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Alternating Copolymerization of Carbon Dioxide and Propylene Oxide with a Rare-Earth-Metal Coordination Catalyst

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ABSTRACT: The copolymerization of carbon dioxide and propylene oxide using rare-earth-metal catalyst systems was investigated in this study. It was found that the ternary rare-earth-metal coordination catalyst consisting of $Y(CF_3CO_2)_3$ (**I**), diethylzinc (**II**), and glycerine (**III**) was the most effective catalyst system to generate an alternating polycarbonate. The effects of the molar ratio of catalyst components, the solvent, and the operating temperature and pressure on the yield and the molecular weight of polycarbonate were systematically studied. At an appropriate combination of all variables, the yield could be as high as 4200 (g/(mol of Y))/h and the molecular weight as high as 1.0×10^5 in a 12 h reaction period. The carbonate content in the resulting polycarbonate was found to be 95.6%.

Introduction

Carbon dioxide is a known greenhouse gas which contributes over half of the greenhouse effect. The necessity to reduce CO_2 emission has gained the consent of most of the countries in the world. One of the means to reduce CO_2 emission is to use CO_2 as a starting material in chemical reactions. In addition to environmental concerns, CO_2 may become a very important raw material in chemical industry in the future, since the sources of coal, petroleum, and natural gas are being quickly exhausted and the carbon content of CO_2 in the atmosphere and in the hydrosphere is by $1^1/_2$ orders of magnitude more than that in coal, petroleum, and gas.[1]

Generally CO_2 is thought of as an inert and relatively unreactive compound; there is no report so far on the homopolymerization of CO_2. However, in 1969, Inoue et al.[2] observed that the copolymerization of CO_2 with epoxide could proceed to form polycarbonate using organometallic compounds as catalysts under relatively mild conditions. Since then, many attempts to develop new catalysts and to copolymerize other monomers with CO_2 have been made, which are described in the excellent reviews of Rokicki and Kuran,[3] Scholsky,[4] and Yamazaki et al.[5]

In the copolymerization reaction of CO_2 with propylene oxide (PO), the effective organometallic catalysts for producing an alternating polycarbonate were found to consist of diethylzinc and a compound having two active hydrogens, such as water,[6] primary amines,[7] di- or trihydroxybenzenes,[8−10] aromatic dicarboxylic acids,[11−13] polymers,[14] etc. However, to carry out this copolymerization reaction, a long reaction time is generally required, and the yield needs to be improved. The reaction mechanism for this kind of catalyst system has been identified as an anionic coordination process.[11]

Recently, Chen et al.[15] successively carried out the copolymerization of CO_2 and propylene oxide by using a rare-earth-metal catalyst system. They found that the ternary rare-earth-metal coordination system $Y(P_{204})_3$−$Al(i\text{-}Bu)_3$−glycerine is the most effective catalyst for the reaction. Despite the fact that random copolymers of polycarbonate were obtained, a higher molecular weight with a narrower molecular weight distribution and a higher yield within a shorter reaction time compared with the previous organometallic compound catalyst systems were observed in their study.

Since an alternating polycarbonate has its special application, the objective of this study is to produce it from the copolymerization of CO_2 and PO by using the rare-earth-metal catalyst systems. As shown in the literature, diethylzinc in organometallic compound systems can generate more alternating copolymers than triisobutylaluminum does.[2,15] Therefore, diethylzinc instead of triisobutylaluminum was employed in the present rare-earth-metal catalyst systems. In addition to $Y(P_{204})_3$, the rare-earth-metal compounds $Y(CH_3CO_2)_3$ and $Y(CF_3CO_2)_3$ were also used. It has been shown that $Y(CF_3CO_2)_3$ is an effective catalyst for the ring opening of tetrahydrofuran (THF) in the polymerization of THF.[16] In this study, the effects of pressure and temperature on yield and molecular weight were also examined.

