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Polymer 42 (2001) 5143–5150

polymer

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Synthesis of polyethercarbonate from carbon dioxide and cyclohexene oxide by yttrium–metal coordination catalyst

Tsung-Ju Hsu, Chung-Sung Tan*

Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30055, Taiwan, ROC

Received 24 October 2000; received in revised form 27 November 2000; accepted 6 December 2000

Abstract

The copolymerization of carbon dioxide and cyclohexene oxide to generate polyethercarbonate using yttrium–metal coordination catalyst was carried out in this study. After testing several catalyst systems, it was found that the system consisting of $Y(CF_3CO_2)_3$(I), $Zn(Et)_2$(II),and glycerine(III) in the solvent of 1,3-dioxolane was the most effective catalyst. The IR and ^1H NMR spectra indicated that the resulting copolymer was indeed a polyethercarbonate with a carbonate content as high as 100%. The weight-average molecular weights observed in a range between 1.9×10^4 and 3.3×10^5 and the dispersity between 3.5 and 12.5. The glass transition temperature of the resulting copolymer was found to locate in a range 105–128°C and the temperature at which 10% weight loss occurred in a range 252–331°C. © 2001 Elsevier Science Ltd. All rights reserved.

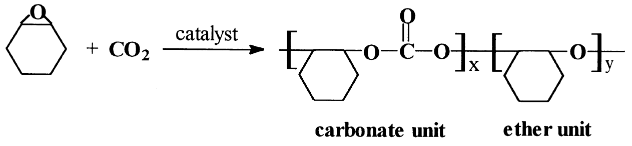
Keywords: Carbon dioxide; Cyclohexene oxide; Yttrium compound

1. Introduction

Carbon dioxide is readily available, inexpensive, nontoxic, and need to be utilized to reduce its emission into atmosphere from global warming point of view, it can be considered as a starting monomer to substitute toxic monomers for synthesis of polymers [1,2]. Due to its inert and relatively unreactive characteristic, a catalyst is generally required to proceed these kind of reactions. Regarding the polymerization of carbon dioxide with epoxide, the first article appeared in 1969 in which an alternating poly(propylene carbonate) was synthesized from carbon dioxide and propylene oxide (PO) using diethyl zinc/water as catalyst [3]. Because of a long reaction time required for a low yield, many attempts to improve activity of catalyst for this copolymerization have been reported in the open literature [4–10]. The most commonly used catalyst systems consist of diethylzinc and a compound having two active hydrogen atoms, such as water, primary amines, carboxylic acids, etc.

Recently, rare-earth metal coordination catalysts were also used to synthesize polyethercarbonate from carbon dioxide and PO [11,12]. While a high molecular weight and a high carbonate content of poly(propylene oxide) could be generated, its application has some limitations due to a low thermal stability. The glass transition temperature T_g of the resulting poly(propylene oxide) is about 35°C, and the temperature at which 10% weight loss occurred (T_{10}) is about 190°C.

To improve thermal stability, cyclohexene oxide (CHO), possessing a rigid six-membered ring, may be used to substitute PO as the starting monomer to synthesize a polyethercarbonate. The copolymerization of carbon dioxide and CHO was carried out according to the scheme



Zinc-based catalysts are generally used in this copolymerization reaction including zinc/water [13], zinc bisphenoxide(base)$_2$ [14–16], zinc crotonate [17], and fluorinated zinc compound [18,19]. In addition to zinc-based catalyst, chromium porphyrinate [20] was also used as the catalyst. As for the copolymerization of CO_2 and PO, a long reaction time is generally required to achieve a desired yield and a high molecular weight is sometimes difficult to obtain. Besides, the thermal properties of the resulting polyethercarbonate were not provided.

Since a rare-earth metal coordination catalyst exhibits its

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* Corresponding author. Tel.: +886-3-572-1189; fax: +886-3-572-1684.
E-mail address: cstan@che.nthu.edu.tw (C.-S. Tan).

PII: S0032-3861(01)00006-4

high activity to the copolymerization of CO_2 and PO, it is expected that this kind of catalyst can also be used in the copolymerization of CO_2 and CHO. The objective of this study is therefore to systematically study the copolymerization of CO_2 and CHO. Several catalyst systems containing different yttrium compounds, diethylzinc, and glycerine were screened out to find the most appropriate one first. After that the effects of temperature, pressure, molar ratio of the catalyst components, and solvent on yield and copolymer properties were examined. The thermal properties such as T_g and T_{10} were also measured and compared with that of the copolymer resulted from CO_2 and PO.

