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Functionalized polycarbonates from dihydroxyacetone: insights into the immortal ring-opening polymerization of 2,2-dimethoxytrimethylene carbonate†

Marion Helou, Jean-Michel Brusson, Jean-François Carpentier and Sophie M. Guillaume*

Received 8th September 2011, Accepted 29th September 2011

DOI: 10.1039/c1py00405k

Functionalized polycarbonates derived from 2,2-dimethoxytrimethylene carbonate (TMC(OMe)₂) have been prepared with controlled molecular features by immortal ring-opening polymerization, under mild conditions (bulk, 60–90 °C), using various (metallo)organic/alcohol (diol) binary catalyst systems: the β -diiminate zinc complex [(BDI^{IPr})Zn(N(SiMe₃)₂)] (BDI = CH(CMeNC₆H₃-2,6-*i*Pr₂)₂), the aluminium triflate, or the organic bases 4-*N,N*-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), as catalyst precursors, combined with benzyl alcohol or 1,3-propanediol acting both as a co-initiator and a chain transfer agent. For the first time, well-defined α -hydroxy- ω -alkoxyester and α,ω -dihydroxy telechelic acetal-functionalized homopolycarbonates were thus prepared with molar mass up to 70 200 g mol⁻¹. These polymers were characterized at the molecular (NMR, SEC), thermal (DSC, TGA) and mechanical levels, and compared to conventional PTMC. P(TMC(OMe)₂) is a rigid and brittle polymer material ($E = 3190 \pm 70$ MPa, $\epsilon_r = 9 \pm 1\%$).

Introduction

Synthetic biodegradable polycarbonates are receiving a topical burst of interest, especially in regard to their great versatility imparted by their tunable physico-chemical and notably thermo-mechanical properties, which make them highly valuable, non-toxic polymer materials. Polycarbonates are targeted in medical and pharmaceutical industries as biocompatible drug delivery systems, tissue repair or tissue regeneration biomaterials. Agricultural, microelectronics and packaging applications are also exploiting and benefiting from their biodegradability, aiming at diversified purposes ranging from specialties to commodities.¹

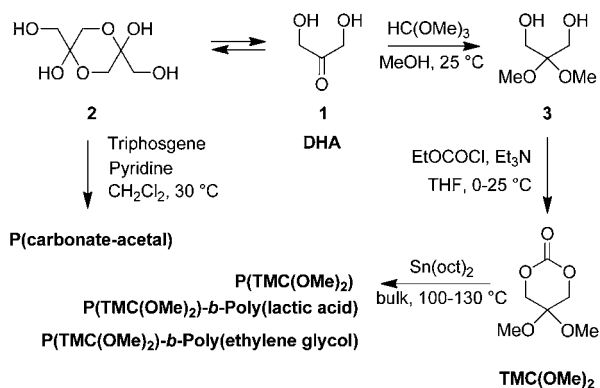
Polycarbonates bearing pendant functionalities along the backbone chain afford the advantage of tailoring the polymer physico-chemical properties to specific needs, thereby broadening and improving their performance characteristics. These can be synthesized either upon direct polymerization of the carefully designed functionalized monomer or upon post-polymerization chemical modification, the former direct polymerization approach being more attractive. Parameters such as solubility, hydrophilicity/hydrophobicity balance, crystallinity, degradation/resorption, permeability, and thermal and mechanical properties can thus be finely modulated. In addition, the side-chain functionalities may serve as further chemical modification sites or as anchoring spots for covalent attachment of e.g. pro-drugs.^{1,2}

In order to address environmental issues, polymers nowadays have to be developed within “green” and sustainable considerations through bio-friendly synthetic approaches. In this regard, we have been (i) valorizing the biomass and (ii) extending ring-opening polymerization (ROP) processes of cyclic esters and carbonates to efficient atom-economic “immortal” procedures, for the controlled elaboration of polyesters/polycarbonates.³ Bio-resourced itaconic or levulinic acids⁴ as well as glycerol⁵ allowed the preparation of seven- and six-membered cyclic carbonates, respectively. Polycarbonates, especially poly(trimethylene carbonate)s (PTMCs), along with other polyesters such as poly(3-hydroxybutyrate)s, have been prepared upon “immortal” ROP (iROP) using several binary catalyst systems based on an alcohol and a metal- or organo-catalyst.^{3–6} We have now extended our investigations to 2,2-dimethoxytrimethylene carbonate (2,2-dimethoxypropane-1,3-diol carbonate, hereafter referred to as TMC(OMe)₂), which is derived from naturally occurring 1,3-dihydroxyacetone (DHA) (Scheme 1).^{5c}

