Polymer Bulletin 61, 679–688 (2008)
DOI 10.1007/s00289-008-0993-8

Polymer Bulletin

The copolymerization of carbon dioxide and propylene oxide with $Y(CCl_3COO)_3$-diphenylzinc-glycerol catalyst

Dong Xie, Xianhong Wang (✉), Xiaojiang Zhao, Fosong Wang

Polymer Engineering Laboratory of Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun, 130022, China
E-mail: xdong@whut.edu.cn; Fax: 86-431-5689095

Received: 12 April 2008 / Revised version: 22 August 2008 / Accepted: 23 August 2008

Summary

Various organometallic compounds (diphenylzinc, dibenzylzinc, dicyclohexylzinc, bis(pentafluorophenyl)zinc, diethylzinc, di(n-butyl)zinc, triethylaluminum) were used to form $Y(CCl_3COO)_3$-organometallic compound-glycerol catalyst for the copolymerization of carbon dioxide and propylene oxide. It was found that $Y(CCl_3COO)_3$-diphenylzinc-glycerol catalyst showed the highest catalytic activity, at optimum conditions the yield could be as high as 478.8 (g polymer/mol Zn h). The catalytic activity sequence of these catalysts decreased as follows: $Y(CCl_3COO)_3$-diphenylzinc-glycerol>$Y(CCl_3COO)_3$-diethylzinc-glycerol>$Y(CCl_3COO)_3$-di-(n-butyl) zinc-glycerol>$Y(CCl_3COO)_3$-dibenzylzinc-glycerol>$Y(CCl_3COO)_3$-dicyclohexylzinc-glycerol>$Y(CCl_3COO)_3$-bis(pentafluorophenyl)zinc-glycerol. ^1H NMR, ^{13}C NMR, TGA, DMA, tensile tests results indicated that microstructure and properties of the polymers varied with catalyst used. Copolymer from $Y(CCl_3COO)_3$-diphenylzinc-glycerol catalyst displayed the highest thermal properties and mechanical properties: the glass transition temperature (T_g) was 50.2°C, the 5% weight loss temperature ($T_{-5\%}$) was 222°C, the tensile strength was 34.7 MPa, the Young's modulus was 298 MPa. The difference between the properties of the polymers was explained relating to the different polycarbonate content in the polymers.

Introduction

Carbon dioxide (CO_2) is an environmental pollutant that causes the greenhouse effect. Thus, the prevention of massive CO_2 emission to the atmosphere has been the subject of a variety of research works. On the other hand, CO_2 is a precious carbon resource, its chemical fixation and utilization is an important subject not only from environmental issue but also from economic view. To our knowledge, CO_2 could be used to produce many useful industrial materials, such as methanol, formic acid, carbonate, urea, salicylic acid etc., among these the most promising example was the copolymerization of CO_2 and epoxides to form biodegradable polymeric material. Since the pioneering work conducted by Inoue [1] in 1969 using $ZnEt_2$-H_2O catalyst, a significant amount of research has been directed toward the synthesis of aliphatic polycarbonates from carbon dioxide and epoxides, and the focus was on the development of catalysts of improved activity and selectivity. To date, a variety of catalysts and catalyst precursors have been revealed such as Et_2Zn-modifiers [2], metalloporphyrins [3], Zinc glutarate [4], rare earth coordination catalyst [5], the well-defined diiminate zinc compounds [6], metal salen complexes [7], bis(phenoxide) derivatives of zinc [8], double metal cyanide complexes etc. [9], which were well reviewed by Beckman [10], Coates [11], Darensbourg [12], Sugimoto [13] in their recent papers. Among all the catalysts reported, rare earth-based ternary catalysts $Y(P_{204})_3$-Al(*i*-Bu)$_3$-glycerine found by Chen et al. are known to catalyze the effective copolymerization of CO_2 and propylene oxide (PO) and produce high molecular weight polycarbonate at relatively short reaction time [5]. Tan etc. [14] developed the rare earth-based catalyst system, utilizing diethylzinc and rare earth compound $Y(CF_3COO)_3$ instead of triisobutylaluminum and $Y(P_{204})_3$, respectively, forming the $Y(CF_3COO)_3$-$ZnEt_2$-glycerine catalyst system. In this case, the catalyst activity was improved to 4200 g/molY per hour, and the resultant copolymer had high carbonate content. In our laboratory, $Y(CF_3COO)_3$ was replaced by $Nd(CCl_3COO)_3$ and the catalytic activity of the resultant catalyst improved to 6875 g/molY per hour at appropriate conditions [15]. $ZnEt_2$ is another crucial component in the rare-earth ternary catalyst, which had been revealed by Tan and Liu [14, 15]. Our previous work had investigated the influence of dialkylzinc in the rare earth ternary catalyst on the copolymerization by using different dialkylzincs, and found that the replacement of $ZnEt_2$ by other dialkylzincs would lead to lower activity [16]. For further investigation of active species and improvement of catalytic activity, in this work many other organometallic compounds including diphenylzinc, dibenzylzinc, dicyclohexylzinc, triethylaluminum, diethylzinc, di(n-butyl)zinc, bis(pentafluorophenyl)zinc were used to form $Y(CCl_3COO)_3$-organometallic compound-glycerol catalyst for the copolymerization of propylene oxide and carbon dioxide. The product microstructure and properties were also studied by ^{1}H NMR, ^{13}C NMR, TGA, DMA, tensile tests.