2. Experimental

2.1. Materials

Cyclohexene oxide of a purity of 98% (TCI) was refluxed over CaH_2 for 4 h and then distilled before use. Diethylzinc, glycerine, and all the solvents, such as benzene, chloroform, 1,2-dichloroethane, 1,3-dioxolane, 1,4-dioxane, dimethylformamide, ethyl acetone, *n*-hexane, tetrahydrofuran, and toluene, were of analytical regent grade and were used without further purification. Carbon dioxide of 99.99% purity (Air Product) was used as received. All yttrium compounds including yttrium trifluoroacetate $Y(CF_3CO_2)_3$, yttrium acetate $Y(CH_3CO_2)_3$, yttrium acetylacetonate $Y(acac)_3$, yttrium hexafluoroacetylacetonate $Y(hf\text{-}acac)_3$, yttrium 2-ethylhexanoate $Y(2\text{-}eha)_3$, yttrium nitrate $Y(NO_3)_3$, and yttrium naphthoate $Y(naph)_3$ purchased form Aldrich were heated in vacuum at 80°C for 40 h before use.

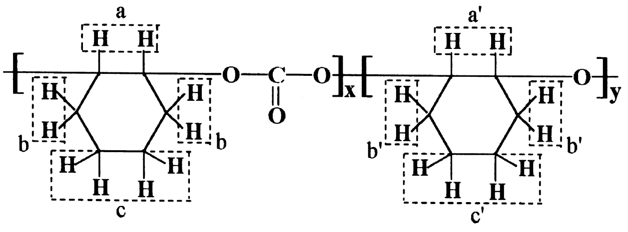
All the catalyst systems containing yttrium–metal compound, diethylzinc, and glycerine were prepared in an atmosphere of argon. Glycerine was added dropwise to a solution of diethylzinc in solvent at room temperature. When evolution of ethane was complete, the solution containing suspended powders resulting from the reaction between diethylzinc and glycerine was heated at 60°C for 2 h. Then the solution was added to an autoclave containing a certain amount of yttrium–metal compound. The resultant catalyst was stirred at 80°C for 1 h before CHO and carbon dioxide were introduced.

2.2. Copolymerization

Copolymerization of carbon dioxide and CHO was carried out in a 300 ml autoclave equipped with a magnetic stirrer (Autoclave Engineers). The spinning speed was kept at 1000 rpm. After a certain operation time, the pressure of carbon dioxide was reduced to atmosphere in order to terminate the polymerization reaction and an excess of methanol containing dilute hydrochloric acid was added to result in a precipitation of the copolymer of CO_2 and CHO. To purify the precipitated copolymer, it was dissolved in THF first and then was reprecipitated by adding an aqueous methanol solution. The resultant copolymer was then dried under vacuum at 60°C for 40 h prior to analysis.

2.3. Analysis of the copolymer

The IR and ^1H NMR spectra were used to determine the structure and the composition of the resulting copolymers. The IR spectra were obtained by a Perkin–Elmer 842 spectrometer and the ^1H NMR spectra of the copolymer in $CDCl_3$ at room temperature by a Bruker AM-400 NMR spectrometer. Suppose the copolymer possesses the following structure:



There are two major peaks in the ^1H NMR spectrum: one is attributed from carbonate unit ($a = 4.8$) and the other from ether unit ($a' = 3.5$). The carbonate content of the

Table 1
Poly(cyclohexene carbonate) synthesized by various catalysts (I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $T = 80$°C, $P = 400$ psi; time = 12 h)

Catalyst system			Yield g of polymer/g of Zn	$Mn \times 10^{-4}$	$Mw \times 10^{-5}$	Mw/Mn	T_g (°C)	T_{10} (°C)	f_{CO_2}
I	II	III							
$Y (CF_3CO_2)_3$	$Zn(Et)_2$	Glycerine	63	3.34	2.48	7.4	123	280	100
$Y(CF_3CO_2)_3$	$Zn(Et)_2$	–	25	0.51	0.19	3.7	117	331	2.4
$Y(CF_3CO_2)_3$	–	Glycerine	–	–	–	–	–	–	–
–	$Zn(Et)_2$	Glycerine	47	2.92	2.02	6.9	115	244	100
$Y(CH_3CO_2)_3$	$Zn(Et)_2$	Glycerine	18	3.67	1.75	4.8	119	283	96.3
$Y(acac)_3$	$Zn(Et)_2$	Glycerine	55	4.24	3.12	7.4	114	288	94.5
$Y(hf\text{-}acac)_3$	$Zn(Et)_2$	Glycerine	58	2.73	2.68	9.8	121	275	93.2
$Y(2\text{-}eha)_3$	$Zn(Et)_2$	Glycerine	50	2.02	1.88	9.3	119	268	88.4
$Y(NO_3)_3$	$Zn(Et)_2$	Glycerine	38	3.24	2.19	6.8	122	279	92.7
$Y(naph)_3$	$Zn(Et)_2$	Glycerine	36	2.24	2.12	9.5	121	272	93.7