DHA, an intermediate in the glucose metabolism derived from plant sources (sugar beets and sugar cane) and obtained directly by oxidation of glycerol, is biologically accepted by the human body and then most widely used as an active ingredient in sunless tanning cosmetics. The solution equilibrium of monomeric DHA (**1**) with its hemiacetal dimer (**2**) has been locked in the dimer form, allowing the preparation of poly(carbonate acetal)s (Scheme 1).⁷ Alternatively, DHA locked into its monomeric form through conversion of its C2 carbonyl into a dimethoxy acetal **3**, led to the formation of TMC(OMe)₂.⁸ Polycarbonates obtained from the bulk ROP of TMC(OMe)₂ at 100 °C using stannous octanoate (Sn(oct)₂; no initiator

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† Electronic supplementary information (ESI) available: Additional NMR and MALDI-ToF mass spectra and thermal properties of the monomer and polymers. See DOI: 10.1039/c1py00405k



Scheme 1 Reported syntheses of (co)polymers derived from TMC(OMe)₂.^{7,8}

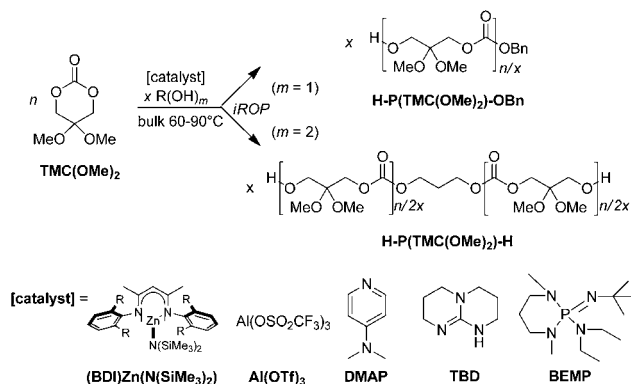
specifically mentioned) have thus been scarcely described, yet quite briefly and with only three homopolymers of molar mass up to 37 500 g mol⁻¹ ($\bar{M}_w/\bar{M}_n \leq 1.5$).⁸ Indeed, the aim of these studies was rather the deprotection of the dimethyl acetal group toward the formation of poly(2-oxypropylene carbonate) to ultimately foster the polymer's surface functionalization through reductive amination of the C2 carbonyl, a nucleophilic addition at the carbonyl without the use of condensation reagents (Scheme 1).^{8a} Diblock copolymers from DHA and ethylene glycol or lactide have also been reported, yet rarely, for amphiphilic nanoparticulate drug delivery vehicles' outcomes (Scheme 1).^{8b,c}

In this work, we report the ROP of TMC(OMe)₂ under "immortal" conditions using various binary catalyst systems based on a metal- or organo-catalyst and an alcohol/diol acting as a co-initiator and a chain transfer agent (Scheme 2).⁹ The catalytic systems were selected among the most active ones in the ROP of the parent trimethylene carbonate (TMC) monomer.³⁻⁵ The polycarbonates were then molecularly, thermally and mechanically characterized.

Experimental section

Materials

All manipulations involving air-sensitive compounds (that is those carried out with the zinc complex) were performed under inert atmosphere (argon, <3 ppm of O₂) using standard Schlenk, vacuum line and glovebox techniques. Solvents were thoroughly dried and



Scheme 2 Schematic representation of the [catalyst/alcohol]-mediated iROP of TMC(OMe)₂: synthesis of P(TMC(OMe)₂).

deoxygenated by standard methods and distilled before use. CDCl₃ was dried over a mixture of 3 and 4 Å molecular sieves. Benzyl alcohol (Acros) was distilled over Mg turnings under argon atmosphere and kept over activated 4 Å molecular sieves. 1,3-Propanediol (Acros) was dried over activated 4 Å molecular sieves. 2,2-Dimethoxypropylene carbonate (TMC(OMe)₂) was prepared according to literature methods^{8a,b} and isolated in 53% yield after 3 recrystallizations in diethyl ether [¹H and ¹³C NMR: δ_{OCH_3} 3.34 ppm, 49.7 ppm; $\delta_{\text{CH}_2\text{OC(O)O}}$ 4.30 ppm, 70.2 ppm, Fig. S1 and S2†]. [(BDI)^{Br}]Zn (N(SiMe₃)₂) was synthesized following the literature procedure.¹⁰ All other reagents were used as received (Aldrich).

Instrumentation and measurements

¹H (300 and 200 MHz) and ¹³C (75 and 50 MHz) NMR spectra were recorded in CDCl₃ on Bruker Avance AM 300 and DPX 200 spectrometers at 23 °C. Chemical shifts (δ) are reported in ppm and were referenced internally relative to tetramethylsilane (δ 0 ppm) using the residual ¹H and ¹³C solvent resonance.

