

# Thermally Stable Poly(propylene carbonate) Synthesized by Copolymerizing with Bulky Naphthalene Containing Monomer

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**ABSTRACT:** To enhance the thermal and mechanical properties of poly(propylene carbonate) (PPC), the terpolymers were synthesized from carbon dioxide, propylene oxide, and a third monomer, [(2-naphthyloxy)methyl]oxirane (NMO) using supported zinc glutarate as catalyst. The structure of these terpolymers was confirmed by  $^1\text{H}$  NMR spectroscopy. The catalytic activity, molecular weight, carbonate unit content, as well as thermal and mechanical properties were investigated extensively. The experimental results showed that the catalytic activity, molecular weight, and carbonate unit content decreased with the incorporation of NMO. DSC measurements indicated that the intro-

duction of NMO increased the glass transition temperature from 38 to 42°C. TGA tests revealed that the thermal decomposition temperature ( $T_{g-5\%}$ ) of the synthesized terpolymer increased significantly, being 34°C higher than that of pure PPC. Accordingly, the mechanical properties proved also to be enhanced greatly as evidenced by tensile tests. These thermal and mechanical improvements are of importance for the practical process and application of PPC. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1037–1043, 2008

**Key words:** terpolymerization; biodegradability; thermal stability; mechanical property

## INTRODUCTION

Carbon dioxide ( $\text{CO}_2$ ) is a main component of greenhouse gases that contributes to global warming, but it is also an inexpensive and abundant one-carbon chemical feedstock. In this sense, the chemical fixation of  $\text{CO}_2$  has become a very attractive subject. One of the most promising approaches to effectively utilize  $\text{CO}_2$  is the synthesis of aliphatic polycarbonates from catalyzed copolymerization of  $\text{CO}_2$  with epoxides. Inspired by the creative work of Inoue and coworkers in 1969,<sup>1</sup> researchers have strived to develop more efficient catalytic systems for the polycarbonate production. Thus, a lot of research work reviewed by Rokicki and Kuran,<sup>2</sup> Beckman,<sup>3</sup> Darensbourg,<sup>4</sup> Sugimoto and Inoue,<sup>5</sup> and Coates<sup>6</sup> has

demonstrated that  $\text{CO}_2$  can be copolymerized with a number of epoxides. As described therein, in most cases propylene oxide and cyclohexene oxide were selected as an epoxide resource. Although magnitude improvements have been obtained in the activity of catalysts in the copolymerization of  $\text{CO}_2$  and cyclohexene oxide, poly(cyclohexene carbonate), their resulting product, is less competitive in the restrictive world of commodity polymers, because of its less biodegradability and the high cost of cyclohexene oxide. It is known that synthetic commodity polymers are in general hardly degradable in nature, causing ecological problems. Therefore, there is a strong need for the polymeric materials, which degrade in nature without producing any harmful stuffs but exhibit superior properties for various purposes. In this respect, poly(propylene carbonate) (PPC) derived from  $\text{CO}_2$  and propylene oxide (PO) as a cheap and technically available comonomer appears to just meet above-said needs.

As disclosed in literature,<sup>7–10</sup> alternating PPC had been synthesized effectively from  $\text{CO}_2$  and PO using zinc glutarate (ZnGA) as catalyst that are considered to be the most commercial suitable catalyst to date. However, when PPC is used for the thermal plastic materials, its glass transition temperature ( $T_g$ ) remained a little low due to its flexible carbonate linkage in the backbone. The practical application of

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PPC has been also limited by the poor thermal stability. To improve the thermal stability, many approaches including physical and chemical ones have been studied. For example, many organic and inorganic components have been compounded with PPC to fabricate blends and composites.<sup>11–13</sup> PPC was also chemically end-capped by maleic anhydride, benzoyl chloride, ethyl silicate, acetic anhydride, and phosphorus oxychloride.<sup>14</sup> Block copolymerization of CO<sub>2</sub> with cyclohexene oxide and 4-vinyl-1-cyclohexene-1,2-epoxide in based PPC by yttrium-metal coordination catalyst was also reported.<sup>15</sup> The modification of PPC with a third comonomer seems to be a potential promising way to improve the properties of PPC extensively.