Table 2
Effect of solvent on copolymerization of CO_2 and CHO using the catalyst system $Y(CF_3CO_2)_3$–$Zn(Et)_2$–glycerine (I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 30 ml; CHO = 30 ml; $T = 80$°C; $P = 400$ psi; time = 12 h)

Solvent	Polarity index	Yield g of polymer/g of Zn	$Mn \times 10^{-4}$	$Mw \times 10^{-5}$	Mw/Mn	T_g (°C)	T_{10} (°C)	f_{CO_2}
n-Hexane	0.1	3	1.14	0.45	3.6	124	283	71.5
Toluene	2.4	62	1.33	1.38	10.4	117	252	62.4
Benzene	2.7	59	1.98	1.87	9.4	122	288	76.1
1,2-Dichloroethane	3.5	57	2.50	2.13	8.5	120	281	60.9
THF	4.0	70	2.07	1.14	5.5	122	253	95.6
Chloroform	4.1	54	2.66	2.61	9.8	119	283	100
Ethyl acetate	4.4	39	1.25	0.44	3.5	118	281	92.5
1,4-Dioxane	4.8	62	2.80	2.20	7.9	116	283	93.9
1,3-Dioxolane	5.3	63	3.34	2.48	7.4	123	272	100
DMF	6.4	Trace	–	–	–	–	–	–

resultant copolymers (f_{CO_2}) could be evaluated based on the following equation [19]:

$$f_{CO_2} = \frac{A_{4.8}}{A_{4.8} + A_{3.5}}.$$

The molecular weights of the copolymers were determined by a gel permeation chromatograph (Shimadzu LC-9A) using polystyrene (Mn varies from 2698 to 650,000) as the standard. THF was used as the solvent with a flow rate of 1.0 ml min^{-1} at 35°C. The glass transition temperature (T_g) and the temperature at which a 10 wt% loss occurs (T_{10}) were measured by a DSC (DuPont 2900) and a TGA (DuPont 951), respectively.

3. Results and discussion

Table 1 shows the experimental results in the copolymerization of CO_2 and CHO by using different yttrium–metal coordination catalysts in 1,3-dioxolane at 80°C and 400 psi. Each experiment was performed in duplicate, the differences in yield, Mw, and T_g were found to be always less than 6.0%. Under this situation, it is concluded that the data on this polymerization reaction could be reproduced. From Table 1, it is seen that the catalyst system $Y(CF_3CO_2)_3$–$Zn(Et)_2$–glycerine provided the highest activity and the highest f_{CO_2}. While polymerization could be proceeded using the catalyst system containing only $Y(CF_3CO_2)_3$ and $Zn(Et)_2$, the resultant polymer had a very low f_{CO_2} indicating that the main reaction was a homopolymerization of cyclohexene oxide rather than a copolymerization. But when the catalyst system consisted of only $Y(CF_3CO_2)_3$ and glycerine, neither poly(cyclohexene oxide) nor polyethercarbonate was found to form. On the other hand a polyethercarbonate could be produced by the catalyst system consisting of $Zn(Et)_2$ and glycerine, though the yield was lower than that by the system containing $Y(CF_3CO_2)_3$, $Zn(Et)_2$, and glycerine. All these results indicated that the active site was on zinc in a compound resulted from either by the reaction between $Zn(Et)_2$ and glycerine or between $Y(CF_3CO_2)_3$ and the compound formed from $Zn(Et)_2$ and glycerine.

Table 1 shows an yttrium compound containing fluorine which was superior to other yttrium compounds for this copolymerization reaction. This is because that the presence of fluorine could induce a more positive charge of yttrium. In a consequence the positive charge of zinc is also increased due to the presence of the bond Y–O–Zn formed by the reaction between the yttrium compound and the compound resulted from $Zn(Et)_2$ and glycerine. Under this situation carbon dioxide could be more easily attracted by the active sites, as a result a high yield and high carbonate content in the copolymer were obtained. Based on yield and f_{CO_2} the system $Y(CF_3CO_2)_3$–$Zn(Et)_2$–glycerine was selected as the most appropriate catalyst system to carry out the copolymerization of CO_2 and CHO.

