Synthesis, Characterization, and Epoxidation of an Aliphatic Polycarbonate from 2,2-(2-Pentene-1,5-diyl)trimethylene Carbonate (^{c}HTC) Ring-Opening Polymerization

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ABSTRACT: 2,2-(2-Pentene-1,5-diyl)trimethylene carbonate (^{c}HTC) was synthesized from cyclohexene-4,4-dimethanol in high yield (>80%). This new carbonate monomer was successfully ring-open polymerized to form P(^{c}HTC) in bulk at 90 °C using various organometallic catalysts including aluminoxanes (methyl and isobutyl), Bu_nSnCl_{4-n} ($n = 1, 2, 3$), $Bu_nSn(OMe)_{4-n}$ ($n = 2, 3$), $ZnEt_2$, and $ZnEt_2-H_2O$. Comparison of these systems showed that the Zn- and Al-based catalysts were preferred for the preparation of high molecular weight polymers in yields ≥89% and reaction times of ≤8 h. For the Bu_nSnX_{4-n} catalysts investigated, values of $n = 1$ when X is Cl and $n = 2$ when X is OMe resulted in relatively greater polymerization rates and higher polymer molecular weights. The effects of reaction time and monomer/catalyst molar ratio were investigated for the Al and Zn catalysts. An outcome of this study was determining that the $ZnEt_2-H_2O$ (1/0.5) catalyst for a monomer/catalyst (M/C) molar ratio of 400 and a 2 h reaction time gave a product with $M_n = 276\,000$ in 98% yield. The P(^{c}HTC) products were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, DSC, TGA, and GPC. NMR results showed that ^{c}HTC decarboxylation did not occur during chain propagation. P(^{c}HTC) has a moderate glass transition temperature ($T_g = 30$ °C) with high thermal stability. ^{13}C NMR at 62.5 MHz did not resolve chain diad sequences although the polymers are likely atactic. Epoxidation of P(^{c}HTC) vinyl side groups was carried out to various extents by using 3-chloroperoxybenzoic acid at room temperature.

Introduction

Aliphatic polycarbonates are of interest for use as bioresorbable biomedical materials.[1−6] Furthermore, they are useful as oligomeric and polymeric additives with plasticizing or thickening properties.[7] Poly(alkylene carbonate)s have been synthesized by (*i*) the reaction of aliphatic diols with phosgene,[8] (*ii*) the copolymerization of epoxides with carbon dioxide in the presence of organometallic catalysts,[9] (*iii*) the ring-opening polymerization (ROP) of cyclic carbonate monomers,[10] (*iv*) carbonate interchange reactions between aliphatic diols and dialkyl carbonates,[11] and (*v*) the direct condensation of diols with CO_2 or alkali metal carbonates.[12−14] Of these, only methods *ii* and *iii* are useful for the preparation of high molecular weight aliphatic poly(carbonate)s. Thus far, method *ii* has been used to prepare high molecular weight aliphatic poly(carbonate)s derived from the epoxides ethylene oxide, propylene oxide and epichlorohydrin.[15−16]

The most commonly used cyclic carbonates for ROPs are the 5- and 6-membered ring monomers. The ROP of 6-membered cyclic carbonates using anionic catalysts is well-known to produce copolymers comprised of repeat units which are identical to those which would be derived from the perfectly alternating copolymerization of the corresponding cyclic ether and CO_2.[10] In other words, no decarboxylation was observed for these anionic polymerizations.[17] In contrast, cationic polymerizations of 6-membered ring cyclic carbonates were accompanied by decarboxylation to yield mixed-linkage polycarbonates containing ether bonds.[18] For example, Kricheldorf and Weegen-Schulz used BF_3OEt_2, BCl_3, and BBr_3 as catalysts for the ROP of trimethylene carbonate (TMC) and neopentylene carbonate to yield polycarbonates containing ether linkages.[19]

The most thoroughly investigated 6-membered cyclic carbonate monomers have been TMC and 2,2-dimethyltrimethylene carbonate (DTC). For TMC, Kricheldorf and Weegen-Schulz[20] reported that $BuSnCl_3$ is a preferred catalyst leading to poly(trimethylene carbonate), PTMC, having a weight average molecular weight (M_w) of about 250 000 and 87.5% monomer conversion in 8 h at 90 °C. Furthermore, they showed that a number of Sn-based catalysts polymerized TMC without decarboxylation. Unfortunately, number average molecular weights (M_n) were not given, and the polymerization mechanism was not elucidated.[20] The majority of efforts directed toward ROPs of DTC and other 2,2-disubstituted carbonates used anionic initiators such as *sec*-BuLi at low temperature.[17] The anionic polymerization of DTC always yields an equilibrium mixture of relatively higher and lower molecular weight (cyclic oligomers) product fractions.[21] Thus, without undertaking fractionation of anionically produced PDTC, high molecular weights ($M_n > 120\,000$) have not been obtained. Enlarging the substituents significantly decreased monomer polymerizability. For example, the anionic (*sec*-BuLi initiated) ROP of 2-methyl-2-phenyltrimethylene carbonate resulted in a lower yield (<50%) and molecular weight ($M_n < 8000$) relative to those for DTC polymerizations under comparable reaction conditions. Furthermore, attempts to homopolymerize 2,2-diphenyltrimethylene carbonate using *sec*-BuLi as catalyst were unsuccessful.[22] Work directed toward the anionic polymerizations of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-diylidene)-1,3-dioxan-2-one (NC) and 2-((allyloxy)methyl)-2-ethyl-1,3-dioxan-2-one (AETC)[23] also showed the lower polymerizability of these monomers relative to DTC. The molecular weight obtained for poly(NC) was in the range 10 000−40 000 using *sec*-BuLi as initiator for 4 h at 0 °C.[24] Similar comparisons for polymerizations of TMC, DTC, 2-methyl-2-propyl-TMC, 2-ethyl-2-propyl-TMC, and 2-methyl-2-phenyl-TMC using amine-based anionic catalysts showed similar detrimental effects on yield

