

# Zinc Lactate-Catalyzed Ring-Opening Polymerization of Trimethylene Carbonate under Microwave Irradiation

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**ABSTRACT:** Microwave-assisted ring-opening polymerization (MROP) of trimethylene carbonate (TMC) was carried out with four different types of zinc lactate, as the catalyst. Poly(trimethylene carbonate)s (PTMC) with a number-average molar mass ranging from 2990 to 75,410 g/mol and a TMC conversion ranging from 85.2% to 98.2% were synthesized effectively in 30 min at 120°C under microwave irradiation. The effects of the catalyst type, catalyst concentration, and microwave irradiation

time on the MROP of TMC were studied. The MROP of TMC was much faster than that under conventional heating conditions. Thermal analysis suggested that PTMC with higher molar mass exhibited higher glass transition temperature ( $T_g$ ) and thermal stability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1236–1241, 2008

**Key words:** trimethylene carbonate; ring-opening polymerization; zinc lactate; microwave irradiation

## INTRODUCTION

Poly(trimethylene carbonate) (PTMC) is one of the most important biodegradable polycarbonates for biomedical purpose.<sup>1</sup> The ring-opening polymerization (ROP) of the corresponding cyclic carbonates is one of the several well-developed methods for synthesizing high molar mass aliphatic polycarbonates. The most widely used catalysts/initiators for the ROP of lactones/lactides/carbonates are tin salts and aluminum alkoxides; however, most of these metal compounds may lead to potentially toxic problems for biomedical applications.<sup>2</sup> Because the application of synthetic polymers in the biomedical fields requires extremely high purity and the absence of any toxic compounds, the use of low-toxic or nontoxic catalysts/initiators, which are composed of cations and anions that are present in human body can have significant benefits.<sup>3</sup>

Zinc is an oligo-element that is required daily by normal metabolism of mammalian bodies; thus, zinc ion with a low concentration may be low toxic or nontoxic to the human body. Several research groups have investigated the zinc and zinc compound catalyzed/initiated ROP of lactones and lactides. Jerome and coworkers studied that the zinc alkoxides initiated ROP of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) in toluene at 25°C,<sup>3</sup> poly( $\epsilon$ -caprolactone)s (PCL) with a

number-average molar mass ( $M_n$ ) ranging from 3100 to 5200 g/mol, and a polydispersity index (PDI) ranging from 1.05 to 1.10 were obtained under this mild condition. The living nature of the polymerization was confirmed by the close agreement between the theoretical and experimental degree of polymerization at a total monomer conversion, as well as the linear dependence of  $M_n$  on the monomer conversion. The proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) analysis of the resulting PCL supported a coordination–insertion mechanism of the polymerization.

Zinc lactate, which contains zinc cation and lactyl anion, is considered as a fully resorbable and biocompatible initiator for the ROP of lactones/lactides.<sup>4–7</sup> Kricheldorf and Damrau first reported the zinc L-lactate (ZnLLa) catalyzed/initiated ROP of L-lactide (L-La) at 120 or 150°C.<sup>4</sup> Poly(L-lactide) of 100% optically pure was obtained with  $M_n$  around 70,000 g/mol at a monomer/initiator molar ratio of 4000. Kricheldorf and Damrau also reported that the ZnLLa catalyzed ROP of 1,4-dioxan-2-one at 100°C in bulk.<sup>5</sup> Polydioxanones with an inherent viscosity of 0.82 dL/g was obtained at a monomer/catalyst molar ratio of 2000, while a 14-day reaction time was required. A coordination–insertion mechanism was proposed for the ZnLLa catalyzed ROP of 1,4-dioxan-2-one.

ZnLLa also proved to be useful for the copolymerization of L-La with glycolide, as well as  $\epsilon$ -CL.<sup>6</sup> The copolymerizations were carried out at 150°C in bulk from 8 to 192 h, which led to copolymers with high yields, high inherent viscosity, and random sequences.