Table 3
Effect of the molar ratio of III to II on copolymerization of CO_2 and CHO (I = 0.0004 mol; II = 0.008 mol; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $T = 80$°C; $P = 400$ psi; time = 12 h)

Molar ratio, III/II	Yield g of polymer/g of Zn	$Mn \times 10^{-4}$	$Mw \times 10^{-5}$	Mw/Mn	T_g (°C)	T_{10} (°C)	f_{CO_2}
0	25	0.51	0.19	3.7	117	331	2.4
0.125	27	0.71	0.32	4.5	115	322	12.3
0.250	55	1.61	1.41	8.8	122	291	51.3
0.375	61	1.78	2.07	11.6	119	292	61.3
0.500	63	3.34	2.48	7.4	123	280	100
0.625	67	2.49	2.70	10.8	122	291	100
0.750	59	2.11	1.79	8.5	122	266	100
0.875	32	1.65	1.59	9.6	120	260	100

Table 4
Effect of the molar ratio of II to I on copolymerization of CO_2 and CHO (II = 0.008 mol; III = 0.004 mol; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $T = 80°C$; $P = 400$ psi; time = 12 h)

Molar ratio, II/I	Yield g of polymer/g of Zn	$Mn \times 10^{-4}$	$Mw \times 10^{-5}$	Mw/Mn	T_g (°C)	T_{10} (°C)	f_{CO_2}
0	–	–	–	–	–	–	–
5	40	1.87	2.34	12.5	121	293	71.5
10	73	3.86	3.27	8.5	122	288	100
15	69	2.82	3.12	11.1	128	285	100
20	63	3.34	2.48	7.4	123	280	100
25	75	3.72	2.79	7.5	121	288	100
30	73	3.50	3.24	9.3	122	287	100
35	70	3.50	3.01	8.6	125	273	100

Table 2 shows that the solvent played an important role. It not only affects the catalyst activity but also the properties of the resulting copolymer. A less polar solvent such as *n*-hexane was not a good candidate to produce a high yield of polyethercarbonate, though it could generate a better dispersity. A lower yield and a better dispersity for the use of *n*-hexane as solvent are attributed to a lower solubility of the resulting copolymer in solvent. This is verified by the fact that white powders suspended in *n*-hexane were observed. The most polar solvent, DMF, could not be used as solvent at all, since no polymer was generated. This result indicates that solvent plays an important role for the formation of active sites for this copolymerization. The other solvents possessing a polarity between *n*-hexane and DMF showed their activity, though the resultant copolymers exhibited different chemical and physical properties. It can also be seen from Table 2 that THF was the solvent to provide the highest yield and 1,3-dioxolane to generate the highest molecular weight, but carbonate contents in these two resultant copolymers were different. Both solvents are classified as cyclic ether indicating that cyclic ether be a suitable solvent for the copolymerization of CO_2 and epoxide. Because 1,3-dioxolane could generate a copolymer with (f_{CO_2}) of 100% and THF has an unpleasant odour, 1,3-dioxolane was chosen as the solvent in this study.

Table 3 shows the effect of the molar ratio of glycerine(III) to $Zn(Et)_2$(II) on yield and the properties of the resultant copolymer when 0.0004 mol of the component I was present. The molar ratio of III to II located around 0.635 was found to provide the highest yield and a relative high molecular weight, though the dispersity was not the smallest. The carbonate content of the resultant copolymer increased with the III/II molar ratio when it was less than 0.5, but after that, the carbonate content could be all reached to 100% at any III/II molar ratio. Since a complex was formed from the reaction between components II and III, a proper stoichiometric ratio should exist. When the amount of component III