Experimental

Materials

Diethylzinc ($ZnEt_2$), di(n-butyl)zinc (Zn(*n*-Bu)$_2$) were prepared from relative alkyl bromide and alkyl iodide [17]. Diphenylzinc ($ZnPh_2$), dibenzylzinc ($Zn(CH_2C_6H_5)_2$), dicyclohexylzinc ($Zn(C_6H_{11})_2$), bis(pentafluorophenyl)zinc ($(C_6F_5)_2Zn$) were prepared from relative Grignard reagent and zinc chloride [18]. $AlEt_3$ was used as received. All these organometallic compounds were purified according to the method described in the reference, and the purities of these compounds were determined from its zinc content by using EDTA titration method [19]. Yttrium trichloroacetate ($Y(CCl_3COO)_3$) was prepared from Y_2O_3 and CCl_3COOH, and was dried at 80°C under vacuum for 48 h prior to use [20]. PO and dioxane were refluxed over CaH_2 for 2 days and distilled before use. Carbon dioxide was commercially obtained (purity>99%) without further purification.

Copolymerization

The rare earth ternary catalyst was prepared according to literature [15]. After adding the catalyst into an oxygen and water free 500 ml autoclave, CO_2 was introduced into the autoclave by pressurization, then the reactor was heated to and kept at the polymerization temperature, with vigorous stirring for a certain period. To terminate the copolymerization reaction, the autoclave was vented, and distilled water was added. The obtained copolymer was purified by several turns of chloroform dissolution and subsequent dilute hydrochloric acid methanol solution precipitation. The methanol-insoluble copolymer was collected and dried at 50°C under reduced pressure till a constant weight was observed.

Characterization

Number average molecular weight and polydispersity of the copolymer were measured from gel permeation chromatography (GPC) on a Waters-400 spectrometer using polystyrene as standard and tetrahydrofuran as eluent. Intrinsic viscosity was obtained in benzene at 35°C using Ubbelohde viscometer.

The ^1H NMR spectra and ^{13}C NMR spectra of the copolymer were recorded on a BRUKER AV 300 NMR spectrometer in deuterochloroform using tetramethylsilane (TMS) as internal reference.

The samples for mechanical properties testing were melt-compression molded using YX-25(D) Semi-Auto matic Moulding Press. The molds were heated to 140°C. The samples were then placed in the hydraulic press and preheated for 3 min. Subsequently, the samples were pressed into sheets in 1 mm thickness at a pressure of 4 MPa for 5 min. All samples were stored in air-tight bags.

The dynamic mechanical behavior of the samples was investigated with a Netzsch DMA 242C (Germany) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.02 mm. The investigated temperature ranged from -30 to 90°C at a heating rate of 2°C/min. The specimen dimension for DMA was $30\times10\times1$ mm^3. At least three samples were tested, and the average value was reported.

The static tensile properties were measured at 23°C and relative humidity of $50\pm5\%$ using an Instron-1121 tensile tester. The cross-head speed was set at 10 mm/min. Five specimens of each sample were tested, and the average results were reported. The samples for mechanical properties test were cut into standard dog-bone tensile bars (ASTM D638) with dimensions of $25\times4\times1$ mm^3.

Thermogravimetric analysis was carried out in a PerkinElmer 7 series thermal analysis system (United States) under a protective nitrogen atmosphere (100 mL/min) at the heating rate of 10°C/min.

Results and discussion

Preparation of various organometallic compounds

$ZnEt_2$, $Zn(n\text{-}Bu)_2$ were prepared according to reaction schematically shown in Eq. 1, while $ZnPh_2$, $Zn(CH_2C_6H_5)_2$, $Zn(C_6H_{11})_2$, $(C_6F_5)_2Zn$ were prepared according to Eq. 2. Table 1 listed the purities and boiling points of these compounds. The purities of these organometallic compounds were higher than 97%, which was good enough for the copolymerization of carbon dioxide and propylene oxide. All these compounds were stored below 5°C in sealed glass vessels.

