

# Heating Characteristics and Polymerization of $\epsilon$ -Caprolactone Under Microwave Irradiation

L. Q. Liao, L. J. Liu, C. Zhang, F. He, R. X. Zhuo

Laboratory of Biomedical Polymers of the Ministry of Education, Department of Polymer Science, College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China

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**ABSTRACT:** The thermal effect of microwave energy on  $\epsilon$ -caprolactone (CL) monomer and polymerization reaction mixture of CL with stannous octoate [Sn(Oct)<sub>2</sub>] intimately depended on the power level of microwaves and the mass scale of materials. When 10 g of CL was heated by microwaves at a power of 680 W, its temperature increased rapidly from 20 to 355°C within 5 min after which it was self-regulated to keep constant at 360°C. Heat generation was observed when a polymerization reaction mixture of 10 g CL with 0.1% (mol/mol) Sn(Oct)<sub>2</sub> was irradiated at 680

W. The exothermic peak was recorded at 2–5 min and its temperature was over 300°C, with the maximum at 343°C. During this period the ring-opening polymerization of CL occurred quickly, resulting in poly( $\epsilon$ -caprolactone) with weight-average molecular weight ( $M_w$ ) of 123,000 g/mol and yield of 95%. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2657–2664, 2003

**Key words:** ring-opening polymerization; polyesters; synthesis; caprolactone; microwaves

## INTRODUCTION

Poly( $\epsilon$ -caprolactone) (PCL) is one of the industrial biopolymers that are used as degradable biomedical materials and packaging materials.<sup>1–3</sup> PCL is generally prepared from catalyzed ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) in bulk or in solution.<sup>4</sup> After Carothers and colleagues<sup>5</sup> reported the ROP of CL, many studies were devoted to this field.<sup>6–12</sup> Young et al.<sup>6</sup> investigated the ROP of CL in melt and in solution and concluded that the pattern of polymerization at high temperature was radically different from the one in solution under mild low-temperature condition. The phenomenon was best explained by assuming that several secondary processes occurred simultaneously with the primary initiation and polymerization reactions. Bassi et al.<sup>7</sup> revealed that the ROP of CL catalyzed by triphenyltin acetate showed zero-order kinetics that could be explained by the formation of an acrylic ester link in the rate-determining step leading to a coordinative unsaturated tin species.

Recently, Kricheldorf and Langanke<sup>8</sup> investigated the germanium alkoxide-initiated ring-opening and

ring-expansion polymerization of CL at six different temperatures and a temperature of 120°C was found to allow for a quantitative conversion after 2 days. Kowalski et al.<sup>9,10</sup> studied the kinetics of polymerization of CL initiated by Sn(Oct)<sub>2</sub> in THF at 80°C and the results strongly suggested that the tin alcoholate active centers were formed from the starting carboxylate and the polymerization proceeded on the tin-alkoxide bond. Storey et al.<sup>11,12</sup> investigated the kinetics and mechanism of stannous octoate [Sn(Oct)<sub>2</sub>] catalyzed bulk polymerization of CL conducted at 130°C and induction periods of polymerization were observed, which were attributed to slow heat transfer and the type of alcohol used as initiator. However, it commonly took over 10 h or several days for the ROP to be completed by conventional heating in the cases mentioned above.

Microwave heating, which presents a totally different heating mode from conventional heating, has been proved to be more rapid and efficient. Since the report by Gedye and coworkers<sup>13</sup> on the use of microwave heating to accelerate organic reactions, a wide variety of chemical reactions have been performed under microwave irradiation. In the field of polymer chemistry, microwave energy was used for enhancing various kinds of polymerizations including addition polymerization,<sup>14–17</sup> condensation polymerization,<sup>18–22</sup> graft polymerization,<sup>23</sup> and ROP.<sup>24–29</sup> Until now, only a few reports were found in the literature concerning microwave-assisted ROP of CL. Albert et al.<sup>24</sup> compared thermal and microwave-activated polymerization of CL at 180°C in the presence of titanium tetrabutylate but the results did not indicate substantial improve-

Correspondence to: L.-J. Liu (liulj@chem.whu.edu.cn).

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ment relating to the use of microwave irradiation. Fang et al.<sup>25,26</sup> studied the ROP of CL and  $\epsilon$ -caprolactam at low forward power in a variable-frequency microwave furnace (frequency range from 2.4 to 7.0 GHz) and found that CL and  $\epsilon$ -caprolactam both exhibited effective absorption of microwaves to induce fast chemical reactions and quality PCL and nylon-6 were produced by the reactions.