Average molar mass (\bar{M}_{SEC}) and molar mass distribution (\bar{M}_w/\bar{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 (\bar{M}_{SEC} values are uncorrected for a 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-[P(TMC(OMe)₂)]-OBn samples were determined by ¹H NMR analysis, from the relative intensity of the signals of either the methylene hydrogens (C(OMe)₂CH₂OC(O), δ 4.23 ppm) or the methyl hydrogens (C(OMe)₂CH₂OC(O), δ 3.28 ppm) of the P(TMC(OMe)₂) main chain relative to the methylene hydrogens of the (CO)OCH₂C₆H₅ (δ 5.19 ppm) or of the C(OMe)₂CH₂OH (δ 3.82 ppm) chain-end. The number-average molar mass values thus obtained by ¹H NMR (\bar{M}_{NMR}) were in close agreement with the ones calculated, as reported in Table 1.

Monomer conversions were calculated from ¹H NMR spectra of the crude reaction mixtures, from the integration (Int.) ratio Int._P(TMC(OMe)₂)/[Int._P(TMC(OMe)₂) + Int._{TMC(OMe)2}], using either the methylene hydrogens (C(OMe)₂CH₂OC(O)) or the methyl hydrogens of the dimethyl acetal of P(TMC(OMe)₂) at δ 4.23 ppm and 3.28 ppm, and of TMC(OMe)₂ at δ 4.30 and 3.34 ppm, respectively.

MALDI-ToF mass spectra were recorded with an AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N₂ laser source (337 nm, 4 ns pulse width) and a 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⁻¹), using aluminium capsules (typically 10 mg of polymer). The thermograms

Table 1 Bulk iROP of TMC(OMe)₂ initiated by various catalytic systems

Entry	Catalyst	Alcohol	[TMC(OMe) ₂] ₀ / [catalyst] ₀ / [alcohol] ₀	Temp/ °C	Reaction time ^a /min	Conv ^b (%)	$\bar{M}_{n,theo}^c$ / g mol ⁻¹	$\bar{M}_{n,NMR}^d$ / g mol ⁻¹	$\bar{M}_{n,SEC}^e$ / g mol ⁻¹	\bar{M}_w/\bar{M}_n^f	TOF ^g / h ⁻¹
1	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 5	60	90	96	15 660	nd	12 450	1.28	320
2	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 10	60	60	45	3750	3570	3000	1.18	225
3	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 1	90	120	92	74 630	nd	70 200	1.79	230
4	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 2	90	60	98	39 800	nd	38 800	1.36	490
5	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 5	90	60	93	15 200	nd	17 000	1.25	465
6	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 15	90	90	95	5240	6120	7100	1.22	317
7	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 25	90	105	89	3000	2980	3130	1.16	254
8	(BDI)Zn(NTMS) ₂	BnOH	500 : 1 : 25	90	120	95	3190	3250	4500	1.12	237
9	Al(OTf) ₃	BnOH	500 : 1 : 5	60	330	28	4650	nd	nd	nd	25
10	Al(OTf) ₃	BnOH	500 : 1 : 5	90	330	96	15 660	nd	10 600	1.18	87
11	Al(OTf) ₃	BnOH	500 : 1 : 5	110	330	0	—	—	—	—	—
12	DMAP	BnOH	500 : 1 : 5	90	330	45	7400	6980	6800	1.23	41
13	TBD	BnOH	500 : 1 : 5	90	180	99	16 150	nd	14 100	1.71	165
14	BEMP	BnOH	500 : 1 : 5	90	180	100	16 300	nd	14 300	1.53	167
15	(BDI)Zn(NTMS) ₂	PPD	500 : 1 : 5	90	3	96	15 630	nd	13 990	1.66	160
16	(BDI)Zn(NTMS) ₂	PPD	500 : 1 : 10	90	1.5	93	7610	5800	6500	1.61	310
17 (ref. 5e)	BEMP	PPD	500 : 1 : 5	90	180	100	16 280	nd	14 300	1.53	167

^a Reaction times were not necessarily optimized. ^b Monomer conversion determined by ¹H NMR spectroscopy. ^c Calculated from [TMC(OMe)₂]₀/[BnOH or PPD]₀ × monomer conversion × M_{TMC(OMe)₂} + M_{BnOH} or M_{PPD} with M_{TMC(OMe)₂} = 162 g mol⁻¹, M_{BnOH} = 108 g mol⁻¹, M_{PPD} = 76 g mol⁻¹. ^d Determined by ¹H 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 Non-optimized turnover frequency expressed in mol_{TMC(OMe)₂} mol_{catalyst}⁻¹ h⁻¹ and calculated over the whole polymerization time.

were recorded according to the following cycles: -40 °C to +180 °C at 10 °C min⁻¹; +180 °C to -40 °C at 10 °C min⁻¹. Thermal gravimetric analyses were performed on a TA Instruments SDT 2960.