$$2RBr + 2RI + 4Zn \xrightarrow{Zn-Cu,\Delta} 2ZnR_2 + ZnBr_2 + ZnI_2 \qquad \textbf{(1)}$$

$$ZnCl_2 + 2RMgBr \longrightarrow ZnR_2 + MgCl_2 + MgBr_2 \qquad \textbf{(2)}$$

Table 1. The purities and boiling points of various organometallic compounds

Organometallic compounds	Boiling point(°C)	zinc content analysis(wt%)		Purity (wt%)
		Determined values	Calculated values	
$ZnEt_2$	116[a]	52.26	52.84	98.90
Zn(n-Bu)$_2$	40[b]	35.66	36.31	98.21
$ZnPh_2$	180[b]	29.35	29.68	98.88
$Zn(CH_2C_6H_5)_2$	--	26.05	26.31	99.01
$Zn(C_6H_{11})_2$	65[b]	27.32	28.14	97.10
$(C_6F_5)_2Zn$	91[c]	15.90	16.36	97.20

[a] measured at 1.01×10^5 Pa; [b] measured at 6.58×10^2 Pa; [c] melting point at 1.01×10^5 Pa.

Copolymerization of CO_2 and PO

Various organometallic compounds ZnR_2 (R is ethyl, n-butyl, phenyl, benzyl, cyclohexyl, pentafluorophenyl) in combination with $Y(CCl_3COO)_3$ and glycerin, were used for the copolymerization of CO_2 and PO in dioxane at 60°C under 30 atm for 8 h. The molar ratio of Zn to Y was fixed at 20, and that of Zn to glycerin was 2, which was the same as the reference [16]. The results were summarized in Table 2. All these rare earth metal coordination catalysts could catalyze the copolymerization of CO_2 with PO. The catalytic activity of $Y(CCl_3COO)_3$-$ZnPh_2$-glycerin catalyst was the highest among the catalysts investigated (320.3(g polymer/mol Zn h)), which was far more than $Y(CCl_3COO)_3$-$ZnEt_2$-glycerin catalyst (221.5(g polymer/mol Zn h)). The catalytic activity of these catalysts decreased according to the following sequence: $Y(CCl_3COO)_3$-$ZnPh_2$-glycerol (320.3(g polymer/mol Zn h))>$Y(CCl_3COO)_3$-$ZnEt_2$-glycerol (221.5(g polymer/mol Zn h))>$Y(CCl_3COO)_3$-Zn(*n*-Bu)$_2$-glycerol (177.3(g polymer/mol Zn h))>$Y(CCl_3COO)_3$-$Zn(CH_2C_6H_5)_2$-glycerol (40.5(g polymer/mol Zn h)) >$Y(CCl_3COO)_3$-$Zn(C_6H_{11})_2$-glycerol (18.7(g polymer/mol Zn h))>$Y(CCl_3COO)_3$-$(C_6F_5)_2Zn$-glycerol (trace). $AlEt_3$ was also used to form $Y(CCl_3COO)_3$-$AlEt_3$-glycerol catalyst for the copolymerization (shown in Table 2), it was found that the activity was low (45.8(g polymer/mol Al h)). At the copolymerization conditions, all the Zn-

Table 2. The copolymerization results with $Y(CCl_3COO)_3$/orgnometallic compound/glycerol ternary catalysts [a]

Orgnometallic Compounds	Catalytic activity (g polymer/molZn h)	$\overline{M_n}$ ($\times10^{-4}$)[b]	PDI[c]	CU%[d]	H-T%[e]
$ZnPh_2$	320.3	9.2	4.5	97.8[g]	71.9
$ZnEt_2$	221.5	11.3	3.9	96.3[g]	72.5
Zn(n-Bu)$_2$	177.3	10.5	5.5	94.3[g]	72.5
$Zn(CH_2C_6H_5)_2$	40.5	4.2	4.5	94.0	72.0
$Zn(C_6H_{11})_2$	18.7	8.3	4.8	92.2[g]	72.8
$(C_6F_5)_2Zn$	trace	\	\	\	\
$AlEt_3$[f]	45.8	\	\	15.0	\

[a] The copolymerization was carried out in dioxane at 60°C under 30 atm for 8 h (The molar ratio of Zn to glycerine to Y was 20 to 10 to 1); [b] number average molecular weight; [c] polydispersity; [d] the polycarbonates content; [e] the head-to-tail structure content; [f] The molar ratio of Al to glycerine to Y was 8 to 4 to 1; [g] methanol insoluble product from diphenylzinc-based catalyst, diethylzinc-based catalyst, di(*n*-butyl)zinc-based catalyst, dicyclohexylzinc-based catalyst were defined as PPC-A, PPC-B, PPC-C, PPC-D, respectively.

based catalysts produced products with high molecular weight (number average molecular weight >42000) and low polydispersity (PDI<5.5). In addition, $ZnPh_2$, $ZnEt_2$, $Zn(n\text{-}Bu)_2$, $Zn(C_6H_{11})_2$ based catalysts generated products with similar number average molecular weight (varied from 83000 to 113000) and polydispersity (PDI varied from 3.9 to 5.5).

