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Metal-free Synthesis of Poly(trimethylene carbonate) by Efficient Valorization of Carbon Dioxide

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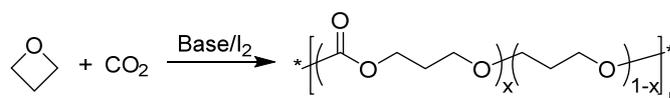
The desire for sustainability drives interest in the production of chemicals from carbon dioxide. The synthesis of poly(trimethylene carbonate), PTMC, by copolymerization of carbon dioxide and oxetane using organocatalysis affords a green route to this important polymer but has proven to be a very challenging process. Herein we report that the application of iodine, in combination with organic superbases provides a highly active system for the direct synthesis of PTMC from CO₂ with very high levels of carbonate linkage (95 % in selectivity). Mechanistic studies reveal the *in-situ* formation of trimethylene carbonate which eventually polymerizes through an active chain-end process from an I₂-oxetane adduct.

Significant progress has been made towards using CO₂ in eco-friendly technologies for replacing conventional phosgene-based processes.¹⁻⁵ In this regard, the use of CO₂ has been extended beyond its initial applications for the preparation of synthon molecules such as linear and cyclic carbonates, ureas and isocyanates, and is now also being used to produce engineering plastics such as polycarbonates. While the copolymerization of epoxides (also referred to as oxiranes) and CO₂ has been the subject of extensive research,⁶ the polymers that result from them require the development of applications and markets for their exploitation. In contrast, poly(trimethylene carbonate), PTMC, has found broad study and commercial application as an implantable biomaterial and as a component in polyurethanes.⁷⁻¹¹ Currently PTMC is accessed via ring-opening polymerization of the 6-membered carbonate,¹²⁻²⁶ trimethylene carbonate (TMC) which requires

the use of phosgene-based CO sources for its synthesis as well as commonly being carried out under anhydrous conditions in toxic solvents using heavy metal catalysts, all of which increase the environmental impact of the process.²⁶⁻²⁹

The derivation of a solvent-free process, using CO₂ as the carbonyl source in the absence of metals would provide a significant advance towards creating this polymer in a more sustainable manner. In an analogous manner to the copolymerization of epoxides and CO₂, PTMC can theoretically be produced by copolymerization of CO₂ with oxetane³⁰ (*i.e.* 1,3-epoxypropane, a four-membered cyclic ether, Scheme 1). Despite this promise, alongside the possibility of producing 6-membered cyclic carbonates,³ which can be readily polymerized by organic catalytic systems,^{31, 32} relatively few studies have focused on this potentially useful synthetic route, probably a consequence of a relative high price of raw materials and the inherent low reactivity of oxetanes that results from their low ring strain (112 vs 106 kJ.mol⁻¹ for oxirane vs oxetane)^{33, 34} and lower acidity^{35, 36}.

Scheme 1. Copolymerization of CO₂ and oxetane using a binary organocatalytic system



On the basis of the pioneering work of Baba *et al.*,^{37, 38} who produced PTMC by coupling CO₂ and oxetane under a vapor pressure method by using organotin halide complexes (100°C, 50 bar in CO₂, 4h, $M_{n,exp} \sim 4,250 \text{ g mol}^{-1}$), Darensbourg and coworkers developed a series of Cr,³⁹⁻⁴¹ Al⁴² and Co-based⁴³ catalytic systems to mediate the copolymerization of CO₂ and oxetane in solution. These organometallic compounds present very good catalytic activity but suffer from their potential toxicity and necessitate costly multi-step syntheses. The development of organocatalytic polymerization has grown significantly over the past 20 years on account of both the green credentials and absence of metals from the resulting

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polymers.⁴⁴ In a seminal advance towards a metal-free catalytic system, Detrembleur and coworkers developed a binary system composed of 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene and tetrabutylammonium iodide to copolymerize oxetane and CO₂ in bulk.⁴⁵ After 24 h at 130 °C under 10 MPa of CO₂ pressure, oligocarbonates of 2,000 g·mol⁻¹ were obtained.