Mechanical properties of the polymers were evaluated at Total Petrochemicals Research Center Feluy, Belgium, using compression molded sheets. These H-shaped samples (length × width × thickness = 17 × 4 × 0.05 mm) were prepared from a mini max molder of Custom Scientific Instruments Inc at 160 °C for P(TMC(OMe)₂), 220 °C for PTMC, using typically 100 mg of the polymer. Tensile tests were then carried out on seven samples at room temperature according to ASTM D 882 using a ZWICK (MEC 125/2) apparatus with a load cell 200 N at a cross-head speed of 10 mm min⁻¹. Strength and elongation at break values were calculated from the dynamic tensile diagrams. The sample specimen deformation was measured from the grip-to-grip separation, which initially was 10 mm.

Typical polymerization procedure

In a typical experiment (Table 1, entry 6), [(BDI)^{Pr}Zn(N(SiMe₃)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 TMC(OMe)₂ (500 equiv. vs. Zn, 0.500 g, 4.3 mmol) were charged in a Schlenk flask in the glovebox. The flask was then immersed in an oil bath preset at the desired temperature (60–90 °C) and the reaction mixture was stirred over the appropriate time (note that reaction times were not systematically optimized). The reaction was quenched by adding an excess of an acetic acid solution (ca. 1 mL of a 16.5 mmol L⁻¹ solution in toluene). The resulting mixture was concentrated under vacuum and the conversion determined by ¹H NMR analysis of the residue. The crude polymer was then dissolved in CH₂Cl₂ and purified upon precipitation in cold methanol, filtered and dried under vacuum. The final polymer was then analyzed by NMR and SEC, DSC and TGA.

Noteworthy, the polycarbonates' purification upon its selective precipitation in MeOH is a procedure that simultaneously allows elimination of catalytic residues within the filtrate. Thus, taken into account that the iROP procedure typically involves very low initial catalytic loading,³ the polymers are thereby recovered with only minor traces—if any—of catalytic residues.

Results and discussion

Binary catalytic systems that proved effective in the (i)ROP of the related unsubstituted TMC⁵ were evaluated in the (i)ROP of TMC(OMe)₂ towards the synthesis of the corresponding homopolycarbonates P(TMC(OMe)₂)_s. Thus the highly active β-diiminate

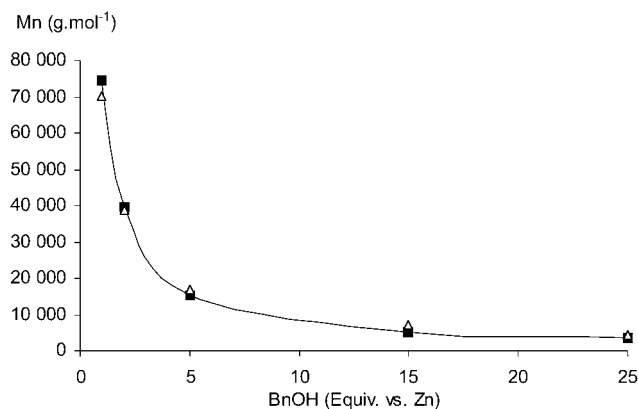


Fig. 1 Dependence of the molar mass \bar{M}_n of P(TMC(OMe)₂)_s synthesized at 90 °C on the benzyl alcohol content at [TMC(OMe)₂]₀/[(BDI)Zn[N(SiMe₃)₂]]₀ of 500 : 1. Δ, Experimental values determined by SEC; ■ theoretical values.

