

# Synthesis and Properties of Aliphatic Polycarbonates Derived from Carbon Dioxide, Propylene Oxide and Maleic Anhydride

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**ABSTRACT:** Terpolymerization of carbon dioxide (CO<sub>2</sub>) with propylene oxide (PO) and maleic anhydride (MA) was successfully carried out using supported zinc glutarate catalyst. Consequently giving high molecular weight poly(propylene carbonate maleate) (PPCMA) in a very high yield (72.5 g polymer/g catalyst). The resulting terpolymers were fully characterized by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and wide-angle X-ray diffraction (WAXD) techniques. NMR measurements showed that PPCMA had an almost alternating structure for the components of carbon dioxide and PO. The influence of molecular weight and MA content on the properties of PPCMA was also investigated. Differential scanning calorimetry (DSC) measurements revealed that the glass transition temperature ( $T_g$ ) of

PPCMA increased with increasing molecular weight. Thermogravimetric analysis (TGA) indicated that PPCMA51 exhibited a very high decomposition temperature (263°C) due to the introduction of the double bond of MA into the backbone of terpolymer. The terpolymers with double bonds can be readily subjected to crosslinking reaction in high temperature to give a slightly crosslinked PPCMA, which exhibit superior thermal stability. Tensile tests also showed that the mechanical properties of PPCMA increased with increasing molecular weight. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4121–4129, 2008

**Key words:** carbon dioxide; terpolymerization; crosslinking; maleic anhydride; aliphatic polycarbonate

## INTRODUCTION

Carbon dioxide is a known greenhouse gas which contributes about 66% of climate warming.<sup>1,2</sup> Moreover, the concentration of CO<sub>2</sub> in the atmosphere is slightly increasing every year because of human activities. It has been reported that the present-day CO<sub>2</sub> level is 345 ppmv (parts per million by volume).<sup>3</sup> Thus, the utilization of CO<sub>2</sub> has attracted increasing attention recently as an effective approach to reduce the release of the greenhouse gas.<sup>4</sup> One possible utilization approach is to use CO<sub>2</sub> as a potential raw material for many fine chemicals, such as urea, salicylic acid, and dimethyl carbonate. Recently, some new processes to convert CO<sub>2</sub> have been exploited, opening a new potential area of

using CO<sub>2</sub> as a source of carbon,<sup>5</sup> a representative example is the copolymerization of carbon dioxide and epoxides to produce biodegradable aliphatic polycarbonate.

Since the creative work of Inoue et al. in 1969,<sup>6</sup> the copolymerization of CO<sub>2</sub> and epoxides has been widely investigated by many research groups. Thus, a large number of scientific works has been reviewed by Inoue, Darensbourg, Beckman, and Coates.<sup>7–10</sup> These papers have demonstrated that CO<sub>2</sub> can copolymerize with epoxides such as ethylene oxide (EO), propylene oxide (PO), isobutylene oxide (BO), or cyclohexene oxide (CHO). In past decades, many researchers focused on finding a highly active catalyst for this copolymerization because CO<sub>2</sub> is relatively stable. A variety of catalysts and catalyst precursors have been reported.<sup>11–14</sup> In recent years, chemists paid much attention to the work about the modification of polycarbonate to enhance the thermal properties and degradability of aliphatic polycarbonates,<sup>15–18</sup> a profitable means is to introduce a third monomer into the copolymerization of CO<sub>2</sub> and epoxides. More recently, Meng and coworkers attempted to terpolymerize CO<sub>2</sub>, PO, and EO to improve the degradability of PPC.<sup>19</sup> Tan and Hsu prepared CO<sub>2</sub>, cyclohexene oxide, and 4-vinyl-1-cyclo-

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hexen-1,2-epoxide terpolymers used  $Y(CF_3CO_2)$  (I)- $Zn(Et)_2$ (II)-*m*-hydroxybenzoic acid(III) as catalyst.<sup>20</sup>

Poly(propylene carbonate) (PPC) derived from  $CO_2$  and PO is known as a cheap and biodegradable polymer material. However, the practical application of PPC has been limited by its poor thermal stability because of the unzipping reaction. We have reported the effective synthesis of PPC from  $CO_2$  and PO in a very high yield using supported glutarate zinc catalyst.<sup>21</sup> In this study, we attempt to terpolymerize  $CO_2$ , PO, and maleic anhydride (MA) using the supported zinc glutarate (s-ZnGA) as catalyst. The objective of this work is to enhance degradability and thermal stability of PPC by introducing ester unit and double bonds of MA into the backbone of terpolymer, respectively. The terpolymers with double bonds can readily subject to crosslinking reaction to give a slightly crosslinked PPCMA, which exhibit superior thermal stability.

