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Aliphatic Polycarbonates Produced from the Coupling of Carbon Dioxide and Oxetanes and Their Depolymerization via Cyclic Carbonate Formation

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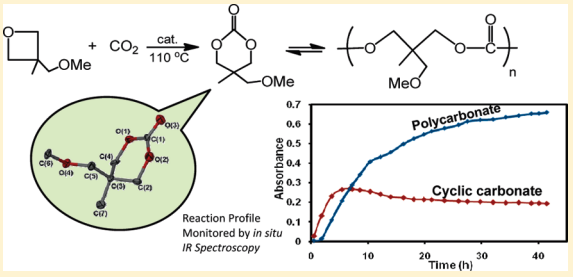
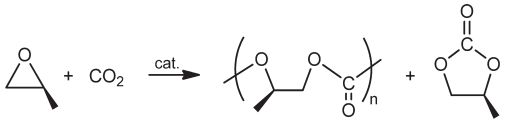
Supporting Information

ABSTRACT: The (salen)CrCl/onium salt catalyzed coupling reactions of several oxetane derivatives and carbon dioxide are reported. The oxetanes investigated contain substituents in the 3-position covering a range of steric requirements. The oxetanes examined include, 3,3-dimethyloxetane, 3-methoxymethyl-3-methyloxetane, and 3-benzyloxymethyl-3-methyloxetane. The rates of reaction of these oxetanes with CO_2 were found to be significantly slower than the corresponding process with the parent oxetane monomer. Furthermore, in these instances the formation of copolymer was found to proceed via the preformed cycloaddition product, i.e., the six-membered cyclic carbonate, to a greater extent and increasing with the steric bulk of the substituents on oxetane. For these sterically more hindered oxetanes, the CO_2 coupling reaction carried out in toluene at 110 °C reached an equilibrium product distribution of copolymer to cyclic carbonate which increased in cyclic carbonate product with increasing steric requirements of the oxetane monomer. For example, the catalyzed coupling of the parent oxetane and CO_2 provides a copolymer to cyclic carbonate ratio of greater than 95%, whereas the corresponding product distribution for 3-benzyloxymethyl-3-methyloxetane was observed to be 60%. The catalytic rate of depolymerization of a purified sample of the copolymer afforded from 3-benzyloxymethyl-3-methyloxetane and CO_2 to the corresponding cyclic carbonate, 5-benzyloxymethyl-5-methyl-1,3-dioxan-2-one, was found to be greatly retarded when carried out in an atmosphere of CO_2.



INTRODUCTION

Four-membered cyclic ethers, oxetanes, have been underutilized because of their commercial inaccessibility and laborious synthesis. Nevertheless, these small molecules are currently receiving much attention in medicinal chemistry and drug delivery studies.[1] Our interest in these cyclic ethers is their ability to react with carbon dioxide to provide polycarbonates.[2] These studies were inspired by the numerous successful catalytic systems investigated for the coupling of oxiranes and CO_2 to yield an array of polycarbonate materials.[3] Equations 1 and 2 illustrate these processes, which are generally carried out at modest pressures of carbon dioxide, i.e., < 3.0 MPa.



(1)

(2)

Although the five-membered cyclic carbonates formed from epoxides and CO_2 are thermodynamically more stable than the corresponding polycarbonate, ring-opening polymerization (ROP) of six-membered cyclic carbonates readily occurs to provide its polycarbonate counterpart with complete retention of carbon dioxide.[4] In previous studies, we have addressed this issue by examining the copolymerization of oxetane with carbon dioxide to determine the origin of the polycarbonate, i.e., whether it is afforded by alternating enchainment of the comonomers CO_2/oxetane or the ROP of initially formed trimethylene carbonate (Scheme 1).[5]

For catalyst systems comprised of (salen)CrCl complexes in the presence of onium salt initiators, the reaction can be tuned to proceed selectively via the route involving the ROP of preformed trimethylene carbonate. This was achieved by the judicious choice of onium salt and reaction conditions of temperature and pressure. In this manner, polycarbonates are afforded which contain only trace quantities of ether linkages in the copolymer backbone. As indicated in eq 2 in most instances the copolymerization of oxetane and CO_2 provides small quantities of trimethylene carbonate (TMC) as a coproduct. This observation suggests that the free energy change associated with the ROP of

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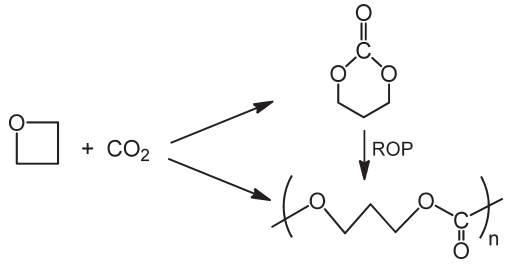
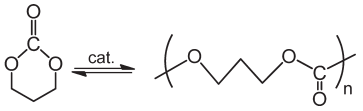
Scheme 1



TMC to poly(TMC), although negative, is not very large in magnitude. Hence, it should in principle be able to depolymerize these polycarbonates into their monomer units, six-membered cyclic carbonate, under suitable reaction conditions (eq 3).[6]



(3)

Herein we wish to explore other four-membered cyclic ether monomers for the synthesis of copolymers from carbon dioxide, thereby generating other polycarbonates with different properties.

EXPERIMENTAL SECTION

Reagents and Methods. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon filled glovebox. Toluene and tetrahydrofuran were freshly distilled from sodium/benzophenone. Ethanol and methanol were freshly distilled from Mg/I_2. Diethyl ether, dichloromethane, and hexanes were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. 1,1,2,2-tetrachloroethane (TCE) (TCI) was freshly distilled over CaH_2. 3-Methyl-3-oxetanemethanol (Alfa Aesar) was used as received. Triethylamine was freshly distilled over CaH_2 before use. Ethyl chloroformate (Aldrich), diethyl methylmalonate (Alfa Aesar), *n*-butyllithium (Aldrich), lithium aluminum hydride (Alfa Aesar), chloromethyl methyl ether (Aldrich), sodium hydride (60% in mineral oil) (Alfa Aesar), dimethyl sulfate (Alfa Aesar), potassium hydroxide (EMD), ethylenediamine (Aldrich), 1,2-phenylenediamine (ACROS), chromium(II) chloride (Alfa Aesar), sodium hydroxide (EMD), sodium sulfate (EMD), and magnesium sulfate (EMD) were used as received. Tetra-*n*-butylammonium azide was stored in the freezer of the glovebox upon arrival. Bone-dry carbon dioxide supplied in a high-pressure cylinder and equipped with a liquid dip tube was purchased from Scott Specialty Gases. The corresponding salen ligands and chromium complexes were synthesized as described in the literature.[7]

^{1}H NMR spectra were acquired on Unity+ 300 MHz and VXR 300 MHz superconducting NMR spectrometers. Molecular weight determinations (M_n and M_w) were carried out with Viscotek Modular GPC apparatus equipped with ViscoGEL I-series columns (H + L), and Model 270 dual detector comprised of RI and Light Scattering detectors. High-pressure reaction measurements were performed using an ASI ReactIR 1000 reaction analysis system with stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo).

