Introduction

Aliphatic polycarbonates are of interest as use for biodegradable biomedical materials.1–6 Furthermore, they are useful as oligomeric and polymeric additives with plasticizing or thickening properties.7 Polyalkylene carbonates 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 CO2 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 epichlorhydrin.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 CO2.10 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 BF3OEt2, BCl3, and BBr3 as catalysts for the ROP oftrimethylene 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-Schulz20 reported that BuSnCl3 is a preferred catalyst leading to poly(trimethylene carbonate), PTMC, having a weight average molecular weight (Mw) 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 (Mn) 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 P(DTC), high molecular weights (Mn > 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 (Mn < 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-diyldene)-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
and/or product molecular weight with increased substitution 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 (Tg) of approximately –18 °C. 29 Relative to PTMC, the 2,2-dimethyl substituents of PDTC result in higher Tg (27 °C) and material crystallinity (Tm = 108 °C, ΔHf = 20 J/g). 17 A further increase in the size of 2,2-substituents for poly(NC) results in Tg and Tm 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 comparison to TMC, the 2,2-dimethyl substituents of DTC created difficulties in high polymer formation using organometallic catalysts such as ZnEt2, Al(O-sec-Bu)3 and Bu2Sn(OMe)2. Furthermore, while PTMC has been reported to be environmentally biodegradable, 30,31 the 2,2-dimethyl substituents within 2-day implants were not observed to degrade and were 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.

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In this paper, we report the preparation and polymerization of the new monomer 2,2-(2-pentene-1,5-diyli)trimethylene carbonate (cHTC; see Results and Discussion for structure). This monomer was selected (i) in comparison to DTC, cHTC contains rigid substituents at the 2-position which maybe useful in increasing the resulting polycarbonate Tg, (ii) the polymerizability of 1HTC by organometallic catalysts was of interest, and (iii) polymers from 1HTC have C=C double bond side groups which were used for polymer modification.

Experimental Section

Instrumental Methods. Fourier Transform-Infrared Spectroscopy (FTIR). A Nicolet 710 Fourier Transform Infrared 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 (1H) NMR spectra were recorded on a Bruker ARX-250 spectrometer at 250 MHz. 1H NMR chemical shifts in parts per million (ppm) are reported downfield fromtetramethylsilane (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 (13C) spectra were recorded at 62.5 MHz on the Bruker ARX-250 spectrometer in 20% w/v chloroform-d solutions. The chemical shifts in ppm were referenced relative to the internal standard CDCl3 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 (Mn, Mw, 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-, 1-, and 10-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 (Polydispersity) 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 same conditions identical with those used for the first scan. Data reported for the glass transition temperature (Tg) 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 (Td) was determined by calculation of the (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 monochromator 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. ZnEt2 (1.1 mol/L in toluene) was purchased from Aldrich and was used as received. Methylaluminoxane (MAO, 2.03 M in heptane) and initiator LAH (1.1, 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 CaH2 under dry argon. Cyclohexene-4,4-dimethanol was purchased from Aldrich and used as received. Chloroform for Sn catalyst preparation was dried by CaH2.

All liquid reagents were transferred by syringe under a dry argon atmosphere.

Synthesis of 1HTC. 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 1HTC was as follows: mp 79.5–80.5 °C; FTIR (spread onto NaCl plates by solution casting from chloroform); 3026 (ν(=C–O), 1737 (ν(C–O), 1654 cm−1 (ν(C=O)); 1H NMR (250 MHz, in chloroform-d, ppm) using the identical lettering system as in Figure 2 but using the subscript m for monomer) 5.60–5.85 (ν(CH2), 2H, m), 4.22 (ν(=O), 4H, s), 2.16 (ν(CH2), 2H, m), 2.08 (ν(CH2), 2H, m), 1.69 ppm (ν(CH2), 2H, t); 13C-NMR (62.5MHz, chloroform-d) carbons are designated using the identical numbering system as in Figure 3.
solution was cooled in an external dry ice solution (99\%)
followed by slowly adding with vigorous stirring a 1,4-dioxane

catalyst (Bu\textsubscript{3}SnCl\textsubscript{2}, Bu\textsubscript{3}SnCl).