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Meanwhile, Vert and coworkers found that only a fraction of the zinc was active in the zinc powder catalyzed ROP of *D,L*-lactide (*D,L*-La); further study revealed that it was zinc *D,L*-lactate (ZnDLLa) rather than zinc that served as the actual catalyst.<sup>7</sup> At a *D,L*-La/catalyst molar ratio of 5000, poly(*D,L*-lactide)s with a  $M_n$  ranging from 2600 to 105,600 g/mol and a monomer conversion ranging from 5.1% to 39.2% were synthesized by hydrated ZnDLLa catalyzed ROP of *D,L*-La at 140°C for 4.2–11.9 h. A polymerization mechanism based on a cationic process cocatalyzed by lactic acid was proposed for the ZnDLLa catalyzed ROP of *D,L*-La.

Although zinc lactate has many advantages such as good stability, biocompatibility, and not catalyzing the back-biting degradation even after 2 weeks' reaction, it is not a highly efficient catalyst for the ROP of lactone/lactides compared with tin(II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>). A long reaction time is needed for the zinc lactate catalyzed ROP to complete under conventional heating.

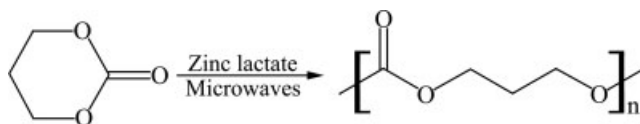
Because of its unique advantages, such as rapid bulk heating capacity compared with the conventional heating method, microwave heating has become one of the most commonly used environmentally benign technologies in the field of synthetic chemistry.<sup>8,9</sup> For monomers containing polar groups that favor the absorption of microwaves, polymerizations including ROP under microwave irradiation have been successfully performed with a dramatically accelerated reaction rate<sup>10–12</sup>; however, to the best of our knowledge, no reports have been published on the zinc lactate-catalyzed/initiated microwave-assisted ring-opening polymerization (MROP) of carbonates.

During this study, four types of zinc lactates, namely, anhydrous zinc *D,L*-lactate (ZnDLLa), hydrated zinc *D,L*-lactate (HZnDLLa), anhydrous zinc *L*-lactate (ZnLLa), and hydrated zinc *L*-lactate (HZnLLa), were used for the first time as a resorbable nontoxic catalyst for the MROP of trimethylene carbonate (TMC). The effects of catalyst type, catalyst concentration, and microwave irradiation time on the polymerization were investigated.

## EXPERIMENTAL

### Materials

TMC was synthesized according to literature<sup>13</sup> and purified three times by recrystallization from anhy-



**Scheme 1** Zinc lactate catalyzed ring-opening polymerization of trimethylene carbonate.

drous ethyl acetate. HZnDLLa was synthesized by reacting *D,L*-lactic acid with zinc oxide.<sup>7</sup> HZnLLa was supplied by PURAC. ZnDLLa and ZnLLa were prepared by dehydration of the corresponding hydrate at 150°C for 24 h. All the other reagents were of analytical grade and used as received.

### Microwave-assisted ring-opening polymerization of trimethylene carbonate

The polymerization was carried out in a CEM Discover<sup>®</sup> mono-mode microwave oven, which contains a built-in infrared thermometer (Scheme 1). Typically, 1.02 g of TMC and varied amounts of zinc lactate were added to a 10 mL vial. Then the vial was closed using the Snap-On<sup>®</sup> cap and purged with high purity (>99.999%) nitrogen flow for 30 min to remove the moisture and oxygen. The vial was then subjected to microwave irradiation at 120°C for different time intervals. After the irradiation was completed, the as-polymerized product was dissolved in chloroform and filtered to remove the catalyst. Part of the solution was taken out and dried to determine the TMC conversion using <sup>1</sup>H NMR. The other part of the solution was condensed in a rotary evaporator and precipitated in excessive methanol. The precipitate was collected by filtration and vacuum-dried at room temperature for gel permeation chromatography (GPC) analysis.

### Ring-opening polymerization of trimethylene carbonate via conventional heating

The ROPs of TMC under conventional heating were conducted in an oil bath at 120°C for 30 min with a monomer/catalyst molar ratio of 500. Four catalysts, namely, ZnDLLa, HZnDLLa, ZnLLa, and HZnLLa, were used in this experiment. All the other procedures were the same as that of microwave-assisted synthesis.

