4204 *Organometallics* **2007,** *26,* 4204−4211

Silica-Grafted Diethylzinc and a Silsesquioxane-Based Zinc Alkyl Complex as Catalysts for the Alternating Oxirane−Carbon Dioxide Copolymerization

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Received April 14, 2007

A novel zinc silsesquioxane complex ($[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Zn_4Me_4$ (**1**)) has been used as a model compound for silica-grafted zinc catalysts in the copolymerization of cyclohexene oxide and CO_2. Complex **1** exists as a dimer in the solid state and is moderately active in the copolymerization, and polycyclohexene carbonates have been obtained with a carbonate content of 79−98%. Polymerizations with $ZnEt_2$-treated silica particles resulted in polymer particles with $\bar{M}_n$ and $\bar{M}_w$ values and carbonate contents comparable to those of the polymers obtained with **1**. It was further demonstrated that CO_2 consumption can be followed online by monitoring the decrease of system pressure during the reaction. CO_2 consumption has been interpreted in relation to both polycarbonate and cyclic carbonate formation. These measurements represent the intrinsic kinetics of this reaction, which appear to be directly related to CO_2 pressure.

Introduction

In the search for new catalysts for the synthesis of aliphatic polycarbonates from carbon dioxide and oxiranes, several classes of catalysts have been developed over the years.[1] Typical examples are the bis(phenoxy)zinc[2] and β-diketiminatozinc[3] catalysts and the porphyrin and salen complexes of several metals.[4,5] More recently, several bimetallic systems based on zinc and magnesium have been reported.[6] All these catalyst systems have in common that they are homogeneous in nature and are used in solution polymerization processes. From an industrial point of view the solution copolymerization of oxiranes and carbon dioxide is not ideal. Even in the presence of additional solvent, the reaction mixtures containing polycarbonate tend to get very viscous already at low conversions. This limits the maximum solid content of the polymerization mixture and complicates processing and purification steps. Viscosity problems during polymerizations can be overcome by, e.g., performing the polymerization in an emulsion or in a nonsolvent, resulting in precipitation of the polymer before it can contribute to the viscosity of the medium. Emulsion polymerization would be highly desirable as it not only retains a low viscosity but also affords good bulk density control and particle morphology. Unfortunately, the oxirane−CO_2 copolymerization is generally

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10.1021/om700367x CCC: $37.00

not compatible with water.[7] This leaves precipitation polymerization as the most obvious choice to circumvent viscosity problems. As is well-known from catalytic olefin polymerization chemistry, precipitation polymerization reactions using homogeneous catalysts suffer from reactor fouling and poor morphology control. The use of heterogeneous catalysts generally helps to solve these problems.[8]

A few examples of heterogeneous catalysts capable of coupling oxiranes and carbon dioxide to either cyclic carbonates or polycarbonates have already been reported.[9] Immobilization of well-defined homogeneous catalysts by tethering of the ancillary ligand system to the support, as, for example, in the case of silica-tethered β-diketiminatozinc or Argogel-supported porphyrinatochromium complexes,[9a,b] is probably the most reliable but also the most laborious method of immobilizing the catalyst. A considerably more simple approach would be to graft zinc alkyls directly onto silica supports. Such a system would resemble the original catalyst as developed by Inoue et al.,[10] consisting of partially hydrolyzed $ZnEt_2$, and related homogeneous catalysts obtained by reacting zinc alkyls with alcohols, phenols, or (di)acids.[2,9c−j] At this point it is important to mention a fundamental difference between, for example, the above-mentioned tethered zinc or chromium complexes and silica-grafted zinc alkyls. In the former case not the metal but the ligand, which remains attached to the metal during the polymerization, is immobilized. In the latter case, the siloxy−zinc bond that binds the metal to the support is the reactive bond (vide infra), and during polymerization the metal center moves away from the support. Hence, for silica-grafted systems any form of chain termination will formally lead to leaching of the catalyst. Besides the fact that the alternating oxirane−CO_2 copolymerization is an intrinsically living polymerization process, encapsulation of the catalyst and growing chain within the growing polymer particle renders actual leaching unlikely.[3]

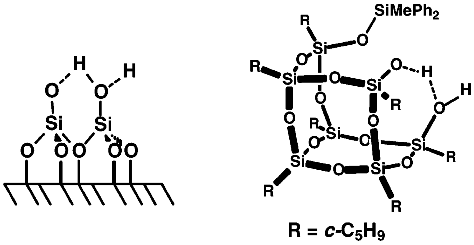

Figure 1. Vicinal silica surface silanols modeled by an incompletely condensed silsesquioxane.

Clearly, the heterogeneous nature of silica-grafted zinc alkyls dramatically hampers the study of such catalysts. Silsesquioxanes have proven to be realistic homogeneous models for silica surface silanols, and to date various heterogeneous catalytic processes such as olefin polymerizations,[11] alkene epoxidation,[12] and methathesis[13] have already successfully been mimicked using silsesquioxanes. The silsesquioxanedisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$ (Figure 1) structurally resembles vicinal silanols widely present on the surface of partly dehydroxylated silicas.[14]

Here we report the use of a silica-supported zinc catalyst and alongside it a homogeneous model system based on an incompletely condensed silsesquioxane ligand, $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$, for the epoxide−$CO_2$ copolymerization. Furthermore, the kinetics of these copolymerizations was studied using a model that enables the conversion to be modeled via the pressure drop during polymerization. The model provides a mathematical description of the relation among system pressure, temperature, initial composition, and actual composition.