## EXPERIMENTAL

### Materials

Carbon dioxide with a purity of 99.99% was used as obtained. PO of 99.5% purity was refluxed over calcium hydride for 4 h. It was then distilled under dry nitrogen gas and stored over 4-Å molecular sieves prior to use. MA of 99.5% purity recrystallized with chloroform. Solvents such as toluene, methanol, acetone, chloroform were of analytical reagent grade and used as received and without further treatment. Glutaric acid of 98.0% purity, zinc oxide of 99.0% purity, and perfluorinated compounds were also used without further treatment.

### Preparation of catalyst

Supported zinc glutarate (s-ZnGA) was prepared according to previous work.<sup>21</sup> That is, to a round-bottom flask equipped with mechanical stirrer, a Dean-Stark trap and a reflux condenser with a drying tube were added zinc oxide (100 mmol) and toluene (150 mL). Then, glutaric acid (98 mmol) and perfluorinated compound (1.96 mmol) was added to the zinc oxide/toluene suspension. Then the slurry mixture was stirred vigorously at 55°C for 8 h. After cooled to room temperature, the reaction mixture was filtered off and washed with acetone three times, followed dried overnight in a vacuum oven at 80°C, giving s-ZnGA as white powder which was stored in a drier prior to use.

### Terpolymerization of $CO_2$ , PO, and MA

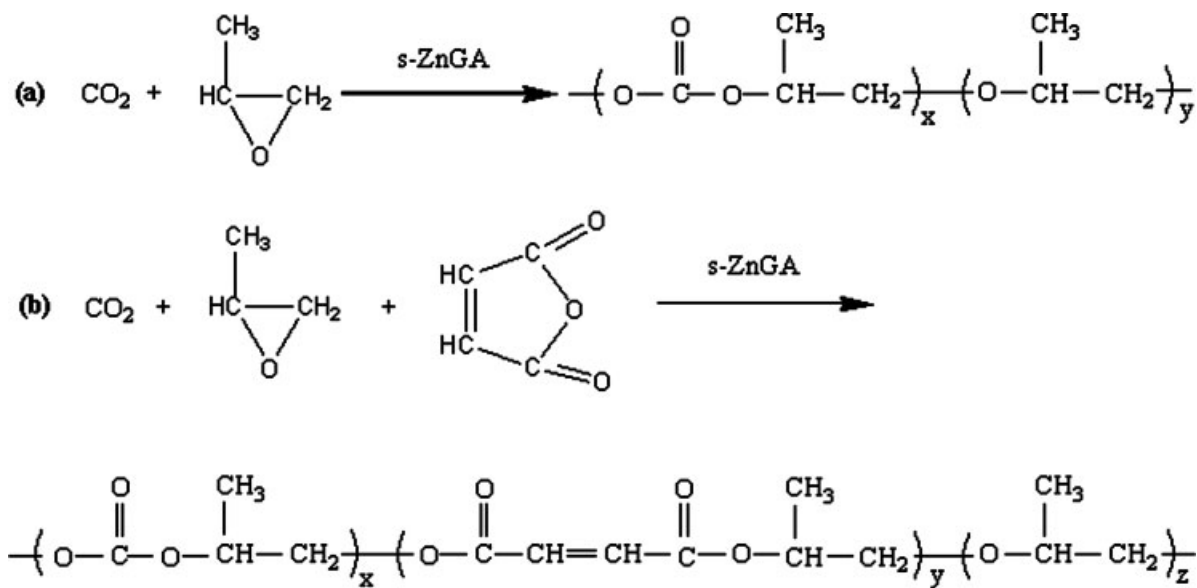
The copolymerization of  $CO_2$ , PO, and MA was carried out in a 500-mL autoclave equipped with a me-

chanical stirrer using PO as both reactant and solvent. The above synthesized supported catalyst zinc glutarate (s-ZnGA) was further dried at 80°C for 24 h prior to being used for the polymerization process. Dry catalyst was then introduced into the autoclave as quickly as possible. The autoclave was finally 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, MA was added to the autoclave. Subsequently, the autoclave was purged with carbon dioxide and alternately evacuated three times, and this was followed by the addition of purified PO with a large syringe. The autoclave was then pressurized to 5.2 MPa via a  $CO_2$  cylinder. The copolymerization was performed at 60°C under stirring for 40 h. Thereafter, the autoclave was cooled to room temperature and the pressure was released. The resulting viscous mixture was removed, dissolved in a proper volume of chloroform and transferred to a separating funnel. The catalyst residual was extracted from the product solution by using 400 mL dilute HCl (5%), followed by washing three times with distilled water. The viscous solution was concentrated by using a rotary evaporator to give a proper concentration. Finally, PPCMA copolymer was precipitated out by pouring the concentrated solution into vigorously stirred methanol. The as-made PPCMA was filtered and dried for 2 days at 80°C under vacuum. Meanwhile, the resulting filtrate was distilled to remove methanol and chloroform to yield a methanol soluble product.

