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Block copolymerization of carbon dioxide with cyclohexene oxide and 4-vinyl-1-cyclohexene-1,2-epoxide in based poly(propylene carbonate) by yttrium–metal coordination catalyst

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Abstract

The coordination system, $Y(CF_3CO_2)_3$ (I)–$Zn(Et)_2$ (II)–*m*-hydroxybenzoic acid (III), was found to be the most active catalyst to generate poly(propylene carbonate) (PPC) from carbon dioxide and propylene oxide (PO) in 1,3-dioxolane. A high yield and a high molecular weight could be obtained at the conditions of a II/I molar ratio of 20, a III/II molar ratio of 1.0, a temperature of 60 °C, and a pressure of 2.76 MPa. The carbonate content in the resultant PPC was found to be nearly 100%.

The block copolymerization in the based PPC was carried out by in situ introducing an epoxide other than PO right after the copolymerization of carbon dioxide with PO using the same catalyst system. The IR and ^{1}H NMR spectra as well as the measured molecular weights verified the resulting copolymers were block copolymers. For the block copolymerization of CO_2 with cyclohexene oxide and CO_2 with 4-vinyl-1-cyclohexene-1,2-epoxide in the based PPC, the yield as well as the cyclohexene carbonate and the 4-vinyl-1-cyclohexene carbonate contents were found to increase with increasing temperature. The most appropriate temperature was around at 80 °C. The weight-average molecular weights of the block copolymers lay in a range from 2.44×10^5 to 3.16×10^5, the polydispersity in a range from 5.0 to 6.3, and the 10% weight loss temperature in a range from 226 to 253 °C. The thermal and mechanical properties of the resultant block copolymers lay between those of PPC, poly(cyclohexene carbonate), and poly(4-vinyl-1-cyclohexene carbonate), indicating the desired properties of a polymer can be achieved via block copolymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon dioxide; Epoxide; Polyethercarbonate

1. Introduction

Carbon dioxide is a major greenhouse gas. Its emission into atmosphere is therefore needed to reduce. One of the means to consume CO_2 is to use it as the starting monomer to synthesize polycarbonate. This means also meets the concept of the cleaner production, because toxic monomers such as phosgene are not environmentally acceptable in preparation of polycarbonate. Due to the inert characteristics of CO_2, an effective catalyst is generally required to proceed this kind of polymerization. The polymerization of CO_2 with propylene oxide (PO) was first reported in 1969 [1]. An alternating poly(propylene carbonate) (PPC) with a carbonate content of 88% was synthesized using diethyl zinc/water as the catalyst. After that, many other catalyst systems including: (a) zinc-based catalyst, such as $Zn(C_2H_5)_2$–H_2O, $Zn(C_2H_5)_2$-di- or tri-hydric phenol, and multiprotic compounds [2–5]; (b) (ttp)AlCl and its derivatives [6]; (c) zinc salts [7] were appeared in the literature for the copolymerization of CO_2 and PO. Due to low yield and long reaction time, many attempts to improve catalyst activity have been made. For the zinc-based catalysts, the use of diethyl zinc/polyhydric phenol [8], zinc glutarate and its derivatives [9,10], and cadmium(II) carboxylates [11] as the catalysts was found to indeed improve the reactivity of CO_2 with PO. For the (tpp)AlCl catalyst systems, the reactivity could also be enhanced using aluminum porphyrin and diethylaluminum chloride-25,27-dimethoxy-26,28-dihydroxy-*p*-*tert*-butyl-calix,4-arene [12,13] as the catalysts.

In recent publications, rate earth coordination catalysts exhibited its high activity in the ring-opening polymerization of epoxides and episulfides [14–18].

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Chen et al. [16] successfully synthesized a random PPC with a high molecular weight and a narrow molecular weight distribution from the copolymerization of CO_2 with PO using the rare-earth coordination catalyst $Y(P_{204})_3-Al(i\text{-}Bu)_3$–glycerine at 60 °C. When yttrium trifluoroacetate $Y(CF_3CO_2)_3$ and $Zn(Et)_2$ were substituted for $Y(P_{204})_3$ and $Al(i\text{-}Bu)_3$, respectively, Tan and Hsu [17] found that an alternating polyethercarbonate with a carbonate content of 95.6% could be obtained at a temperature of 60 °C and a pressure of 2.76 MPa. The catalyst system $Zn(Et)_2$-*m*-hydroxybenzoic acid has been shown to possess a higher catalyst activity than the system $Zn(Et)_2$–glycerine [4,19], it is therefore speculated that the catalyst activity towards the copolymerization of CO_2 and PO be improved if *m*-hydroxybenzoic acid is substituted for glycerine in a rare-earth coordination catalyst system. One of the objectives in this study is to verify this speculation. Besides, the effects of different components including rare-earth compound and multiprotic compound as well as solvent on yield and molecular weight of the resulting PPC were also systematically studied.