The ^1H NMR spectra of various methanol insoluble copolymers obtained with rare earth ternary catalyst were shown in figure 1. The polycarbonate unit content of the copolymer (CU%) was calculated from the area ratio of peaks at 5.0, 4.2, and 3.5 ppm in the ^1H NMR spectrum according to the following equation (Eq. 3) [5]:

$$CU\% = \frac{A_{5.0} + A_{4.2}}{A_{5.0} + A_{4.2} + A_{3.5}} \qquad \mathbf{(3)}$$

As shown in Figure 1 and Table 2, the content of polycarbonate unit in the copolymer varied with catalyst used. When the copolymerization was catalyzed by $Y(CCl_3COO)_3$-$AlEt_3$-glycerol catalyst, the product was mainly random copolymer with very low polycarbonate unit content (CU% was 15.0%). With $Y(CCl_3COO)_3$-$Zn(C_6H_{11})_2$-glycerol catalyst, the CU% of the methanol insoluble product was 92.2%, and when $Y(CCl_3COO)_3$-$ZnEt_2$-glycerol, $Y(CCl_3COO)_3$-$Zn(n\text{-}Bu)_2$-glycerol, or $Y(CCl_3COO)_3$-$Zn(CH_2C_6H_5)_2$-glycerol catalyst was used, the CU% of the corresponding product was 96.3%, 94.3%, 94.0%, respectively. $Y(CCl_3COO)_3$-$ZnPh_2$-glycerol catalyst produced copolymer with the highest CU% content (97.8%). It was

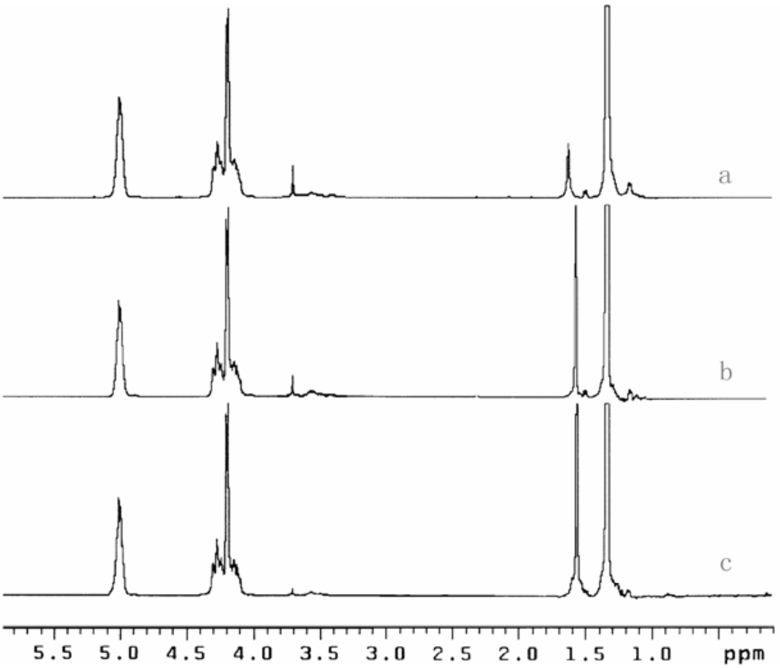
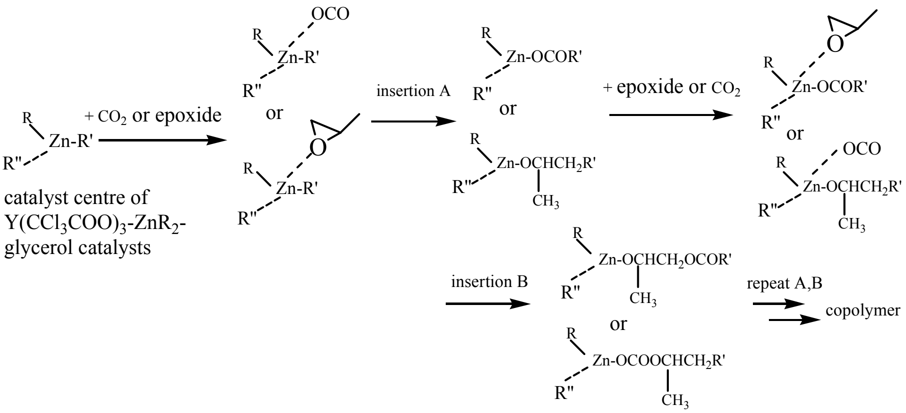


Figure 1. The typical ^1H NMR spectra of the methanol insoluble copolymer obtained with rare earth ternary catalyst; a. dicyclohexylzinc-based catalyst; b. di(n-butyl)zinc-based catalyst; c. diphenylzinc-based catalyst.

rational to speculate that $Y(CCl_3COO)_3$-$ZnPh_2$-glycerol catalyst system could more easily attract carbon dioxide to participate in copolymerization.