### Measurements

FTIR spectra were recorded on an Analect RFX-65A FTIR spectrophotometer, using the KBr pellet. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-400 NMR spectrometer using tetramethylsilane as an internal standard and D-chloroform ( $CDCl_3$ ) as solvent. Molecular weight ( $M_w$  and  $M_n$ ) of a polymer product was measured using a gel permeation chromatography (GPC) system (Waters 515 HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 500, 10,000, and 100,000 Å). 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-1200 to analyze the structure. 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 determined by differential scanning calorimetry (DSC) measurements were carried out under



**Scheme 1** (a) Copolymerization between carbon dioxide and propylene oxide, (b) Terpolymerization of carbon dioxide, propylene oxide and maleic anhydride.

nitrogen flow on a Netzsch calorimeter (Model 204) from  $-30$  to  $100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .  $T_g$  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  $50$  to  $500^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ .

The static mechanical properties of the PPCMA copolymer performed at  $25^\circ\text{C}$  and relative humidity of  $50\% \pm 5\%$  using a computer-controlled Instron mechanical tester (Model 5566) 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

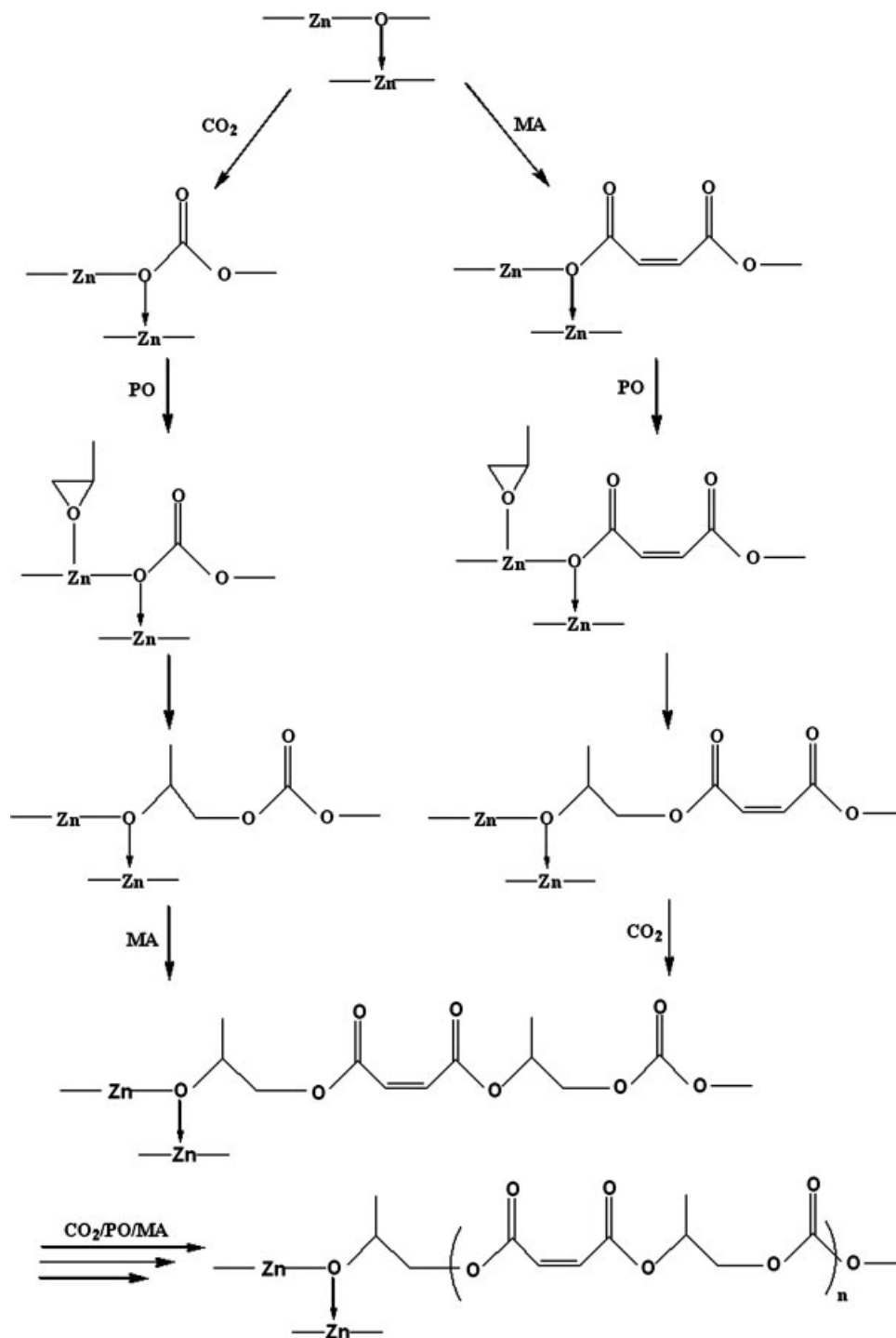
### Proposed reaction mechanism of terpolymerization

