

# Kinetics Study of $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ Initiated Ring-Opening Polymerization of $\epsilon$ -Caprolactone by Differential Scanning Calorimetry

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**ABSTRACT:** The ring-opening polymerization of  $\epsilon$ -caprolactone initiated by  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  was investigated by differential scanning calorimetry (DSC). Both isothermal and dynamic experiments have been applied to obtain the kinetic parameters. The apparent polymerization rate constant for different experiments was determined; the activation energy determined is 76–88 kJ/mol by the isothermal method and 75–86 kJ/mol by the dynamic method. Using the obtained kinetic parameters, a model to predict the polymerization process was developed and can well describe

the polymerization process, which demonstrates that DSC is a convenient and reliable method to study the kinetics of ring-opening polymerization. The kinetic results also demonstrate that  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  is an efficient initiator in the ring-opening polymerization of  $\epsilon$ -caprolactone. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3990–3998, 2008

**Key words:** titanium alkoxide;  $\epsilon$ -caprolactone; ring-opening polymerization; kinetics (polym.); differential scanning calorimetry (DSC)

## INTRODUCTION

Because of their biodegradability, permeability, and good compatibility with many other polymers, poly( $\epsilon$ -caprolactone) (PCL), its copolymers, and PCL-based blends have been investigated worldwide for all kinds of purpose, such as pharmacological, biomedical, agricultural, and environmental,<sup>1–5</sup> which provide PCL a great potential of application. Up to now, there are many ways to prepare PCL, but the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone initiated by metal alkoxides, such as aluminum,<sup>6,7</sup> tin,<sup>8</sup> magnesium,<sup>9</sup> zinc,<sup>10</sup> and titanium derivatives,<sup>8,11</sup> is the most practical and convenient strategy. Among those initiators, titanium alkoxides attract much attention because of their good initiating activities. The first report on the use of titanium alkoxide in ROP was published in 1958 by Hall and Schneider.<sup>12</sup> Since then great effort had been spent on the design and synthesis of the new initiators derived from titanium alkoxide, especially which can provide good control of the polymerization or can be used to prepare functional PCL.

For a long time, differential scanning calorimetry (DSC) has been applied as an efficient and reliable method to study the kinetics of polymeric materials. DSC provides a continuous history of the heat evolved during the polymerization, which can be interpreted into the information concerning the kinetics of the polymerization.<sup>13–17</sup> In this study, both isothermal and dynamic DSC experiments were carried out to investigate the ROP kinetics of  $\epsilon$ -caprolactone initiated by  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ , a new initiator which is expected to be used to prepare double-bond capped PCL.

## EXPERIMENTAL

### Materials

$\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  was synthesized according to the method described in the previous study.  $\epsilon$ -Caprolactone (Solvay Company, Warrington, United Kingdom, 99%) was dried over calcium hydride ( $\text{CaH}_2$ ) for 1 day at room temperature, then vacuum distilled, and stored in a well-sealed bottle.

### Polymerization of $\epsilon$ -caprolactone

The mixture of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  and  $\epsilon$ -caprolactone used in DSC experiments is prepared according to the following description:  $\epsilon$ -caprolactone (50 g,

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TABLE I  
Molecular Weight of PCL from Isothermal and Dynamic DSC Polymerization

DPn(set)	$M_n^T$	Isothermal DSC polymerization				Dynamic DSC polymerization			
		$T$ ( $^{\circ}\text{C}$ )	$M_n$	$M_w$	$M_w/M_n$	Ramp ( $^{\circ}\text{C}/\text{min}$ )	$M_n$	$M_w$	$M_w/M_n$
100	11,500	170	9,800	22,800	2.33	2	9,700	21,600	2.05
		175	9,800	20,600	2.10	5	9,500	20,700	1.97
		180	9,400	22,200	2.36	10	9,800	19,900	2.03
		185	9,600	20,800	2.17	15	10,100	20,900	2.07
		190	10,800	20,000	1.85	20	96,00	19,200	2.00
150	17,200	170	16,800	36,400	2.17	2	15,800	37,200	2.35
		175	16,000	36,300	2.27	5	16,600	34,500	2.09
		180	15,600	34,700	2.22	10	16,500	38,200	2.32
		185	20,300	41,400	2.04	15	15,900	35,700	2.25
		190	15,100	34,800	2.30	20	16,700	37,200	2.23
200	22,900	170	21,200	39,500	1.86	2	19,100	39,600	2.07
		175	20,900	39,100	1.87	5	19,300	39,900	2.07
		180	23,700	45,300	1.91	10	21,300	41,900	1.97
		185	21,300	40,600	1.91	15	22,400	39,500	1.76
		190	24,000	46,800	1.95	20	19,300	38,500	1.99

