nH,  $\text{CH}_3\text{CHCH}_2\text{OC}(\text{O})\text{O}$ ), 4.00 (m,  $J$  = 7 Hz, 4nH,  $\text{OC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)$ ), 3.84 (t,  $J$  = 5 Hz,  $\text{CH}_3\text{CHCH}_2\text{OH}$ ), 3.71 (m,  $J$  = 7 Hz,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 2.00 (m,  $J$  = 5 Hz, 2nH,  $\text{CH}_3\text{CHCH}_2\text{OC}(\text{O})\text{O}$ ), 1.84, 1.55 (m,  $J$  = 7 Hz, 4nH,  $\text{OC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$ ), 1.02 (d,  $J$  = 6 Hz, 6nH,  $\text{CHCH}_3\text{O}$ ) (Figure 7).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  155.8 ( $\text{C}=\text{O}$ ), 128.0 ( $\text{C}_6\text{H}_5$ ), 72.3 ( $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{OH}$ ), 71.8 ( $\text{CH}(\text{CH}_3)\text{CH}_2\text{OC}(\text{O})\text{O}$ ), 67.2 ( $\text{OCH}_2\text{Ph}$ ), 66.0 ( $\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ ), 65.4 ( $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{O}$ ), 59.9 ( $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ ), 36.0 ( $\text{OC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ ), 32.6 ( $\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ ),  $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{OH}$ ), 32.2 ( $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ ),  $\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$ ), 31.9 ( $\text{OC}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$ ),  $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{O}$ ), 29.7 ( $\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$ ),  $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{O}$ ), 16.4, 16.2 ( $\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ ),  $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{OH}$ ; 16.0 ( $\text{OC}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{O}$ ),  $\text{OC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$ ) (Figure S8, Supporting Information).

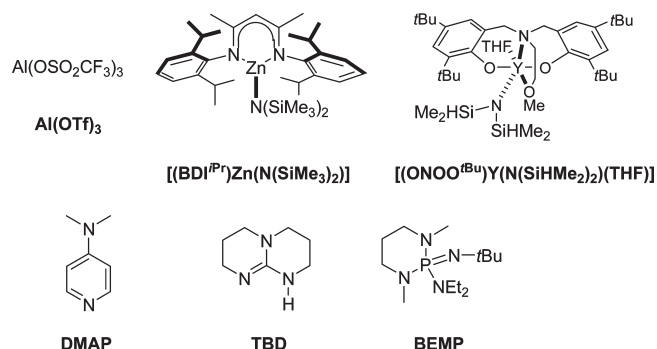
## Results and Discussion

**Synthesis of the Monomers.**  $\alpha$ - and  $\beta$ -Methyl-tetramethylene carbonates ( $\alpha$ -Me7CC and  $\beta$ -Me7CC) were synthesized from 1,4-pentanediol and 2-methyl-1,4-butanediol, respectively, using regular academic (not green) routes, upon cyclization with triphosgene in the presence of pyridine at –78 °C, as initially reported by Burk and Roof for the synthesis of cyclic carbonates from 1,2- and 1,3-diols (Scheme 3).<sup>11</sup> Treatment of the diols at such a temperature, lower than that reported in the original preparation of  $\alpha$ -Me7CC (45–50 °C),<sup>4</sup> allowed higher yields to be reached (at best 57%) upon minimizing the side formation of oligocarbonates which is favored at higher temperatures.  $\beta$ -Me7CC, first synthesized in the present work, was isolated in slightly higher yields (up to 70%), possibly because of the different position of the methyl group which may sterically disfavor the formation of oligomers. The use of antipyrine as the base in place of pyridine, under the reaction conditions previously reported (45–50 °C, THF or  $\text{CHCl}_3$ ), did not give satisfactory yields of pure 7CCs. Note also that the chloroformate route commonly employed for the synthesis of six-membered cyclic carbonates<sup>3</sup> proved to be inefficient in this case (see the Experimental Section). Like other seven-membered tetramethylene carbonates,<sup>3</sup> both monomers  $\alpha$ -Me7CC and  $\beta$ -Me7CC are rather tricky to manipulate and especially to purify because of their strong ability to polymerize.

**Polymerization of  $\alpha$ -Me7CC and  $\beta$ -Me7CC.** The ROP of  $\alpha$ -Me7CC and  $\beta$ -Me7CC was investigated with some well-established metal-based catalysts, namely, the Lewis acid  $\text{Al}(\text{OTf})_3$ ,<sup>10f,g</sup> and the organometallic complexes  $[(\text{BDI}^{\text{IPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$ <sup>10a-e,12</sup> ( $\text{BDI}^{\text{IPr}}$  = 2-((2,6-diisopropylphenyl)-amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene] and  $[(\text{ONOO}^{\text{tBu}})\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})]$ <sup>13</sup> ( $\text{ONOO}^{\text{tBu}}$  = amino-alkoxy-bis(phenolate)) (Scheme 4). These zinc and yttrium catalysts were selected because of their high performances in the stereoselective ROP of racemic lactide,<sup>12,13</sup> and of racemic  $\beta$ -butyrolactone.<sup>14</sup> Representative results obtained with these catalysts are reported in Tables 1 and 2. The more recently unveiled organocatalysts such as amines, guanidines,

Scheme 3. Synthesis of  $\alpha$ - and  $\beta$ -Methyl Tetramethylene Carbonates,  $\alpha$ -Me7CC and  $\beta$ -Me7CC