It is well known that the side chains have significant influence on the thermal properties of polymers. (2-Naphthoxy) methyl oxirane (NMO) belongs to a kind of PO with proper size condensed ring substituent, which makes it not only can take part in the copolymerization but also act as bulky side groups. Herein, we selected NMO as a third comonomer to be incorporated into the PPC backbone using supported zinc glutarate (*s*-ZnGA) catalyst, resulting in a novel terpolymer, poly(PO-*co*-CO<sub>2</sub>-*co*-NMO) (PPCN). This chemical modification is expected to further enhance  $T_g$  and thermal stability of PPC for the need of extensive practical applications.

## EXPERIMENTAL

### Materials

CO<sub>2</sub> of a purity of 99.99% was commercially obtained without further purification. PO of 95.0% purity was pretreated by potassium hydroxide and refluxed over calcium hydride for 24 h. It was then distilled under dry nitrogen gas and stored over 4 Å molecular sieves prior to use. Glutaric acid (GA) of 98.0% purity, zinc oxide of 99.0% purity, 2-naphthol, epichlorohydrin, potassium carbonate, and solvents such as toluene, methanol, acetone, chloroform, were of analytical reagent grade and used as received. Silica gel of 60–120 mesh for column chromatography was commercially obtained without further treatment.

### Preparation of catalyst

Supported ZnGA was synthesized according to previous work.<sup>10</sup> To a round-bottom flask equipped with mechanical stirrer, a Dean–Stark trap and a reflux condenser with a drying tube were added ZnO (100 mmol) and toluene (150 mL). Then, to the ZnO/toluene suspension was added GA (98 mmol) and perfluorinated compound (1.96 mmol). After the addition was complete, the slurry mixture was

stirred vigorously at 55°C for 8 h. Upon cooling down, the reaction mixture was filtered off and washed with acetone several times, dried overnight in a vacuum oven at 80°C, giving *s*-ZnGA as white powder that was stored in a drier prior to use.

### Synthesis of NMO

NMO was prepared as described in the literature.<sup>16</sup> A mixture of 2-naphthol (30.0 g, 0.1734 mmol), epichlorohydrin (68 mL, 0.8680 mmol), and potassium carbonate (28.8 g, 0.2084 mmol) was stirred at 120°C for 5 h. Then, the mixture was diluted with distilled water (170 mL) and extracted with ethyl acetate (3 × 200 mL). Organic layer was washed with distilled water, dried with anhydrous magnesium sulfate, and concentrated to give the crude compound, which was purified by chromatography (10% v/v ethyl acetate–hexane) on a silica gel column to give the product (28.1 g, yield 81%). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 2.82 (dd,  $J = 2.7$  and 5.1 Hz, 1H, CH–O–CHH), 2.95 (t,  $J = 4.8$  Hz, 1H, CH–O–CHH), 3.44 (m, 1H, Ar–O–CH<sub>2</sub>–CH–O–CH<sub>2</sub>), 4.06 (dd,  $J = 5.7$  and 10.8 Hz, 1H, Ar–O–CHH–CH–O–CH<sub>2</sub>), 4.35 (dd,  $J = 3.3$  and 11.1 Hz, 1H, Ar–O–CHH–CH–O–CH<sub>2</sub>), 7.14 (d,  $J = 2.4$  Hz, 1H, Ar–H), 7.19 (dd,  $J = 8.9$  and 2.5 Hz, 1H, Ar–H), 7.34 (dd,  $J = 7.0$  and 1.0 Hz, 1H, Ar–H), 7.44 (td,  $J = 7.0$  and 1.1 Hz, 1H, aryl), 7.75 (m, 3H, Ar–H). NMO was dried for 5 h under vacuum at 60°C and stored in a drier prior to use.