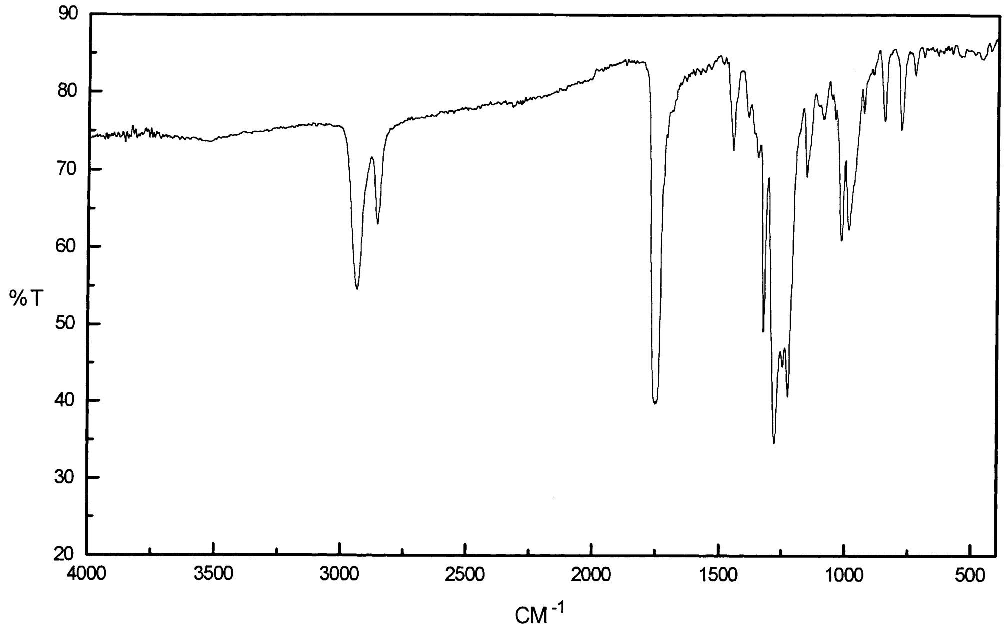


Fig. 1. IR spectra of the resulting copolymer. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 1,3-dioxolane; CHO = 30 ml; $T = 80°C$; $P = 400$ psi; time = 12 h.

