

SYNTHESIS AND CHARACTERIZATION OF HIGH MOLECULAR WEIGHT POLY(1,2-PROPYLENE CARBONATE-*co*-1,2-CYCLOHEXYLENE CARBONATE) USING ZINC COMPLEX CATALYST*

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Abstract Using supported multi-component zinc dicarboxylate catalyst, poly(1,2-propylene carbonate-*co*-1,2-cyclohexylene carbonate) (PPCHC) was successfully synthesized from carbon dioxide (CO₂) with propylene oxide (PO) and cyclohexene oxide (CHO). The conversion of epoxides dramatically increased up to 89.7% (yield: 384.2 g of polymer per g of Zn) with increasing reaction temperature from 60°C to 80°C. The optimized reaction temperature is 80°C. The chemical structure, the molecular weight, as well as thermal and mechanical properties of the resulting terpolymers were investigated extensively. When CHO feed content (mol%) is lower than 10%, the PPCHC terpolymers have number average molecular weight (M_n) ranging from 102×10^3 to 202×10^3 and molecular weight distribution (MWD) values ranging from 2.8 to 3.5. In contrast to poly(propylene carbonate) (PPC), the introduction of small amount of CHO leads to increase in the glass transition temperature from 38.0°C to 42.6°C. Similarly, the mechanical strength of the synthesized terpolymer is greatly enhanced due to the incorporation of CHO. These improvements in mechanical and thermal properties are of importance for the practical application of PPC.

Keywords: Carbon dioxide; Cyclohexene oxide; Catalysis; Terpolymerization; Propylene oxide.

INTRODUCTION

Recently the observed increase in atmospheric carbon dioxide (CO₂) is believed to contribute about 66% of climate warming^[1–4]. On the other hand, CO₂ is an inexpensive and abundant one-carbon resource, its storage on the earth is more than the sum of petroleum and coal. In this respect, numerous scientists put the attractiveness in the utilization of CO₂ as environmentally benign, inexhaustibly available, and generating environmental benefits^[5–9].

Since Inoue's discovery that ZnEt₂/H₂O was active for the copolymerization of propylene oxide (PO) and CO₂^[10], a green route to high molecular weight polycarbonates has received much attention. One of the challenges in this area has been directed to finding an effective catalyst for the alternating polymerization. Many efforts have been devoted to develop active heterogeneous catalysts (*e.g.*, zinc, chromium, aluminum, iridium, cobalt, iron, magnesium, *etc.*)^[11–14]. Furthermore, the elegant mechanism investigations performed independently by Darensbourg^[15–17], Coates^[18], Chisholm^[19] and others^[20–24] have provided valuable insights

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into the corresponding processes.

Poly(propylene carbonate) (PPC) derived from CO₂ and PO is known as a cheap and biodegradable material which has found usages in many applications, such as ceramic binders, evaporation mold and adhesives^[25–27]. However, owing to the existence of carbonate linkage in the backbone of PPC resulting in the relatively poor mechanical properties and thermal stability, varying attempts are recognizable to modify the pure PPC to reach related properties that fit to existing applications, either by blending or by terpolymerization. The introduction of a third monomer including cyclic epoxides, cyclic anhydrides, acrylates and lactones into the copolymerization of CO₂ and PO is a feasible means to enhance the thermal properties of PPC^[28–32]. More recently, we have reported the terpolymerization of CO₂, PO, and anhydrides to improve the properties of PPC^[33, 34]. In our previous works, we have successfully synthesized high molecular weight alternating PPC in very high yield in presence of supported zinc glutarate (s-ZnGA) catalyst^[35–37]. By using the same catalyst, PPC has already been commercialized in Henan Tianguan Enterprise Group Co. Ltd, Nanyang, China in a production capacity of 5000 t/a.

In this work, herein, we selected CHO as a third comonomer to be incorporated into the PPC backbone using new supported multi-component zinc dicarboxylate catalyst. The thermal and mechanical properties of the resultant terpolymers were fully characterized accordingly. The reaction mechanism was also investigated and discussed.