### General polymerization procedure

The synthesis of PPC and PPCN were carried out in a 500 mL autoclave equipped with a mechanical stirrer using PO as both reactant and solvent.

The *s*-ZnGA pre-dried was introduced into the autoclave as quickly as possible. The autoclave was 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 100°C and then was cooled to 30°C. Subsequently, the autoclave was purged carefully with CO<sub>2</sub> and evacuated alternatively for three times, followed by adding purified quantitative PO with a large syringe. The autoclave was then pressurized to 5.2 MPa via a CO<sub>2</sub> cylinder. The copolymerization was performed at 60°C under stirring for 40 h and afterwards 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 the polymer. The precipitated polymer was additionally washed with MeOH several times and dried at 80°C under vacuum to a constant weight. The as-made copolymer was weighed to calculate the yield of the copolymer.

PPCN was synthesized in the similar procedure to that of PPC, except that the required NMO was quickly added into the autoclave when the autoclave was cooled to 30°C.

## Measurements

$^1\text{H}$  NMR spectra were recorded on a Bruker NMR spectrometer (Model: DRX 400 MHz) using tetramethylsilane as standard and D-chloroform ( $\text{CDCl}_3$ ) as solvent. Molecular weight distribution ( $M_w$  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 A, 10,000 A, and 100,000 A). 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.

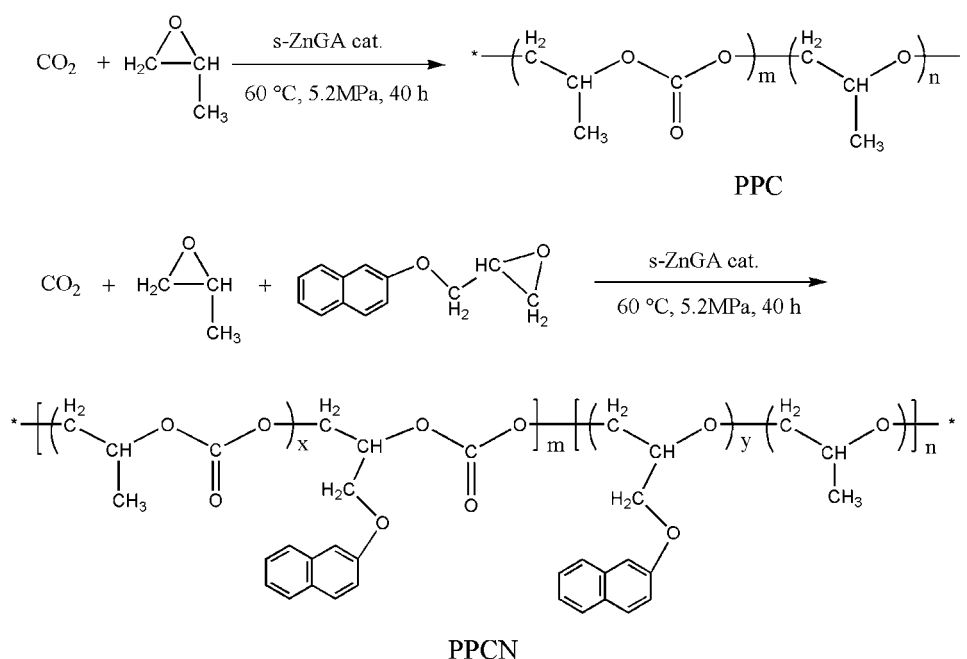
Differential Scanning Calorimetry (DSC) measurements were carried out under nitrogen flow on a Netzsch calorimeter (Model 204) from  $-30$  to  $100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . Thermogravimetric analysis (TGA) measurements were performed in a PerkinElmer TGS-2 under a protective nitrogen atmosphere. The temperature ranged from 30 to  $400^\circ\text{C}$  with a heating rate of  $20^\circ\text{C}/\text{min}$ .

