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Organocatalysts for the Controlled "Immortal" Ring-Opening Polymerization of Six-Membered-Ring Cyclic Carbonates: A Metal-Free, Green Process

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Abstract: Six-membered cyclic carbonates, namely trimethylene carbonate (TMC), 3,3-dimethoxytrimethylene carbonate (DMTMC) and 3-benzyloxytrimethylene carbonate (BTMC), undergo controlled "immortal" ring-opening polymerization (iROP) under mild conditions (bulk, 60–150 °C), by using organocatalysts, including an amine [4-*N*,*N*-dimethylaminopyridine (DMAP)], a guanidine [1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD)], or a phosphazene [2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP)], in the presence of an alcohol [benzyl alcohol (BnOH), 1,3-propanediol (PPD), glycerol (GLY)] that acts as both a co-initiator and a chain-transfer agent. Remarkably, such organocatalysts remain highly active in the iROP of technical-grade, unpurified TMC. Under optimized conditions, as much as 100000 equivalents of TMC were fully converted by as little as 10 ppm of BEMP with the simultaneous growth of as many as 200 polymer chains, allowing the preparation of high molar mass poly(trimethylene carbonate)s (up to 45800 g mol^{-1}). These catalyst systems enable among the highest activities (TOF = 55800 h^{-1}) and productivities (TON = 95000) ever reported for the ROP of TMC.

Keywords: carbonates · organocatalysis · polycarbonates · ring-opening polymerization · trimethylene carbonate

Introduction

Aliphatic polycarbonates, like polyesters, are a highly valuable class of polymers and, in light of their outstanding properties, find applications in a wide array of fields, ranging from biomedical uses to textiles, microelectronics, and packaging.[1] Polycarbonates derived from renewable resources have recently appeared as valuable potential alternatives to petrochemical thermoplastics, thereby becoming an attractive, topical research field. For higher added-value materials, the polymerization procedure should enable optimum control over macromolecular parameters, that is, well-defined molar mass, narrow molar-mass distribution, and variable, yet reliable, topology of the macromolecule, including end-group fidelity and sequence of monomer units along the main polymer chain. In addition to these selectivity criteria, the catalyst/initiator system must feature high activity and productivity.

Among living polymerization techniques accessing polycarbonates, ring-opening polymerization (ROP) stands out as the leading approach to satisfy such challenges.[1a,2,3] While state-of-the-art organometallic polymerization catalysis provides various proficient systems based on nontoxic metal centers, such as zinc, magnesium, calcium, or rare-earth metals, bearing suitable ancillary ligands, attention is currently aimed at the development of metal-free catalytic systems to avoid issues revolving around residual metal traces in the final polymer.

To face this concern, one recently established approach is the "immortal" ROP (iROP) of carbonates; this technique allows the use of a catalytic amount of metal complex and a protic source, such as an alcohol, used in large excess (compared with the metal catalyst), which behaves both as a co-initiator and as a chain transfer agent.[4,5] By enabling the growth of as many polymer chains as the number of equiva-

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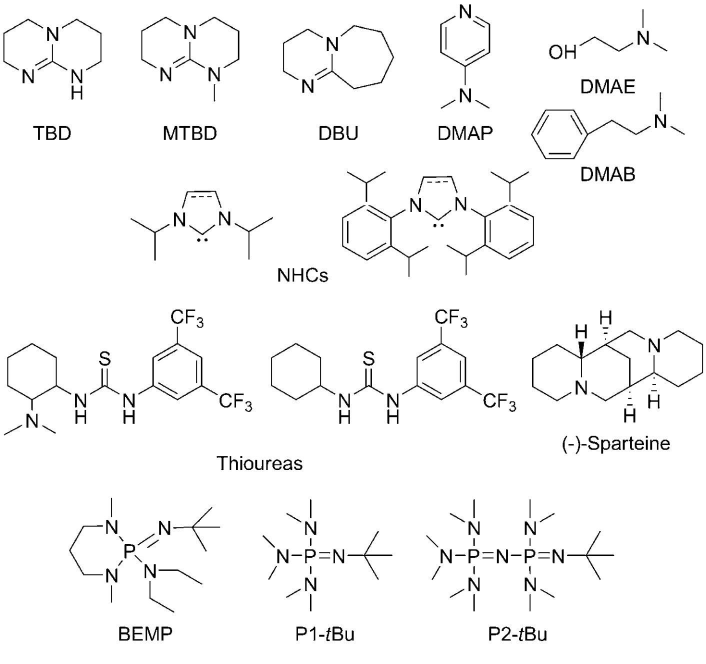
lents of alcohol introduced per unique metal center, one can lower the loading of metal pre-catalyst used to amounts as low as 20 ppm, while maintaining very high activities and productivities.[5] In such situations, the metal species becomes catalytic with respect to the polymer chains, in addition to the monomer units. Also, the ancillary ligand present in the metal coordination sphere affords the possibility of efficiently achieving the aforementioned control and selectivity criteria.[5,6] Such iROPs, including fast and reversible transfer reactions,[3a,7] offer the great advantage of combining high efficiency and control of macromolecular features, as well as resulting in nontoxic polymers.

Another approach is the development of metal-free catalytic systems. Recent advances in the ROP of cyclic esters have led to the emergence of a variety of mono- and bicomponent organocatalysts, as well as enzymes.[8,9] Although generally organocatalysts do not perform as well as organometallic catalysts if stereo/regioselectivity is considered, some of these organocatalyst systems have shown notable activity and degree of control for the ROP of lactones and cyclic carbonates, as well as siloxanes. Such polymerizations, promoted by simple organic molecules, might appear good alternatives to those employing metal-based catalysts/initiators.

Regarding the controlled ROP of trimethylene carbonate (TMC), some organocatalysts have been shown to lead to well defined poly(trimethylene carbonate)s (PTMCs) of high molar mass (up to 72 000 $\mathrm{g\,mol^{-1}}$), with relatively narrow molar-mass distributions ($M_w/M_n = 1.04$–1.8) and good end-group fidelity.[8,10] These include commercially available guanidines (TBD, MTBD), amidine (DBU), tertiary amines (DMAE, DMAEB), some N-heterocyclic carbenes (NHCs), and bifunctional thiourea–tertiary amine catalysts.[8,10] These organocatalysts, used in presence of an alcohol (e.g., $HOCH_2Ph$, $HO(CH_2)_4OH$; up to 20 equiv),[10b] in solution or in bulk, at 20–65 °C, operate through an activated-monomer mechanism. Similarly, some of these organocatalysts, including TBD,[11a] DBU,[11a–d,12] DMAP, and other amines (aniline, *N*,*N*-dimethylaniline, triethylamine, pyridine, quinuclidine, 1,4-diazabicyclo[2.2.2]octane, sparteine)[11d,g] or amino acids,[11e] possibly in the presence of tin(octoate)$_2$,[12] have been investigated in the ROP of various substituted TMCs. From these studies, TBD, DBU, and, to a lesser extent, DMAP have been shown to offer the best compromise in terms of activity and controlled polycarbonate molecular features.[8,10,11]

A category of organocatalysts that has recently emerged, namely phosphazene bases (BEMP, P1-*t*Bu and its dimeric analogue P2-*t*Bu), has demonstrated remarkably high activity at low temperatures, along with excellent stereocontrol for the ROP of *rac*-lactide, most likely as a consequence of its high basicity and steric hindrance.[13] Yet, such organocatalysts remain unexplored towards the ROP of cyclic carbonates.