In addition to copolymerization of CO_2 and PO, the rare-earth catalyst system $Y(CF_3CO_2)_3-Zn(Et)_2$–glycerine was also shown to be active for the copolymerization of CO_2 with cyclohexene oxide (CHO) as well as the copolymerization of CO_2 with both PO and CHO [18,20]. While the thermal stability of the obtained polyethercarbonate was found to enhance significantly compared to that of PPC, mainly due to a rigid six-membered ring possessed by CHO, its application is still limited because of brittleness and poor transparency. Besides, one and two glass transition temperatures (T_g) were also observed in the copolymerization of CO_2 with both PO and CHO, indicating that the resultant copolymer might not be a block copolymer. In order to enhance both thermal and mechanic properties, a block copolymer resulted from the copolymerization of CO_2 with CHO in a living PPC may be an alternative. The study on this kind of block copolymerization is the other objective in this note. The block copolymerization was carried out using the same catalyst system for the synthesis of PPC.

Because 4-vinyl-1-cyclohexene-1,2-epoxide (VCHO) possesses a side chain containing carbon–carbon double bond, the properties of the resultant copolymer from the block copolymerization may be easily varied by insertion of other species thereafter when VCHO instead of CHO is used. Under this circumstance, the application of the resultant copolymer can be enhanced [21]. The last objective of this study is to generate a block copolymer from the copolymerization of CO_2 with VCHO in a living PPC. The thermal and mechanical properties of the resultant block copolymers were also measured in this study to see the improvement over the based PPC.

2. Experiment

2.1. Materials

PO of a purity 99.5% (Acros Organics), CHO of a purity of 98% (Tokyo Chemical Industry), and VCHO of a purity of 98% (Aldrich) were refluxed over CaH_2 for 4 h and then distilled before use. Diethyl zinc (Strem Chemicals) was used as received. The multiprotic compounds including glucose (Aldrich), *m*-hydroxybenzoic acid (Tokyo Chemical Industry), 1,3-phenylene diamine (Tokyo Chemical Industry), pyrogallol (Aldrich), and resorcinol (Aldrich) were heated in vacuum at 80 °C, except 1,2,3-benzenetricarboxylic acid (Tokyo Chemical Industry) that was heated in vacuum at 105 °C, for 24 h and were stored in dry boxes before use, glycerine (Tokyo Chemical Industry) and all the solvents including acetone, 1,3-dioxolane, ethyl acetate (EA), and tetrahydrofuran (THF) were analytical regent grade and were used without further purification. Carbon dioxide of 99.99% purity (Air Product) was used without further treatment. All the rare-earth compounds including cerium acetylacetonate $Ce(acac)_3$, cerium trifluoroacetylacetonate $Ce(trifluoro\text{-}acac)_3$, lanthanum acetylacetonate $La(acac)_3$, neodymium acetylacetonate $Nd(acac)_3$, neodymium trifluoroacetylacetonate $Nd(trifluoro\text{-}acac)_3$, samarium acetylacetonate $Sm(acac)_3$, samarium trifluoroacetylacetonate $Sm(trifluoro\text{-}acac)_3$, yttrium acetylacetonate $Y(acac)_3$, and yttrium trifluoroacetate $Y(CF_3CO_2)_3$ were purchased from Aldrich and were heated in vacuum at 80 °C for 40 h before use.

All the coordination catalyst systems containing a rare-earth compound, diethyl zinc, and a multiprotic compound were synthesized in an atmosphere of argon. The preparation was done by dissolving a multiprotic compound in a solvent first. The resultant solution was then added dropwise to the solution of diethyl zinc and the same solvent at room temperature. In this step, ethane was observed to evolve and the temperature of the solution was observed to rise indicating the occurrence of a reaction between diethyl zinc and multiprotic compound. The solution containing the suspended powders resulted from diethyl zinc and multiprotic compound was heated at 60 °C for 2 h after the evolution of ethane was complete. This solution was added to a 300 ml autoclave equipped with a magnetic stirrer (Autoclave Engineers Inc.) in which a known amount of a rare-earth compound was present. Before the addition of the solution, this autoclave was heated in vacuum at 100 °C for 4 h in order to remove oxygen and moisture. The resultant rare-earth catalyst solution was stirred at 60 °C for 1 h before CO_2 and epoxide were introduced.

2.2. Copolymerization

The reason to study the copolymerization of CO_2 with PO was to search for the most effective catalyst for synthesis of an alternating polyethercarbonate. The copolymerization

Table 1
Effect of rare-earth compound (I) on the copolymerization of CO_2 with PO (I = 0.0004 mol; II = 0.008 mol; III = 0.008 mol; solvent = 30 ml of 1,3-dioxolane; PO = 30 ml; $T = 60$ °C; P = 2.76 MPa; time = 12 h)

Catalyst system			Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}
I	II	III				
$Y(CF_3CO_2)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	50	13.5	4.7	100
$Ce(acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	9	8	5.3	96
$La(acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	29	12.2	3.9	96
$Nd(acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	23	5.6	2.9	96
$Sm(acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	8	7.1	3.9	93
$Y(acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	23	7.5	3.3	91
$Ce(trifluoro\text{-}acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	27	8.3	4.2	94
$Nd(trifluoro\text{-}acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	31	13.3	4.4	96
$Sm(trifluoro\text{-}acac)_3$	$Zn(Et)_2$	*m*-Hydroxybenzoic acid	12	3.0	2.1	93

was carried out in the autoclave containing the prepared catalyst system at a spinning speed of 1000 rpm. After a certain period of reaction time, the pressure was reduced to atmosphere to terminate the copolymerization and an excess of aqueous methanol solution containing dilute hydrochloric acid was added to result in a precipitation of the copolymer. To purify the precipitated crude copolymer, it was dissolved in THF first and then was precipitated again by adding an aqueous methanol solution. After three-time purification treatment, the resultant copolymer was dried under vacuum at 50 °C for 40 h prior to analysis.