The copolymerization of  $\text{CO}_2$  and PO to produce PPC using ZnGA as catalyst has been extensively investigated.<sup>5,11,22–25</sup> The synthesis of PPC and PPCMA are described in Scheme 1. As depicted in literature,<sup>8,16</sup> the mechanism of this reaction is considered to be anionic coordination mechanism. In this work, the third monomer MA was introduced into the copolymerization of  $\text{CO}_2$  and PO, and MA was activated by anionic coordination catalyst *s*-ZnGA. Therefore, an anionic coordination mechanism for this terpolymerization of  $\text{CO}_2$ , PO, and MA is proposed here as follows. The proposed mechanism is described in Scheme 2. The Zn—O bond of *s*-ZnGA catalyst accounts for the active center for the terpolymerization of  $\text{CO}_2$  with PO and MA. First,

both  $\text{CO}_2$  and MA were activated by coordinating with Zn metal active centers of catalyst, and then inserted into Zn—O bond leading to produce carbonate anion. Second, PO 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. Either  $\text{CO}_2$  or MA could not homopolymerize and copolymerize under this polymerization conditions. Therefore, both of them are competing to be inserted into Zn—O bond. On the other hand, PO could homopolymerize to give polyether linkage, which existed in the resulted terpolymer in a small amount. Because of the very small amount of MA used, thus the terpolymerization of  $\text{CO}_2$ , PO, and MA can be thought to proceed via the alternating repeating insert of  $\text{CO}_2$  and PO into growing polymer backbone.

### About the terpolymerization

As disclosed in literature,<sup>21</sup> the catalysis behavior of *s*-ZnGA to synthesis PPC has been discussed. In this work, therefore, the optimum conditions for the terpolymerization of  $\text{CO}_2$  with PO and MA are as follows:  $60^\circ\text{C}$ , 40 h, 5.2 MPa  $\text{CO}_2$  pressure, and the stirring rate of 100 rpm. The terpolymerization results of  $\text{CO}_2$ , PO, and MA are summarized in Table I. It is apparent that the yields and molecular weight of resulting PPCMAs are related with their composition. PPCMA301 with a high molecular weight of 67.1 k was obtained in an extremely high yield (72.5 g polymer/g catalyst) when PO/MA molar ratio was fixed at 30/1. Smaller PO/MA molar ratio resulted in both lower yield and lower molecular



**Scheme 2** The supposed mechanism of terpolymerization of carbon dioxide, propylene oxide and maleic anhydride.

weight, owing to the decrease in the relative concentration of PO in the terpolymerization mixture with increasing MA concentration. This is because PO was used as both monomer and reaction medium, small amount of PO may restrict the diffusion of living polymer end and then reduce the yield of terpolymer. Moreover, excessive MA in the reaction mixture could form a complex with Zn metal active centers of *s*-ZnGA catalyst, which then keeps CO<sub>2</sub> apart

from Zn—O bond and prevents PO insertion into the growing terpolymer backbone. In this sense, MA cannot homopolymerize under this polymerization conditions, thus leading to the decline of the yield and molecular weight of PPCMA. However, the yields still keep quite high in case of very small amount of MA used (such as the case of PO : MA = 30 : 1). The objective of the incorporation of MA is to introduce double-bond moieties into the copolymer between PO

TABLE I  
The Results of Terpolymerization of CO<sub>2</sub>, PO, and MA with Varying PO/MA Ratio

Copolymer	PO : MA (Molar Ratio)	Yield <sup>a</sup> (g/g of catalyst)	$M_n/M_w/PI^b$	Composition <sup>c</sup> (Molar Fraction in %)		
				$f_{PO}$	$f_{MA}$	$f_{CO_2}$
PPC	—	103.5	54.7K/73.3K/1.34	50.05	0	49.95
PPCMA301	30 : 1	72.5	67.1K/220.4K/3.28	50.39	2.03	47.58
PPCMA201	20 : 1	68.2	63.2K/213.3K/3.37	50.41	2.86	46.73
PPCMA101	10 : 1	63.8	52.9K/235.6K/4.45	50.42	3.27	46.31
PPCMA81	8 : 1	60.8	49.6K/221.0K/4.45	50.75	4.27	44.98
PPCMA51	5 : 1	56.6	29.3K/190.5K/6.49	51.04	7.99	40.97

<sup>a</sup> Copolymerization conditions: CO<sub>2</sub> pressure 5.2 MPa, temperature 60°C, reaction time 40 h, stirred at 100 rpm in a 500-mL autoclave.

<sup>b</sup> Molecular weight was determined by GPC.

