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Copolymerization of carbon dioxide and propylene oxide with neodymium trichloroacetate-based coordination catalyst

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Abstract

The copolymerizations of carbon dioxide (CO_2) and propylene oxide (PO) were performed using new ternary rare-earth catalyst. It was found that the rare-earth coordination catalyst consisting of $Nd(CCl_3COO)_3$, $ZnEt_2$ and glycerine was very effective for the copolymerization of PO with CO_2. The effects of the relative molar ratio and addition order of the catalyst components, copolymerization reaction time, and operating pressure as well as temperature on the copolymerization were systematically investigated. At an appropriate combination of all variables, the yield could be as high as 6875 g/mol Nd per hour at 90 °C in a 8 h reaction period.

Keywords: Carbon dioxide; Poly (propylene carbonate); Rare-earth metal coordination catalyst

1. Introduction

Chemical fixation of CO_2 is a very attractive subject not only from viewpoint of carbon resource utilization, but also from increasing environmental concerns. As a kind of potential approach, one of the most promising areas of CO_2 utilization is its application as a direct material for polymer synthesis. The past three decades witnessed the great progress in fixation of CO_2 into aliphatic polycarbonates since the creative work of Inoue in 1969 [1,2]. To date, many excellent reviews in different period contributed by Kuran [3], Super [4] and Darensbourg [5] have made good description of this topic, where the importance of catalyst was never overestimated.

Among all the catalysts reported, the rare earth-based ternary catalysts are known to produce high molecular weight polycarbonate at mild conditions [6,7]. Chen et al. [6], using $Y(P_{204})_3-Al(i\text{-Bu})_3-$glycerine system, first successfully carried out the copolymerization of CO_2 and PO under mild conditions to yield high molecular weight random copolymers with narrow distribution. However, the catalytic activity and the carbonate unit content in copolymer were low. Subsequently, Tan [7] developed the rare earth-based catalyst system, utilizing diethylzinc ($ZnEt_2$) 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/mol Y per hour, and the resultant copolymer had high carbonate content.

In the present paper, the exploitation of new rare-earth metal catalyst composed of rare-earth metal carboxylates were investigated for the copolymerization of CO_2 and PO. The catalytic systems, especially, $Nd(CCl_3COO)_3-ZnEt_2-$glycerine, showed high activity for the copolymerization of carbon dioxide and propylene oxide, whose catalytic activity could be reached to 6875 g/mol Nd per hour at 90 °C in a 8 h reaction period. Meanwhile, The influence of copolymerization variables like catalyst component, operating pressure and temperature on the yield, the molecular weight, and copolymer structure have been discussed. The resultant copolymers were subjected to ^1H NMR spectroscopy, infrared spectroscopy, gel

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permeation chromatography, differential scanning calorimetry, thermogravimetry, and stress-strain analyses.

2. Experimental

2.1. Materials

Propylene oxide was pretreated by potassium hydroxide and refluxed over calcium hyride (CaH_2) for 48 h, it was then distilled and stored over 4 Å molecular sieve. 1,4-Dioxane was refluxed over CaH_2 and distilled before use. Carbon dioxide of 99.99% purity was used without further purification. Glycerine was of analytic purity and distilled under reduced pressure prior to use.

Diethyl-zinc was prepared by reaction of the mixture of ethyl bromide and ethyl iodide with zinc–copper couple according to literature [8]. It was distilled under reduced pressure prior to use.

Lanthanide carboxylates ($Ln(RCOO)_3$) were synthesized according to the literature [9]. They were dried at 80 °C for 40 h prior to use.

2.2. Catalyst preparation

The $Ln(RCOO)_3$–$ZnEt_2$–glycerine coordination catalysts were prepared under a nitrogen atmosphere according to Refs. [10,11]. All catalysts were prepared at 60 °C for 2 h. If $Nd(CCl_3COO)_3$ and $ZnEt_2$ were first reacted in dioxane, and glycerine was sequentially introduced into above mixture, the addition order was denoted as $Nd(CCl_3COO)_3 + ZnEt_2 +$ glycerine. If diethyl zinc reacted with glycerine in dioxane at first, and then the dioxane solution of $Nd(CCl_3COO)_3$ was added, the addition order was denoted as $ZnEt_2 +$ glycerine $+ Nd(CCl_3COO)_3$. If glycerine was firstly added to the dioxane solution of $Nd(CCl_3COO)_3$, and then $ZnEt_2$ was added into this mixture, the addition order was denoted as $Nd(CCl_3COO)_3 +$ glycerine $+ ZnEt_2$.