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and/or product molecular weight with increased substituent size.[25]

Surprisingly, the use of coordination−insertion type organometallic catalysts for substituted cyclic carbonate ROPs[26,27] have received relatively little attention compared to anionic initiators. Specific examples that describe Sn-, Al-, and Zn-based catalyzed carbonate ROPs are given below (see Results and Discussion).

PTMC has been reported either as having low crystallinity or as being amorphous.[28] Furthermore, PTMC is a rubbery material with low tensile strength[28] and a glass transition temperature (T_g) of approximately −18 °C.[29] Relative to PTMC, the 2,2-dimethyl substituents of PDTC result in higher T_g (27 °C) and material crystallinity (T_m = 108 °C, ΔH_f = 20 J/g).[17] A further increase in the size of 2,2-substituents for poly(NC) results in T_g and T_m values of 60 and 117 °C, respectively.

A number of aliphatic polycarbonates or their copolymers were reported to be environmentally biodegradable.[30,31] The bioresorption of poly(ethylene carbonate) pellets in the peritoneal cavity in rats was apparent within 2 days of implantation and was nearly complete within 2 weeks.[5] For PTMC, a film incubated in pH 7.4 buffer solution for 30 weeks at 37 °C resulted in only 9% weight loss and 7% molecular weight decrease.[28] However, a number of research groups[28,32,33] reported that the *in vitro* hydrolytic degradation of PTMC and TMC-LA copolymers were comparatively slower than the degradation resulting from *in vivo* exposures under comparable pH/temperature conditions. For example, Zhu *et al.*[28] showed that implantation of PTMC in rats over 26 weeks resulted in a weight loss and decrease in molecular weight of 21% and 55%, respectively. These studies demonstrate the potential utility of PTMC, other polycarbonates, and copolymers containing carbonate linkages for use as bioresorbable implant materials.

In comparsion to TMC, the 2,2-dimethyl substituents of DTC created difficulties in high polymer formation using organometallic catalysts such as $ZnEt_2$, Al(O-*sec*-Bu)$_3$ and $Bu_2Sn(OMe)_2$. Furthermore, while PTMC has at best low crystallinity, PDTC is semicrystalline and has a relatively higher T_g. Considering that aliphatic polycarbonates are important candidates for use as bioresorbable implant and environmentally degradable materials, we have initiated a program to expand the currently limited data base which relates cyclic carbonate structure, polymerizability, and polycarbonate properties.[34] In this paper, we report the preparation and polymerization of the new monomer 2,2-(2-pentene-1,5-diyl)trimethylene carbonate (^{c}HTC; see Results and Discussion for structure). This monomer was selected for study since (i) in comparison to DTC, ^{c}HTC contains rigid substituents at the 2-position which may be useful in increasing the resulting polycarbonate T_g, (ii) the polymerizability of ^{c}HTC by organometallic catalysts was of interest, and (iii) polymers from ^{c}HTC have C=C double bond side groups which were used for polymer modification.

Experimental Section

Instrumental Methods. Fourier Transform-Infrared Spectroscopy (FTIR). A P-E 1720 FTIR spectrometer was used to obtain the spectra (16 scans, resolution 2 cm^{-1}) of the monomer and polymers over the range from 4000 to 400 cm^{-1}. Films of polymers were cast from chloroform solution directly onto a NaCl crystal plate for transmission measurements.

Nuclear Magnetic Resonance (NMR) Spectroscopy. Proton (^{1}H) NMR spectra were recorded on a Bruker ARX-250 spectrometer at 250 MHz. ^{1}H NMR chemical shifts in parts per million (ppm) are reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference. The concentration used was 4% w/v in chloroform-*d*. The instrumental parameters were as follows: temperature 300 K, pulse width 7.80 μs (30°), 32 K data points, acquisition time 3.18 s, 1 s relaxation delay, and 32 transients. Carbon-13 (^{13}C) spectra were recorded at 62.5 MHz on a Bruker ARX-250 spectrometer in 20% w/v chloroform-*d* solutions. The chemical shifts in ppm were referenced relative to the internal standard $CDCl_3$ at 77.00 ppm. Polymer spectral acquisitions were conducted using the following parameters: temperature 300 K, 30° pulse width, 64K data points, acquisition time 1.638 s, delay time 1 s, and 15 000−20 000 transients.

Molecular Weight Measurements. Number and weight average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (GPC) utilizing a Waters Model 510 pump, Model 410 differential refractometer, Waters 486 tunable absorbance detector, and a Model 717 Plus autosampler with 500-, 10^3-, 10^4-, and 10^5-Å ultrastyragel columns placed in series. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. The injection volume was 100 μL, and sample concentrations were ~0.5% w/v. Polystyrene standards with a low dispersity (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows-based Millenium 2.0 software package.