Scheme 4. Metal-Based and Organic ROP Catalysts Used in the Present Study



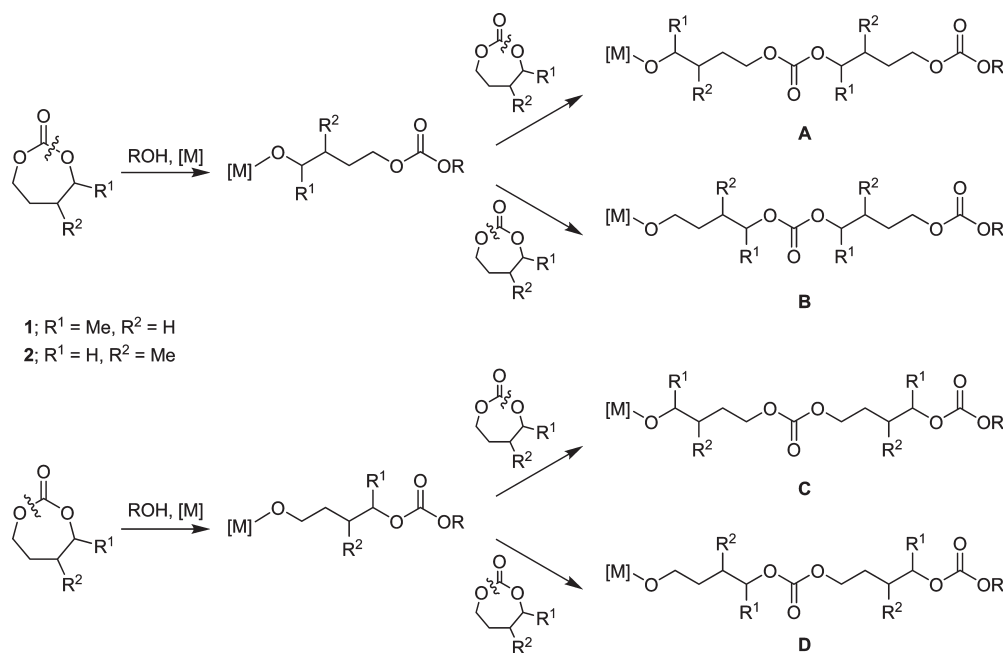
or phosphazenes have similarly been explored in the ROP of  $\beta$ -Me7CC using 4-dimethylaminopyridine (DMAP), 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD), and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) (Scheme 4, Table 3).<sup>10h,i,15</sup> All these catalytic species have been used in association with benzyl alcohol (BnOH) or isopropanol (*i*PrOH) acting both as a co-initiator and as a chain transfer agent (CTA), thereby making the present investigations the pioneering approach of the “immortal” ROP (iROP) of 7CCs. Our concern in preferentially using “immortal” in place of “classical” ROP is to develop the ROP of heterocyclic monomers, among which carbonates, within rather “green” considerations.<sup>10e,16</sup> Addition of a protic source, to play the dual role of a co-initiator and of a CTA, in a minute amount relative to the monomer loading, drives the number of macromolecular chains growing per initiator to an amount equalizing the original amount of alcohol initially added to the whole catalytic system. Hence, iROP allows lowering the amount of catalytic species to quantities as low as 10 ppm, thus alleviating possible issues revolving around the toxicity of the catalytic (metallic or organic) residues.<sup>10</sup> In addition, the operating conditions of iROP enable efficient bulk procedures (i.e., solvent free), thereby further improving safety and environmental concerns.

As can be seen from Tables 1–3, the molar mass values determined from NMR ( $\overline{M}_{n,NMR}$ , refer to the Experimental Section) were in quite close agreement with the ones calculated ( $\overline{M}_{n,theo}$ ), assuming that all the added alcohol molecules contribute to the immortal polymerization. Note that in the case of iROP, the expected molar mass value  $\overline{M}_{n,theo}$  is calculated from the initial concentration in CTA, that is in  $[BnOH]_0$ , rather than from that of the catalyst. These observations indicate that BnOH is the actual ROP initiator and that a fast and reversible exchange takes place between the growing polymer chains and the free alcohol moieties.<sup>10a–c</sup>

The SEC traces of the poly(7CC)s all exhibited a unimodal and symmetrical peak. The moderate broadness of molar mass distribution values observed for bulk polymerizations, as compared to those measured for solution polymerization, is typical and reflects the more frequent occurrence of side processes (transfer and/or transesterification/transcarbonation reactions) all along the propagation step.<sup>3,17</sup> The molar mass values determined by SEC ( $\overline{M}_{n,SEC}$ ) were referenced to poly(styrene) standards and were not corrected for possible difference in hydrodynamic radius of these poly(7CC)s. These values often deviate quite significantly from the calculated ones ( $\overline{M}_{n,theo}$ ), especially for the poly( $\alpha$ - and  $\beta$ -Me7CC)s anticipated with a relatively high  $\overline{M}_n$  value and seem to reach a limit around  $\overline{M}_{n,SEC} = 16\,000\text{ g}\cdot\text{mol}^{-1}$  (Tables 1–3). Attempts to determine the molar mass of these polycarbonates by performing SEC in solvents different from THF ( $CHCl_3$ ,  $CH_2Cl_2$ , DMF) led to quite different  $\overline{M}_n$  and  $\overline{M}_w/\overline{M}_n$  values (see the Supporting Information, Table S1). The behavior of these poly(7CC)s, which display a molar mass remaining constant at a ceiling value even though increasing amounts of monomer are quantitatively converted, suggests that somehow these polycarbonates adsorb (more or less depending on the eluting solvent) onto the eluting SEC columns with a cutoff limit of the polymer molar mass being effectively eluted at  $16\,000\text{ g}\cdot\text{mol}^{-1}$ .<sup>18</sup>

Evaluation of the catalyst most resistant to impurities, namely,  $Al(OTf)_3$ ,<sup>10f</sup> at a  $[monomer]_0/[catalyst]_0/[BnOH]_0$  ratio of 500:1:5 revealed the activity of this system toward both monomers at temperatures as low as 40 °C (solution or bulk, Table 1, entries 1–3; Table 2, entries 2–3). Reactions with this system were, however, better conducted at higher temperatures (110 °C) under bulk (solvent-free) conditions. As expected, this Lewis acid catalysts is more active with the larger carbonates 7CCs than with TMC: at 110 °C, for the same  $[monomer]_0/[catalyst]_0/[BnOH]_0$  ratio of 500:1:5, whereas 88% of TMC conversion was observed after 30 min,<sup>10f</sup> quantitative conversion of  $\alpha$ -Me7CC and  $\beta$ -Me7CC was reached within 15 min.

The zinc  $\beta$ -diiminate complex  $[(BDI^{IPr})Zn(N(SiMe_3)_2)]$  successfully used in the iROP of the six-membered ring monomer TMC<sup>10a–c</sup> was similarly active toward the (i)ROP of  $\alpha$ - and  $\beta$ -Me7CC under very mild conditions (20–60 °C), either in toluene solution or in bulk (Table 1, entries 4–16; Table 2, entries 4–17). In the presence of 1 equiv of BnOH, the ROP of  $\alpha$ -Me7CC (100–500 equiv) in toluene or in bulk proceeded quantitatively within 5–180 min (Table 1, entries 4–9, 13–14). Likewise, the ROP of  $\beta$ -Me7CC, in solution as well as in bulk, gave almost quantitative conversions within similar reaction times (5 to 50 min; Table 2, entries 4–10, 13–15). Performing the ROP reactions in bulk required shorter reaction times to reach full conversion, as compared

Scheme 5. Possible Regioselectivities for ROP of  $\alpha$ -Me7CC and  $\beta$ -Me7CC

to solution process (Table 1, compare entry 4 vs 5, 8 vs 9, 13 vs 14; Table 2, compare entry 8 vs 10, 14 vs 15).

Using an excess (5–10 equiv) of benzyl alcohol, that is under “immortal” conditions, both in solution ( $[\alpha\text{-Me7CC}]_0/[(\text{BDI})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]_0$  ratio of 200:1; Table 1, entries 10–11) or in bulk ( $[\alpha\text{- or } \beta\text{-Me7CC}]_0/[(\text{BDI})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]_0$  ratio of 500:1; Table 1, entries 15–16; Table 2, entries 11–12, 16–17), the zinc catalytic system remained similarly active. The molar mass values determined by NMR spectroscopy were in quite good agreement with the calculated ones ( $\overline{M}_{n,\text{theo}}$ ), determined from the initial monomer-to-alcohol ratio. As the concentration in CTA increased, for a given monomer-to-Zn ratio, the molar mass of the resulting poly( $\alpha$ - or  $\beta$ -Me7CC), determined by NMR decreased proportionally to the number of added BnOH molecules, further evidencing the chain transfer efficiency. The results also demonstrated that the iROP of  $\alpha$ - and  $\beta$ -Me7CC with BnOH remained fairly well controlled in terms of molar mass distributions ( $\overline{M}_w/\overline{M}_n < 1.36$ ). As much as 10 macromolecular chains could thus be grown from a single zinc center by the  $(\text{BDI}^{\text{IPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)/\text{BnOH}$  system in the presence of up to 500 equiv of  $\alpha$ - or  $\beta$ -Me7CC.