Recently, some of us reported on the catalytic activity of an equimolar mixture of iodine and the 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) superbase to perform the cycloaddition of various epoxides and CO₂, in bulk, to yield 5-membered cyclic carbonates.⁴⁶ The efficiency of that binary catalyst system enabled a working pressure of CO₂ as low as 0.1 MPa, and was justified by the ability of DBU to properly activate CO₂ as part of a zwitterionic adduct⁴⁷ simultaneously with the formation of a carbon-oxonium bond interaction between I₂ and the oxirane through σ -hole (halogen) bonding.⁴⁸⁻⁵⁰ Very importantly, iodine is an inexpensive and environmentally friendly catalyst, which is currently applied in food,⁵¹ polymer,⁵² and pharmaceutical industries.⁵¹ The increased Lewis basicity of the oxetane monomers (compared to epoxides),⁵³ in combination with the high efficiency for the concomitant activation of both CO₂ and oxiranes of this catalytic system suggested that organocatalytic copolymerization of oxetane and CO₂ may be possible. Herein, we describe the use of various dual catalytic systems composed by iodine and different organic bases to promote the copolymerization of CO₂ and oxetane. We show that with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), highly efficient

copolymerization is possible under mild conditions with fast kinetic. Mechanistic investigations reveal that TMC is formed and polymerized instantaneously to produce PTMC, initiated from an *in situ*-generated iodine/oxetane adduct in the system.

Polymerizations of oxetane and CO₂ were first attempted with the I₂/DBU catalytic system. Reactions were performed in bulk, at 105 °C, under a 1 MPa CO₂ atmosphere. Arbitrarily, the catalytic loading content was fixed to 2.5 mol% of each I₂ and DBU with respect to the oxetane monomer. After 24 h, SEC analysis of the resulting material revealed the presence of oligomers, with a number-average molar mass (M_n) of 1,360 g·mol⁻¹ and a dispersity value ($M_w/M_n = \mathcal{D}_M$) of 1.71 (Table 1, entry 1). ¹H NMR spectroscopic analysis of the oligomers (Figure S1) revealed that 72% of the polymerized oxetane was selectively incorporated through carbonate linkages while 20% resulted in

the production of ether bonds in the polymer. The remaining converted oxetane (8 mol% of total) was converted into the 6-membered cyclic carbonate, trimethylene carbonate (TMC). We postulated that, similarly to the I₂-initiated ROP of tetrahydrofuran,⁴⁹ the self-oligomerization of oxetane in presence of iodine could explain the presence of ether bonds in the copolymer structure. This hypothesis was verified by addition of I₂ to oxetane ([oxetane]₀/[I₂]₀ = 40) in absence of CO₂ which resulted in production of oligomeric polyoxetane after 8 minutes at 105 °C (Figure S2), albeit in low yield (10 mol% of oxetane was converted).

Table 1. Copolymerization of oxetane and CO₂ catalyzed by I₂ and base in bulk. ^[a]

Entry	Base	pK_a ^[d]	Time (h)	Oxetane Conversion (%) ^[b]	TOF (h ⁻¹)	Selectivity (%) ^[b]			M_n (SEC) ^[c] g mol ⁻¹	\mathcal{D}_M ^[c]
						TMC	Carbonate Linkages	Ether Linkages		
1	DBU	24.3	24	82	1.37	8	72	20	1,360	1.71
2	MTBD	25.5	24	46	0.77	11	71	18	5,240	1.35
3	MTBD	25.5	44	80	0.73	9	73	18	6,000	1.45
4	TBD	26.0	24	88	1.61	<1	88	12	4,630	1.32
5	P ₄ - <i>tert</i> -Bu	42.7	24	15	0.25	>99	0	0	NA	NA
6	P ₄ - <i>tert</i> -Bu	42.7	168	83	0.20	71	19	10	320	1.42

^[a] Copolymerization conditions: 7.88 mmol oxetane, 2.5 mol% I₂ and base cocatalyst, 1 MPa CO₂, 105 °C. ^[b] Oxetane conversion and selectivity were determined from ¹H NMR spectroscopy of crude mixture; ^[c] Determined by SEC in tetrahydrofuran (THF) with polystyrene standard; ^[d] pK_a of bases in acetonitrile.⁵⁰