Thermal Analysis. Differential scanning calorimetry (DSC) studies were conducted on a DuPont DSC 912 equipped with a TA 2000 data station. Experiments were conducted using between 5 and 8 mg of sample, a heating rate of 10 °C/min, and a nitrogen purge. During the first heating scan the samples were heated to 200 °C. The samples were then rapidly quenched with liquid nitrogen to −60 °C and then heated once again to 200 °C (second heating scan) under the running conditions identical with those used for the first scan. Data reported for the glass transition temperature (T_g) were taken from the midpoint of the transition in the second scan. Thermal gravimetric analyses (TGA) were conducted from room temperature to 500 °C using a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments). Samples were heated at 10 °C/min under a nitrogen atmosphere. The onset decomposition temperature (T_d) reported was calculated by the instrument (program TGA-5.0) as the point of intersection between the two tangents.

X-ray Analysis. Wide-angle X-ray scattering (WAXS) of a solution cast film aged for 2 weeks at 40 °C was performed using a Philips Vertical Diffractometer with Bragg−Brentano geometry and a graphite diffracted beam monochrometer at 40 kV/20 mA and Cu Kα radiation(1.5405 Å). A scanning speed of 2°/min with a sample interval of 0.05° was used.

Materials. $ZnEt_2$ (1.1 mol/L in toluene) was purchased from Aldrich and was used as received. Methylaluminoxane (MAO, 2.03 M in heptane) and isobutylaluminoxane (IBAO, 0.95 M in heptane) were from Akzo Chemical Inc. All of the Sn catalysts were purchased as neat liquids or solids from Aldrich and were used as received. 1,4-Dioxane was dried by distillation over CaH_2 under dry argon. Cyclohexene-4,4-dimethanol was purchased from Aldrich and used as received. Chloroform for Sn catalyst preparation was dried by CaH_2. All liquid reagents were transferred by syringe under a dry argon atmosphere.

Synthesis of ^{c}HTC. The monomer was prepared as described by Ariga *et al.*[18] except that the reaction was conducted at 0 °C instead of room temperature. The crude product was washed with ether and recrystallized from dry tetrahydrofuran (0 °C) to give white needle-like crystals (81% yield). Characterization of ^{c}HTC was as follows: mp 79.5−80.5 °C; FTIR (spread onto NaCl plates by solution casting from chloroform): 3026 ($\nu_{H-C=}$), 1737 ($\nu_{C=O}$), 1654 cm^{-1} ($\nu_{C=C}$); ^{1}H-NMR (250 MHz, in chloroform-*d*, protons are designated using the identical lettering system as in Figure 2 but using the subscript m for monomer) 5.60−5.85 (c$_m$/d$_m$, 2H, m), 4.22 (a$_m$, 4H, s), 2.16 (e$_m$, 2H, m), 2.08 (b$_m$, 2H, m), 1.69 ppm (f$_m$, 2H, t); ^{13}C-NMR (62.5MHz, chloroform-*d*, carbons are designated using the identical numbering system as in Figure 3

Table 1. Ring-Opening Polymerization of 2,2-(2-Pentene-1,5-diyl)trimethylene Carbonate (^{c}HTC) by Different Catalysts[a]

entry	catalyst	time (h)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	MAO[d]	2	88	77 100	2.1
2	IBAO[d]	2	66	79 200	2.0
3	Bu_3SnCl	48	15	6 030	1.3
4	Bu_2SnCl_2	48	70	30 800	2.6
5	$BuSnCl_3$	48	93	98 400	3.4
6	Bu_3SnOMe	48	40	7 530	1.8
7	$Bu_2Sn(OMe)_2$	48	88	20 000	2.1
8	$ZnEt_2$	2	100	240 000	1.8
9	$ZnEt_2-H_2O$ (1/0.5)	2	100	106 000	3.0

[a] Monomer to catalyst ratio (M/C) was 100 mol/mol; reactions were conducted in bulk at 90 °C. [b] 100 × methanol-insoluble product (g)/initial monomer charged (g). [c] Determined by GPC, see Experimental Section. [d] MAO, methylaluminoxane; IBAO, isobutylaluminoxane; C is taken as the concentration of [Al].

Table 2. Effect of Reaction Time on the Ring-Opening Polymerization of ^{c}HTC by Aluminoxanes[a]

entry	catalyst	time (h)	yield (%)[b]	M_n[b]	M_w/M_n[b]
1	MAO	1	42	25 300	1.6
2	MAO	2	88	77 100	2.1
3	MAO	8	89	101 000	1.8
4	MAO	24	95	85 400	1.9
5	IBAO	1	57	37 900	2.2
6	IBAO	2	66	79 200	2.0
7	IBAO	8	93	142 000	2.0
8	IBAO	24	98	134 000	2.0

[a] M/C = 100 mol/mol, in bulk, 90 °C. [b] See Table 1 footnotes.

Table 3. Effect of M/C Molar Ratio on the Ring-Opening Polymerization of ^{c}HTC by Zn(II) Catalysts[a]

entry	catalyst	M/C	yield (%)[b]	M_n[b]	M_w/M_n[b]
1	$ZnEt_2$	100	100	240 000	1.8
2	$ZnEt_2$	200	96	204 000	2.2
3	$ZnEt_2$	400	91	255 000	2.1
4	$ZnEt_2$	800	80	200 000	1.8
5	$ZnEt_2-H_2O$ (1/0.5)	100	100	106 000	3.0
6	$ZnEt_2-H_2O$ (1/0.5)	200	99	151 000	2.2
7	$ZnEt_2-H_2O$ (1/0.5)	400	98	276 000	1.9
8	$ZnEt_2-H_2O$ (1/0.5)	800	33	64 100	2.3

[a] In bulk, 90 °C, 2 h. [b] See Table 1 footnotes.