Propylene oxide has one asymmetric carbon atom, the selective incorporation of propylene oxide monomer is a determining factor to influence the microstructure of the copolymer. The ^{13}C NMR spectrum of carbonyl region was used to determine the content of tail-to-tail (T–T), head-to-tail (H–T) and head-to-head (H–H) structures in the copolymer, and the value of (H–T)/[(H–H) + (H–T) + (T–T)] (H-T%) could be chosen to evaluate the regioselective insertion of propylene oxide in the copolymerization [21]. As shown in Table 1, the content of H–T unit in the copolymer were all above 70%, indicating that the bond cleavage of propylene oxide occurs with certain regioselectivity during the formation of polycarbonate. But all the Zn-based catalysts didn't generate products with significant change in head-to-tail structure (less than 2%).

In our preformed research we had witnessed that $Y(CCl_3COO)_3$-ZnR_2-glycerol catalyst system has similar structure, and there is a Zn-R bond in the catalytic center which is supposed to be charged for the different catalytic activity [16]. As shown in scheme 1, when different organozinc including $ZnEt_2$, Zn(*n*-Bu)$_2$, $ZnPh_2$, $Zn(CH_2C_6H_5)_2$, $(C_6F_5)_2Zn$, $Zn(C_6H_{11})_2$ were used to prepare $Y(CCl_3COO)_3$-ZnR_2-glycerol catalyst, the catalyst was supposed to have a structure with a zinc centre bonded or coordinated to R, R' and R'' group, where R group was originated from ZnR_2, R' was a group containing glyceryl group and R'' was a complex compound containing rare earth salt, in spite of the structure of R' and R'' hadn't been fully characterized at present. That is to say, when organozinc changes from $ZnEt_2$, Zn(*n*-Bu)$_2$, $ZnPh_2$, $Zn(CH_2C_6H_5)_2$, $(C_6F_5)_2Zn$ to $Zn(C_6H_{11})_2$, the R group in the catalyst centre changes from Et, n-Bu, phenyl, benzyl, pentafluorophenyl to cyclohexyl group, with R' and R'' group remaining unchanged. Thus, from the copolymerization results that the catalytic activity sequence: $Y(CCl_3COO)_3$-$ZnPh_2$-glycerol>$Y(CCl_3COO)_3$-$ZnEt_2$-glycerol>$Y(CCl_3COO)_3$-$Zn(CH_2C_6H_5)_2$-glycerol>$Y(CCl_3COO)_3$-$(C_6F_5)_2Zn$-glycerol, was in accord with the electron donating ability of the following groups: phenyl>ethyl>benzyl>pentafluorophenyl, we could draw a conclusion that the catalytic activity of $Y(CCl_3COO)_3$-ZnR_2-glycerol catalysts increased with the electron donating ability of R group. As is known, with the increase of electron donating ability of R group in the catalyst (Scheme 1), the catalytic active centre is rich in electron, its coordination ability to CO_2 increases; while with the increase of electron withdrawing ability of R group, the catalytic active centre is short of electron, its coordination ability to PO increases. In addition, it is well known that to form alternating copolymer the catalytic active centre must have appropriate coordination ability to PO and carbon dioxide, and the insertion of CO_2 and epoxide into the catalytic active centre must proceed alternatively [22]. Thus, although the exact thermodynamic and kinetic mechanisms were not clear for the copolymerization with $Y(CCl_3COO)_3$-ZnR_2-glycerol catalysts, we concluded that carbon dioxide insertion was the rate–determining step. Besides the electron effect of R group, the bulk effect of R group also played a role on the catalytic activity of $Y(CCl_3COO)_3$-ZnR_2-glycerol catalysts. The following catalytic activity sequence: $Y(CCl_3COO)_3$-$ZnEt_2$-glycerol> $Y(CCl_3COO)_3$-Zn(*n*-Bu)$_2$-glycerol>$Y(CCl_3COO)_3$-$Zn(C_6H_{11})_2$-glycerol, was due to the bulk effect differences of the following groups: ethyl<n-butyl<cyclohexyl. The catalytic activity of $Y(CCl_3COO)_3$-$AlEt_3$-glycerol catalyst and the CU% of the corresponding product were lower compared with Zn-based catalysts was relating to different electron structure of aluminum and zinc catalytic active centre [14].



Scheme 1 Suggested schematic picture as reaction pathways for CO$_2$/PO copolymerization catalyzed by Y(CCl$_3$COO)$_3$-ZnR$_2$-glycerol catalysts (R group was originated from ZnR$_2$, R' was a group containing glyceryl group and R'' was a complex compound containing rare earth salt).