Longer reaction times, as well as higher temperatures and bulk procedure, led, as anticipated, to the occurrence of some side reactions (transfer or inter/intramolecular transesterification/transcarbonation reactions), as evidenced by the slightly larger  $\overline{M}_w/\overline{M}_n$  values. This is illustrated, for instance, by the broadening of the molar mass distribution from 1.36 to 1.68 and concomitant decrease in  $\overline{M}_n$  values from 15 700 to 9000  $\text{g}\cdot\text{mol}^{-1}$  over a prolonged reaction time from 15 min to 24 h, respectively (Table 2, entry 6 vs 7). Running the polymerization of  $\alpha$ -Me7CC in bulk rather than in diluted medium led to a slight increase of the  $\overline{M}_w/\overline{M}_n$  value (e.g., from 1.58 to 1.68; Table 1, entry 8 vs 9 and from 1.13 to 1.27, Table 1, entry 13 vs 14). Also, the lowering of the temperature resulted in a slightly narrower molar mass distribution value (1.17 at 0 °C vs 1.23 at 20 °C), yet at the logical expense of activity (76 turnovers within 25 min vs 200 turnovers within 10 min, respectively) (Table 2, entry 9 vs 10).

The solution ROP of  $\alpha$ -Me7CC mediated by the {aminoalkoxy-bis(phenolate)}-yttrium amido, or its alkoxide analogue

prepared in situ upon addition of BnOH, proceeded at room temperature within a few minutes (Table 1, entries 17–20).<sup>19</sup> The molar mass distribution values were slightly larger than those obtained with the zinc or triflate salt catalytic systems.

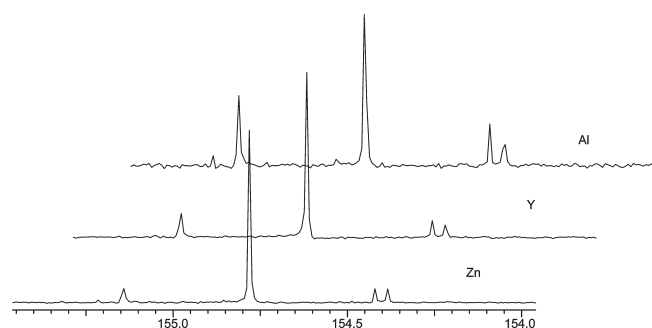
The ROP of  $\beta$ -Me7CC using the organocatalysts DMAP, TBD, and BEMP in the presence of BnOH was found to be effective only at higher temperatures (Table 3). For all catalyst systems, running the experiments at 20 or 60 °C did not afford any polymer. However, at 110 °C, 100 turnovers were easily reached within 1 h affording well-defined poly( $\beta$ -Me7CC). All three organocatalytic systems exhibited similar activities.

**Microstructural Analyses. Regioselectivity of the O–C(O)O Bond Cleavage in Cyclic Carbonates  $\alpha$ - and  $\beta$ -Me7CC.** One aim of this study was to explore the regioselectivity of the O–C(O)O bond cleavage in these dissymmetric cyclic carbonates. It was anticipated that the zinc and yttrium organometallic catalysts supported by the bulky ancillaries {BDI<sup>IPr</sup>} and {ONOO}, respectively, may be more discriminating than simple Lewis acids or organic catalysts. The microstructure of the prepared poly( $\alpha$ - and  $\beta$ -7CC)s was investigated by <sup>13</sup>C NMR spectroscopy. In a previous study on the cationic ROP of  $\alpha$ -Me7CC promoted by TfOH or TfOMe, Endo et al. reported that the carbonyl region of the 22.5 MHz spectra of poly( $\alpha$ -Me7CC) in CDCl<sub>3</sub> contains three resonances at  $\delta$  155–156 ppm, which are diagnostic of the diad sequences (Scheme 5).<sup>4</sup> The central, most intense resonance was assigned to indistinguishable diads **A** and **D** that arise from regioregular enchainment of the monomer units, that is, regioregular cleavage of either of the O–C(O)O bonds in  $\alpha$ -Me7CC. In addition, they observed two other resonances, at higher and lower field apart from the aforementioned central resonance respectively ( $\Delta\delta = \text{ca. } 0.5$  ppm). Consistent with previous assignments made for a polymer derived from a norbornene-based six-membered cyclic carbonate,<sup>20</sup> those two resonances were assigned to the two magnetically inequivalent carbonyl groups that result from regioirregular enchainment of the monomer units, that is, alternated cleavage of the two O–C(O)O bonds in  $\alpha$ -Me7CC. Because those two carbonyl groups belong to



the same sequence (“diads” **B** and **C** in Scheme 5), the corresponding resonances necessarily have an equal intensity. On the other hand, the relative intensity of these two resonances, as compared to that of the central resonance, reflects the regioregularity in the ROP. To quantify the latter characteristics, we have introduced in this microstructural study the degree of regioregularity,  $X_{\text{reg}}$  (as opposed to the degree of randomness,  $X_{\text{rand}} = 1 - X_{\text{reg}}$ ).<sup>21</sup> For a perfectly statistical ROP process (i.e.,  $X_{\text{reg}} = 0$ ,  $X_{\text{rand}} = 1$ ), the probability of formation of these sequences is equal and a 1:2:1 distribution for the three resonances is expected. On the other hand, when the ROP proceeds in a more regioregular fashion (i.e.,  $X_{\text{reg}} \rightarrow 1$ ,  $X_{\text{rand}} \rightarrow 0$ ), the relative intensity of the high and low field carbonyl resonances progressively decreases; in other words, only the central resonance should be observed for a perfectly regioregular ROP. On that basis, we estimated the degree of regioselectivity achieved in the cationic ROP of  $\alpha$ -Me7CC promoted by TfOH or TfOMe at 20 °C<sup>4</sup> to  $X_{\text{reg}} = \text{ca. } 0.50$ .<sup>22</sup>