In order to limit the formation of ether linkages during the copolymerization, we sought to more efficiently activate the CO₂ towards incorporation into the resulting polymer. Guanidine-CO₂ complexes are known to be produced more easily as compared to amidine-CO₂ adducts,⁵⁴ and hence bicyclic guanidines such as 7-methyl-1,5,7-triazabicyclo-[4.4.0]-dec-5-ene (MTBD) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were chosen to examine their catalytic efficiencies for the copolymerization of CO₂ and oxetane as part of the binary catalyst system with I₂ (Table 1, entries 2 to 4). Both guanidine

bases were efficient for the copolymerization. After 24 h, MTBD allowed the production of a copolymer characterized by a M_n of 5,240 g·mol⁻¹ (\mathcal{D}_M of 1.35) and a copolymer composition similar to the one obtained by DBU. Attempts to further increase the molar mass of the polymer by prolonging the reaction time (from 24 to 44 h) led to a slightly broader dispersity ($\mathcal{D}_M \sim 1.45$) and enhancement of molar mass ($M_n = 6,000$ g·mol⁻¹), which is comparable with the highest M_n reported ($M_n = 7,100$ g·mol⁻¹) so far by using CO₂.³⁹ Interestingly, calculated turn over frequencies (TOF) associated

to that catalytic system (Table S1, entries 2 & 3) are double (TOF $\sim 0.7 - 0.8 \text{ h}^{-1}$, 1 MPa, 105 °C) that calculated from the 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene/tetrabutylammonium iodide catalytic system reported previously (TOF = 0.35 h^{-1} , 2 MPa, 130°C) under comparable experimental conditions (Table S1, entry 10)⁴⁵ demonstrating the highly efficient nature of such I_2 -based catalytic systems.

Replacing MTBD by the more basic TBD resulted in a significant enhancement of the overall conversion after 24 h (Table 1) yielding a polymer with a comparable molar mass and dispersity ($M_n = 4,630 \text{ g mol}^{-1}$, $D_M = 1.32$) but characterized by a further increase in TOF to 1.61 h^{-1} (Table 1, entry 4). Most notably however, the application of TBD as the basic cocatalyst, limited the ether linkages in the polymer to *ca.* 10 mol% thus resulting in a carbonate content of *ca.* 90 mol% (Table 1, entry 4). Note here that polymerization reactions were also performed from pristine I_2 and TBD for comparison (Table S3, entries 5 and 6).

Reasoning that the inherent basicity of the basic cocatalyst could explain the overall activity and selectivity of the process, we also applied 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethyl amino)-phosphoranylideneamino]-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (P_4 -*tert*-Bu) as a cocatalyst for this process (Table 1, entries 5 & 6). Unexpectedly, under the same experimental conditions, copolymerization failed, limiting the reaction to the *in-situ* production of TMC monomer in low yield ($\sim 15\%$). Interestingly, extending the reaction from 1 to 5 days allowed conversion of 30% of oxetane to TMC with no trace of polymerization (Table S2, entries 1 to 3). After 7 days (Table 1, entry 6 and Table S2, entry 4), traces of oligomers were

polycarbonates using such binary systems requires a balance of basicity to both enable polymer formation and reduce ether linkage formation.

Since the CO_2 -based copolymers generated from the I_2 /TBD catalytic system are produced with both high yield and selectivity for carbonate linkages, we selected to study this system with the aim of further enhancing molar mass control and carbonate selectivity. Studies of the influence of CO_2 pressure were conducted retaining equimolar ratios of I_2 and TBD in bulk oxetane at 105 °C (Table 2). By performing reactions under a reduced catalyst loading of 1.25 mol% for 1 and 3 days with 1.5 MPa pressure of CO_2 , 83 mol% of carbonate linkages were obtained (Table 2, entries 1 & 2). As may be expected, a further increase in both carbonate content (90 mol%) and overall conversion (86%) were observed when the CO_2 pressure was increased to 3 MPa (Table 2, entry 3). Notably, by further reducing catalyst loading to 1 mol%, 95% carbonate linkages resulted after 3 and 7 days (Table 2, entry 4-5). Notably, the M_n values of the resulting materials were slightly lower at higher oxetane conversions, *i.e.* for a higher pressure in CO_2 .