The $ZnEt_2$–glycerine catalyst was prepared by dropwise addition of glycerine into $ZnEt_2$ in dioxane solution, the mixture was kept stirring for 2 h at 60 °C.

2.3. Copolymerization

Copolymerization of CO_2 and PO was carried out in a 500 ml autoclave at elevated pressure and temperature. After a certain period, the copolymerization reaction was terminated by addition of methanol solution containing 5% dilute hydrochloric acid. The copolymer was purified by dissolving the crude copolymer in $CHCl_3$ and precipitated in dilute hydrochloric acid methanol solution. The resulted copolymers were dried at 40 °C in vacuum till constant weight.

2.4. Measurement

^1H NMR spectra of the copolymers were recorded at room temperature on a Unity-400 spectrometer using tetramethylsilane as internal reference. The carbonate or ether unit content in the copolymerization product was calculated from ^1H NMR spectra according to literature [1,6]. 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 glass transition temperature was determined from Perkin–Elmer 7 Differential Scanning Calorimetry. The thermal decomposition temperature was measured using thermogravimetric analyzer (Model: Perkin–Elmer 7) under protective nitrogen atmosphere. Static mechanical properties were measured on Instron-1121 Material Testing Machine at 20 °C. The examination was performed at cross head speed at 10 mm/min. The thin film specimens with dimensions of $20 \times 4 \times 1.25$ mm^3. The residual metal ion was determined on TJA-POEMS Plasma and Mass Spectroscopy.

3. Results and discussion

3.1. Copolymerization of carbon dioxide and propylene oxide using various rare earth metal coordination catalysts

Rare-earth carboxylates $Ln(RCOO)_3$ ($R = CCl_3$, Ln = Y, La, Nd, Sm, Gd, Dy, and Ho; $R = CH_2Cl$–, $CHCl_2$–, or CF_3, Ln = Nd) in combination with $ZnEt_2$ and glycerine, were used for the copolymerization of CO_2 and PO in dioxane at 60 °C under 30 atm for 12 h. The molar ratio of Zn to Ln was fixed at 20, and that of Zn to glycerine was 2. The results are summarized in Table 1. All these rare-earth metal coordination catalysts are effective for the copolymerization of CO_2 with PO, and $Nd(CCl_3COO)_3$–$ZnEt_2$–glycerine catalyst shows the highest catalytic

Table 1
Copolymerization of CO_2 and PO with various rare earth catalysts

Rare-earth-based ternary catalyst	Yield (g/mol Ln h)
$Y(CCl_3COO)_3$–$ZnEt_2$–glycerine	2833
$La(CCl_3COO)_3$–$ZnEt_2$–glycerine	3416
$Nd(CCl_3COO)_3$–$ZnEt_2$–glycerine	3833
$Sm(CCl_3COO)_3$–$ZnEt_2$–glycerine	3000
$Gd(CCl_3COO)_3$–$ZnEt_2$–glycerine	3083
$Dy(CCl_3COO)_3$–$ZnEt_2$–glycerine	3666
$Ho(CCl_3COO)_3$–$ZnEt_2$–glycerine	3600
$Nd(CH_2ClCOO)_3$–$ZnEt_2$–glycerine	1916
$Nd(CHCl_2COO)_3$–$ZnEt_2$–glycerine	1833
$Nd(CF_3COO)_3$–$ZnEt_2$–glycerine	2916

Notes: The copolymerization was carried out in dioxane at 60 °C under 30 atm for 12 h. The molar ratio of Zn to glycerine to Ln was 20 to 10 to 1.