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of our poly( $\alpha$ -Me7CC) samples, recorded at 125 MHz in  $\text{CDCl}_3$ , show four resonances for the carbonyl groups instead of the aforementioned three resonances observed at 22.5 MHz<sup>4</sup> (Figure 1). As revealed by their relative intensity, independently measured from different samples (Table 4), it is obvious that, at this higher field, the single upfield resonance observed at 22.5 MHz has split into two distinct resonances ( $\delta$  154.42 and 154.38 ppm, most likely reflecting triad sequences).<sup>23</sup> In fact, the intensity of those two resonances each equals (within experimental uncertainty) half that of the low field resonance ( $\delta$  155.14 ppm).<sup>23</sup> In addition, in the present 125 MHz  $^{13}\text{C}$  NMR spectra, the  $\text{OCHCH}_3$  and  $\text{OCH}_2$  groups also appeared each as a set of independent resonances that can be assigned to regioregular (two single resonances at  $\delta$  74.50 and 67.22 ppm, respectively) and regioirregular (several overlapping

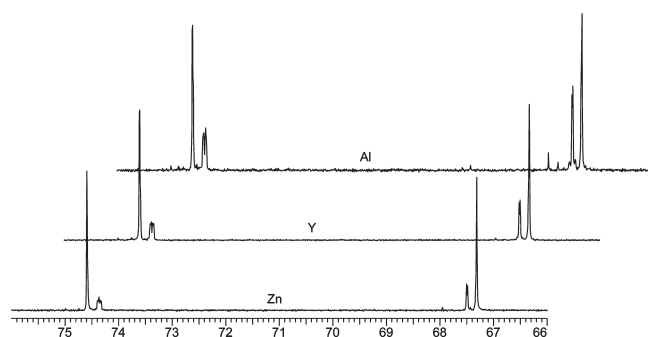


**Figure 1.** Details of the carbonyl region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (125 MHz,  $\text{CDCl}_3$ , 20 °C) of  $\text{BnO}$ -[poly( $\alpha$ -Me7CC)]-H samples prepared from  $[\alpha\text{-Me7CC}]/[\text{catalyst}]/[\text{BnOH}]$  systems; bottom: [Zn] (Table 5, entry 1) ( $X_{\text{reg}} = 0.71$ ), middle: [Y] (Table 5, entry 3) ( $X_{\text{reg}} = 0.58$ ), top: [Al] (Table 5, entry 4) ( $X_{\text{reg}} = 0.27$ ).

resonances at  $\delta$  74.20–74.35 and 67.40–67.45 ppm, respectively) enchainments of monomer units (Figure 2). These assignments were confirmed by the relative intensity of the two resonances for each of these individual groups,<sup>24</sup> which was found to agree well (within experimental accuracy) to the relative intensity for the resonances of the carbonyl group in regioregular ( $\delta$  154.78 ppm) and regioirregular ( $\delta$  155.14, 154.42, and 154.38 ppm) sequences, respectively (Table 4).

With these probes in hands, we could evaluate with a significant reliability the degree of regioregularity ( $X_{\text{reg}}$ )<sup>21</sup> and eventually probe the effect of the catalytic system onto the microstructure of the poly( $\alpha$ -Me7CC) samples. The  $X_{\text{reg}}$  values reported in Table 4 show that, among the systems investigated, the  $[(\text{BDI}^{\text{Pr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$  is the one that allowed to achieve the most regioselective ROP of  $\alpha$ -Me7CC. The degree of regioselectivity of this given catalyst system decreased with increasing temperature ( $X_{\text{reg}} = 0.71$  at 20 °C vs 0.51 at 60 °C). In comparison, the  $[\text{Y}(\text{ONOO}^{\text{tBu}})(\text{N}(\text{SiHMe}_2)_2)(\text{THF})]/\text{BnOH}$  system led to a lower regioselectivity ( $X_{\text{reg}} = 0.58$  at 20 °C), while the  $\text{Al}(\text{OTf})_3/\text{ROH}$  system was hardly regioselective whichever the temperature ( $X_{\text{reg}} = 0.27$  at 40 °C, 0.21 at 90 °C). We assume that these results most likely reflect the different bulkiness of the initiators/catalysts. In this regard, it is interesting to note that the selectivity trend observed in the ROP of  $\alpha$ -Me7CC qualitatively follows the one observed with the same initiators/catalysts for the stereoselective ROP of racemic lactide to form heterotactic-enriched polylactides.<sup>25</sup>

The regioregularity of poly( $\beta$ -Me7CC) samples was similarly investigated by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. In contrast to poly( $\alpha$ -Me7CC), irrespective of the operating conditions and catalyst systems used, the carbonyl region of the 125 MHz spectra of the poly( $\beta$ -Me7CC)s systematically featured three resonances in a 1:2:1 relative intensity ratio (Figures 3 and S8). In addition, the  $\text{OCHCH}_3$  and



**Figure 2.** Details of the  $\text{CH}_3\text{CHO}$  and  $\text{OCH}_2$  region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (125 MHz,  $\text{CDCl}_3$ , 20 °C) of  $\text{BnO}$ -[poly( $\alpha$ -Me7CC)]-H samples prepared from  $[\alpha\text{-Me7CC}]/[\text{catalyst}]/[\text{BnOH}]$  systems; bottom: [Zn] (Table 5, entry 1) ( $X_{\text{reg}} = 0.71$ ), middle: [Y] (Table 5, entry 3) ( $X_{\text{reg}} = 0.58$ ), top: [Al] (Table 5, entry 4) ( $X_{\text{reg}} = 0.27$ ).

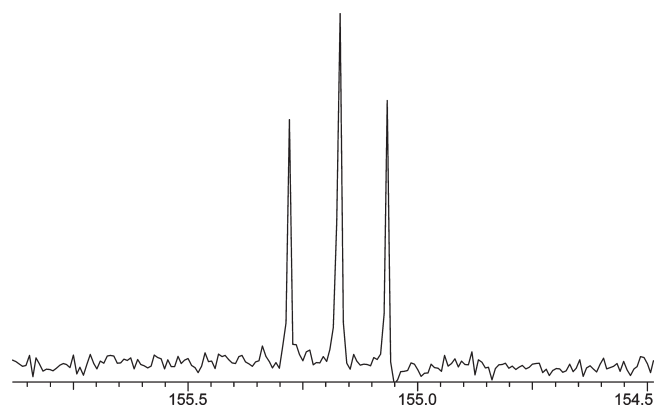
**Table 4.**  $^{13}\text{C}$  NMR Chemical Shifts and Relative Integrals of Diagnostic Resonances of  $\text{BnO}$ -[poly( $\alpha$ -Me7CC)]-H<sup>a</sup>

		entry 1 ( $\text{BDI}^{\text{Pr}}\text{Zn}(\text{N}(\text{TMS})_2)$ 200:1:1, 20 °C	entry 2 ( $\text{BDI}^{\text{Pr}}\text{Zn}(\text{N}(\text{TMS})_2)$ 200:1:1, 60 °C	entry 3 ( $\text{ONOO}^{\text{tBu}}\text{Y}(\text{NR}_2)(\text{THF})$ 200:1:1, 20 °C	entry 4 [ $\text{Al}(\text{OTf})_3$ ] 500:1:5, 40 °C	entry 5 [ $\text{Al}(\text{OTf})_3$ ] 500:1:5, 90 °C
	chem shift (ppm)					
<b>C=O</b>	155.14	0.109	0.240	0.222	0.409	0.434
	154.78	1	1	1	1	1
	154.42	0.074	0.112	0.092	0.202	0.222
	154.38	0.082	0.120	0.117	0.186	0.207
<b>OCH</b>	74.50	1	1	1	1	1
	74.20–74.35	0.317	0.486	0.443	0.717	0.809
<b>OCH<sub>2</sub></b>	67.40–67.45	0.304	0.499	0.389	0.683	0.701
	67.22	1	1	1	1	1
<b><math>X_{\text{reg}}</math></b>		$0.71 \pm 0.03$	$0.51 \pm 0.02$	$0.58 \pm 0.02$	$0.27 \pm 0.07$	$0.21 \pm 0.09$