Synthesis of 3-Methoxymethyl-3-methyloxetane. This derivative of oxetane was prepared according to the procedure reported by McAlees with some modifications.[8] A solution of 3-methyl-3-oxetanemethanol (50 g, 0.489 mol) in THF (~100 mL) was added via syringe to a suspension of sodium hydride (23.5 g, 60% in mineral oil) in THF (1 L) that was previously cooled to 0 °C using an ice/water bath. After the reaction mixture was allowed to warm to room temperature, the solution was stirred for 24 h. Dimethyl sulfate (86.4 g, 0.685 mol) was added dropwise (exothermic reaction) via syringe to the reaction solution that was previously cooled to 0 °C using an ice/water bath. After warming the solution to room temperature, the mixture was stirred for 24 h at ambient temperature. A solution of sodium hydroxide (30 g in 50 mL of water) was then added, and most of the THF was removed by distillation. The residue was extracted with diethyl ether, and the ether extract was dried over Na_2SO_4 and vacuum distilled to give 3-methoxymethyl-3-methyloxetane (MMO) (36 g, 63.3%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.45 (d, 2H, OCH_2), 4.30 (d, 2H, OCH_2), 3.40 (s, 2H, CH_2), 3.35 (s, 3H, OCH_3), 1.26 (s, 3H, CH_3).

Synthesis of 3-Benzyloxymethyl-3-methyloxetane. A benzene solution (50 mL) of 3-methyl-3-oxetanemethanol (20 g, 0.20 mol) and benzyl bromide (33.5 g, 0.20 mol) was stirred with 50% sodium hydroxide aqueous solution (80 mL) and tetra-*n*-butylammonium bromide (9.5 g 0.03 mol). After stirring for 2 days at room temperature, the organic layer was collected and the organic solvent was removed. The desired product was afforded as a colorless liquid in 70% yield (27.1 g) after distillation under reduced pressure. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.24 (m, 5H, −Ar), 4.58 (s, 2H, $-CH_2-$Ar), 4.54 (d, 2H, $-OCHH_2$), 4.37 (d, 2H, $-OCHH_2$), 3.53 (s, 2H, CH_2), 1.34 (s, 3H, CH_3).

Synthesis of 2-Methoxymethyl-2-methyl Malonic Acid Diethyl Ester. This compound was prepared according to the procedure reported by Doherty.[9] A tetrahydrofuran solution (40 mL) of diethyl methylmalonate (5 g, 0.0287 mol) was cooled to −78 °C and treated with a 1.64 M solution of *n*-butyllithium in hexanes (17.5 mL, 0.0287 mol). The resulting mixture was stirred rapidly and after warming to room temperature, was transferred dropwise *via* cannula to a tetrahydrofuran solution (30 mL) of chloromethyl methyl ether (2.9 g, 0.0287 mol). After the reaction solution was stirred overnight, the solvent was removed under vacuum and the residue extracted into diethyl ether (2 × 30 mL), washed with water (2 × 30 mL), dried over $MgSO_4$, filtered, and the solvent was removed to afford the desired ester as a pale yellow/colorless oil in 80% yield (5.02 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.13 (quart, 4H, J = 7.0 Hz, CH_2CH_3), 3.66 (s, 2H, CH_2), 3.28 (s, 3H, OCH_3), 1.42 (s, 3H, CH_3), 1.19 (t, 6H, J = 7.1 Hz, CH_2CH_3).

Synthesis of 2-Benzyloxymethyl-2-methyl Malonic Acid Diethyl Ester. In a similar manner to that above, a tetrahydrofuran solution (40 mL) of diethyl methylmalonate (5 g, 0.0287 mol) was cooled to −78 °C and treated with a 2.5 M solution of *n*-butyllithium in hexanes (11.5 mL, 0.0287 mol). The mixture was stirred and after warming to room temperature, was transferred dropwise *via* cannula to a tetrahydrofuran solution (35 mL) of chloromethoxymethylbenzene (4.50 g, 0.0287 mol). After being stirred overnight, the solvent was removed under vacuum and the residue extracted into diethyl ether (2 × 30 mL), washed with water (2 × 30 mL), dried over $MgSO_4$, and filtered. The solvent was removed to afford the product as a colorless oil in 96% yield (8.14 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.24 (m, 5H, −Ar), 4.54 (s, 2H, $-CH_2-$Ar), 4.18 (q, 4H, $-CH_2CH_3$), 3.81 (s, 2H, CH_2), 1.53 (s, 3H, CH_3), 1.23 (t, 6H, $-CH_2CH_3$).

Synthesis of 2-Methoxymethyl-2-methyl-1,3-propanediol. This compound was prepared according to the procedure reported by Doherty.[9] A solution of 2-methoxymethyl-2-methyl malonic acid diethyl ester (5 g, 0.0229 mol) in tetrahydrofuran (20 mL) was added dropwise via cannula to a stirred suspension of $LiAlH_4$ (4.36 g, 0.115 mol) in tetrahydrofuran (80 mL), at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 4 h.

After cooling to 0 °C, the resulting suspension was diluted with diethyl ether (100 mL) and quenched by addition of water (10 mL), followed by KOH (2.8 g in 10 mL of water), and finally water (10 mL), and stirred for 1 h. After hydrolysis was complete, the resulting mixture was filtered and the solids were washed with diethyl ether (2 × 25 mL). The organic fractions were combined, and dried over $MgSO_4$, and the solvent was removed to afford 2-methoxymethyl-2-methyl-1,3-propanediol as a colorless oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (d, 2H, J = 10.7 Hz, OCH_2), 3.54 (d, 2H, J = 10.7 Hz, OCH_2), 3.37 (s, 2H, CH_2), 3.33 (s, 3H, OCH_3), 0.79 (s, 3H, CH_3).

Synthesis of 2-benzyloxymethyl-2-methyl-1,3-propanediol. A tetrahydrofuran solution (30 mL) of 2-benzyloxymethyl-2-methylmalonic acid diethyl ester (8.14 g, 0.0277 mol) was added dropwise via cannula to a stirred suspension of $LiAlH_4$ (5.25 g, 0.138 mol) in tetrahydrofuran (100 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After cooling to 0 °C, the resulting suspension was diluted with diethyl ether (100 mL) and quenched by addition of water (10 mL), followed by KOH (3 g in 1 0 mL of water), and finally water (10 mL), and stirred for a further 1 h. After hydrolysis was complete, the resulting mixture was filtered and the solids were washed with diethyl ether (2 × 25 mL). The organic fractions were combined, and dried over $MgSO_4$. The solvent was removed to afford 2-benzyloxymethyl-2-methyl-1,3-propanediol as a white solid in 87% yield (5.06 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.28 (m, 5H, −Ar), 4.52 (s, 2H, $-CH_2$Ar), 3.70 (d, 2H, $-OCHH_2$), 3.61 (d, 2H, $-OCHH_2$), 3.47 (s, 2H, CH_2), 2.39 (m, 2H, OH), 0.83 (s, 3H, CH_3).