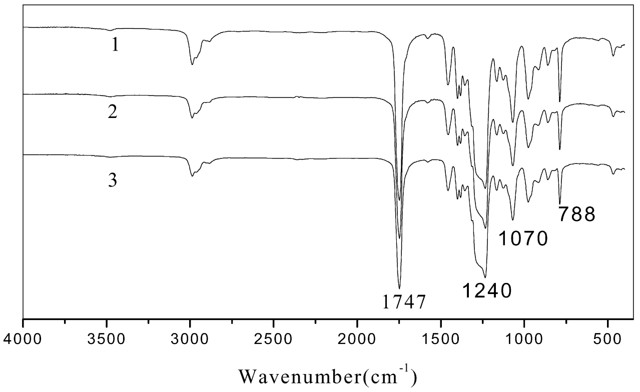


Fig. 1. The typical IR spectra of the methanol insoluble copolymer obtained with various $Ln(CCl_3COO)_3$-based catalyst. (1) $Sm(CCl_3COO)_3$-based catalyst; (2) $Gd(CCl_3COO)_3$-based catalyst; (3) $Dy(CCl_3COO)_3$-based catalyst. Reaction condition: time: 12 h; other conditions see Table 2.

activity. Therefore, the following studies were focused on this Nd catalyst.

The typical IR and ^1H NMR spectra of the resultant copolymers obtained from $Ln(CCl_3COO)_3$-based ternary catalyst system were shown in Figs. 1 and 2, respectively. It was found that all the IR spectra showed the strong absorption band at 1747 and 1240 cm^{-1} characteristic of stretching vibration of C=O bond and C–O–C bond of the carbonate group, respectively. Moreover, the 3.4–3.9 ppm peaks characteristic of neighbouring more than two ether linkage were insignificant for all the ^1H NMR spectra [12], indicating that the copolymers were mainly alternative ones of PO and CO_2.

3.2. Copolymerization of CO_2 and PO using $Nd(CCl_3COO)_3$–$ZnEt_2$–glycerine

The component of the catalyst is one of the most important factors influencing the copolymerization for the rare earth coordination catalyst, as observed earlier by Chen and Tan et al. [6,7], respectively. Therefore, the effect of molar ratio of the $ZnEt_2$ to glycerine on the copolymerization was first studied and summarized in Table 2. It has significant influence on the yield and molecular weight of the copolymers, the optimal molar ratio of glycerine/$ZnEt_2$ is 0.5 where the yield and molecular weight of the copolymer reached the maximum, which is in good agreement with literature [7].

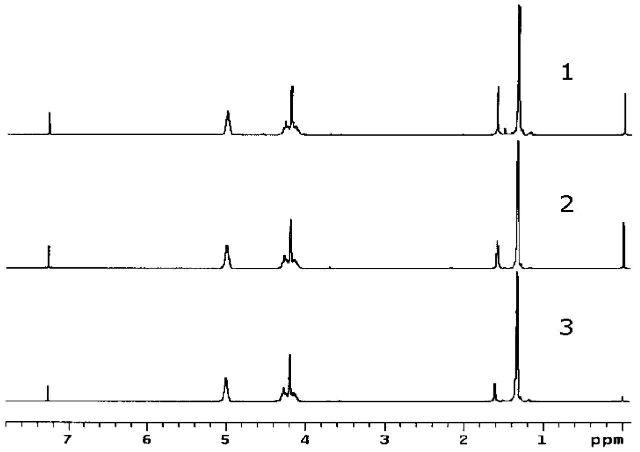


Fig. 2. The typical ^{1}HMR spectra of the methanol insoluble copolymer obtained with various $Ln(CCl_3COO)_3$-based catalyst. (1) $Sm(CCl_3COO)_3$-based catalyst; (2) $Gd(CCl_3COO)_3$-based catalyst; (3) $Dy(CCl_3COO)_3$-based catalyst. Reaction condition: time: 12 h; other conditions see Table 2.

Table 2
Effect of the molar ratio of glycerine to $ZnEt_2$ on the copolymerization of CO_2 and PO

Molar ratio glycerine/$ZnEt_2$	Yield (g/mol Nd h)	$\bar{M}_n \times 10^{4a}$	$\bar{M}_w/\bar{M}_n$
0.3	Trace	–	–
0.4	2083	5.99	3.58
0.5	4375	6.77	4.34
0.6	2750	3.32	4.60
0.8	400	2.66	2.95
0.9	86	–	–

Notes: Reaction condition: PO: 50 ml; solvent: 1,4-dioxane; P_{CO_2}: 3.0 atm; temperature: 60 °C; time: 8 h; $ZnEt_2 = 1.86$ ml; $ZnEt_2/Nd(CCl_3COO)_3 = 20$ (molar ratio).
[a] Data from GPC.