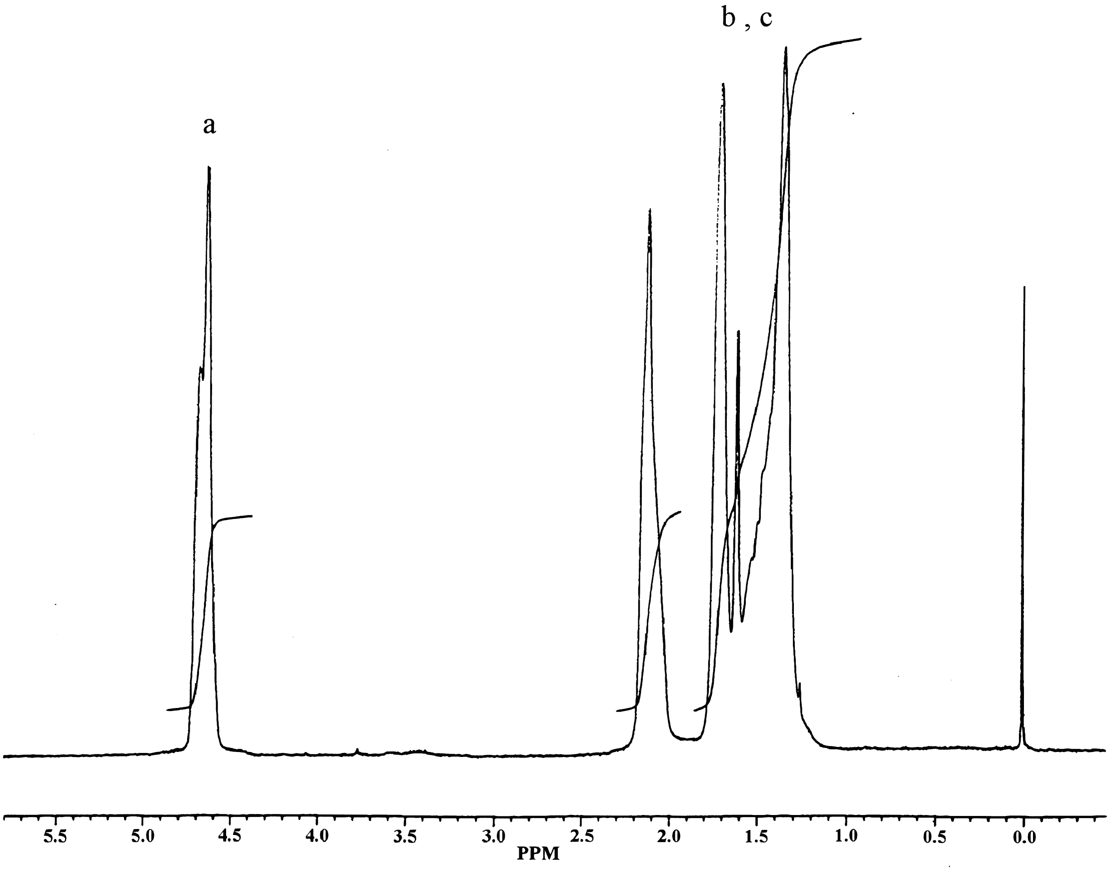


Fig. 2. ^{1}H NMR spectra of the resulting copolymer. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 1,3-dioxolane; CHO = 30 ml; T = 80°C; P = 400 psi; time = 12 h.

less than the stoichiometric requirement was used, the complex formed which would react further with $Y(CF_3CO_2)_3$ to generate active sites for the copolymerization of CO_2 and CHO became less. As a result a significant portion of ether unit in the resulting copolymer, i.e. f_{CO_2} is less than 1.0, was observed. On the other hand, when more glycerine was used, it would hinder the attraction of CO_2 and CHO by the active sites in the coordination catalyst, the

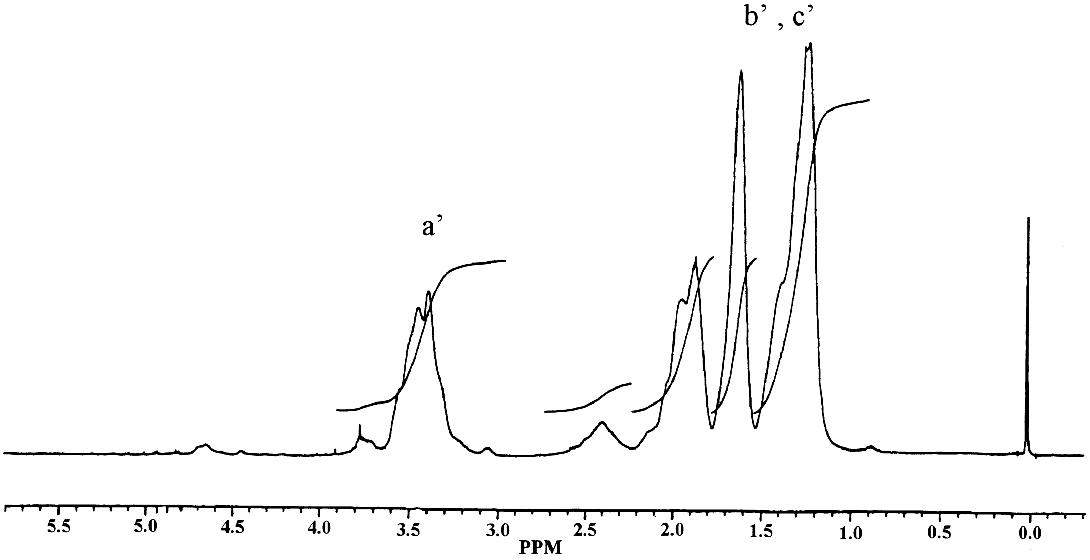


Fig. 3. ^{1}H NMR spectra of the resulting copolymer. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0 mol; solvent = 1,3-dioxolane; CHO = 30 ml; T = 80°C; P = 400 psi; time = 12 h.

Table 5
Poly(cyclohexene carbonate) synthesized at various temperatures (I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $P = 400$ psi; time = 12 h)

T (°C)	Yield g of polymer/g of Zn	Mn × 10^{-4}	Mw × 10^{-5}	Mw/Mn	T_g (°C)	T_{10} (°C)	f_{CO_2}
40	–	–	–	–	–	–	–
50	8	2.12	1.70	8.0	126	272	100
60	29	2.12	2.15	10.1	123	278	100
70	51	2.00	2.27	11.4	122	264	84.7
80	63	3.34	2.48	7.4	123	280	100
90	61	2.35	1.83	7.8	122	281	100
100	55	1.60	1.25	7.8	116	283	100
110	47	1.73	0.72	4.1	108	278	84.9
120	17	0.70	0.36	5.1	105	258	84.7

yield therefore decreased. The results shown in Table 3 indicate that the presence of glycerine is essential to generate a high yield and a high f_{CO_2} in this copolymerization.

