Organocatalytic Ring Opening Polymerization of Trimethylene Carbonate

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Received August 14, 2006; Revised Manuscript Received September 18, 2006

A variety of organocatalysts has been surveyed in the ring opening polymerization of trimethylene carbonate. Excellent control was found for several of these catalysts yielding well-defined polycarbonates with molecular weights up to 50 000 g mol^{-1}, polydispersities below 1.08, and high end-group fidelity. Melt or bulk polymerization was accomplished without loss of control of molecular weight or polydispersity, and random ester−carbonate bulk polymerizations were also demonstrated. Furthermore, by combining disparate polymerization techniques using bifunctional initiators, the mild polymerization conditions allow for the preparation of new block copolymers. Hydrogen-bond activation of monomer and initiator/propagating species is proposed as the underlying mechanism, which can be tuned to mitigate adverse side reactions.

Introduction

Aliphatic polycarbonates are employed in many biomedical applications, owing to their high biocompatibility, facile (bio) degradation, low toxicity, and superior mechanical properties as compared to those of structurally similar polyesters.[1] They can be prepared by chain copolymerization of, for example, diols and carbonates, cyclic ethers, and carbon dioxide as well as by ring opening polymerization (ROP) of suitable cyclic carbonates such as trimethylene carbonate (TMC).[2] For ROP, cationic,[3] anionic,[4] coordination−insertion,[5] and enzyme−catalyst[6] polymerization routes have been described, with moderate success in terms of control over molecular weight, polydispersity (PDI $\geq$ 1.2), and end-group fidelity of the resulting polycarbonates.[2] Side reactions involving decarboxylation, leading to ether formation or carbonate interchanges, are typical. An important aspect for materials with applications in the biomedical field is the use of nontoxic catalysts. Biologically nontoxic magnesium and calcium based complexes have been successfully employed for the ROP of TMC; however, the toxicity of the salen ligands has not been assessed, and polymerization control was limited as judged from the polydispersities of the precipitated polymers ($\sim$1.6).[7] In our own work, we have focused on the development of completely metal-free or organocatalytic ROP of cyclic esters such as lactide, various lactones, and cyclic silyl ethers such as hexamethyltrisiloxane and carbosilanes, motivated primarily by applications for the microelectronics industry.[8] We have investigated known transesterification agents such as 4-dimethylaminopyridine (DMAP),[9] phosphines,[10] *N*-heterocyclic carbenes[11] (NHCs), bifunctional amino−thioureas,[12] and guanidines.[13] NHCs and guanidines were found to be active for the ROP of cyclic silyl ethers as well.[14] Recent advances in the use of organocatalysts to complement or supplant classic organic synthetic methods based on metal-containing reagents have had a significant recent impact, particularly in the development of pharmaceuticals.[15] Application of organocatalysis to the ROP of cyclic carbonates to prepare polymers of predictable molecular weight and narrow polydispersities would be highly desirable. Herein, we report results on the ROP of TMC using several of the organocatalysts in our toolbox such as NHCs, guanidine and amidine bases, and the bifunctional thiourea-tertiary amine system (Scheme 1).

Results and Discussion

We have surveyed a number of organocatalysts for the ROP of TMC (Scheme 1). Two commercially available guanidines, 1.5.7-triazabicyclo-[4.4.0]dec-5-ene (**1**, TBD) (pK_a = 26.0) and 7-methyl-1.5.7-triazabicyclo-[4.4.0]dec-5-ene (**2**, MTBD) (pK_a = 25.5) were investigated together with a structurally similar amidine base 1,8-diazabicyclo[5.4.0]undec-7-ene (**3**, DBU) (pK_a = 24.3).[16] Two selected NHCs with either alkyl or aryl substituents, 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (**4**) (pK_a = 30.4) and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (**5**) (pK_a $\sim$22.0),[17] were also evaluated for the ROP of TMC. Last, the bifunctional thiourea-tertiary amine catalyst (**6**) and catalyst mixture (**7**) were investigated, as they were found to be successful for lactide polymerization. Takemoto et al.[18] have demonstrated the utility of such catalysts in asymmetric synthesis.

Table 1 summarizes the results of the different catalysts polymerizing TMC in solution (2.0 M in methylene chloride) using benzyl alcohol as an initiator and with a targeted degree of polymerization (DP) of 50.

All catalysts surveyed were active for the ROP of TMC, differing mainly in polymerization time. The experimentally measured DPs and number average molecular weight (M_n) closely matched the targeted values with extraordinarily low polydispersities (PDIs) for catalysts **3** and **7**. As a major concern for carbonate polymerization is decarboxylation (leading to ether bond formation), it is noteworthy that for all organocatalysts

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10.1021/bm060795n CCC: $37.00
Published on Web 12/07/2006

Scheme 1. Organocatalysts Surveyed for ROP of TMC Initiated by Benzyl Alcohol

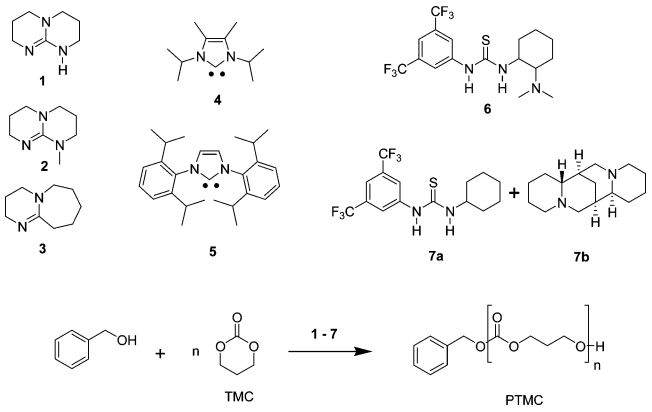


Table 1. Catalyst Screening for Polymerization of TMC

catalyst	target DP	time	conversion (%)	reached DP	PDI
(**1**)[a]	50	15 min	>99	50	1.31
(**1**)[a]	100	60 min	>99	97	1.32
(**1**)[a]	250	360 min	>99	~240	1.32
(**1**)[a]	500	360 min	>99	~420	1.31
(**2**)[a]	50	180 min	>99	48	1.28
(**3**)[a]	50	480 min	>99	51	1.04
(**4**)[b]	50	0.1 min	>99	50	broad >2
(**5**)[b]	50	30 min	>99	49	1.06
(**6**)[c]	50	6 days	88	45	1.09
(**7a**) + (**7b**)[d]	50	720 min	>99	49	1.07