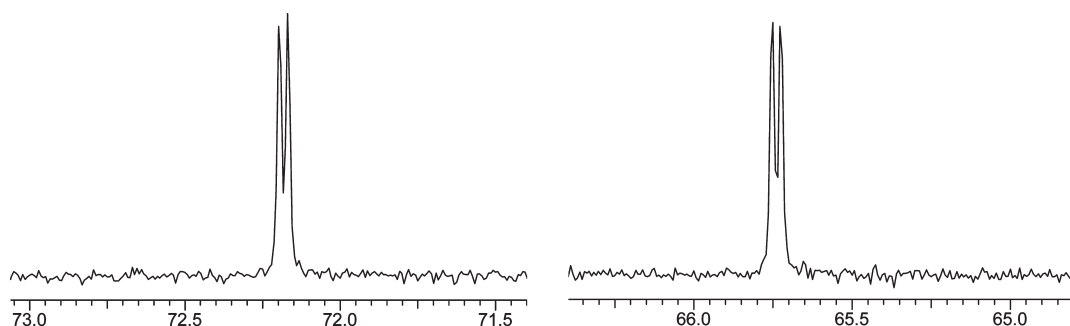
<sup>a</sup>  $X_{\text{reg}}$  = average value calculated from the relative intensities of the C=O, OCH and  $\text{OCH}_2$  resonances.<sup>21</sup>



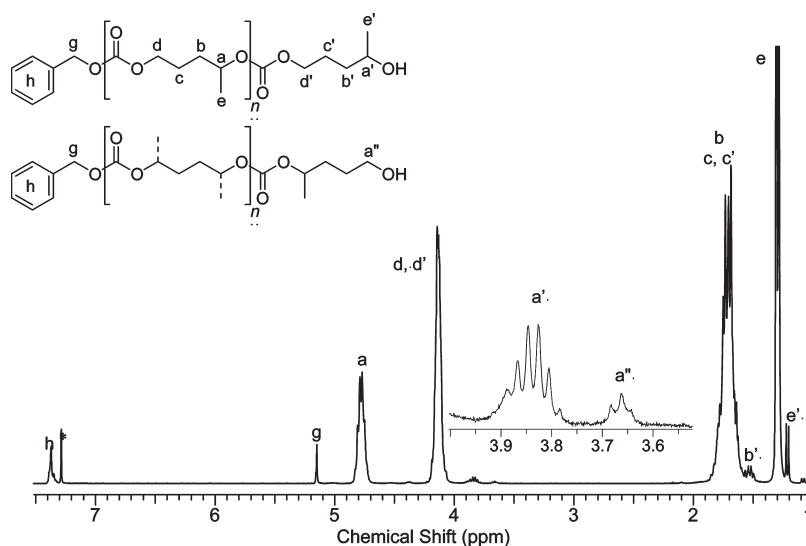
OCH<sub>2</sub> groups also appeared each as two equally intense resonances ( $\delta$  72.13 and 72.10,  $\delta$  65.69 and 65.66 ppm, respectively) (Figure 4). As explained above, these data indicate that the ROP of  $\beta$ -Me7CC always proceeded in a perfectly statistical fashion (i.e.,  $X_{\text{reg}} = 0$ ). The absence of regioselectivity in the ROP of  $\beta$ -Me7CC can be accounted for by the  $\beta$ -position of the methyl group. As opposed to  $\alpha$ -Me7CC that has an  $\alpha$ -methyl substituent, that is, a methyl closer to the carbonate function, and for which  $X_{\text{reg}}$  values



**Figure 3.** Detail of the carbonyl region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ , 20 °C) of a BnO-[poly( $\beta$ -Me7CC)]-H sample prepared from the  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$  system (Table 2, entry 4) ( $X_{\text{reg}} = 0$ ).



**Figure 4.** Details of the  $\text{CH}_3\text{CHO}$  and  $\text{OCH}_2$  regions of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ , 20 °C) of a BnO-[poly( $\beta$ -Me7CC)]-H sample prepared from the  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$  system (Table 2, entry 4) ( $X_{\text{reg}} = 0$ ).

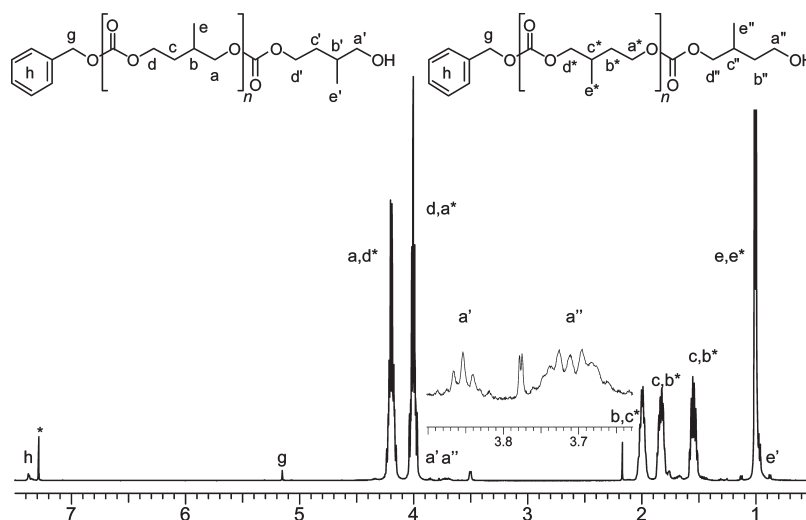


**Figure 5.**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ , 20 °C) of a BnO-[poly( $\alpha$ -Me7CC)]-H sample prepared from the  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$  system (Table 1, entry 10) showing assignments of main-chain and terminal groups (\* refers to the residual  $\text{CHCl}_3$  resonance).