The tensile tests were performed at  $23^\circ\text{C}$  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 was  $10\text{ mm}/\text{min}$ . Five specimens of each sample were tested, and the average results were reported.

## RESULTS AND DISCUSSION

### Structural characterization

The synthesis of PPC and PPCN are depicted as Scheme 1. The resulting methanol-insoluble polymer products were characterized by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR spectrum (Fig. 1, top) confirmed the existence of carbonate linkages and small fraction of random incorporated ether units in PPC, suggesting that the resulting polymer from  $\text{CO}_2$  and PO is almost the alternating PPC. Figure 1 (bottom) shows representative  $^1\text{H}$  NMR spectra for the terpolymer obtained from  $\text{CO}_2$  with NMO and PO with a molar feed ratio of 1:50:  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ), 1.3 [3H,  $\text{CH}_3$ (13)], 4.2 [2H,  $\text{CH}_2\text{CH}$  (9)], 4.6 [2H,  $\text{CH}_2\text{CH}$  (9')], 5.0 [1H,  $\text{CH}_2\text{CH}$  (10)], 5.3 [1H,  $\text{CH}_2\text{CH}$  (10')], 7.16 [4H; Ar—H (1, 7, 1', 7')], 7.34 [2H, Ar—H (4, 4')], 7.44 [1H, Ar—H (5, 5')], 7.75 [3H, Ar—H (3, 2, 6, 3', 2', 6')], 1.16 [3H,  $\text{CH}_3$  (13')], 3.4–4.4 [protons in all ether linkages (8, 9, 11, 12, 8', 11', 12')]. Compared with the  $^1\text{H}$  NMR spectrum for PPC, the emergent peaks at 5.3, 4.6, and 7.1–7.8 ppm are observed, indi-



Scheme 1 Syntheses of PPC (top) and PPCN (bottom).