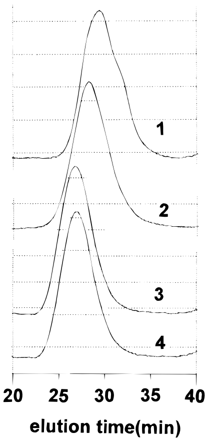


Figure 1. GPC traces of poly(^{c}HTC)s prepared using IBAO (90 °C, M/C = 100) and reaction times of (1) 1 h (Table 2, entry 5), (2) 2 h (Table 2, entry 6), (3) 8 h (Table 2, entry 7), and (4) 24 h (Table 2, entry 8).

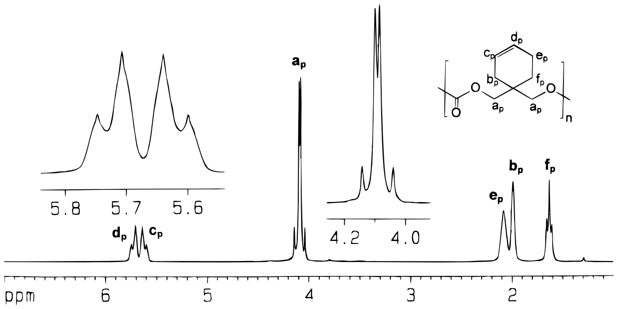


Figure 2. 250 MHz ^{1}H-NMR spectrum of P(^{c}HTC) (Table 1, entry 1) in chloroform-*d*.

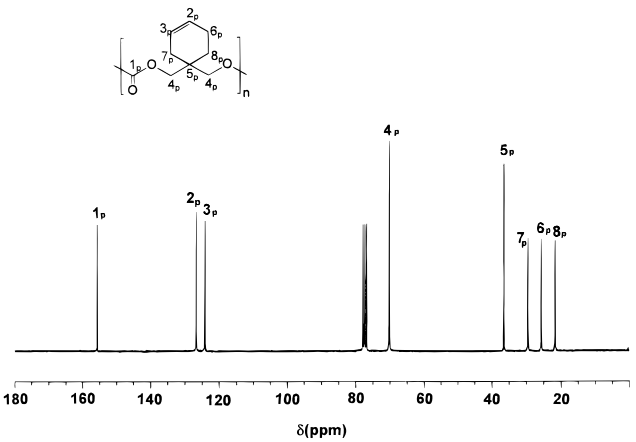


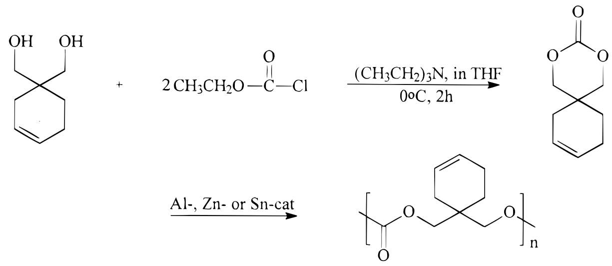
Figure 3. 62.5 MHz ^{13}C-NMR spectrum of P(^{c}HTC) (Table 1, entry 1) in chloroform-*d*.

but using the subscript m for monomer) 148.77 (1_m), 127.00 (2_m), 123.37 (3_m), 75.77 (4_m), 30.29 (5_m), 29.97 (7_m), 26.21 (6_m), 21.58 ppm (8_m).

Preparation of Catalysts. The catalyst $ZnEt_2-H_2O$ (1:0.5) was prepared by modification of a literature procedure.[35] Into a previously silanized and flame-dried 10 mL Schlenk tube, 1 mL $ZnEt_2$ (1.1 M in toluene) was injected via syringe. The solution was cooled in an external dry ice–acetone bath followed by slowly adding with vigorous stirring a 1,4-dioxane solution (99 μL) containing 9.9 μL distilled water. After 15 min, the dry ice bath was removed and the temperature was increased to 25 °C. The resulting clear solution was stored in the refrigerator (about 4 °C) for up to 2 weeks prior to use without loss of catalytic activity. Solutions (1 mol/L) of Sn catalysts (Bu_nSnCl_{4-n} $\{n = 1, 2, 3\}$ and Bu_nSnOMe_{4-n} $\{n = 2, 3\}$) were prepared in dry chloroform.

Polymerizations. The following is the general procedure used for ^{c}HTC polymerizations. Additional information on polymerization conditions, catalyst concentrations, and monomer to catalyst ratios are given in Tables 1–3. The polymerization ampules (10 mL) were treated with trimethylsilyl chloride, washed with three 5 mL portions of methanol, dried at 100 °C in an oven, and flame-dried while purging with dried argon. ^{c}HTC (0.84 g) and the catalyst solution (see Tables 1–3) were transferred into the ampule using a glovebox to maintain an inert nitrogen atmosphere. The ampule was degassed by several vacuum-purge cycles which also removed solvent introduced in the catalyst solution. The ampule was then sealed under argon and placed in an oil bath maintained at 90 °C for a predetermined reaction time. At the end of the reaction period, the contents of the ampule was dissolved in chloroform (8 mL), the chloroform solution was added to methanol (80 mL) to precipitate the polymer, the precipitate was washed with several portions of methanol, and then the volatiles were removed in a vacuum oven (<3 mmHg, 40 °C, 24 h). ^{1}H and ^{13}C NMR of a polymer product (Table 2, entry 2) were shown in Figures 2 and 3, respectively. FTIR spectra (thin film, prepared by solution casting from chloroform onto a NaCl plate) had the following characteristic absorption bands: 3026 ($\nu_{H-C=}$), 1748 ($\nu_{C=O}$), 1652 cm^{-1} ($\nu_{C=C}$).