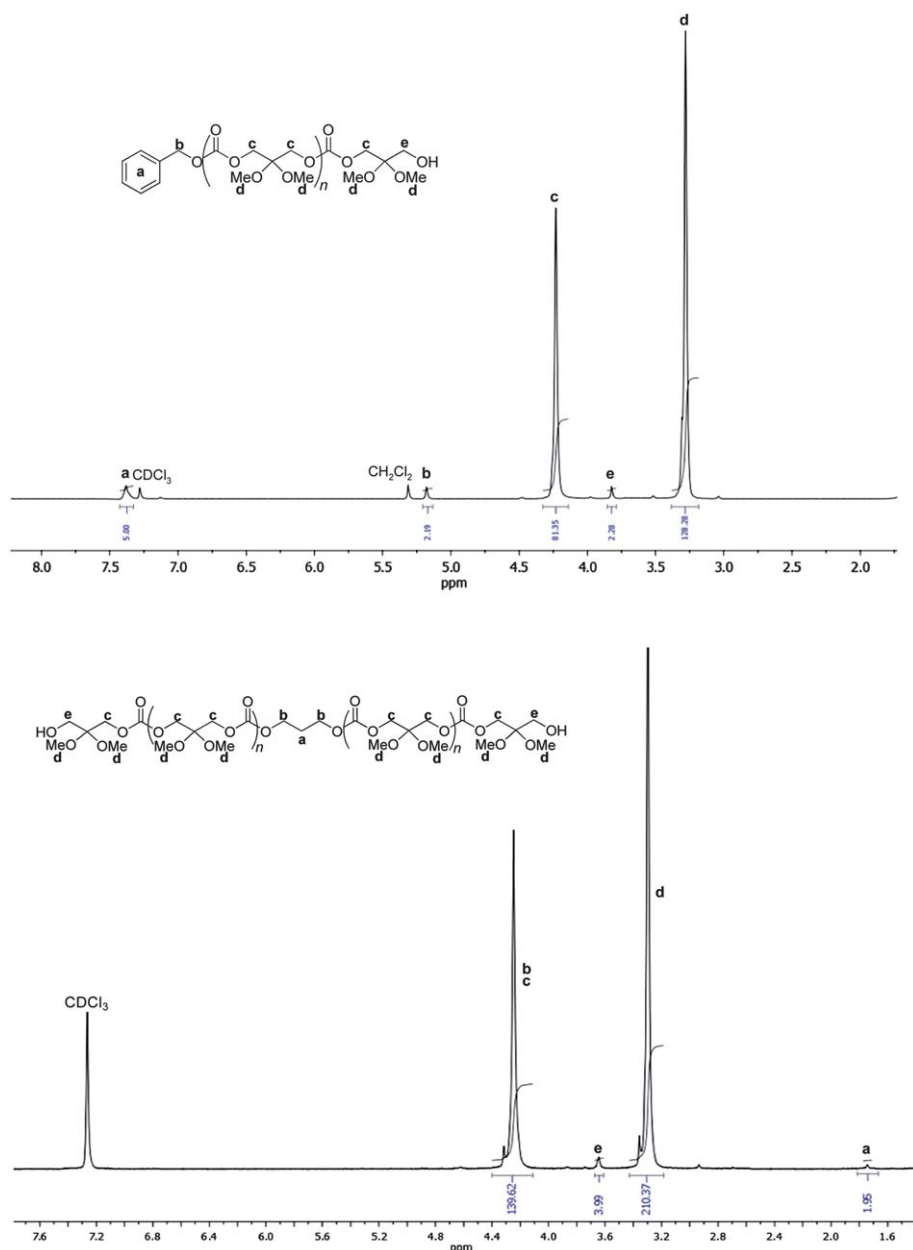


Fig. 2 ^1H NMR (300 MHz, CDCl_3 , 23°C) spectra of a H-P(TMC(OMe) $_2$)-OBn (top) and H-P(TMC(OMe) $_2$)-H (bottom) (Table 1, entries 2 and 16).

discrete zinc complex, $[(\text{BDI}^{\text{Pr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$ ($\text{BDI}^{\text{Pr}} = 2-((2,6\text{-diisopropylphenyl})\text{amido})-4-((2,6\text{-diisopropylphenyl})\text{-imino})-2\text{-pentene}$), the Lewis acidic triflate salt $\text{Al}(\text{OTf})_3$, and the organic bases, 4-*N,N*-dimethylaminopyridine (DMAP), 1.5.7-triazabicyclo-[4.4.0]dec-5-ene (guanidine, TBD) and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (phosphazene, BEMP), were successfully combined with a monoalcohol (benzyl alcohol, BnOH) or a diol (1,3-propanediol, PPD). The P(TMC(OMe) $_2$)s thus synthesized displayed various molar masses ranging from 3000 to 70 200 g mol^{-1} and showed a quite good degree of control over the molecular features. Selected results at a typical catalyst loading of 0.2 mol% ($[\text{TMC}(\text{OMe})_2]_0/[\text{catalyst}]_0 = 500 : 1$) are reported in Table 1.

Although the bulk 11 iROP of TMC(OMe) $_2$ was successfully carried out at 60°C , raising the polymerization temperature to 90°C

significantly improved the activity of both metallic catalytic systems, $[(\text{BDI}^{\text{Pr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]/\text{BnOH}$ and $\text{Al}(\text{OTf})_3/\text{BnOH}$ (Table 1, entries 1 vs. 5, 9 vs. 10). At this latter temperature, the molar mass values measured by NMR and SEC were in good agreement with the ones expected (as determined from the monomer-to-alcohol ratio and the conversion), whereas the molar mass distribution values generally remained quite narrow. An increase in the relative amount of alcohol/chain transfer agent led to proportionally lower molar mass polycarbonates, as depicted in Fig. 1, in agreement with a controlled iROP process. 3 This adequate compromised reaction temperature of 90°C is higher than the one suitable for the iROP of TMC with this system under similar operating conditions. Indeed, at 60°C , at $[\text{monomer}]_0/[(\text{BDI}^{\text{Pr}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]_0/[\text{BnOH}]_0 = 500 : 1 : 5$, complete TMC conversion was reached within 7 min ($\text{TOF}_{\text{TMC}} = 4240 \text{ h}^{-1}$), 3,5a,b whereas 90 min were required to achieve almost