However, the number-average molecular weight ( $M_n$ ) of the obtained PCL was only around  $10^4$  g/mol after CL was irradiated by microwave for 2 h with  $\text{Sn}(\text{Oct})_2$  as a catalyst at 150, 180, and 200°C, respectively. Barbier-Baudry et al.<sup>28</sup> synthesized PCL macromonomers with a weight-average molecular weight ( $M_w$ ) of 3000–5000 g/mol under microwave irradiation from commercial CL, using commercial hydrated lanthanide halides as catalysts. We investigated the  $\text{Sn}(\text{Oct})_2$  and zinc powder catalyzed ROP of CL in a microwave oven with a frequency of 2.45 GHz, resulting in a PCL with high  $M_w$  [124,000 g/mol for  $\text{Sn}(\text{Oct})_2$  and 92,300 g/mol for zinc powder, respectively] at around 200°C,<sup>29</sup> indicating that dielectric heating has great influence on the ROP.

Based on our previous work, the heating characteristics of CL monomer and polymerization reaction mixture of CL with  $\text{Sn}(\text{Oct})_2$  under microwave irradiation were examined in a multimode microwave oven with various amounts of materials and microwave power levels. The vacuum  $\text{Sn}(\text{Oct})_2$ -catalyzed ROP of CL was investigated as well. A high effective ROP of CL was induced by a 680-W microwave irradiation, resulting in PCL with  $M_w$  of 123,000 g/mol and yield of 95% within 5 min. The results are presented in this study.

## EXPERIMENTAL

### Materials

$\epsilon$ -Caprolactone (99%; Aldrich, Milwaukee, WI) was used without further purification.  $\text{Sn}(\text{Oct})_2$  was distilled under vacuum and dissolved in freshly dried toluene. PCL ( $M_w = 80,000$  g/mol) was a gift of Solvay (Brussels, Belgium). All other reagents were analytical grade and used as received.

### Microwave equipment

A 2.45-GHz multimode microwave oven (Whirlpool-JA203) with a maximum output power of 850 W was applied in our study. The output power could be performed at 10 different levels by a power on-off cycle. The temperature of materials was measured by inserting a thermocouple into a self-made ampoule.

### Measurement

A  $^1\text{H}$ -NMR spectrum was recorded on a Mercury VX-300 spectrometer using tetramethylsilane (TMS) as

an internal standard and  $\text{CDCl}_3$  as solvent. Weight-average molar mass ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) of PCL were determined by gel permeation chromatography (GPC) on a Waters (Milford, MA) HPLC system equipped with a Model 2690D separation module, a Model 2410 refractive index detector, and a Shodex K803 column. Chloroform was used as eluant at a flow rate of 1.0 mL/min. GPC data were calibrated by standard polystyrene.

### Thermal effect of microwave on $\epsilon$ -caprolactone

A certain amount of CL was put into a vacuum-sealed silanized ampoule, after which it was irradiated at pointed microwave power for 30 min and the temperature was recorded every minute.

### Microwave-assisted ROP

The typical procedure was as follows. A mixture of CL with 0.1% of  $\text{Sn}(\text{Oct})_2$  was put into a silanized ampoule that was sealed under vacuum after three dry-nitrogen/exhaust cycles. The mixture in the vacuum-sealed ampoule was irradiated at pointed microwave power for a predetermined time. During the polymerization, the temperature was measured every minute and the data were collected. At the end of the reaction, the ampoule was immediately removed from the microwave oven and immersed in ice water. The crude solid product was dissolved in methylene chloride and precipitated by methanol. The precipitate was filtrated out and dried under vacuum at ambient temperature.

### ROP by conventional heating method

The thermal polymerization was carried out with a salt bath at 210°C for 60 min. The temperature of polymerization was measured every minute and the data were collected. The purification procedure was the same as that of the microwave method.

## RESULTS AND DISCUSSION

The structure of the precipitate was confirmed as PCL by  $^1\text{H}$ -NMR and the spectrum accorded with that of the standard sample ( $M_w = 80,000$ ; Solvay).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 1.4 (Ha, 2H), 1.7 (Hb+c, 4H), 2.3 (Hd, 2H), 4.1 (He, 2H) (Fig. 1).

### Thermal effect of microwave energy on $\epsilon$ -caprolactone

The heating characteristics of CL under microwave irradiation (MI) were investigated at four levels of microwave power (170, 340, 510, and 680 W) with CL in the amount of 1, 5, 10, 15, and 20 g, designated as