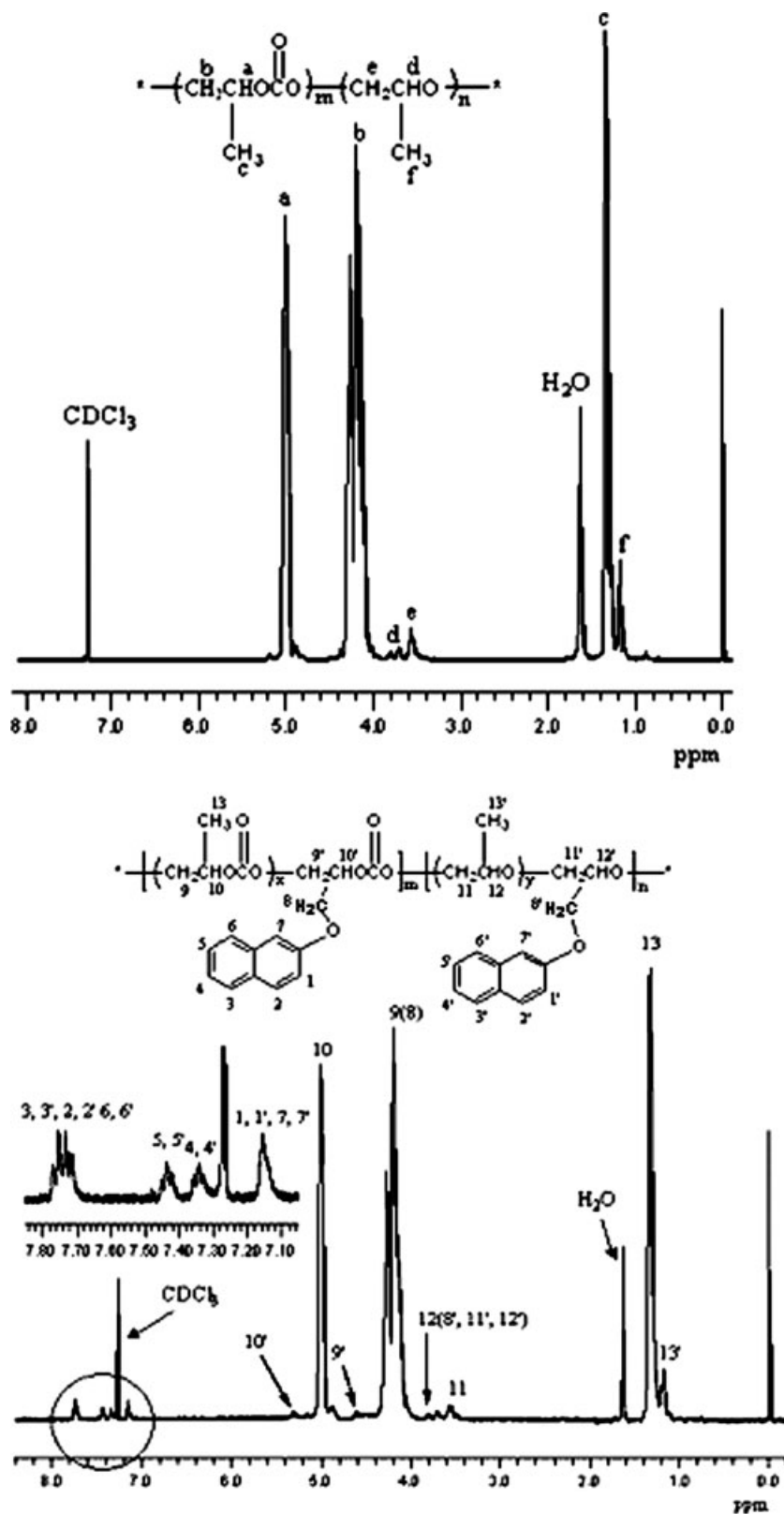


Figure 1 <sup>1</sup>H NMR spectra of PPC (top) and PPCN (bottom) terpolymer.

cating that NMO was successfully incorporated into the terpolymer backbone. These signals are assigned as the methine and methylene of [(2-naphthyl)oxy-

methyl]ethylene carbonate units and aromatic protons from NMO units according to the references.<sup>17,18</sup>

**TABLE I**  
The Results of the Terpolymerization of CO<sub>2</sub> With PO and NMO by s-ZnGA Catalyst<sup>a</sup>

Feed NMO content (%) <sup>b</sup>	Yield <sup>c</sup>	$M_n/M_w$ /MWD <sup>d</sup>	Composition of the polymer (molar fraction in %) <sup>e</sup>			
			$f_{\text{NMEC}}$ (%)	$f_{\text{PC}}$ (%)	$f_{\text{PE}}$ (%)	$f_{\text{NMO}}$ (%)
0	110	113K/405K/3.58		98.0	2.0	
1.0	100	104K/262K/2.52	0.5	96.1	3.5	0.5
2.0	89	103K/263K/2.55	0.7	93.4	5.8	0.8
2.9	80	84K/311K/3.70	1.3	91.8	6.9	1.3
4.4	68	67K/243K/3.63	1.4	91.3	6.0	2.7
6.2	61	35K/112K/3.20	1.6	85.5	10.2	4.3

<sup>a</sup> Polymerization was conducted at 60°C for 40 h under 5.2 MPa CO<sub>2</sub> pressure using 0.5 g of catalyst and 70 mL of PO.

<sup>b</sup> NMO molar fraction in both PO and NMO stocks.

<sup>c</sup> As g of polymer/g of cat.

<sup>d</sup> Determined by gel-permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.

<sup>e</sup> Determined by <sup>1</sup>H NMR spectroscopy.