### Characterizations

The products were characterized by <sup>1</sup>H NMR at 300 MHz and carbon nuclear magnetic resonance spectroscopy (<sup>13</sup>C NMR) at 75.5 MHz on a Bruker DPX300 spectrometer with tetramethylsilane as an internal standard and CDCl<sub>3</sub> as a solvent.

$M_n$  and the PDI of the polymers were determined by GPC on a Viscotek HPLC system equipped with a model VE3580 refractive-index detector and an I-MBHMW-3078/I-MBLMW-3078 column set. Tetrahydrofuran was used as an eluent (flow rate 1.0 mL min<sup>-1</sup>) at 35°C. The molar mass was calibrated by polystyrene standards.

Differential scanning calorimetry (DSC) analysis was performed on a TA Q10 DSC at a heating rate

TABLE I  
Poly(trimethylene carbonate)s Obtained by Zinc Lactate Catalyzed Ring-Opening  
Polymerization under Microwave Irradiation (120°C, 30 min)

Entry no.	Catalyst	Monomer/catalyst ratio	$M_n$	PDI	Conversion (%)
01	HZnLa	50	4,220	1.6	96.1
02	HZnLa	100	6,800	1.8	96.1
03	HZnLa	200	10,790	1.6	95.4
04	HZnLa	500	20,700	1.5	93.6
05	ZnLa	50	19,410	1.6	98.0
06	ZnLa	100	36,300	1.6	97.7
07	ZnLa	200	49,490	1.7	97.4
08	ZnLa	500	75,410	1.9	95.2
09	HZnDLLa	50	2,990	1.7	95.9
10	HZnDLLa	100	3,750	2.3	94.2
11	HZnDLLa	200	12,520	1.4	95.0
12	HZnDLLa	500	22,000	1.6	95.9
13	ZnDLLa	50	18,150	1.6	96.7
14	ZnDLLa	100	27,720	1.7	98.2
15	ZnDLLa	200	32,050	1.8	96.3
16	ZnDLLa	500	19,910	1.7	97.1

of 10°C min<sup>-1</sup>. All samples were heated to 100°C at a rate of 10°C min<sup>-1</sup> and kept isothermal for 3 min to erase previous thermal history, then cooled down to -60°C at a rate of 10°C min<sup>-1</sup>, and subsequently heated to 100°C at a rate of 10°C min<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a SDT 2960 simultaneous DSC-TGA TA instrument under argon flux at 100 mL min<sup>-1</sup>. Samples of ~18–20 mg were heated up from room temperature to 500°C at a rate of 10°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Characterization of the poly(trimethylene carbonate)

The  $M_n$  of the precipitates measured by GPC ranged from 2990 to 75,410 g/mol with a PDI ranging from 1.4 to 2.3 (Table I). The chemical structure of the precipitate obtained was characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR (Fig. 1). <sup>1</sup>H NMR ( $\delta$ , ppm): 2.03 (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 4.23 (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 3.73 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—OH); <sup>13</sup>C NMR ( $\delta$ , ppm): 28.03 (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 31.63 (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—OH), 58.88 (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—OH), 64.28 (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 154.90 (—CO—OCH<sub>2</sub>CH<sub>2</sub>—). The NMR data were in agreement with the literature.<sup>14</sup>

### Influence of the catalyst type and concentration on the microwave-assisted ring-opening polymerization of trimethylene carbonate

The influence of the zinc lactate catalyst concentration on the MROP of TMC was investigated at four monomer/catalyst molar ratios: 50, 100, 200, and 500. Four types of zinc lactates, ZnDLLa, HZnDLLa,

ZnLa, and HZnLa, were investigated as the catalysts. The microwave irradiation time was 30 min.