EXPERIMENTAL

Materials

CO₂ with a purity of 99.99% was used as received. Both CHO and PO of 99.5% purity were refluxed over calcium hydride for 4 h. They were then distilled under dry nitrogen gas and stored over 0.4 nm molecular sieves prior to use. Solvents such as methanol, acetone and chloroform were of analytical reagent grade and used without further treatment.

Supported multi-component zinc dicarboxylate catalyst was prepared according to previous work^[32]. The catalyst was white powder with the Zn weight content of 11.6%.

Terpolymerization of CHO, PO and CO₂

The terpolymerization of CO₂, PO and CHO was performed in a 500 mL autoclave equipped with a mechanical stirrer. First, dry supported multi-component zinc dicarboxylate catalyst was introduced into the autoclave as quickly as possible. The autoclave was then capped with its head, and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave with catalyst inside was further dried for 24 h under vacuum at 80°C. Upon cooling down, CHO and PO were added to the autoclave. Subsequently, the autoclave was then pressurized to 5.2 MPa *via* a CO₂ cylinder. The terpolymerization was performed under stirring for 40 h. Thereafter, when the reaction finished, the autoclave was cooled to room temperature and the pressure was released. The resulting viscous mixture was unloaded and dissolved in a sufficient volume of chloroform containing 5% solution of hydrochloric acid to decompose the catalyst. The transparent organic layer was washed to the neutral reaction and slowly added to excess vigorously stirred MeOH to precipitate out the resulting terpolymer. Finally, the as-made PPCHC was filtered and dried for 24 h at 80°C under vacuum.

Instrumental Analysis

¹H-NMR spectra were recorded on a Bruker NMR spectrometer using tetramethylsilane as an internal standard and D-chloroform (CDCl₃) as solvent. Molecular weight (M_w and M_n) of polymer products was measured using a gel permeation chromatography (GPC) system (Waters 515 HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 50 nm, 1000 nm, and 10000 nm). The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02, which were supplied from Shodex Inc. THF (HPLC grade) was used as an eluent. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a Rigaku D/max-III power X-ray diffractometer. The 2θ scan data were collected at 0.05° intervals over a range of 2°–40°. The glass transition temperature (T_g) of the copolymers was determined by

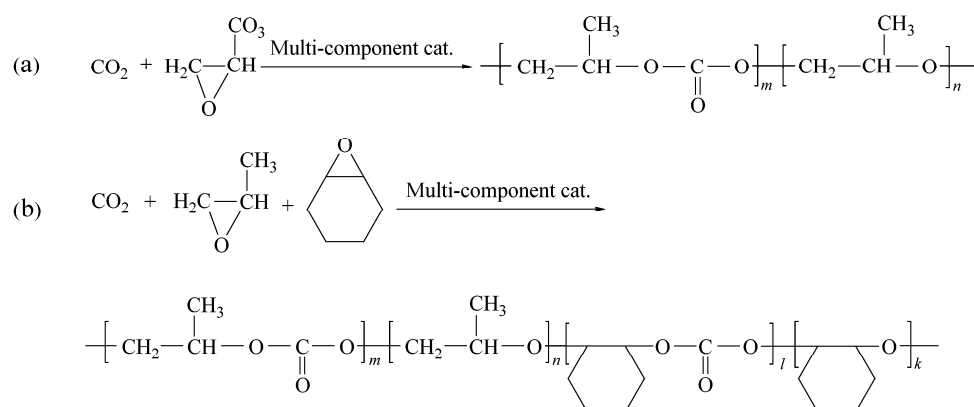
differential scanning calorimetry (DSC) measurements which were carried out under nitrogen flow on a Netzsch calorimeter (Model 204) from -30°C to 150°C at a heating rate of 10 K/min. T_g of the samples was determined from the second run. Thermogravimetric analysis (TGA) measurements were performed in a Perkin-Elmer TGS-2 under a protective nitrogen atmosphere. The temperature ranged from 50°C to 500°C with a heating rate of 10 K/min.