2.3. Block copolymerization

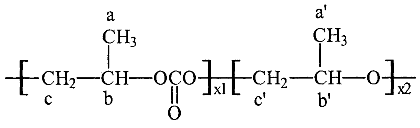
The block copolymerization was carried out by in situ introducing the epoxide other than PO into the autoclave at a time when the based PPC had been synthesized via the copolymerization of carbon dioxide and PO. After a certain period, the pressure in the autoclave was reduced to atmosphere to terminate the block copolymerization. The resulting block copolymer was obtained and purified by the same procedures as mentioned for the synthesis of PPC.

2.4. Analysis of the copolymer

The structure and the composition of the resulting copolymers were determined by the IR and ^1H NMR spectra. The IR spectra were obtained by a Perkin–Elmer 842 spectrometer and the ^1H NMR spectra of the copolymer in D-chloroform at room temperature using tetramethylsilane as the internal reference were obtained by a Varian Unityinova 500 NMR spectrometer.

2.4.1. PPC synthesized from CO_2 and PO

Suppose the resultant PPC possessed the following structure:



$$-\!\left[\underset{c}{CH_2}-\underset{b}{\overset{\overset{a}{CH_3}}{CH}}-O\underset{\underset{O}{\|}}{C}O\right]_{x1}\!\left[\underset{c'}{CH_2}-\underset{b'}{\overset{\overset{a'}{CH_3}}{CH}}-O\right]_{x2}\!-$$

Three major peaks should be present in the ^1H NMR spectrum. One was attributed from CH in carbonate unit (b: $\delta = 5.0$), the other from CH_2 in carbonate unit (c: $\delta = 4.1-4.25$), and the third one from CH and CH_2 in ether unit

Table 2
Effect of multiprotic compound (III) on the copolymerization of CO_2 with PO (I = 0.0004 mol of $Y(CF_3CO_2)_3$; II = 0.008 mol of $Zn(Et)_2$; solvent = 30 ml of 1,3-dioxolane; PO = 30 ml; $T = 60$ °C; $P = 2.76$ MPa; time = 12 h)

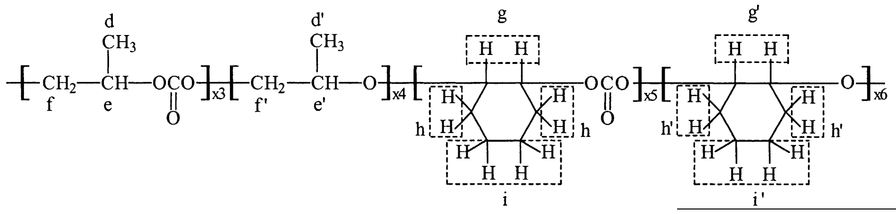
Multiprotic compound	Molar ratio, III/II	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}
1,2,3-Benzenetricarboxylic acid	0.5	–	–	–	–
1,2,3-Benzenetricarboxylic acid	0.34	6	6.8	3.4	100
Glycerine	0.5	28	6.4	3.4	100
Glucose	0.5	–	–	–	–
Glucose	0.375	–	–	–	–
Glucose	0.25	–	–	–	–
m-Hydroxybenzoic acid	0.75	19	8.2	4.3	100
m-Hydroxybenzoic acid	1	50	13.5	4.7	100
m-Hydroxybenzoic acid	1.25	39	11.6	4.8	100
1,3-Phenylene diamine	0.625	32	13.4	5.4	94
1,3-Phenylene diamine	0.5	38	14.0	5.2	98
1,3-Phenylene diamine	0.375	30	12.3	5.3	92
Pyrogallol	0.5	45	7.9	3.4	100
Resorcinol	1	49	11.1	4.6	100

(c′ and b′: $\delta = 3.5-3.8$). The carbonate content of PPC (f_{CO_2}) could be calculated based on the following equation [16]:

$$f_{CO_2} = \frac{A_{5.0} + A_{4.2}}{A_{5.0} + A_{4.2} + A_{3.5}} \qquad (1)$$

2.4.2. Block copolymer synthesized from CO_2 and CHO in the based PPC

Suppose the resultant block copolymer possessed the following structure:



Four major peaks were present in the ^{1}H NMR spectrum of the block copolymer. One was attributed from CH in propylene carbonate unit (e: $\delta = 5.0$), the other from CH in cyclohexene unit (g: $\delta = 4.6$), the third one from CH_2 in propylene carbonate unit (f: $\delta = 4.1-4.25$), and the fourth one from CH and CH_2 in ether unit (e′, f′, and g′: $\delta = 3.5-3.8$). The propylene carbonate content (F_{PC}) and the cyclohexene carbonate content (F_{CHC}) could be calculated based on the following equation:

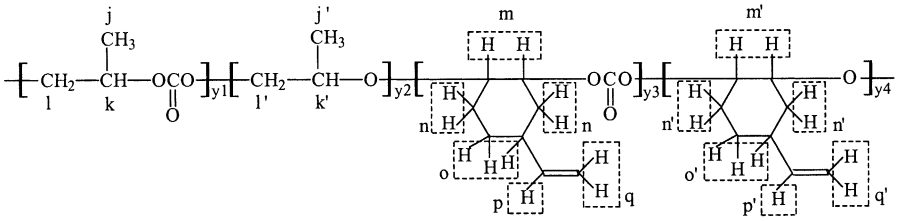
$$F_{PC}/F_{CHC} = A_{4.2}/A_{4.6} \qquad (2)$$

The carbonate content of the resultant block copolymers could be estimated by:

$$f_{CO_2} = \frac{A_{4.6} + A_{4.2}}{A_{4.6} + A_{4.2} + 0.8A_{3.5}} \qquad (3)$$

2.4.3. Block copolymer synthesized from CO_2 and VCHO in the based PPC

Suppose the resultant block copolymer possessed the following structure:



Seven major peaks were present in the ^{1}H NMR spectrum of the block copolymer. One was attributed from CH of vinyl group in 4-vinyl-1-cyclohexene carbonate unit (p: $\delta = 5.7$), the other from CH of vinyl group in 4-vinyl-1-CHO unit (p′: $\delta = 5.3$), the third one from CH in propylene carbonate (k: $\delta = 5.0$), the fourth one from CH in 4-vinyl-1-cyclohexene carbonate unit (m: $\delta = 4.7$), the fifth one from CH_2 of vinyl group in 4-vinyl-1-cyclohexene carbonate unit and 4-vinyl-1-CHO unit (q and q′: $\delta = 4.8$), the sixth one from CH_2 in propylene carbonate unit (l: $\delta = 4.1-4.25$), and the seventh one from CH and CH_2 in ether units (k′, l′, and m′: $\delta = 3.5-3.8$). The propylene carbonate content (F_{PC}) and the 4-vinyl-1-cyclohexene carbonate content (F_{VCHC}) could be calculated based on the following equation

$$F_{PC}/F_{VCHC} = 0.5A_{4.2}/A_{5.7} \qquad (4)$$

and the carbonate content of the obtained block copolymers could be calculated by

$$f_{CO_2} = \frac{A_{5.7} + A_{5.0} + A_{4.7} + A_{4.2}}{A_{5.7} + A_{5.3} + A_{5.0} + A_{4.7} + A_{4.2} + A_{3.5}} \qquad (5)$$

In order to verify the above-mentioned formula be effective in calculation of carbonate content, the elemental analysis was also carried out in this study. The percentages of the elements C and H were measured by a Perkin–Elmer 2400 CHN elemental analyzer. The gel permeation chromatograph (Shimadzu LC-9A and Shimadzu RID-6A) was used to measure the molecular weights of the resultant copolymers using polystyrene ($M_n = 2698-650\,000$) as the standard and THF as the solvent with a flow rate of 1.0 ml/min at 40 °C. The glass transition temperature (T_g) was measured by a differential scanning calorimeter (DuPont 2900) and the 10% weight loss temperature (T_{10}) was measured by a TGA (DuPont 951). The mechanical properties including tensile strength, tensile modulus, and elongation at break were measured with an Instron Model 4468. The crosshead speed was kept at 10 mm/min. The Izod impact strength (un-notched) was determined with an impact tester (TMI 43-01).

3. Results and discussion

Table 1 shows the experimental results in the

Table 3
Effect of solvent on the copolymerization of CO_2 with PO by the catalyst system $Y(CF_3CO_2)_3-Zn(Et)_2-m$-hydroxybenzoic acid (I = 0.0004 mol of $Y(CF_3CO_2)_3$; II = 0.008 mol of $Zn(Et)_2$; III = 0.008 mol of *m*-hydroxybenzoic acid; PO = 30 ml; $T = 80$ °C; $P = 2.76$ MPa; time = 12 h)

Solvent	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}
1,3-Dioxolane (30 ml)	50	13.5	4.7	100
EA (3 ml) + 1,3-dioxolane (27 ml)	39	8.6	3.7	96
EA (7.5 ml) + 1,3-dioxolane (22.5 ml)	35	6.0	3.2	100
EA (15 ml) + 1,3-dioxolane (15 ml)	22	4.9	2.5	98
Acetone (30 ml)	–	–	–	–
THF (30 ml)	20	11.5	2.9	97
Acetone (15 ml) + THF (15 ml)	–	–	–	–
Acetone (15 ml) + 1,3-dioxolane (15 ml)	–	–	–	–

copolymerization of CO_2 and PO using different rare-earth compounds in the solvent of 1,3-dioxolane at 60 °C and 2.76 MPa. Each experiment was performed in duplicate, the differences in yield, M_w, M_n, and T_{10} were found to be always less than 6.0%, indicating that the data could be reproduced. From Table 1, it is seen that the rare-earth metal trifluoroacetate and trifluoroacetylacetonates were more active than the rate-earth-metal acetylacetonates for this copolymerization. This might be due to the presence of fluorine induced a more positive charge of the rare-earth metal. In a consequence the positive charge of zinc was also increased due to the presence of the bond rare-earth metal–O–Zn formed in the catalyst preparation step. In the comparison of the rare-earth metal coordination systems, it can be seen that the system $Y(CF_3CO_2)_3-Zn(Et)_2-m$-hydroxybenzoic acid provided the highest activity, molecular weight, and f_{CO_2}, though the polydispersity (M_w/M_n) was not the best.