The activity of Y(CCl$_3$COO)$_3$-ZnPh$_2$-glycerin catalyst was further investigated for the copolymerization of PO and CO$_2$ by varying reaction conditions. It is well known that solvent plays an important role during the process of the copolymerization. In this work dioxane, diethyl ether, toluene and PO were chosen as the reaction medium, as shown in table 3. It was found that the catalytic activity in different solvents decreased in the following sequence (see table 3): PO (340.2 g polymer/(mol Zn h)), 1,4-dioxane (320.3 g polymer/(mol Zn h)), diethyl ether (305.8 g polymer/(mol Zn h)), toluene (295.6 g polymer/(mol Zn h)). The cause was supposed relating to the solubility of CO$_2$ in the solvent and/or the coordination between the active species and solvent [5, 23]. The effect of reaction temperature on the copolymerization was also studied with other conditions unchanged (reaction medium was PO, reaction time was 8 h, CO$_2$ pressure was 30 atm), which was also listed in Table 3. The yield increased when the reaction temperature increased from 40 to 80°C, and it finally reached 478.8 (g polymer/mol Zn h) in 8 h run at 80°C, or 9576 (g polymer/mol Y h), which was far more than the highest value with rare-earth ternary catalyst system mentioned in the reference [15]. The intrinsic viscosity of the resulting polymers dropped from 1.66 dL/g to 0.75 dL/g when the copolymerization temperature increased from 40 to 80°C, which was similar with Liu's report [15].

Table 3. The copolymerization results with Y(CCl$_3$COO)$_3$/ZnPh$_2$/glycerol catalyst[a]

No.	Reaction temperature(°C)	Reaction medium	Catalytic activity (g polymer/molZn h)	[η] (dL/g)
1	60	toluene	295.6	0.44
2	60	diethyl ether	305.8	0.98
3	60	dioxane	320.3	1.12
4	60	PO	340.2	1.20
5	40	PO	235.4	1.66
6	80	PO	478.8	0.75

[a] The copolymerization was carried out under 30 atm for 8 h (The molar ratio of Zn to glycerine to Y was 20 to 10 to 1).

Properties of Polymers

The methanol insoluble products from $ZnPh_2$-based, $ZnEt_2$-based, Zn(*n*-Bu)$_2$-based, $Zn(C_6H_{11})_2$-based catalyst were defined as PPC-A, PPC-B, PPC-C, PPC-D, respectively. The DMA curves of storage modulus and tan δ versus temperature curves of these poly(propylene carbonates) (PPCs) were shown in Fig. 2a and Fig. 2b, respectively. From the storage modulus curve, storage modulus decreased with increasing temperature. Moreover, over the whole measurement temperature, the softening temperature and storage modulus of the PPCs appeared to increase with the following sequence, PPC-A>PPC-B>PPC-C>PPC-D. The differences were supposed mainly relating to the CU% content of PPC, since the molecular weight, molecular weight distribution and tacticity of all the PPCs were similar (see table 2). The results showed that the storage modulus and softening temperature increased with the CU% content of PPC. Accordingly, at 30°C, the storage modulus of PPC-A, PPC-B, PPC-C, PPC-D was 3.4 GPa, 3.1 GPa, 2.3 GPa, 1.9 GPa (Fig. 2a), respectively. This means that high alternate PPC is applicable at temperatures higher than room temperature. The glass transition temperature (T_g), as identified by the tanδ peak, showed the same sequence as storage modulus. With the increase of CU% of PPC (from 92.2% to 97.8%), T_g of PPC increased from 41°C to 50.2°C, correspondingly (see Table 4). Copolymer produced from $Y(CCl_3COO)_3$-$ZnPh_2$-glycerin catalyst (PPC-A) exhibited the highest T_g (50.2°C).

The static mechanical properties of various PPCs produced from different catalysts were shown in Table 4. For copolymer produced from $Zn(C_6H_{11})_2$-based catalyst (PPC-D), the tensile strength and Young's modulus were the lowest (24.7 Mpa and 218 MPa, respectively). The tensile strength and Young's modulus of copolymer produced from $ZnEt_2$-based catalyst (PPC-B) displayed higher values (31.0 Mpa and 267 MPa, respectively). While copolymer produced from $ZnPh_2$-based catalyst (PPC-A) showed the highest tensile strength and Young's modulus (34.7 MPa and 298 MPa, respectively). The cause was also relating to the CU% content of the PPCs. The strength and modulus of PPC improved with the increase of CU% content. However, the elongation at break of the PPCs with different CU% content did not show much difference (around 400%).