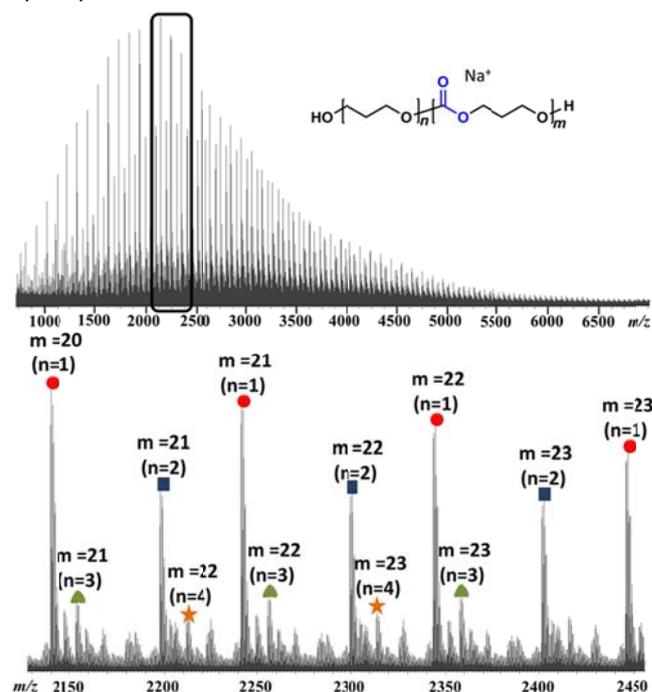
To obtain more information on the polymer structure, MALDI-ToF mass spectrometry analyses of the resultant polymers were realized. As a representative example (Figure 1) the polymer produced with the highest carbonate linkages (Table 2, entry 3) displays a main population that corresponds to an almost perfectly alternating structure of carbon dioxide and oxetane, with signals spaced by $m/z = 102$ (Figure 1, red-dotted distribution) corresponding to a sodium-charged PTMC end-capped by two hydroxy groups. Such a structure may be explained by the initiation of the copolymerization from a hydrolyzed oxetane molecule with one more oxetane than CO_2

Table 2. Copolymerization of oxetane and CO_2 catalyzed by different loadings of I_2 /TBD and CO_2 pressure at 105°C. [a]

Entry	catalysts loading/mol%	Time (day)	CO_2 Pressure (MPa)	Con. [b] %	Sele. c. % [b]	M_n SEC [c] $\text{g}\cdot\text{mol}^{-1}$	D_M SEC [c]
1	1.25	1	1.5	53	84	5,070	1.54
2	1.25	3	1.5	76	83	5,340	1.53
3	1.25	3	3	86	90	4,000	1.38
4	1	3	3	78	92	6,500	1.55
5	1	7	3	97	95	4,000	1.60

[a] Copolymerization conditions: 7.88 mmol of oxetane, 105 °C, $[\text{I}_2]_0/[\text{TBD}]_0 = 1$; [b] Conversion of oxetane and selectivity of carbonate linkage were determined from ^1H NMR spectroscopy of product mixture; [c] Determined by SEC in tetrahydrofuran (THF) with polystyrene standard.

detectable while maintaining a high selectivity in the production of TMC monomer. Such lack of copolymerization activity and the unique selectivity towards TMC are probably the result of a strong complexation between the P_4 -*tert*-Bu and the I_2 which suggests that the selective production of



($n = 1$, with n representing the number of pristine oxetane in the copolymer).

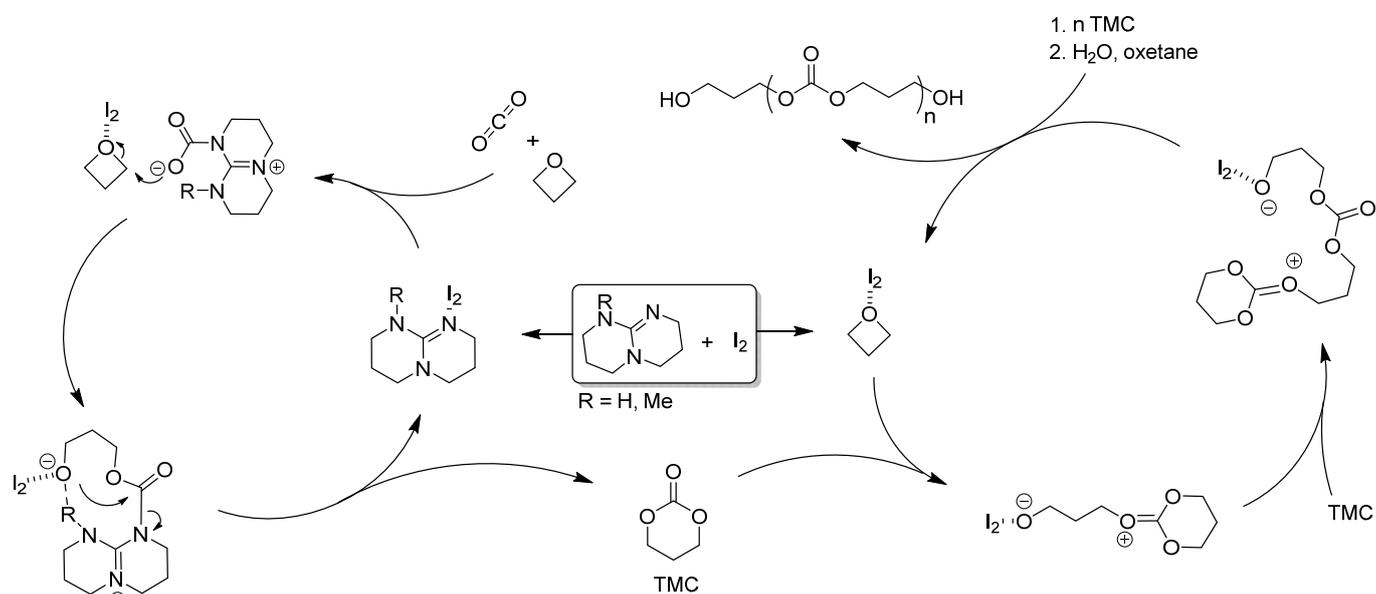
Figure 1. MALDI mass spectrum recorded for sample 3 (Table 2), global mass spectrum (upper) and magnification between $m/z = 2130$ and $m/z = 2450$ (bottom). "m" represents the polymerization degree in TMC and "n" the number of missing CO_2 molecule per structure.

