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Summary

Our original thrust, that of developing a direct route to diphenyl carbonate (the monomer for bisphenol A polycarbonate) using carbon dioxide as a raw material, was unsuccessful. The appendix describes the experiments that were tried in this regard. The primary problem was that we were unable to replicate the literature results of Yamazaki, et al., despite using their conditions and reactants, which form the basis for the proposed work. Despite this setback, we have derived a new route to diphenyl carbonate, which we have described in a proposal to the NSF/EPA partnership for environmental research (the sustainable technology section) which was submitted in April, 1995. This route would incorporate carbon dioxide into a dialkyl carbonate using a tin catalyst, followed by transesterification using an enzyme to diphenyl carbonate. Thus, this work may continue on the future. However, despite the setbacks in the original proposed work, we set up two new collaborations with both Miles (now Bayer) and Exxon which employ CO₂ as both monomer and solvent in polymer processing.

The Exxon Collaboration

Although the original thrust of the research proved very disappointing, we began two new collaborations regarding use of carbon dioxide in polymer systems, one with our old collaborators at Miles (now Bayer), and the other with a group at Exxon research in Annandale, NJ. In the Exxon work, we evaluated the use of CO₂ as both monomer and sole solvent in the copolymerization of CO₂ with cyclohexane oxide to form the polymer, poly(cyclohexane carbonate). Previous patents by ARCO and Air Products had described zinc-based catalysts which would prove effective in this copolymerization, yet these catalysts were uncharacterized mixtures of several materials. Staff at
Exxon isolated the active ingredient of the catalyst, the adduct of zinc oxide plus the half-ester of a diacid, eg., maleic acid. This catalyst proved very active in the synthesis of polycyclohexane carbonate from cyclohexene oxide and carbon dioxide, but was insoluble in carbon dioxide, and thus required use of an additional organic solvent in order to generate high yield. This, we employed an old trick used by our group to solubilize materials in CO₂; that of fluorinating the catalyst ligands. We have previously shown that fluorinated and silicone-containing compounds exhibit very high solubility in carbon dioxide, much higher than their alkyl-functional analogs. Consequently, Exxon staff prepared the fluorinated version of the half-ester/zinc catalyst, which, upon testing proved to be quite CO₂-soluble (over 1 wt% solubility at 2000 psi).

Following this development, we conducted a number of polymerizations of CO₂ with cyclohexene oxide in carbon dioxide at pressures ranging from 1000 to 5000 psi, and temperatures ranging from 70 to 170°C. We also investigated the phase behavior of the cyclohexene oxide-CO₂ binary, and are preparing to examine the polymer-cyclohexene oxide-CO₂ ternary system. Major findings include:

1. The polymerization reaction produces both high molecular weight polymer ($M_w = 50,000$ to $100,000$) plus cyclic carbonate. The extent to which the reaction produces polymer over cyclics is dependent upon temperature, with the maximum selectivity towards polymer occurring at 110 to 120°C (at 2000 psi).

2. The overall yield of products is also temperature dependent, with a maximum at 110°C (at 2000 psi). The plot of yield vs temperature indicates a shallow minimum at 90°C, which we at first thought was an artifact, but later proved to be reproducible. This remained a mystery until we conducted experiments on the phase behavior of the cyclohexene oxide-CO₂ binary. At 2000 psi, the run at 90°C was conducted at a point which falls almost exactly on the phase boundary, which could lead to large concentration fluctuations and thus stoichiometric imbalances, and thus the low yield.

3. At a maximum yield, the catalyst produces nearly 400 grams of polymer per gram of zinc, an order of magnitude improvement over those catalysts mentioned in the Air Products or ARCO patents.
4. As pressure increases above 3500 psi (at 100°C), the yield of both overall products and polymer drops, a result which is reproducible but as yet not entirely explained. It may be due to the fact that at a constant initial loading of cyclohexene oxide, as pressure increases, the molar ratio of CO₂:cyclohexene oxide will increase. In a subsequent series of experiments, we found that as the CO₂:cyclohexene oxide ratio increases (at constant pressure and temperature), the yield does decrease. Another possible explanation is that the volume change upon activation for the polymerization is positive, which would mean that the rate constant of the reaction would decline with increasing pressure. Most volume changes upon activation for polymerizations that have been measured are negative, however.