In an effort to promote efficient procedures for the synthesis of polycarbonates, we have extended the iROP concept, so far essentially developed with metal-based catalytic systems,[5,10b] to organic ones. Herein, we present the results of our investigations into the iROP of different six-membered cyclic carbonates, including TMC, 3-benzyloxytrimethylene carbonate (BTMC), and 3,3-dimethoxytrimethylene carbonate (DMTMC), promoted by organocatalysts that appear to be the most promising for the ROP of cyclic esters, namely an amine (DMAP), a guanidine (TBD), and a phosphazene (BEMP);[14] various alcohols (benzyl alcohol (BnOH), 1,3-propanediol (PPD), glycerol (GLY)) have been used as chain transfer agents.



Experimental Section

Materials: All manipulations were performed under inert atmosphere (argon, <3 ppm of O_2) by using standard Schlenk, vacuum line, and glovebox techniques. Solvents were thoroughly dried and deoxygenated by standard methods and distilled before use. $CDCl_3$ was dried over a mixture of 3 and 4 Å molecular sieves. TMC (technical grade, Labso Chimie Fine) was first dissolved in THF and stirred over CaH_2 for 2 days, before being filtered and dried; TMC was then recrystallized from cold THF. Alcohols (BnOH, PPD, GLY), organocatalysts (DMAP, TBD, BEMP), and $Al(OTf)_3$ (all purchased from Aldrich) were used as received. The six-membered-ring carbonate monomers BTMC[15] and DMTMC[16] were synthesized as previously reported.

Instrumentation and measurements: ^1H (500 or 200 MHz) and $^{13}C\{^1H\}$ (125 or 50 MHz) NMR spectra were recorded in $CDCl_3$ on Bruker Avance AM 500 and DPX 200 spectrometers at 23 °C and were referenced internally by using the residual ^1H and ^{13}C solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm).

Average molar mass ($\bar{M}_n$) and molar-mass-distribution ($\bar{M}_w/\bar{M}_n$) values were determined from chromatogram traces recorded by size-exclusion chromatography (SEC) in THF at 20 °C (flow rate = 1.0 $\mathrm{mL\,min^{-1}}$) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a PLgel 5 Å MIXED-C column. The polymer samples were dissolved in THF (2 $\mathrm{mg\,mL^{-1}}$). All elution curves were calibrated with polystyrene standards. $\bar{M}_{n\,SEC}$ values for PTMCs were calculated by using the average correction coefficient previously reported ($\bar{M}_{\mathrm{nSEC}}=\bar{M}_{\mathrm{nSEC\,raw\,data}}\times 0.73$; 0.73 = average of the coefficients determined from low molar-mass PTMCs (0.57; $\bar{M}_{\mathrm{n}}<5000$) and from high molar-mass PTMCs (0.88; $\bar{M}_{\mathrm{n}}>10000$) by using MALDI-TOF mass spectrometry and viscosimetry analyses, respectively).[17] The SEC traces of the polymers all exhibited a unimodal, symmetrical peak.

The molar-mass values of short-chain H-PTMC-OR samples were determined by ^{1}H NMR analysis from the relative intensities of the signals of PTMC methylene protons (-$CH_2OC(O)$; at $\delta = 4.24$ ppm) to those of the α-hydroxymethyl (CH_2OH; at $\delta = 3.76$ ppm). The number-average molar-mass values obtained by ^{1}H NMR, $\bar{M}_{\mathrm{nNMR}}$, were in close agreement with those calculated; for instance, $\bar{M}_{\mathrm{nNMR}} = 7340\ \mathrm{g\,mol^{-1}}$ for Table 1, entry 11. Monomer conversions were calculated from ^{1}H NMR spectra of the crude polymer samples by using the integration (Int.) ratio (Int.$_{\mathrm{PTMC}}$/[Int.$_{\mathrm{PTMC}}$+Int.$_{\mathrm{TMC}}$]), of the methylene group in the α-position of the (poly)carbonate ($CH_2OC(O)$; $\delta = 4.24$ ppm for polymer, 4.45 ppm for monomer).

MALDI-TOF mass spectra were recorded with an AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N_2 laser source (337 nm, 4 ns pulse width) and a time-delayed extracted-ion source. Spectra were recorded in the positive-ion mode by using the reflectron mode and an accelerating voltage of 19 kV. The polymer sample was dissolved in THF (10 mg mL^{-1}) and a solution of α-cyano-4-hydroxycinnamic acid (2:1 v/v; 10 mg mL^{-1}) in acetonitrile/0.1 % trifluoroacetic acid (TFA) was prepared. Both solutions were then mixed in a 1:1 volume ratio, deposited sequentially on the sample target and then air-dried.

Typical ROP of TMC—synthesis of H-PTMC$_{\mathbf{PPD}}$-H from BEMP/PPD: TMC (500 equiv, 1.12 g, 10.9 mmol) was added to PPD (10 equiv, 16 μL, 0.219 mmol) and BEMP (1 equiv, 6.3 μL, 21.9 μmol) in toluene (0.1 mL). The mixture was then stirred at 60 °C for the appropriate time (see Table 2; reaction times were not systematically optimized). The reaction was quenched with excess acetic acid (ca. 2 mL of a 1.74 mol L^{-1} solution in toluene). The resulting mixture was concentrated under vacuum and the conversion determined by ^{1}H NMR analysis of the residue. This crude polymer was then dissolved in CH_2Cl_2, purified by precipitation from cold methanol, filtered, and dried under vacuum. NMR data for H-PTMC-OBn[5a–c] and PPD-(PTMC-H)$_2$[5c] were in agreement with previously reported data.

GLY-(PTMC-H)$_3$: $(PolO)CH_2CH(OPol)CH_2(OPol)$ (Pol = polymer), ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.96$ (m, 1 H, $(PolO)CH_2C\mathit{H}(OPol)CH_2(OPol)$), 4.42 (m, 4 H, $(PolO)C\mathit{H}_2CH(OPol)C\mathit{H}_2(OPol)$), 4.26 (t, J = 6.5 Hz, 3(4n+2)H, $\{C(O)OC\mathit{H}_2CH_2C\mathit{H}_2\}$, $HOCH_2CH_2C\mathit{H}_2$), 3.75 (t, J = 6 Hz, 6 H, $HOC\mathit{H}_2CH_2CH_2$), 2.07 (quint, J = 6 Hz, 3(2n)H, $\{C(O)OCH_2C\mathit{H}_2CH_2\}$), 1.94 ppm (quint, J = 6 Hz, 6 H, $HOCH_2C\mathit{H}_2CH_2$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 154.0$ ($\{\mathit{C}(O)OCH_2CH_2CH_2\}$), 70.5 ($(PolO)CH_2\mathit{C}H(OPol)CH_2(OPol)$), 66.9 ($(PolO)\mathit{C}H_2CH(OPol)\mathit{C}H_2(OPol)$), 65.1 ($\{C(O)O\mathit{C}H_2CH_2\mathit{C}H_2\}$), 63.3 ($C(O)O\mathit{C}H_2CH_2CH_2OH$), 59.6 ($C(O)OCH_2CH_2\mathit{C}H_2OH$), 31.2 ($C(O)OCH_2\mathit{C}H_2CH_2OH$), 27.4 ppm ($\{C(O)OCH_2\mathit{C}H_2CH_2\}$).