Results and Discussion

Reaction of silsesquioxanedisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$ with 2 equiv of dimethylzinc afforded the zinc silses-

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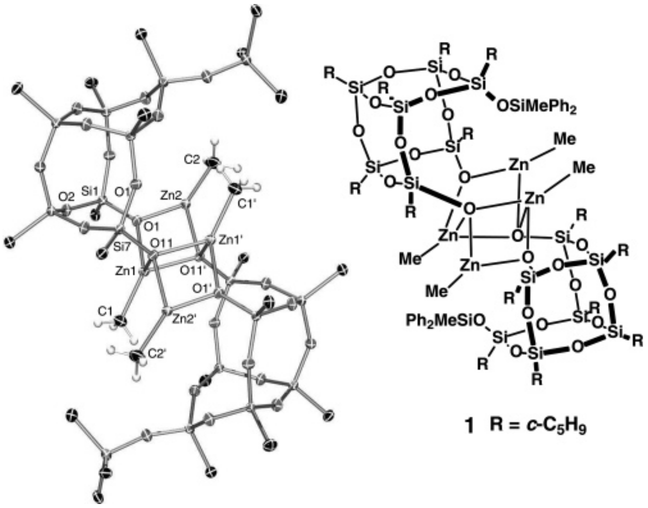


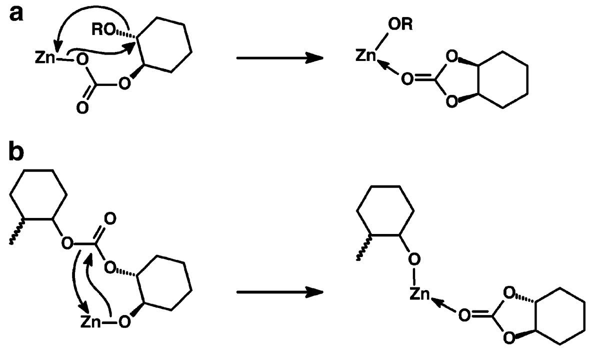
1 R = *c*-C_5H_9

Figure 2. Schematic presentation and molecular structure of [(c-C_5H_9)$_7$$Si_7O_{11}$($OSiMePh_2$)]$_2$$Zn_4Me_4$ (**1**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): Zn1−O1, 1.9767(11); Zn1−O11, 2.1764(12); Zn1−C1, 1.948(2); Zn1−O11, 2.1324(11); Zn2−O1, 1.9254(12); Zn2−C2, 1.922(2); Zn2−O11′, 2.0518(11); Si1−O1, 1.6281(13); Si1−O2, 1.6307(13); Si7−O11, 1.6431(12). Selected bond angles (deg): O1−Zn1−C1, 133.03(8); O11−Zn1−C1, 114.35(8); O11′−Zn1−C1, 129.73(7); O1−Zn1−O11, 100.81(5); O1−Zn1−O11′, 82.28(5); O11−Zn1−O11′, 83.76(4); O1−Zn2−*C*2, 141.76(8); O11′−Zn2−C2, 132.42(8); O1−Zn2−O11′, 85.69(5); Zn1−O1−Zn2, 100.36(6); Zn1−O11−Zn1′, 96.24(4); Zn1−O11−Zn2′, 98.54(5); Zn1′−O11−Zn2′, 91.48(4); Zn1−O1−Si1, 133.01(7); Zn2−O1−Si1, 126.03(7); Zn1−O11−Si7, 117.32(6); Zn1′−O11−Si7, 127.54(6); Zn2′−O11−Si7, 119.21(6).

quioxane complex [(c-C_5H_9)$_7$$Si_7O_{11}$($OSiMePh_2$)]$_2$$Zn_4Me_4$ (**1**) in moderate isolated yield. Crystals of **1** suitable for X-ray crystal structure determination were grown from a mixture of hexane/toluene.[15]

Complex **1** (Figure 2) is a dimeric species containing two silsesquioxane cages bound together by four zinc atoms. The molecule has a crystallographically imposed center of inversion in the center of the Zn1−O11−Zn1′−O11′ plane. Two of the four zinc atoms are distorted trigonal planar, whereas the other two are tetrahedrally coordinated. Consequently, O1 is μ_2-bridged and O11 is μ_3-bridged between the zinc atoms. Accordingly, the Zn1−μ_2-O1 (1.9767(11) Å), Zn1−μ_3-O11 (2.1764(12) Å), and Zn1−C1 (1.948(2) Å) distances are longer than the corresponding Zn2−μ_2-O1 (1.9254(12) Å), Zn2−μ_3-O11′ (2.0518(11) Å), and Zn2−C2 (1.922(2) Å) bond lengths. The Zn2−C2 and Zn2−μ_2-O1 bond lengths are significantly shorter than the corresponding Zn−C and Zn−μ_2-O distances of the trigonal planar zinc centers in [(*c*-C_5H_9)$_7$$Si_7O_{12}$]$_2$$Zn_4Me_2$ (Zn−C$_{av}$ = 1.942(5) Å, Zn−μ_2-O$_{av}$ = 1.955(3) Å)[16] and, for example, [(MeZn)$_2$Zn(OSi^{i}Pr$_3$)$_4$] (Zn−C$_{av}$ = 1.946(3) Å, Zn−μ_2-O$_{av}$ = 1.975(2) Å).[17] The Zn−μ_3-O bond lengths in **1** are similar to the Zn−μ_3-O bond distances in, e.g., [MeZn(μ_3-OSiEt$_3$)]$_4$ (Zn−μ_3-O$_{av}$ = 2.090(4) Å). Si−O$_{av}$ (1.6244(13) Å) is normal within the range found for silsesquioxane compounds. The C−Zn−O and O−Zn−O angles in **1** are comparable to those in the above-mentioned zinc silsesquioxane and siloxane complexes.