<sup>c</sup> Molar fractions of CO<sub>2</sub>, PO, and MA calculated by integrating areas of <sup>1</sup>H NMR spectra of PPC and PPCMA.

and carbon dioxide. The terpolymers with double-bonds can subject to further crosslinking, consequently overcoming the disadvantages such as low  $T_g$  and poor mechanical strength. Moreover, the molecular weight can be readily increased by simply crosslinking reaction of PPCMA.

### Structure and characterization of PPCMA

As described in experimental section, the structure of methanol-insoluble terpolymer was investigated by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and WAXD spectra. Figure 1 shows the representative FTIR spectra of PPC and PPCMA51. Both copolymers had characteristic FTIR absorptions at around 1750 (s, C=O), 1250 (s, C—O), 1074, and 790 cm<sup>-1</sup> (s, C—O—C). Moreover, the arrowhead-marked absorption peak at 1645 cm<sup>-1</sup> of PPCMA is attributed to the C=C vibration, indicating the presence of MA in PPCMA.

Figure 2 shows the typical <sup>1</sup>H NMR spectra for the copolymer of PPC and PPCMA51. The <sup>1</sup>H NMR spectrum of PPC [Fig. 2(a)] indicates the existence of carbonate linkages on PPC backbone, the main signals are assigned as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) 1.3 (d, 3H, —CH<sub>3</sub>), 3.5 (m, 3H, —CH<sub>2</sub>CH—), 4.2 (m, 2H, —CH<sub>2</sub>CH—), and 5.0 (m, 1H, —CH<sub>2</sub>CH—). The characteristic peaks of PPCMA51 [Fig. 2(b)] correspond to the follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) 1.3 (d, 3H, —CH<sub>3</sub>), 3.5 (m, 3H, —CH<sub>2</sub>CH—), 4.2 (m, 2H, —CH<sub>2</sub>CH—), 5.0 (m, 1H, —CH<sub>2</sub>CH—), and 6.2 (d, 2H, —CH=CH—), all of which are similar to those of PPC. An extra absorption peak at 6.2 ppm (d, 2H, —CH=CH—) was observed, demonstrating the presence of MA unit in the resultant terpolymers.

Figure 3(a) shows the <sup>13</sup>C NMR spectrum of PPC copolymer: <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) 16.2 (—CH<sub>3</sub>), 69.0 (—CH<sub>2</sub>CH—), 72.3 (—CH<sub>2</sub>CH—), 154.1 (—OCOO—), and Figure 3(b) gives the <sup>13</sup>C NMR spectrum of PPCMA51 terpolymer: <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm) 16.1 (—CH<sub>3</sub>), 69.0 (—CH<sub>2</sub>CH—),

72.3 (—CH<sub>2</sub>CH—), 128.7–129.9 (—CH=CH—), 154.1 (—OCOO—), 164.5 (—COO—). Compared with PPC, the <sup>13</sup>C NMR signals at 128.7–129.9 (—CH=CH—) and 164.5 (—COO—) also indicates that MA terpolymerize or insert into the backbone of terpolymers.

Based on the information of <sup>1</sup>H NMR spectra, the composition of terpolymers can be estimated from the following equations:

$$f_{PO} = (A_{5.0} + A_{4.2} + A_{3.5}) / [2(A_{5.0} + A_{4.2}) + A_{3.5}] \times 100\% \quad (1)$$

$$f_{MA} = (3A_{6.2}/2) / [2(A_{5.0} + A_{4.2}) + A_{3.5}] \times 100\% \quad (2)$$

$$f_{CO_2} = 1 - f_{PO} - f_{MA} \quad (3)$$

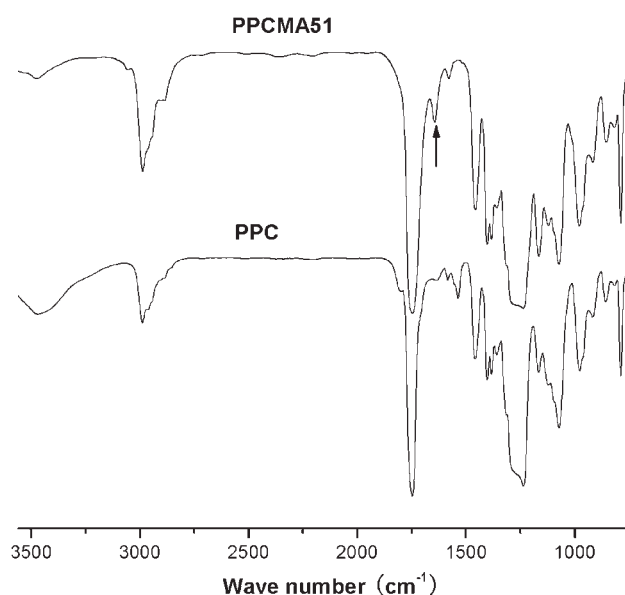


Figure 1 FTIR spectra of PPC and PPCMA51.