Epoxidation of P(^{c}HTC). To a 20 mL vial containing 0.3 g of P(^{c}HTC) dissolved in 3.0 mL of $CHCl_3$ was added 0.093, 0.187, 0.279 or 0.372 g of 3-chloroperoxybenzoic acid (Aldrich, as received). After reactions were maintained with magnetic stirring at room temperature for 30 h, the products were precipitated by addition of the reaction solutions to 30 mL of



Scheme 1. Synthesis and Polymerization of ^{c}HTC

methanol. The precipitates were washed with methanol and then dried *in vacuo* to give between 0.30 and 0.31 g of products.

Results and Discussion

Synthesis of 2,2-(2-Pentene-1,5-diyl)trimethylene Carbonate (^{c}HTC). The monomer ^{c}HTC was synthesized in 81% yield by a one-pot reaction from cyclohexene-4,4-dimethanol (see Scheme 1 and the Experimental Section for additional details). The structure and purity of ^{c}HTC was confirmed by FTIR, ^{1}H-NMR, ^{13}C-NMR. and melting point analyses (see Experimental Section).

Polymerization of ^{c}HTC with Different Catalysts. A number of organometallic catalysts including aluminoxanes and Zn-based and Sn-based systems were selected to study their abilities to catalyze ^{c}HTC ring-opening polymerization (see Table 1). Reactions were conducted in bulk at 90 °C with a monomer to catalyst molar ratio (M/C) of 100. Polymerizations were either terminated immediately after gelation or, when gelation was not observed, at 48 h. The Zn-based catalysts resulted in quantitative polymer yield within 2 h and gave P(^{c}HTC) with M_n values >100 000. A comparison of the results obtained using $ZnEt_2$ and $ZnEt_2-H_2O$ (1/0.5) showed that the latter gave P(^{c}HTC) of relatively lower molecular weight. The Al-based catalysts MAO and IBAO also gave promising results. Specifically, the former catalyst resulted in 88% polymer yield in 2 h with an M_n of 77 100. Reactions conducted with Sn-catalysts were relatively slow and, with the exception of $BuSnCl_3$, gave M_n values ≤30 800. For Bu_nSnCl_{4-n}, increasing the number of Cl ligands attached to Sn from 1 to 3 resulted in a significant increase in both P(^{c}HTC) yield and molecular weight. This trend for Bu_nSnCl_{4-n} catalysts was the same as that observed by Kricheldorf *et al.*[20] for TMC polymerizations. Similarly, increasing the number of methoxy ligands from 1 to 2 for $Bu_nSn(OMe)_{4-n}$ catalysts resulted in increased P(^{c}HTC) yield and molecular weight (see Table 1). A previous report showed that the polymerizations (90 °C, M/C = 154) of DTC by $ZnEt_2$ (20 h), Al(O-*sec*-Bu)$_3$ (36 h), and $Bu_2Sn(OMe)_2$ (45 min) gave PDTC in yields (M_n) of 88% (35 000), 89% (20 000), and 45% (21 200), respectively.[27] Therefore, even though ^{c}HTC has relatively larger substituents than DTC, a comparison of these Al- and Zn-catalyzed polymerizations indicates that ^{c}HTC gave relatively higher product yields and molecular weights. However, it appears that the larger substitutents of ^{c}HTC relative to DTC may be detrimental to its polymerization by $Bu_2Sn(OMe)_2$ and other Sn-based catalysts. It is noteworthy to mention that the use of anionic initiators such as *sec*-BuLi for polymerizations of other disubstituted carbonates such as NC often gave high yields >90% in ≤3 h but resulted in polymers of relatively low molecular weight (10 000 to 40 000) due to backbiting reactions.[24] On the basis of the above, further studies of ^{c}HTC polymerization described below were focused on the Zn(II)- and Al(III) catalysts.