Scheme 1. Cyclic Carbonate Formation: (a) Direct Yielding *cis*-Cyclohexene Carbonate, (b) via Back-Biting, Affording *trans*-Cyclohexene Carbonate



Copolymerization of Cyclohexene Oxide and CO_2. The silsesquioxane-based zinc complex **1** has been tested for its activity in the copolymerization of cyclohexene oxide and carbon dioxide. The results of these experiments are summarized in Table 1. Polymerization experiments were carried out under conditions that are generally used for two well-known catalyst systems, the β-diketiminatozinc system (10 bar, 50 °C)[3b] and the bis(phenoxy)zinc complexes (55−80 bar, 80−120 °C).[2e] To compare the results with the most similar system known, a reference polymerization with the Darensbourg [($F_2C_6H_3O$)$_2$-Zn·THF]$_2$ was carried out.

At 120 °C in the absence of CO_2, **1** is a moderately active catalyst for the homopolymerization of cyclohexene oxide (CHO) to poly(cyclohexene oxide) (PCHO). Applying a CO_2 pressure of 10 bar inhibits the formation of PCHO significantly, and although the activity is low, poly(cyclohexene carbonate) (PCHC) is formed with a carbonate content of around 80%. MALDI-TOF-MS confirmed that a poly(ether-*co*-carbonate) is formed and not a blend of polyether and polycarbonate. Increasing the pressure has a significant positive effect on the activity and selectivity of the catalyst, and at 80 bar PCHC with a carbonate content around 98% was obtained. Raising the temperature from 50 to 120 °C while maintaining the pressure at 10 bar (or from 80 to 120 °C at 80 bar) has a negligible effect on the activity and selectivity, demonstrating that pressure has a more pronounced influence on the activity than temperature. In this respect, catalyst **1** resembles the zinc phenoxide catalyst rather than the β-diketiminatozinc catalyst that was found to be zeroth-order in CO_2.[2,3]

Depolymerization of aliphatic polycarbonates via back-biting and formation of cyclic carbonates is a well-known thermal decomposition reaction. Interestingly, at 120 °C cyclic carbonate formation is more pronounced at high carbon dioxide pressure (80 bar), which suggests that a zinc carbonate species is involved in this back-biting process. The thus proposed back-biting process would resemble the direct formation of cyclic carbonate, which is known to be a double-inversion process leading to *cis*-cyclic carbonate. However, the fact that only *trans*-cyclohexene carbonate was obtained excludes the double inversion process and strongly points to a normal chain-end back-biting process (Scheme 1). Although there is a clear promoting effect of increased CO_2 pressure on formation of *trans*-cyclic carbonate, the origin of this effect is not straightforward.

The polymerization carried out at 120 °C and 80 bar of CO_2 catalyzed by **1** was followed in more detail. Sampling at regular

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[15] ($C_{50}H_{82}O_{12}Si_8Zn_2$)$_2$, M_r = 2461.32, monoclinic, $P21/n$, a = 14.8772(6) Å, b = 17.9401(7) Å, c = 21.9733(8) Å, β = 90.006(1)°, V = 5864.6(4) Å^3, Z = 2, D_x = 1.394 g·cm^{-3}, F(000) = 2600, μ = 10.38 cm^{-1}, T = 110 K, 53279 reflections measured, GOF = 1.041, $R_w(F^2)$ = 0.0869, $R(F)$ = 0.0327. Data were collected on a Nonius Kappa CCD area detector with a graphite monochromator (λ = 0.71073 Å).

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Table 1. Selected Copolymerization Results with Cyclohexene Oxide and CO_2

entry	catalyst[a]	time (h)	pressure (bar)	temp (°C)	CHO conversion[b] (%)	CHC fraction[b] (%)	CO_2 fraction (%)	TOF[c] (h^{-1})	$\bar{M}_n$[d] ($g \cdot mol^{-1}$)	$\bar{M}_w/\bar{M}_n$
1	none	24	80	120	2	0	0			
2	$[(F_2C_6H_3O)_2Zn \cdot THF]_2$	28	80	80	19	0	98	15.4	25800	18.4
3	**1**	24	0	120	13	0	0	4.0		
4	**1**	24	10	50	9	2	79	2.8	*e*	*e*
5	**1**	24	10	120	8	2	80	2.5	13900	3.8
6	**1**	24	80	80	34	2	92	10.1	10600	10.8
7	**1**	24	80	120	44	14	98	13.5	11600	10.0
8	SiO_2-ZnEt_2	24	80	120	6		93	0.7	9000	5.3
9	SiO_2-ZnEt_2	48	80	120	6		85	0.6	8400	5.0

[a] All polymerizations were performed with 200 μmol of the catalyst (calculated for the monomeric form), 35 mL of toluene, and 15 mL of CHO. [b] The conversion and amount of CHC were determined by integration of methine peaks in the ^1H NMR spectra. [c] Units of mol of $CHO \cdot mol \cdot cat^{-1} \cdot h^{-1}$ (referring to the monomeric catalyst species). [d] PS equivalents. [e] The high molecular weight fraction of the distribution was outside the exclusion limit of the used SEC columns.

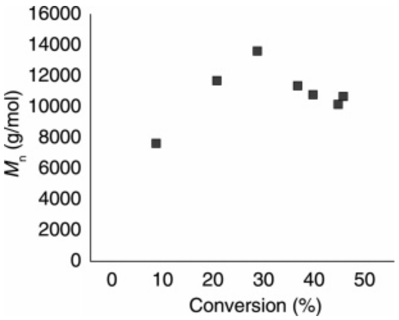

Figure 3. $\bar{M}_n$ development plotted versus the conversion for **1**.

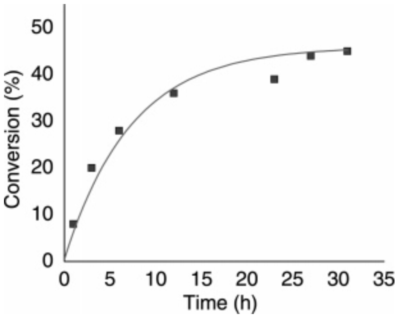

Figure 4. Conversion development over time for **1**.