Synthesis of 5-Methoxymethyl-5-methyl-1,3-dioxan-2-one. This compound was synthesized according to the procedure reported by Endo for the synthesis of trimethylene carbonate with a slight modification.[10] Triethylamine (21.4 g, 0.211 mol) was added dropwise via syringe to a solution of 2-methoxymethyl-2-methyl-1,3-propanediol (13.5 g, 0.100 mol) and ethyl chloroformate (21.7 g, 0.201 mol) in 700 mL of THF at 0 °C over a period of 30 min. The reaction mixture was stirred overnight at room temperature. The precipitated triethylamine hydrochloride salt was isolated by filtration, and the filtrate was concentrated under vacuum. The oily residue was vacuum distilled to afford 5-methoxymethyl-5-methyl-1,3-dioxan-2-one as colorless oil. After a period of several months colorless crystals grew and were successfully analyzed by X-ray crystallography. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.27 (d, 2H, OCH_2), 4.02 (d, 2H, OCH_2), 3.31 (s, 3H, OCH_3), 3.28 (s, 2H, CH_2), 1.03 (s, 3H, CH_3).

Synthesis of 5-Benzyloxymethyl-5-methyl-1,3-dioxan-2-one. Triethylamine (5.11 g, 0.05 mol) was added dropwise via syringe to a solution of 2-benzyloxymethyl-2-methyl-1,3-propanediol (5.06 g, 0.0241 mol) and ethyl chloroformate (5.25 g, 0.0483 mol) in 50 mL of tetrahydrofuran at 0 °C over a period of 30 min. The reaction mixture was stirred overnight at ambient temperature. The precipitated triethylamine hydrochloride salt was removed by filtration, and the filtrate was concentrated under vacuum. Colorless oil of 5-benzyloxymethyl-5-methyl-1,3-dioxan-2-one (3.85 g, 70%) was afforded after chromatography purification (EA:hexane = 1:1, $R_f \sim 0.45$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42−7.26 (m, 5H, −Ar), 4.53 (s, 2H, CH_2−Ar), 4.36 (d, 2H, $-OCHH_2$), 4.07 (d, 2H, $-OCHH_2$), 3.41 (s, 2H, CH_2), 1.11 (s, 3H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 148.17, 137.38, 128.34, 127.86, 127.49, 73.86, 73.48, 71.01, 32.92, 17.32. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found C, 66.14; H, 7.04.

Substrate Binding and Ring-Opening Step Examined by Infrared Spectroscopy. 3-methoxymethyl-3-methyloxetane binding and ring-opening step studies were examined by solution infrared spectroscopy. The catalytic system used in these studies was a (salen)$Cr^{III}Cl$ (50 mg) complex (*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine chromium(III) chloride) in the presence of n-Bu_4NN_3 as cocatalyst and using TCE as the solvent (4 mL).

X-ray Structural Studies. Single crystals of (salen)Cr(III)-Cl·oxetane (complex **6**) were obtained by layering hexanes into a saturated dichloromethane solution of the corresponding (salen)Cr(III)Cl complex (*N*,*N*′-bis(3-methoxy-5-*tert*-butylsalicylidene)-1,2-phenylenediimine chromium(III) chloride) containing 20 equiv of MMO. Single crystals of 5-methoxymethyl-5-methyl-1,3-dioxan-2-one were isolated after several months.

For both structures, a Bausch and Lomb 10× microscope was used to identify suitable crystals. Each crystal was coated in paratone, affixed to a nylon loop, and placed under streaming nitrogen (110 K) in a Bruker-D8 Adv GADDS X-ray diffractometer. Space group determinations were made on the basis of systematic absences and intensity statistics. Both crystal structures were solved by direct methods and were refined by full-matrix least-squares on F^2. All hydrogen atoms were placed in idealized positions and refined with fixed isotropic displacements parameters equal to 1.2 (1.5 for methyl protons), times the equivalent isotropic displacements parameters of the atoms to which they were attached. All non-hydrogen atoms were refined with anisotropic displacement parameters.

The following are the programs that were used: data collection and cell refinements; FRAMBO Version 4.1.05 (GADDS),[11] data reductions; SAINTPLUS Version 6.63,[12] absorption correction; SADABS,[13] structural solutions; SHELXS-97,[14] structural refinement; SHELXL-97;[15] molecular graphics and preparation of material for publication; SHELXTL, version 6.14,[16] and X-Seed, version 1.5.[17]

General Procedure for Copolymerization Reactions of 3-methoxymethyl-3-methyloxetane and CO_2. In a typical experiment, the appropiate amount of catalyst, cocatalyst (n-Bu_4NN_3), and 4 g of MMO were delivered via the injection port into a 300 mL stainless steel Parr autoclave reactor that was previously dried in vacuo overnight at 80 °C. The autoclave was then pressurized with 3.5 MPa of CO_2 and the temperature was increased to 110 °C. The monomer:catalyst:cocatalyst ratio was maintained at 275:1:2, and the reaction was run for the corresponding reaction time. After the reaction was stopped, the autoclave was put into ice, cooled down to 10 °C, and vented in a fume hood. The percent conversion to products was determined based on the amount of oxetane monomer left in the reaction solution as ascertained by ^{1}H NMR in $CDCl_3$:MMO: δ 4.45 (d, 2H, OCH_2), 4.30 (d, 2H, OCH_2), 3.40 (s, 2H, CH_2), 3.35 (s, 3H, OCH_3), 1.26 (s, 3H, CH_3). Furthermore, the quantities of 5-methoxymethyl-5-methyl-1,3-dioxan-2-one, polycarbonate, and ether linkages in the copolymer were determined by integrating the peak area of the corresponding resonances in $CDCl_3$: Polycarbonate: δ 4.07 (s, 4H, OCH_2), 3.31 (s, 3H, OCH_3), 3.26 (s, 2H, CH_2), 1.0 (s, 3H, CH_3), cyclic carbonate: δ 4.27 (d, 2H, OCH_2), 4.02 (d, 2H, OCH_2), 3.31 (s, 3H, OCH_3), 3.28 (s, 2H, CH_2), 1.03 (s, 3H, CH_3), and ether linkages: δ 0.9 (s, 3H, CH_3), with other resonances being obscured by the intense polymer signals.

Copolymerization Reaction Monitored by *in situ* IR Spectroscopy. In a typical experiment, the appropiate amount of complex **5a**, cocatalyst, (n-Bu_4NN_3), and oxetane monomer (8 g) were dissolved in 6 mL of toluene and delivered via the injection port into a 300 mL stainless steel Parr autoclave reactor that was previously dried in vacuo overnight at 80 °C. The monomer:catalyst:cocatalyst ratio was maintained at 150:1:2. The autoclave is modified with a 30 bounce SiComp window to allow for the use of an ASI ReactIR 1000 system equipped with a MCT detector. In this manner a 128-scan background spectrum was collected after the reaction mixture was heated to 110 °C. The autoclave was pressurized with 3.5 MPa of CO_2, and the infrared spectrometer was set to collect one spectrum every 3 min the corresponding reaction time. Profiles of the absorbance at 1750 cm^{-1} (polymer) and at 1770 cm^{-1} (cyclic carbonate) with time were recorded after baseline correction. After the reaction was stopped, the autoclave was cooled down to room temperature and vented in a fume hood. The reaction solution was analyzed by ^{1}H NMR spectroscopy in the same manner as

above, to determine the percent conversion to products, and the percentages of polycarbonate, cyclic carbonate, and ether linkages.