When $Y(CF_3CO_2)_3$ was used as the rare-earth metal compound in the catalyst system, several multiprotic compounds and different ratios of III/II were tested to see their effects on yield and molecular weight of the resultant copolymers. Table 2 shows that the use of *m*-hydroxybenzoic acid with a molar ratio of *m*-hydroxybenzoic acid to $Zn(Et)_2$ as 1.0 resulted in the highest yield and molecular weight compared to other multiprotic compounds. Besides, the yield was found to be much higher than that using glycerine reported by Tan and Hsu [17]. A possible reason was that more positive charge of zinc was generated by *m*-hydroxybenzoic acid compared to glycerine because *m*-hydroxybenzoic acid is a more acidic compound. It is surprised to see from Table 2 that glucose could not proceed the copolymerization at all even it possesses six –OH bonds. It is known that a compound possessing more active hydrogen was beneficial for the copolymerization when organometallic catalyst consisting of diethylzinc was employed [4,19,22–24]. While polyethercarbonate could be generated using a tetraprotic compound 1,3-phenylene diamine, the yield and molecular weight were not comparable to *m*-hydroxybenzoic acid. Though pyrogallol could generate a high f_{CO_2} and a narrow polydispersity, the molecular weight was found to be less than 80 000. A very low yield was observed when 1,2,3-benzenecarboxylic acid was used. The reason was that this compound became an acid anhydride after the removal of the crystalline water from its structure by heating before it was used. In a comparison of the acidity of the multiprotic compounds, it can be seen that the acidity increases in the following order: glycerine, pyrogallol, resorcinol, *m*-hydroxybenzoic acid. The present results indicated that a multiprotic compound with a high acidity was essential to yield a large amount of PPC.

Table 3 shows that solvent not only affected the catalyst activity but also the properties of the resultant copolymers. When a mixture of EA and 1,3-dioxolane was used as the solvent, it is seen that the catalyst activity decreased but the polydispersity became narrower when the EA content was increased. This was because that EA was a poor solvent for the resulting copolymer. The addition of EA therefore reduced the solubility of the resultant copolymer in the mixture. Under this circumstance, the molecular weight could not become very large and the polydispersity of the resultant copolymer therefore became narrower. On the other hand, acetone is a very good solvent for PPC; however, no PPC was generated when acetone was used either as the solvent or as the cosolvent. It seems that the copolymerization cannot be carried out in a very polar solvent. Regarding yield and molecular weight, Table 3 shows 1,3-dioxolane was the most appropriate solvent for this copolymerization compared to the other solvents and mixtures. It was therefore chosen for the subsequent block copolymerization.

The IR and ^1H NMR spectra of the resulting copolymer for the II/I molar ratio of 20 and the III/II molar ratio of 1.0 are shown in Figs. 1 and 2, respectively. The two adsorption peaks at 1250 and 1750 cm^{-1} in Fig. 1 provided an evidence for the presence of carbonate unit in the resultant copolymer. The carbonate content could be evaluated from Fig. 2 with Eq. (1), and was found to be nearly of 100%. It should be mentioned that due to the peak areas at $\delta = 3.5-3.8$ were nearly 0, the contribution to the carbonate content by the structures other than the previously

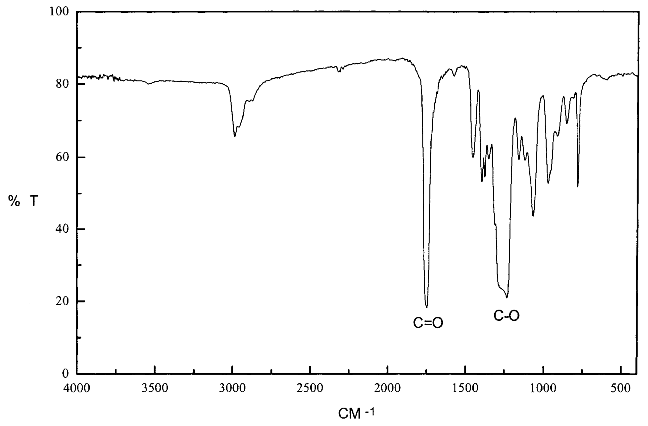
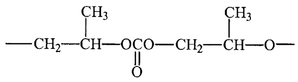
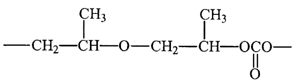


Fig. 1. The IR spectrum of the synthesized poly(propylene carbonate). (Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.008 mol; solvent = 1,3-dioxolane; PO = 30 ml; $T = 60$ °C; $P = 2.76$ MPa; time = 12 h.)

mentioned, such as


$-CH_2-\overset{CH_3}{\overset{|}{CH}}-O\underset{\overset{\|}{O}}{C}O-CH_2-\overset{CH_3}{\overset{|}{CH}}-O-$


$-CH_2-\overset{CH_3}{\overset{|}{CH}}-O-CH_2-\overset{CH_3}{\overset{|}{CH}}-O\underset{\overset{\|}{O}}{C}O-$

was negligible. Under this situation, the resulting copolymer was an alternating polyethercarbonate. To assure the calculation of the carbonate content be reliable, the elemental ratios of C (%) to H (%) were also evaluated from the ^{1}H NMR spectrum and the elemental analysis which were 47.0:5.9 and 46.5:5.6, respectively. This comparison verified the reliability of the calculated carbonate content in the resultant copolymer. These results accompanying with a yield higher than that reported at the same operating conditions [15,25] indicated that the coordination system $Y(CF_3CO_2)_3-Zn(Et)_2-m$-hydroxy-benzoic acid was a very active catalyst for generating an alternating polyethercarbonate from CO_2 and PO. This catalyst system was therefore used for the block copolymerization.