Copolymerization of CO_2 with PO has been considered to proceed via a coordination anionic process [13,14], which requires a certain Lewis acidity of the catalyst. Therefore, a suitable Lewis acidity of the catalyst is favorable for the coordination polymerization of CO_2 with PO. Tsuruta et al. [15] found that the homo-polymerization of PO proceeded by a cationic polymerization or a coordination polymerization under $ZnEt_2$–H_2O catalyst. It has been found that varying molar ratio of H_2O to $ZnEt_2$ resulted in the change of Lewis acidity of the catalyst, where the Lewis acidity increased when the molar ratio of H_2O to $ZnEt_2$ increased from 0 to 1, leading to the increase of poly (propylene oxide) yield. However, the yield of poly (propylene oxide) decreased when the molar ratio of H_2O to $ZnEt_2$ was over 1. Considering the similarity of glycerine and H_2O when they reacted with $ZnEt_2$, it is reasonable to speculate that the effect of the molar ratio of glycerine to $ZnEt_2$ on the copolymerization of CO_2 and PO is due to the difference of Lewis acidity of the catalyst.

The influence of the molar ratio of Zn to Nd on the copolymerization of CO_2 and PO was also investigated. For convenience, the contents of $ZnEt_2$ and glycerine were kept constant (glycerine/$ZnEt_2 = 0.5$ mol/mol), whereas the concentration of $Nd(CCl_3COO)_3$ in the catalyst was changed. The results are summarized in Table 3, the catalytic activity is only 1318 g/mol Nd h when the ratio of Zn to Nd is 180, it increases to 1758 g/mol Nd h when the ratio of Zn to Nd drops to 20. It is clear that $Nd(CCl_3COO)_3$ plays a key role to improve the catalytic activity. The change of rare earth metal content in the catalyst altered the Lewis acidity of the catalyst. Such change was observed in polymerization of epichlorohydrin with neodymium acetyl acetonate catalyst ($Nd(acac)_3$)–$Al(i\text{-}Bu)_3$–H_2O [16].

Table 3
Effect of molar ratio of $ZnEt_2$ to $Nd(CCl_3OO)_3$ on copolymerization of CO_2 and PO

Run	Molar ratio $ZnEt_2/Nd(CCl_3COO)_3$	Yield (g/mol of Zn)	$M_n \times 10^{-4a}$	$\bar{M}_w/\bar{M}_n$
1	180	1318	6.21	3.12
2	120	1467	6.93	3.14
3	40	1648	7.69	2.67
4	20	1758	6.77	4.34
5	14	1373	9.31	2.51

Notes: Reaction condition: same as in Table 2.

[a] Data from GPC.

Fig. 3 shows the dependence of yields on the copolymerization time under ternary or binary catalysts. The yield increases with increasing reaction time both in ternary catalyst and binary catalyst system. However, as shown in Fig. 3, the copolymerization reaction proceeded much faster with $Nd(CCl_3COO)_3$-based ternary catalyst than that with $ZnEt_2$–glycerine binary catalyst, especially in the first 4 h, suggesting that the $Nd(CCl_3COO)_3$–$ZnEt_2$–glycerine ternary catalyst promote CO_2 and PO to participate in the copolymerization reaction than $ZnEt_2$–glycerine binary catalyst.