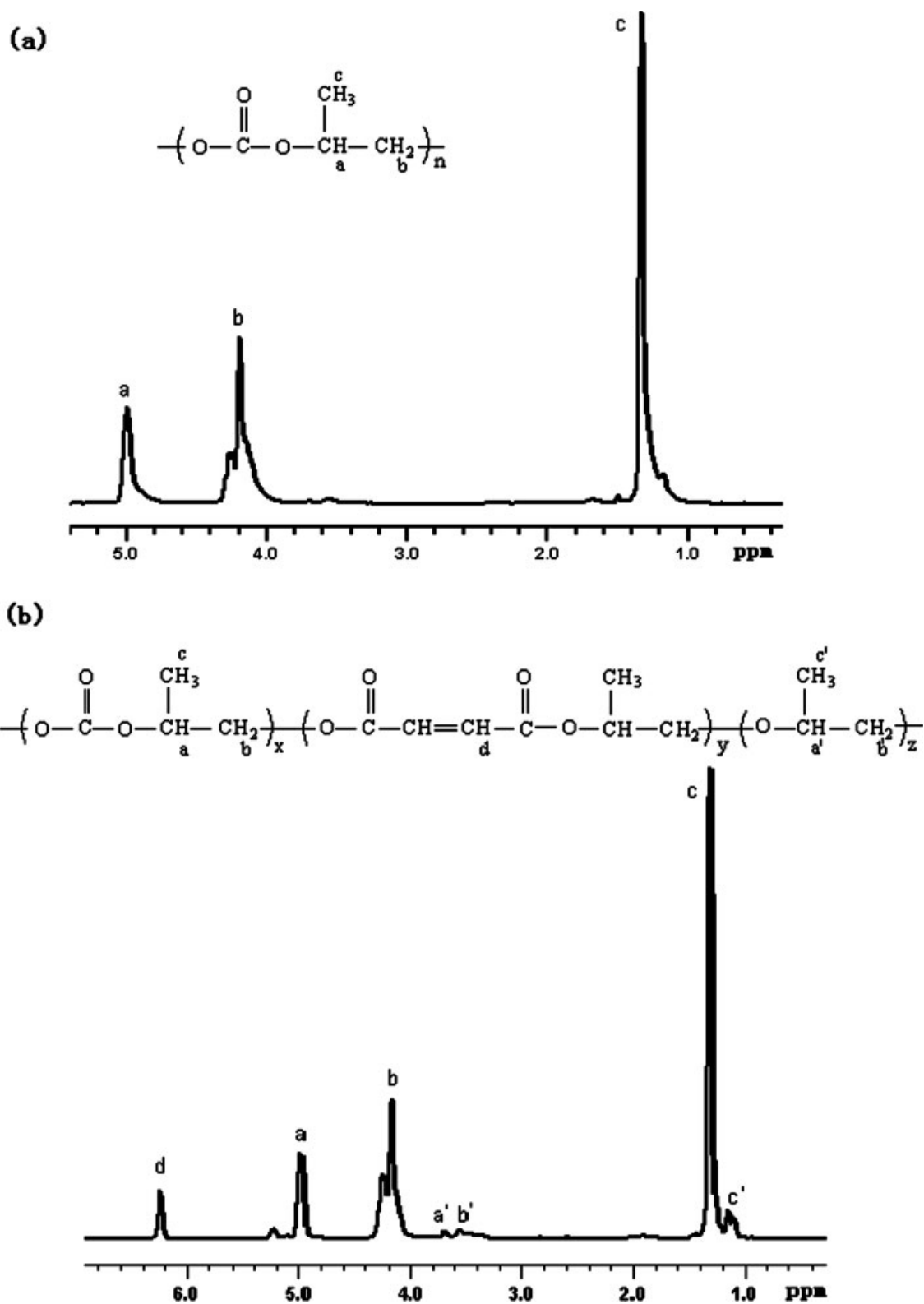


Figure 2 (a)  $^1\text{H}$  NMR spectrum of PPC, (b)  $^1\text{H}$  NMR spectrum of PPCMA51.

The compositions of terpolymers including the molar fractions of PO ( $f_{\text{PO}}$ ), MA ( $f_{\text{MA}}$ ) and CO<sub>2</sub> ( $f_{\text{CO}_2}$ ) are listed in Table I. It can be seen that the existence of small fraction of random incorporated

ether units in PPC backbone, indicating the almost alternative structure of PPC. However,  $f_{\text{CO}_2}$  in PPCMA terpolymer decreased with the introduction of MA into its backbone. Because MA and CO<sub>2</sub> play