The IR spectra of the block copolymers resulting from the copolymerization of CO_2 with CHO and CO_2 with VCHO in the based PPC for the II/I molar ratio at 20 and the III/II molar ratio at 1.0 are shown in Figs. 3 and 4, respectively. The existence of two adsorption peaks carbonyl group (C=O) and ether group located at 1750 and 1250 cm^{-1} provided an evidence for the presence of carbonate unit in the resultant block copolymers. It can also be seen from Fig. 4 that there existed an adsorption peak at 1645 cm^{-1}, indicating the presence of a vinyl group in the resultant block copolymer using VCHO as the monomer.

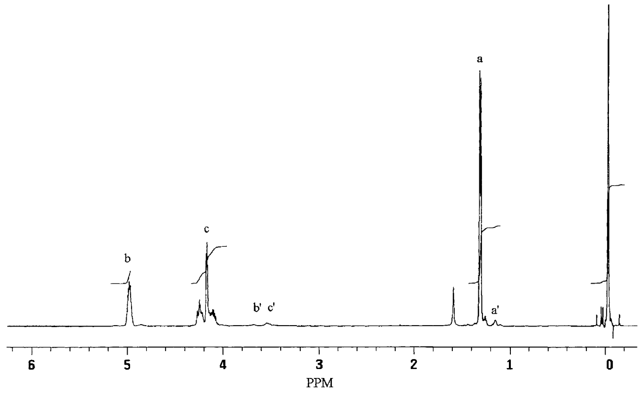


Fig. 2. The ^{1}H NMR spectrum of the synthesized PPC. (Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.008 mol; solvent = 1,3-dioxolane; PO = 30 ml; $T = 60$ °C; $P = 2.76$ MPa; time = 12 h.)

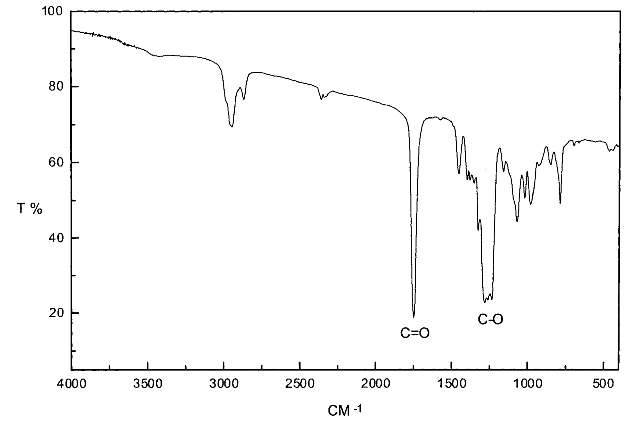


Fig. 3. The IR spectrum of the block copolymer synthesized from CO_2 and CHO in the based poly(propylene carbonate). (Reaction conditions: CHO = 30 ml; $T = 80$ °C; $P = 4.14$ MPa; time = 12 h.)

The ^{1}H NMR spectra of the resulting block copolymers are shown in Figs. 5 and 6. The two peaks in Fig. 5, one was attributed from CH in propylene carbonate unit and the other from CH in cyclohexene carbonate unit, indicated that the resultant polymer was a PPC-*block*-poly(cyclohexene carbonate), PPC-*block*-PCHC. The two peaks in Fig. 6, one was attributed from CH of vinyl group in 4-vinyl-1-cyclohexene carbonate unit and the other from CH_2 in propylene carbonate unit, verified the generated polymer was a PPC-*block*-poly(4-vinyl-1-cyclohexene carbonate), PPC-*block*-PVCHC.

Tan and Hsu [17,18] pointed out degradation occurred in

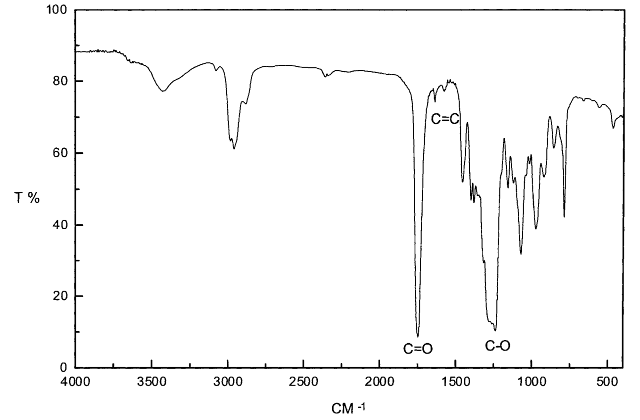


Fig. 4. The IR spectrum of the block copolymer synthesized from CO_2 and VCHO in the based poly(propylene carbonate). (Reaction condition: VCHO = 30 ml; $T = 80$ °C; $P = 4.14$ MPa; time = 12 h.)

