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The Copolymerization of Carbon Dioxide and [2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane Catalyzed by (Salen)CrCl. Formation of a CO_2 Soluble Polycarbonate

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The copolymerization of 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane and carbon dioxide catalyzed by (salen)$Cr^{III}Cl$ (H_2salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine) with 2.5 equiv of *N*-MeIm as cocatalyst affords a polycarbonate devoid of polyether linkages, along with only a trace quantity of cyclic carbonate. The presence of the trimethoxysilane functionality in the epoxide not only provided the reactant monomer and product copolymer high solubility in liquid carbon dioxide but also provided the ability to cross-link the copolymer and thereby greatly alter the physical properties of the thus formed polycarbonate. In addition, the enhanced solubility of the copolymer in liquid CO_2 furnishes a ready means of removing the highly colored metal catalyst from the polycarbonate product.

Recent advances in catalyst design for the copolymerization of epoxides and carbon dioxide have led to the feasibility of synthesizing a new generation of thermoplastics with interesting characteristics and physical properties. Most of the fundamental studies in this area have focused on copolymers derived from cyclohexene oxide and propylene oxide monomers.[1] Previously, we have shown that poly(cyclohexylene carbonate) in general has inferior corresponding properties with the widely applied bisphenol-A-polycarbonate produced from bisphenol A and phosgene.[2] However, the copolymers produced from propylene oxide or ethylene oxide and carbon dioxide, i.e., poly(propylene carbonate) and poly(ethylene carbonate), have several useful applications, including binders, lost foam casting, and coatings.[3] The search for other copolymers prepared via this environmentally benign route which possess even greater commercial value is one of our active research goals. Relevant to this objective, the epoxy-functionalized silanes, [2-(3,4-epoxycyclohexyl)ethyl]triethoxysilane and [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane, are designed as cross-linkers for coating formulations.[4] Herein, we report our initial findings on the copolymerization reactions of these epoxy silanes with carbon dioxide in the presence of (salen)$Cr^{III}Cl$.

Copolymerization reactions of **1** and carbon dioxide were carried out in a 300 mL stainless steel Parr reactor modified to accommodate an ASI ReactIR SiCOMP probe.[5] In a typical experiment 10 mL of **1** was added to the reactor, which was heated to 80 °C, and a background spectrum was recorded. The catalyst, (salen)$Cr^{III}Cl$ (H_2salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine) (50 mg, 0.086 mmol), and 17 μL (0.21 mmol, 2.5 equiv) of *N*-methylimidazole (*N*-MeIm) in 10 mL of **1** were added to the reactor via the injection port. The reaction vessel was pressurized with bone dry carbon dioxide to 55 bar and maintained at 80 °C. Figure 1 illustrates the three-dimensional stack plot of the infrared spectra taken in the $\nu(CO_2)$ region as a function of time, where the major absorbance at 1748 cm^{-1} is due to the polycarbonate. Noted as well in Figure 1 is the formation of a very small quantity

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(1) (a) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577. (b) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368. (c) Super, M.; Beckman, E. *Macromol. Symp.* **1998**, *127*, 89. (d) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018. (e) Beckman, E. *Science* **1999**, *283*, 946. (f) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107. (g) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487. (h) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, B. E.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738. (i) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007. (j) Eberhardt, R.; Allmendinger, M.; Luinstra, G. A.; Rieger, B. *Organometallics* **2003**, *22*, 211. (k) Inoue, S. *J. Polym. Sci.: A* **2000**, *38*, 2861. (l) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725. (m) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. *Macromolecules* **2000**, *33*, 303. (n) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284. (o) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 581.

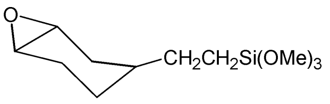
(2) Koning, C.; Wildeson, J. R.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. *Polymer* **2001**, *42*, 3995.

(3) Empower Materials, 100 Interchange Boulevard, Newark, DE 19711. A subsidiary of Axess Corporation of Greenville, Delaware. http://www.empowermaterials.com.

(4) (a) OSi Specialties, One American Lane, Greenwich, CT 06831-2559. http://www.eastechchemical.com. (b) Crivello, J. V.; Mao, Z. *Chem. Mater.* **1997**, *9*, 1554.

(5) Monomer **1** was obtained as a mixture of cis and trans isomers from Gelest, Inc., and purified by vacuum distillation over CaH_2.