[a] Catalyst concentration was 1 mol % to initiator. [b] Catalyst concentration was 5 mol % to initiator. [c] Catalyst concentration was 10 mol % vs TMC. [d] Catalyst and cocatalyst concentration was 5 mol % to TMC.

surveyed, the ^{1}H− NMR spectra show the desired end-groups and no indication of competitive side reactions. Benzyl carbonate was observed at the α-chain position and gave the same integral value as the respective methylene group adjacent to the hydroxyl at the ω-chain position, indicating a controlled initiation and end-group fidelity (Figure 1). Moreover, using pyrene butanol as an initiator in the presence of DBU, the gel permeation chromatography (GPC) traces from the ultraviolet/visible (UV−vis) and refractive index (RI) detector overlay indicate that pyrene is on the chain end to further confirm end-group fidelity (Figure 1).

To examine the control over the polymerization, the molecular weight was monitored as function of monomer conversion for selected catalysts. A linear correlation between the molecular weight and the monomer conversion for both **3** and **7** is observed, as measured by ^{1}H− NMR (Figure 2). Moreover, the PDI values gradually decrease with increasing conversion and, even at high monomer conversion and/or reaction completion, remain low, even after full conversion of the monomer and standing of the reaction mixture for 3 days. All of these details indicate an absence of molecular scrambling, which otherwise would broaden the molecular weight distribution.

As bulk polymerization provides a commercially suitable pathway and is of great importance from an application point of view, the versatility of the catalysts was examined in conditions requiring no solvents. To avoid auto-initiation, the bulk polymerization was carried out at 65 °C. Compound **3** was used as the catalyst in the presence of benzyl alcohol, and TMC was polymerized within minutes, yielding polymers with controlled molecular weight and end-group fidelity. The PDIs were in general slightly higher (~1.09−1.15) as compared to solution conditions. To demonstrate the living nature of the polymerization under bulk conditions, a chain extension experiment was conducted. Polymerization was initiated from benzyl alcohol for a target DP of 30. After complete monomer conversion, the flask was cooled, and an additional 30 monomer equiv was added and allowed to polymerize (65 °C, 30 min). The cycle was repeated, and the results are shown in Figure 3. Polymer growth proceeded in a linear fashion, and notably, it was proven that the intermediate chains can be employed for further growth, simply by the addition of more monomers. The molecular weight distribution remained narrow, monomodal, and shifted accordingly upon chain extension (PDI from ~1.09−1.15).

Because poly(trimethylene carbonate) (PTMC) only degrades hydrolytically through a surface erosion type mechanism, it would be desirable to tune the degradability by incorporating other monomers via random copolymerization.[19] To this end, we employed δ-valerolactone (VL) as a reactive solvent for TMC using TBD as a catalyst and benzyl alcohol as an initiator. After 2 h at room temperature, the ^{1}H− NMR spectra showed complete monomer conversion, and the polymer composition (50:50 PTMC to polyvalerolactone (PVL)) was identical to the target value. In addition, two types of initiating species were observed, presumably originating from the benzyl ester and benzyl carbonate and suggesting a random structure of the formed polymer. Further support of the sequence distribution was obtained from ^{13}C− NMR (Figure 4), as the carbonyl in both carbonate and ester showed expected shifts due to the existence of predicted dyad sequences: carbonate−carbonate−carbonate, carbonate−carbonate−ester, ester−carbonate−carbonate, ester−carbonate−ester, ester−ester−ester, ester−ester−carbonate, carbonate−ester−ester, and carbonate−ester−carbonate, respectively.[20] The ester dyads were observed upfield relative to the all ester chain and the carbonate dyads observed downfield relative to the all carbonate chain according to previous reports.[21] Moreover, differential scanning calorimetry (DSC) showed a fully amorphous copolymer with only one glass transition temperature (T_g) at about −43 °C, well-matched to the T_g predicted by the Fox equation,[22] and no melting point associated with PVL was observed. Conversely, a DSC analysis of a 50:50 blend of PTMC and PVL homopolymers revealed the respective T_g values of the homopolymers and the melting transition of PVL, indicating immiscibility (Figure 4).

To further demonstrate the versatility of these catalysts for the ROP of TMC and to extend the possible macromolecular architectures, we have prepared a series of block copolymers using disparate polymerization techniques. In recent years, controlled radical polymerization techniques have enabled the preparation of an enormously wide spectrum of possible macromolecular architectures.[23] From both microelectronic and biomedical points of view, metal-free controlled radical polymerization techniques such as nitroxide mediated polymerization (NMP) and reversible addition fragmentation and chain transfer polymerization (RAFT) are clearly the techniques of choice. Hydroxyl-functionalized polymers can be generated by using hydroxyl-functionalized initiators and agents (Scheme 2).[24]

Here, we have used hydroxyl-functionalized polystyrene (PS) and poly(*N*,*N*-dimethylacrylamide) (PDMA) macroinitiators made by NMP,[25] hydroxyl-functionalized poly(methyl methacrylate) (PMMA) and poly(2-vinylpyridine) (P2VP) macroinitiators from RAFT polymerization,[26] and commercially available poly(ethylene oxide) (PEO) for the preparation of PTMC block copolymers using catalyst **7** (Scheme 3).