Experimental Section

Materials. Propylene oxide of a purity of 99.5% (Janssen Chimica) was refluxed over CaH_2 and 4A molecular sieves and was distilled before use. Diethylzinc, glycerine, and all of the solvents, such as *n*-hexane, benzene, toluene, DMSO, and 1,3-dioxolane, were of analytical reagent grade and were used without further purification. CO_2 of a purity higher than 99.99% (Air Product Co.) was used as received. $Y(P_{204})_3$ was prepared as follows: YCl_3 was first produced from an aqueous solution containing 0.01 mol of Y_2O_3 and 0.06 mol of HCl at 100 °C, and then 0.03 mol of phosphoric acid bis(2-ethylhexyl) ester was added into the resulting YCl_3 solution at room temperature to produce $Y(P_{204})_3$. The resultant $Y(P_{204})_3$, $Y(CF_3CO_2)_3$, and $Y(CH_3CO_2)_3$ purchased from Aldrich Chemical Co. were heated in vacuum at 80 °C for 40 h before use.

The catalyst system $Y(CF_3CO_2)_3$−$Zn(Et)_2$−glycerine was prepared in an atmosphere of purified argon. Glycerine was added dropwise to a solution of $Zn(Et)_2$ in solvent at room temperature. After ethane gas evolution had ceased, the solution containing white powders resulting from the reaction between $Zn(Et)_2$ and glycerine was heated at 60 °C for 2 h. This solution was then added to an autoclave which contained a known amount of $Y(CF_3CO_2)_3$. The resultant catalyst was stirred at 60 °C for 1 h prior to CO_2 and PO being introduced.

Copolymerization. Copolymerization of CO_2 and PO was carried out in a 300 mL autoclave which was equipped with a magnetic stirrer (Autoclave Engineers Inc.). The spinning

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Table 1. Copolymerization of CO_2 and PO by Various Catalysts[a]

catalyst system			yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
I	II	III				
$Y(CF_3CO_2)_3$	$Zn(Et)_2$	glycerine	1600	3.0	1.2	4.00
$Y(CF_3CO_2)_3$	$Zn(Et)_2$		trace			
$Y(CF_3CO_2)_3$		glycerine	trace			
	$Zn(Et)_2$	glycerine	80	3.5	1.35	3.85
$Y(CF_3CO_2)_3$	$Zn(Et)_2$	PO	Trace			
$Y(P_{204})_3$	$Zn(Et)_2$	glycerine	170	4.7	2.0	4.26
$Y(CH_3CO_2)_3$	$Zn(Et)_2$	glycerine	Trace			

[a] **I** = 0.00055 mol; **II** = 0.011 mol; **III** = 0.0055 mol; solvent = 20 mL of toluene; PO = 30 mL; T = 60 °C; P = 400 psi; time = 6 h.

speed was kept at 1000 rpm. The polymerization reaction was terminated by adding an excess of ethanol containing dilute hydrochloric acid, and the resulting copolymer of CO_2 and PO could be precipitated by adding more ethanol to the solution. To purify the precipitated copolymer, it was dissolved in THF first and then was reprecipitated by adding aqueous ethanol solution. After the purification, the copolymer collected was dried under vacuum at 50 °C for 40 h prior to analysis.

Analysis of the Copolymer. To determine the structure and the composition of the prepared copolymers, the NMR spectra of the copolymer in deuteriochloroform at room temperature were measured with a Burker AM-400 NMR spectrometer using tetramethylsilane as the standard, and the IR spectra were measured by a Perkin-Elmer 842 spectrometer. The molecular weights were determined with a Shimadzu C-R4A chromotopac by using THF as the solvent and polystyrene (M_n = 4000 to 6.5 × 10^5) as the standard.

Results and Discussion

Table 1 shows the results in copolymerization of CO_2 and PO by using several rare-earth-metal coordination catalysts in toluene at 60 °C and 400 psi. Each experiment was performed in duplicate; the difference in yield was observed to be less than 7.0%. From Table 1 it can be seen that only the catalyst system $Y(CF_3CO_2)_3-Zn(Et)_2-$glycerine could offer a high yield. It is also seen that the copolymerization could proceed for the catalyst system $Zn(Et)_2-$glycerine, though the yield was low, but not for the systems $Y(CF_3CO_2)_3-$glycerine and $Y(CF_3CO_2)_3-Zn(Et)_2$. This indicates that the active site might be on zinc in the compound formed by the reaction between $Zn(Et)_2$ and glycerine. A high yield resulting from the presence of $Y(CF_3CO_2)_3$ might be due to the fact that fluorine could induce a more positive charge of yttrium, or a bimetallic catalyst compound between $Y(CF_3CO_2)_3$ and the compound from the reaction between $Zn(Et)_2$ and glycerine could be formed. Further work is underway to identify the exact molecular structure and active site of this ternary catalyst system.