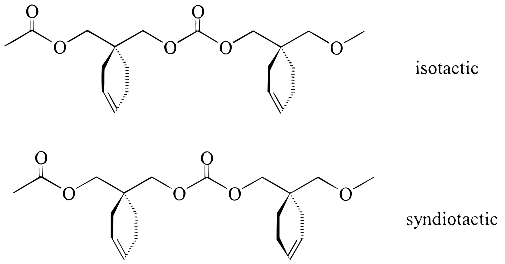
Effect of Reaction Time. Table 2 shows the effect of reaction time on the polymerization of ^{c}HTC catalyzed by MAO and IBAO at 90 °C (^{c}HTC:Al mol/mol = 100). For IBAO-catalyzed polymerizations, the P(^{c}HTC) yield increased rapidly to 57% from 0 to 1 h and, subsequently, increased slowly (to 93%) from 1 to 8 h. Product M_n also increased from 37 900 to 142 000 for reaction times of 1−8 h. Further increasing the reaction time to 24 h resulted in a small decrease in product molecular weight. GPC traces (Figure 1) showed that, with the exception of trace 1 (entry 5, Table 2), which had a low molecular weight shoulder, the other P(^{c}HTC) products from IBAO catalysis (entries 6−8, Table 2) had unimodal distributions. The molecular weight dispersities (M_w/M_n) of these products ranged from 2.0 to 2.2. For MAO, the polymer yield increased rapidly to 88% during the first 2 h and, subsequently, increased slowly (88−95%) from 2 to 24 h. The maximum MAO-catalyzed P(^{c}HTC) M_n was at 8 h (101 000 g/mol). The small decrease in M_n from 8−24 h observed for both MAO and IBAO catalysis might result from thermal or catalytic degradation of the preformed polymer. Decreased molecular weight with extended reaction time for carbonate ROPs was similarly observed for Bu_nSnCl_{4-n} catalyzed TMC polymerizations.[20] Comparision of MAO- and IBAO-catalyzed ^{c}HTC polymerizations showed that M_n and M_w/M_n varied in a similar manner as a function of time. However, at 8 h, IBAO catalysis produced P(^{c}HTC) of relatively higher molecular weight (142 000).

Interestingly, an increase in the reaction time from 2 to 24 h for $ZnEt_2-H_2O$-(1/0.5) catalyzed ^{c}HTC polymerization (M/C 400) did not alter product M_n, M_w/M_n, or yield (results not shown). Therefore, $ZnEt_2-H_2O$ (1/0.5) at 90 °C over 24 h did not result in the depolymerization of preformed P(^{c}HTC) chains for extended reaction times.

Effect of Monomer/Catalyst Molar Ratio. The effects of the M/C molar ratio for $ZnEt_2$ and $ZnEt_2-H_2O$(1/0.5) catalyzed ^{c}HTC polymerizations (90 °C, 2 h) on P(^{c}HTC) yield and molecular weight are shown in Table 3. For $ZnEt_2$, the polymer yield decreased from 100% to 80% as M/C increased from 100 to 800. However, P(^{c}HTC) M_n remained high (≥200 000) and the polydispersity varied little as a function of M/C. Similarly, Kricheldorf and Weegen-Schulz[20] reported that for Bu_nSnCl_{4-n}-catalyzed TMC polymerizations, the M/C molar ratio had little influence on the yield and PTMC molecular weight. Such molecular weight behavior may be a consequence of the fact that the number of initiation events and total number of chains is a function of monomer impurities and not the $ZnEt_2$ concentration.

For $ZnEt_2-H_2O$ (1/0.5) catalysis, P(^{c}HTC) yield showed no substantial change to M/C 400. However, increasing M/C from 400 to 800 decreased P(^{c}HTC) yield from 98% to 33%. This decrease in polymer yield is likely associated with a corresponding decrease in the rate of monomer conversion at high M/C. In contrast to results presented above for the nonhydrolyzed catalyst, partial hydrolysis resulted in increased M_n (by 2.6×) and decreased polydispersity (3.0 to 1.9) as M/C was increased from 100 to 400. The increase in M_n may be due to a decrease in the number of chain initiation events caused by $ZnEt_2-H_2O$ (1/0.5) at a lower catalyst concentration. This explanation is consistent with an increase in polydispersity at low M/C since initiation caused by monomer impurities may occur at a different

Chart 1. Tacticity of P(^{c}HTC)



rate than initiation due to added catalyst, resulting in a broadened molecular weight distribution. The relatively lower molecular weight for M/C 800 likely results from low monomer conversion. In comparison, increasing M/C from 100 to 200 for the aluminoxane catalysts (MAO and IBAO) resulted in a decrease by >50% in yield as well as M_n (data not shown).

Structural Characterization. All of the P(^{c}HTC) products described in Tables 1−3 have indistinguishable FTIR (see Experimental Section), ^{1}H-NMR and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of P(^{c}HTC) formed by MAO catalysis (Table 2, entry 2) is shown in Figure 2. Assignments of protons were based on ^{1}H−^{1}H COSY NMR spectra (not shown) and literature spectra of related structures.[24] Each of the methylene groups (a_p, b_p, f_p, and e_p) consist of protons which are chemically nonequivalent (diasteromeric relationship) since the repeat units of P(^{c}HTC) contain stereogenic centers (carbon 5_p; see Figure 3). For example, protons a_p appear as a skewed doublet of doublets which deviates from simple first-order splitting behavior due to coupling of diastereotopic protons which have slightly differing chemical shifts. The corresponding protons of the monomer (a_m) appear as a singlet when observed at 250 MHz NMR but were resolved into a triplet at 500 MHz (spectrum not shown). This triplet is similarly explained by the coupling behavior of diastereomeric a_m protons. However, in the latter case, a higher field was needed to resolve the small differences in chemical shift. Other protons such as c_p, d_p, e_p, and b_p show broad absorption signals that are devoid of coupling features. Once again, repeat unit stereogenic centers which result in chemical nonequivalence and complex coupling behavior explain these spectral characteristics.

The prochiral faces of ^{c}HTC differ only by the spatial arrangement of the double bond within the cyclohexene ring. Therefore, it is likely that there is little or no discrimination between ^{c}HTC prochiral faces during additions of monomer to the chiral propagating chain end. In other words, the difference in activation energy between additions of the dissimilar prochiral face orientations to the chiral propogating chain end is expected to be small resulting in atactic P(^{c}HTC)s with equivalent fractions of isotactic and syndiotactic diads. Structures of P(^{c}HTC) isotactic and syndiotactic diads are shown in Chart 1.