0.44 mol) and  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  (1.1137 g,  $2.19 \times 10^{-3}$  mol) were charged into a dry flask and stirred for 15 min at room temperature to get a homogeneous solution. For the other mixtures, only the molar ratio of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  to  $\epsilon$ -caprolactone was changed according to the set degree of polymerization, DPn(set), which is defined by the following equation.

$$\text{DPn(set)} = \frac{w_{\text{CL}}/M_{\text{CL}}}{4 \times w_{\text{Ti}}/M_{\text{Ti}}} = \frac{M_0}{4 \times I_0} \quad (1)$$

where  $w_{\text{CL}}$  is the mass of  $\epsilon$ -caprolactone, g;  $M_{\text{CL}}$  is the molecular weight of  $\epsilon$ -caprolactone, g/mol;  $w_{\text{Ti}}$  is the mass of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ , g;  $M_{\text{Ti}}$  is the molecular weight of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ , g/mol;  $M_0$  is the mol quantity of  $\epsilon$ -caprolactone; and  $I_0$  is the mol quantity of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ .

All DSC experiments were performed on a TA DSC Q10 differential scanning calorimeter running under the nitrogen atmosphere (50 mL/min), and the DSC data were analyzed by TA Universal Analysis software, but the linear-fitting analysis was performed with OriginPro7.5 software. For each experiment, about 8 mg mixture was injected into an aluminum hermetic capsule and sealed with a corresponding lid. For the isothermal polymerization, the samples were heated in the DSC cell from the standby temperature  $40^{\circ}\text{C}$  to the specific temperatures at a heating rate of  $30^{\circ}\text{C}/\text{min}$  and were held at the set temperature for 120 min, which ensures the completion of the polymerization. For dynamic polymerization, the samples were heated from  $40$  to  $300^{\circ}\text{C}$  at five different heating rates, 2, 5, 10, 15, and  $20^{\circ}\text{C}/\text{min}$ , respectively.

### Characterization of molecular weight

The number-average molecular weight  $M_n$ , the weight-average molecular weight  $M_w$ , and the poly-

dispersity  $M_w/M_n$  were determined on Waters Alliance GPCV 2000 size exclusion chromatography (SEC) equipped with refractive index detector and viscometer detector. The elution was performed on three 7.8 mm  $\times$  300 mm Waters Styragel columns, Styragel<sup>®</sup> HT 2, Styragel<sup>®</sup> HT 4, and Styragel<sup>®</sup> HT 6E. 1,2,4-Trichlorobenzene (TCB, >99%) was used as an eluent at  $135^{\circ}\text{C}$  and the flow rate was 1.0 mL/min. The instrument was calibrated by narrow standard polystyrene. PCL prepared in DSC experiment was first hydrolyzed and vacuum dried, then solutions of PCL were prepared in TCB, and filtered on a filter plate (0.45  $\mu\text{m}$  pore size) before injection.

## RESULTS AND DISCUSSION

### Molecular weight of PCL

As shown in Table I, the molecular weight determined by SEC was corrected by PCL standards and they are compared with the theoretical number-average molecular weight,  $M_n^T$ , which is calculated by eq. (2).

$$M_n^T = \text{DPn(set)} \times M_{\text{CL}} + M_{-\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2} \quad (2)$$