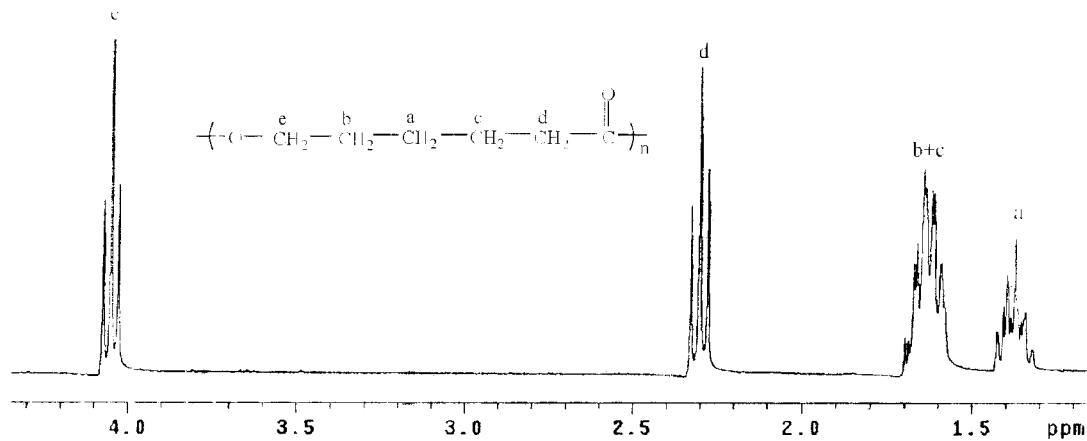


Figure 1 <sup>1</sup>H-NMR spectrum of poly(ε-caprolactone) with  $M_w$  123,000 g/mol.

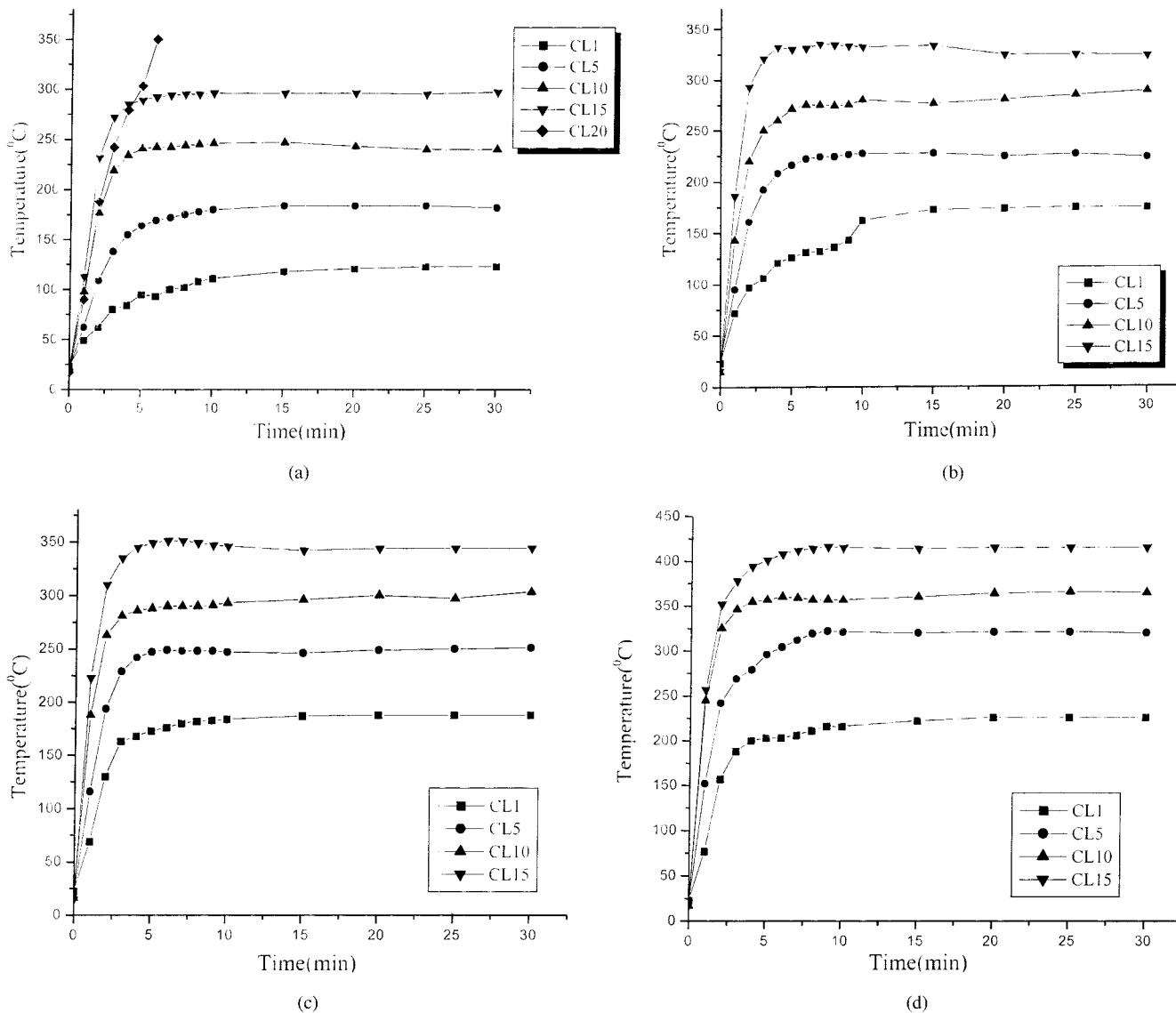
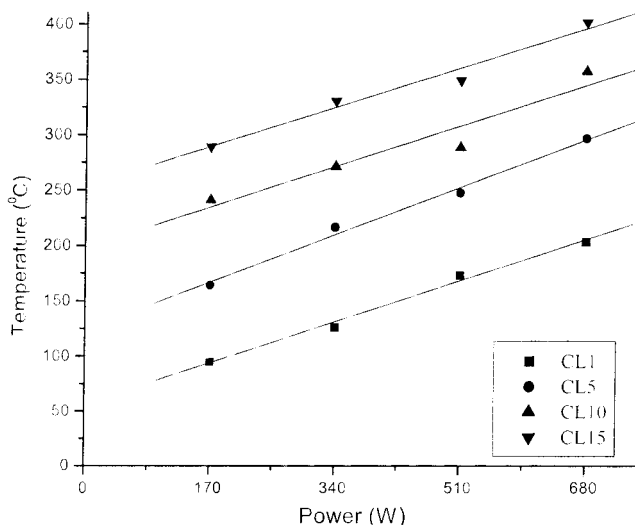