On the basis of the above <sup>1</sup>H NMR spectra information, the compositions, including [(2-naphthoxy)methyl]ethylene carbonate molar fraction ( $f_{\text{NMEC}}$ ), propylene carbonate molar fraction ( $f_{\text{PC}}$ ), PO ether molar fraction ( $f_{\text{PE}}$ ), and the overall incorporated NMO molar fraction ( $f_{\text{NMO}}$ ) of the resulted terpolymer, can be estimated via the relative intensity ( $A$ ) of the correlated protons of the terpolymer according to the following equation.

$$f_{\text{NMEC}} = A_{5.3} / [A_{5.3} + A_{5.0} + (A_{1.16}/3) + (A_{7.34} - A_{5.3})] \times 100\% \quad (1)$$

$$f_{\text{PC}} = A_{5.0} / [A_{5.3} + A_{5.0} + (A_{1.16}/3) + (A_{7.34} - A_{5.3})] \times 100\% \quad (2)$$

$$f_{\text{PE}} = (A_{1.16}/3) / [A_{5.3} + A_{5.0} + (A_{1.16}/3) + (A_{7.34} - A_{5.3})] \times 100\% \quad (3)$$

$$f_{\text{NMO}} = A_{7.34} / [A_{5.3} + A_{5.0} + (A_{1.16}/3) + (A_{7.34} - A_{5.3})] \times 100\% \quad (4)$$

For PPC, the values of  $A_{5.3}$  and  $A_{7.34}$  are zero due to the absence of NMO units in the PPC backbone.

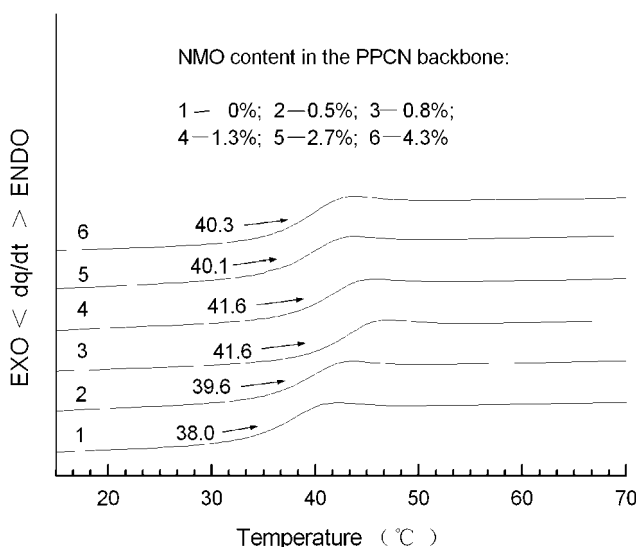
The results of the polymerization are summarized in Table I. It can be seen that the PPCN terpolymers

were successfully synthesized with number average molecular weight ( $M_n$ ) ranging from 35K to 113K and molecular weight distributions (MWD) of 2.52–3.70. The MWD tends to be broader with decreasing  $M_n$ . The catalytic activity decreased from 110 to 61 g of polymer per gram of catalyst with increasing the feed NMO monomer content from 0% to 6.2%. The overall incorporated NMO molar fraction of the resulted terpolymers was always smaller than the corresponding feed NMO monomer content. It can be also observed that the incorporated NMO existed in both carbonate linkages and ether linkages, but the NMEC moiety content changed in a very limited range from 0.5% to 1.6%. It is apparent that the total NMEC and propylene carbonate (PC) contents decreased with increasing feed NMO monomer content. These results demonstrated that NMO exhibited less reactivity than PO in the terpolymerization reaction. This could be explained by the fact that (2-naphthoxy)methyl is a weaker electron donor compared with the methyl of PO, because the increasing electron-donor character of the substituent at the oxirane ring can result in an enhanced reactivity of the oxirane in the copolymerization reaction.<sup>2</sup> On the other hand, the NMO ring contains a bulky substituent that might be another cause due to the steric effect that is unfavorable for the NMO monomer to