H-PDMTMC-OBn: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.39$ (m, 5 H, $C_6\mathit{H}_5$), 5.19 (s, 2 H, $C_6H_5C\mathit{H}_2$), 4.24 (s, (4n+2)H, $\{C(O)OC\mathit{H}_2C(OCH_3)_2C\mathit{H}_2\}$, $C\mathit{H}_2C(OCH_3)_2CH_2OH$), 3.87 (s, 2 H, $HOC\mathit{H}_2C(CH_3)_2CH_2$), 3.30 ppm (s, (6$n$+6)H, $\{C(O)OCH_2C(OC\mathit{H}_3)_2CH_2\}$, $HOCH_2C(C\mathit{H}_3)_2CH_2$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 155.3$ ($\{\mathit{C}(O)OCH_2C(OCH_3)_2CH_2\}$), 138.9 ($\mathit{C}_{6\mathrm{ortho}}H_5$), 129.0 ($\mathit{C}_{6\mathrm{meta}}H_5$), 128.1 ($\mathit{C}_{6\mathrm{para}}H_5$), 102.3 ($HOCH_2\mathit{C}(OCH_3)_2CH_2OC(O)$), 99.8 ($\{C(O)OCH_2\mathit{C}(OCH_3)_2CH_2\}$), 72.7 ($Ph\mathit{C}H_2OC(O)$), 67.9 ($\{C(O)O\mathit{C}H_2C(OCH_3)_2\mathit{C}H_2\}$), 51.0 ppm ($\{C(O)OCH_2C(O\mathit{C}H_3)_2CH_2\}$).

PPD-(PDMTMC-H)$_2$: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.24$ (s, (4n+4)H, $\{C(O)OC\mathit{H}_2C(OCH_3)_2C\mathit{H}_2\}$, $HOCH_2C(OCH_3)_2C\mathit{H}_2$), 3.78 (m, 4 H, $OC\mathit{H}_2CH_2C\mathit{H}_2O$), 3.63 (s, 4 H, $HOC\mathit{H}_2C(OCH_3)_2CH_2$), 3.31 (s, (6$n$+6)H, $\{C(O)OCH_2C(OC\mathit{H}_3)_2CH_2\}$, $HOCH_2C(OC\mathit{H}_3)_2CH_2$), 1.88 ppm (m, 2 H, $OCH_2C\mathit{H}_2CH_2O$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 155.2$ ($\{\mathit{C}(O)OCH_2C(OCH_3)_2CH_2\}$), 102.6 ($HOCH_2\mathit{C}(OCH_3)_2CH_2$), 99.8 ($\{C(O)OCH_2\mathit{C}(OCH_3)_2CH_2\}$), 69.0 ($\{C(O)O\mathit{C}H_2C(OCH_3)_2\mathit{C}H_2\}$), 63.3 ($O\mathit{C}H_2CH_2\mathit{C}H_2O$), 50.8 ($\{C(O)OCH_2C(O\mathit{C}H_3)_2CH_2\}$), 26.9 ppm ($OCH_2\mathit{C}H_2CH_2O$).

H-PBTMC-OBn: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.28$–7.34 (m, (5n+5)H, $\{C(O)OCH_2C(OCH_2C_6\mathit{H}_5)CH_2\}$, $(C_6\mathit{H}_5CH_2)$), 4.67 (s, 2 H, $\{C(O)OCH_2C(OC\mathit{H}_2C_6H_5)CH_2\}$), 4.33–4.14 (m, (4$n$+2)H, $\{C(O)OC\mathit{H}_2CH(OCH_2C_6H_5)C\mathit{H}_2\}$, $HOCH_2CH(OCH_2C_6H_5)C\mathit{H}_2$), 3.86–3.91 ppm (m, ($n$+3)H, $\{C(O)OCH_2C\mathit{H}(OCH_2C_6H_5)CH_2\}$, $HOC\mathit{H}_2C\mathit{H}(OCH_2C_6H_5)CH_2$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 155.2$ ($\{\mathit{C}(O)OCH_2CH(OCH_2C_6H_5)CH_2\}$), 137.9 ($\mathit{C}_{6\mathrm{ortho}}H_5$), 128.9 ($\mathit{C}_{6\mathrm{meta}}H_5$), 128.3 ($\mathit{C}_{6\mathrm{para}}H_5$), 74.4 ($\{C(O)OCH_2CH(O\mathit{C}H_2C_6H_5)CH_2\}$), 72.7 ($\{C(O)OCH_2\mathit{C}H(OCH_2C_6H_5)CH_2\}$), 66.9 ppm($\{C(O)O\mathit{C}H_2CH(O\mathit{C}H_2C_6H_5)\mathit{C}H_2\}$).

PPD-(PBTMC-H)$_2$: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35$–7.24 (m, (5n+10)H, $\{C(O)OCH_2CH(OCH_2C_6\mathit{H}_5)CH_2\}$, $HOCH_2CH(OCH_2C_6\mathit{H}_5)CH_2$), 4.36 (m, (2$n$+4)H, $\{C(O)OCH_2CH(OC\mathit{H}_2C_6H_5)CH_2\}$, $HOCH_2CH(OC\mathit{H}_2C_6H_5)CH_2$), 4.34–4.19 (m, (4$n$+8)H, $\{C(O)OC\mathit{H}_2CH(OCH_2C_6H_5)C\mathit{H}_2\}$, $HOC\mathit{H}_2CH(OCH_2C_6H_5)C\mathit{H}_2$, $OC\mathit{H}_2CH_2C\mathit{H}_2O$), 3.91–3.84 (m, ($n$+2)H, $\{C(O)OCH_2C\mathit{H}(OCH_2C_6H_5)CH_2\}$, $HOCH_2C\mathit{H}(OCH_2C_6H_5)CH_2$), 1.90 ppm (m, 2 H, $OCH_2C\mathit{H}_2CH_2O$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 155.4$ ($\{\mathit{C}(O)OCH_2CH(OCH_2C_6H_5)CH_2\}$), 137.6 ($\mathit{C}_{6\mathrm{ortho}}H_5$), 128.8 ($\mathit{C}_{6\mathrm{meta}}H_5$), 128.3 ($\mathit{C}_{6\mathrm{para}}H_5$), 74.4 ($\{C(O)OCH_2CH(O\mathit{C}H_2C_6H_5)CH_2\}$), 72.5 ($\{C(O)OCH_2\mathit{C}H(OCH_2C_6H_5)CH_2\}$), 66.9 ($\{C(O)O\mathit{C}H_2CH(OCH_2C_6H_5)\mathit{C}H_2\}$), 63.6 ($O\mathit{C}H_2CH_2\mathit{C}H_2O$), 61 ($HO\mathit{C}H_2CH(OCH_2C_6H_5)CH_2$), 26.9 ppm ($OCH_2\mathit{C}H_2CH_2O$).