Solutions (1 mol/L) of SnCl\textsubscript{4} in acetone were prepared in dry chloroform.

For cHTC polymerizations, additional information on
catalyst concentrations, and monomer to catalyst ratios are given in Tables 1
and 2. The catalyst ZnEt\textsubscript{2} was used for cHTC polymerizations. Additional information on
polymerization conditions, catalyst concentrations, and monomer to catalyst ratios are given in Tables 1–3.

Preparation of Catalysts. The catalyst ZnEt\textsubscript{2}–H\textsubscript{2}O (1:0.5) was prepared by modification of a literature procedure.\textsuperscript{50}

Monomer to catalyst ratio (M/C) was 100 mol/mol; reactions were conducted in bulk at 90 °C, \( 100 \times \) methanol-insoluble product (g)/initial monomer charged (g).\textsuperscript{1d} Determined by GPC, see Experimental Section.\textsuperscript{4d} MAO, methylaluminoxane; IBAO, isobutylaluminoxane; C is taken as the concentration of [Al].

Table 2. Effect of Reaction Time on the Ring-Opening Polymerization of cHTC by Aluminoxanes\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>( M_\text{n} )</th>
<th>( M_w/M_\text{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MAO</td>
<td>1</td>
<td>42</td>
<td>25 300</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>MAO</td>
<td>2</td>
<td>88</td>
<td>77 100</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>MAO</td>
<td>5</td>
<td>89</td>
<td>101 000</td>
<td>1.8</td>
</tr>
<tr>
<td>4</td>
<td>MAO</td>
<td>24</td>
<td>95</td>
<td>85 400</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>IBAO</td>
<td>1</td>
<td>57</td>
<td>37 900</td>
<td>2.2</td>
</tr>
<tr>
<td>6</td>
<td>IBAO</td>
<td>2</td>
<td>66</td>
<td>79 200</td>
<td>2.0</td>
</tr>
<tr>
<td>7</td>
<td>IBAO</td>
<td>8</td>
<td>93</td>
<td>142 000</td>
<td>2.0</td>
</tr>
<tr>
<td>8</td>
<td>IBAO</td>
<td>24</td>
<td>98</td>
<td>134 000</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\( a \) M/C = 100 mol/mol, in bulk, 90 °C.\textsuperscript{b} See Table 1 footnotes.

Table 3. Effect of M/C Molar Ratio on the Ring-Opening Polymerization of cHTC by Zn(II) Catalysts\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>M/C</th>
<th>yield (%)</th>
<th>( M_\text{n} )</th>
<th>( M_w/M_\text{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnEt\textsubscript{2}</td>
<td>100</td>
<td>100</td>
<td>240 000</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>ZnEt\textsubscript{2}</td>
<td>200</td>
<td>96</td>
<td>204 000</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>ZnEt\textsubscript{2}</td>
<td>400</td>
<td>91</td>
<td>255 000</td>
<td>2.1</td>
</tr>
<tr>
<td>4</td>
<td>ZnEt\textsubscript{2}</td>
<td>800</td>
<td>80</td>
<td>200 000</td>
<td>1.8</td>
</tr>
<tr>
<td>5</td>
<td>ZnEt\textsubscript{2}–H\textsubscript{2}O (1:0.5)</td>
<td>100</td>
<td>100</td>
<td>106 000</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>ZnEt\textsubscript{2}–H\textsubscript{2}O (1:0.5)</td>
<td>200</td>
<td>99</td>
<td>151 000</td>
<td>2.2</td>
</tr>
<tr>
<td>7</td>
<td>ZnEt\textsubscript{2}–H\textsubscript{2}O (1:0.5)</td>
<td>400</td>
<td>98</td>
<td>276 000</td>
<td>1.9</td>
</tr>
<tr>
<td>8</td>
<td>ZnEt\textsubscript{2}–H\textsubscript{2}O (1:0.5)</td>
<td>800</td>
<td>33</td>
<td>64 100</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\( a \) In bulk, 90 °C, 2 h.\textsuperscript{b} See Table 1 footnotes.