Catalyst **7** was previously shown to be tolerant to the

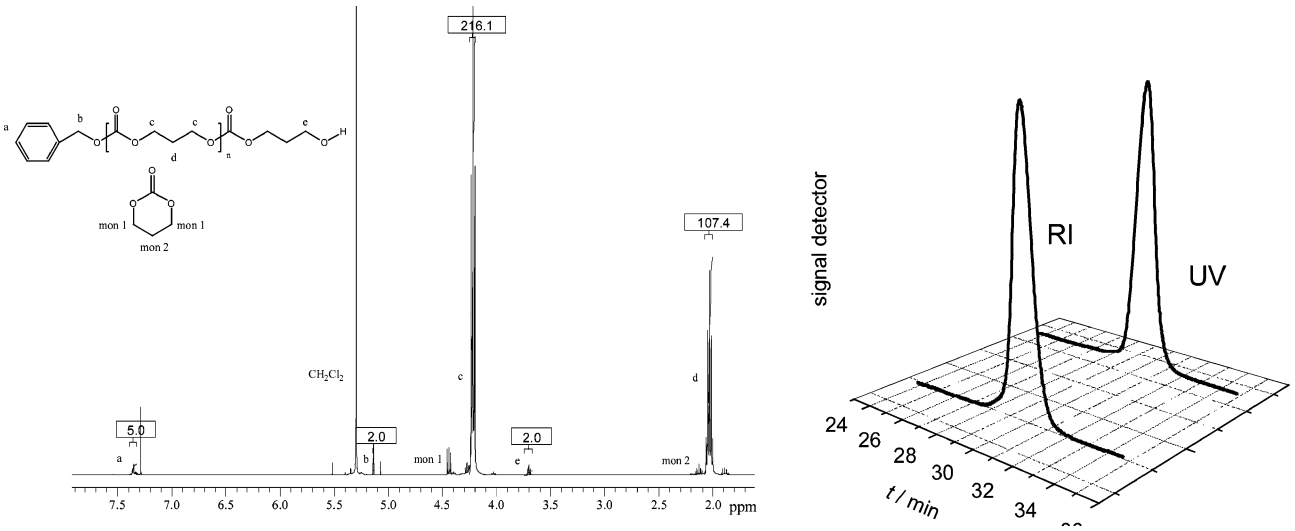


Figure 1. ^{1}H NMR spectrum in $CDCl_3$ of PTMC initiated from benzyl alcohol after 98% conversion (left) and overlay of the GPC traces from the UV and RI detector of a polymerization initiated from pyrene butanol (right).

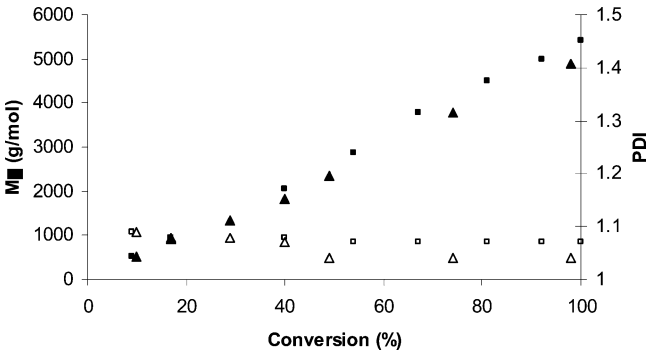


Figure 2. M_n and PDI vs monomer conversion for polymerization of TMC catalyzed with **3** (triangles) and **7** (squares). Open symbols represent the obtained PDIs.

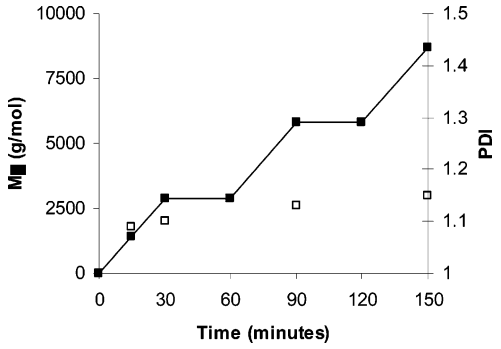


Figure 3. Bulk chain extension experiment. Molecular weight M_n (filled squares) and PDI (open squares) as a function of time.

dithioester chain end of the macroinitiators prepared by RAFT as well as the methyl esters in the backbone of PMMA. The characteristic red color of the macroinitiator is retained throughout the polymerization of TMC by the thiourea systems in contrast to the other catalysts in this study. Successful block copolymerization is evident from Table 2. No macroinitiator residues were found, which points to excellent end-group fidelity of the controlled radical polymerization techniques. Thermal properties were investigated by DSC: two glass transition temperatures indicative of a phase separated microstructure were observed in all cases, except for PDMA−PTMC, which displayed a single glass transition at −12 °C, well in between the T_g values of the constituting homopolymers, which shows the compatibility between PTMC and PDMA blocks.

The organocatalysts used in this study have been proposed to function along different pathways that also reflect upon the polymerization of TMC. Scheme 4 illustrates and summarizes the different modes of action for the different organocatalysts in the ROP of trimethylene carbonate. When comparing the two guanidines and the amidine base (**1**−**3**), polymers synthesized with **1** propagate very rapidly (minutes), whereas **2** and **3** are less active and need a few hours to reach completion. It has previously been shown in the context of ROP of lactide that **1** is capable of acyl transfer reactions.[13] An NMR scale model reaction of ethyl chloroformate and a 2-fold excess of **1** demonstrated that an alkoxycarbonyl group can be transferred to **1** (Scheme 5). The HCl salt of **1** precipitates out of the C_6D_6 solution, leaving the tertiary-urethane Etoc-**1** in solution. The addition of benzyl alcohol results in the formation of the mixed carbonate and regeneration of **1** (Figures S2 and S3). It should further be noted that upon standing of the NMR solution of the mixed carbonate and **1** for 30 min, ether formation was observed.