Since the catalyst is composed of three components, the catalyst preparation method, especially the addition order of the catalyst components may have important influence on the copolymerization reaction. In the following, the catalyst was prepared in three different addition orders, $Nd(CCl_3COO)_3 + ZnEt_2 +$ glycerine (catalyst I), $ZnEt_2 +$ glycerine $+ Nd(CCl_3COO)_3$ (catalyst II), and $Nd(CCl_3COO)_3 +$ glycerine $+ ZnEt_2$ (catalyst III), all the catalysts were heterogeneous suspensions in 1,4-dioxane. As summarized in Table 4, catalyst III gave the highest yield of the copolymer, whereas catalyst I showed the lowest catalyst activity. According to the addition order, catalyst II and III permit the first reaction between $ZnEt_2$ and glycerine, forming continuous Zn–O–Zn aloxane structure in situ. Because of the oxygen bridge between the two Zn atoms, aloxane can be considered as electron donors [17]. Therefore, they can coordinate with neodymium to form bimetallic-like catalyst compound, and this feature may be responsible for the high catalyst activity [6,18]. When $Nd(CCl_3COO)_3$ reacts with $ZnEt_2$ at first, the amount of $ZnEt_2$ to react with glycerine is greatly reduced, therefore the amount of continuous structure of Zn–O–Zn bond is reduced, which is supposed to be the active center for the binary catalyst system [3]. Therefore, the catalytic activity for catalyst I is low.

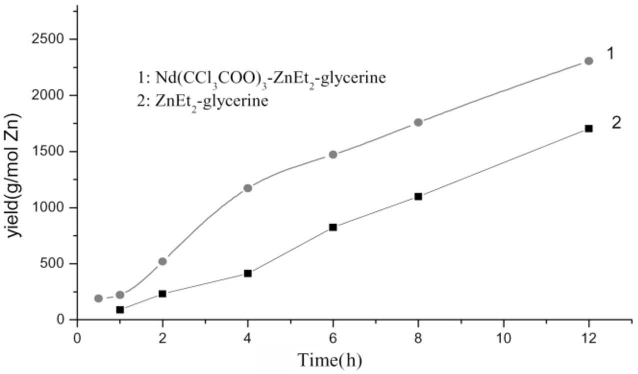


Fig. 3. The effect of the reaction time on the copolymer yield with different catalysts. Reaction condition: temperature: 60 °C; other conditions see Table 2.

The influence of reaction temperature on the copolymerization reaction was investigated with temperature change from 50 to 90 °C. The results are summarized in Table 5. The yield increased when the reaction temperature increased from 50 to 80 °C, and it finally reached 6875 g/mol of Nd in 8 h run at 90 °C. This result was quite different from the earlier report [7] where the yield of the copolymer had maximum value at 60 °C and decreased with higher temperature. When the structure of the methanol insoluble copolymer was investigated, it was found that the carbonate content was from 95.6 to 96.9%, indicating that the copolymer obtained by $Nd(CCl_3COO)_3$–$ZnEt_2$–glycerine catalyst was highly alternative, which was not sensitive to temperature change.

As listed in Table 5, the intrinsic viscosity of the resulting polymers was significantly influenced by the copolymerization temperature. Copolymer of higher intrinsic viscosity was obtained at lower temperature. The intrinsic viscosity of the copolymer reached 1.92 dl/g at 50 °C. According to the literature [19], this viscosity corresponds to an average number molecular weight of 2.0×10^5. The intrinsic viscosity dropped rapidly to 0.75–0.82 dl/g, when the temperature increased from 70 to 90 °C. This is probably due to the polymer degradation at high temperature [3]. However, higher reaction temperature is still practical in case the balance between yield and molecular weight is maintained.

Table 4
Dependence of the yield of copolymer on the addition order of the catalyst components

Addition order	Yield (g/mol/h Nd)	η (dl/g)
$Nd(CCl_3COO)_3 + ZnEt_2 +$ glycerine	3159	0.48
$ZnEt_2 +$ glycerine $+ Nd(CCl_3COO)_3$	3472	1.07
$Nd(CCl_3COO)_3 +$ glycerine $+ ZnEt_2$	4395	1.04

Notes: other reaction conditions: same as in Table 2.

Table 5
Effect of reaction temperature on the copolymerization yield and carbonate content

Run	T (°C)	Yield (g/mol Nd h)	Carbonate (%)	η (dl/g)[a]
1	50	3500	95.6	1.92
2	60	4375	96.7	1.13
3	70	5250	96.5	0.80
4	80	6500	96.7	0.82
5	90	6875	95.6	0.75

Notes: Other reaction condition same in Table 2.

[a] Measured in benzene at 35 °C.