polymerizations. The following is the general procedure used for cHTC 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.\textsuperscript{9} cHTC (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

0 °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).\textsuperscript{1h} \( ^{1}H \) 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 \( (\nu_{\text{C-H}}) \), 1748 \( (\nu_{\text{C} = \text{O}}) \), and 1652 cm\textsuperscript{-1} \( (\nu_{\text{C} = \text{C}}) \).

Figure 1. GPC traces of poly(cHTC)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(cHTC) (Table 1, entry 1) in chloroform-d.

Figure 3. 62.5 MHz \( ^{13}C \)-NMR spectrum of P(cHTC) (Table 1, entry 1) in chloroform-d.
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 (‘HTC’). The monomer ‘HTC was synthesized in 81% yield by a one-pot reaction from cyclohexene, 4,4-dimethylaniline (see Scheme 1 and the Experimental Section for additional details). The structure and purity of ‘HTC was confirmed by FTIR, 1H-NMR, 13C-NMR, and melting point analyses (see Experimental Section).

Polymerization of ‘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 ‘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(‘HTC) with Mₙ values >100 000. A comparison of the results obtained using ZnEt₂ and ZnEt₂·H₂O (1/0.5) showed that the latter gave P(‘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 Mₙ of 77 100. Reactions conducted with Sn-catalysts were relatively slow and, with the exception of Bu₂SnCl₃, gave Mₙ values ≤30 800. For Bu₂SnCl₄, increasing the number of Cl ligands attached to Sn from 1 to 3 resulted in a significant increase in both P(‘HTC) yield and molecular weight. This trend for Bu₂SnCl₄ 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 Bu₂Sn(OMe)₄-catalysts resulted in increased P(‘HTC) yield and molecular weight (see Table 1). A previous report showed that the polymerizations (90 °C, M/C = 154) of DTC by ZnEt₂ (20 h), Al(2-sec-Bu)₃ (36 h), and Bu₂Sn(OMe)₂ (45 min) gave P(DTC) in yields (Mₙ) of 88% (35 000), 89% (20 000), and 45% (21 200), respectively.²⁷ Therefore, even though ‘HTC has relatively larger substituents than DTC, a comparison of these Al- and Zn-catalyzed polymerizations indicates that ‘HTC gave relatively higher product yields and molecular weights. However, it appears that the larger substituents of ‘HTC relative to DTC may be detrimental to its polymerization by Bu₂Sn(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.²⁸

Effect of Reaction Time. Table 2 shows the effect of reaction time on the polymerization of ‘HTC catalyzed by MAO and IBAO at 90 °C (‘HTC:Al mol/mol = 100). For IBAO-catalyzed polymerizations, the P(‘HTC) yield increased rapidly to 57% from 0 to 1 h and, subsequently, increased slowly (to 93%) from 1 to 8 h. Product Mₙ 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(‘HTC) products from IBAO catalysis (entries 6–8, Table 2) had unimodal distributions. The molecular weight dispersities (Mₘ/Mₙ) of these products ranged from 2.0 to 2.2.

Interestingly, an increase in the reaction time from 2 to 24 h for ZnEt₂·H₂O (1/0.5) catalyzed ‘HTC polymerization (M/C 400) did not alter product Mₙ, Mₘ/Mₙ, or yield (results not shown). Therefore, ZnEt₂·H₂O (1/0.5) at 90 °C over 24 h did not result in the depolymerization of preformed P(‘HTC) chains for extended reaction times.