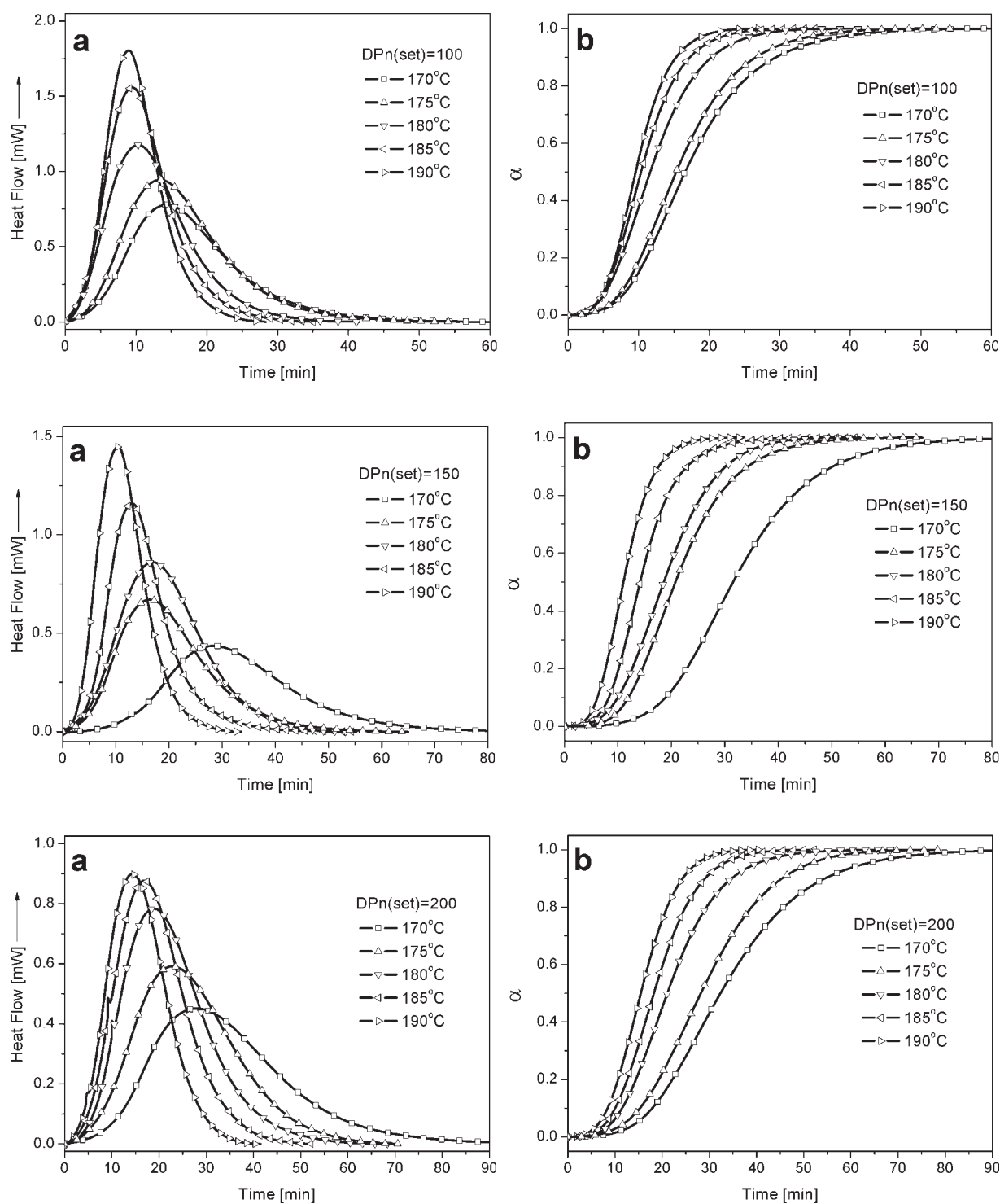
where  $M_{\text{CL}}$  is the molecular weight of  $\epsilon$ -caprolactone,  $M_{-\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2}$  is the molecular weight of one alkoxide arm in  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ .

The results in Table I show that the molecular weight of PCL from DSC polymerization is close to  $M_n^T$ , this agreement indicates that all alkoxy groups of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  are active in initiation of the polymerization in DSC.

### Polymerization kinetics evaluated by DSC

Isothermal DSC polymerization of  $\epsilon$ -caprolactone

In the isothermal DSC polymerization of  $\epsilon$ -caprolactone, the measured heat flow,  $\Delta H_t/\Delta H$ , is



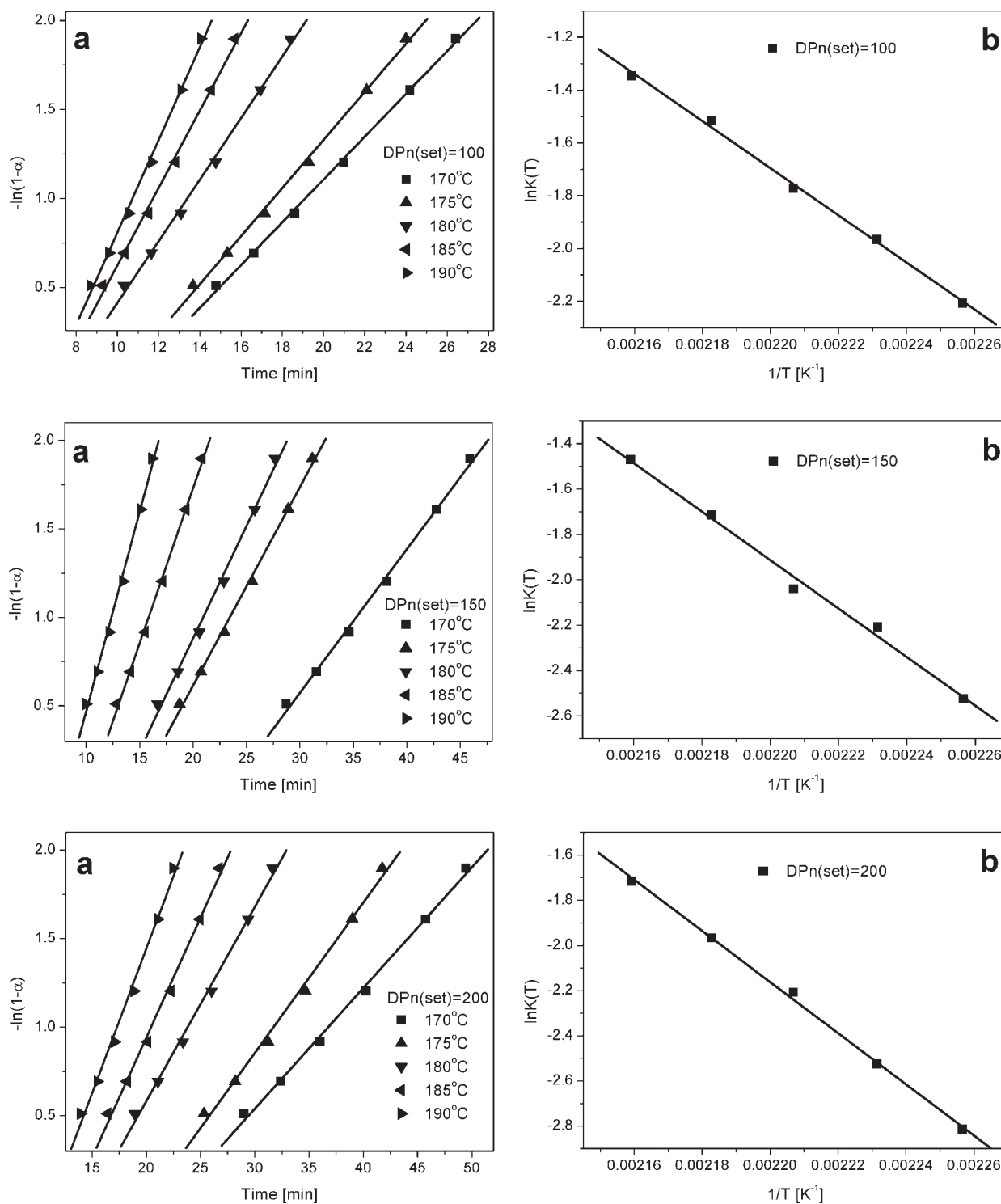
**Figure 1** (a) Thermograms of isothermal DSC polymerization; (b) conversion  $\alpha$  as a function of polymerization time of isothermal DSC polymerization.