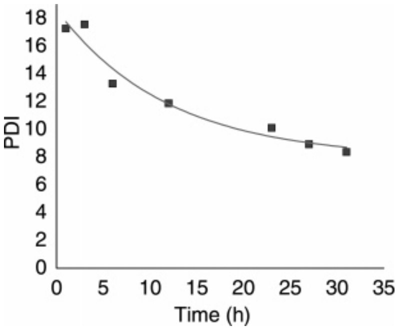

Figure 5. Polydispersity development over time for **1**.

intervals during the polymerization allowed us to follow the conversion and molecular weight buildup of the polymerizations over a prolonged period of time (Figures 3−5).[18]

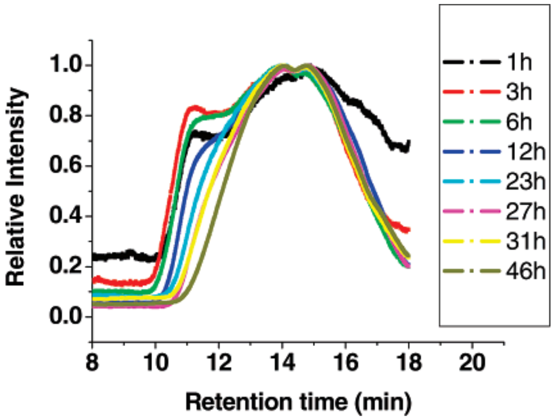

Figure 6. SEC traces showing the PCHC molecular weight development over time for a copolymerization of cyclohexene oxide and carbon dioxide with **1** as the catalyst.

A good indication for a living, single-site character of a catalyst is the linear behavior of $\bar{M}_n$ plotted versus the conversion. As is clear from Figure 3, this is not the case for **1** (vide infra). $\bar{M}_n$ values around 10000 $g \cdot mol^{-1}$ are already reached at the beginning of the polymerization, and an ill-defined maximum value can be seen around 25% conversion. Figure 4 shows a typical development of conversion with time for **1** with a strong decrease in the polymerization rate when conversion approaches 50%. The strong decrease in the polymerization rate above 40% conversion is attributed to mass-transfer limitation as a result of the high viscosity. The PDI development over time (Figure 5) shows a maximum value in the beginning of the polymerization and a gradual decrease during polymerization. In the beginning of the polymerization complex **1** apparently has a tendency to make both short and some very long chains. This leads to a high $\bar{M}_w$ and a relatively low $\bar{M}_n$. Over time the lower molecular weight chains predominate, leading to a drop in $\bar{M}_w$, while the $\bar{M}_n$ values still average around 11000 $g \cdot mol^{-1}$, causing a reduction of the polydispersity index. This behavior can also be seen in Figure 6, showing the size exclusion chromatography (SEC) plots of the same samples taken at selected time intervals for the construction of Figures 3−5.

With respect to activity and optimal polymerization conditions, **1** resembles the bis(phenoxide)zinc system more than the β-diketiminatozinc system. This is also expected assuming that, similar to that for the bis(phenoxide)zinc system, initial insertion occurs in the zinc−siloxide bond, after which the ligand is separated from the zinc center and any further influence of the ligand is negligible. Also the broad polydispersity observed for **1** resembles that of the bis(phenoxide)zinc catalyst.[19] Such broad distributions are characteristic for multiple active sites and/or slow competing processes during the polymerization such as slow initiation, chain scission, and transesterification. The

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(18) Reaction conditions: 100 μmol of the dimeric catalyst, 15 mL of CHO, 35 mL of toluene, 120 °C, 80 bar.

(19) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. C. *Inorg. Chem.* **2001**, *40*, 986−993.

dimeric silsesquioxane zinc catalyst **1** consists of four zinc centers each with potential initiating sites and likely to result in a multimodal distribution. Furthermore, possible dissociation of the dimer during polymerization will afford an even larger variety of active sites each with its own activity that will also contribute to a multimodal distribution. To elucidate whether chain scission reactions are responsible for the gradual lowering of $\bar{M}_w$, a MALDI-TOF-MS study was performed on the polycarbonates formed with **1** to determine the end groups of the polymer chains.

MALDI-TOF-MS Analysis. The MALDI-TOF-MS of the polycarbonate in Figure 7 shows a nonperfectly alternating oxirane−CO_2 copolymer, as could also be seen by ^1H NMR. Although only one combination of end groups was expected, actually three different end groups can be assigned. During the workup procedures the polymer−silsesquioxane bonds were expected to be readily hydrolyzed to give hydroxide end groups (Figure 7A).[20] Indeed, the MALDI-TOF-MS did not show any silsesquioxane end groups.