Additionally, other distributions are clearly visible which can be assigned to the same polymer unit but with 2, 3 and 4 molecules of CO_2 'missing' from the polymer chain (Figure 1, bottom, $n = 2$, $n = 3$ and $n = 4$). Notably, the absence of a population that has an equal number of oxetane and CO_2 units may indicate that oxetane is involved in the initiation step of the polymerization.

Scheme 2. First step of copolymerization from CO_2 /oxetane: generation of TMC and oligoetherification of oxetane. Second step of copolymerization from CO_2 /oxetane: generation of copolymer by an "ACE" mechanism.

and initiating steps, polymerization was realized in the

These observations, added to that of the formation of TMC



presence of benzyl alcohol (BnOH) and 1,4-butanediol (BuOH) as potential exogenous initiators. Reactions were performed at 105°C for 24h and for an initial oxetane-to-catalyst-to-initiator molar ratio of 100/2.5/1 (Table S4, entries 1-3). While a slight depression of molar mass of the resultant PTMC was indicated by SEC analysis (down to $3,100\text{ g}\cdot\text{mol}^{-1}$), no trace of incorporated alcohol was observed in the ^1H NMR spectra of the precipitated copolymers (Figure S4), suggesting that exogenous alcohols are only acting as protic sources. To further test this hypothesis, adding 1.25 mol% of exogenous water led to the isolation of oligomers with significantly lower molar mass ($1,000\text{ g}\cdot\text{mol}^{-1}$, $D_M = 1.79$, Table S4, entry 4) which suggests that the limitation of the molar mass can be simply overcome by the application of higher purity CO_2 and that initiation of the polymerization does not involve a nucleophilic source and that exogenous alcohols as well as residual water (mainly present in the CO_2 gas) limits the PTMC molar masses by proton transfer. Inefficiency of the nucleophilic alcohols to end-cap PTMC chains may find origin in their deactivation when they are in presence of both CO_2 and superbase catalysts.⁵⁵

in the process, led us to further investigate the mechanism by which the copolymerisation was occurring, with the aim to elucidate if the copolymers were mainly produced by ring-opening polymerization (ROP) of the TMC produced *in situ* or by a direct copolymerization by "chain up" process involving both oxetane and CO_2 . To this end, the copolymerization was followed by ^1H NMR spectroscopy (Figure 2, Figure S6). After 30 minutes of reaction, both TMC monomer and copolymer