**TABLE II**  
The Thermal and Mechanical Properties of the PPCN Terpolymers

NMO unit content (%) <sup>a</sup>	$T_g$ (°C)	$T_{-5\%}$ (°C)	Tensile strength (MPa)	Elongation at break (%)
0	38.0	238	31.7	544.1
0.5	39.6	243	33.8	2.7
0.8	41.6	272	34.5	3.3
1.3	42.0	257	34.8	3.1
2.7	40.3	250	35.9	302.3
4.3	40.1	247	21.8	566.8

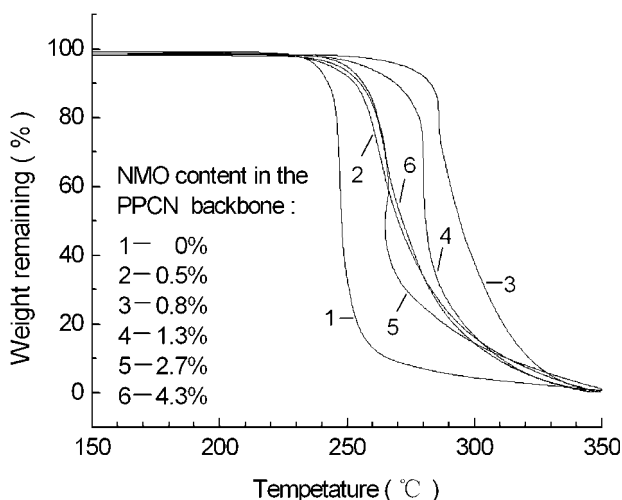
<sup>a</sup> NMO molar fraction in the PPCN backbone.



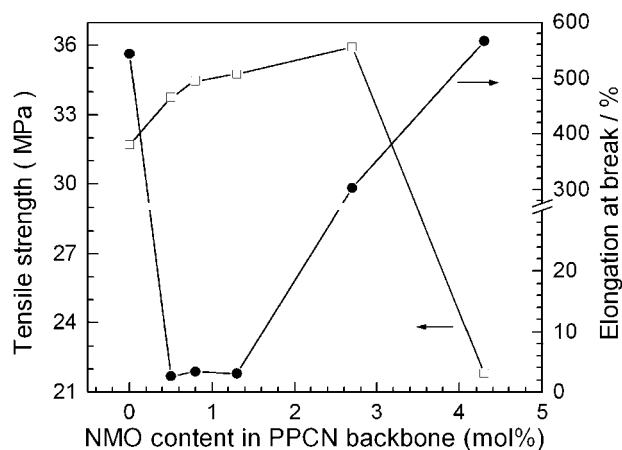
**Figure 2** DSC curves for the resulted PPCN terpolymers with different NMO content.

coordinate with metal in the active site, which is necessary for oxiranes prior to insertion into metal-oxygen bond.<sup>19</sup> Taking these factors into account, the NMO monomer is expected to be incorporated randomly into the PPC backbone, resulting in the terpolymers with superior thermal and mechanical characters.

The bulky aromatic rings containing NMO monomer was introduced on to the PPC backbone as side groups, showing steric obstruct effect to prevent the flexible PPC backbone from rotating. Therefore, the physical properties such as  $T_g$  and thermal stability of PPC can be tailored by adjusting the incorporated NMO content.



**Figure 3** TGA curves for the resulted PPCN terpolymers with different NMO content.

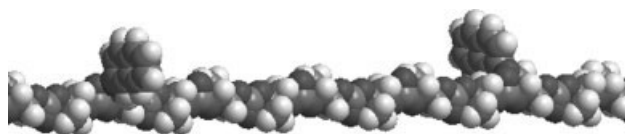


**Figure 4** Tensile strength and elongation at break of the resulted PPCN terpolymers versus the NMO units content in PPCN.