Figure 2 Temperature profile of ε-caprolactone under microwave irradiation: (a) 170 W; (b) 340 W; (c) 510 W; (d) 680 W.



**Figure 3** Temperature–power curve of  $\epsilon$ -caprolactone (5 min).

CL1, CL5, CL10, CL15, and CL20, respectively (Fig. 2). A rapid increase in temperature was recorded within 5 min. For example, when CL15 was irradiated at 170 W for 5 min its temperature increased to 289°C, which was 271° higher than that before irradiation (18°C). At this moment, the increased temperature was 72° for CL1, 143° for CL5, 219° for CL10, and 286° for CL20 [Fig. 2(a)]. After that period of time the temperature of all samples of CL, except CL20, increased slowly and steadily. The difference in temperature between the second 5 min (from 5 to 10 min) was only 6, 16, 5, and 7° for CL1, CL5, CL10, and CL15, respectively. Irradiated for only 6 min, CL20 exploded and was not investigated further in the present study. The temperature of each sample of CL was self-regulated to wave around a constant value when the irradiation time lasted more than 15 min, which indicated that a thermal equilibrium was established. The mode of increase in temperature of CL at the other three power levels was the same as that at 170 W (Fig. 2).

As a rule, for the four power levels, the higher the power, the higher the temperature. A linear relationship between the temperature of CL and the power level was observed when it was irradiated for 5 min (Fig. 3). The differences in temperature by power increasing from 170 to 680 W ranged from 80 to 120° for the four samples.

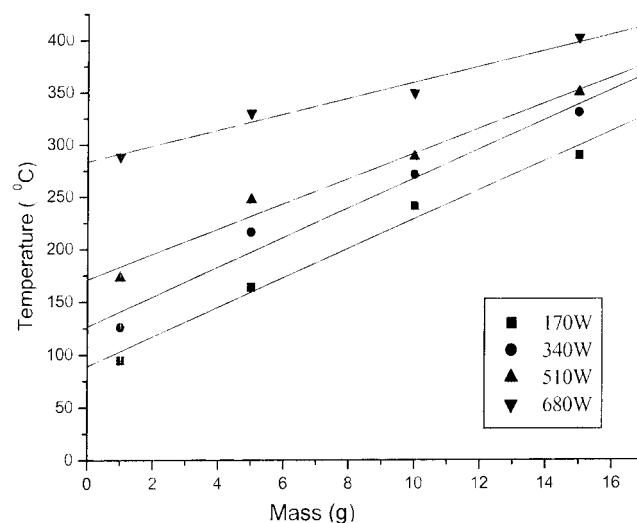
The mass of CL also had a strong influence on its heating characteristics and an increase in temperature was induced by increased amounts. Irradiated at 170 W for 5 min, the temperature of CL increased from 95 to 250°C when the mass of CL was increased from 1 to 15 g, which meant a difference of 155°. At 340, 510, and 680 W, the difference was 150, 150, and 100°, respectively (Fig. 4).