Using ZnDLLa as the catalyst, PTMCs with a  $M_n$  of 18,150, 27,720, 32,050, and 19,910 g/mol and a TMC conversion of 96.7%, 98.2%, 96.3%, and 97.1% were obtained at a monomer/catalyst molar ratio of 50, 100, 200, and 500, respectively [Fig. 2(a)]. When the monomer/catalyst ratio increased from 50 to 200, the  $M_n$  of the PTMC increased with the monomer/catalyst ratio; however, when the monomer/catalyst ratio was increased from 200 to 500, the  $M_n$  of the PTMC decreased from 32,050 to 19,910 g/mol.

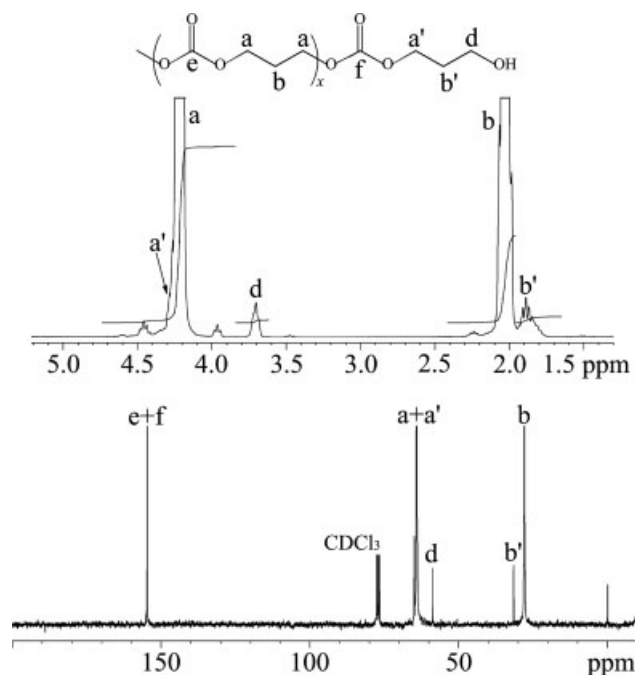
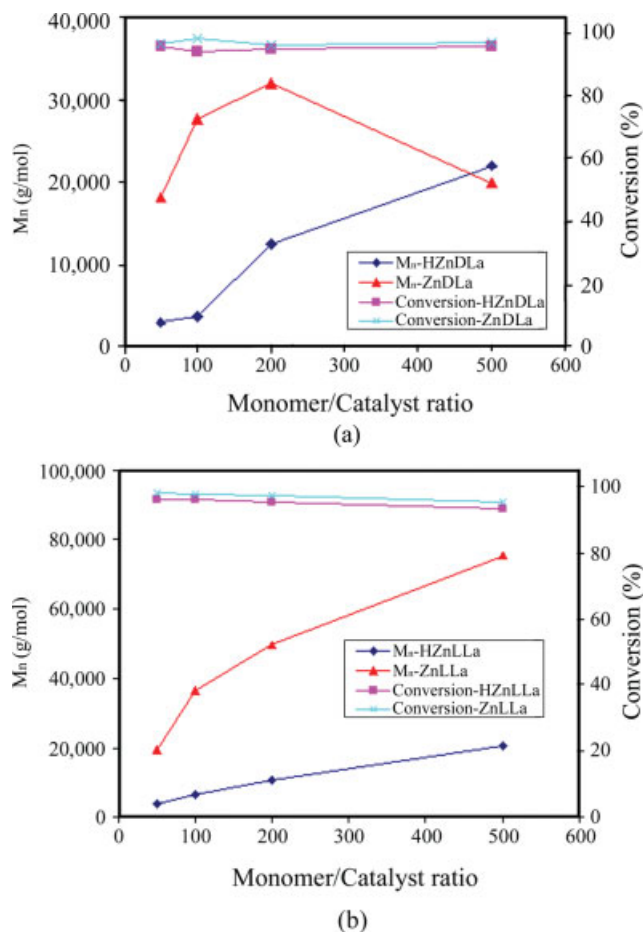


Figure 1 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of No. 02 PTMC sample: (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR.