Results and Discussion

The catalytic performances of DMAP, TBD, and BEMP for the ROP of TMC—purified or unpurified—were evaluated in bulk at 60–150 °C by first using benzyl alcohol as an initiator/chain-transfer agent. The $[TMC]_0/[catalyst]_0/[BnOH]_0$ ratio was varied from 500:1:5 up to 10000:1:200 and 100000:1:100. The most significant results are gathered in Table 1. All organocatalysts surveyed were active, with slightly variable activities (vide infra), and exhibited controlled behavior. This control is shown by the good agreement between the molar masses determined (and corrected)[17] by SEC analysis ($\bar{M}_{\mathrm{nSEC}}$) and those calculated ($\bar{M}_{\mathrm{ntheo}}$), as well as by the quite narrow molar-mass distribution values. As expected for polymerizations performed in bulk, the molar-mass distributions were slightly larger than those commonly obtained with procedures performed in solution, as a result of more important side reactions, yet within the common range, and still all monomodal ($\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} < 1.85$).[5,10a,17]

At a typical $[TMC]_0/[catalyst]_0/[BnOH]_0$ ratio of 500:1:5, selected from our previous work on the iROP of TMC mediated by [{BDI}Zn] ({BDI} = β-diiminate) catalysts,[5] DMAP only partly (50 %) polymerized purified TMC within 30 min at 60 °C (Table 1, entry 1). Raising the temperature to 110 °C led to almost quantitative monomer conversion within 15 min, with only minor amounts of transesterification reactions appearing over prolonged reaction times, as indicated by the slightly broadened molar-mass distribution values and the, still good, agreement of experimental and calculated $\bar{M}_{\mathrm{n}}$ values (Table 1, entries 1–4). Similarly, TBD allowed faster ROP at 110 °C (as compared to 60 °C), readily converting 500 equivalents of monomer within 5 min (vs. 30 min at 60 °C; Table 1, entries 7 and 8). In comparison with the data reported for "classical" (i.e., "non-immortal") solution ROP of purified TMC with a similar

Table 1. Bulk iROP of purified and unpurified TMC mediated by various organocatalyst–BnOH or $[\{BDI\}Zn\{N(SiMe_3)_2\}]$–BnOH[5a,b] systems.

Entry	Catalyst	$[TMC]_0/[Catalyst]_0/[BnOH]_0$	T [°C]	t [min][a]	Conversion[b] [%]	$\bar{M}_{n\,theo}$[c] [$g\,mol^{-1}$]	$\bar{M}_{n\,SEC}$[d] [$g\,mol^{-1}$]	$\bar{M}_w/\bar{M}_n$[e]	TOF [h^{-1}]
1	DMAP	500:1:5	60	30	50	5210	5050	1.18	500
2	DMAP	500:1:5	110	5	87	9000	11850	1.46	5220
3	DMAP	500:1:5	110	15	97	10000	13200	1.53	1940
4	DMAP	500:1:5	110	150	98	10100	13700	1.62	196
5[f]	DMAP	500:1:5	110	150	98	10100	12400	1.46	196
6[10a]	TBD (in CH_2Cl_2)	500:1:1	RT	360	99	50600	42850	1.31	83
7	TBD	500:1:5	60	30	99	10210	10900	1.85	990
8	TBD	500:1:5	110	5	99	10210	12700	1.52	5940
9[f]	TBD	500:1:5	110	5	100	10310	9950	1.71	6000
10	BEMP	500:1:5	60	10	69	7150	6650	1.32	2070
11	BEMP	500:1:5	60	30	80	8270	7300	1.27	800
12	BEMP	500:1:5	60	60	85	8780	8250	1.25	425
13[f]	BEMP	500:1:5	60	60	78	8060	8050	1.23	390
14	BEMP	500:1:5	110	5	80	8270	6950	1.43	4800
15[5a,b]	$[\{BDI\}Zn\{N(SiMe_3)_2\}]$	500:1:5	60	7	99	10210	12400	1.55	4245
16	$[\{BDI\}Zn\{N(SiMe_3)_2\}]$	500:1:5	110	3	100	10320	11750	1.77	10000
17	DMAP	10000:1:20	110	120	97	49580	42050	1.56	4850
18	DMAP	10000:1:20	150	10	93	47540	30050	1.47	55800
19	TBD	10000:1:20	110	120	98	50090	44850	1.52	4900
20	TBD	10000:1:20	150	10	82	41930	19300	1.65	49200
21	BEMP	10000:1:20	110	60	60	30710	29400	1.40	6000
22	BEMP	10000:1:20	150	30	65	33260	30200	1.61	13000
23[5a,b]	$[\{BDI\}Zn\{N(SiMe_3)_2\}]$	10000:1:20	60	180	89	45500	43300	1.90	2967
24[5b]	$[\{BDI\}Zn\{N(SiMe_3)_2\}]$	5000:1:200	60	180	100	2660	1500	1.23	1665
25[f],[5a–e]	$[\{BDI\}Zn\{N(SiMe_3)_2\}]$	10000:1:100	60	180	0	–	–	–	0
26[f]	TBD	10000:1:200	110	60	100	5210	5300	1.58	10000
27[f]	BEMP	10000:1:200	110	60	98	5100	5550	1.49	9800
28[f]	TBD	100000:1:100	150	15 × 60	91	92930	25410	1.54	6067
29[f]	BEMP	100000:1:100	110	26 × 60	82	83750	45800	1.49	3154
30[f]	BEMP	100000:1:100	150	15 × 60	95	97000	24300	1.51	6330
31[5f–g]	$Al(OTf)_3$	500:1:5	110	60	96	9900	13800	1.62	480
32[5f–g]	$Al(OTf)_3$	500:1:5	150	5	98	10100	10950	1.55	5880
33[f],[5f–g]	$Al(OTf)_3$	10000:1:10	110	120	75	76610	45200	1.53	3750
34[f],[5f–g]	$Al(OTf)_3$	10000:1:10	150	20	92	93950	61200	1.42	27600
35[f]	$Al(OTf)_3$	100000:1:100	150	15 × 60	87	88850	41400	1.66	5800

[a] Reaction times were not necessarily optimized. [b] Monomer conversion determined by ^1H NMR spectroscopy. [c] Calculated from $[TMC]_0/[BnOH]_0 \times$ monomer conversion $\times M_{TMC} + M_{BnOH}$, with $M_{TMC} = 102\ g\,mol^{-1}$ and $M_{BnOH} = 108\ g\,mol^{-1}$. [d] Determined by SEC vs. polystyrene standards and corrected by a factor of 0.73.[17] [e] Molar-mass distribution calculated from SEC traces. [f] Experiment ran with technical grade TMC.

$[TMC]_0/[TBD]_0$ ratio of 500:1 in the presence of 1 equivalent of BnOH (Table 1, entry 6),[10a] the guanidine was clearly much more active in the bulk "immortal" process that uses a fivefold excess of BnOH (TOF = 83 h^{-1} vs. 5940 h^{-1}, Table 1, entries 6[10a] vs. 8). Likewise, the BEMP–BnOH system allowed faster ROP of purified TMC at 110 °C than at 60 °C (Table 1, entries 10–12, and 14). Comparison of the activity of these three organocatalysts within 30 min at 60 °C [TOF: TBD (990 h^{-1}) > BEMP (800 h^{-1}) > DMAP (500 h^{-1}); Table 1, entries 1, 7, and 11] or within 5 min at 110 °C [TOF: TBD (5940 h^{-1}) > DMAP (5220 h^{-1}) > BEMP (4800 h^{-1}); Table 1, entries 2, 8, and 14) reveals the slight superiority of TBD. Regarding molar-mass distribution values, BEMP gave narrower values as compared with DMAP or TBD.