The static mechanical properties of the poly(1,2-propylene carbonate-co-1,2-cyclohexylene carbonate) (PPCHC) were measured at 25°C and relative humidity of $(50 \pm 5)\%$ using an SANS CMT tester according to the ASTM E-104 standard. The cross-head speed employed was 10 mm/min. Five specimens of each sample were tested, and the average results were reported.

RESULTS AND DISCUSSION

Structural Characterization of PPCHC

The synthesis of PPC and PPCHC is described in Scheme 1. As disclosed in literature^[29, 35, 38, 39], the catalytic behavior and reaction mechanism of ZnGA to synthesis PPC have been extensively investigated. In this work, therefore, the terpolymerization of CO_2 , PO, and CHO is performed in the presence of supported multi-component zinc dicarboxylate catalyst at varying reaction temperature, 40 h, 5.2 MPa CO_2 pressure and with a stirring rate of 100 r/min. The copolymerization conditions are same as those reported in above literature.



Scheme 1 (a) Copolymerization of carbon dioxide and propylene oxide; (b) Terpolymerization of carbon dioxide, propylene oxide and cyclohexene oxide

As described in experimental section, the structure of methanol-insoluble terpolymer was investigated by ^1H -NMR. Figure 1(a) shows the ^1H -NMR spectrum of PPC. It confirms the existence of carbonate linkages and small fraction of random incorporated ether unit in PPC backbone, suggesting that the resulting copolymer is almost an alternated one. The major signals are assigned as follows: ^1H -NMR (CDCl_3) δ , 1.3 (3H, $-\text{CH}_3$), 3.5 (3H, $-\text{CH}_2\text{CH}-$), 4.2 (2H, $-\text{CH}_2\text{CH}-$), and 5.0 (1H, $-\text{CH}_2\text{CH}-$). Figure 1(b) shows the ^1H -NMR spectrum of the resulting methanol-insoluble terpolymers obtained from the terpolymerization with CHO molar feed content of 5%. The major characteristic peaks of PPCHC are assigned as follows: ^1H -NMR (CDCl_3) δ , 1.3 (3H, $-\text{CH}_3$), 2.2 (2H, in 1,2-cyclohexene unit), 3.5 (3H, $-\text{CH}_2\text{CH}-$; 1H, in 1,2-cyclohexene ether unit), 4.2 (2H, $-\text{CH}_2\text{CH}-$), 4.6 (1H, in 1,2-cyclohexylene carbonate unit), 5.0 (1H, $-\text{CH}_2\text{CH}-$). Compared with the ^1H -NMR spectrum of PPC, the observed emergent peaks at $\delta = 4.6$ and 2.2 demonstrate that CHO was successfully incorporated into the backbone of terpolymer.