The mass of the second simulated chain structure (Figure 7B) corresponds to either a cyclic structure, $[OC_6H_{10}]_n[CO_2]_m$ ($n \geq m$), or a linear polymer containing a proton and a cyclohexenolate as end groups, $H[OC_6H_{10}]_{n-1}[CO_2]_mOC_6H_9$ ($n \geq m$). Although cyclic poly(cyclohexene carbonate) structures have not been reported to date, their existence is not unlikely. Cyclic carbonate formation by the back-biting mechanism (Scheme 1) is actually the most simple example of this process. Intramolecular transesterification at other carbonate functionalities along the polymer chains has a 50% chance to afford cyclic structures. However, leaving the reaction mixture at 80 °C for two weeks did not result in a significant lowering of the polydispersity index, excluding possible transesterification reactions being of great importance in this system. As already mentioned, the mass also corresponds to a polymer structure containing a cyclohexenolate end group. Previously, for Lewis acidic zinc bis(aryl oxide) and β-diketiminatozinc catalysts, we have reported the presence of a combination of cyclohexenolate and cyclohexanolate end groups. It was proposed that these end groups were the result of oxirane rearrangement and Meerwein−Ponndorf−Verley−Oppenhauer (MPVO) reduction/oxidation.[21] As no cyclohexanolate end group could be found here,[22] it is likely that the origin of the observed OC_6H_9 end group is different in this case. A possible explanation for the presence of the cyclohexenolate end groups is a thermal chain scission process as reported by Liu et al. for poly(propylene carbonate),[23] where a carbon dioxide molecule is released from the polycarbonate chain by a mechanism as depicted in Scheme 2. Both end groups (cyclohexenolate and cyclohexanol) formed in such a process can be observed by MALDI-TOF-MS (Figure 7). At this point no conclusive evidence for either decarboxylation or formation of cyclic structures is present. The existence of the third polymer structure containing a proton and a menthyl end group ($H[OC_6H_{10}]_n[CO_2]_mCH_3$) is interesting and proves that insertion of carbon dioxide even into zinc−carbon bonds is possible upon pretreatment of the catalyst with CO_2 (10 bar, 50 °C, 30 min). So far we had assumed the zinc−siloxide bond to be the sole reactive bond in these catalysts. This assumption was based on the fact that dialkylzinc and β-diketiminatozinc alkyls are inactive in CO_2−oxirane copolymerizations. Treatment of the zinc alkyls with a protic reagent (carboxylic acid, alcohol, or water in the case of the original Inoue system) or SO_2 prior to the polymerization was required to obtain an active catalyst.[3]

Zinc-Modified Silica Particles. A heterogeneous silica-supported zinc catalyst has been prepared by modifying mesoporous silica particles (50 μm, 304 $m^2 \cdot g^{-1}$) with $ZnEt_2$. Analysis of the zinc content of the catalyst by means of ICP-MS showed a content of 1.82 mmol of $Zn \cdot g^{-1}$. Literature values of the silanol content of unmodified Sylopol 948 silica, calcined under the same conditions we used (250 °C for 3 h), were found to be 3.2 mmol of hydroxyl $groups \cdot g^{-1}$, which would imply a silanol conversion with zinc of around 56%. Polymerizations with the silica-supported zinc catalyst were performed in a high-pressure reactor equipped with a sapphire view cell to visually follow the polymerizations (Table 1, entries 8 and 9). To enhance the probability that the polycarbonate would precipitate during the polymerization, the reactions were performed in heptane as a nonsolvent. The morphology of the formed polymer is clearly different compared to that of the polymers obtained with complex **1**. The polymer particles formed have a significantly higher bulk density compared to the light and fluffy polymers obtained after precipitation in petroleum ether of the viscous reaction mixture. Unfortunately, despite the use of heptane as a nonsolvent, the monomer itself is a very good solvent for the polymer, and its presence resulted in the formation of sticky polymer particles. As is commonly observed for heterogeneous catalysts, the activity of the silica-supported catalyst is lower compared to that of its homogeneous analogue **1**.[9] The molecular weight of the polymer is comparable to that obtained with **1**, and the polydispersity of the polymer is, with a value of 5 in heptane, lower than that of **1** under similar conditions in toluene. The carbonate contents also remained at the same level as found for **1**. This contrasts the results obtained by Lu et al. for the silica-tethered β-diketiminatozinc system, where a considerable drop in CO_2 content was observed compared to that of the homogeneous analogue.[9b]

Kinetics. A kinetic study on the copolymerization of cyclohexene oxide and carbon dioxide with catalyst **1** was performed. The pressure drop that was measured during the reactions was interpreted in terms of a change in liquid-phase composition and was used to calculate the CHO and CO_2 conversion. As the vapor pressure of the system is mainly determined by the CO_2 to CHO ratio in the liquid phase, it serves as a primary indication of the composition of this phase. The PCHC concentration can be calculated from the difference between the actual and initial CO_2 to CHO ratios. The use of this approach is restricted by the validity of the assumption of thermodynamic equilibrium between the vapor and liquid phases, knowledge of the stoichiometry of the reaction, and knowledge of the initial composition. In this work the effect of polymer concentration is neglected as it is expected to influence the vapor pressure by less than 2%.[24] This assumption seems valid, because the conversion of CHO is typically below 30%. Additionally, the transfer of components between the liquid and vapor phases is assumed to be negligible, as the pressure drop and change in volume of the liquid phase are relatively small.

The experimental conditions and results of these experiments are summarized in Table 2. The results of these kinetic

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(20) A silanol group is more acidic than a cyclohexanol, which is a good indication that the silanol is a better leaving group. See ref 14.

(21) Meerendonk, W. J.; van Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2005**, *38*, 7306−7313.

(22) Recently, we discovered that chains with the combination of cyclohexyl/cyclohexenyl end groups originate from the reaction of the catalyst with CHO in the absence of CO_2. As done in this study, these end groups are absent when the CHO is added after the reactor is charged with the catalyst and CO_2.

(23) Liu, B.; Chen, L.; Zhang, M.; Yu, A. *Macromol. Rapid Commun.* **2002**, *23*, 881−884.

(24) The effect of PCHC on the vapor pressure of similar CHO/CO_2 mixtures at 120 °C and 20% conversion is typically lower than 2%.