Table 2 shows the experimental results for different solvents. It is seen that less polar solvents, such as hexane and benzene, are not good candidates to make a polycarbonate from CO_2 and PO. While DMSO is the most polar solvent compared with the others, however, a yellowish copolymer rather than polycarbonate was obtained. This indicates that a proper choice of solvent is essential. When 1,3-dioxolane instead of toluene was used as the solvent, the yield and molecular weight of the resulting copolymer under the same operating conditions were found to improve significantly. The yield was increased from 3000 to 4200 (g/(mol of Y))/h and M_n from 5.0 × 10^4 to 1.0 × 10^5. As we were concerned with yield and molecular weight, further runs were focused on the use of $Y(CF_3CO_2)_3-Zn(Et)_2-$glycerine as catalyst and 1,3-dioxolane as solvent. Chen et al.[15] pointed out that the component ratios in the $Y(P_{204})_3-Al(i\text{-}Bu)_3-$glycerine system have a significant effect on yield in production of a random polycarbonate; the same conclusion can be drawn in production of an alternating polycarbonate using the present catalyst system. Table 3 shows that the optimum $Zn(Et)_2/Y(CF_3CO_2)_3$ molar ratio was 20 at which the yield and the molecular weight of the copolymer were highest though the dispersity was not at a maximum. The effect of the molar ratio of glycerine to $Zn(Et)_2$ is shown in Table 4. The most appropriate ratio providing the highest yield and M_w as well as the lowest dispersity was found to be at 0.5. The yield of 4200 (g/(mol of Y))/h obtained in this study is much higher than that reported by Chen et al.[15] (2451 g/(mol of Y) for a 16 h run) despite the fact that the carbonate contents in these two copolymers are quite different.

Table 2. Effect of Solvent on Copolymerization of CO_2 and PO Using the Catalyst System $Y(CF_3CO_2)_3-Zn(Et)_2-$Glycerine[a]

solvent	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
toluene	3000	5.0	1.55	3.10
1,3-dioxolane	4200	10.0	2.85	2.85
n-hexane	trace			
benzene	680	5.1	1.68	3.29
DMSO	trace			

[a] **I** = 0.00055 mol; **II** = 0.011 mol; **III** = 0.0055 mol; **II/I** = 20; **III/II** = 0.5; PO = 30 mL; solvent = 20 mL; T = 60 °C; P = 400 psi; time = 12 h.

Table 3. Effect of the Molar Ratio of II to I on Copolymerization of CO_2 and PO[a]

molar ratio, **II/I**	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
10	1900	6.0	2.40	4.00
15	2450	7.9	2.50	3.16
20	4200	10.0	2.85	2.85
25	2400	11.0	2.55	2.31
30	1840	11.5	2.79	2.42

[a] **II** = 0.011 mol; **III** = 0.0055 mol; **III/II** = 0.5; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi; time = 12 h.

Table 4. Effect of the Molar Ratio of III to II on Copolymerization of CO_2 and PO[a]

molar ratio, **III/II**	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
0.25	1000	3.0	1.06	3.52
0.375	2000	7.3	2.30	3.15
0.5	4200	10.0	2.85	2.85
0.625	1400	4.5	2.50	5.55
0.75	450	2.4	0.95	3.95

[a] **I** = 00055 mol; **II** = 0.011 mol; **II/I** = 20; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi; time = 12 h.

The IR and NMR spectra of the resulting copolymer for the **II/I** molar ratio at 20 and the **III/II** molar ratio at 0.5, shown in Figures 1 and 2, indicate that the copolymer was indeed an alternating polycarbonate and the ratio of carbonate unit in total polymer calculated according to the reference[2] was 95.6%. Compared to the 10−30% of carbonate unit in a random polycarbonate as reported by Chen et al.,[15] it is rational to speculate that the present catalyst system could more easily attract carbon dioxide to participate in copolymerization. Under this situation, the polypropylene oxide content in the resulting polycarbonate should be small. The