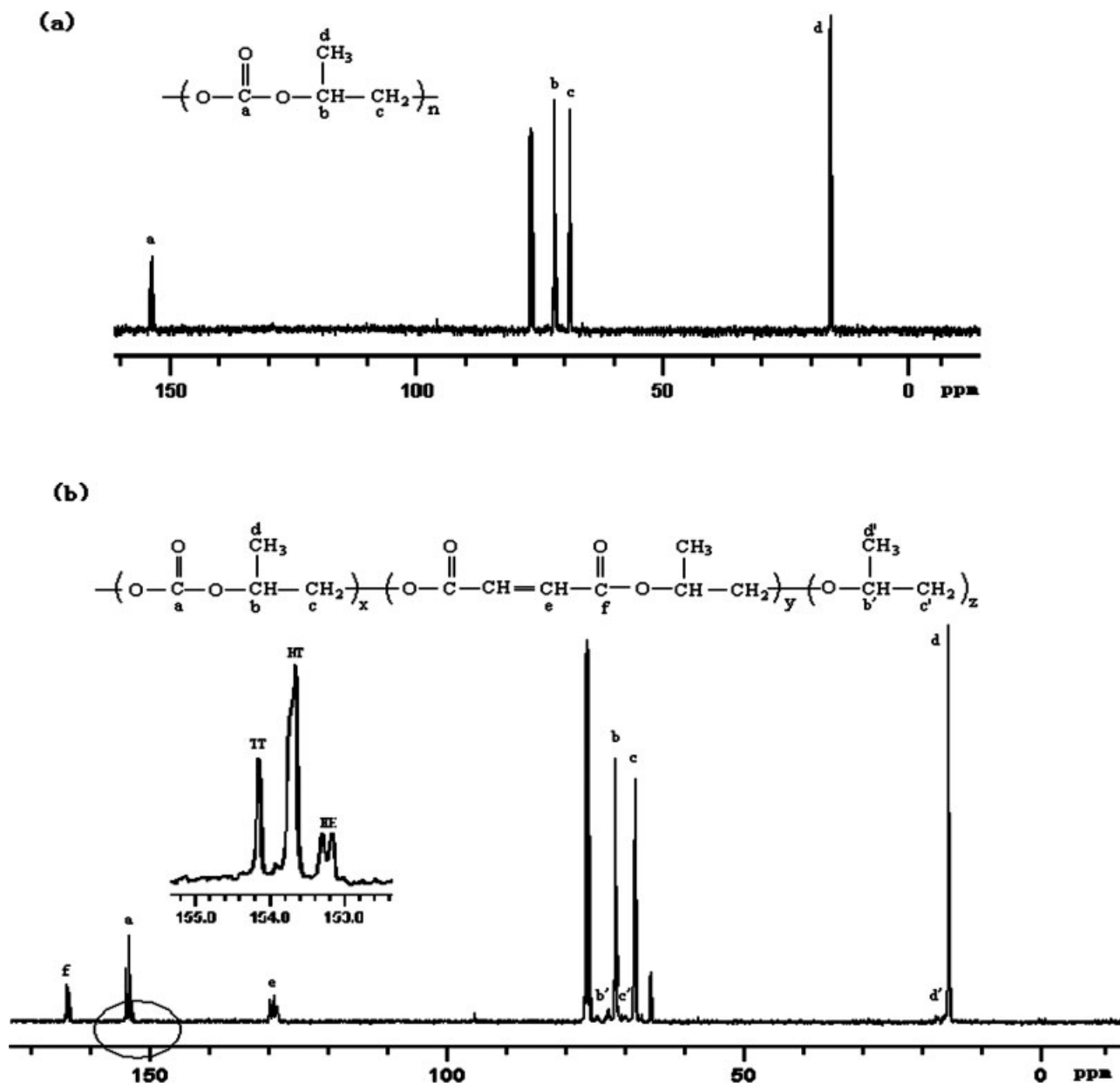


Figure 3 (a)  $^{13}\text{C}$  NMR spectrum of PPC, (b)  $^{13}\text{C}$  NMR spectrum of PPCMA51.

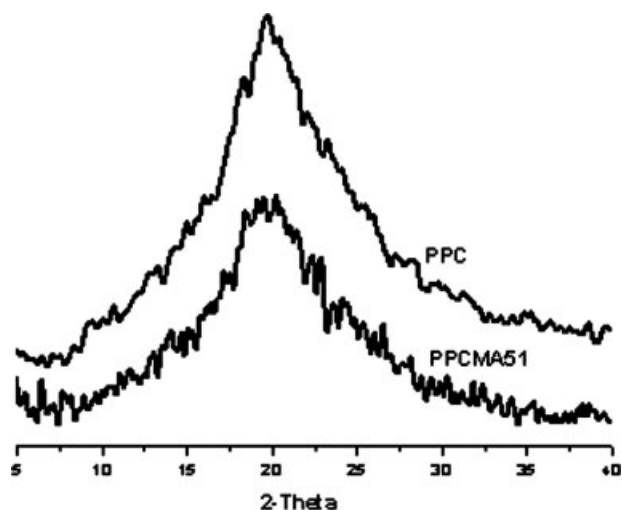
the same role in the copolymerization with PO, that is, MA competes with  $\text{CO}_2$  to copolymerize with PO in the terpolymerization. Thus, the value of  $f_{\text{CO}_2}$  decreased with the increased amount of MA in terpolymer. The results also show that the  $f_{\text{PO}}$  in PPCMA is about 50%, indicating the almost alternative structure of PPCMA.