proportional to the extent of polymerization, i.e., the conversion of monomer. Therefore, the conversion of  $\epsilon$ -caprolactone  $\alpha$  during the polymerization at a specific time  $t$  can be defined by the following equation.

$$\alpha_t = \frac{\Delta H_t}{\Delta H} \quad (3)$$

where  $\Delta H_t$  is the heat generated up to time  $t$  and  $\Delta H$  is the total heat generated during the entire polymerization.

Meanwhile, the measured heat flow,  $dH/dt$ , is proportional to the polymerization rate, which can be obtained by differentiating  $\alpha$  with respect to  $t$ , as expressed by eq. (4).



**Figure 2** (a)  $-\ln(1-\alpha)$  as a function of polymerization time  $t$ ; (b)  $\ln[k(T)]$  as a function of  $1/T$ .

$$\frac{d\alpha}{dt} = k(T)f(\text{cat})f(\alpha) \quad (4)$$

where  $k(T)$  is the rate constant,  $f(\text{cat})$  is the concentration dependent function of catalyst, and  $f(\alpha)$  is the concentration dependent function of  $\epsilon$ -caprolactone

monomer. The dependence of  $k(T)$  on temperature can be given by Arrhenius expression.

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

**TABLE II**  
The Apparent Polymerization Rate Constant  $K(T)$   
Determined by Isothermal DSC Polymerization

$T$ (°C)	DPn(set)		
	100 (s <sup>-1</sup> )	150 (s <sup>-1</sup> )	200 (s <sup>-1</sup> )
170	0.11	0.08	0.06
175	0.14	0.11	0.08
180	0.17	0.13	0.11
185	0.22	0.18	0.14
190	0.26	0.23	0.18

where  $E_a$  is the activation energy,  $k_0$  is the frequency factor,  $T$  is the Kelvin temperature, and  $R$  is the universal gas constant.

As proved in the previous study, for  $\epsilon$ -caprolactone,  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  initiated bulk ROP is first order in monomer, the rate of reaction is proportional to the concentration of unreacted monomer. Therefore,  $f(\alpha)$  can be given by eq. (6).

$$f(\alpha) = (1 - \alpha) \quad (6)$$

Assuming that the growing species have the same catalytic activities with that of alkoxy groups of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  throughout the polymerization,  $f(\text{cat})$  can be given by eq. (7).

$$f(\text{cat}) = [\text{C}_{\text{cat}}]^n \quad (7)$$

where  $n$  is the reaction order of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$ .

Combining eqs. (4)–(7), the polymerization rate can be described by the following equation.

$$\frac{d\alpha}{dt} = k(T)[\text{C}_{\text{cat}}]^n(1 - \alpha) = k_0 \exp\left(-\frac{E_a}{RT}\right)[\text{C}_{\text{cat}}]^n(1 - \alpha) = K(T)(1 - \alpha) \quad (8)$$

where  $K(T)$  is the apparent polymerization rate constant, as given by eq. (9).

$$K(T) = k(T)[\text{C}_{\text{cat}}]^n = k_0 \exp\left(-\frac{E_a}{RT}\right)[\text{C}_{\text{cat}}]^n \quad (9)$$

From eq. (8), the following equation can be obtained, which can be used to determine  $K(T)$ .

$$\ln(1 - \alpha) = K(T)(t - t_0) \quad (10)$$

where  $t_0$  is the time delay in DSC polymerization.