The NHC catalysts also showed a high activity in the polymerization of TMC. Catalyst **4** needed seconds to reach full conversion, but at the sacrifice of control as evidenced by the broad molecular weight distributions (PDI >2). The high reactivity of catalyst **4** is believed to stem from the high basicity, typical of NHCs with alkyl substituents. The lower activity of catalyst **5** is reflective of the decreased basicity and steric encumberance and was accompanied by a higher level of control as indicated by the narrower molecular weight distribution (PDI ∼1.06). Nucleophilic mechanisms have been demonstrated for the NHCs in a variety of transformations, including benzoin and formoin condensation and Stetter and transesterification reactions.[27] More recently, NHCs have been shown to be strong hydrogen-bond acceptors as well.[28]

The last catalysts surveyed in the polymerization of TMC were the bifunctional thiourea-tertiary amine catalysts. Although **6** and **7** had the highest catalyst loading, they had the lowest polymerization rates and needed 12 h and 6 days, respectively, to reach completion. We have demonstrated that the carbonyl group of lactide is activated by **7a** toward electrophilic attack and that both the initiating as well as the concurrent propagating alcohol is activated by **7b** toward nucleophilic attack.[12] These are results that in the present case translate directly to activation of the TMC carbonyl and propagating alcohol. Hydrogen-bond activation of benzyl alcohol by the various basic catalysts was

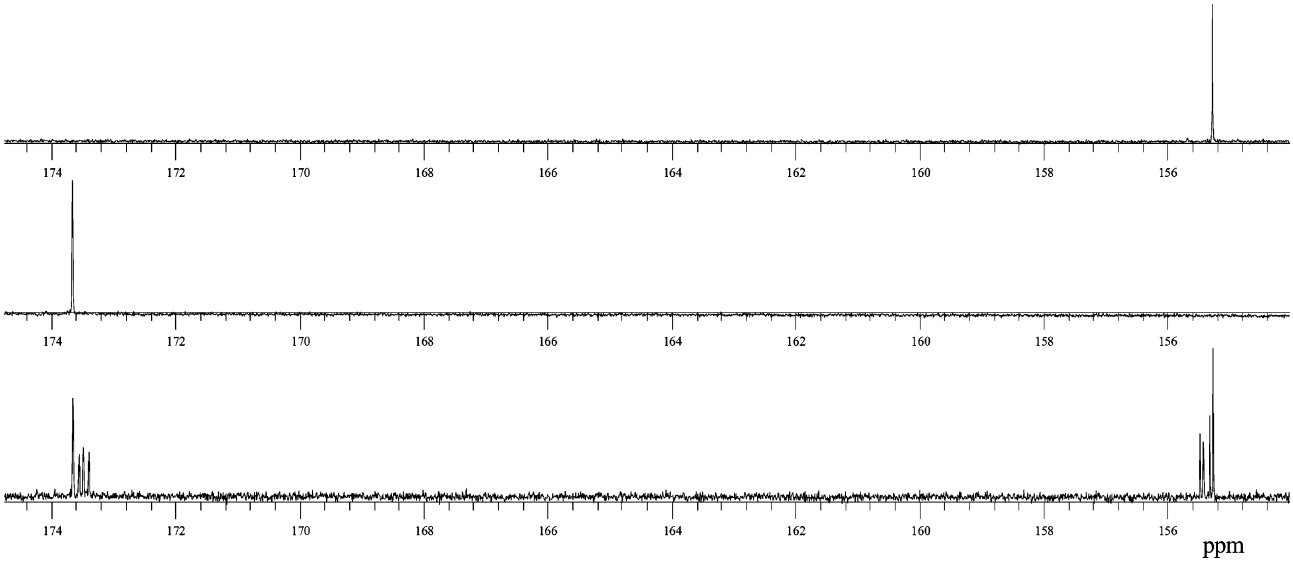
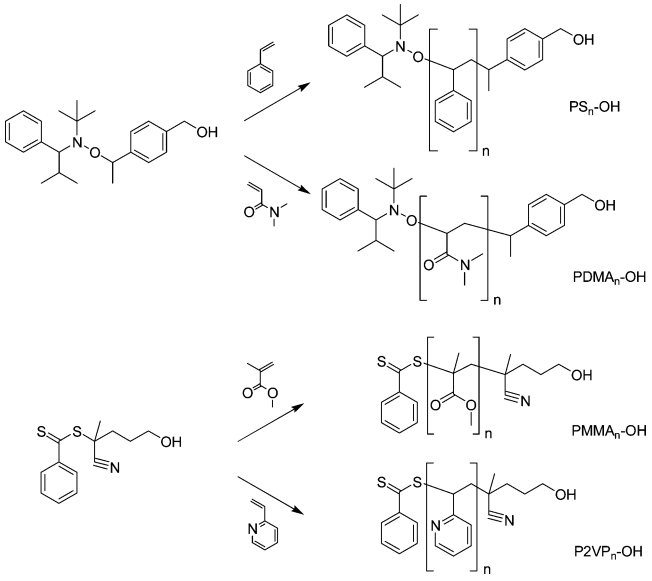
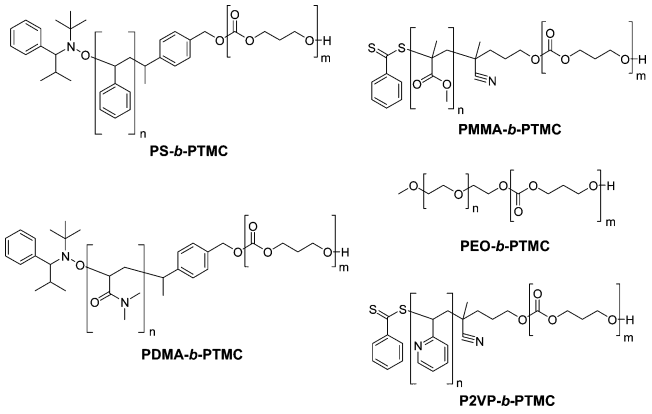


Figure 4. ^{13}C NMR carbonyl region of PTMC, PVL, and PTMC−PVL copolymer.

Scheme 2. Synthesis of Hydroxyl-Functionalized Macroinitiators by NMP and RAFT



Scheme 3. Synthesis of a Variety of PTMC−Block Copolymers Using Catalyst **7**



probed by measuring the proton shift of the hydroxyl of benzyl alcohol in 1:1 complexes, keeping the concentration at 0.05 M in C_6D_6 in all cases (Table 3). A trend is visible between the difference in chemical shift ($\Delta\delta$) and polymerization time. Organocatalyst **4**, which has the highest literature pK_a value, gives the largest downfield shift of the OH proton resonance and has the highest polymerization rate. (−)-Sparteine has the lowest literature pK_a -value, gives the smallest downfield shift and will not polymerize TMC without addition of the thiourea catalyst for simultaneous monomer activation. The only catalyst in Table 3 not following this trend is **3**, for which we currently do not have a satisfactory explanation.