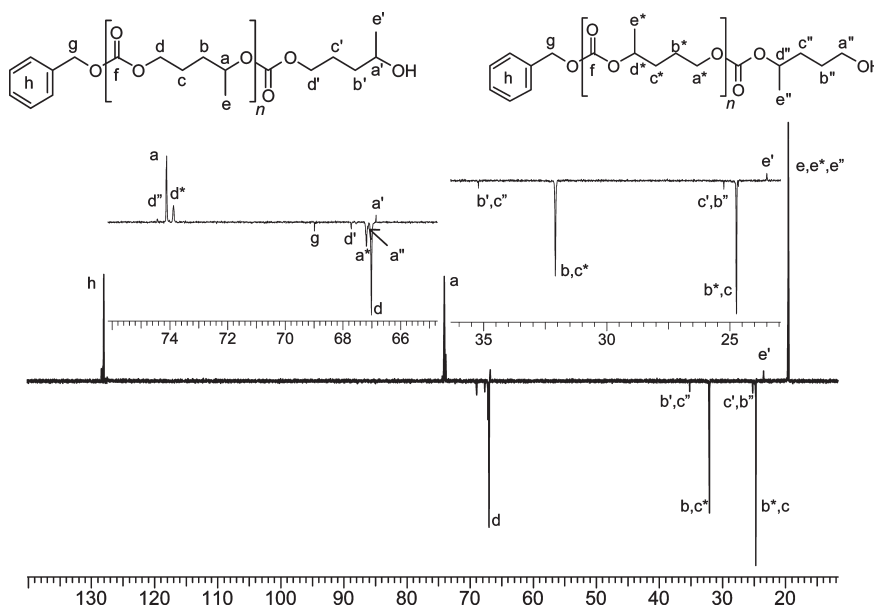
range up to 0.71, the remote position of the methyl substituent in  $\beta$ -Me7CC most likely does not allow the catalyst/initiator to discriminate between the two  $\text{O}-\text{C}(\text{O})\text{O}$  bonds.

**Nature of the Terminal Monomer Units and End-Groups.** The nature of the terminal monomer units and end-groups in poly( $\alpha$ -Me7CC) and poly( $\beta$ -Me7CC) was carefully investigated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and MALDI-ToF mass spectrometry on low molar mass polymers (typical theoretical degrees of polymerization  $\approx 20$ ). Both benzyloxy and isopropoxy-terminated polymers were studied to facilitate NMR and MALDI-ToF-MS investigations.

The  $^1\text{H}$  NMR spectra of regioregular ( $X_{\text{reg}} = \text{ca. } 0.7$ ) poly( $\alpha$ -Me7CC) samples prepared in the presence of  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$  combined with BnOH or  $i\text{PrOH}$ , respectively, are depicted in Figures 5, S5, and S6, respectively. In both cases, the terminal benzyloxy or isopropoxy carbonate end-groups were evidenced by a single set of low intensity resonances at  $\delta$  7.40 (m) and 5.15 (s) ppm for  $\text{C}_6\text{H}_5\text{CH}_2\text{O}$  [labeled h and g, respectively] and  $\delta$  4.85 (hept) ppm for  $(\text{CH}_3)_2\text{CHO}$  [labeled g] (the  $\text{CH}_3$   $i\text{Pr}$  [labeled h] resonances overlapped with those of the main-chain  $\text{CH}_3$  groups). In addition, these NMR spectra featured two well-resolved signals at  $\delta$  3.82 and 3.65 ppm, which can be assigned to the other chain termini, that is  $\text{CH}(\text{CH}_3)\text{OH}$  (major) and  $\text{CH}_2\text{CH}_2\text{OH}$  (minor),<sup>26</sup> respectively [labeled a' and a'', respectively]. Close examination of the spectra also showed the resonances for the methine adjacent methylene and methyl groups in the  $\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$  terminal group [a multiplet and a doublet, labeled b' and e', respectively]. All



**Figure 6.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ) of a  $\text{BnO}$ -[poly( $\beta$ -Me7CC)]-H sample prepared from the  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$  system (Table 2, entry 4) (\* refers to the residual  $\text{CHCl}_3$  resonance).



**Figure 7.**  $^{13}\text{C}$  DEPT (100 MHz,  $\text{C}_6\text{D}_6$ , 20  $^\circ\text{C}$ , bottom) NMR spectrum of a  $\text{BnO}$ -[poly( $\alpha$ -Me7CC)]-H sample prepared from the  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$  system (Table 1, entry 10).

these assignments, especially those of the  $\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$  terminal group, were confirmed by  $^1\text{H}$  homodecoupling (Figure S6, Supporting Information) and  $^{13}\text{C}$ - $^1\text{H}$  HMQC NMR experiments.

Similarly,  $^1\text{H}$  NMR signals of chain ends of regioirregular ( $X_{\text{reg}} = 0$ ) poly( $\beta$ -Me7CC) samples, prepared likewise from  $[(\text{BDI}^{\text{iPr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$  combined with  $\text{BnOH}$  or  $i\text{PrOH}$ , exhibited analogous chain ends. Typical resonances for the benzyloxy groups ( $\delta$  7.38 (m) and 5.17 (s) ppm for  $\text{C}_6\text{H}_5\text{CH}_2\text{O}$ , labeled **h** and **g**, respectively) were clearly observed. In addition, the resonances corresponding to the other chain termini ( $(\text{CH}_3)\text{CHCH}_2\text{OH}$  at  $\delta$  3.84 ppm and  $\text{CH}_2\text{CH}_2\text{OH}$  at  $\delta$  3.71 ppm [labeled **a'** and **a''**, respectively]) showed up as well-resolved resonances of equal intensity (Figure 6).

The  $^{13}\text{C}$  DEPT NMR spectra of poly( $\alpha$ -Me7CC) samples confirmed the previous assignments of the polymer chain termini (Figure 7). In addition to the most intense resonances that reflect the regioselectivity of the polymer main chain (vide supra), a series of lower intensity resonances was observed that could be assigned to the benzyloxy moiety ( $\delta$  68.9 ppm) and to the

different terminal monomer units:  $\text{O}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{OH}$  ( $\delta$  66.8 ppm) and  $\text{OCH}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{OH}$  ( $\delta$  67.6 ppm) (labeled **a'** and **d'**, respectively), and  $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  ( $\delta$  67.0 ppm) and  $\text{OCH}(\text{CH}_3)(\text{CH}_2)_3\text{OH}$  ( $\delta$  74.4 ppm) (labeled **a''** and **d''**, respectively) (Figure 7). Another characteristic trend that supports this assignment is the downfield shift between the main chain and terminal resonance for the  $\text{CH}_3$  groups ( $\delta(\text{e})$  19.6 vs  $\delta(\text{e}')$  23.4 ppm) and the adjacent methylene group ( $\delta(\text{b})$  32.0 vs  $\delta(\text{b}')$  35.1 ppm), which reflects replacement of an ester by a hydroxyl group, respectively.