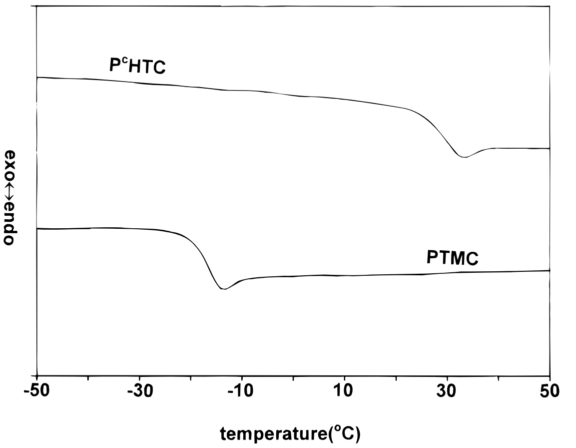
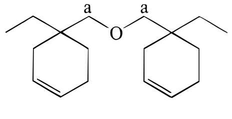


Figure 4. Second heating scan DSC thermograms (10 °C/min heating rate, N_2 atmosphere) of P(^{c}HTC) and PTMC.

Chart 2. Ether Linkage



The ^{13}C-NMR spectrum of P(^{c}HTC) (Table 2, entry 2) is shown in Figure 3. Assignments of carbons were based on a correlated ^{1}H−^{13}C 2D NMR spectrum (not shown). Expansion of P(^{c}HTC) carbon signals showed no additional signals which might have resulted from differing stereochemical relationships between adjacent repeat units. The same was true from inspection of ^{13}C-NMR spectra of selected P(^{c}HTC) products prepared by using MAO, IBAO, $BuSnCl_3$, $ZnEt_2$, and $ZnEt_2$−H_2O (1:0.5) catalysts. Thus, the spatial arrangement of alkene functionalities along the chain seems to have little affect on the ^{13}C-NMR chemical shifts of P(^{c}HTC). Since tacticity was not observable by ^{13}C NMR, the likeness of ^{13}C-NMR spectra for P(^{c}HTC) formed by differing catalysts (see Table 1) cannot be taken as evidence for similar repeat unit sequence distributions. However, as discussed above, we believe that atactic polymers were formed for all of the polymerizations described herein. Also, both ^{1}H- and ^{13}C-NMR spectra of selected P(^{c}HTC) homopolymers prepared by using MAO, IBAO, $BuSnCl_3$, $ZnEt_2$, and $ZnEt_2$−H_2O (1:0.5) catalysts showed no evidence for decarboxylation during propagation. If decarboxylation had occurred, calculations using empirical equations for model compounds[36] predicted that ^{1}H- and ^{13}C-NMR signals at ca. 3.5 and ca. 73.3 ppm, respectively, would have been observed. These signals would result from main chain methylenes of ether linked repeat units (see Chart 2).

The polymerization of ^{c}HTC without decarboxylation is consistent with previous reports for DTC and TMC polymerizations. Specifically, Schmilt *et al.*[27] showed that DTC polymerization by Al-, Sn-, and Zn-based catalysts occurred without decarboxylation. Similarly, decarboxylation during propagation was not observed for Sn-catalyzed TMC polymerizations.[20]

Thermal and Crystalline Properties. Solution cast films of P(^{c}HTC) (Table 2, entry 7) and PTMC (M_n = 80 500, M_w/M_n = 1.9) were aged at 40 °C for 2 weeks and then analyzed by DSC and WAXS. The second heating scan is shown in Figure 4. The P(^{c}HTC) film did not show a melting transition during the first heating scan. The WAXS diffractogram of this P(^{c}HTC) film gave an amorphous halo for $2\theta = 14-25°$ devoid of crystalline reflections. Therefore, it was concluded that the P(^{c}HTC) film was amorphous. PTMC showed a weak endotherm transition (peak at 40 °C, ΔH_f = 1 J/g) that was likely due to melting. Analysis of the thermal transitions of PTMC by others gave similar results.[29] The second heating scans (Figure 4) showed that P(^{c}HTC) had a T_g value which was 46 °C higher than that of PTMC (+30 and −16 °C, respectively). However, the T_g values for P(^{c}HTC) and PDTC (T_g = 27 °C) were similar while the latter was semicrystalline (T_m = 108 °C, ΔH_f = 20 J/g).[17]

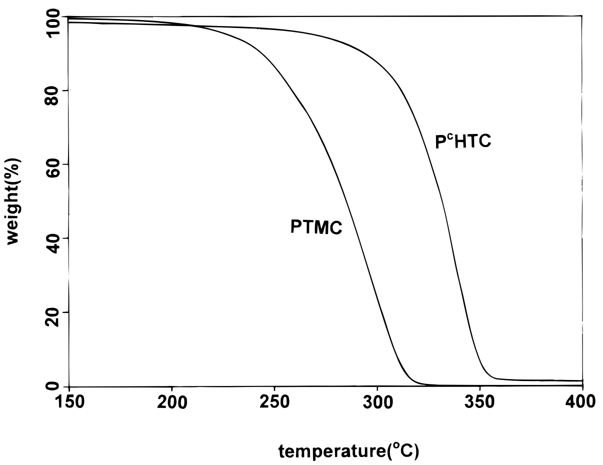


Figure 5. TGA analyses of P(^{c}HTC) and PTMC (10 °C/min heating rate, N_2 atmosphere).