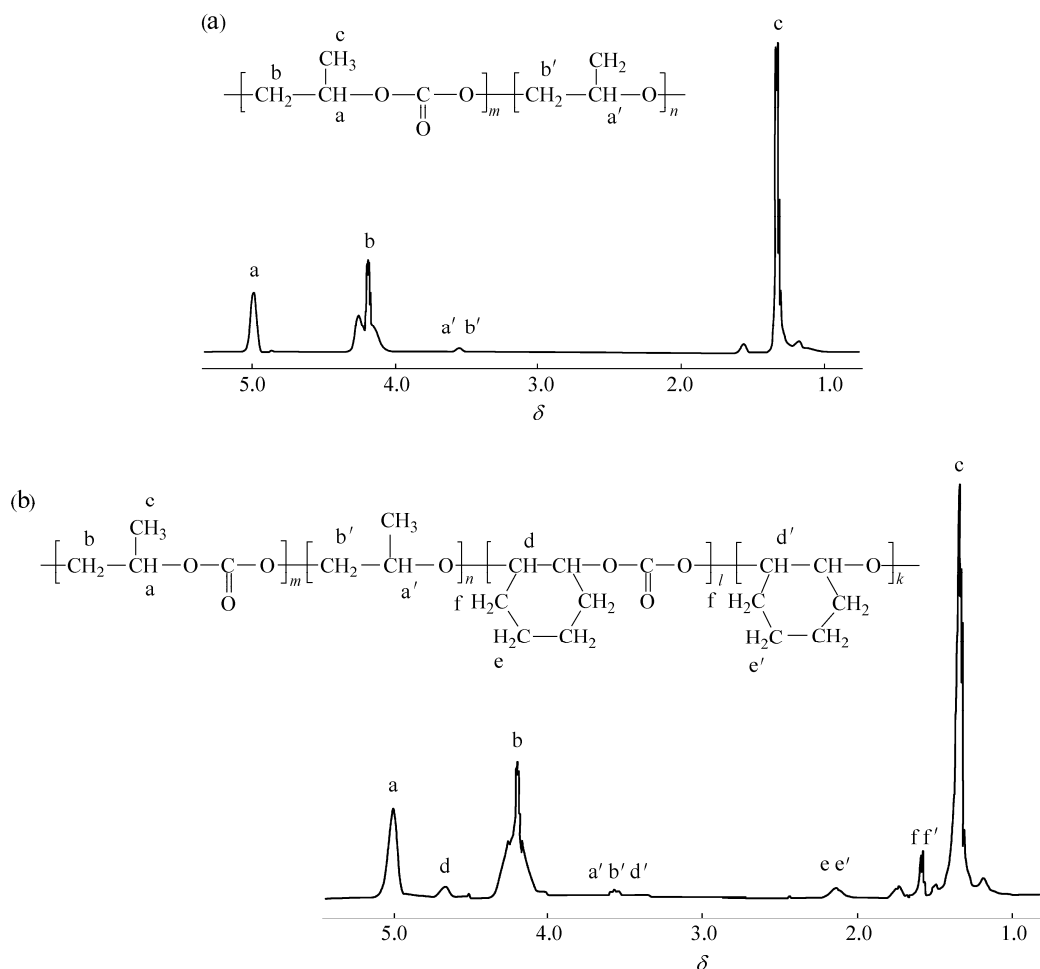


Fig. 1 (a) ^1H -NMR spectrum of PPC; (b) ^1H -NMR spectrum of PPCHC

Based on the ^1H -NMR spectra, the compositions, including 1,2-cyclohexylene carbonate unit molar fraction (f_{CHC}), carbonate unit molar fraction (f_{CO_2}) and ether molar (both PO and CHO) unit fraction (f_{PE}) of the resulted terpolymers can be estimated by the relative integration (A) of the correlated protons of the terpolymer according to the following equations:

$$f_{\text{CHC}} = \frac{A_{4.6}}{[(A_{4.6} + A_{4.2}) \times 2 + 0.8 \times A_{3.5}] \times 100\%}$$

$$f_{\text{CO}_2} = \frac{A_{4.6} + A_{4.2}}{[(A_{4.6} + A_{4.2}) \times 2 + 0.8 \times A_{3.5}] \times 100\%}$$

$$f_{\text{PE}} = \frac{0.8 \times A_{3.5}}{[(A_{4.6} + A_{4.2}) \times 2 + 0.8 \times A_{3.5}] \times 100\%}$$

Table 1 displays the experimental results of the terpolymerization at 60°C . It is apparent that the supported multi-component zinc dicarboxylate catalyst prepared from ZnO, glutaric acid and other coordinating agents has been readily found to provide the most effective heterogeneous catalyst to produce PPC and PPCHC with ultra-high molecular weight. From Table 1, it can be seen that the terpolymers were successfully synthesized with number average molecular weight (M_n) ranging from 54 K to 201 K and molecular weight distributions (MWD) ranging from 2.3 to 5.8 respectively. Regarding the yield, the results show that the catalytic activity decreased from 302.8 g to 87.2 g of polymer per g of Zn depending on increasing the CHO feed content from 0% to 15% with respect to the total moles of epoxides. Owing to the six-membered ring steric obstruct effect, CHO

coordinates difficultly with metal at active site, which is necessary for oxiranes to insert into metal-oxygen bond. This reveals that in comparison with PO, CHO exhibits less reactivity during the terpolymerization reaction at 60°C. The molar fractions of the CHO content in the resulted terpolymers increase with increasing CHO feed content. The ether content within the terpolymer is limited to a few mol%. In addition, the total yield of polymer product (polycarbonate) that was insoluble in methanol was greater than 98%. It indicates that in the terpolymerization, methanol-soluble products that contain polyethers and cyclic carbonate are obtained only in small quantities.