### Heating characteristics of microwave ROP of $\epsilon$ -caprolactone

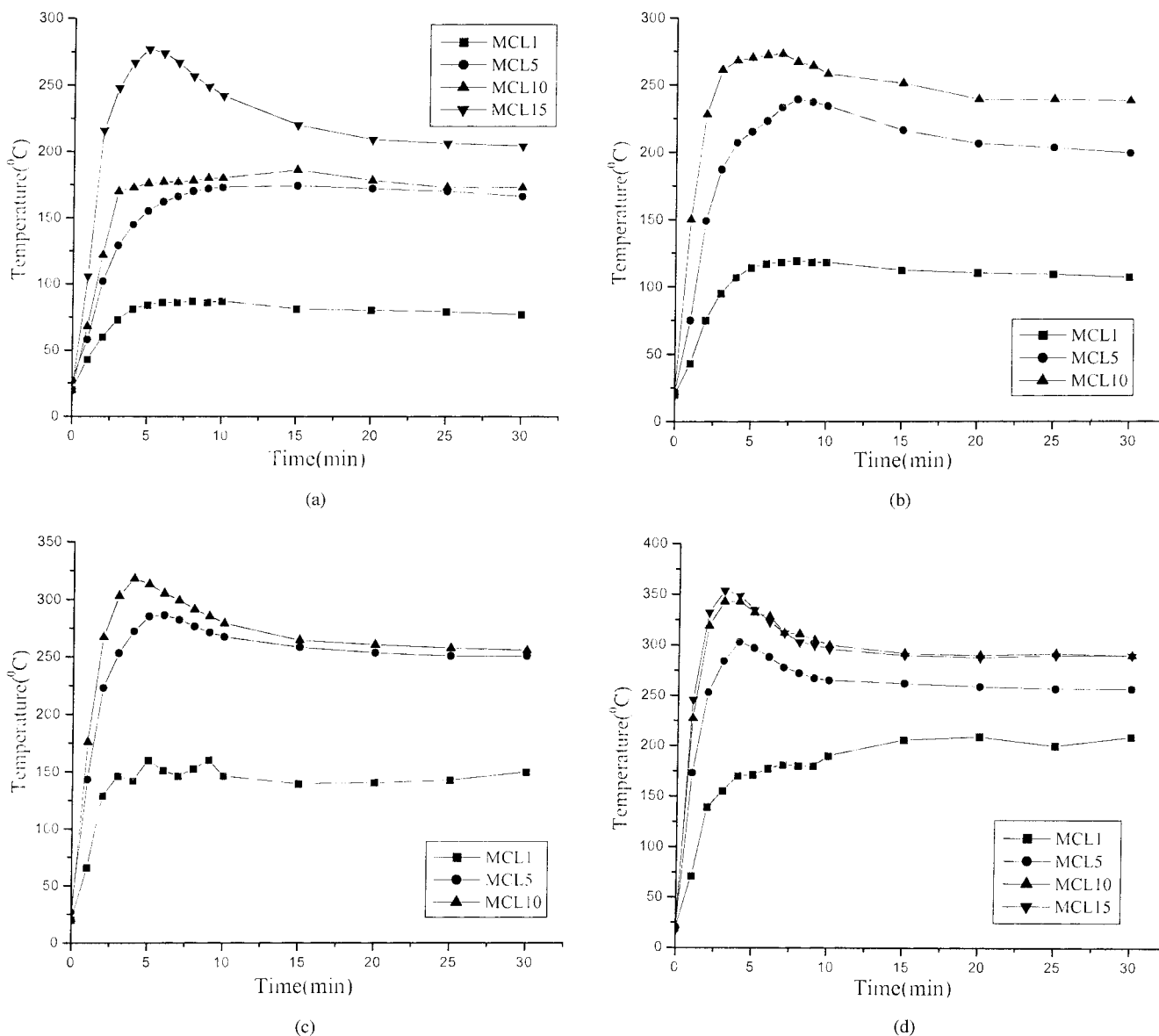
It was reported that the heating characteristics of ROP of CL with  $\text{Sn}(\text{Oct})_2$  as catalyst under MI were similar to those of pure CL and the equilibrium temperature was slightly lower.<sup>29</sup> Our present investigation revealed that in some cases the heat generation of a mixture of CL with  $\text{Sn}(\text{Oct})_2$  (MCL), which underwent a ROP under MI, was observed before the temperature was self-regulated to equilibrium.

The polymerization mixture of CL1 with  $\text{Sn}(\text{Oct})_2$  is designated as MCL1 in the discussion below and MCL5, MCL10, and MCL15 are defined accordingly. The results in Figure 5 show that an exothermic peak appeared in the thermograms of MCL10 at four power levels (although that at 170 W was small), and it was also observed from the thermograms of MCL5 at 340, 510, and 680 W as well as MCL15 at 170 and 680 W (Table I). An exothermic peak appeared when the equilibrium temperature of MCL was over 170°C except for MCL1 at 680 W, which had an equilibrium temperature of 209°C but without an obvious exothermic peak in the thermogram. The time for highest temperature of the exothermic peak ranged from 3 to 13 min, depending on both mass of MCL and irradiation power.