### Improved thermal properties of PPCN

The thermal properties are related to the structure and composition of the resulted terpolymers. By adjusting the molar proportion of NMO, varying properties of PPCN terpolymers can be obtained as shown in Table II. Generally, PPC with high molecular weight shows higher  $T_g$  than that with low molecular weight. As shown in Figure 2, although the PPC has higher molecular weight than those modified PPCN terpolymers, all the PPCN showed higher  $T_g$  to certain extent compared with the PPC. This implies that the NMO monomer incorporated randomly into the PPC backbone indeed acted an important function to increase  $T_g$ . In fact, the bulky naphthyl groups originated from NMO monomer exert steric obstruct effect to prevent the flexible PPC backbone from rotating (see Fig. 3). The PPCN terpolymers showed the highest  $T_g$  of 42°C when the incorporated NMO content was about 1% in PPCN. Beyond this value, the  $T_g$  of the PPCN terpolymers decreased with further increasing NMO unit content. It is believed that the decrement in  $T_g$  was resulted from the decrease in the molecular weight of the PPCN terpolymers.

As shown in Figure 4, the 5% weight loss temperature ( $T_{-5\%}$ ) of the PPCN terpolymer was greatly increased up to about 272°C, being 34°C higher than that of pure PPC at the NMO content of 2.7%. The



**Figure 5** Energy minimized space filling structure of PPCN segment with bulky naphthyl groups on the flexible PPC backbone.

highly thermal decomposition temperature ensures that the PPCN terpolymer could be safely melt-processed at 150–180°C without decomposition. According to previous work,<sup>20</sup> the thermal decomposition of PPC obeys two kinds of mechanism, the main chain scission reaction and the unzipping reaction. Although the unzipping reaction involves the backbiting of the terminal hydroxyl groups at the carbon in carbonate linkage leading to the formation of cyclic PC. When introducing the NMO units into the PPC backbone, thus the formed bulky naphthyl side groups can suppress the backbiting process and diminish the unzipping reaction. This effect is obviously favorable for increasing the thermal decomposition temperature. However, when the NMO units content exceed the value of 1.3%, the decrease in molecular weight becomes a dominant factor. It is known that the polymer with low molecular weight has more hydroxyl terminal groups that accelerate the unzipping reaction, resulting in low thermal decomposition temperature.

### Mechanical properties

The mechanical properties of the resulted PPCN terpolymers were measured in terms of tensile strength ( $\sigma_a$ ) and elongation at break ( $\epsilon$ ). Figure 5 shows both the tensile strength and elongation at break versus the NMO content. It can be seen that the tensile strength of the PPCN terpolymer increased up to 36 MPa which was 4 MPa higher than that of pure PPC at the NMO unit content of 4.3%, together with an elongation at break of about 300%. It also reveals that the incorporation of NMO leads to the PPCN terpolymers more brittle due to the presence of bulky and rigid naphthyl groups. However, when the incorporated NMO content exceed 2.7%, the elongation at break of the PPCN terpolymers increased again owing to the rapid decrease in molecular weight.

### CONCLUSIONS

The PPCN terpolymers from the copolymerization of CO<sub>2</sub> with PO and [(2-naphthyloxy)methyl]oxirane were successfully synthesized using supported ZnGA as catalyst. The resulted terpolymers exhib-

ited greatly enhanced thermal and mechanical properties over pure PPC due to the incorporation of NMO monomer. However, the addition of NMO resulted in the decrease in the molecular weight of the PPCN terpolymers. The highest  $T_g$  and the weight loss temperature of the PPCN terpolymers are 42 and 272°C, respectively. High tensile strength of 36 MPa can be achieved at a NMO content of 4.3% in PPCN terpolymer. Very small amount of NMO moiety in the synthesized PPCN can greatly enhance the thermal properties of PPC, demonstrating the effective way to endow the potential and practical application of PPC.

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