Table 4. Epoxidation of P(^{c}HTC) by 3-Chloroperoxybenzoic Acid (3-CPBA)^a

entry	3-CPBA (g)	mol % of C=C^b	mol % of epoxy^b	M_n^{c}	M_w/M_n^{c}
epoxy-1	0.093	78	22	34 800	1.4
epoxy-2	0.187	55	45	30 500	1.5
epoxy-3	0.279	31	69	29 300	1.6
epoxy-4	0.372	5	95	34 400	1.6

[a] 0.30 g polymer (M_n = 35 700, M_w/M_n = 1.7) in 3 mL of chloroform, room temperature, and 30 h; the products obtained were in the range 0.30−0.31 g. [b] Calculated by ^{1}H-NMR spectral integration; see text. [c] See Table 1 footnotes.

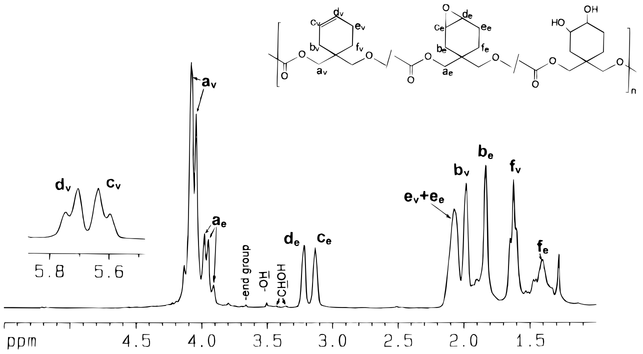


Figure 6. 250 MHz ^{1}H-NMR spectrum of epoxy-2 in chloroform-*d*.

The thermal stabilities of P(^{c}HTC) and PTMC were compared by TGA (see Figure 5). The onset of decomposition temperatures for P(^{c}HTC) and PTMC were 300 and 260 °C, respectively. Our results on the thermal stability of PTMC was consistent with a previous report.[37] It may be that substituents at the 2,2-position of poly(trimethylene carbonates) stabilize the chain from thermal unzipping to cyclic oligomers.

Epoxidation of Pendant P(^{c}HTC) Vinyl Side Groups. The pendant C=C double bonds in P(^{c}HTC) provide a variety of opportunities for further modifications. The epoxidation of a P(^{c}HTC) product (M_n = 35 700, M_w/M_n = 1.7; synthesized by MAO, M/C = 50, reaction time 2 h, 90 °C) was successfully carried out by using 3-chloroperoxybenzoic acid at room temperature (see Table 4 and Experimental Section).

Figure 6 shows the 250 MHz ^{1}H-NMR spectrum of the product with 45 mol % epoxide side groups (epoxy-2). Assignments of signals shown in Figure 6 were primarily based on comparisons to P(^{c}HTC) homopolymer and a ^{1}H−^{1}H COSY NMR spectrum (not shown). The chemical shifts of main chain methylenes of ^{c}HTC (a_v) and epoxy−^{c}HTC (a_e) units were partially resolved into two sets of multiplets. The very weak signals at 3.50 ppm (−O*H*) and 3.43/3.35 ppm (>C*H*−OH) which were observed for all the epoxide derivatives showed that low levels (<2% by integration) of epoxide hydrolysis occurred under the acidic conditions for epoxide formation and polymer isolation (see Experimental Section). The assignments of chemical shifts at 3.50, 3.43, and 3.35 ppm were based on ^{1}H-NMR spectra recorded using D_2O exchange (disappearance of the signal at 3.50 ppm) and derivatization with trifluoroacetic anhydride (downfield shift of signals at 3.50, 3.43, and 3.35 ppm). The spectral integration of signal regions between 3.1 and 3.3 ppm (protons c_e and d_e) and the multiplet between 5.5 and 5.8 ppm (protons c_v and d_v) were used to determine the mol % of vinyl and epoxide side groups of the products (see Table 4). Degrees of vinyl group epoxidation from 22 to 95 mol % (low-level epoxide hydrolysis was neglected) resulted by varying the quantity of 3-chloroperoxybenzoic acid in reactions. It is important to note that acidic conditions during epoxidation reactions and polymer isolation did not result in a substantial change in product molecular weight (see Table 4).

Summary of Results. The new aliphatic cyclic carbonate ^{c}HTC was prepared by a one-step reaction from cyclohexene-4,4-dimethanol in high yield (>80%). This monomer was designed to (i) gain additional information on the polymerizability of 2,2-disubstituted-propylene carbonates by organometallic catalysts and (ii) investigate modification of C=C double bond side groups that result from ^{c}HTC polymerization. On the basis of a comparison of the different catalysts with respect to monomer conversion and high molecular weight polymer synthesis, the Zn-based catalysts were most effective. ^{1}H-NMR and ^{13}C-NMR analyses showed that the polymers formed did not contain ether linkages. Thus, it was concluded that for all of the catalysts studied, chain propagation occurred without decarboxylation.

Studies by DSC and WAXS showed that P(^{c}HTC) was amorphous and the glass transition temperature was 30 °C. In addition, analyses by TGA showed that P(^{c}HTC) had a higher thermal stability than PTMC. Variable mole percentages (22−95%) of the vinyl P(^{c}HTC) side groups were transformed to epoxide functionalities by reaction with 3-chloroperoxybenzoic acid. This side chain modification was accomplished without a substantial change in the product molecular weight.

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