To obtain the kinetics parameters, isothermal DSC experiments have been performed at five different temperatures on  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  initiated polymerization of  $\epsilon$ -caprolactone with three different DPn(set). The isothermal DSC thermograms are shown in Figure 1.

The plots of  $-\ln(1 - \alpha)$  vs.  $t$  are shown in Figure 2(a) and  $K(T)$  is determined from the slope of those plots. The results are summarized in Table II.

The  $E_a$  determined from the slope of  $\ln[K(T)]$  vs.  $1/T$  plot, as shown in Figure 2(b), is presented in Table III.

From the plot of  $\ln[K(T)]$  vs.  $1/T$ , the dependence of  $K(T)$  on temperature for the polymerization of DPn(set) = 100, 150, 200 can be given by the following equations.

$$K(T)_{\text{DPn(set)=100}} = 1.70 \times 10^7 \exp\left(-\frac{9156}{T}\right) \quad (11)$$

$$K(T)_{\text{DPn(set)=150}} = 1.38 \times 10^8 \exp\left(-\frac{10209}{T}\right) \quad (12)$$

$$K(T)_{\text{DPn(set)=200}} = 2.38 \times 10^8 \exp\left(-\frac{10556}{T}\right) \quad (13)$$

According to eq. (8), the conversion  $\alpha$  of  $\epsilon$ -caprolactone can be determined by the following expression.

$$\alpha = 1 - \exp[-K(T)(t - t_0)] \quad (14)$$

where  $t_0$  is the time delay in DSC polymerization, which is equal to the intercept of time axis in the plot of  $-\ln(1 - \alpha)$  vs.  $t$ , as shown in Figure 2.

Combining eqs. (11)–(13) and eq. (14), the model for predicting the monomer conversion as a function of reaction time can be developed, and Figure 3 shows the comparison between the DSC experiment and polymerization process described by the model. It shows that for all the polymerization, the developed model can well describe the polymerization process when the monomer conversion is higher than 20%.

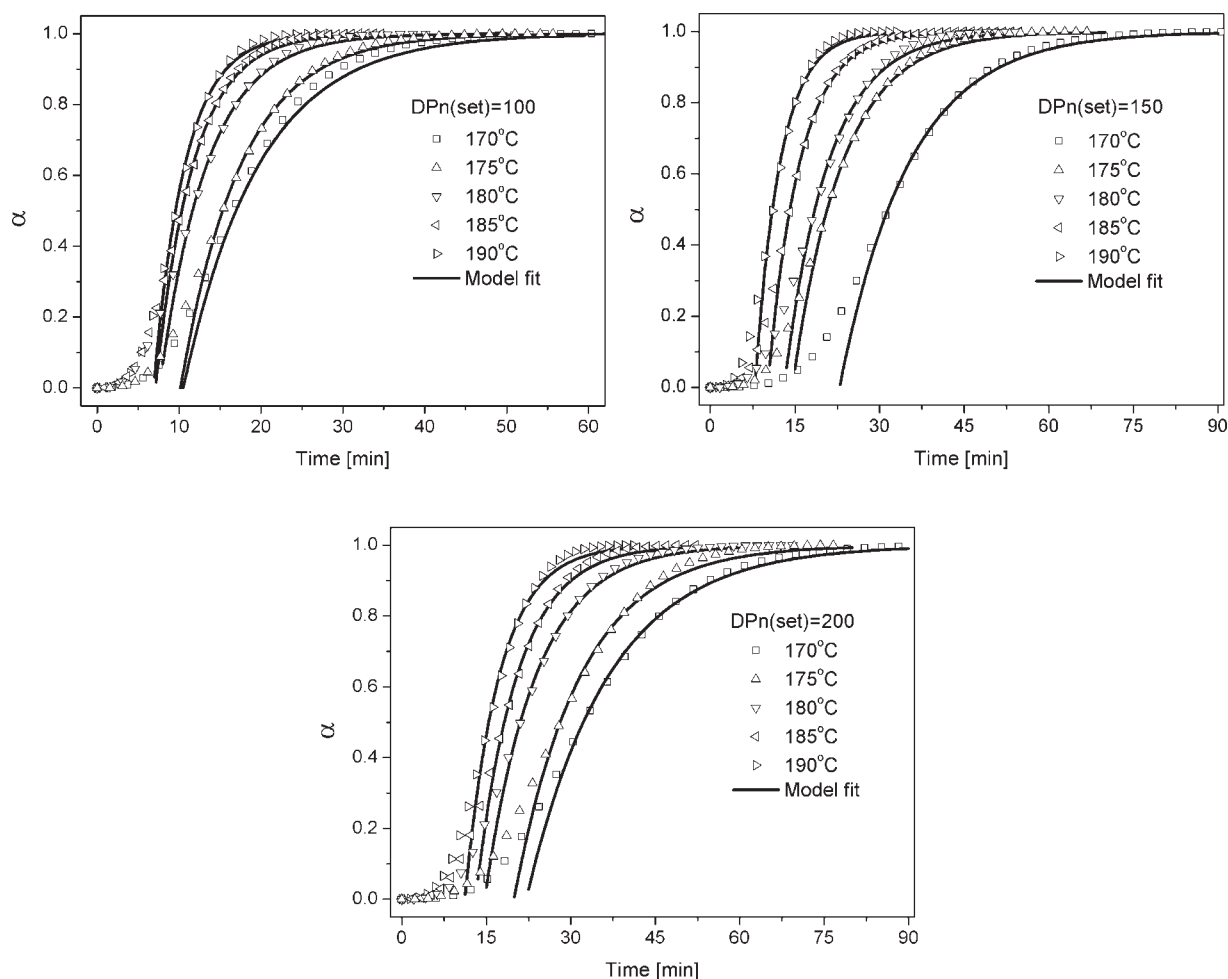
According to eq. (9), the reaction order of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  in the ROP of  $\epsilon$ -caprolactone can be derived from the slope of the  $\ln[K(T)]$  vs.  $\ln[\text{C}_{\text{cat}}]$  plot. For a certain DPn(set), the catalyst concentration  $[\text{C}_{\text{cat}}]$  can be calculated by the following equation.