Table 1. Terpolymerization of CO₂, PO, and CHO with varying CHO feed content^a

CHO molar feed content ^b (%)	Yield ^c	$M_n/M_w/MWD^d$	Composition ^e (molar fraction in %)		
			f_{CHC}	f_{CO_2}	f_{PE}
0	302.8	$138 \times 10^3/749 \times 10^3/5.4$	0	47.2	2.8
5	204.4	$198 \times 10^3/455 \times 10^3/2.3$	2.4	48.4	3.3
10	110.8	$201 \times 10^3/707 \times 10^3/3.5$	3.5	47.4	5.1
15	87.2	$54 \times 10^3/313 \times 10^3/5.8$	3.7	48.9	2.1

^a Polymerization conditions: CO₂ pressure 5.2 MPa, reaction time 40 h, stirring at 100 r/min in a 500 mL autoclave;

^b The molar fraction of the loaded CHO with respect to the total moles of CHO and PO; ^c As g of polymer per g of Zn;

^d Determined by GPC; ^e Determined by ¹H-NMR spectroscopy

Due to the terpolymerization conducted in the relatively low yield, we have tried to evaluate the effect of temperature on terpolymerization and optimize the appropriate temperature for synthesis of PPCHC. The terpolymerization is investigated by varying reaction temperature above 60°C.

Table 2 lists the yield and properties of the resulting PPCHCs which performed at 60°C, 70°C, and 80°C respectively. It can be observed that both the yield and the epoxides monomer conversion increased with temperature. To our delight, at 80°C, the maximum yield reaches 384.3 g of polymer per g of Zn, as well as the epoxides monomer conversion is up to 89.97%. The terpolymerization was thus accelerated with increasing temperature. Because the activation barrier for the CHO insertion is higher in energy than that of PO insertion into metal-oxygen bond, the increase in temperature is an effective way to improve the CHO reactivity. However, it can be seen that the molecular weight decreases with increasing temperature. We have ascribed this to the formation of cyclic carbonate. At elevated temperatures, it has been proposed that the production of cyclic carbonates during the copolymerization reaction is the result of a unimolecular depolymerization reaction of the polymer catalyst complex, *i.e.*, a backbiting mechanism^[40].

Table 2. Results of terpolymerization of CO₂, PO, and CHO at different temperatures^a

CHO molar feed content ^b (%)	T (°C)	Yield ^c	Epoxides conversion (%)	$M_n/M_w/MWD^d$	Composition ^e (molar fraction in %)		
					f_{CHC}	f_{CO_2}	f_{PE}
0	60	302.8	67.14	$138 \times 10^3/749 \times 10^3/5.4$	0	47.2	2.8
5%	60	204.4	53.05	$198 \times 10^3/457 \times 10^3/2.3$	2.4	48.4	3.3
5%	70	266.0	70.12	$136 \times 10^3/465 \times 10^3/3.4$	1.9	47.2	5.6
5%	80	295.6	77.83	$102 \times 10^3/249 \times 10^3/2.4$	3.5	47.2	5.7
10%	60	110.8	29.76	$202 \times 10^3/713 \times 10^3/3.5$	3.5	47.4	5.1
10%	70	201.9	45.38	$198 \times 10^3/418 \times 10^3/2.1$	4.0	47.1	4.8
10%	80	384.2	89.97	$143 \times 10^3/332 \times 10^3/2.3$	3.7	47.7	4.6