On the other hand, the equilibrium temperature of MCL was not always below that of CL during the irradiation. The relationship between the temperatures of MCL and CL is summarized as four types in Figure 6 by simplified models. Type 1 and Type 2 both show that the temperature of MCL was below that of CL during the whole period of irradiation time, although Type 2 contained an exothermic peak. Type 3 shows that the temperature of the exothermic peak of MCL was greater than the equilibrium temperature of



**Figure 4** Temperature–mass curve of  $\epsilon$ -caprolactone (5 min).



**Figure 5** Temperature profile of microwave-assisted ROP of  $\epsilon$ -caprolactone [0.1% Sn(Oct)<sub>2</sub>, 30 min]: (a) 170 W; (b) 340 W; (c) 510 W; (d) 680 W.

CL. By Type 4, both the temperature of the exothermic peak and the equilibrium temperature of MCL were greater than the equilibrium temperature of CL within 20 min. The classification of MCL and detailed data are listed in Table I.

#### Rapid ROP under microwave irradiation

In our previous study,<sup>29</sup> it was revealed that ROP of CL was carried out effectively under microwave irradiation and no decomposition of the monomer and polymer occurred even if the temperature of polymerization mixture was around 200°C. However, by the conventional heating method, the color of polymerization mixture quickly turned yellow, brown, and dark when its temperature was over 140°C, indicating the

occurrence of decomposition. As a result of that, commercial PCL was generally prepared below that temperature for 10 h or days to obtain a product with high  $M_w$  and yield.

To understand the influence of microwave thermal effect on the ROP, it was carried out around 80, 110, 140, and 210°C, respectively, regulated simply by irradiating MCL1 at 170, 340, 510, and 680 W (Fig. 5). The  $M_w$ -temperature curve (Fig. 7) shows that the  $M_w$  of PCL depended on polymerization temperature, which increased from below 40,000 to over 120,000 g/mol with the temperature from 110 to 210°C. It was deduced that the ROP was greatly enhanced at high temperature.

As shown in Figure 5, two kinds of thermograms were recorded from MCL attributed to its heating

**TABLE I**  
**Temperature of  $\epsilon$ -Caprolactone (CL) and Polymerization Reaction Mixture (MCL) Under Microwave Irradiation**

Type	CL mass (g)	Power (W)	$T_{CL}^a$ ( $^{\circ}C$ )	$T_{MCL}^b$ ( $^{\circ}C$ )	$T_{EXO}^c$ ( $^{\circ}C$ )
1	1	170	123	77	—
	1	340	174	107	—
	1	510	188	149	—
	1	680	226	209	—
	5	170	182	166	—
2	10	170	240	173	186
	10	340	288	238	286
	10	680	365	290	362
	15	170	297	204	285
	15	680	415	290	391
3	5	340	223	199	238
	5	680	320	257	321
	10	510	303	255	335
4	5	510	251	251	288

<sup>a</sup> Temperature of CL at 30 min.

<sup>b</sup> Temperature of MCL at 30 min.

<sup>c</sup> The highest temperature of exothermic peak of MCL.

characteristics under MI. It was noted that an exothermic peak was observed from all the thermograms of MCL10 but not from that of MCL1. Thus, the ROPs of MCL10 and MCL1 were selected as models to investigate the effect of MI.

Irradiated at 680 W for only 1 min, MCL10 turned viscous, confirming the occurrence of polymerization. At 3 min, the yield reached 90%, resulting in PCL with  $M_w$  of 52,400 g/mol ( $M_w/M_n$  1.82). Irradiated for 5 min, the ROP was nearly completed and PCL with high  $M_w$  and yield (123,000 g/mol and 95%) was obtained. When the ROP of MCL10 at 680 W extended to 15 and 60 min,  $M_w$  of PCL decreased to 65,800 g/mol ( $M_w/M_n$  2.60) and 33,000 g/mol ( $M_w/M_n$  2.65) and the yield also decreased to 92 and 86%, respectively [Fig. 8(a)]. The results showed that the polymerization accelerated between 3 and 5 min. Interestingly, the exothermic peak appeared just within the same period of time (from 2 to 5 min) and the temperature of the exothermic peak was over 300 $^{\circ}C$  with the maximum of 343 $^{\circ}C$  at 3 min [Fig. 8(a)]. The exothermic peak seemed to be induced by a rapid polymerization of CL at high temperature. Meanwhile, at 680 W for 15 min PCL with  $M_w$  70,000 g/mol and yield of 80% was formed from the polymerization of MCL1, which was carried out around 210 $^{\circ}C$ , and for 30 min its  $M_w$  increased to over 120,000 g/mol and the yield was around 90% [Fig. 8(b)].