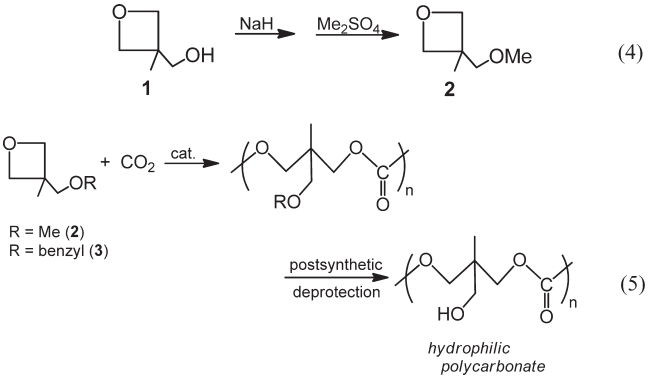
Depolymerization of Poly(3-benzyloxymethyl-3-methyloxetane carbonate). Poly(3-benzyloxymethyl-3-methyloxetane carbonate) (60 mg, 0.25 mmol), (*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine chromium(III) chloride (3 mg, 0.005 mmol), and *n*-Bu_4NN_3 (2.8 mg, 0.01 mmol) were dissolved in 2.4 mL of *d*-toluene in the glovebox and transferred into a J. Young NMR tube (1.2 mL). The tube was evacuated at liquid nitrogen temperature and refilled with argon or CO_2. The tube was placed in a 110 °C oil bath and the reaction was monitored by ^{1}H NMR spectroscopy.

Polymerization of Poly(3-benzyloxymethyl-3-methyloxetane carbonate) from 5-Benzyloxymethyl-5-methyl-1,3-dioxan-2-one. 5-Benzyloxymethyl-5-methyl-1,3-dioxan-2-one (60 mg, 0.25 mmol), (*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine chromium(III) chloride (3 mg, 0.005 mmol), and *n*-Bu_4NN_3 (2.8 mg, 0.01 mmol) were dissolved in 2.4 mL of *d*-toluene in the glovebox and transferred into a J. Young NMR tube (1.2 mL). The tube was placed in a 110 °C oil bath and the reaction was monitored by ^{1}H NMR spectroscopy.

Statistical Deconvolution of FTIR Spectra. FTIR spectra were deconvoluted using Peakfit, version 4.12 (Peakfit for Windows, v. 4.12; SYSTAT Software Inc., San Jose, CA, 2003). Statistical treatment was a residuals method utilizing a combination Gaussian−Lorentzian summation of amplitudes with a linear baseline and Savitsky-Golay smoothing.

RESULTS AND DISCUSSION

The oxetane, 3-methyl-3-oxetane methanol (**1**), is commercially available and can be readily converted to the corresponding methoxy or *O*-benzyl derivatives. Derivatization of **1** prior to copolymerization with CO_2 is required in order to avoid rapid chain transfer reactions between the growing polymer chain and the alcoholic monomer, thereby prohibiting polymer formation. For example, depronation of **1** with NaH in mineral oil followed by the treatment with dimethyl sulfate generated 3-methoxymethyl-3-methyl oxetane (MMO) (**2**) in 63% yield (eq 4).[8] In subsequent postsynthetic modification of these copolymers via deprotection of the −OH function it is possible to prepare hydrophilic polycarbonates (eq 5).[18,19]



The corresponding six-membered cyclic carbonates can be prepared from the respective 1,3-propanediol with ethylchloroformate in the presence of stoichiometric quantities of triethylamine.[10] For example, 5-methoxymethyl-5-methyl-1,3-dioxan-1-one (**4**), was prepared from 2-methoxymethyl-2-methyl-1,3-propanediol and its structure was confirmed by X-ray crystallography. Figure 1 contains a thermal ellipsoid drawing of **4** with a list of selected bond distances and bond angles provided in Table 1.

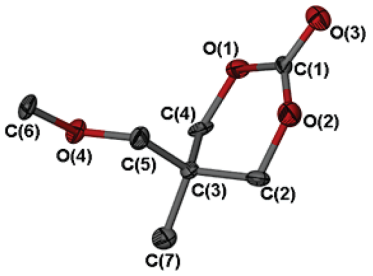


Figure 1. Thermal ellipsoid plot of 5-methoxymethyl-5-methyl-1,3-dioxan-2-one. Ellipsoids are at the 50% level. H atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for 5-Methoxymethyl-5-methyl-1,3-dioxan-2-one[a]

O(1)−C(1)	1.357(12)
O(3)−C(1)	1.187(12)
O(1)−C(4)	1.460(12)
O(4)−C(6)	1.418(13)
O(3)−C(1)−O(1)	118.3(10)
O(2)−C(1)−O(1)	119.7(9)
C(2)−C(3)−C(4)	105.6(8)
C(5)−O(4)−C(6)	111.4(8)

[a] Units of bond angles and bond distances are deg and Å, respectively.

As illustrated in Figure 2 the oxetane monomer and products from the coupling reactions of monomer **2** with carbon dioxide are easily accounted for using ^{1}H NMR spectroscopy. In this instance the relative quantities of copolymer along with any accompanying ether linkages and cyclic carbonate can be assessed by integrating the areas under the peaks of the corresponding resonances at 1.00, 0.90, and 1.03 ppm, respectively. *In situ* infrared monitoring of the reaction's progress can be achieved by observing the growth of the carbonyl vibrations of the copolymer and cyclic carbonate in a mixture of toluene and oxetane monomer at 1750 and 1770 cm^{-1}, respectively.

We present here copolymerization studies of oxetane derivatives and CO_2 employing the (salen)CrCl/onium salt catalyst systems utilized in our previous investigations (Figure 3). Initially complex **5a** in the presence of *n*-Bu_4NN_3 was used to examine the selectivity and catalytic activity for copolymer formation from the coupling of monomer **2** and carbon dioxide. The copolymerization reactions were performed under identical reaction conditions, i.e., 110 °C, 3.5 MPa CO_2 pressure, and the monomer:catalyst:cocatalyst ratio was maintained at 275:1:2. The results of this study are summarized in Table 2. The product mixtures were analyzed by ^{1}H NMR spectroscopy, with quantities of copolymer, cyclic carbonate and ether linkages in the copolymer determined by integrating the proton resonances at 1.00, 1.03, and 0.90 ppm, respectively. As is readily evident from Table 2, the yield of copolymer greatly exceeds the cyclic carbonate in all instances. It should also be pointed out that the reaction occurs on a much slower time scale than the oxetane/CO_2 process and results in a much greater amount of cyclic carbonate product at high conversion.[2,5] 100% CO_2 content corresponds to a *completely alternating* copolymer with *no* ether linkages; i.e., it represents the maximum allowable CO_2 content in the copolymer. Some researchers prefer to define a completely alternating copolymer with a CO_2 content of 50%.