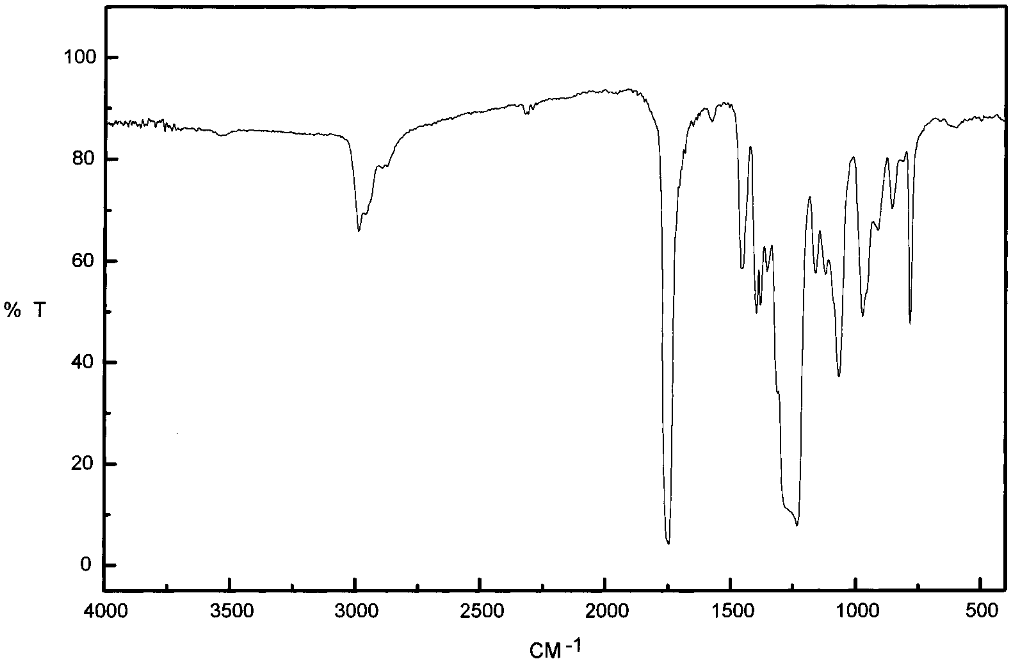

Figure 1. IR spectrum of the resulting copolymer. Reaction conditions: **I** = 0.00055 mol; **II** = 0.011 mol, **III** = 0.0055 mol; solvent = 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi; time = 12 h.

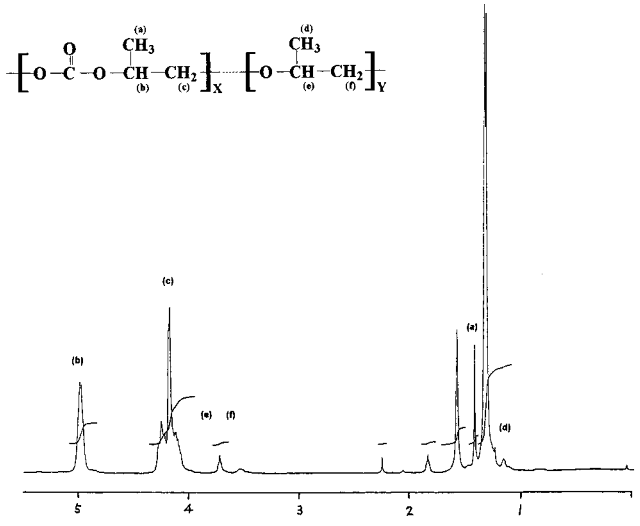

Figure 2. NMR spectrum of the resulting copolymer. Reaction condition: **I** = 0.00055 mol; **II** = 0.011 mol; **III** = 0.0055 mol; solvent = 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi; time = 12 h.

NMR spectrum in Figure 2 verifies this speculation. If the yield is based on the PO monomer used, a 63.5% yield in a 12 h run and a 72% yield in a 24 h run were observed for the proposed catalyst system with the most appropriate **II**/**I** and **III**/**II** molar ratios. Compared to the 88% content of carbonate unit in an alternating polycarbonate for the catalyst system $Zn(Et)_2-H_2O^2$ and the 71.7% yield in a 44 h run for the catalyst system $Zn(Et)_2$–m-hydroxybenzoic acid,[11] which is one of the best binary catalyst systems,[3] the proposed ternary catalyst system seemed to be rather effective for generation of an alternating polycarbonate from CO_2 and PO.

Table 5. Effect of Temperature on Copolymerization of CO_2 and PO[a]

T, °C	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
40	470	3.2	1.60	5.00
50	995	5.1	2.55	4.90
60	4200	10.0	2.85	2.85
70	1600	3.5	1.60	4.57
80	1100	3.0	1.20	4.00
100	trace			

[a] **I** = 0.00055 mol; **II** = 0.011 mol; **III** = 0.0055 mol; **II**/**I** = 20; **III**/**II** = 0.5; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; P = 400 psi; time = 12 h.