It has been reported that the copolymer yield increased with increasing pressure till 20 atm and then leveled off [2,13]. When the copolymerization of CO_2 with PO was performed using Nd-based ternary catalyst under pressure of 4–42 atm at 80 °C for 8 h, an interesting phenomenon on the yield and structure of copolymer was observed. As shown in Fig. 4, the yield of the copolymer increased slightly while the operating pressure was above 24 atm, the carbonate structure in the copolymer kept increasing till 42 atm. However, the conversion of monomer PO(c%) was maintained between 65% and 67% according to the following equation:

$$c\% = \frac{\text{Total[Polymer]}}{\text{Total[PO]}} \times \frac{58(x+y)}{44x+58(x+y)} \tag{1}$$

where x and y are the contents of carbonate unit and ether unit in the copolymer, respectively (see Scheme 1). The values of x and y can be calculated by integrated areas in the ^{1}H NMR spectrum, corresponding to peaks at 5.0, 4.2, and 3.4–3.9 ppm, respectively [6].

$$x = \frac{A_{5.0} + A_{4.2}}{A_{5.0} + A_{4.2} + A_{3.4-3.9}} \tag{2}$$

$$y = 1 - x \tag{3}$$

In order to explain the above phenomenon, water-insoluble copolymer prepared at different pressure was subjected to ^{1}H NMR spectra. As shown in Fig. 5, the chemical shifts at 1.3, 4.2 and 5.0 ppm have been assigned to hydrogen in CH_3, CH_2 and CH in the carbonate unit of the copolymer, respectively [1,2], and those around 3.4–3.9 ppm have been assigned to hydrogen in CH_2 and CH in ether unit from more than two neighboring PO units [11]. The coexistence of the above two groups of peaks in ^{1}H NMR spectra clearly indicates that the resulting copolymer contains carbonate linkage as well as ether linkage. As estimated from the integration of the characteristic peaks, the ether unit in the water-insoluble polymer was between 40.8 and 10.8% when the CO_2 pressure varied from 4 to 42 atm, in other words, the ether unit in the copolymer decreased with the increase of operating pressure. One possible explanation for the increase of carbonate content in the resultant copolymer at higher pressure was due to the increase of the solubility of CO_2 in the solvent and propylene oxide [20,21], which led to higher CO_2 concentration in polymerization media, beneficial to CO_2 incorporation into copolymer.

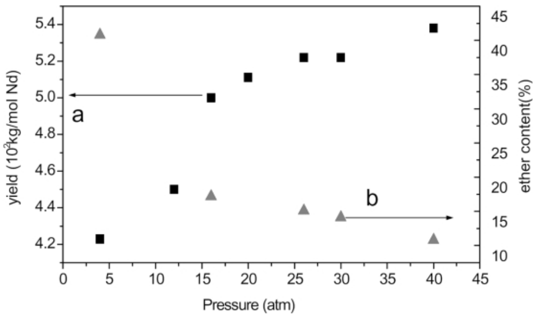
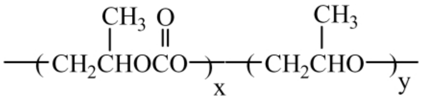


Fig. 4. The effect of operating pressure on the yield and ether unit content of the copolymer. Reaction condition: temperature: 80 °C; other conditions see Table 2.



$$-\!\left(\mathrm{CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HO\overset{\overset{\displaystyle O}{\|}}{C}O}\right)_x\!\!-\!\left(\mathrm{CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HO}\right)_y\!-$$

Scheme 1. Structure of the copolymer.

3.3. Characterization of the thermal and mechanical properties of the copolymer

The obtained copolymer was amorphous at room temperature [3,22]. Its glass transition temperature (T_g) (see Fig. 6) was between 37.0 and 41.5 °C, depending on its molecular weight. It was 37.0 °C for number average molecular weight of 7.9×10^4 and increased to 41.5 °C for number average molecular weight of 1.3×10^5. The copolymer exhibited good mechanical properties with