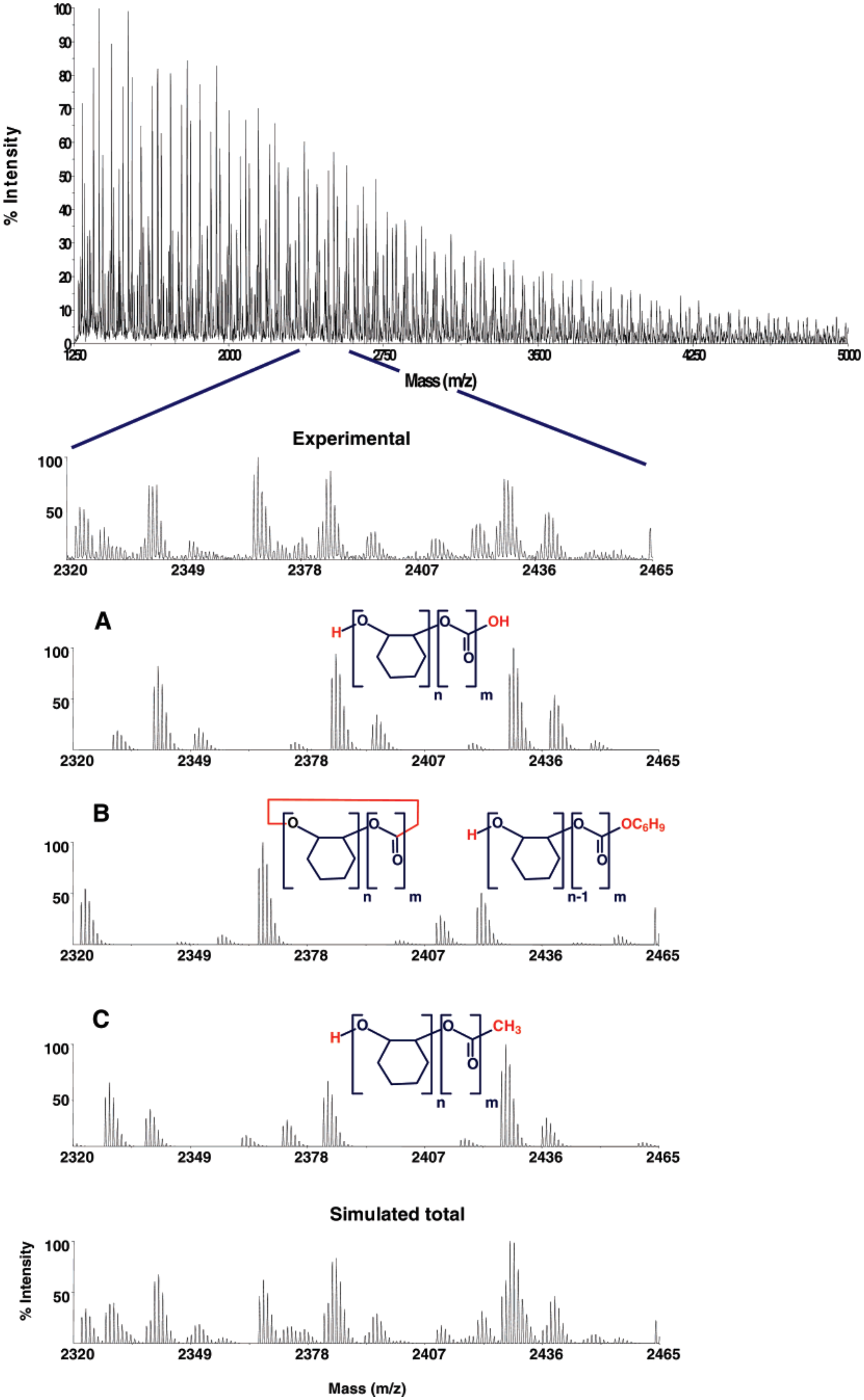
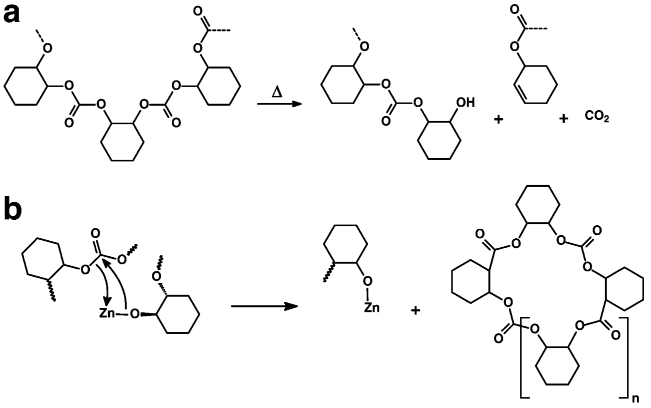


Figure 7. MALDI-TOF-MS spectrum and an enlargement of a part of the spectrum of the K^+ adduct of PCHC obtained with catalyst **1** at 120 °C and 80 bar. Also shown are simulated spectra (A−C) for different end groups.

experiments are graphically presented in Figure 8. As was found by Darensbourg for the bis(phenoxide)zinc systems,[2f] comparison of entry 1 with entries 2−5 (Table 2) indicates that addition of PCy_3 strongly improves the selectivity of polycarbonate over polyether formation. Addition of a stoichiometric ratio of PCy_3 to Zn (entry 2) resulted in perfectly alternating copolymers for

Scheme 2. Possible Side Reactions: (a) Chain Scission via Decarboxylation, (b) Formation of Cyclic Structures by Transesterification



catalyst **1**. For entry 2 the observed decrease in cyclic carbonate formation can be attributed to the lower reaction temperature. Entries 3−5 demonstrate that the formation of ether linkages for **1** can also be inhibited by adding PCy_3 to Zn in a 1:2 ratio. In this case catalyst activities are significantly higher. Entries 3−5 also demonstrate the positive effect of CO_2 pressure on catalyst activity, which indicates that CO_2 is involved in the rate-determining step of this reaction.