$$[\text{C}_{\text{cat}}] = \frac{1}{4} \times \frac{1000 \times D_{\text{CL}}}{\text{DPn(set)} \times M_{\text{CL}}} = \frac{1030}{4 \times 114.14 \times \text{DPn(set)}} \quad (15)$$

where  $D_{\text{CL}}$  is the density of  $\epsilon$ -caprolactone, 1.03 g/mL at 25°C.

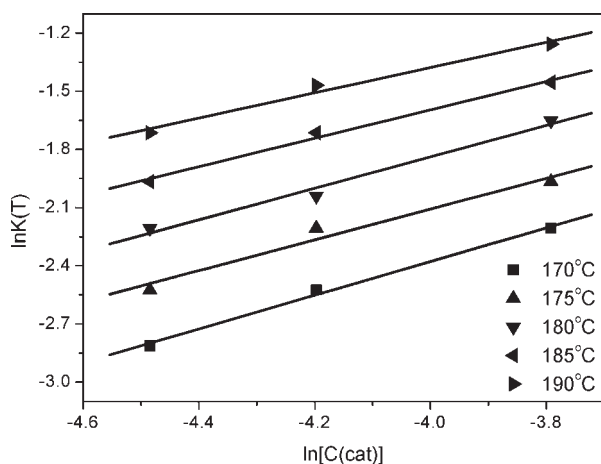
**TABLE III**  
The Activation Energy  $E_a$  Determined by Isothermal  
DSC Polymerization

DPn(set)	$E_a$ (KJ/mol)
100	76
150	84
200	88



**Figure 3** Comparison of conversion versus time between the isothermal DSC experiment data and calculated data using the kinetic parameter determined.

The plots of  $\ln[K(T)]$  vs.  $\ln[C_{\text{cat}}]$  at five different temperatures are shown in Figure 4. The reaction order of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$  was determined by the linear fitting of  $\ln[K(T)]$  vs.  $\ln[C_{\text{cat}}]$  plot, and the