The hydrogen-bonding ability of the thiourea catalyst to the cyclic carbonate monomer was also investigated in more detail. Figure 5 shows the results of a titration of TMC to the thiourea catalyst. The chemical shifts of the NH protons of **7b** change as a function of the TMC/catalyst ratio (Figure 5).

Host−guest NMR analysis software yielded a value of 45 for the association constant at room temperature,[31] which is comparable to other thiourea-carbonyl hydrogen-bonding association constants.[31,32] This clearly demonstrates that the NH protons of the catalyst are involved in hydrogen bonding to the carbonyl of the monomer, and hence, nucleophilic attack is facilitated. In comparison, diethyl carbonate, with a contrasting transoid form to the cisoid conformation of TMC, causes less pronounced shifts for the NH protons, indicating weaker hydrogen bonds to the thiourea. This explains the excellent selectivity of **6** and **7** for cyclic carbonates, the low polydispersity of the obtained polymers, and the absence of adverse carbonate interchange reactions.

Conclusion

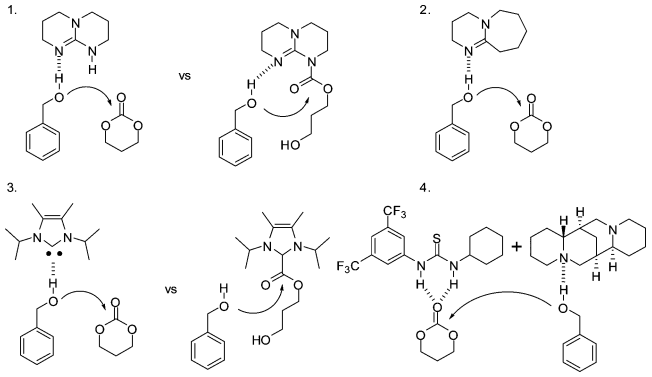
In conclusion, we have extended organocatalytic ROP to a new class of cyclic monomers. This work demonstrates the highly controlled and versatile ability to selectively polymerize TMC using a variety of organic catalysts. Polymerization conditions have been established such that solution and bulk polymerization can afford polymers with a precise molecular weight and narrow molecular weight distributions. TMC was in addition copolymerized using both macro-initiators and comonomers to establish block and random copolymers, demonstrating the ease with which block formation and composition can be tailored. Precision of polymerization, versatility of catalysis, optimization of copolymerization, and the unique biodegradability of the polymer could have a siginificant impact on emerging bioorganic and biomedical applications as well as finding a place in microelectronics.

Table 2. Characterization of Macroinitiators and PTMC Block Copolymers

macroinitiator	[TMC]/[MI][a]	conversion (%)	DP_{PTMC}[b]	M_n[c]	PDI	T_g[d]
PEO_{110}-OH[e]	50	75	40	9500	1.03	−34 °C (PTMC) 52 °C (T_m PEO)
PS_{80}-OH[f]	50	>99	52	21900	1.08	−32 °C (PTMC) 91 °C (PS)
$PDMA_{70}$-OH[g]	50	>99	45	14800	1.06	−12 °C
$PMMA_{140}$-OH[h]	100	>99	102	30800	1.11	−36 °C (PTMC) 107 °C (PMMA)
$P2VP_{90}$-OH[i]	50	>99	50	20200	1.09	−36 °C (PTMC) 77 °C (P2VP)

[a] Targeted degree of polymerization. [b] Experimentally determined degree of polymerization by ^{1}H NMR. [c] Obtained by GPC in THF. [d] Scan rate of 10 °C/min, second heating run. [e] Poly(ethylene oxide) (DP = 125; M_n = 5 kg mol^{-1}; and PDI = 1.03). [f] Polystyrene (DP = 80; M_n = 8.3 kg mol^{-1}; and PDI = 1.07). [g] Poly(*N*,*N*-dimethylacrylamide) (DP = 70; M_n = 7.1 kg mol^{-1}; and PDI = 1.08). [h] Poly(methyl methacrylate) (DP = 140; M_n = 14.5 kg mol^{-1}; and PDI = 1.12). [i] Poly(2-vinylpyridine) (DP = 90; M_n = 9.2 kg mol^{-1}; and PDI = 1.06).

Scheme 4. Various Catalysts and Their Mechanism in the Polymerization of TMC[a]



[a] (1) **1**, (2) **2** or **3**, (3) **4** or **5**, and (4) **6** or **7**.

Scheme 5. Reaction of **1** with Ethyl Chloroformate Followed by Addition of Benzyl Alcohol

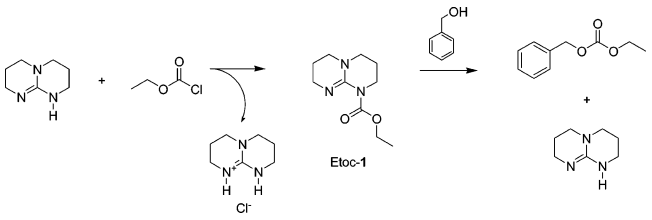


Table 3. Hydrogen-Bonding Shifts of Catalysts Used in Polymerization of TMC

catalyst	δ (ppm)	$\Delta\delta$ (ppm)	pK_a catalyst-H$^+$ (CH_3CN)	pK_a catalyst-H$^+$ (DMSO)	pK_a catalyst-H$^+$ (THF)
1	5.90	4.89	26.0[16]		21.0[29]
2	4.76	3.75	25.5[16]		17.9[29]
3	6.09	5.08	24.3[16]	13.9[16]	16.8[29]
4	9.61	8.60	35.8[17]	24.5[17]	
5	5.22	4.21	28.2[17]	16.8[17]	
sparteine	1.56	0.55	17.5[30]		