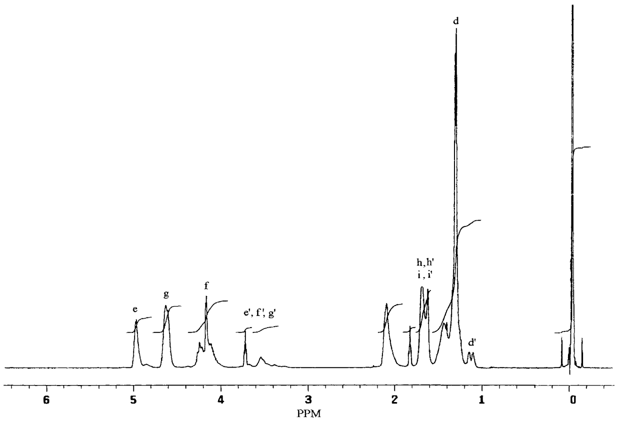


Fig. 5. The ^{1}H NMR spectrum of the block copolymer synthesized from CO_2 and CHO in the based poly(propylene carbonate). (Reaction conditions: CHO = 30 ml; $T = 80$ °C; $P = 4.14$ MPa; time = 12 h.)

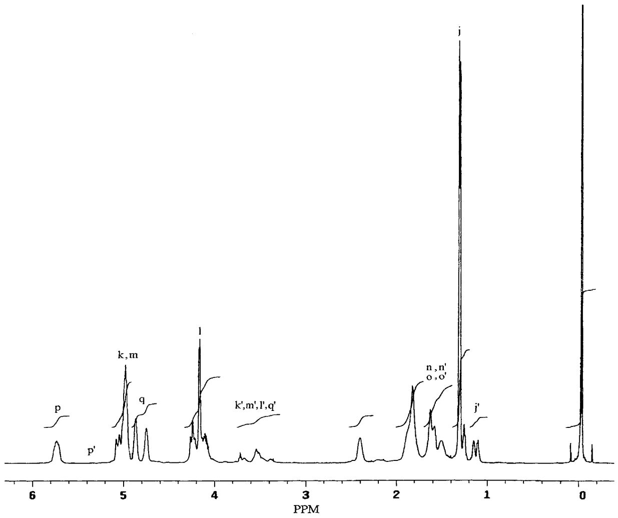


Fig. 6. The ^{1}H NMR spectrum of the block copolymer synthesized from CO_2 and VCHO in the based PPC. (Reaction conditions: VCHO = 30 ml; $T = 80$ °C; $P = 4.14$ MPa; time = 12 h.)

the copolymerization of CO_2 with PO and CO_2 with CHO when the temperature was higher than 60 and 80 °C, respectively. The block copolymerization was therefore carried out between 60 and 80 °C in this study. Table 4 shows the yield and properties of the resulting PPC-*block*-PCHC at 60, 70, and 80 °C. It can be seen that both the yield and weight-average molecular weight increased with temperature and the best polydispersity occurred at 70 °C. The carbonate content lying between 86 and 92% at these temperatures indicated the presence of PO unit and CHO unit in the resultant block copolymer. It was also observed that the ratios of carbon and hydrogen atoms evaluated by the ^{1}H NMR spectrum and the elemental analysis were 55.0:6.9 and 53.4:7.0, respectively. The small differences in carbon and hydrogen atoms between these two calculation means indicated the calculated carbonate content be reliable. Table 4 shows more PO and CHO units were present at 80 °C. As indicated by Hsu and Tan [18], the most appropriate temperature for the copolymerization of CO_2 with CHO occurred at 80 °C. The copolymerization of CO_2 with CHO was thus accelerated with increasing temperature. As a result, F_{CHC} increased with increasing temperature. On the other hand, the degradation of the based PPC became more severe at the temperatures higher than 60 °C, F_{PC} thus decreased with increasing temperature. Due to an increase in weight-average molecular weight with temperature as shown in Table 4, the copolymerization rate of CO_2 with CHO was believed to be higher than the degradation rate of PPC at 80 °C. Table 5 shows similar results for the synthesis of PPC-*block*-PVCHC. A high carbonate content lying between 89 and 92% was present in the resultant block copolymer and F_{VCHC} increased with increasing temperature. Due to the copolymerization rate of PVCHC was lower than that of PCHC in the present temperature range [25], F_{VCHC} in this block copolymerization was found to be lower than F_{CHC} in the block copolymerization of CO_2 with CHO at these temperatures.

The glass transition temperatures (T_g) of the resultant copolymers and block copolymers based on PPC are shown in Table 6. It is seen that the resultant PPC-*block*-PCHC and PPC-*block*-PVCHC possessed two T_g that lay between those of the copolymers and were not equal to those of the polyethers, indicating that block copolymerization could be carried out using the present technique. Table 4 shows the T_{10} of PPC-*block*-PCHC were in a range 236–253 °C that was higher than that of the PPC (about 195 °C) but lower than that of PCHC (about 280 °C). It was also the case for the PPC-*block*-PVCHC, as shown in Table 5. These results indicated that the thermal property of the block copolymer could be varied by addition of a proper portion of the copolymer resulted from the copolymerization of CO_2 with CHO or VCHO.