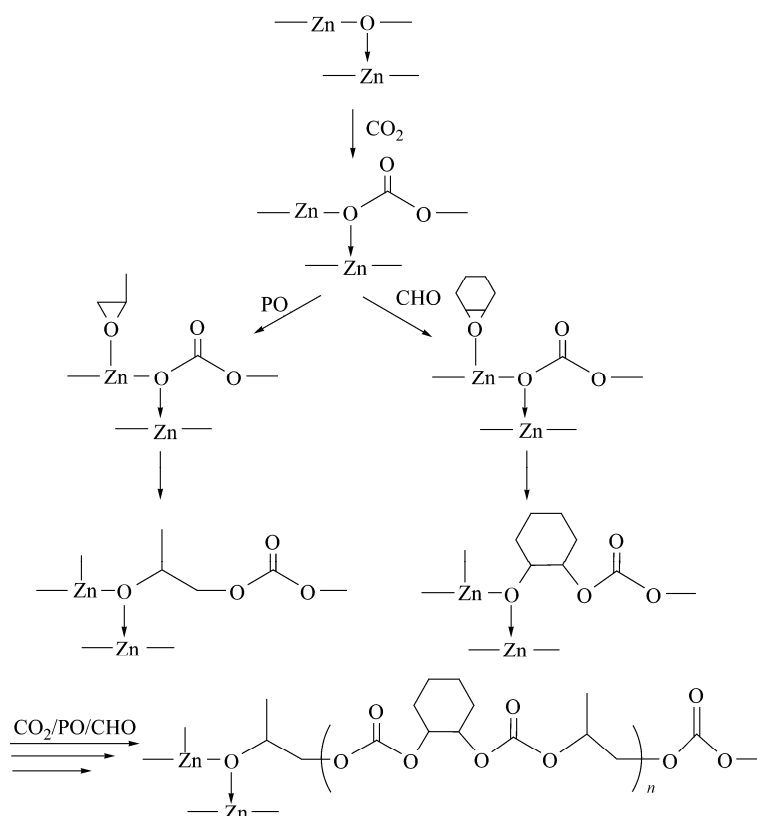
^a Polymerization conditions: CO₂ pressure 5.2 MPa, reaction time 40 h, stirring at 100 r/min in a 500 mL autoclave;

^b The molar fraction of the loaded CHO with respect to the total moles of CHO and PO; ^c As g of polymer per g of Zn;

^d Determined by GPC; ^e Determined by ¹H-NMR spectroscopy

Proposed Reaction Mechanism of Terpolymerization

On the basis of the literature^[23, 41], the mechanism of the terpolymerization of CO₂, PO and CHO is considered to be anionic coordination mechanism. In this work, we tentatively proposed a possible mechanism for the terpolymerization as summarized in Scheme 2.



Scheme 2 The supposed mechanism of terpolymerization of CO₂, PO and CHO

The Zn—O bond of supported multi-component zinc dicarboxylate catalyst accounts for the active center for the terpolymerization of CO₂ with PO and CHO. First, compared to PO and CHO, CO₂ was found to be more easily activated by coordinating with Zn metal active centers of catalyst, and inserted into Zn—O bond leading to produce carbonate anion. Then, PO and CHO could also be activated by Zn(II) active centers, which could be attacked by carbonate anion following the ring-open reaction and the insertion into growing main chain. We believe that PO and CHO insertion is a rate-determining step, whereas CO₂ insertion is a fast step. Because CO₂ can not be homopolymerized under any polymerization conditions, subsequent alternating enchainment of CO₂, PO and CHO forms the alternating polycarbonate. On the other hand, consecutive epoxides enchainment leads to a small percentage of ether linkage in the resulting terpolymer.

Thermal and Mechanical Properties of PPCHC

The thermal properties of the resulting terpolymers are summarized in Table 3. It is known that the major factors influencing thermal properties are the mobility of polymer chains, as reflected in many cases by glass transition temperature of the polymer, and polymer chain interactions, as reflected by the thermal degradation activation energy^[42]. It can be seen that the PPCHC exhibits higher T_g than PPC, although PPC has higher molecular weight than that of PPCHC terpolymers. The possible reason is that the rigid C₆ confining the motions of the main chain leads to the relatively higher glass transition temperature. Moreover, the experimental results demonstrate that the resulting terpolymer possesses only one T_g , indicating there is no block terpolymerization formed using the present technique. In addition, the thermal decomposition of polymer is thus of crucial importance for defining a processing window. According to previous work^[43], the thermal decomposition of PPC obeys two kinds of mechanism, the main chain scission reaction and the unzipping reaction. As shown in Table 3, the 5% weight loss temperatures ($T_{-5\%}$) of the PPC and PPCHC terpolymer greatly increase up to about 260°C, which is higher than that of pure PPC ($T_{-5\%}$ being 233°C) using the supported zinc dicarboxylate catalyst