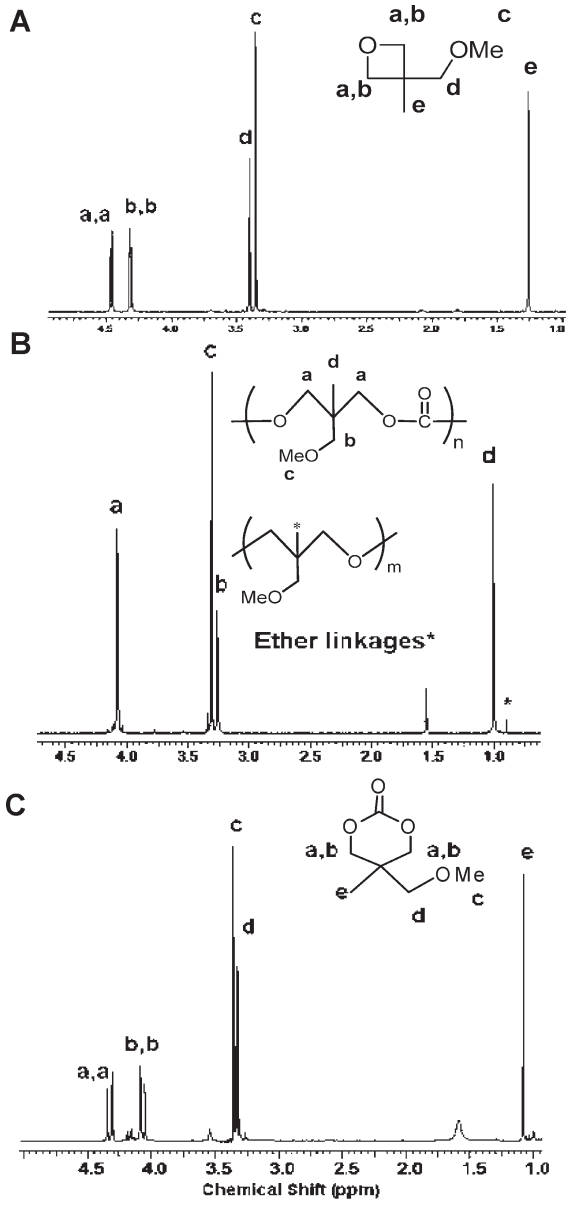
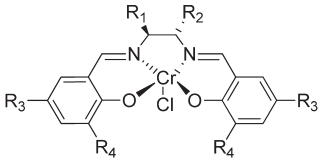


Figure 2. ^{1}H NMR in $CDCl_3$ of (A) MMO, (B) polycarbonate obtained from MMO and CO_2, and (C) cyclic carbonate.

In subsequent studies, the effects of altering the nature of the substituents on the phenolate rings and the diimine backbone of the salen ligand in the (salen)CrCl complex on the reactivity and selectivity of the coupling reaction of **2** and CO_2 were examined. The results of this investigation are summarized in Table 3. As noted in Table 3, upon retaining the phenylene backbone of the diimine while changing the substituents in the 3,5-positions of the phenolate groups (entries 1 and 2 in Table 3) reveals the Cr(III) salen derivative containing the bulky di-*tert*-butyl groups to be more active. This is consistent with previous observations reported for the copolymerization of oxetane and CO_2 catalyzed by the (salen)CrCl catalyst system.[2,5] On the other hand, for the copolymerization of cyclohexene oxide and CO_2 catalyzed by chromium salen complexes, higher catalytic activity was obtained in complexes containing methoxy and *tert*-butyl groups in the 3 and 5 positions of the phenolate rings.[20] We have also studied the



Complex **5a**: $R_1 = R_2 = H$; $R_3 = R_4 = t$-Bu
5b: $R_1, R_2 = -C_4H_4-$; $R_3 = R_4 = t$-Bu
5c: $R_1, R_2 = -C_4H_4-$; $R_3 = OMe$; $R_4 = t$-Bu
5d: $R_1, R_2 = (1R,2R)-C_4H_8-$; $R_3 = R_4 = t$-Bu

Figure 3. Structures of the (salen)Cr^{III} chloride complexes utilized as catalysts for the copolymerization of oxetanes and CO_2.

effects of altering the diimine backbone of the Cr(III) salen complex while maintaining the di-*tert*-butyl groups in the 3,5-positions of the phenolate moiety (entries 3 and 4, Table 3). As is seen in Table 3, the catalytic behavior of the chromium salen complexes is greatly affected by changing the diimine backbone from cyclohexylene to ethylene, with the chromium salen complex with the ethylene backbone displaying higher catalytic activity. This is most likely due to the flexibility imparted to the chromium salen complex by the ethylene backbone compared to the cyclohexylene backbone. Hence, binding of a bulkier oxetane to the chromium center would be more feasible. It is important to point out that the percentage of CO_2 incorporation in the copolymers was lower than the typical CO_2 fixation observed in polycarbonates obtained from oxetane and CO_2 catalyzed by the (salen)CrCl catalytic system. In general, the observed M_n values were found to be significantly lower than the theoretical value. For example, an observed M_n value for the copolymer afforded in entry 3 of Table 3 of 11 400 is considerably lower than the anticipated value of 34 000. This is thought to be due to a chain transfer mechanism arising from the presence of trace quantities of water in the system.[21−23] The polydispersity indices were general around 1.30.

Substrate Binding and Ring-Opening Studies. Since oxetane monomers containing substituents in the 3-position are sterically more encumbering than oxetane, a comparative study of the binding of monomer **2** with that of the parent oxetane to the Cr(III) center in (salen)CrCl was conducted employing infrared spectroscopy.[2c] For this investigation complex **5a** in the presence of 2 equiv of *n*-Bu_4NN_3 was utilized, where the ν_{N_3} stretching vibrations provide accessible probes for both binding and ring-opening steps. The results of this study are depicted in Scheme 2 and Figure 4.