Table 6. Effect of Pressure on Copolymerization of CO_2 and PO[a]

P, psi	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
200	3765	7.4	2.10	2.83
400	4200	10.0	2.85	2.85
600	4150	11.0	3.30	3.00
800	3350	8.0	2.90	3.62
1200	1890	7.9	3.30	4.17
1600	1390	7.0	2.66	3.80

[a] **I** = 0.00055 mol; **II** = 0.011 mol; **III** = 0.0055 mol; **II**/**I** = 20; **III**/**II** = 0.5; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; T = 60 °C; time = 12 h.

When the molar ratios of **II**/**I** and **III**/**II** were maintained at 20 and 0.5, respectively, and the pressure was fixed at 400 psi, Table 5 shows that the yield increased with increasing temperature in a lower temperature range, reached a maximum at about 60 °C, and then dropped rapidly as the temperature further increased. The decrease of yield with increasing temperature is probably due to polymer degradation reactions. The location of the optimum temperature for production of an alternating polycarbonate is the same as that for production of a random polycarbonate.[15]

For a polymerization reaction, the difference in the partial molar volumes of the activated complex and the reactants is generally negative; consequently, the reaction rate is more often enhanced by pressure according to the transition state theory.[4,17,18] For this copolymerization reaction, the yield was indeed enhanced with pressure as the pressure is less than 600 psi, but after that pressure was reached, the yield was decrease with increasing pressure, as shown in Table 6. One of the possible reasons is due to the swelling of the solvent

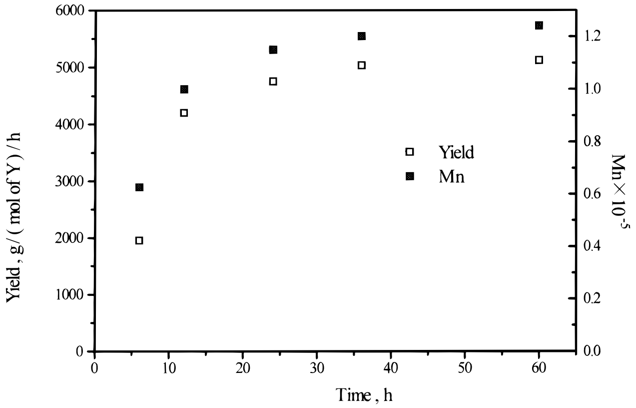

Figure 3. Reaction time dependence of the yield and molecular weight of the copolymer. Reaction conditions: **I** = 0.00055 mol; **II** = 0.011 mol; **III** = 0.0055 mol; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi.

because more CO_2 is dissolved in solvent at high pressures.[19,20] As a result, the solubility of the copolymer is decreased. This explanation might be supported by the fact that the molecular weight of copolymer decreased with increasing pressure as $P > 600$ psi, shown in Table 6. Further studies are required to clarify the effects of pressure on yield and molecular weight.

Figure 3 illustrates the reaction time dependence of yield and molecular weight. Both the yield and molecular weight of the copolymer were found to increase with increasing reaction time. This indicates that the reaction mechanism for the copolymerization of CO_2 and PO is an anionic coordination process.[10]

Conclusion

An alternating polycarbonate was produced from the copolymerization of carbon dioxide and propylene oxide in the presence of the rare-earth-metal catalyst system $Y(CF_3CO_2)_3$ (**I**)−diethylzinc (**II**)−glycerine (**III**). The optimum yield and a high molecular weight of polycarbonate were obtained when the molar ratios of **II**/**I** and **III**/**II** were at 20 and 0.5, respectively, and the operating temperature and pressure were at 60 °C and 400 psi, respectively, by using 1,3-dioxolane as solvent. The yield at those combined conditions in a 12 h run was 4200 (g/(mol of Y))/h. The carbonate content in the resulting copolymer was found to be 95.6%.

The use of CO_2 as a monomer to produce polycarbonate as investigated in this study may provide a means to consume CO_2, which is a known contributor to global warming. Since the rare-earth-metal catalyst systems are so effective, more attention should be paid to apply this kind of catalyst system to other copolymerization reactions using CO_2 as the starting monomer.

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