Finally, Figure 4 shows the WAXD spectra of PPC and PPCMA51. It is clear that both PPC and PPCMA are amorphous.

### Properties of PPCMA

The thermal properties for the obtained PPCMA are listed in Table II. It can be seen that the  $T_g$  of

PPCMA increased with the increasing molecular weight. PPCMA301 with a molecular weight of 67.1 k exhibits the highest  $T_g$  of 37.5°C. However, the  $T_g$  of PPCMA decreased with increasing MA content. The possible reason is that more MA ester unit in the backbone of PPCMA results in the relatively lower glass transition temperature. The thermal decomposition temperature (5% weight loss temperature,  $T_{-5\%}$ ; and maximum weight loss temperature,  $T_{\text{max}}$ ) for PPCMA was very high and increased with increasing MA content. PPCMA51 with molecular weight of 29.3 k exhibits  $T_{-5\%}$  of 263°C and  $T_{\text{max}}$  of 277°C, respectively. According to previous work,<sup>26</sup> the thermal decomposition of PPC obeys two kinds of mechanism, the main chain scission reaction and



**Figure 4** The wide-angle X-ray diffraction spectra of PPC and PPCMA51.

the unzipping reaction. Presumably, with  $f_{MA}$  increasing, PPCMA can be readily crosslinked at high temperature. Similarly, MA unit restrains the backbiting process and depresses the unzipping reaction, leading to a highly thermal stable terpolymer.

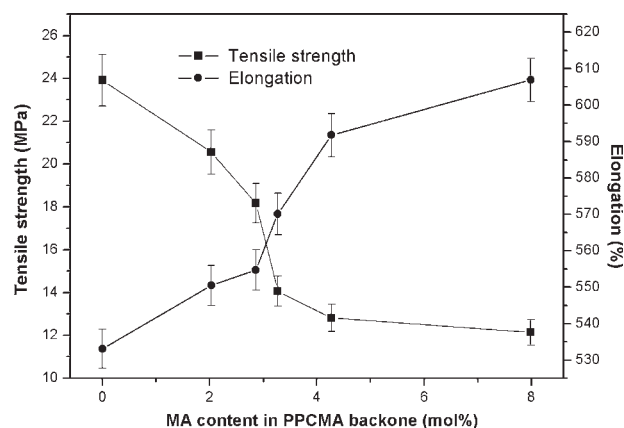
The static mechanical properties of the resulted PPCMA terpolymers were measured in terms of tensile strength and elongation at break. As shown in Figure 5, the highest tensile strength of PPCMA301 reached 20.55 MPa, together with an elongation at break of 550%. Then the tensile strength of PPCMA decreased with decreasing molecular weight. However, the tensile strength can be increased by simply the crosslinking reaction of PPCMA with the presence of double-bonds. The results also revealed that the tensile strength of PPCMA was very close to that of PPC with the same molecular weight.

## CONCLUSIONS

PPCMA can be readily synthesized from the terpolymerization of  $CO_2$  with PO and MA using *s*-ZnGA as catalyst. PPCMA terpolymer with high molecular weight can be afforded in an extremely high yield of 72.5 g polymer/g catalyst. The alternating structure

**TABLE II**  
Thermal Properties of PPC and PPCMA Copolymers

Copolymer	$T_g$ (°C) (N <sub>2</sub> )	$T_{-5\%}$ (°C) (N <sub>2</sub> )	$T_{max}$ (°C) (N <sub>2</sub> )
PPC	37.8	233	249
PPCMA301	37.5	235	253
PPCMA201	37.0	234	252
PPCMA101	36.3	234	250
PPCMA81	35.9	257	273
PPCMA51	35.2	263	277



**Figure 5** Mechanical properties of PPCMA terpolymers versus the MA content in PPCMA.

of the PPCMA terpolymers was confirmed by FTIR,  $^1H$  NMR,  $^{13}C$  NMR, and WAXD measurements. The molecular weight or MA content in PPCMA has dramatic influence on the properties of PPCMA. The mechanical properties of PPCMA are much dependent on molecular weight and very close to that of PPC with the same molecular weight. Thermal stability of PPCMA increased greatly with increasing MA content due to the introduction of the double bond of MA into the backbone of terpolymer. The terpolymers with double bonds can readily subject to crosslinking reaction in high temperature to give a slightly crosslinked PPCMA, which exhibit superior thermal stability. The terpolymerization by the introduction of MA provides an effective way to synthesize highly thermal stable PPC copolymer from  $CO_2$  and PO, and broadens the potential application of PPC as a new biodegradable thermoplastic material.

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