As indicated by Tan and Hsu [12], the molar ratio of Zn(Et)$_2$(II) to Y(CF$_3$CO$_2$)$_3$(I) has a significant effect on yield in the copolymerization of CO$_2$ and propylene oxide and the physical properties of the resultant copolymer. It was also the case in this copolymerization using Y(CF$_3$CO$_2$)$_3$–Zn(Et)$_2$–glycerine as catalyst and 1,3-dioxolane as solvent, shown in Table 4. The highest yield was found at the II/I molar ratio of 25, and the highest molecular weight at 10. When the II/I molar ratio was larger than 5, the carbonate contents of all the copolymers generated were 100% indicating that the resultant copolymers were an alternating polyethercarbonate.

The IR spectra of the resultant copolymer for the II/I molar ratio at 20 and the III/II molar ratio at 0.5 were shown in Fig. 1. The two absorption peaks at ca. 1250 and 1750 cm^{-1} provide an evidence for the existence of carbonate units in the resulting copolymer. The ^{1}H NMR spectra of the copolymers generated by using the catalyst system containing the components I, II, and III as well as by the system containing only I and II were shown in Figs. 2 and 3, respectively. The carbonate content was as high as 100% for the first case, shown in Fig. 2, but was only 2.4% for the latter case indicated in Fig. 3. These results indicated that glycerine is an indispensable compound for the generation of an alternating polyethercarbonate from CO$_2$ and CHO.

When the pressure was maintained at 400 psi and the II/I and III/II molar ratios were fixed at 20 and 0.5, respectively, the yield and the physical and chemical properties of the resultant copolymer at various temperatures were shown in Table 5. It can be seen that the yield increased with temperature in a lower temperature range, reached a maximum at about 80°C, and then decreased rapidly as the temperature further increased. The existence of an optimum temperature regarding yield was also observed in the copolymerization of CO$_2$ and propylene oxide [12], but the location of the maximum temperature is 20°C higher in the present copolymerization reaction. The molecular weight was found to drop rapidly when the temperature was higher than 80°C, indicating degradation reactions occurred at higher temperatures.

Table 6 shows the pressure effect on this copolymerization reaction. According to the transition state theory [21], reaction rate for a polymerization reaction was generally accelerated by pressure. For this copolymerization reaction, the yield indeed increased with the increasing pressure when the pressure was less than 800 psi, but after that the yield decreased with the increasing pressure. A possible reason for a decrease in yield at higher pressures is due to a decrease in solubility of copolymer resulting from the swelling of the solvent caused by the dissolution of CO$_2$. A more pronounced swelling is always happened near the critical pressure of CO$_2$.

When 0.008 mol of Zn(Et)$_2$ was employed, the effect of the molar ratio of CHO to Zn(Et)$_2$ on yield at 80°C and 400 psi for a 12 h run is shown in Fig. 4. It can be seen that the yield was increased with the increasing molar

Table 6
Poly(cyclohexene carbonate) synthesized at various pressures (I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $T = 80$°C; time = 12 h)

P (psi)	Yield g of polymer/g of Zn	Mn × 10^{-4}	Mw × 10^{-5}	Mw/Mn	T_g (°C)	T_{10} (°C)	f_{CO_2}
200	53	2.02	2.15	10.6	122	289	100
400	63	3.44	2.48	7.8	123	280	100
600	64	2.17	2.38	11.0	123	281	100
800	67	1.82	1.87	10.3	123	280	100
1100	53	1.77	2.16	12.2	125	275	100
1300	49	2.30	1.48	6.4	126	283	100
1600	29	2.31	1.85	8.0	125	285	100