The results verified that ROP of CL under MI was much faster than that by the conventional heating method. At the same power level (680 W), the thermal effect of microwave energy on the larger-scale monomer (MCL10, 300 $^{\circ}C$ ) was stronger than that on the smaller one (MCL1, 210 $^{\circ}C$ ) and the polymerization at higher temperature (>300 $^{\circ}C$  for 5 min,  $M_w$  123,000

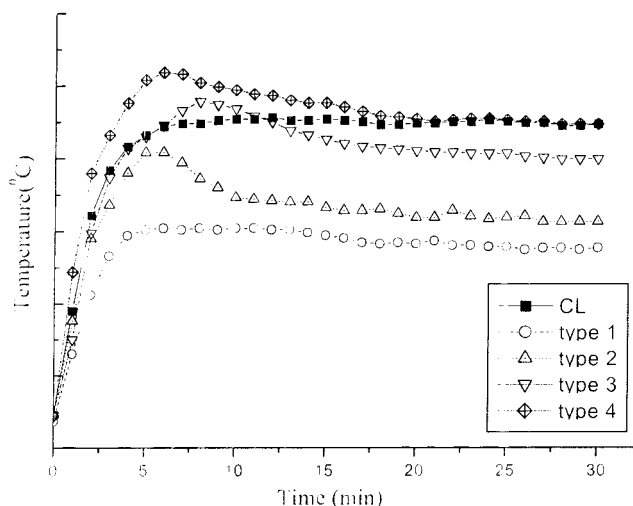
g/mol) was much faster than that at the lower (210 $^{\circ}C$  for 15 min, 70,000 g/mol); the greatest  $M_w$  of PCL from MCL10 (123,000 g/mol) was nearly the same as that from MCL1 (124,000 g/mol at 30 min). It is concluded that under MI, PCL with a high  $M_w$  can be synthesized either by conducting ROP of CL over 300 $^{\circ}C$  in several minutes or by prolonging its time to tens of minutes around 200 $^{\circ}C$ .

When MCL10 was irradiated at 170 W for 5 min, its temperature was only 175 $^{\circ}C$  and  $M_w$  of the obtained PCL was 51,500 g/mol ( $M_w/M_n$  1.97) with a yield of 90%. The result showed that for the same scale of CL (MCL10), a lower microwave power (170 W) produced a lower thermal effect (175 $^{\circ}C$ ) and thus slower polymerization compared with the result at 680 W.

As shown in Figure 9, an exothermic peak was also observed at 4–10 min when MCL10 was heated at 210 $^{\circ}C$  by the conventional method. The temperature of MCL10 rose to the highest temperature of 229 $^{\circ}C$  at 7 min and then remained at 210 $^{\circ}C$  for the subsequent 50 min. The temperature–time curve was similar to that of MCL5 under MI at a power of 340 W (Fig. 5). Irradiated at 340 W, the equilibrium temperature of MCL5 was around 200 $^{\circ}C$  and an exothermic peak appeared between 4 and 15 min with the maximum at 8 min. Obviously, the similarity between the heating characteristics of the two systems was induced mainly by the temperature factor.

## CONCLUSIONS

The thermal equilibrium was established when  $\epsilon$ -caprolactone was under microwave irradiation for more than 15 min. A higher level of microwave power and a larger amount of CL induced higher equilibrium temperature. Stannous octoate-catalyzed ring-opening polymerization of CL under microwave irradiation