Experimental Procedures

Methods and Materials. Reagents were available commercially and used as received unless otherwise noted. Solvents were dried using activated alumina columns. 4-Pyrene-1-butanol was stirred in dry THF with CaH_2, filtered, and freed of solvent in vacuo. Catalysts **6**,[12] 7a,[12] and **1** were dissolved in dry THF, stirred with CaH_2, filtered, and freed of solvent in vacuo. Catalysts **2**, **3**, and benzyl alcohol were twice distilled from CaH_2 under dry N_2 and stored over molecular sieves (3 Å). NHC's **4**[33] and **5**[34] were prepared in a glovebox according to literature procedures. Styrene, methyl methacrylate (MMA), 2-vinylpyridine (2VP), and *N*,*N*-dimethylacrylamide (DMA) were passed through a plug of neutral activated aluminum oxide prior to use and used as such. Technical quality 4,4′-bisazo(4-cyanopentan-1-ol) (containing ~30% water by weight) was bought from Langfang Hawk Ltd. (China) and dissolved in methylene chloride, and the organic layer was separated and dried over $MgSO_4$, filtered, and evaporated in vacuo. The resulting solid was recrystallized twice from methylene chloride/hexanes yielding off-white crystals. The hydroxy-functionalized alkoxyamine, 2,2,5-trimethyl-3-(4′-*p*-hydroxymethylphenylethoxy)-4-phenyl-3-azahexane,[35] for NMP and the hydroxy-functionalized RAFT-agent, 4-cyano-4-((thiobenzoyl)sulfanyl)-pentan-1-ol,[36] were prepared according to literature procedures. Hydroxyfunctional PS and PDMA were prepared by NMP, whereas hydroxyfunctional PMMA[37] and P2VP[38] were prepared by RAFT polymerization according to literature procedures. Macroinitiators from NMP and RAFT polymerizations as well as commercially avaible poly(ethylene oxide) (Fluka) were dried in a vacuum oven and further dried by coevaporation of dry distilled toluene 3 times before transferring to a glovebox for assembly of the ROP reaction. ^{1}H− NMR spectra were obtained on a Bruker Avance 400 instrument at 400 MHz. Gel permeation chromatography was performed in THF using a Waters chromatograph equipped with four 5 μm Waters columns (300 mm × 7.7 mm) connected in series with an increasing pore size (10, 100, 1000, 10^5, and 10^6 Å), a Waters 410 differential refractometer, and a 996 photodiode array detector and calibrated with polystyrene standards (750 −to 2 × 10^6 g mol^{-1}). Differential scanning calorimetry (DSC) was performed using a TA Differential Scanning Calorimeter 1000 that was calibrated using high purity indium at a heating rate of 10 °C/min. Melting points were determined from the second scan following slow cooling (to remove the influence of thermal history) at a heating rate of 10 °C/min.

General Procedure for Polymerization of TMC in Solution. In a glovebox, initiator and catalysts were weighed in stoichiometric amounts and dissolved in dry benzene-d_6 or dry methylene chloride until a clear solution was obtained. The crystalline monomer was dissolved separately in the same solvent and added to the catalyst/initiator solution. Polymerizations were carried out for a given amount of time after which an excess of benzoic acid was added to quench the polymerization by protonating the catalyst. The polymer was collected by precipitation in methanol. Analytical data using benzyl alcohol as initiator: ^{1}H− NMR ($CDCl_3$): δ = 7.35−7.25 (m, 5H, ArH- α-end), 5.12 (s, 2H, $ArCH_2$- α-end), 4.20 (m, 4H, -$H_2COCOOCH_2$- pol), 3.68 (t, 2H, -CH_2-OH ω-end), 2.04 (m, 2H, -CH_2- pol), 1.88 (m, 2H, -CH_2CH_2OH ω-end).

General Procedure for Polymerization of TMC in Bulk. In a glovebox, initiator, catalyst, and trimethylene carbonate were weighed in stoichiometric amounts and charged in a dry Schlenk-flask equipped with a stir bar. Outside the glovebox, the flask was heated to 65 °C using an oil bath. Polymerizations were carried out for a given amount of time after which an excess of benzoic acid was added to quench the polymerization by protonating the catalyst. The polymer was dissolved in methylene chloride and collected by precipitation in methanol. For analytical data using benzyl alcohol as initiator, see previous discussion. For bulk copolymerization, VL was initially used to dissolve TMC. The polymerization was conducted at ambient temperature inside the