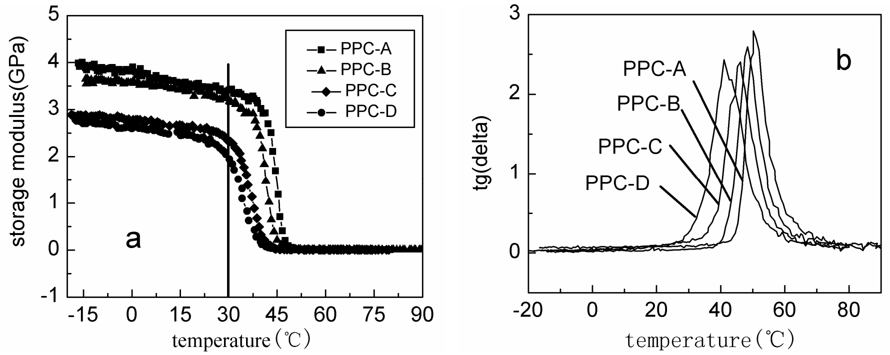


Fig 2a. Storage modulus versus temperature curves of various PPCs; Fig 2b. Tan δ versus temperature curves of various PPCs (PPC-A, copolymer produced from diphenylzinc-based catalyst; PPC-B, copolymer produced from diethylzinc-based catalyst; PPC-C, copolymer produced from di(n-butyl)zinc-based catalyst; PPC-D, copolymer produced from dicyclohexylzinc-based catalyst).

Table 4. Static mechanical properties and thermal properties of various PPCs

Polymer	CU%	T_g (°C)	σ (MPa)	E (MPa)	ε (%)	$T_{-5\%}$ (°C)	T_{max} (°C)
PPC-A	97.8	50.2	34.7	298	365	222	246, 271
PPC-B	96.3	48.4	31.0	267	355	215	237, 267
PPC-C	94.3	44.5	28.9	227	420	207	221, 263
PPC-D	92.2	41.0	24.7	218	415	190	205, 245

T_g, glass transition temperature determined by DMA; σ, tensile strength; E, Young's modulus; ε, elongation at break; $T_{-5\%}$, 5% weight loss temperature; T_{max}, maximum weight loss temperature; PPC-A, copolymer produced from diphenylzinc-based catalyst; PPC-B, copolymer produced from diethylzinc-based catalyst; PPC-C, copolymer produced from di(*n*-butyl)zinc-based catalyst; PPC-D, copolymer produced from dicyclohexylzinc-based catalyst.

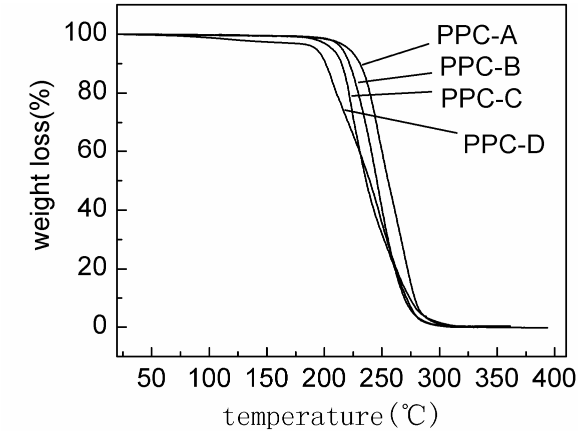


Figure 3. TGA curves of various PPCs (PPC-A, copolymer produced from diphenylzinc-based catalyst; PPC-B, copolymer produced from diethylzinc-based catalyst; PPC-C, copolymer produced from di(n-butyl)zinc-based catalyst; PPC-D, copolymer produced from dicyclohexylzinc-based catalyst).

Figures 3 showed the TGA curves for PPC-A, PPC-B, PPC-C, PPC-D, respectively. The 5% weight-loss temperature ($T_{-5\%}$) and maximum weight-loss temperatures (T_{max}) were listed in Table 4. As shown in Figure 3 and Table 4, copolymer produced from $ZnPh_2$-based catalyst (PPC-A) exhibited the highest thermal stability ($TGA_{-5\%}$ of >222°C, T_{max} of 246°C and 271°C), copolymer produced from $ZnEt_2$-based catalyst (PPC-B) took second place ($TGA_{-5\%}$ of 215°C, T_{max} of 237°C and 267°C), copolymer produced from Zn(*n*-Bu)$_2$-based catalyst (PPC-C) was more junior ($TGA_{-5\%}$ of 207°C, T_{max} of 221°C and 263°C), and copolymer produced from $Zn(C_6H_{11})_2$-based catalyst (PPC-D) showed the lowest thermal stability ($TGA_{-5\%}$ of 190°C, T_{max} of 205°C and 245°C). These results reveal that thermal properties depend greatly upon the molecular structure, both $T_{-5\%}$ and T_{max} of PPC increase steadily with increasing CU% content. The alternating PPC shows superior thermal properties.