As indicated in Scheme 2, upon addition of 2 equiv of *n*-Bu_4NN_3 to (salen)CrCl in weakly coordinating tetrachloroethane solvent, the anionic six-coordinate bis(azide) species (salen)$Cr(N_3)_2^-$ readily forms at ambient temperature. This is apparent in the ν_{N_3} stretching region with the appearance of an infrared band at 2047 cm^{-1} with a shoulder at 2057 cm^{-1}. It should be noted here that the *n*-Bu_4N^+ salt of (salen)$Cr(N_3)_2^-$ anion has been fully characterized by X-ray crystallography.[2c,24] Addition of 100-fold excess of 3-methoxymethyl-3-methyloxetane to the bis(azide) complex displaces some of the azide anion as seen by an increase in the ν_{N_3} absorption of the free azide ion concentration at 2009 cm^{-1}, with a concomitant decrease in the concentration of (salen)$Cr(N_3)_2^-$ (yellow line, Figure 4). Moreover, a new ν_{N3} stretching band appears at 2061 cm^{-1} which is assigned to (salen)$Cr(N_3)\cdot$oxetane. Upon stirring of this reaction mixture for 24 h at ambient temperature, no significant changes in the infrared spectrum resulted, indicative of the ring-opening

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Table 2. Copolymerization of 3-Methoxymethyl-3-methyloxetane (MMO) and CO_2 Catalyzed by Complex 5a in the Presence of *n*-Bu_4NN_3 at Various Reaction Times[a]

time (days)	% polycarbonate	% cyclic carbonate	% CO_2 content	% conversion
1	77.6	22.4	75.4	23.3
2	85.4	14.5	73.6	52.7
3	85.7	14.2	87.6	76.7

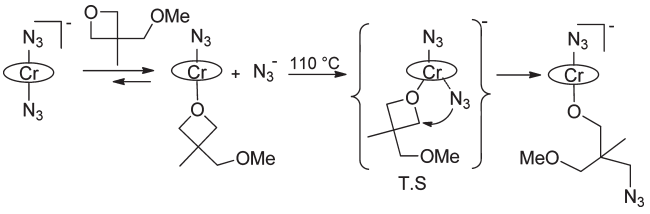
[a] Copolymerization conditions: Catalyst loading = 0.012 mol %, 4 g of MMO, 2 equiv of *n*-Bu_4NN_3, M/I = 275, 3.5 MPa of CO_2, at 110 °C. Percent conversion to products, product distributions, and % of CO_2 content were determined by ^{1}H NMR spectroscopy.

Table 3. Copolymerization of 3-Methoxymethyl-3-methyloxetane (MMO) and CO_2 Catalyzed by (salen)$Cr^{III}Cl$ Complexes.[a]

entry	complex	R_1	R_2	R_3	R_4	% poly carbonate[b]	% cyclic carbonate[b]	% CO_2 content[b]	% conversion[b]
1	**5b**	$-C_4H_4-$		*tert*- butyl	*tert*- butyl	87.3	12.7	80.5	42.4
2	**5c**	$-C_4H_4-$		OCH_3	*tert*- butyl	85.1	14.9	64.3	38.3
3	**5a**	H	H	*tert*- butyl	*tert*- butyl	85.7	14.2	87.6	76.7
4	**5d**	(1*R*,2*R*)-C_4H_8-		*tert*- butyl	*tert*- butyl	84.1	15.9	81.6	37.2

[a] Copolymerization conditions: Catalyst loading = 0.012 mol %, 4 g of MMO, 2 equiv of *n*-Bu_4NN_3, M/I = 275, 3.5 MPa of CO_2, at 110 °C for 3 days. [b] Percent conversion to products, product distributions, and % of CO_2 content were determined by ^{1}H NMR spectroscopy.

Scheme 2. Ring-Opening Step of MMO Catalyzed by (salen)$Cr(N_3)_2^-$



process of MMO requiring higher temperatures. Indeed, heating the reaction mixture at 110 °C led to oxetane ring-opening by azide as indicated by the organic azide band at 2100 cm^{-1}. After the reaction solution was heated for 24 h at 110 °C, the main infrared stretching band observed was that of organic azide. It should be noted that an analogous experiment employing oxetane as monomer, led to oxetane ring-opening by azide at 110 °C after only 3 h.[2c] Hence, these results indicate that the ring-opening of monomer **2** by azide is much slower than that of the parent oxetane. This is consistent with 3-methoxymethyl-3-methyloxetane being more sterically hindered than oxetane. Additionally, the presence of electron donating substituents on the 3-position of trimethylene oxide electronically retards the ring-opening step.

X-ray crystallography was utilized in conjunction with the ν_{N_3} infrared spectral data (*vide supra*) to verify that MMO binding to the chromium center occurs without ring-opening at ambient temperature, similar to what was observed for the oxetane monomer.[2b] X-ray quality single crystals of the adduct (complex **6**) formed between complex **5c** and monomer **2** were isolated from a hexanes layered saturated dichloromethane solution of **5c** and a 20-fold excess of **2**. A thermal ellipsoid representation of complex **6** is depicted in Figure 5, with selected bond distances and bond angles listed in Table 4. This clearly shows that the sterically encumbering 3-methoxymethyl-3-methyloxetane monomer is capable of strongly binding to the (salen)Cr(III) center prior to ring-opening. Noteworthy is the observation that the Cr−O(oxetane) bond distances in the parent oxetane and the 3-methoxymethyl-3-methyloxetane

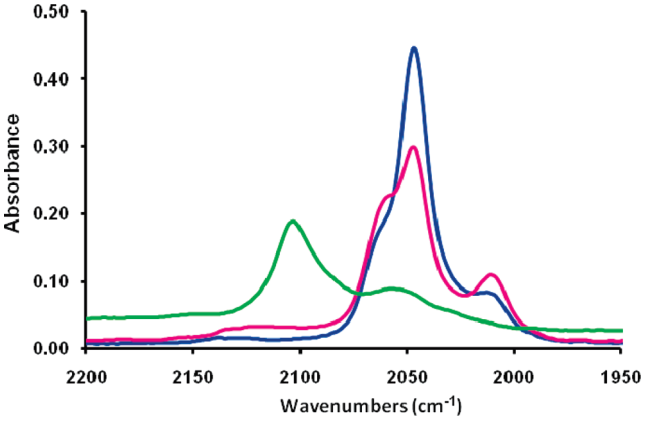


Figure 4. Spectra of TCE solutions of chromium salen chloride complex with 2 equiv of *n*-Bu_4NN_3 (blue line), after addition of 100 equiv of MMO at ambient temperature and stirred for 3 h (pink line), and after stirring the reaction solution at 110 °C for 24 h (green line).

derivatives do not differ significantly, i.e., 2.0492 (11) and 2.056 (8) Å, respectively.

Copolymerization of 2 and Carbon Dioxide Monitored by *in situ* IR Spectroscopy. Figure 6 shows the reaction profiles of both copolymer and cyclic carbonate formation for the copolymerization reaction of MMO and CO_2 carried out at 110 °C and 3.5 MPa in the presence of complex **5a** along with 2 equiv of *n*-Bu_4NN_3. It is clearly observed under these reaction conditions that the formation of cyclic carbonate is enhanced over the formation of copolymer during the early stages of the coupling reaction, followed by a slow decrease in cyclic carbonate concentration over time. Concomitantly, the formation of polycarbonate is initially inhibited, followed by rapid copolymer production over the remaining course of the reaction. These results are consistent with formation of copolymer at least in part via ring-opening of the preformed cyclic carbonate and the presence of an equilibrium between the cyclic carbonate and the copolymer products which only slightly favors the copolymer product at equilibrium. Importantly, the percentage of copolymer in the product mixture is about 80% at 110 °C based on the assumption

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Table 4. Selected Bond Distances and Angles for Complex 6[a]

Cr(1)−Cl(1)	2.297(3)
Cr(1)−O(1)	2.056(8)
Cr(1)−O(5)	1.920(6)
O(1)−C(1)−C(2)	94.5(8)
O(1)−C(3)−C(2)	94.4(8)
C(3)−C(2)−C(1)	78.9(9)
C(3)−O(1)−C(1)	89.6(10)

[a] Units for bond distances and bond angles are Å and deg, respectively.