The ROP of purified TMC by using DMAP, TBD, or BEMP was next evaluated upon raising the amounts of monomer and chain-transfer agent to a $[TMC]_0/[catalyst]_0/[BnOH]_0$ ratio of 10000:1:20. To counteract the low catalyst loading, the reaction temperature was raised to 110–150 °C (Table 1, entries 17–22). As anticipated, the reaction proceeded faster at higher temperatures with neither loss of the control of the polymer molar mass nor broadening of the molar-mass distribution for this quite large amount of monomer. Under these experimental conditions, DMAP and TBD exhibited the highest activities (TOF = 55800 h^{-1}, Table 1, entry 18 and 49200 h^{-1}, Table 1, entry 20, respectively), while the BEMP-based system appeared to be less efficient (TOF ≤ 13000 h^{-1}, Table 1, entry 22).

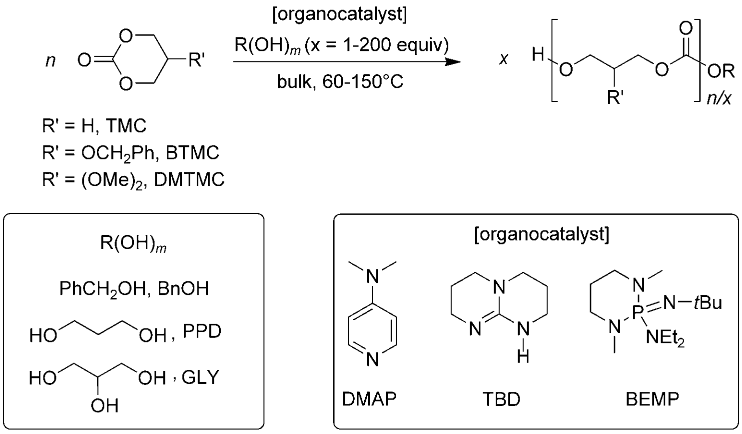
In an attempt to further evaluate the ability of such organocatalysts to resist reaction with trace impurities that might be present in the monomer and/or the alcohol, the iROP of technical-grade TMC, that is, of a raw, unpurified monomer batch, was investigated (Table 1, entries 5, 9, 13, and 26–30). Most interestingly, DMAP, TBD, and BEMP underwent successful iROP of TMC at $[TMC]_0/[catalyst]_0/[BnOH]_0$ ratios of either 500:1:5 (Table 1, entries 5 vs. 4, 9 vs. 8, and 13 vs. 12) or as high as 10000:1:200 (Table 1, entries 26 and 27). No significant difference in activity among these three organocatalysts, or in comparison to the corresponding experiments performed with purified TMC, was observed. PTMCs with controlled molecular features ($\bar{M}_n$, $\bar{M}_w/\bar{M}_n$ and molecular structure) were systematically obtained. This ability to perform iROP of unpurified monomers represents another significant advantage to the organocatalysts compared with organometallic systems, such as, for example, the zinc system [{BDI}Zn{N(SiMe$_3$)$_2$}]/BnOH, which almost instantaneously decomposes in the presence of crude TMC. For instance, with [TMC]$_0$/[{BDI}Zn{N(SiMe$_3$)$_2$}]$_0$/[BnOH]$_0$ = 10000:1:10, the iROP of unpurified TMC at 60 °C failed to give any polymer within 3 h (Table 1, entry 25),[5a–e] whereas the iROP initiated by TBD–BnOH or BEMP–BnOH systems converted 98–100 % of the 10000 equivalents of unpurified TMC over 60 min, in the presence of 200 equivalents of alcohol (Table 1, entries 26 and 27). These observations further highlight the greater stability of these DMAP, TBD, and BEMP with alcohol systems towards impurities that makes these catalysts highly valuable.

Further investigations focused on BEMP for several reasons. First, as mentioned above, among the organocatalysts investigated herein, BEMP affords the narrowest molar-mass distribution values. Second, BEMP has, thus far, never been evaluated in polymerizations involving cyclic carbonates, as opposed to DMAP, which has already been studied with various (di)lactones,[13a,b] although not with TMC, and to TBD, which has previously been evaluated with (di)lactones[13c–g] and TMC.[10a,11a] Our first experiments involved higher loadings of unpurified TMC and alcohol in order to further increase the number of growing polymer chains per organocatalyst-based initiating system (Table 1, entries 27, 29, and 30). At a [TMC]$_0$/[BEMP]$_0$/[BnOH]$_0$ ratio of 10000:1:200, the iROP remained controlled, as implied by the good agreement between the expected molar mass and the one measured by SEC, as well as by the relatively narrow molar-mass distribution[5,10a,17] (Table 1, entry 27). This was no longer the case when an even larger amount of monomer (100000 equiv) was polymerized, as shown by the experimentally measured molar mass, which was much lower than the expected value (Table 1, entries 29 and 30). This apparent discrepancy highlights the fact that the larger the monomer loading, the greater the total amount of impurities inherent in the unpurified monomer batch and thus present in the reaction medium.[18] Since some of these impurities (supposedly protic reagents, such as water or residual alcohol) may behave as additional chain-transfer agents in a similar manner to the purposely added alcohol, they may contribute to the lowering of the molar mass. We have previously demonstrated that a more accurate theoretical molar mass of the polymer ($\bar{M}'_{\text{n theo}}$) can be determined upon taking into account the amount ($\bar{X}$) of these "transfer-active" impurities.[5e–g] The amount of impurities, being determined as 0.056 % (average value)[5e–g] of the technical-grade TMC batch used for this study, gives an expected molar mass ($\bar{M}'_{\text{n theo}}$) of 53720 g mol^{-1} ($\bar{M}'_{\text{n theo}}$ = [TMC]$_0$/{[ROH]$_0$ + ($\bar{X}$ × [TMC]$_0$)} × monomer conversion × M_{TMC} + M_{ROH} with $\bar{X}$ = 0.056). This gave a value in good agreement with the molar mass experimentally obtained ($\bar{M}_{\text{n SEC}}$ = 45800, Table 1, entry 29). Remarkably, under our experimental conditions, PTMCs with a molar mass as high as 45800 g mol^{-1} could thus be prepared from such technical-grade, unpurified TMC, while growing as many as 200 polymer chains from the phosphazene catalyst, introduced at loadings as low as 10 ppm (i.e., 2 mg of BEMP used to polymerize, quantitatively, 74.4 g of TMC).