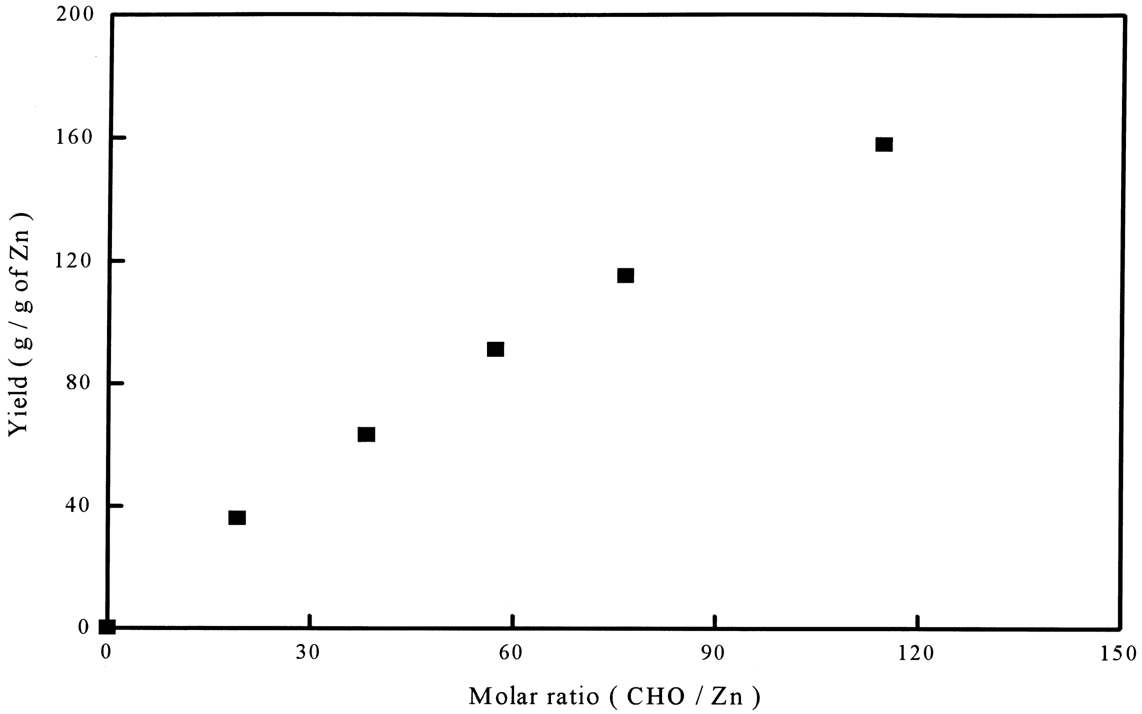


Fig. 4. The effect of the molar ratio of CHO to $Zn(Et)_2$ on yield. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 1,3-dioxolane; $T = 80°C$; $P = 400$ psi; time = 12 h.

ratio. These results indicate that sorption of CHO by the catalyst was crucial for this copolymerization. Due to volume limitation of the reactor, the molar ratio higher than 120 for an initial charge of $Zn(Et)_2$ of 0.008 mol could not be obtained. In order to see this effect at higher molar ratios, 0.004 mol of $Zn(Et)_2$ was charged initially into the reactor. When the molar ratio of CHO to $Zn(Et)_2$ was at 300, the yield was observed to be 310.4 g/(g of Zn). This result is higher than or comparable to those reported in the literature [14,16,18,19]. It should also be noted that the operation time to achieve this high yield using the present catalyst system is less than those in the above-mentioned literature. In addition, the recovery of catalyst is relatively easy for the present catalyst due to its heterogeneity as compared to the homogenous catalyst reported.

It can be seen from Tables 1–6 that the glass transition temperature T_g of the resulting copolymer at any operating condition is higher than 105°C, which is significant larger than that of the copolymer generated from CO_2 and PO (about 35°C). In addition to T_g, T_{10} of the resultant polyethercarbonate was found to be higher than 252°C at any reaction condition exhibiting at least 60°C higher than that of the copolymer resulted from CO_2 and PO. These results indicated the copolymerization of CO_2 and CHO be a feasible means to generate a polyethercarbonate with a high T_g. The enhancement of thermal property for the present copolymer was attributed to the presence of a bulky group in CHO.

4. Conclusions

The polyethercarbonate could be generated from the copolymerization of carbon dioxide and cyclohexene oxide in 1,3-dioxolane by a catalyst system consisting of $Y(CF_3CO_2)_3$, diethylzinc, and glycerine. For this catalyst system, sorption of carbon dioxide onto active sites is believed to be fast, thus an alternating instead of a random polyethercarbonate could be obtained. With a proper combination of temperature, pressure, and molar ratio of the catalyst components for a 12 h run in a batch-mode operation a yield higher than 310.4 g/(g of Zn) could be obtained, indicating that this copolymerization is an effective means to utilize the major greenhouse gas carbon dioxide. Besides, the thermal stability of the copolymer resulted from CO_2 and CHO was also found to be better than that of the copolymer from CO_2 and PO via a comparison of T_g and T_{10}. These results indicate that not only a high yield and a high molecular weight of the copolymer can be obtained, but also the thermal properties can be adjusted as desired by a proper choice of an epoxide or a combination of epoxides in a copolymerization reaction with CO_2.

Acknowledgements

Financial support from the National Science Council of Republic of China, Grant NSC89-2214-E007-009, is gratefully acknowledged.

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