5. The polymer which is produced exhibits a glass transition temperature of 120°C. While this is higher than most commodity thermoplastics, the price of the cyclohexene oxide may not allow the material to be produced economically, despite the use of the inexpensive CO₂ as co-reactant.

6. Subsequent phase behavior of the cyclohexene oxide-CO₂ binary revealed that we conducted polymerizations in both the one phase and two phase regions – it is not clear yet what role this has played in the overall yield of product, or of the selectivity towards polymer.

In addition to the work we performed at the University of Pittsburgh, Exxon employed a staff member and technician on the project, and designed and built a high pressure reactor system for use at Annandale. They also provided us with cash gifts totalling $29,000 and access to some of their corporate analytical facilities. Thus their expenditures on the project likely dwarfed ours. We have recently submitted a paper to Macromolecules regarding this work. A presentation has also been made at the CO₂ Chemistry conference recently held in Norman, OK.

The Miles Collaboration

Although the originally-proposed path to diphenyl carbonate was not successful, we embarked on a new area in conjunction with Miles, to employ carbon dioxide as the sole blowing agent for polyurethane foam. Further, we proposed to generate the polymer in carbon dioxide, i.e., CO₂ was
to be the solvent for the reactants and the pore-forming agent. A Miles employee, Kristin Parks, was given a leave of absence at 80% salary, to pursue this research to fulfill the requirements for her PhD degree. Further, Miles has supplied us with raw materials and allowed us access to their corporate SEM facilities for foam characterization. Thus, Miles's contribution has been much greater than what I originally expected.

To date, we have measured the phase behavior of the urethane precursors in carbon dioxide, and have generated a number of microcellular foams via conducting a polymerization in carbon dioxide at high pressure. The foams exhibit a relatively low density (approx. 0.2 g/cm$^3$) and cell sizes less than what can be achieved in commercial materials (less than 50 microns).

The most exciting result concerns the behavior of the system during polymerization. We expected that during the course of the polymerization, the system would undergo phase separation (which would produce the pores) owing to be rapidly increasing molecular weight and the fact that the system produces a cross-linked polymer. However, when we ran the reaction in a high pressure view cell, we found that the polymer remained in solution (a perfectly clear, homogeneous solution) through the end of the reaction. The foam appeared immediately upon reduction of the pressure. Thus we have generated a CO$_2$-sprayable urethane foam system, and the patenting process has begun at the University.

**Summary**

In summary, our original target of a CO$_2$-based route to diphenyl carbonate proved unsuccessful, yet the funds received from DOE allowed us to develop collaborations with both Exxon and Miles which were not anticipated in the original proposal. Each of these projects is continuing via support from these companies, and will likely conclude with the PhD defenses of the students involved in 1996. Miles currently has an active program underway involving polymerization in carbon dioxide, as does Exxon. Although I am familiar with the commercial goals of each of these programs, I do not think I am at liberty to say what they are at this time.
Appendix I:

Summary of Experimental Findings on Use of CO₂
to Generate Diphenyl Carbonate
I. **Dialkyl Carbonate from CO$_2$, EtOH, (Bu)$_2$Sn(OMe)$_2$.**

The first try at dialkyl carbonate synthesis was through the attempted reproduction of some work found in the literature. The reference [Yamazaki, N., Nakahama, S. and Higashi, F. "Polymers Derived from CO$_2$ and Carbonates", *Ind. Eng. Chem. Prod. Res. Dev.*, Vol 18, No. 4, 1979] was referred to which described the formation of dibutyl, diethyl and diphenyl carbonates using di-$n$-butyltin dialkoxides.