As compared to the best organometallic initiating systems reported to date for the iROP of purified TMC, namely those based on β-diiminate[5a–e] or bis(morpholinomethyl)-phenoxide ({LO^1})[5e] zinc derivatives, for a [TMC]$_0$/[catalyst]$_0$/[BnOH]$_0$ ratio of 500:1:5, these organocatalysts appear less active, at both 60 °C (TOF = 4200–4245 h^{-1} for both [Zn]/ROH[5e] vs. 500 h^{-1} for DMAP, 990 h^{-1} for TBD, and 2070 h^{-1} for BEMP; Table 1, entries 15, 1, 7, and 10, respectively) and at 110 °C (TOF = 10000 h^{-1} for [{BDI}Zn{N(SiMe$_3$)$_2$}] vs. 5220 h^{-1} for DMAP, 5940 h^{-1} for TBD, and 4800 h^{-1} for BEMP; Table 1, entries 16, 2, 8, and 14, respectively). However, upon raising either the initial amount of monomer or alcohol (both purified), the BEMP and TBD systems resist the problems caused by the potential impurities inherent to such large quantities of reagents better than the zinc systems. In fact, at a [TMC]$_0$/[catalyst]$_0$/[BnOH]$_0$ ratio of 5000:1:200, the [{BDI}Zn{N(SiMe$_3$}$_2$]/BnOH system is already much less active (TOF = 1665 h^{-1}, Table 1, entry 24)[5b] than that based upon either TBD (TOF = 10000 h^{-1}, entry 26) or BEMP (TOF = 9800 h^{-1}, Table 1, entry 27) evaluated with an amount of unpurified TMC twice as large (10000:1:200).

Comparison of the performance of these organocatalysts to those of systems based upon metal triflates[5f,g] for the iROP of purified TMC at 60–110 °C at a [TMC]$_0$/[catalyst]$_0$/[BnOH]$_0$ ratio of 500:1:5, revealed similar activities within the range TOF = 425–500 h^{-1} for DMAP, BEMP, and Al(OTf)$_3$ (Table 1, entries 1, 11, and 31) and a slightly higher one for TBD (TOF = 990 h^{-1}, Table 1, entry 7). With unpurified TMC at a [TMC]$_0$/[catalyst]$_0$/[BnOH]$_0$ ratio of 100000:1:100, TBD (TOF = 6067 h^{-1}, Table 1, entry 28), BEMP (TOF = 6330 h^{-1}, Table 1, entry 30) and Al(OTf)$_3$ (TOF = 5800 h^{-1}, Table 1, entry 35) displayed similar activities at 150 °C. Comparing all catalytic organometallic ([{BDI}Zn{N(SiMe$_3$)$_2$}], [{LO^1}ZnEt]),[5a–e] Lewis acidic metal triflate (M(OTf)$_n$),[5f,g] and organocatalyst (DMAP, TBD, BEMP) systems combined with an alcohol, the highest activity ever obtained with purified TMC was reached with the organic-based systems of TBD and DMAP at 150 °C (TOF$_{\text{max}}$ = 49200–55800 h^{-1}, Table 1, entries 18 and 20). On the other hand, when using technical-grade, unpurified TMC, Al(OTf)$_3$ afforded the best activity at 150 °C (TOF$_{\text{max}}$ = 27600 h^{-1}, Table 1, entry 34). Whereas the bis(morpholinomethyl)phenoxide–zinc system gave the best productivity with purified TMC (TON$_{\text{max}}$ = 96000 in 8 h),[5e] the metal triflates and the organocatalyst systems afforded the largest turnovers with unpurified TMC (TON$_{\text{max}}$ = 82000 in 26 h, 87000–95000 in 15 h, Table 1, entries 28–30 and 35). In summary, while the significant advantage of the zinc organometallic catalytic systems[5a–e] remains their activity towards purified monomers, both the metal triflates and organocatalysts are highly valuable for their robustness, as well as their high activities and productivities, especially with technical-grade, unpurified reagents.

To design hydroxy-telechelic PTMCs with different topologies, and to further underline the versatility of these organocatalyst–alcohol systems in the iROP of TMC, we next selected 1,3-propanediol (PPD) and glycerol (GLY) as chain-transfer agents (Scheme 1).[5c] Also, PPD and GLY are two alcohols derived from the biomass, and their use remains in line with our efforts to promote renewable resources for the development of "green" polymers.[19] This also provided easier identification, by NMR spectroscopy, of the organic branching points of the PTMC chains originating from the alcohol.



Scheme 1. Schematic representation of the [organocatalyst/alcohol]-mediated iROP of six-membered-ring cyclic carbonates.

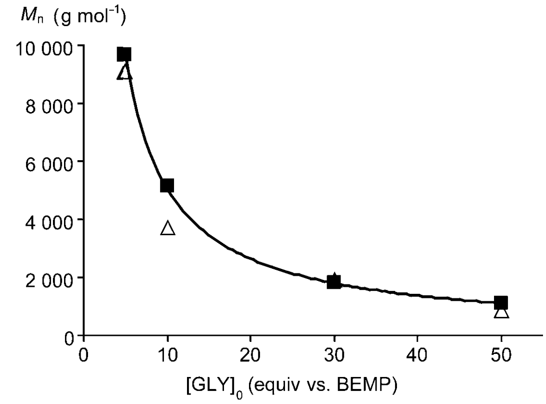


Figure 1. Dependence of the molar mass ($\bar{M}_n$) on the glycerol concentration at a $[TMC]_0/[BEMP]_0/[GLY]_0$ ratio of 500:1:5. △ = experimental values determined by SEC; ■ = theoretical values.

The results gathered in Table 2,[20] obtained by using BEMP as the organocatalyst, show that the iROP of purified TMC at 110 °C proceeded in an "immortal"-controlled manner when either PPD or GLY were used as the chain-transfer agent. Thus, as the concentration of PPD or GLY increased, the molar mass of the resulting PTMC decreased in inverse proportion, as illustrated for GLY in Figure 1. Thus, the molar mass of PTMCs could be effectively tuned on demand by adjusting the $[TMC]_0/[BEMP]_0/[PPD$ or $GLY]_0$ ratio. It appears that increasing the number of arms in the growing polymer chain from one (BnOH) to two (PPD) to three (GLY) does not affect the efficiency of the transfer reaction. The nature of the alcohol also had a limited influence on the reaction rate, as the reactions conducted with PPD or GLY proceeded only slightly faster than those with BnOH ($TOF_{PPD} = 5280\,h^{-1}$, Table 2, entry 1 vs. $TOF_{BnOH} = 4800\,h^{-1}$, Table 1, entry 14; $TOF_{GLY} = 1410\,h^{-1}$, Table 2, entry 5 vs. $TOF_{BnOH} = 800\,h^{-1}$, Table 1, entry 11). These experiments represent the first controlled iROP of TMC that uses an organocatalyst with a branched alcohol as the chain-transfer agent, affording multihydroxy-telechelic PTMCs. To the best of our knowledge, the use of GLY as a chain-transfer agent has only been reported once, for the preparation of trifunctional polycarbonates from the bulk iROP of TMC; however, it involved the heavy, possibly toxic, tin derivative $[Sn(octoate)_2]$, and led to PTMCs with quite large molar-mass distributions ($\bar{M}_w/\bar{M}_n = 1.5$–$2.6$).[21] In comparison to our previously reported, analogous iROP of TMC using the organometallic-based systems $[\{BDI\}Zn\{N(SiMe_3)_2\}]$/PPD or GLY,[5c] the present organocatalyst systems show similar control of the polymer's molar features, but slightly better activities [with $[\{BDI\}Zn\{N(SiMe_3)_2\}]$:[5c] $TOF_{PPD} = 653\,h^{-1}$ at a ratio of 500:1:10 over 45 min at 60 °C, $TOF_{GLY} = 1164\,h^{-1}$ at a ratio of 500:1:5 over 25 min at 60 °C; vs. with BEMP: $TOF_{PPD} = 1860\,h^{-1}$ at a ratio of 500:1:10 over 15 min at 60 °C (Table 2, entry 3), $TOF_{GLY} = 2000\,h^{-1}$ at a ratio of 500:1:10 over 15 min at 60 °C (Table 2, entry 6)].