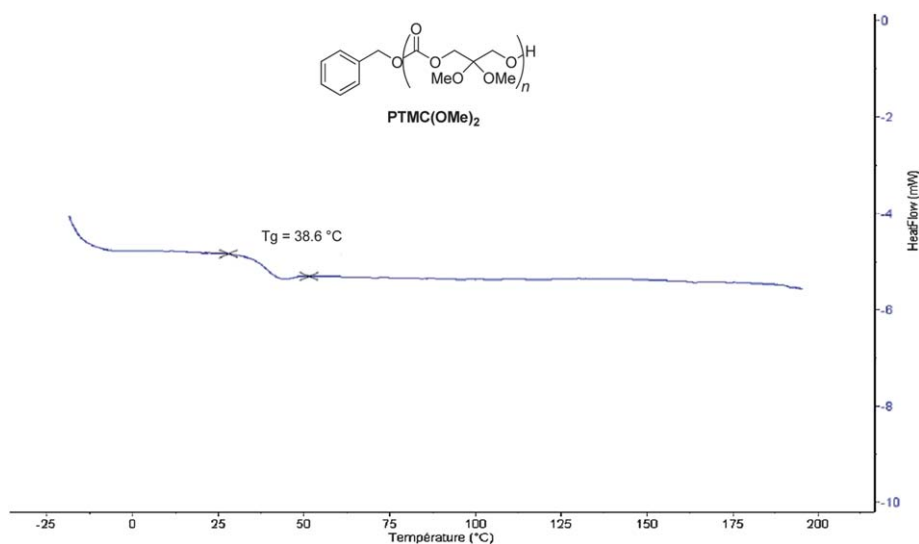


Fig. 3 DSC trace of a H-P(TMC(OMe)₂)-OBn ($\bar{M}_{n\text{SEC}} = 38\,800\text{ g mol}^{-1}$; Table 1, entry 4; $10\text{ }^{\circ}\text{C min}^{-1}$, He).

quantitative TMC(OMe)₂ conversion ($\text{TOF}_{\text{TMC(OMe)}_2} = 320\text{ h}^{-1}$; Table 1, entry 1).

Similarly, with the aluminium-based catalyst system, better activities were (more easily) obtained in the iROP of TMC than in that of TMC(OMe)₂. At $[\text{monomer}]_0/[\text{Al(OTf)}_3]_0/[\text{BnOH}]_0 = 500 : 1 : 5$, 480 TMC equiv. were polymerized at $110\text{ }^{\circ}\text{C}$ ($\text{TOF}_{\text{TMC}} = 480\text{ h}^{-1}$)^{3,5d} while in the iROP of TMC(OMe)₂, the highest—yet moderate—activity was observed at $90\text{ }^{\circ}\text{C}$ ($\text{TOF}_{\text{TMC(OMe)}_2} = 87\text{ h}^{-1}$; Table 1, entry 10). Raising the temperature to $110\text{ }^{\circ}\text{C}$ in the ROP of TMC(OMe)₂ with this catalyst system led to degradation of the polycarbonate upon cleavage of the acetal group (Table 1, entry 11), whereas this same aluminium catalytic system was revealed to be most effective at $150\text{ }^{\circ}\text{C}$ in the iROP of unsubstituted TMC ($\text{TOF}_{\text{TMC}} = 5880\text{ h}^{-1}$).^{3,5d}

The decreased polymerization activities observed with TMC(OMe)₂ as compared to TMC and metal-based catalysts most likely

result from unfavorable interactions of the additional methoxy functionalities with the Lewis acidic metal centers, which compete with the effective activation of the carbonate moiety.

DMAP, TBD and BEMP, in association with BnOH at $90\text{ }^{\circ}\text{C}$, all ring-opened TMC(OMe)₂ with the guanidine ($\text{TOF}_{\text{TMC(OMe)}_2} = 165\text{ h}^{-1}$; Table 1, entry 13) and phosphazene ($\text{TOF}_{\text{TMC(OMe)}_2} = 167\text{ h}^{-1}$; Table 1, entry 14) being both more active than the amine ($\text{TOF}_{\text{TMC(OMe)}_2} = 41\text{ h}^{-1}$; Table 1, entry 12). The organic bases were then revealed to be significantly more effective than the aluminium-based system ($\text{TOF}_{\text{TMC(OMe)}_2} = 87\text{ h}^{-1}$; Table 1, entry 10), but still less active than the zinc-based system ($\text{TOF}_{\text{TMC(OMe)}_2} = 465\text{ h}^{-1}$; Table 1, entry 5).¹²