**Figure 2** Influence of the catalyst concentration on the microwave-assisted ring-opening polymerization of TMC (a) ZnDLA series and (b) ZnLLa series. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Using HZnDLA as the catalyst, at a monomer/catalyst molar ratio of 50, 100, 200, and 500, the corresponding  $M_n$ s were 2990, 3750, 12,520, and 22,000 g/mol with conversions of 95.9%, 94.2%, 95.0%, and 95.9%, respectively [Fig. 2(b)]; thus, the  $M_n$  increased with the monomer/catalyst molar ratio. A decreasing HZnDLA concentration would result in lower water concentration and lead to an increasing polymer molar mass.

Using ZnLLa as the catalyst, similar trends of  $M_n$  as a function of the monomer/catalyst ratio were observed [Fig. 2(b)]. PTMCs with a  $M_n$  of 19,410, 36,300, 49,490, and 75,410 g/mol and a corresponding TMC monomer conversion of 98.0%, 97.7%, 97.4%, and 95.2% were obtained at a monomer/catalyst molar ratio of 50, 100, 200, and 500, respectively. For the HZnLLa-catalyzed MROP of TMC, the  $M_n$ s of PTMCs synthesized at monomer/catalyst molar ratios of 50, 100, 200, and 500 were 4,220, 6,800, 10,790, and 20,700 g/mol with corresponding monomer conversions of 96.1%, 96.1%, 95.4%, and 93.6%, respectively.

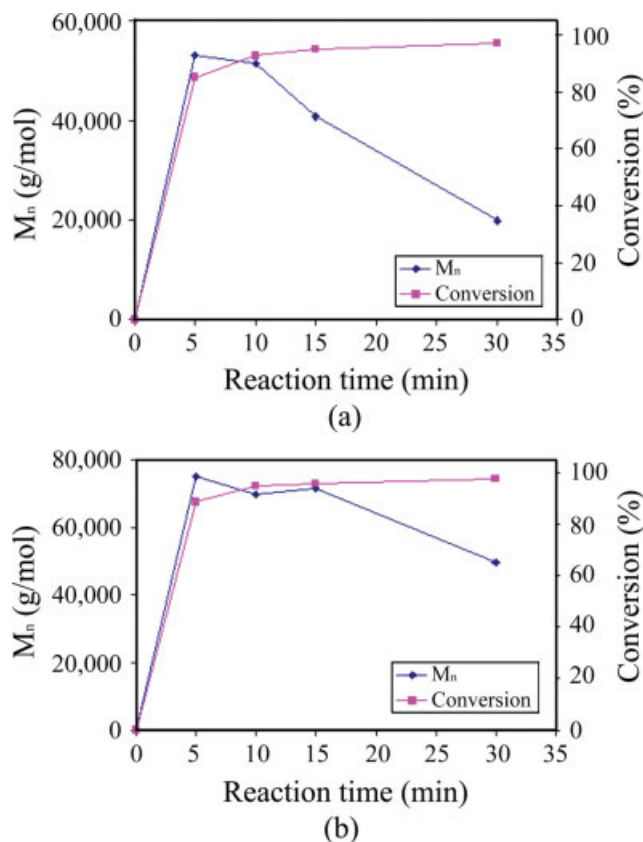
For these four types of catalysts, it can be observed that the  $M_n$ s with anhydrous zinc lactate were significantly higher than those with hydrated zinc lactate, which is similar to what was reported on zinc lactate catalyzed ROP of lactide under conventional heating.<sup>7</sup> This can be explained by the difference in the catalyst chemical structure. In the hydrated zinc lactate, the H<sub>2</sub>O molecules in the hydrated catalyst, which has a molar ratio to the zinc lactate of at least two, may react with the TMC monomer and subsequently form cointiators for the ROP of TMC and thereby lowering the  $M_n$  of the resulting polymer. Another trend in these experiments is that the  $M_n$ s showed a high deviation from the monomer/catalyst molar ratio, and were much lower than those calculated from the monomer/catalyst ratio, this could be attributed to the spontaneous polymerization of the TMC. At a temperature higher than 100°C, TMC was reported to undergo a spontaneous polymerization in bulk following an anionic mechanism.<sup>1,15</sup> By this spontaneous polymerization, more PTMC chains were formed during the ROP process and led to lowered  $M_n$  of the resulting polymer.