Conclusions

Different organometallic compounds combining with yttrium trichloroacetate and glycerin were used as catalysts for the copolymerization of carbon dioxide and propylene oxide, where organometallic compounds were diethylzinc, di(n-butyl)zinc, diphenylzinc, dibenzylzinc, dicyclohexylzinc, bis(pentafluorophenyl)zinc, triethylaluminum. It was found that the catalytic activity and content of polycarbonate unit of the corresponding product varied with catalysts used. $Y(CCl_3COO)_3$-diphenylzinc-glycerol catalyst displayed the highest catalytic activity, at optimum conditions the yield attained 478.8 (g polymer/mol Zn h). The thermal properties and static and dynamic mechanical properties of the products varied with CU% content, the alternating PPC produced from diphenylzinc-based catalyst exhibited superior mechanical performance and thermal properties.

Acknowledgements. The financial supports from the key project of Chinese Academy of Science (grant No. KJCX2-206A) and Natural Science Foundation of China (grant No.50003009) are gratefully acknowledged.

References

1. Inoue S, Koinuma H, Tsuruta T (1969) J Polym Sci Polym Lett 7: 287
2. Rokicki A, Kuran W (1981) J Macromol Sci Rev Macromol Chem C21: 135
3. a. Aida T, Inoue S (1983) J Am Chem Soc 105: 1304; b. Sugimoto H, Ohshima H, Inoue S (2003) J Polym Sci Part A Polym Chem 41: 3549
4. a. Meng YZ, Du LC, Tiong SC (2002) J Polym Sci Part A Polym Chem 40: 3579; b. Chisholm MH, Navarro-Llobet D, Zhou ZP (2002) Macromolecules 35: 6494; c. Ree M, Bae JY, Jung JH (2000) Polym Eng Sci 40: 1542
5. Chen XH, Shen ZQ, Zhang YF (1991) Macromolecules 24: 5305
6. Cheng M, Lobkovsky EB, Coates GW (1998) J Am Chem Soc 120: 11018
7. Darensbourg DJ, Yarbrough JC (2002) J Am Chem Soc 124: 6335
8. Darensbourg DJ, Holtcamp M (1999) J Am Chem Soc 121: 107
9. a. Kim I, Yi MJ, Byun SH, Park DW, Kim BU, Ha CS (2005) Macromol Symp 224: 181; b. Chen S, Hua ZJ, Fang Z, Qi GR (2004) Polymer 45: 6519; c. Yang SY, Fang XG, Chen LB (1996) Polym Adv Technol 7: 605
10. a. Super MS, Beckman EJ (1997) Trends Polym Sci 5: 236; b. Beckman EJ (1999) Science 283: 946
11. a. Moore DR, Cheng M, Lobkovsky EB, Coates GW (2003) J Am Chem Soc 125: 11911; b. Coates GW, Moore DR (2004) Angew Chem Int Ed 43: 6618
12. Darensboug DJ, Mackiewicz RM, Phelps AL, Billodeaux DR (2004) Acc Chem Res 37: 836
13. Sugimoto H, Inoue S (2004) J Polym Sci Part A Polym Chem 42: 5561
14. Tan CS, Hsu TJ (1997) Macromolecules 30: 3147
15. a. Liu BY, Zhao XJ, Wang XH, Wang FS (2001) J Polym Sci Part A Polym Chem 39: 2751; b. Liu BY, Zhao XJ, Wang XH, Wang FS (2003) Polymer 44: 1803
16. Xie D, Wang XH, Zhao XJ, Wang FS (2005) Chin J Polym Sci 23: 671
17. a. Krug R, Tang P (1954) J Am Chem Soc 76: 2262; b. Soroos H, Morgana M (1944) J Am Chem Soc 66: 893
18. a. Hofstee H, Boersma J, Van der Kerk G (1978) J Orgmet Chem 144: 255; b. Hofstee H, Boersma J, Van der Meulen JD, Van der Kerk GJM (1978) J Orgnomet Chem 153: 245; c. Schrock RR (1976) J Orgnomet Chem 122: 209; d. Thiele K, Wilcke S, Ehrhardt M (1968) J Orgnomet Chem 14: 13; d. Noltes JG, Van den Hurk JWG (1964) J Orgnomet Chem 1: 377
19. Ren XD, Liu W, Hu J, Zhao Y (2001) Liaoning Chem Ind 30: 375
20. Tilley G, Roberts J (1963) Inorg Chem 2: 745
21. Lednor PW, Rol NC (1985) J Chem Soc Chem Commun 9: 598
22. Liu ZW, Torrent M, Morokuma K (2002) Organometallics 21: 1056
23. Quan ZL, Wang XH, Zhao XJ, Wang FS (2003) Polymer 44: 5605