Table 2. Bulk iROP of purified TMC mediated by various BEMP–alcohol systems.[19]

Entry	Alcohol	$[TMC]_0/[Catalyst]_0/[Alcohol]_0$	T [°C]	t [min][a]	Conversion[b] [%]	$\bar{M}_{n\,theo}$[c] [g mol^{-1}]	$\bar{M}_{n\,SEC}$[d] [g mol^{-1}]	$\bar{M}_w/\bar{M}_n$[e]
1	PPD	500:1:5	110	5	88	9050	8100	1.50
2	PPD	500:1:5	60	10	81	8340	10450	1.54
3	PPD	500:1:10	60	15	93	4820	5050	1.48
4	PPD	500:1:50	60	15	100	1100	1300	1.30
5	GLY	500:1:5	60	20	94	9680	9100	1.57
6	GLY	500:1:10	60	15	100	5200	3700	1.44
7	GLY	500:1:30	60	30	100	1790	1900	1.43
8	GLY	500:1:50	60	20	100	1110	850	1.54

[a] Reaction times were not necessarily optimized. [b] Monomer conversion determined by ^1H NMR. [c] Calculated from $[TMC]_0/[alcohol]_0 \times$ monomer conversion $\times M_{TMC} + M_{Alcohol}$, with $M_{TMC} = 102\,g\,mol^{-1}$, $M_{PPD} = 76\,g\,mol^{-1}$, $M_{GLY} = 92\,g\,mol^{-1}$. [d] Determined by SEC vs. polystyrene standards and corrected by a factor of 0.73.[17] [e] Molar-mass distribution calculated from SEC traces.

The mono-, bi-, or trifunctional alcohols, BnOH, PPD, or GLY, respectively, all allowed the synthesis of the mono-, bi-, or trihydroxy-functionalized, linear or three-arm star polymers BnO-PTMC-H, PPD-(PTMC-H)$_2$, or GLY-(PTMC-H)$_3$, respectively. NMR spectroscopy enabled the identification of characteristic resonances corresponding to the *n* terminal α-hydroxymethylene hydrogen atoms -(CH_2-OH)$_n$ at $\delta = 3.76$ ppm (refer to the experimental section), as well as of the organic moiety arising from the corresponding alcohol (BnO, PPD, or GLY). Thus, the use of an *n*-functional alcohol in combination with an organic catalyst allowed easy access to an *n*-hydroxy-telechelic polycarbonate.

Next, the use of the organocatalysts to promote the iROP of cyclic carbonates, in the presence of alcohols as chain-transfer agents, was extended towards other, related six-membered ring carbonate monomers, namely 3-benzyloxytrimethylene carbonate (BTMC) and 3,3-dimethoxytrimethylene carbonate (DMTMC; Table 3). So far, the ring-opening (co)polymerization of BTMC has essentially revolved around enzymes or metal-based catalysts, such as [Sn(octoate)$_2$] and [Al(O*i*Pr)$_3$], with operating temperatures typically in the range of 140–150 °C over quite extended reaction times (up to 72 h).[16,22] The interest in this monomer arises from the possibility of deprotecting the resulting PBTMC of its benzyl groups, resulting in polymers exhibiting better degradation properties, as well as greater hydrophilicity, due to their pendant hydroxyl groups. In comparison to TMC, the ROP of DMTMC has been studied considerably less, most likely because of the delicate synthesis of this monomer through the monomeric form of dihydroxyacetone.[16] The only report we are aware of mentions the preparation of PDMTMC with a molar mass as high as $\bar{M}_w = 37500$ g mol^{-1} from bulk ROP with [Sn(octoate)$_2$] as the catalyst (no initiator mentioned) at 100 °C over a couple of hours.[16b] The deprotection of PDMTMC by removal of the dimethoxyacetal group leads to the corresponding poly(2-oxypropylene carbonate), which is of great interest as a potential biomaterial.

Table 3. Bulk iROP of six-membered ring carbonates mediated by various BEMP–alcohol systems at a [monomer]$_0$/[BEMP]$_0$/[alcohol]$_0$ ratio of 500:1:5.

Entry	[Monomer]	Alcohol	T [°C]	t [min][a]	Conversion[b] [%]	$\bar{M}_{\text{ntheo}}$[c] [g mol^{-1}]	$\bar{M}_{\text{nSEC}}$[d] [g mol^{-1}]	$\bar{M}_w/\bar{M}_n$[e]
1	DMTMC	BnOH	90	180	96	15660	14000	1.66
2	DMTMC	PPD	90	180	100	16280	14300	1.53
3	BTMC	BnOH	60	240	100	20910	13000	1.65
4	BTMC	PPD	60	240	100	20880	15100	1.62

[a] Reaction times were not necessarily optimized. [b] Monomer conversion determined by ^{1}H NMR spectroscopy. [c] Calculated from [monomer]$_0$/[alcohol]$_0$ × monomer conversion × $M_{\text{Monomer}} + M_{\text{Alcohol}}$, with $M_{\text{DMTMC}} = 162$ g mol^{-1}, $M_{\text{BTMC}} = 208$ g mol^{-1}, $M_{\text{BnOH}} = 108$ g mol^{-1}, and $M_{\text{PPD}} = 76$ g mol^{-1}. [d] Determined by SEC vs. polystyrene standards. [e] Molar-mass distribution calculated from SEC traces.

By using either BnOH or PPD as the chain-transfer agent, both BTMC and DMTMC underwent selective, quantitative iROP initiated at a [BEMP]$_0$/[alcohol]$_0$ ratio of 1:5 at 60 or 90 °C (Scheme 1). Under such conditions, conversion of 500 equivalents of monomer into the corresponding polycarbonates proceeded within 240 min (Table 3).[23] Taking into account that the molar-mass values were determined by SEC from a calibration curve established from polystyrene standards with a distinct hydrodynamic radius, the polymer molar-masses measured agreed quite well with the calculated values for DMTMC, whereas the data obtained with BTMC were somewhat different. For both polymers, the molar-mass distribution remained comparable to that observed for PTMCs prepared from bulk experiments.