without multi-component part^[33]. Presumably, the presence of the multi-component part and rigid C₆ rings on the chain restrains the backbiting process and depresses the unzipping reaction, resulting in a highly thermal stable terpolymer.

Table 3. The mechanical and thermal properties of PPCHC with varying CHO molar feed content

CHO molar feed content (%)	<i>T</i> (°C)	<i>T_g</i> (°C)	<i>T</i> _{-5%} (°C) (N ₂)	<i>T</i> _{max} (°C) (N ₂)	Tensile strength (MPa)	Elongation at break (%)
0	60	38.1	260.6	290.4	24.17	695.45
5%	60	41.4	257.4	291.4	34.22	2.76
5%	70	39.5	255.2	290.3	29.06	3.11
5%	80	39.1	258.7	289.8	33.32	4.48
10%	60	40.8	267.7	292.7	29.76	4.72
10%	70	42.6	267.1	295.4	30.33	3.52
10%	80	40.1	265.5	288.8	35.42	4.41

The results of the static mechanical properties tests are also listed in Table 3. The mechanical properties of the synthesized PPCHC terpolymers were measured in terms of tensile strength (σ_a) and elongation at break (ε). The highest tensile strength of PPCHC with CHO molar feed content of 10% reached 35.42 MPa, together with an elongation at break of 4.41%. From the low record values of the elongation at break, the data clearly show the brittle behavior of PPCHC as the presence of bulky rigid C₆ groups in its main chain. The results also revealed that the tensile strength of PPCHC is significantly higher than that of PPC with the corresponding molecular weight.

Figure 2 shows the WAXD spectrum of PPCHC with CHO molar feed content of 5%. There is no any peak observed, indicating the terpolymer is amorphous.

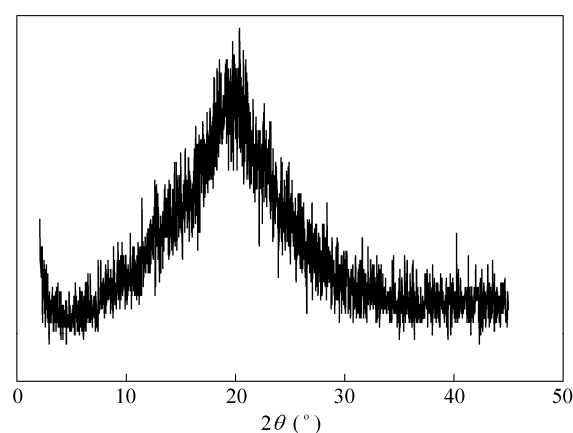


Fig. 2 The wide-angle X-ray diffraction spectra and PPCHC

CONCLUSIONS

PPCHC can be readily synthesized from the terpolymerization of CO₂ with PO and CHO using supported multi-component zinc dicarboxylate as catalyst. The optimal reaction conditions of the terpolymerization are at 80°C and under 5.2 MPa, and the resultant terpolymers have ultra-high molecular weight together with an extremely high yield of 384.2 g polymer per g Zn. On the premise of high monomer conversion, the glass transition temperature and the 5% weight loss temperature of the PPCHC terpolymers are 42.6°C and 267.7°C, respectively. High tensile strength of 35.42 MPa can be achieved with 10% molar content of CHO in PPCHC terpolymer. In conclusion, the incorporation of CHO provides an effective way to improve the thermal and mechanical properties of PPC copolymers derived from CO₂ and PO, which are a new kind of biodegradable thermoplastic material.

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