The results of the model calculations that provide a mathematical description of the relation among system pressure, temperature, initial composition, and actual composition are presented in Figure 8. Although the model does not account for cyclohexene carbonate (CHC) formation, Figure 8 indicates that the total carbonate yield (PCHC + CHC), calculated from vapor pressure data, agrees well with the results of the ^{1}H NMR analysis. This is probably due to the very low vapor pressure of CHC and similar interaction toward CO_2, which allows us to treat CHC like carbonate fragments in the polymer chain. The development of conversion over time suggests that there is no significant change of the reaction rate. As diffusion coefficients are expected to decrease significantly in this regime, this indicates that reaction rates are not determined by mass-transfer limitations and therefore represent intrinsic kinetics of this reaction.

Conclusions

It can be concluded that the zinc silsesquioxane complex **1** is active in the copolymerization of cyclohexene oxide and CO_2 and resembles the zinc bis(phenoxide) system. Polydispersities are broad and typical for multisite catalysts. The presence of three different types of end groups not only revealed that both the Zn−O and Zn−C bond can initiate the polymerization but also demonstrated that thermal chain scission by either transesterification leading to ring structures or thermal decarboxylation and dehydrogenation occurs. Precipitation polymerization with $ZnEt_2$-treated silica particles indeed results in a lowering of the viscosity of the medium with respect to the system using homogeneous catalysts. Due to the presence of excess CHO during the polymerization the product was obtained as sticky polymer particles, but this problem can probably be tackled by optimization of process conditions. Reaction kinetics were determined by following the pressure drop, which is related to the change of composition during the reaction. These measurements appear to represent the intrinsic kinetics of this reaction, which is directly influenced by CO_2 pressure.

Experimental Section

Materials. CHO (Aldrich) was dried over CaH_2, distilled, and stored under argon on molecular sieves (4 Å) prior to use. Carbon dioxide (>99.9993% pure) was purchased from HoekLoos and was used without any further purification. Toluene and petroleum ether (40−70) were dried over an alumina column and stored on molecular sieves (4 Å). Heptane and benzene-d_6 were dried by distillation from Na/K alloy. Chloroform-d_1 was dried on molecular sieves (4 Å). Unless mentioned otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox (Braun MB-150-GI). Commercial silica gel (Grace Davison, Sylopol 948, 50 μm, 304 $m^2 \cdot g^{-1}$) was used as the support. All other chemicals were purchased from Aldrich and were used as received. The silsesquioxane ligand $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$[25] and the bis(phenoxy)zinc complex $[(2,6\text{-}F_2C_6H_3O)_2Zn \cdot THF]_2$[2e] were prepared according to literature procedures.

Analytical Techniques. ^{1}H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz), a Varian Mercury Vx (400 MHz), and a Varian Mercury Plus (200 MHz) spectrometer. Size exclusion chromatographs were recorded on a Waters GPC instrument equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$. A set of two linear columns (Mixed C. Polymer Laboratories, 30 cm, 40 °C) were used. Molecular weights were calculated relative to polystyrene standards. Data acquisition and processing was performed using Waters Millennium32 software. MALDI-TOF-MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix, DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was synthesized according to literature procedures.[26] The matrix was dissolved in THF at a concentration of 40 $mg \cdot mL^{-1}$. Potassium trifluoroacetate (Aldrich, >99%) was used as the cationization agent and dissolved in THF at typical concentrations of 1 $mg \cdot mL^{-1}$. Polymer was dissolved in THF at approximately 1 $mg \cdot mL^{-1}$. In a typical MALDI-TOF-MS analysis, the matrix, potassium trifluoroacetate, and the polymer solution were premixed in a ratio of 10:1:5. The premixed solutions were hand-spotted on the target well and left to dry. Spectra were recorded in both the linear and reflector modes. Baseline corrections and data analyses were performed using Data Explorer version 4.0 from Applied Biosystems. Elemental analyses were carried out at the Analytical Department of the University of Groningen and at ALControl BV.

$[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Zn_4Me_4$ (1). To a cooled (−80 °C) solution of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$ (2.14 g, 2.0 mmol) in toluene (20 mL) was added $ZnMe_2$ (2.2 mL, 2.0 M in toluene, 4.4 mmol). The mixture was allowed to warm to room temperature, upon which evolution of gas was visible. After being stirred for 30 min, the mixture was gently heated, and when gas evolution ceased, it was heated to reflux for 1 min. After evaporation of the volatiles, the last traces of toluene were removed by dissolving the product in hexane (5 mL) and subsequent evaporation of the volatiles. The residue was dissolved in a hot mixture of hexane (50 mL) and toluene (10 mL), and the solution was filtered. Colorless crystals of **1**, suitable for an X-ray diffraction study (1.27 g, 0.52 mmol, 52%), were obtained after crystallization at −30 °C. ^{1}H NMR (benzene-d_6): $\delta = 7.80$ (d, 8 H, Ph), 7.25 (m, 12 H, Ph), 1.70 (m, 112 H, $CH_2C_5H_9$), 1.25 (m, 14 H, CHC_5H_9), 0.95 (s, 6 H, $SiCH_3$), 0.05 (s, 12 H, ZnMe). $^{13}C\{^1H\}$ NMR (benzene-d_6): $\delta = 137.82$, 134.73, 129.69, 128.14 (Ph), 28.62, 28.43, 28.26, 28.17, 27.94, 27.89, 27.46, 27.42, 27.36, 27.33, 27.30, 27.17, 26.95, ($CH_2C_5H_9$), 25.65, 25.17, 24.16, 23.04, 22.82 (1:2:2:1:1, CHC_5H_9), 0.41

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(26) Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *Eur. J. Mass Spectrom.* **2000**, *6*, 49−52.