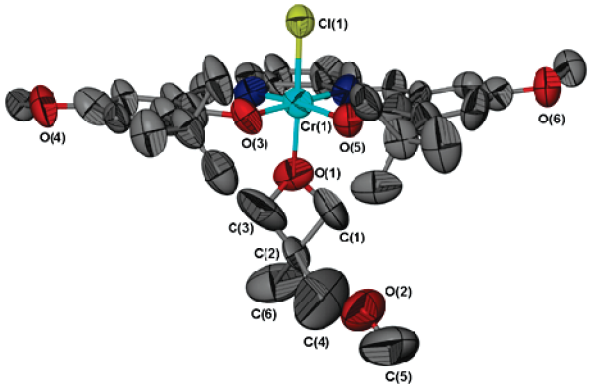


Figure 5. Thermal ellipsoid plot of complex **6**. Ellipsoids are at the 50% level.H atoms are omitted for clarity.

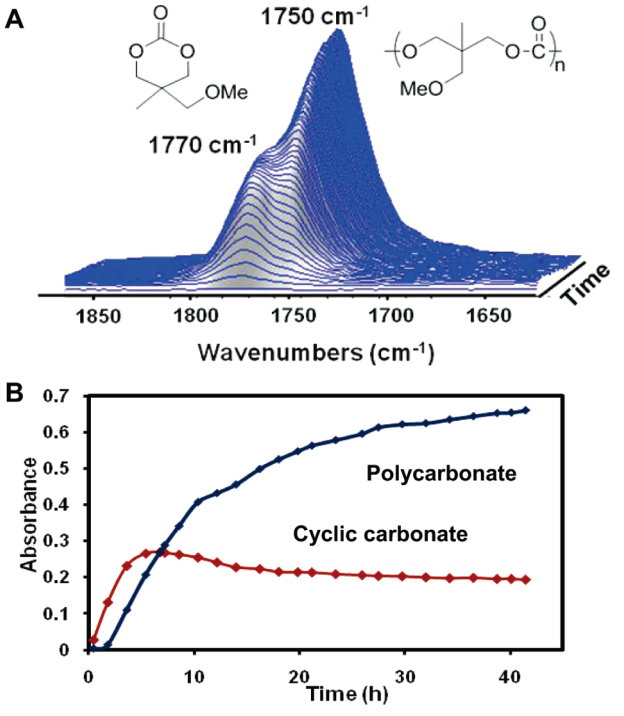


Figure 6. (A) Three-dimensional stack plot of IR spectra collected every 3 min during the copolymerization reaction of MMO and CO_2. (B) Reaction profiles obtained after deconvolution of selected IR spectra, indicating copolymer and cyclic carbonate formation with time.

that the extinction coefficients for the $\nu_{c=o}$ vibrations in the two products are similar. This observation in turn is consistent with more definitive quantification of the product distribution based

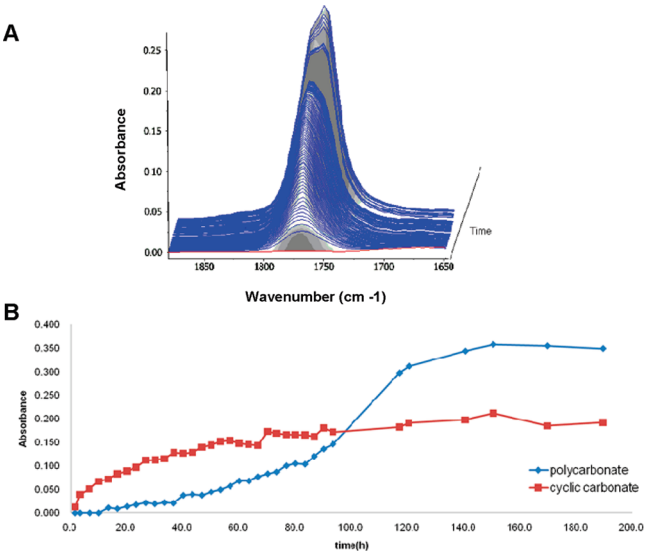
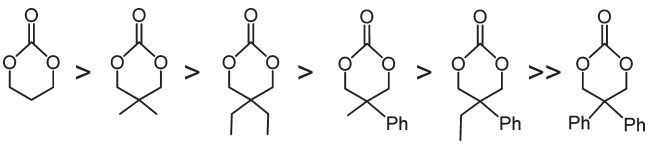


Figure 7. (A) Three-dimensional stack plot of IR spectra collected every 3 min during the copolymerization reaction of 3-benzyloxymethyl-3-methyloxetane and CO_2. (B) Reaction profiles obtained after deconvolution of selected IR spectra, indicating copolymer and cyclic carbonate formation with time. Reaction carried out at 110 °C in toluene, at 3.5 MPa of CO_2 pressure, in the presence of complex **5a** and 2 equiv of *n*-Bu_4NN_3.

on ^{1}H NMR experiments as presented in Table 2. It is also to be noted here that the product apportionment is much more in favor of the copolymer (>95%) for the reaction involving CO_2 and the parent oxetane monomer.[2]

On the other hand, the coupling reaction of CO_2 with the sterically more bulky oxetane, 3-benzyloxymethyl-3-methyloxetane (**3**), afforded an equilibrium distribution of copolymer to cyclic carbonate of about 60% at 110 °C. The reaction profiles for the production of copolymer and cyclic carbonate from the coupling of monomer **3** and CO_2 are illustrated in Figure 7. These observations strongly suggest that the steric requirements of the substituents on the 3-position of oxetane govern the relative stabilities of the cyclic carbonate and polycarbonate afforded from CO_2 and oxetanes. Consistent with these qualitative observations is the data reported in Figure 8 for the reaction between 3,3-dimethyloxetane and carbon dioxide carried out under similar catalytic conditions as those in Figure 6. In this instance the equilibrium product distribution was observed to be 88% in favor of copolymer. Hence, the equilibrium distribution of copolymer to cyclic carbonate produced from the coupling of oxetanes and CO_2 was found to decrease in the order: oxetane >3,3-dimethyloxetane >3-methoxymethyl-3-methyloxetane >3-benzyloxymethyl-3-methyloxetane. A similar observation was reported by Endo and co-workers when examining the ring-opening polymerization of a series of six-membered cyclic carbonates.[6] In the study by Endo and co-workers the order of percent conversion of cyclic carbonate to polycarbonate was:



We have initiated an investigation of the equilibrium process in reaction 6 as catalyzed in toluene by complex **5a** in the presence