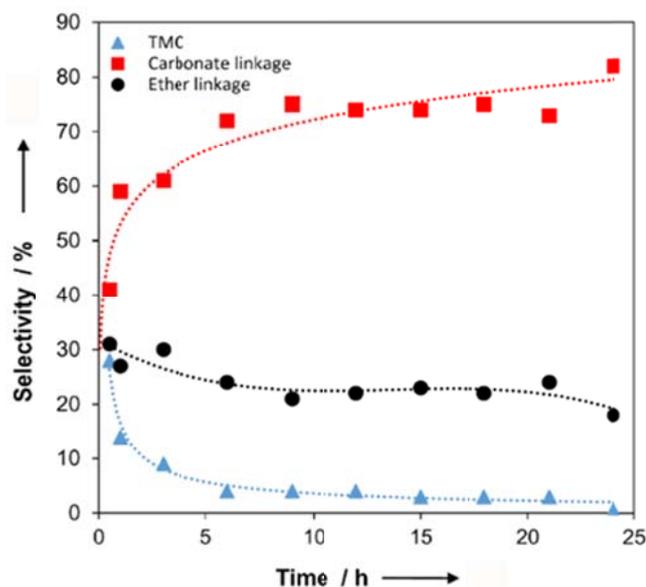


Figure 2. Chart of selectivity of product against time. Conditions of reaction: Copolymerization conditions: 197 μmol of I_2 (2.5 mol%), 7.88 mmol of oxetane, $[\text{M}]/[\text{I}_2]_0/[\text{TBD}]_0 = 40/1/1$, 1 MPa of CO_2 , at 105 $^\circ\text{C}$.

coexist, before the relative quantity of TMC drops and copolymer increases. These observations are in agreement with Darensbourg's observations,⁴⁰ alongside the high selectivity to TMC with the $\text{P}_4\text{-tert-Bu}$ cocatalyst, and suggest that TMC is formed before being polymerized through a secondary catalytic cycle (Scheme 2) to yield PTMC.

Notably, the high quantity of TMC monomer initially produced is accompanied by the presence of oligomers composed by ~ 40 mol% of carbonate that increase throughout the polymerization and ~ 30 mol% ether linkages that decrease throughout the reaction. These observations prompt us to propose a two-step process mechanism in which oxetane is activated by halogen bonding by I_2 while a zwitterionic species is created by activation of CO_2 by the TBD. The electrophilic activation of the oxetane allows it to undergo a nucleophilic attack from the CO_2 -adduct zwitterion thus leading to an alkoxide intermediate that is stabilized by hydrogen bonding from the TBD N-H hydrogen. Finally, TMC is produced from an intramolecular nucleophilic substitution on the carbonyl group. As the CO_2 is in an excess, it is anticipated that free TBD will not be available to initiate ROP of the resulting TMC and instead, an active chain end (ACE) mechanism,⁵⁶ initiated by the I_2 -oxetane adduct operates to produce PTMC, consistent with our observation of I_2 -initiated oxetane ROP. The observation that exogenous alcohols do not act as initiators in the polymerization supports this mechanism.

To support the postulated ACE ROP initiated from the I_2 -oxetane adduct, the ROP of commercially available TMC monomer was undertaken in presence of a freshly prepared 1:1 I_2 /oxetane adduct (Table S5, entry 1), under 1 MPa of nitrogen atmosphere at 105 $^\circ\text{C}$ and from an initial $[\text{TMC}]_0/[\text{I}_2\text{-oxetane adduct}]_0$ of 40. Interestingly, after 24 h, quantitative conversion of the TMC monomer yielded a PTMC with $M_n = 6,000 \text{ g mol}^{-1}$, comparable to that observed from the CO_2 -based polymerization procedure. Interestingly a few percent of

ether linkages were also observed in the polymer by ^1H NMR spectroscopic analysis which could indicate exchange to form an I_2 -TMC adduct or partial decarboxylation of the TMC monomer under these conditions (Figure S5). Notably, only 50 mol% of the initially used adduct were consumed during the polymerization. Increasing the ratio of $[\text{TMC}]_0/[\text{I}_2\text{-oxetane adduct}]_0$ to 80 resulted in a PTMC with $M_n = 10,000 \text{ g mol}^{-1}$ suggesting the initiation capability of I_2 /oxetane adduct in absence of water (Table S5, entry 2). It is worthy to note that no decarboxylation was observed while the experiment was carried out under CO_2 atmosphere (Table S5, entry 3). Importantly, this polymerization proceeds efficiently in the absence of the TBD and hence demonstrates that the base is probably used during the first part of the process only, reinforcing then our hypothetical two-step mechanism.

In conclusion, the synthesis of poly(trimethylene carbonate) is reported through a green route using CO_2 and commercially available organocatalysts. The study reveals that the combination of iodine and the bicyclic guanidine, TBD, provides an efficient synthesis with high carbon dioxide incorporation and a high TOF value under such mild conditions. Mechanistic studies revealed that polymerization most likely proceeds by formation of trimethylene carbonate monomer that is polymerized *in situ* via an activated chain end mechanism, initiated from an I_2 /oxetane adduct. These advances afford a great opportunity to expand the scope of CO_2 utilization in polymer synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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TABLE OF CONTENT ENTRY

The green I_2 /TBD catalytic complex is demonstrated competitive to metal-based systems in the preparation of PTMC through a two-step process mechanism.