Similarly, in the  $^{13}\text{C}$  NMR spectra of poly( $\beta$ -Me7CC), the regions at  $\delta$  60–75 and 35–25 ppm contained several low intensity resonances assignable to methyl, methylene, and methine  $\text{OC}(=\text{O})\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$  and  $\text{OC}(=\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$  groups in terminal units based on similar DEPT investigations (Figures S8, S9, S10, Supporting Information). This indicates also cleavage of both oxygen-acyl  $\text{O}-\text{C}(\text{O})\text{O}$  bonds.<sup>27</sup>

Overall, these  $^1\text{H}$  and  $^{13}\text{C}$  NMR data strongly suggest that  $\alpha$ -Me7CC is preferentially ring-opened at the most hindered

**Table 5.** Thermal Properties of poly( $\alpha$ - or  $\beta$ -Me7CC) Prepared from Various Catalytic Systems As Determined by DSC

polycarbonate	entry	catalyst	$\overline{M}_{n,theo}$ (g·mol <sup>-1</sup> )	$T_g$ (°C)
poly( $\alpha$ -Me7CC)	Table 1, entry 2	Al(OTf) <sub>3</sub>	11050	-18
	Table 1, entry 6	(BDI <sup>IPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	22750	-14
	Table 1, entry 7	(BDI <sup>IPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	24300	-14
	Table 1, entry 19	(ONOO <sup>tBu</sup> )Y(N(SiHMe <sub>2</sub> ) <sub>2</sub> )(THF)	25350	-11
poly( $\beta$ -Me7CC)	Table 2, entry 3	Al(OTf) <sub>3</sub>	13100	28
	Table 2, entry 4	(BDI <sup>IPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	13100	30
	Table 2, entry 15	(BDI <sup>IPr</sup> )Zn(N(SiMe <sub>3</sub> ) <sub>2</sub> )	56650	36

oxygen-acyl O—C(O)O bond, that is, close to the  $\alpha$ -Me substituent (A, Scheme 5). On the other hand, the simpler <sup>13</sup>C NMR spectra of poly( $\beta$ -Me7CC) samples are rather indicative of a lack of regioselectivity in the ROP of  $\beta$ -Me7CC.

MALDI-ToF-MS spectra of poly( $\alpha$ -Me7CC) and poly( $\beta$ -Me7CC) samples prepared from [catalyst]/BnOH systems (catalyst = [(BDI<sup>IPr</sup>)Zn(N(SiMe<sub>3</sub>)<sub>2</sub>)] or Al(OTf)<sub>3</sub>) featured one major distribution of peaks assignable to BnO-[poly( $\alpha$ - or  $\beta$ -Me7CC)]-H molecules cationized by Na<sup>+</sup> ions (Figure S11, Supporting Information). Because the molar mass of [BnOH + Na<sup>+</sup>] (131 g·mol<sup>-1</sup>) is incidentally close to that of the repeat unit ( $M_{Me7CC} = 130$  g·mol<sup>-1</sup>), another series of polymers were prepared from the [(BDI<sup>IPr</sup>)Zn(N(SiMe<sub>3</sub>)<sub>2</sub>)]/*i*PrOH system so that the molar mass of [*i*PrOH + Na<sup>+</sup>] (83 g·mol<sup>-1</sup>) is then well-differentiated from that of the repeating unit. The MS spectra then displayed a major series of peaks unambiguously assigned to *i*PrO-[poly( $\alpha$ - or  $\beta$ -Me7CC)]-H molecules cationized by Na<sup>+</sup> ions (Figure S12, Supporting Information). The other minor population observed in this case could not be assigned to specific end-groups or macromolecules (cyclic polymers, decarboxylated polymers...). It is yet unestablished whether this second set of macromolecules reflects the formation of different macromolecules during the polymerization process or during the ionization process. In all cases, the  $\overline{M}_n$  values observed by MALDI-ToF-MS were in good agreement with those determined by NMR.

The thermal properties of the poly( $\alpha$ - and  $\beta$ -Me7CC) prepared were investigated by DSC. All the DSC traces displayed a single glass transition at low temperature. The  $T_g$  values for poly( $\alpha$ -Me7CC) ranged from -18 to -11 °C, with the lower  $T_g$  values observed for the less regioregular polymers. The transition temperature of the poly( $\beta$ -Me7CC)s varied from +28 to +36 °C for poly( $\beta$ -Me7CC) upon increasing the molar mass of the polycarbonate (Table 5). No melting temperature transition was detected with any of these the poly( $\alpha$ - and  $\beta$ -Me7CC)s highlighting their amorphous feature.

## Conclusion

$\alpha$ -Me7CC and the newly synthesized  $\beta$ -Me7CC have been prepared in high yield from the corresponding  $\alpha,\omega$ -diols issued from green renewable acids. Subsequent ("immortal") ring-opening polymerization using various (organo)metallic and organic catalysts afforded the corresponding polycarbonates, poly( $\alpha$ - and  $\beta$ -Me7CC)s, with quite good control and activities. Detailed NMR and MALDI-ToF-MS analyses revealed that  $\alpha$ -Me7CC was preferentially ring-opened at the most hindered oxygen-acyl O—C(O)O bond, with greater regioselectivity obtained from the zinc and yttrium based catalysts. On the other hand, the  $\beta$ -Me7CC did not exhibit any favored cleavage, no matter which catalytic system was used. Such a lack of regioselectivity during the ROP of  $\beta$ -Me7CC most likely originates from the more remote methyl-substitution of the carbonate.

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**Supporting Information Available:** Additional NMR spectra of monomers and polymers, and MALDI-ToF-MS spectra of polymers. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Bhanage, B. M.; Fujita, S.-I.; Ikushima, Y.; Arai, M. *Green Chem.* **2003**, *5*, 429–432. (b) Ariga, T.; Takata, T.; Endo, T. *Macromolecules* **1997**, *30*, 737. (c) Carothers, W. H.; Van Natta, F. J. *J. Am. Chem. Soc.* **1930**, *52*, 314–326. (d) Zhou, C.-H.; Beltrami, J. N.; Fan, Y.-X.; Lu, G. Q. *Chem. Soc. Rev.* **2008**, *37*, 527–549. (e) Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008**, *10*, 13–30.
- (2) Werpy, T.; Petersen, G., Principal Investigators; Aden, A.; Bozell, J. (NREL); Holladay, J.; White, J. (PNNL); Manheim, A. (DOE-HQ), Contributing Authors; *Results of Screening Potential Candidates from Sugars and Synthesis Gas*; U. S. Department of Energy, Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL): Washington, DC, **2004**; Vol. 1. (b) Bozell, J. J.; Petersen, G. R. *Green Chem.* **2010**, *12*, 539–554.
- (3) Rokicki, G. *Prog. Polym. Sci.* **2000**, *25*, 259–342.
- (4) Matsuo, J.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **2000**, *201*, 585–596.
- (5) (a) Wu, R.; Al-Azemi, T. F.; Bisht, K. S. *Biomacromolecules* **2008**, *9*, 2921–2928. (b) Wu, R.; Al-Azemi, T. F.; Bisht, K. S. *Macromolecules* **2009**, *42*, 2401–2410.
- (6) (a) Ochiai, B.; Yoshii, K.; Nagai, D.; Endo, T. *Macromolecules* **2004**, *37*, 2329–2331. (b) Matsuo, J.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A* **1997**, *35*, 1375–1380. (c) Takeuchi, D.; Aida, T.; Endo, T. *Macromol. Chem. Phys.* **2000**, *201*, 2267–2275. (d) Takeuchi, D.; Aida, T.; Endo, T. *Macromol. Rapid Commun.* **1999**, *20*, 182–184. (e) Mikayama, M.; Mitani, M.; Yamada, T.; Mukaiyama, T. *Macromol. Rapid Commun.* **1996**, *17*, 865–870.
- (7) (a) Matsuo, J.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1998**, *199*, 97–102. (b) Shibasaki, Y.; Sanada, H.; Yokoi, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 4316–4320. (c) Shibasaki, Y.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 3590–3593. (d) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900–904. (e) Shibasaki, Y.; Sanda, F.; Endo, T. *Macromol. Rapid Commun.* **2000**, *21*, 489–492. (f) Matsuo, J.; Nakano, S.; Sanda, F.; Endo, T. *J. Polym. Sci.* **1998**, *36*, 2463–2471. (g) Morikawa, H.; Sudo, A.; Nishida, H.; Endo, T. *Macromol. Chem. Phys.* **2005**, *206*, 592–5999. (h) Nagai, D.; Yokota, K.; Ogawa, T.; Ochiai, B.; Endo, T. *J. Polym. Sci.* **2007**, *46*, 733–739.
- (8) (a) Takata, T.; Matsuo, H.; Endo, T. *Chem. Lett.* **1991**, 2091–2094. (b) Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci.* **2001**, *39*, 4091–4100.
- (9) Anderson, E. A.; Davidson, J. E. P.; Harrison, J. R.; O'Sullivan, P. T.; Burton, J. W.; Collins, I.; Holmes, A. B. *Tetrahedron* **2002**, *58*, 1943–1971.
- (10) (a) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Chem.—Eur. J.* **2008**, *14*, 8772–8775. (b) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Adv. Synt. Cat.* **2009**, *351*, 1312–1324. (c) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Macromol. Rapid Commun.* **2009**, *30*, 2128–2135. (d) Carpentier, J.-F.; Guillaume, S.; Helou, M.; Miserque, O.; Sarazin, Y. *Eur. Pat. Appl.* 08-290187-7; (e) Carpentier, J.-F.; Guillaume, S.; Guillaume, S.; Helou, M.; Poirier, V.; Sarazin, Y. *J. Chem. Soc., Dalton Trans.* **2010**, DOI: 10.1039/