**Figure 4**  $\ln[K(T)]$  as a function of  $\ln[C_{\text{cat}}]$ .

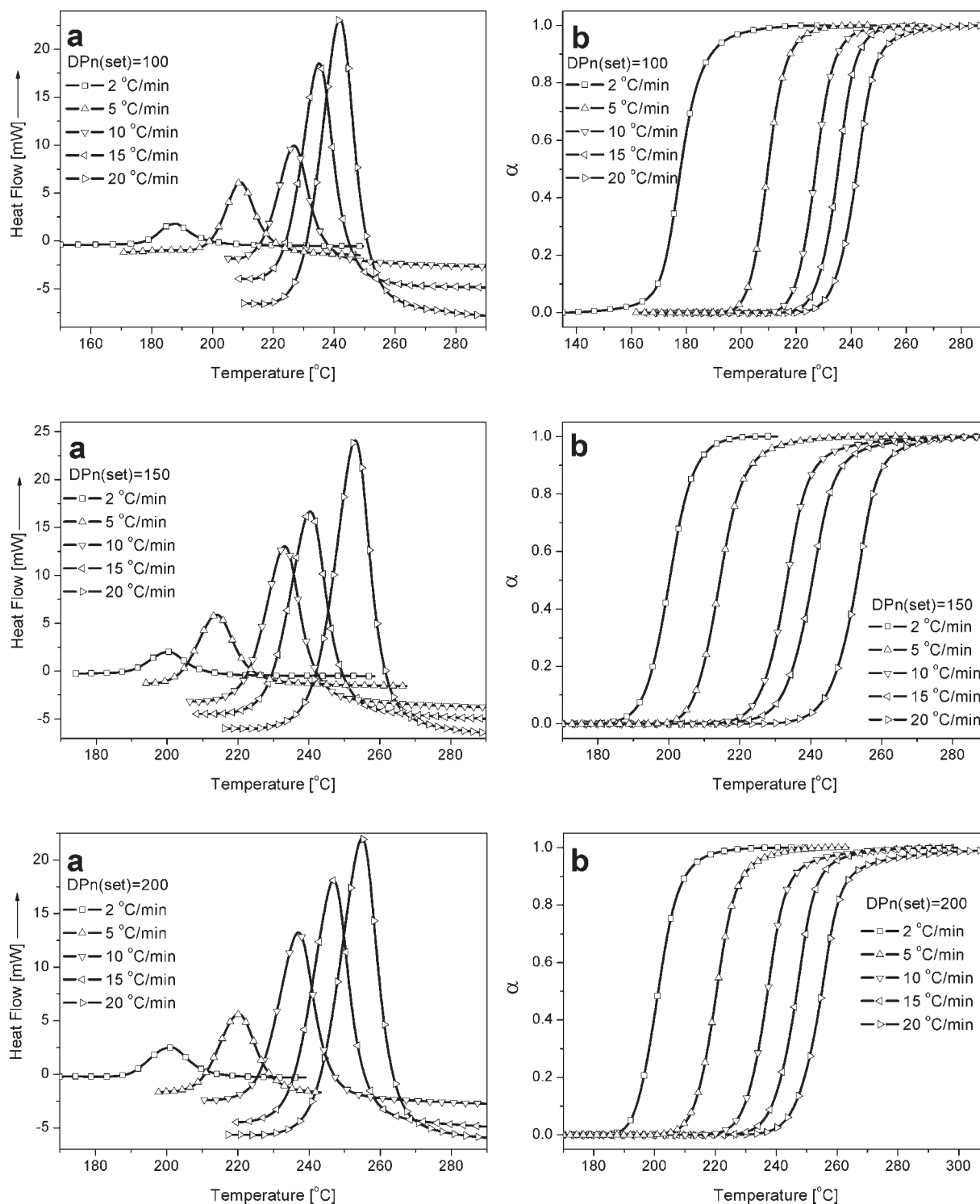
results are presented in Table IV. The results show that for five temperatures, the reaction order is around 0.7.

#### Dynamic DSC polymerization of $\epsilon$ -caprolactone

To compare with the kinetic results determined from isothermal DSC polymerization, dynamic DSC polymerization of  $\epsilon$ -caprolactone has been performed, and the DSC thermograms are shown in Figure 5. For a certain DPn(set), the beginning temperature of

**TABLE IV**  
The Reaction Order of  $\text{Ti}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_4$   
Determined by Isothermal DSC Polymerization

$T$ ( $^{\circ}\text{C}$ )	$n$
170	0.7
175	0.7
180	0.7
185	0.7
190	0.7



**Figure 5** (a) Thermograms of dynamic DSC polymerization; (b) conversion  $\alpha$  as a function of temperature  $T$  in dynamic DSC polymerization.

polymerization increases with increasing of the heating rate and the position of the peak shifts with the heating rate.

During the dynamic experiment, at the specific temperature  $T$ , the conversion  $\alpha$  of  $\epsilon$ -caprolactone can be determined by eq. (16).

$$\alpha_T = \frac{\Delta H_T}{\Delta H} \quad (16)$$

where  $\Delta H_T$  is the heat generated up to temperature  $T$ , and  $\Delta H$  the total heat generated in the dynamic DSC polymerization.

TABLE V  
Values of  $T_m$  and  $T_{50\%}$  at Different Heating Rate

Ramp ( $^{\circ}\text{C}/\text{min}$ )	DPn(set) = 100		DPn(set) = 150		DPn(set) = 200	
	$T_m$ ( $^{\circ}\text{C}$ )	$T_{50\%}$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$T_{50\%}$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$T_{50\%}$ ( $^{\circ}\text{C}$ )
2	187.81	188.19	200.62	200.23	201.33	201.23
5	209.26	209.68	214.26	214.43	220.46	220.43
10	226.82	227.12	233.15	233.35	237.05	237.20
15	235.07	235.25	240.40	240.47	246.89	246.84
20	241.89	242.18	253.11	253.08	254.89	254.99

At the specific temperature, the rate of the polymerization can be given by eq. (17).

$$\frac{d\alpha}{dt} = k(T)f(\text{cat})f(\alpha) = \frac{dH}{dt} \cdot \frac{1}{\Delta H} \quad (17)$$

Incorporating the heating rate, the rate expression can be given by eq. (18).

$$\frac{d\alpha}{dt} = \varphi \frac{d\alpha}{dT} \quad (18)$$

where  $\varphi$  is the linear heating rate,  $dT/dt$ .