Table 2. Kinetic Experiments of the Copolymerization of Cyclohexene Oxide and CO_2

entry	amt of **1**[a] (μmol)	PCy_3:Zn (mol/mol)	time (h)	pressure (bar)	temp (°C)	conversion[b] (%)	CHC fraction[b] (%)	CO_2 fraction[b] (%)	TOF[c] (h^{-1})	$\bar{M}_n$[d] ($g{\cdot}mol^{-1}$)	$\bar{M}_w/\bar{M}_n$
1	227	0.0	22	124	125	47	14	65	4.3	10400	4.3
2	222	1.0	5	49	80	8.7	0.6	>99	0.36	11400	7.3
3	189	0.57	95	50	121	13	9.9	>99	0.60	8100	4.8
4	188	0.53	95	76	116	33	13	>99	1.20	7200	3.2
5	189	0.50	39	104	116	22	8.0	>99	4.43	10600	3.7

[a] Referring to the monomeric catalyst species. [b] As determined by integration of the methine peaks of the different species. [c] Units of mol of CHO·mol·cat^{-1}·h^{-1} (referring to the monomeric catalyst species). [d] PS equivalents.

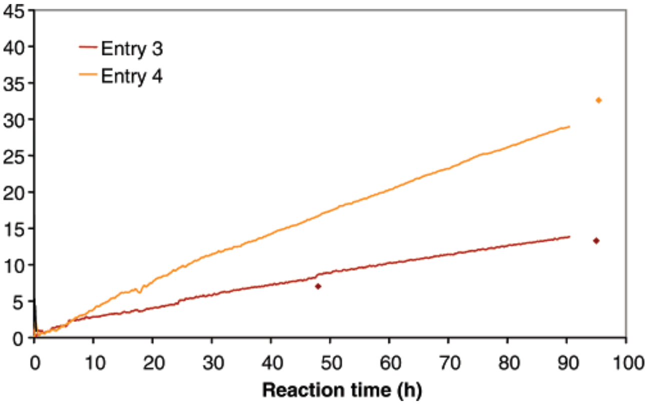

Figure 8. Carbonate (PCHC + CHC) yield as a function of the reaction time for entries 3 and 4 (Table 3). The lines are calculated from vapor pressure data. Symbols represent results from ^{1}H NMR analysis.

(SiCH_3), −10.39 (ZnCH_3). ^{29}Si{^{1}H} NMR(benzene-d_6 vs $SiMe_4$) δ = −10.77 (*Si*$MePh_2$), −57.33, −63.26, −64.12, −65.20, −65.60 (2:1:1:1:2). Anal. Cald for $C_{100}H_{164}O_{24}Si_{16}Zn_4$ (2461.28 g·mol^{-1}): C, 48.80; H, 6.72. Found: C, 48.19; H, 6.56.

$ZnEt_2$-Treated Silica (2). To a suspension of predried silica (250 °C, 3 h, vacuum) in heptane (25 mL) was slowly added $ZnEt_2$ (25 mL, 1 M solution in hexane). The suspension was stirred overnight, decanted, washed with 2 × 10 mL of heptane to remove unreacted $ZnEt_2$, and dried in vacuo. The sample was analyzed by ALControl BV using the following method. A 108.9 mg sample of the diethylzinc-treated silica was extracted in the course of 1 h by 10 mL of a 1% solution of HNO_3. The solution was then filtered (0.45 μm) and analyzed by ICP-MS (according to NEN 6426). The found concentration of zinc was 1.82 mmol of zinc·g of silica^{-1}.

Example of a Typical Copolymerization Using Complex 1. The dimeric compound **1** (240 mg, 100 μmol) was dissolved in toluene (35 mL) and injected into a 380 mL steel autoclave. The autoclave was pressurized to 10 bar and heated to 50 °C for 30 min. Next the cyclohexene oxide (15 mL) was injected into the reactor with a CO_2 overpressure (50 bar). All valves were closed, and the reactor was further heated to 120 °C, resulting in a pressure of about 80 bar. After a set polymerization time, a sample was taken for ^{1}H NMR analysis (300 MHz, chloroform-d_1) to determine the conversion. Conversions were determined by integration of the methine peaks in the ^{1}H NMR spectra. ^{1}H NMR (300 MHz, chloroform-d_1): δ 4.65 (br, CH (PCHC), 2H), 3.11 (s, CH (CHO), 2H). The samples for SEC analysis were prepared as follows: About 0.5 mL of each of the reaction mixtures was added dropwise to a 10-fold excess of petroleum ether (40−70), upon which the PCHC precipitated. After separation, the polymer was redissolved in the SEC eluent (THF). Polymer solutions for MALDI-TOF-MS analyses were prepared in a manner similar to that described above.

Example of a Typical Copolymerization for Kinetic Measurements. The initial CO_2 to cyclohexene oxide ratio for the kinetic experiments was controlled by preparation of a liquid feed in a separate autoclave. For this purpose dry CHO (300 mL) was added to a dry 500 mL autoclave, which was subsequently pressurized with CO_2. The composition of the liquid phase in this reactor was controlled by temperature and pressure.[27] Thermodynamic equilibrium was assumed after 12 h of intensive mechanical stirring. Prior to the catalytic experiments, the 100 mL autoclave was dried overnight at 120 °C under an argon flow. Upon transfer of a mixture of catalyst **1** and PCy_3 to the autoclave, the complete system was rinsed during three repetitive cycles of vacuum and CO_2 atmosphere. While the autoclave was maintained at room temperature, the liquid feed was added and subsequently heated to the desired reaction temperature. It should be noted that for these copolymerizations no additional solvents were used. After each experiment the conversion as calculated from the vapor pressure was verified using ^{1}H NMR. The products were purified by the dropwise addition of a 10-fold volumetric dilution of the reaction mixture in THF to a 10-fold excess of petroleum ether. The precipitated poly(cyclohexene carbonate) was subsequently separated and dissolved in THF for analysis by SEC, as described earlier.

Acknowledgment. We thank the Dutch Polymer Institute (DPI) for their financial support. This research forms part of the research program of the DPI, Project No. 286.

Supporting Information Available: Complete crystallographic data for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700367X

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