Table 7 shows the mechanical properties of the resultant

Table 4
Experimental results for the block copolymerization of CO_2 with CHO in the based PPC at different temperatures (I = 0.0004 mol of $Y(CF_3CO_2)_3$; II = 0.008 mol of $Zn(Et)_2$; III = 0.008 mol of *m*-hydroxybenzoic acid; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $P = 4.14$ MPa; time = 12 h)

T (°C)	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}	F_{PC}	F_{CHC}	$F_{PO} + F_{CHO}$	T_{10} (°C)
60	48	24.4	6.1	91	72	19	9	236
70	59	27.7	5.0	92	65	27	8	253
80	69	31.0	6.2	86	47	39	14	248

Table 5
Experimental results for the block copolymerization of CO_2 with VCHO in the based PPC at different temperatures (I = 0.0004 mol of $Y(CF_3CO_2)_3$; II = 0.008 mol of $Zn(Et)_2$; III = 0.008 mol of *m*-hydroxybenzoic acid; solvent = 30 ml of 1,3-dioxolane; VCHO = 30 ml; $P = 4.14$ MPa; time = 12 h)

T (°C)	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}	F_{PC}	F_{VCHC}	$F_{PO} + F_{VCHO}$	T_{10} (°C)
60	52	30.0	6.3	88	75	13	12	227
70	60	31.6	6.0	92	75	17	8	235
80	79	27.0	5.6	89	62	27	11	226

Table 6
The glass transition temperatures of the resultant copolymers

Copolymers	Glass transition temperature, T_g (°C)
PPC	38
PCHC	125
PVCHC	107
PPC-*block*-PCHC[a]	41,89
PPC-*block*-PVCHC[b]	43,90

[a] $F_{PC}/F_{CHC}/F_{PO} + F_{CHO} = 47:39:14$.

[b] $F_{PC}/F_{VCHC}/F_{PO} + F_{VCHO} = 63:28:9$.

copolymers and block copolymers. PVCHC and PCHC exhibited a superior tensile strength to PPC. This was because that CHO and VCHO possess a rigid six-membered ring. The tensile strength of PPC could be enhanced via a block copolymerization of CO_2 with CHO or VCHO. Table 7 shows that the tensile strengths of the resultant copolymers PPC-*block*-PCHC and PPC-*block*-PVCHC were higher than those of PPC and the commercial LDPE (Exxon Chemical Co.), but were lower than those of PCHC, PVCHC, and the commercial polycarbonate (PC, optical grade, Bayer). On the other hand, PPC possessed the highest elongation indicating PPC had the highest toughness. Elongation of the block copolymers resulted in more rigid CHO or VCHO and was thus reduced and found to be less than PPC and LDPE but higher than PCHC, PVCHC, and PC. Due to possession of the largest tensile modulus, PCHC was the most stiffness copolymer. The stiffness of the copolymer PPC-*block*-PCHC was therefore enhanced compared to PPC itself. The Izod impact strengths of the resultant copolymers shown in Table 7 indicated that PPC had the highest impact strength, given that PPC was a rubbery copolymer. Though the Izod impact strengths of the PPC-*block*-PCHC and PPC-*block*-PVCHC were lower than that of PPC, they were higher than those of PCHC, PVCHC, and PC.

4. Conclusions

An alternating PPC with a 100% carbonate content could be effectively generated from the copolymerization of CO_2 and PO in 1,3-dioxolane using the coordination system $Y(CF_3CO_2)_3$ (I)–$Zn(Et)_2$ (II)–*m*-hydroxybenzoic acid (III) as the catalyst. At a temperature of 60 °C, a pressure of 2.76 MPa, and the molar ratios of II/I and III/II of 20 and 1, respectively, both the yield and molecular weight of the resultant PPC were higher than that reported in the literature.

The block copolymerization of CO_2 with CHO and VCHO in the based PPC were found to be effectively carried out by the same catalyst system for the copolymerization of CO_2 and PO. From the IR and ^1H NMR spectra and the measured molecular weights, the resulting copolymers were identified as block copolymers. The T_g, T_{10}, tensile strength, elongation, and Izod impact strength of the resulting block copolymers were found to lie between those of the copolymers resulted from CO_2 and individual monomers such as PO, CHO, and VCHO. These results indicated that block copolymerization was an effective means to generate

Table 7
The mechanical properties of the resultant copolymers and block copolymers

Copolymers	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Impact strength (ft-lb/in.)
PPC	14.7	203.1	1353	3.89
PCHC	29.4	1.3	2707	0.70
PVCHC	36.7	1.3	2110	1.02
PPC-*block*-PCHC[a]	15.2	2.0	2033	2.22
PPC-*block*-PVCHC[b]	18.4	1.7	1811	2.28
Commercial LDPE	8.1	124.3	251	–
Commercial PC	18.9	1.4	1573	1.26

[a] $F_{PC}/F_{CHC}/F_{PO} + F_{CHO} = 47:39:14$.

[b] $F_{PC}/F_{VCHC}/F_{PO} + F_{VCHO} = 63:28:9$.

a polymer with the desired thermal and mechanical properties.

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