**Figure 6** Comparison of thermograms of  $\epsilon$ -caprolactone and polymerization reaction mixture.

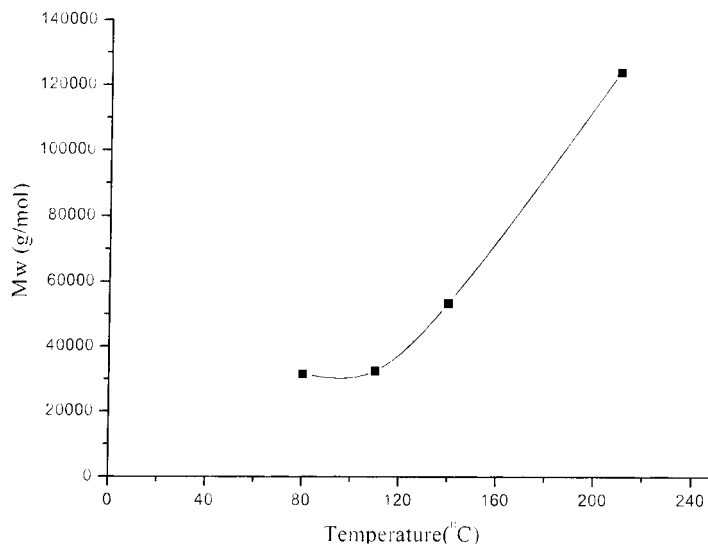
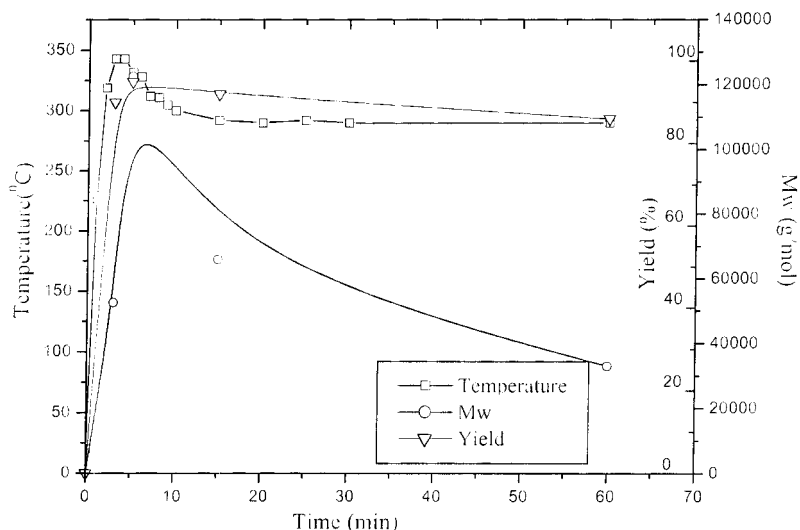
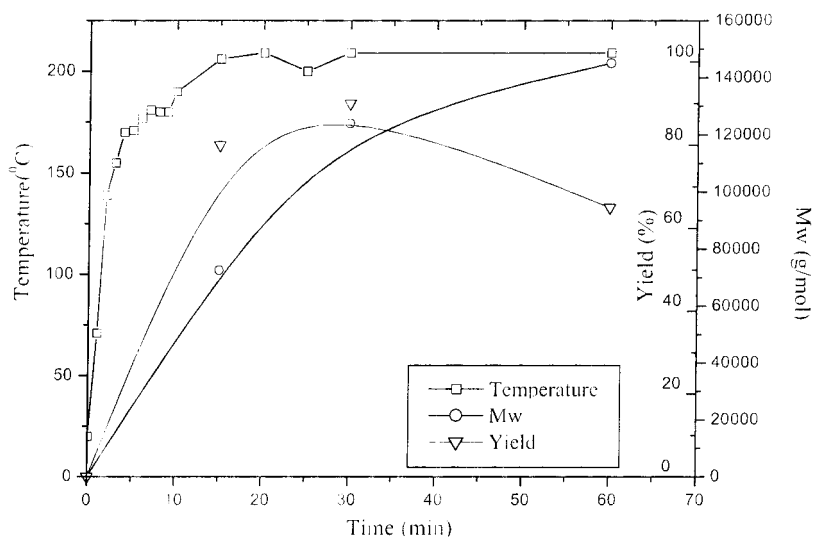


Figure 7 Thermal effect of microwave on ROP of  $\epsilon$ -caprolactone [0.1% Sn(Oct)<sub>2</sub>, 30 min].

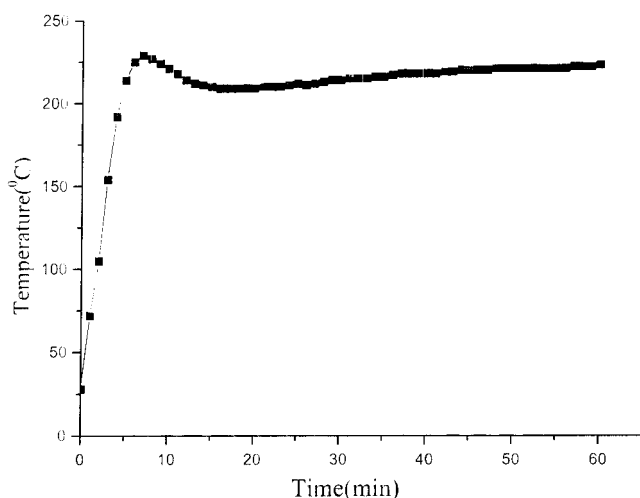


(a)



(b)

Figure 8 Temperature, yield, and  $M_w$  versus time plots of ROP (680 W): (a) MCL10; (b) MCL1.



**Figure 9** Temperature profile of ROP of  $\epsilon$ -caprolactone by conventional method (MCL10, 210°C, 60 min).

tion was determined to be heat generating by an exothermic peak in its thermogram, which was recorded when the equilibrium temperature of the polymerization reaction mixture was more than 170°C. PCL with high  $M_w$  can be synthesized either by conducting ROP of CL under microwave irradiation over 300°C in several minutes or by prolonging its time to tens of minutes around 200°C.

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