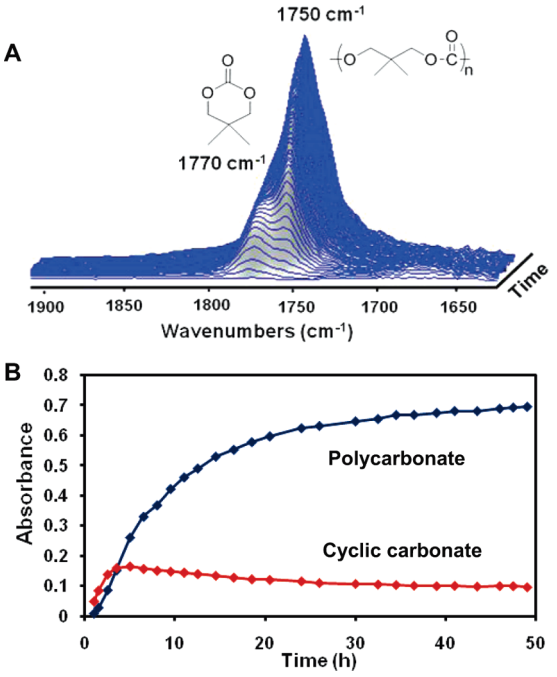
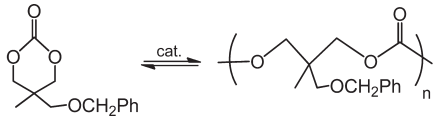


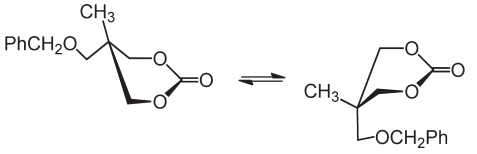
Figure 8. (A) Three-dimensional stack plot of IR spectra collected every 3 min during the copolymerization reaction of 3,3-dimethyloxetane and CO_2. (B) Reaction profiles obtained after deconvolution of selected IR spectra, indicating copolymer and cyclic carbonate formation with time. Reaction carried out at 110 °C in toluene, at 3.5 MPa of CO_2 pressure, in the presence of complex **5a** and 2 equiv of *n*-Bu_4NN_3.

of two equivalents of *n*-Bu_4NN_3. It is noteworthy that computational studies have shown that conformational isomerization between the two



(6)

conformers of closely related six-membered cyclic carbonates occurs with a low activation barrier and with little thermodynamic difference between the equatorial vs axial conformers.[25] It is of interest to note here that the crystals isolated of 5-methoxymethyl-5-methyl-1,3-dioxan-2-one (**4**) were of the axial conformer.



(7)

Figure 9 depicts the rates of depolymerization of poly(5-methyl-5-benzyloxymethyl-1,3-dioxan-2-one) and the concomitant formation of the corresponding cyclic carbonate for reactions carried out in toluene at 110 °C in both argon and CO_2 atmospheres.[26] As is evident in Figure 9 the rate of depolymerization to cyclic monomer is greatly retarded by carbon dioxide. This is consistent with views based on cycloaddition studies involving epoxides and CO_2, where the process proceeding via the carbonate species has a significantly higher energy of activation compared to that occurring by way of an alkoxy species (Scheme 3).[27] On the other hand, the forward reaction in eq 6 to provide copolymer from the cyclic carbonate proceeds at 110 °C at a faster rate than

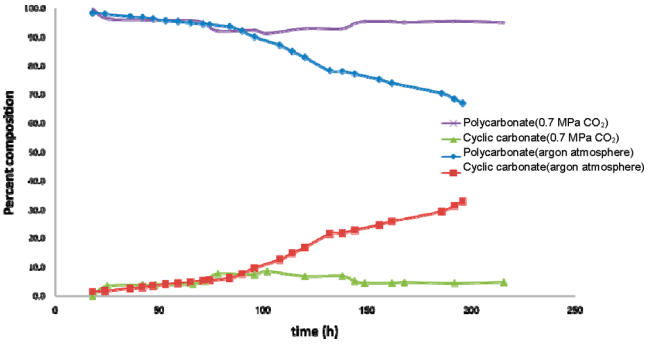
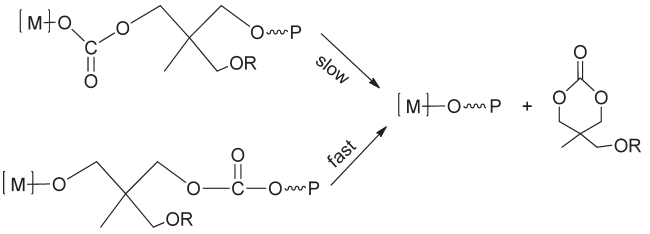


Figure 9. Depolymerization of poly(5-benzyloxymethyl-5-methyl-1,3-dioxan-2-one) to the corresponding cyclic carbonate in toluene at 110 °C as catalyzed by complex **5a** in the presence of 2 equiv of *n*-Bu_4NN_3.

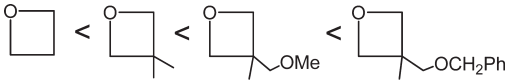
Scheme 3



the reverse process. This fits with our observation of the oxetane/CO_2 coupling process, where the reaction appears to be proceeding by initial formation of cyclic carbonate prior to ring-opening polymerization to copolymer since these reactions were performed at elevated pressures of CO_2.

CONCLUSIONS

Herein, we have extended our studies of the coupling reaction of CO_2 with oxetanes, focusing on oxetanes that are doubly substituted at the 3-position with substituents of varying steric requirements. Presented in these investigations were 3-methyloxetanes further substituted at the 3-position with methyl, $-CH_2OMe$, and $-CH_2OCH_2Ph$. Formation of the copolymer was found to proceed via preformed six-membered cyclic carbonate to a greater extent as the steric bulk of the substituents in the 3-position increased. That is, the degree of copolymer formation from oxetane and CO_2 by way of ring-opening polymerization of the first formed cyclic carbonate increased in the order listed below at 110 °C. Furthermore, the rate of the CO_2/oxetane coupling process was found to decrease in this order.



The thermal stability of the six-membered cyclic carbonate vs copolymer increased as well with an increase in the steric requirements of the substituents in the 3-position of the oxetane

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monomer. For example, only a trace of trimethylene carbonate is seen upon copolymerizing oxetane and CO_2, whereas, the coupling of 3-benzyloxymethyl-3-methyloxetane and CO_2 afforded an equilibrium product distribution of copolymer to cyclic carbonate of 60% at 110 °C. A noteworthy observation was that the rate of the isolated purified polycarbonate proceeding to the equilibrium distribution of polycarbonate and cyclic carbonate was greatly retarded by the presence of carbon dioxide. An ongoing effort in our laboratory is to develop an effective postsynthetic hydrogenation process for converting the benzyloxymethyl copolymer to the hydrophilic polycarbonate containing pendant hydroxyl groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables and cif files providing crystallographic data for compound **4** and complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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