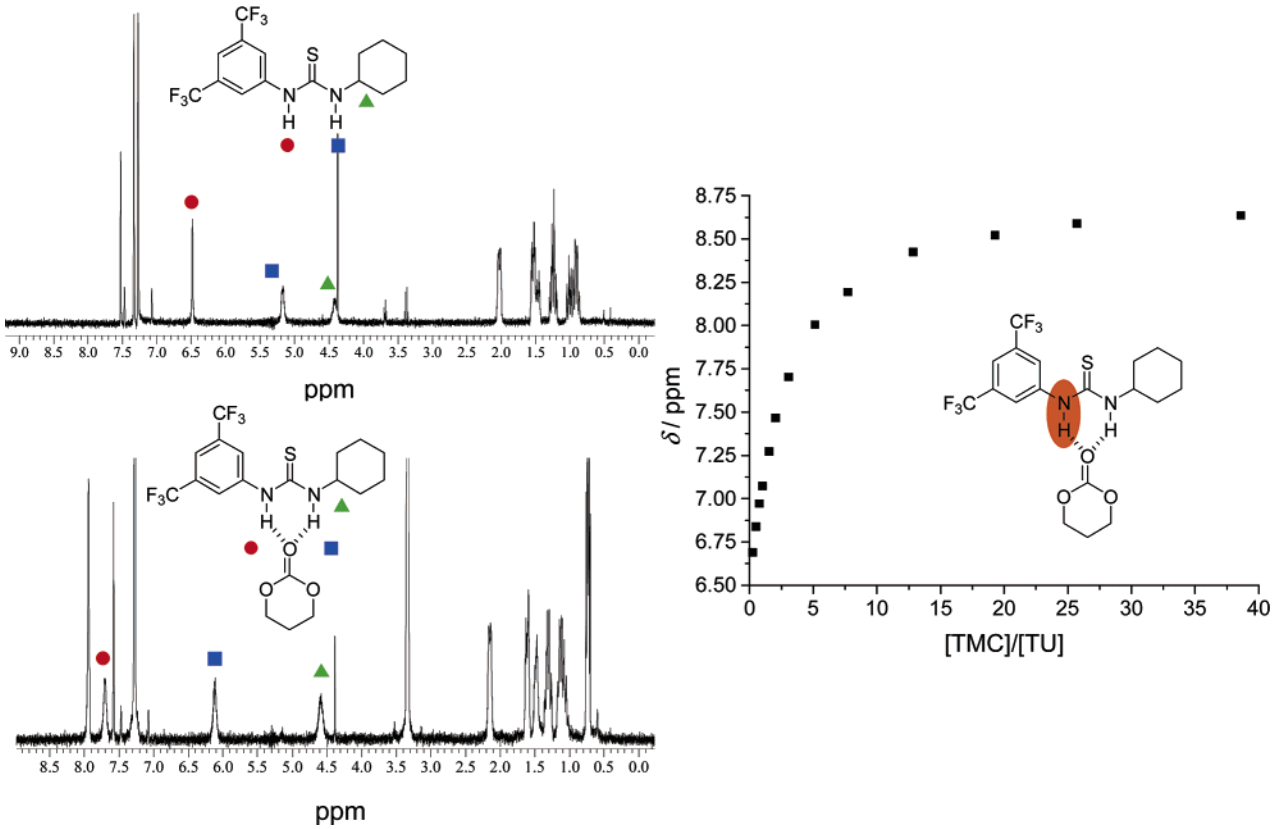


Figure 5. ^{1}H NMR spectrum in C_6D_6 of 3-fold excess of TMC over thiourea showing the shifts of the NH protons at 7.7 and 6.1 ppm (left) and the complete titration curve. Curve-fitting gives a association constant of 45.

glovebox, and the reaction was started by the addition of initiator and catalyst. The polymerization was conducted for a given amount of time, and benzoic acid was added in excess to quench the reaction. The copolymer was collected by precipitation in methanol from a methylene chloride solution. Analytical data using benzyl alcohol as initiator: ^{1}H− NMR ($CDCl_3$): δ = 7.35−7.25 (m, 5H, ArH- α-end), 5.15 (s, 2H, $ArCH_2OCO$- α-end), 5.10 (s, 2H, $ArCH_2OCO$- α-end), 4.25−4.15 (m, 4H, -H $_2COCOOCH_2$- pol), 4.15−4.0 (m, 2H, -H_2COCO- pol), 3.72 (t, 2H, -CH_2OH ω-end), 3.67 (t, 2H, -CH_2OH ω-end), 2.35 (m, 2H, -$OCOCH_2$- pol), 2.04 (m, 2H, -CH_2- pol), 1.80−1.60 (m, 4H, -CH_2CH_2- pol). ^{13}C− NMR ($CDCl_3$) 21.8, 28.3, 28.4, 34.2, 64.3, 64.6, 155.2, 173.6.

Synthesis of Block Copolymers. Poly(ethylene oxide) (100 mg, M_n = 5000 g mol^{-1}, PDI = 1.03), thiourea **7a** (37 mg, 100 μmol), (−)-sparteine (11.2 mg, 50 μmol), and TMC (102 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (1 mL). After 24 h, benzoic acid (20 mg) was added. ^{1}H− NMR ($CDCl_3$): δ = 4.50−4.42 (m, ∼160H; OC(═O)-OCH_2 PTMC, $OCH_2CH_2OC(═O)O$), 3.92−3.48 (m, ∼440H; $CH_2CH_2O_{PEO}$, CH_2OH), 3.37 (s, 3H; OCH_3), 2.16 (m, ∼80H; $CH_2CH_2CH_2$ PTMC). GPC (RI): M_n (PDI) = 9500 g mol^{-1} (1.03). Polystyrene (160 mg, M_n = 8300 g mol^{-1}, PDI = 1.07), **7** (37 mg, 100 μmol), (−)-sparteine (11.2 mg, 50 μmol), and TMC (102 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (1 mL). After 24 h, benzoic acid (20 mg) was added. ^{1}H− NMR ($CDCl_3$): δ = 7.47−6.32 (m, ∼400H; $H_{aromatic}$, C_6H_5 PS), 5.17−5.12 (m, 3H; HC−ON, $PhOCH_2$), 4.44−4.07 (m, ∼200H; $OC(═O)OCH_2$ PTMC, ON−-CH), 3.50−0.53 (m, ∼360H; CH_2 PS, CH PS, CH_3 ini, CH_3CHCH_3, $C(CH_3)_3$), $CH_2CH_2CH_2$ PTMC, CH_3CHCH_3, CH_3CHCH_3). GPC (RI): M_n (PDI) = 21 900 g mol^{-1} (1.08). Poly(*N*,*N*-dimethylacrylamide) (140 mg, M_n = 7000 g mol^{-1}, PDI = 1.07), **7a** (37 mg, 53 μmol), (−)-sparteine (11.2 mg, 50 μmol), and TMC (102 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (1 mL). After 24 h, benzoic acid (20 mg) was added. ^{1}H− NMR ($CDCl_3$): δ = ^{1}H− NMR ($CDCl_3$): δ = 7.24−7.06 (m, 9H; $H_{aromatic}$), 5.22−5.08 (m, 3H; HC−-ON, $PhOCH_2$), 4.53−4.41 (m, ∼180H; $OC(═O)OCH_2$ PTMC), 3.22−0.42 (m, ∼740H; $N(CH_3)_2$ PDMAA, CH_2 PDMAA, CH PDMAA, ON−-CH, CH_3 initiating fragment, CH_3CHCH_3, $CH_2CH_2CH_2$ PTMC $C(CH_3)_3$), CH_3CHCH_3, CH_3CHCH_3). GPC (RI): M_n (PDI) = 14 800 g mol^{-1} (1.06). Poly(methyl methacrylate) (140 mg, M_n = 14 500 g mol^{-1}, PDI = 1.12), **7a** (37 mg, 53 μmol), (−)-sparteine (11.2 mg, 50 μmol), and TMC (102 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (1 mL). After 24 h, benzoic acid (20 mg) was added. ^{1}H− NMR ($CDCl_3$): δ = 7.83 (b, 2H; $H_{2,6\ aromatic\ RAFT}$), 7.63 (b, 1H; $H_{4\ aromatic\ RAFT}$), 7.48 (b, 2H; $H_{3,5\ aromatic\ RAFT}$), 4.50−4.40 (m, ∼400H; $OC(═O)OCH_2$ PTMC), 3.59−3.51 (bs, ∼420H; OCH_3 PMMA), 2.22−2.04 (m, ∼50H; $CH_2CH_2CH_2$ PTMC), 1.95−0.78 (m, ∼905H; CH_2 PMMA, CH_3 PMMA, $H_{aliphatic\ RAFT}$). GPC (RI): M_n (PDI) = 30 800 g mol^{-1} (1.11). Poly(2-vinylpyridine) (90 mg, M_n = 9200 g mol^{-1}, PDI = 1.06), thiourea catalyst **7a** (37 mg, 100 μmol), (−)-sparteine (11.2 mg, 50 μmol), and TMC (102 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (0.8 mL). After 24 h, benzoic acid (20 mg) was added to the orange viscous reaction mixture. ^{1}H− NMR ($CDCl_3$): δ = 8.53−6.12 (m, ∼365H; $H_{aromatic\ RAFT}$, $H_{aromatic\ P2VP}$), 4.48−4.40 (m, ∼200H; $OC(═O)OCH_2$ PTMC), 2.22−0.51 (m, ∼375H; $CH_2CH_2CH_2$ PTMC, $H_{aliphatic\ RAFT}$, $H_{aliphatic\ P2VP}$). GPC (RI): M_n (PDI) = 20 200 g mol^{-1} (1.09).