Replacing benzyl alcohol with 1,3-propanediol in the iROP of TMC(OMe)₂ promoted by $[(\text{BDI}^{\text{Ar}})\text{Zn}(\text{N}(\text{SiMe}_3)_2)]$ or BEMP afforded the corresponding α - ω -dihydroxy telechelic polycarbonates, H-P(TMC(OMe)₂)-H. Similar to the data obtained with BnOH,

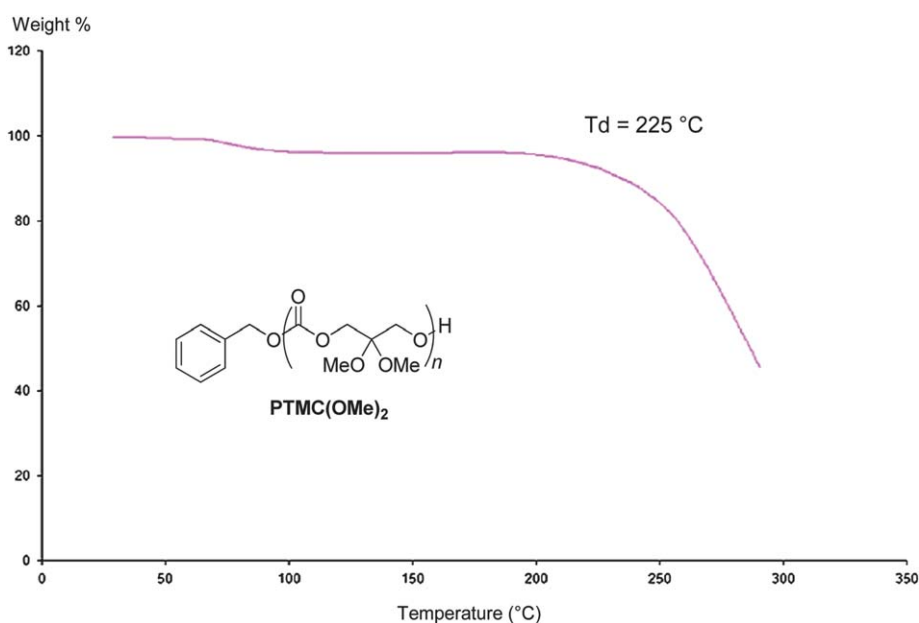


Fig. 4 TGA trace of a H-P(TMC(OMe)₂)-OBn ($\bar{M}_{n\text{SEC}} = 38\,800\text{ g mol}^{-1}$; Table 1, entry 4).

Table 2 Mechanical parameters of P(TMC(OMe)₂), PTMC and PLLA determined by tensile tests

Entry	Polymer ($\bar{M}_n/\text{g mol}^{-1}$)	Injection conditions		Tensile parameters		
		Polymer temp/ $^{\circ}\text{C}$	Molding temp/ $^{\circ}\text{C}$	E^a/MPa	σ_r^b/MPa	ε_r^c (%)
1	PTMC (95 000)	220	23	4.5 ± 1	1.8 ± 0.7	650 ± 77
2	PTMC(OMe) ₂ (70 200)	160	23	3190 ± 70	126 ± 3	9 ± 1
3	PLLA ³ (95 000)	190	23	3427 ± 71	140 ± 7	6 ± 1

^a Elastic modulus. ^b Strain at break. ^c Elongation at break.

good activities and control in terms of molar mass and molar mass distribution of P(TMC(OMe)₂) were reached with the diol, as previously observed in the corresponding PTMC syntheses^{5c,f} (Table 1, entries 15–17).

¹H NMR analyses of the precipitated polycarbonates prepared from these binary catalyst systems showed the main polymer chain typical resonances (δ 4.23, 3.28 ppm; $\text{CH}_2\text{C}(\text{OMe})_2\text{CH}_2\text{OC}(\text{O})\text{O}$), indicating that no side processes (e.g., hydrolysis of the 2,2-dimethyl acetal functionalities) occurred, despite the use of relatively large amounts of alcohol (diol) and the presence of Lewis acidic metal centers (Fig. 2 and ESI†). Besides, low intensity resonances for both a hydroxymethyl (δ 3.82 ppm; CH_2OH) and a benzyloxy carbonate group (δ 7.38, 5.19 ppm; $\text{PhCH}_2\text{OC}(\text{O})\text{O}$) were observed, in agreement with the expected formation of H-P(TMC(OMe)₂)-OBn (Scheme 2).^{5e} When PPD was used, the unique polymer chain-end identified by the characteristic triplet at δ 3.76 ppm representative of a hydroxymethyl end-group, supported the formation of α,ω -dihydroxy telechelic H-P(TMC(OMe)₂)-H (Scheme 2, Fig. 2 and ESI†). No ether linkages (δ_{IH} 3.4–3.1 ppm; $\delta_{13\text{C}}$ 66.5–67.7 ppm) were detected in any spectrum of the polymers, thereby highlighting the ability of all initiating systems to prevent decarboxylation. The molar mass values of short-chain P(TMC(OMe)₂)s, as determined by ¹H NMR spectroscopy, were in close agreement with the ones calculated $\bar{M}_{n,\text{theo}}$ and the one measured by SEC, $\bar{M}_{n,\text{SEC}}$ as well (Table 1).