10.1021/ic034363m CCC: $25.00



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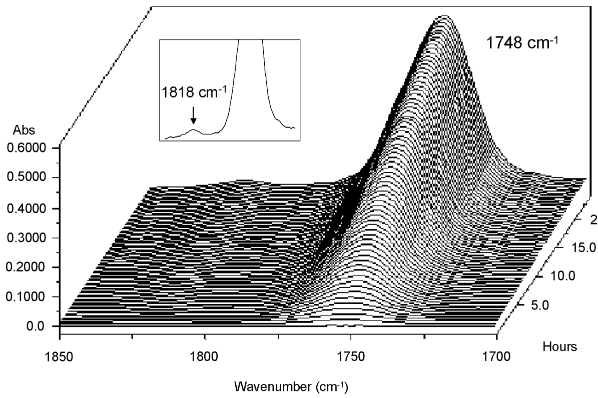

Figure 1. In situ infrared monitoring in the $\nu(CO_2)$ region for polycarbonate formation. The weak band at 1818 cm^{-1} due to cyclic carbonate is barely discernible. This product is better seen in the inset.

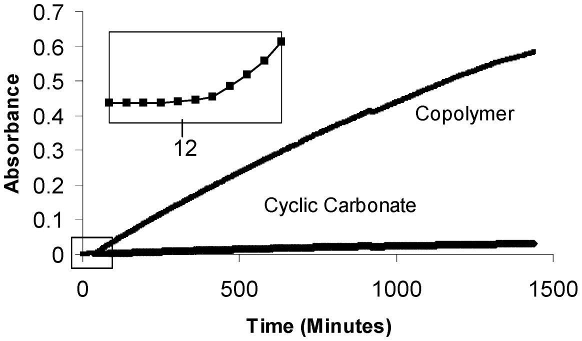

Figure 2. Reaction profile indicating the infrared absorbance of the band at 1748 cm^{-1} due to the copolymer product as a function of time, as well as that at 1818 cm^{-1}, due to cyclic carbonate. The inset shows an enlarged view of the catalyst activation period.

of cyclic carbonate as indicated by the infrared absorption at 1818 cm^{-1}. Figure 2 depicts the reaction profiles for the formation of the copolymer and cyclic carbonate with time. From the overlay in Figure 2 it is apparent that the time period to activate the catalyst (*the initiation step*) is greatly reduced (~12 min) as compared to that seen for its 1,2-cyclohexene diimine chromium(III) analogue (>60 min) employing cyclohexene oxide as monomer under identical reaction conditions.[6] This may be the consequence of a decrease in steric crowding about the metal center in the former case. Recall that the initiation step displays a second-order rate dependence on [catalyst], i.e., it proceeds via a dinuclear transition state.[6,7] More extensive ongoing studies in our laboratory show this initiation period to be dependent on several variables, including the salen ligand, the ring-opening nucleophile attached to chromium, and the epoxide. It is noteworthy that the reaction's liquid phase is monophasic as evidenced by the observation that upon stirring of the

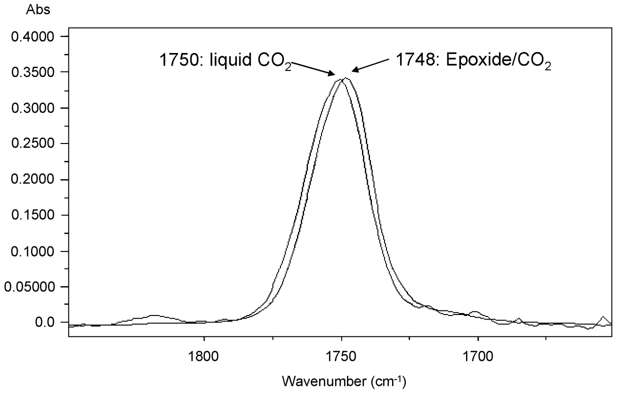

Figure 3. Infrared spectra of polycarbonate in epoxide/CO_2 solution and in pure liquid CO_2 at 55 bar pressure and ambient temperature.

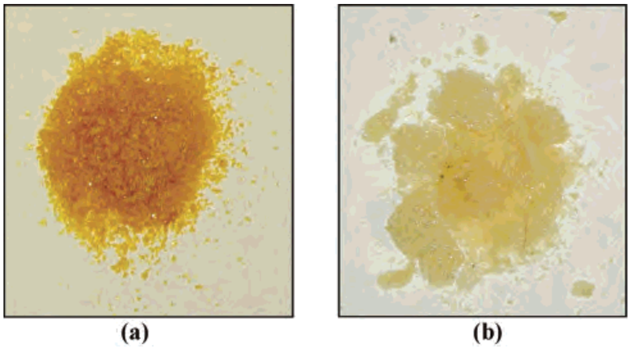

Figure 4. (a) Copolymer originally isolated from reaction. (b) As obtained after dissolution in liquid carbon dioxide and release of CO_2 pressure.

solution there are no changes in the infrared spectral characteristics. This is to be contrasted with the analogous cyclohexene oxide/carbon dioxide reaction system, where at 80 °C and 55 bar there exists a dense cyclohexene oxide rich phase (which contains the catalyst) and a less dense cyclohexene oxide poor liquid phase.[1c] The infrared probe is situated to sample the more dense phase. Furthermore, the reaction mixture remains monophasic as the reaction proceeds, i.e., because of the silane groups the polycarbonate is highly miscible with carbon dioxide (see Figure 3).[8]