- c001226b; (f) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Chem. Cat. Chem.* **2010**, *2*, 306–313. (g) Carpentier, J.-F.; Guillaume, S.; Helou, M.; Miserque, O. Eur. Pat. Appl. 08-290749-4; (h) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Chem.—Eur. J.*, in press; (i) Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S.; Helou, M. Eur. Pat. Appl. 09-290655-1.
- (11) (a) Burk, R. M.; Roof, M. B. *Tetrahedron Lett.* **1993**, *34*, 395–398. (b) Wu, R.; Al-Azemi, T. F.; Bisht, K. S. *Biomacromolecules* **2008**, *9*, 2921–2928.
- (12) (a) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238. (b) Rieth, L. R.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 15239–15248.
- (13) (a) Cai, C.-X.; Toupet, L.; Carpentier, J.-F. *J. Organomet. Chem.* **2003**, *683*, 131–136. (b) Cai, C.-X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J.-F. *Chem. Commun.* **2004**, 330–331. (c) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169–179. (d) Amgoune, A.; Thomas, C. M.; Carpentier, J.-F. *Macromol. Rapid Commun.* **2007**, *28*, 693–697.
- (14) (a) Amgoune, A.; Thomas, C. M.; Ilinca, S.; Roisnel, T.; Carpentier, J.-F. *Angew. Chem., Int. Ed.* **2006**, *45*, 2782–2784. (b) *Angew. Chem.* **2006**, *118*, 2848–2850; (c) Ajellal, N.; Bouyahyi, M.; Amgoune, A.; Thomas, C. M.; Bondon, A.; Pillin, I.; Grohens, Y.; Carpentier, J.-F. *Macromolecules* **2009**, *42*, 987–993.
- (15) For a recent review on Organocatalytic Ring-Opening Polymerization, see Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093–2107.
- (16) (a) Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301–312. (b) Jenck, J. F.; Agterberg, F.; Droscher, M. J. *Green Chem.* **2004**, *6*, 544–556.
- (17) Edlund, U.; Albertsson, A.-C. *Adv. Polym. Sci.* **2002**, *157*, 68–112.
- (18) A similar “cut off” phenomenon has been reported for poly(3-hydroxybutyrate); see refs 12b and 14.
- (19) In the absence of added benzyl alcohol, ROP reactions mediated by such yttrium-amido compounds are initiated via nucleophilic attack of the bis(silyl)amido group; see refs 13 and 14.
- (20) Kühling, S.; Keul, H.; Höcker, H.; Buysch, H. J.; Schön, N.; Leitz, E. *Macromolecules* **1991**, *24*, 4229–4235.
- (21) The degree of regioregularity was calculated by the formula  $X_{\text{reg}} = 1 - (\text{relative intensity of the related regioirregular resonances})$ , the resonance for regioregular enchainment being setup to 1 (see Table 5).
- (22) The exact integration of the three resonances in the carbonyl region was not mentioned in the original manuscript.<sup>4</sup> The reported <sup>13</sup>C NMR spectrum was digitalized and processed, giving a 1:4:1 ratio.
- (23) A partial splitting of the low field resonance ( $\delta$  155.14 ppm) is also observed in some spectra.
- (24) No comparison of the absolute intensity of each of these individual resonances (CO, OCH, OCH<sub>2</sub>) can be done due to the obviously different relaxation times of these inherently different groups.
- (25) Typical  $P_r$  values achieved in the ROP of racemic lactide:  $P_r = 0.90$  for [(BDI<sup>IPr</sup>)Zn(O<sup>i</sup>Pr)]<sub>2</sub> (20 °C in CH<sub>2</sub>Cl<sub>2</sub>; see ref 12a),  $P_r = 0.80$  for [(ONOO<sup>tBu</sup>)Y(O<sup>i</sup>Pr)] (20 °C in THF, see refs 13b, 13c), while simple metal triflate/ROH combinations do not lead to noticeable heterotactic enrichment ( $P_r = \text{ca. } 0.50$ ). Formation of such stereoregular PLAs results from alternated incorporation of L- and D-lactide (as expressed by the probability of racemic linkage,  $P_r$ ) and requires chain-end control, which is known to depend crucially on the bulkiness of substituents installed on ancillary ligands in the metal initiators.<sup>12,13</sup> Yet, the pertinence of this parallel between the regioselective ROP of  $\alpha$ -Me7CC and the stereoselective ROP of racemic lactide remains limited.
- (26) The integral ratio for the resonances of the terminal groups CH-(CH<sub>3</sub>)OH and CH<sub>2</sub>CH<sub>2</sub>OH of poly( $\alpha$ -Me7CC) samples ranges from 1:0.70 to 1:0.25.
- (27) For a poly( $\beta$ -Me7CC) sample prepared from the [(BDI<sup>IPr</sup>)Zn(N-(SiMe<sub>3</sub>)<sub>2</sub>)]/BnOH system, an additional resonance for the PhCH<sub>2</sub>O moiety was also observed in the same region ( $\delta$  70.6 ppm).