^{1}H NMR Experiments. Determination of K_{ass} by Titration of TMC to Thiourea 7a. A total of 1.8 mg of thiourea catalyst **7a** was dissolved in 605 μL of C_6D_6 and transferred to an NMR tube. A stock solution of 27.3 mg of TMC in 2.013 mL of C_6D_6 was prepared. After the addition of an aliquot of this TMC−stock solution to the thiourea-containing NMR tube, a ^{1}H− NMR-spectrum was taken. In total, 13 points were obtained (see Figure S1). The following successive aliquots of stock solution were added: 10, 10, 10, 10, 20, 20, 40, 80, 100, 200, 250, 250, and 500 μL. In another experiment, 27.0 mg of diethyl carbonate and 2.1 mg of thiourea catalyst **7a** were dissolved in 0.7 mL of C_6D_6 (50-fold excess). The NH protons of the thiourea shifted from 5.20 to 5.80 and from 6.67 to 7.27 ppm, respectively, which is significantly less than the shifts observed in the titration experiment described previously.

1:1 Mixtures of Organocatalyst with Benzyl Alcohol. A stock solution of 0.05 M benzyl alcohol (28.0 mg) in C_6D_6 (4.5 mL) was prepared. This stock solution was transferred to seven different vials containing the different organocatalysts and a blank to determine the shift of the OH proton in the absence of any catalyst; subsequently,

they were transferred to seven NMR tubes. The following quantities were used: 5.1 mg of **1**, 5.8 mg of **2**, 5.8 mg of **3**, 6.7 mg of **4**, 14.4 mg of **5**, and 8.3 mg of **7b**.

Model Reaction. A total of 14.0 mg of **1** was dissolved in 0.5 mL of C_6D_6. A total of 5.0 mg of ethylchloroformate in 0.25 mL of C_6D_6 was added with stirring. A precipitate formed immediately and was filtered off. The mother solution was measured by ^{1}H− NMR, and an intermediate, presumably Etoc-**1** could be observed. ^{1}H− NMR (C_6D_6): δ = 4.32 (q, 2H; OC*H*$_2$CH$_3$), 3.61 (m, 4H; C*H*$_2$NC(═O), C*H*$_2$N═C), 2.64 (t, 2H; NC*H*$_2$CH$_2$CH$_2$NC(═O)), 2.47 (t, 2H; NC*H*$_2$-CH$_2$CH$_2$N═C), 1.61 (quint, 2H; NCH$_2$C*H*$_2$CH$_2$NC(═O)), 1.39 (quint, 2H; NCH$_2$C*H*$_2$CH$_2$N═C), 1.22 (t, 3H; OCH$_2$C*H*$_3$). To this solution, a 3-fold excess of benzyl alcohol was added and besides peaks for TBD and benzyl alcohol, the mixed carbonate (i.e., benzylethylcarbonate) could be observed. ^{1}H− NMR (C_6D_6): δ = 5.06 (s, 2H; PhC*H*$_2$), 3.98 (q, 2H; OC*H*$_2$CH$_3$), 1.02 (t, 3H; OCH$_2$C*H*$_3$). See also Figures S2 and S3.

Acknowledgment. Debbi Price and Boehringer-Ingelheim are gratefully acknowledged for kindly donating the trimethylene carbonate monomer. NSF-CPIMA and NSF-GOALI are acknowledged for funding, and Teddie Magbitang and Dolores Miller (IBM Almaden Research Center) are thanked for analytical support. John Logan (San Jose State University) and Al Nelson (IBM Almaden Research Center) are thanked for helpful discussions and help with the NMR software. F.N. acknowledges the Swedish Research Council (VR) for financial support.

Supporting Information Available. DSC curves representing PTMC, PVL, PTMC−PVL copolymer, and PTMC/PVL blend, ^{1}H NMR spectrum in C_6D_6 of the reaction product of **1** and ethylchloroformate after 15 min at room temperature, and ^{1}H NMR spectrum of benzylethylchloroformate after reaction of the compound in Figure S2 with excess benzyl alcohol. This material is available free of charge via the Internet at http://pubs.acs.org.

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BM060795N