Following a 3-day reaction period, at which time all of the epoxide monomer was consumed, the reactor was cooled and vented to release the carbon dioxide.[9] The resulting yellow polymer was extracted from the reactor via dissolution in methylene chloride and maintained under anhydrous conditions to avoid premature cross-linking. Upon removal of the solvent under vacuum, 21.7 g (86% yield with a TON of 4815 g of polymer/g of Cr or 862 mol of CHO/mol of Cr) of yellow polycarbonate solid was isolated and shown by ^{1}H NMR in $CDCl_3$ to contain less than 1% ether linkages. Because the reaction was carried out for an extended period of time in order to consume all of the epoxide, it is possible to only report a minimum value for the TOF of 66.9 g of polymer/g of Cr/h or 12.0 mol of CHO/mol of Cr/h. A

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(6) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335.

(7) (a) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897−5898. (b) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 10924−10925. (c) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421−431.

(8) (a) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature (London)* **2000**, *405*, 6783. (b) Beckman, E. J.; Sarbu, T.; Styranec, T. *Polym. Mater. Sci. Eng.* **2001**, *84*, 269.

(9) The reaction was allowed to go to completion since the starting epoxide monomer is difficult to remove from the copolymer via distillation without cross-linking the silane groups.

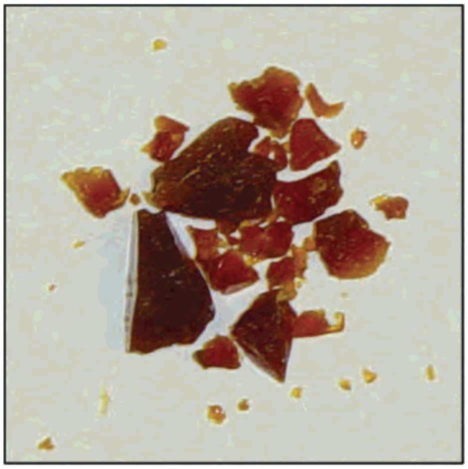

Figure 5. The randomly cross-linked copolymer afforded from a polycarbonate product where no attempt was made to remove the metal catalyst.

preliminary M_w value of ~21000 was determined by GPC. An authentic sample of the polyether was prepared from the neat monomer in the presence of zinc chloride as catalyst. The polyether protons on the cyclohexane backbone appear as a broad group of resonances between 3.2 and 3.5 ppm in $CDCl_3$. The silane methoxy protons in the monomer appear at 3.49 ppm in $CDCl_3$ and are unshifted in either the polycarbonate or polyether.

Nozaki and co-workers have synthesized *syndio*- and *iso*-dyad model carbonates and provided spectral assignments for the carbonate resonances in the copolymer obtained from cyclohexene oxide and carbon dioxide.[10] In this instance the carbonate ^{13}C NMR signal for the m-centered tetrad was found at 153.7 ppm, whereas the signals at higher field (153.3−153.1 ppm) were due to r-centered tetrads. For the copolymer produced from cyclohexene oxide and CO_2 in the presence of (salen)CrCl, the ^{13}C NMR spectrum displays its most intense carbonate signal at 153.7 ppm, with the upfield signals being less intense.[6] However, *assuming* these ^{13}C signals are similarly assigned for the copolymer derived from **1** and carbon dioxide using (salen)CrCl as catalyst, the intensity pattern is reversed, indicative of a reversal in stereoselectivity of monomer enchainment.

The enhanced solubility of the polycarbonate afforded by the monomer **1** in carbon dioxide has allowed for the ready removal of the highly colored catalyst remains from the copolymer. That is, upon dissolving the crude polymer in liquid CO_2 and releasing the pressure, the catalyst material settles out first, with *one* dissolution cycle leading to a greatly decolorized material (See Figure 4). Upon allowing the polycyclohexylene carbonate derived from carbon dioxide and the epoxide bearing trimethoxysilane functionality to stand in moist air for extended periods of time, or during drying of the copolymer under vacuum at elevated temperatures, random cross-linking of the trimethoxysilane units occurs to provide a tough polymeric material possessing a $T_g > 180$ °C (see Figure 5). Present studies are aimed at investigating controlled hydrolytic cross-linking to incorporate silsesquioxane groups into the polycarbonate, thereby providing materials with potentially useful properties.[11]

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(10) Nakano, K.; Nozaki, K.; Hiyana, T. *Macromolecules* **2001**, *34*, 6325.

(11) These studies are being performed collaboratively with C. E. Koning and R. Duchateau at the Laboratory of Polymer Chemistry, Eindhoven University of Technology, The Netherlands.