Effect of Monomer/Catalyst Molar Ratio. The effects of the M/C molar ratio for ZnEt₂ and ZnEt₂·H₂O (1/0.5) catalyzed ‘HTC polymerizations (90 °C, 2 h) on P(‘HTC) yield and molecular weight are shown in Table 3. For ZnEt₂, the polymer yield decreased from 100% to 80% as M/C increased from 100 to 800. However, P(‘HTC) Mₙ remained high (≥200 000) and the polydispersity varied little as a function of M/C. Similarly, Kricheldorf and Weegen-Schulz²⁰ reported that for Bu₂SnCl₄-catalyzed TMC polymerizations, the M/C molar ratio had little influence on the yield and P(‘HTC) 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 ZnEt₂ concentration.

For ZnEt₂·H₂O (1/0.5) catalysis, P(‘HTC) yield showed no substantial change to M/C 400. However, increasing M/C from 400 to 800 decreased P(‘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 M₉ (by 2.6×) and decreased polydispersity (3.0 to 1.9) as M/C was increased from 100 to 400. The increase in Mₙ may be due to a decrease in the number of chain initiation events caused by ZnEt₂·H₂O (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
Structures of P(cHTC) isotactic and syndiotactic diads
equivalent fractions of isotactic and syndiotactic diads.
expected to be small resulting in atactic P(cHTC) with orientations to the chiral propagating chain end is.
In other words, the difference in activation energy
additions of monomer to the chiral propagating chain
behavior of diastereomeric am.
- NMR spectra. The 1H-NMR spectrum of P(cHTC)
protons. However, in the latter case, a higher field was needed to resolve the small differences in chemical shift.
Other protons such as cp,d p,e p, and bp 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 cHTC 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 1H-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 propagating chain end is expected to be small resulting in atactic P(cHTC)s with equivalent fractions of isotactic and syndiotactic diads. Structures of P(cHTC) isotactic and syndiotactic diads are shown in Chart 1.
The 13C-NMR spectrum of P(cHTC) (Table 2, entry 2) is shown in Figure 3. Assignments of carbons were based on a correlated 1H-13C 2D NMR spectrum (not shown).
- NMR spectra of selected P(cHTC) products prepared by using MAO, IBAO, BuSnCl3, ZnEt2, and ZnEt2-H2O (1:0.5) catalysts showed no evidence for decarboxylation during propagation. If decarboxylation had occurred, calculations using empirical equations for model compounds predicted that 1H- and 13C-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 HTCT without decarboxylation is consistent with previous reports for DTC and TMC polymerizations. Specifically, Schmilt et al. 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.

Thermal and Crystalline Properties. Solution cast films of P(cHTC) (Table 2, entry 7) and PTMC (Mn = 80 500, Mw/Mn = 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(cHTC) film did not show a melting transition during the first heating scan. The WAXS diffractogram of this P(cHTC) film gave an amorphous halo for 2θ = 14–25° devoid of crystalline reflections. Therefore, it was concluded that the P(cHTC) film was amorphous. PTMC showed a weak endotherm transition (peak at 40 °C, ΔHf = 1 J/g) that was likely due to melting. Analysis of the thermal transitions of PTMC by others gave similar results.

The second heating scans (Figure 4) showed that P(cHTC) had a Tg value which was 46 °C higher than that of PTMC (+30 and −16 °C, respectively). However, the Tg values for P(cHTC) and PDTC (Tg = 27 °C) were similar while the latter was semicrystalline (Tm = 108 °C, ΔHf = 20 J/g).
The thermal unzipping to cyclic oligomers. of poly(trimethylene carbonates) stabilize the chain from low levels (<2% by integration) of epoxide hydrolysis which occurred under the acidic conditions for epoxide formation and polymer isolation (see Experimental Section). The assignments of chemical shifts at 3.50 ppm (protons c, d) and the multiplet between 5.5 and 5.8 ppm (protons c and d) 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 4HTC 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 4HTC 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. 1H-NMR and 13C-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(4HTC) was amorphous and the glass transition temperature was 30 °C. In addition, analyses by TGA showed that P(4HTC) had a higher thermal stability than PTMC. Variable molar percentages (22–95%) of the vinyl P(4HTC) 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.

### References and Notes


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