#### Influence of microwave irradiation time on the microwave-assisted ring-opening polymerization of trimethylene carbonate

The influence of microwave irradiation time on the MROP of TMC were examined at 5, 10, 15, and 30 min using two anhydrous zinc lactates, ZnDLA, and ZnLLa as the catalysts at a monomer/catalyst molar ratio of 200 (Fig. 3).

Using ZnDLA as the catalyst, the  $M_n$  of the PTMC reached 53,080 g/mol after the reaction mixture was irradiated for only 5 min with a TMC conversion of 85.2%, indicating that the MROP of TMC proceeded rapidly [Fig. 3(a)]. By increasing the reaction time to 10 min, PTMC with a slightly lower  $M_n$  of 51,360 g/mol and a TMC conversion of 92.7% was obtained, indicating that the ROP of the TMC monomer was the dominant reaction during the first 10 min of microwave irradiation. After 15 min of microwave irradiation, the  $M_n$  decreased to 40,760 g/mol with a conversion of 95.0%, suggesting the degradation of the resulting polymer became significant at prolonged irradiation times. When the microwave irradiation time was prolonged to 30 min, the  $M_n$  of the PTMC dropped significantly to 19,910 g/mol with a conversion of 97.1%. By increasing the microwave irradiation time, the phenomenon observed with the continuously increasing monomer conversion, coupled with the continuously decreasing  $M_n$ , suggests that the degradation was attributed to a random thermal degradation rather than an unzipping depolymerization mechanism.





**Figure 3** Influence of microwave irradiation time on the microwave-assisted ring-opening polymerization of trimethylene carbonate (a) ZnDLa and (b) ZnLa. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Using ZnLa as the catalyst, the  $M_n$ s of the PTMC polymers produced at 5, 10, 15, and 30 min were 75,120, 69,600, 71,420, and 49,490 g/mol, respectively, which showed a trend similar to ZnDLa [Fig. 3(b)]. At the same time, the TMC monomer conversions at 5, 10, 15, and 30 min were 85.5%, 94.6%, 95.7%, and 97.4%, respectively, which increased with the microwave irradiation time.

Similar to our previous findings on the MROP of lactide,<sup>16,17</sup> with increasing reaction time, the  $M_n$  of the resulting PTMC decreased while the TMC monomer conversion increased. This observation strongly suggested that two competitive reactions, namely, the MROP of TMC and the random thermal degradation caused by the *trans*-esterification of the resulting PTMC undergone simultaneously. During the first 5 min of microwave irradiation, the MROP reaction was the dominant reaction; during prolonged times, the degradation reaction became stronger.

#### Ring-opening polymerization of trimethylene carbonate via conventional heating

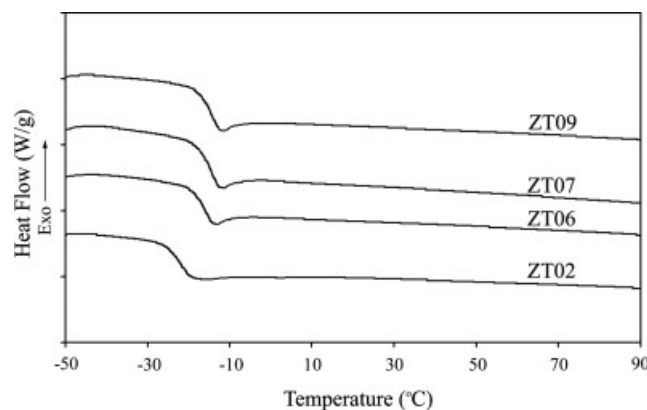
The ROP of TMC was conducted in an oil bath at 120°C for 30 min using ZnDLa, HZnDLa, ZnLa, and HZnLa as the catalysts with a monomer/catalyst molar ratio of 500/1. No precipitate was obtained in the process of precipitation in methanol. GPC results of the reaction mixture showed that PTMC polymers with  $M_n$  of 1240, 1240, 1260, and 1260 g/mol were obtained for ZnDLa, HZnDLa, ZnLa, and HZnLa, respectively, with corresponding TMC conversions of 3.0%, 1.8%, 3.1%, and 1.9%. For their counterparts under microwave heating, the  $M_n$  of the PTMC polymers was 19,910, 22,000, 75,410, and 20,700 g/mol with corresponding TMC conversions of 97.1%, 95.9%, 95.2%, and 93.6%, respectively. Compared with the MROP under the same conditions, the ROP of TMC under conventional heating conditions proceeded much slower in terms of  $M_n$  and monomer conversion.