MALDI-TOF-MS analyses of a low molar mass H-PDMTMC-OBn sample prepared by using the BEMP/BnOH catalytic system[24] showed a main envelope corresponding to H-PDMTMC-OCH$_2$Ph·Na$^+$ (Figure 2; the second/minor distribution (*m/z*: $[M+\text{Na}]^+ + 16 = [M+\text{K}]^+$) corresponds to the analogous H-PDMTMC-OCH$_2$Ph·K$^+$ series) with a repeat unit of approximately 162.2 g mol^{-1}, which is the molar mass of DMTMC. The most intense signal detected, *m/z*: 3209.5 g mol^{-1}, corresponds to the sodium species containing 20 monomer units and benzyloxy and hydroxyl end groups. This observation agrees with the molar mass measured by SEC analysis ($\bar{M}_{\text{nSEC}} = 3130$ g mol^{-1}). Notably, in agreement with the NMR data, no decarboxylation of the carbonate chains was observed under the operating conditions. The chemical structure of H-PDMTMC-OBn was further confirmed by NMR analysis, as depicted in Figure 3.

Conclusion

We have demonstrated that the commercially available organocatalysts DMAP, TBD, and BEMP allow the controlled iROP of several six-membered-ring cyclic carbonates, such as TMC, DMTMC, or BTMC, under mild operating condi-

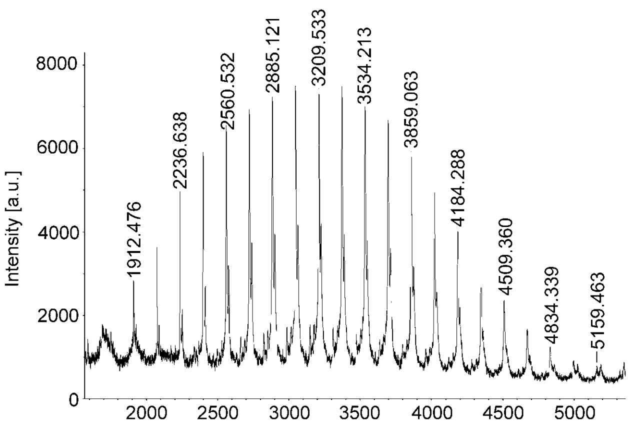


Figure 2. MALDI-TOF mass spectrum of a H-PDMTMC-OBn sample ($\bar{M}_{\text{nSEC}} = 3130$ g mol^{-1}).

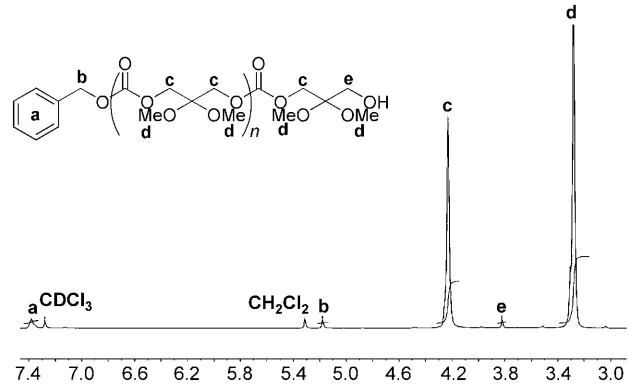


Figure 3. ^{1}H NMR (300 MHz, CDCl$_3$, 23 °C) spectrum of a H-PDMTMC-OBn sample ($\bar{M}_n$ = 4500 g mol^{-1}).

tions (solvent free, 60–150 °C) by using an alcohol, such as BnOH, PPD, or GLY, as a co-initiator and chain-transfer agent. This is the first report of the iROP of a cyclic carbonate by a phosphazene. Remarkably, such organocatalysts remained highly efficient in the iROP of technical-grade, unpurified TMC, with high activities and productivities similar to those reached with metal triflate based systems.[5f,g] Under optimized conditions, as much as 100 000 equivalents of TMC were fully converted from as little as 10 ppm of BEMP with the simultaneous growth of up to 200 polymer chains, allowing the preparation of high molar mass PTMCs. Activities among the highest reported thus far, as high as 55 800 h^{-1}, were reached. Well-defined α-hydroxy-ω-alkoxy- and α,ω-hydroxy-telechelic linear or three-armed star polycarbonates, including, in particular, HO-PDMTMC-OH and the first HO-PBTMC-OH, with tunable molar masses, were synthesized.[25]

Since these polycarbonates have been synthesized under solvent-free conditions, from a metal-free organocatalyst precursor, which, in addition, can be used in very small quantities thanks to its high activity and to the "immortal" conditions established, such macro-*n*-ols can be qualified as "green" polycarbonates. Also, thanks to their biocompatibility, they are promising candidates for biomaterials.

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[18] Note that ROP experiments conducted with purified TMC, under the same operating conditions, with a zinc-catalyst showed a much better agreement between the experimental molar masses determined by SEC and those calculated; in fact, the use of [{4-*tert*-butyl-2,6-bis(morpholinomethyl)phenoxy}ZnEt]/*i*PrOH in a 1:100 ratio, with 100000 equivalents of purified TMC, gave $\bar{M}_{\text{nSEC}}$ = 94400 g mol^{-1} for $\bar{M}_{n\text{theo}}$ = 98000 g mol^{-1}.[5e] The organocatalysts described here behave similarly towards purified TMC, that is, affording PTMC with $\bar{M}_{\text{n}}$ values in close agreement with the $[\text{TMC}]_0/[\text{ROH}]_0$ ratio.

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[20] Similar experiments performed with a $[\text{TMC}]_0/[\text{TBD}]_0/[\text{PPD}$ or $\text{GLY}]_0$ ratio of 500:1:5 gave quantitative conversion of purified TMC with PPD at 110°C over 60 min ($\bar{M}_{\text{ntheo}}$ = 10290 g mol^{-1}, $\bar{M}_{\text{nSEC}}$ = 13140 g mol^{-1}, $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$ = 1.91), or with GLY at 60°C over 20 min ($\bar{M}_{\text{ntheo}}$ = 10290 g mol^{-1}, $\bar{M}_{\text{nSEC}}$ = 10100 g mol^{-1}, $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$ = 1.72). These results are quite similar to those obtained with BEMP (Table 2, entries 1 and 5, respectively).

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[23] Similar experiments performed with a $[\text{DMTMC}]_0/[\text{TBD}]_0/[\text{BnOH}]_0$ ratio of 500:1:5 gave quantitative conversion of DMTMC at 90°C over 180 min ($\bar{M}_{\text{ntheo}}$ = 16050 g mol^{-1}, $\bar{M}_{\text{nSEC}}$ = 14100 g mol^{-1}, $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$ = 1.71), and with a $[\text{DMTMC}]_0/[\text{DMAP}]_0/[\text{BnOH}]_0$ ratio of 500:1:5 gave a 45% conversion of DMTMC at 90°C over 330 min ($\bar{M}_{\text{ntheo}}$ = 7400 g mol^{-1}, $\bar{M}_{\text{nSEC}}$ = 6800 g mol^{-1}, $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$ = 1.23). Compared to the analogous BEMP experiment (TOF = 160 h^{-1}, Table 3, entry 1), these results show that TBD displays a similar activity (TOF = 163 h^{-1}), whereas the DMAP catalytic system remains much less efficient (TOF = 41 h^{-1}).

[24] The MALDI-TOF mass spectrum of an H-PDMTMC-OCH_2Ph was acquired from a low molar mass sample $\bar{M}_{\text{ntheo}}$ = 3750 g mol^{-1}, $\bar{M}_{\text{nSEC}}$ = 3130 g mol^{-1}, $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$ = 1.18.

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