These results were confirmed by MALDI-ToF mass spectrometry analyses of low molar mass P(TMC(OMe)₂) samples. Analyses of a H-P(TMC(OMe)₂)-OBn sample prepared from the BEMP/BnOH catalytic system (Table 1, entry 7) featured a major distribution of peaks unambiguously assignable to H-P(TMC(OMe)₂)-OBn molecules cationized by Na⁺ ions (H-P(TMC(OMe)₂)-OCH₂Ph·Na⁺; main peak centered at m/z : 3209.5 g mol⁻¹) with a repeat unit of 162.2 g mol⁻¹ (i.e., the molar mass of TMC(OMe)₂; Fig. S3†).^{5e} This clearly demonstrated that BnOH indeed acted as an effective co-initiator and a chain transfer agent in the iROP of TMC(OMe)₂, ultimately end-capping the polycarbonate.

The thermal properties of P(TMC(OMe)₂) samples were next investigated by DSC and TGA (see also Table S1 in the ESI†). The DSC trace of the polymer (Fig. 3) featured a relatively high temperature glass transition at $T_g = 39\text{ }^{\circ}\text{C}$, in comparison to the negative T_g value ($-15\text{ }^{\circ}\text{C}$; $\bar{M}_n = 10\,000\text{ g mol}^{-1}$)¹³ of TMC. The absence of a melting temperature transition highlighted the amorphous character of these functional polycarbonates similarly to PTMCs. The degradation temperature of PTMC(OMe)₂, $T_d = 225\text{ }^{\circ}\text{C}$, measured by TGA (Fig. 4) is slightly lower than that of PTMC ($T_d = 230\text{ }^{\circ}\text{C}$).¹⁴

Mechanical properties of the P(TMC(OMe)₂)s, especially the elastic modulus (E), the strain at break (σ_r) and the elongation at

break (ε_r), were determined from tensile tests and compared to those of PTMC and poly(L-lactide). Illustrative values of each parameter are reported in Table 2 for all three polymers. PTMC exhibits both a very small elasticity modulus ($E = 4.5 \pm 1\text{ MPa}$) and a quite high elongation at break ($\varepsilon_r = 650 \pm 77\%$) value, thus demonstrating its well known elastomeric characteristics (Table 2, entry 1). On the contrary, samples of PTMC(OMe)₂ displayed a high E ($3190 \pm 70\text{ MPa}$) value along with a low ε_r ($9 \pm 1\%$) (Table 2, entry 2), characteristic of a rigid material much like poly(L-lactide) (Table 2, entry 3). This was rather unexpected considering the amorphous nature of this polymer.

Conclusions

Well-defined homopolymers derived from 2,2-dimethoxytri-methylene carbonate TMC(OMe)₂ have been prepared with controlled molecular features by immortal ROP, under mild conditions (bulk, 60–90 $^{\circ}\text{C}$), from various binary (metallo)organic catalysts/alcohol systems: H-P(TMC(OMe)₂)-OBn and α,ω -dihydroxy telechelic H-P(TMC(OMe)₂)-H of various molar masses ranging from 3000 to 70 200 g mol⁻¹ and quite narrow molar mass distribution values ($\bar{M}_w/\bar{M}_n \leq 1.79$) were thus synthesized. These acetal-functionalized homopolycarbonates were all characterized at the molecular (NMR, SEC, MALDI-ToF-MS), thermal (DSC, TGA) and mechanical levels. Unlike PTMC which is elastomeric, mechanical properties of amorphous P(TMC(OMe)₂) evidenced a rigid and brittle polymer material ($E = 3190 \pm 70\text{ MPa}$, $\varepsilon_r = 9 \pm 1\%$), much like semi-crystalline poly(L-lactide).

Acknowledgements

Financial support of this research (PhD grant to M. H.) from Total Petrochemicals Co. is gratefully acknowledged. S.M. G gratefully acknowledges the Region Bretagne ACOMB research program and Rennes Métropole for equipment support.

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