**Thermal properties of the poly(trimethylene carbonate)**

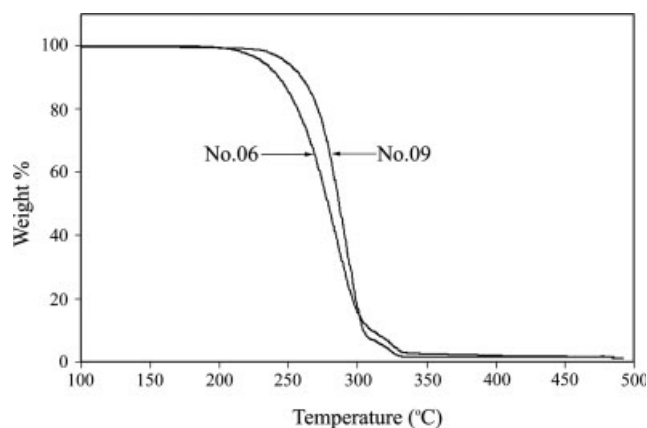
The DSC thermograms of the PTMC obtained by the MROP of the TMC with different molar mass were recorded. PTMC samples No. 09, No. 07, No. 06, and No. 02 as listed in Table I with corresponding  $M_n$  of 75,410, 36,300, 19,410, and 6,800 g/mol were selected for this study. As shown in Figure 4, no melting peaks were observed in the DSC curves; this was in accordance with the literature, which reported that PTMC is amorphous in the relaxed state and crystalline in the stretched state.<sup>18</sup> The glass transition temperature ( $T_g$ ) of the PTMC polymer with a  $M_n$  of 75,410, 36,300, 19,410, and 6,800 g/mol were -14.3°C, -14.8°C, -15.74°C, and -21.98°C, respectively. The DSC results suggested that PTMC with higher  $M_n$  possessed higher  $T_g$  as expected.

#### Thermal properties of the poly(trimethylene carbonate)

TGA analysis was performed for PTMC No. 09 and No. 06 (Fig. 5) with a corresponding  $M_n$  of 75,410 and 19,410 g/mol. Thermal degradation was detectable above 200°C for each of the two samples. The temperature at 5 wt % weight loss for No. 09 and No. 06 are 247.8 and 230.8°C, respectively; the



**Figure 4** DSC thermograms of No. 09, No. 07, No. 06, and No. 02 as listed in Table I.



**Figure 5** TGA curves of No. 09 and No. 06 as listed in Table I.

temperature at 50 wt % weight loss for No. 09 and No. 06 are 286.8 and 278.8°C, respectively. Apparently, PTMC with a higher  $M_n$  has a higher thermal stability.

### CONCLUSIONS

Using four types of zinc lactates as the catalyst, PTMCs with a number-average molar mass ranging from 2990 to 75,410 g/mol and a TMC conversion ranging from 85.2% to 98.2% were synthesized effectively in 30 min at 120°C under microwave irradiation. The catalyst type and concentration had an important influence on the MROP of TMC. It was found that the anhydrous zinc lactates were more effective in the synthesis of high molecular molar mass polymers, and higher monomer/catalyst ratio led to higher molecular molar mass for both types of catalysts. Prolonged microwave irradiation time led to the degradation of the polymers because the MROP and thermal degradation reactions occurred simultaneously during the later stage of the reaction

process. PTMC with higher molar mass exhibited higher  $T_g$  and thermal stability. The MROP proceeded much faster than that under conventional heating method. The cytotoxicity of the products of polymerization with different concentrations of zinc ion is worthy for further study.

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