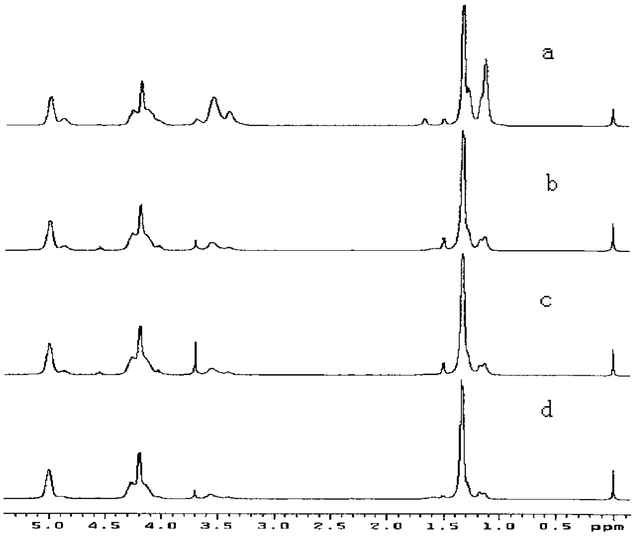


Fig. 5. ^{1}H NMR spectra of PO/CO_2 water-insoluble copolymers obtained at various CO_2 pressure. (a) 4 atm; (b) 12 atm; (c) 30 atm; (d) 40 atm. Reaction conditions: temperature: 80 °C; other conditions see Table 2.

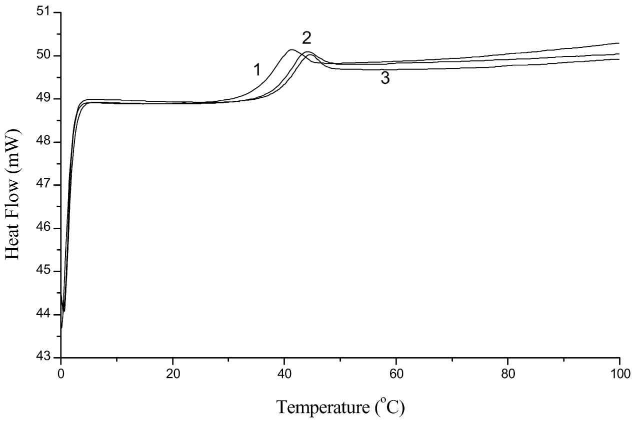


Fig. 6. DSC curves of different number average molecular weight copolymer (N_2, 10 °C/min) $\bar{M}_n$ ($\times 10^{-4}$) was: (1): 7.9; (2): 9.7; (3): 13.

Table 6
Dependence of the thermal decomposition temperature on the residual metal ion in the copolymer

Run	Residual metal ion ($\times 10^5$g/g)		T_d (°C, 5%)
	Zn^{2+}	Nd^{3+}	
1	1905	0.045	187.2
2	30.08	0.059	213.7
3	8.18	Trace	222.8
4	6.72	Trace	233.6

Notes: The residual metal ion in the resulting copolymer from Plasma Mass Spectroscopy. Purification process: Sample 1: water-insoluble; Sample 2: 5 g sample1 + 100 ml acetone + 200 ml ethanol; Sample 3: 5 g sample1 + 100 ml chloroform + 200 ml ethanol; Sample 4: 5 g sample 1 + 100 ml chloroform + 200 ml methanol (two cycles).

tensile modulus of 1.3 GPa, tensile strength of 30.6 MPa, and elongation rate at break of 3.5% at 20 °C.

Kuran et al. [23] noticed the influence of catalyst residue on the thermal stability of the copolymer. As listed in Table 6, it was also observed that the residual metal ion in the resulting copolymer showed significant influence on the onset decomposition temperature of the copolymer. As listed in Table 6, though the content of Nd^{3+} did not show significant change with the purifying process, the content of residual Zn in the copolymer was closed related to the purity process, it was variable between 1.9×10^{-2} and 6.7×10^{-5} g/g, corresponding to the increase of 5% decomposition temperature from 187.2 to 233.6 °C, indicating that the thermal stability of the copolymer was significantly affected by the residual metal ion in the copolymer.

4. Conclusions

The rare earth coordination catalyst composed of $Nd(CCl_3COO)_3$, $ZnEt_2$ and glycerine was very efficient for the copolymerization of CO_2 and PO, which showed catalytic activity as high as 6875 g/mol of Nd in 8 h run at 90 °C. The carbonate unit content in the copolymer was very sensitive to CO_2 pressure. Meanwhile, the obtained copolymer had a T_g above 37.0 °C. The thermal stability was greatly affected by the metal ion residue in the copolymer.

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