Reactions using the same molar ratios of components and the same conditions as those reported in the literature were tried with very poor success. Reactions were run from 25 to 50 hours. All products were analyzed using a Mattson Polaris FTIR and initially some very small absorbance peaks at 1750 wavenumbers and a large flat peak is found in the hydroxyl region above 3000 wavenumbers possibly due to water formation. Subsequently, reactions were run using first 4A molecular sieves and then CaSO$_4$ in an attempt to remove the water and promote carbonate production. Products formed show small peaks at 1655 wavenumbers from these reactions, but amount of product formed is so small that none could be recovered. No other attempts were made at reproducing the dialkyl carbonate synthesis from the Yamazaki paper.

II. **Synthesis of Diphenyl Carbonate from Bis(tributyltin) Carbonate, CO$_2$, and Phenol**

The next approach was to insert CO$_2$ into a bi-tin compound and from there generate the dialkyl carbonate. The synthesis was attempted in two steps, one reproduced from literature [Bloodworth, A., Davies, A., Vasishtha, S., "Organometallic Reactions. Part VII. Further Addition Reactions of Tributyltin Methoxide and of Dibutyltin Oxide", *J. Chem. Soc. (C)*, pp. 1309-13, 1967] and one developed by us.

The first step involved the insertion of CO$_2$ into the center of a Bis(tributyltin) Oxide molecule to form Bis(tributyltin) Carbonate. Insertion proceeds under a low CO$_2$ pressure (~500 psig) for ~10 hours, as described in the paper. The product displays the FTIR peaks mentioned in the paper as characteristic of the desired Bis(tributyltin) Carbonate.

Step two is a little more difficult and was attempted in several different ways. At first the Bis(tributyltin) Carbonate was reacted phenol using hexane as a solvent. The reaction was run under
a CO₂ atmosphere (~1000 psig) and CaSO₄ was included to remove any water formed. On analysis of products peaks at 1609 and 1595 wavenumbers show up that aren't attributable to solvent or reactants (Diphenyl Carbonate has its' carbonate peak at 1768 wavenumbers). The same reaction was run using ether as a solvent with the products giving same spectrum as those synthesized in hexane. A slightly different approach was taken after these two failures.

Reactions were attempted in the hood under elevated temperatures to study if substitution to diphenyl carbonate could be achieved. Using the TGA a CO₂ release temperature was detected at 110-160°C. Using toluene as the solvent, the tin carbonate and phenol were mixed and heated under a CO₂ atmosphere. A Dispersion IR (DIR) spectrum was made of the initial pot mixture for comparison. After heating the mixture slowly to 106°C and letting the system reflux overnight (13 hours), the spectrum remains the same. The mixture was then cooled to 80°C and p-toluene sulfonic acid was added and a spectrum was taken. The mixture was again heated, this time to 114°C and the system was allowed to react overnight (12 hours). After the first 2 hours a possible carbonate peak at 1780 wavenumbers appeared, but after 12 hours the spectrum had changed, but there was no sign of a diphenyl carbonate peak. The reaction was repeated letting temperature get no higher than 100°C, but with the same results.

Dr. Heirum Bormann starts at this point and all the step two work is hers, I only synthesized the tin carbonate. From this point the same reaction utilizing THF as the solvent and Imidazole as the catalyst was attempted with no success. [Note: for this reaction it was determined that Thin Layer Chromatography (TLC) could be used to test for products and was employed for analysis of products]. I'm not familiar with any other work Heidrun might have done with this system, this is the only thing I have written down concerning her work.

III. Lactone Formation as a Route to Polyester Production Using CO₂

2,3-Dimethyl-1,3-Butadiene (DMB) was reacted with CO₂ under various conditions to study the possibility of polyester formation through a lactone intermediate. We started by trying to reproduce the work of [Soga, K., Hosoda, S., and Ikeda, S., "Copolymerization of CO₂ and Some Diene Compounds", Die Makromolekulare Chemie, Vol. 176, pp. 1907-1911, 1975] with little success.

At first CO₂ and the DMB was reacted at 80°C and ~2500 psig for something like 4 days.
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