From eq. (18), the temperature dependence of the conversion  $\alpha$  can be given by the following equation.

$$\frac{d\alpha}{dt} = \frac{k(T)f(\text{cat})f(\alpha)}{\varphi} \quad (19)$$

When eq. (5) is substituted into eq. (19), the following expression is obtained.

$$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E_a}{RT}\right) f(\text{cat})f(\alpha) \frac{1}{\varphi} \quad (20)$$

When eq. (20) is integrated with respect to temperature  $T$  and conversion  $\alpha$ ,  $g(\alpha)$  is obtained.

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^T \left\{ k_0 \exp\left(\frac{-E_a}{RT}\right) f(\text{cat}) \frac{1}{\varphi} \right\} dT \quad (21)$$

Assuming  $x = -E/RT$  and differentiating  $x$  with respect to  $T$ , eq. (22) is obtained, which can be reorganized into eq. (23).

$$dx = \frac{E_a}{RT^2} dT \quad (22)$$

$$dT = \frac{E_a}{R} \frac{1}{x^2} dx \quad (23)$$

Substituting eq. (23) into eq. (21), and integrating with respect to  $x$ , the following equation is obtained.

$$g(\alpha) = \frac{k_0 f(\text{cat}) E_a}{\varphi R} p(x) \quad (24)$$

where

$$p(x) = \int_{\infty}^x (\exp(-x)/x^2) dx$$

Because the equation  $p(x)$  has no exact integral, several attempts were tried and the results have

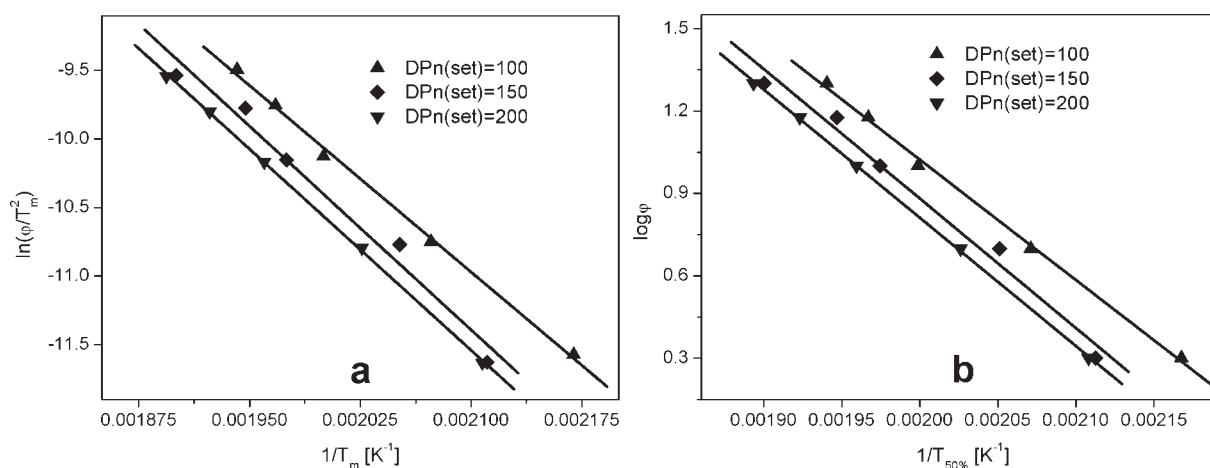


Figure 6 (a)  $\ln(\varphi/T_m^2)$  as a function of  $1/T_m$  according to the Kissinger method; (b)  $\log[\varphi]$  as a function of  $1/T_{50\%}$  according to the Flynn-Wall method.



**TABLE VI**  
The Activation Energy  $E_a$  Determined by Dynamic DSC Polymerization

DPn(set)	$E_a$ (KJ/mol)	
	Kissinger	Flynn–Wall
100	75	80
150	82	86
200	81	85

been used for extensive kinetics studies of polymeric systems.<sup>18,19</sup>

Kissinger<sup>20</sup> used the temperature at which the rate of polymerization is at the maximum and obtained the following relationship regardless of reaction order.

$$\frac{d[\ln(\varphi/T_m^2)]}{d(1/T_m)} = -\frac{E_a}{R} \quad (25)$$

where  $T_m$  is the temperature at which the maximum polymerization rate occurs. The results were showed in Table V. Therefore, the  $E_a$  can be obtained from the slope of a plot of  $\ln(\varphi/T_m^2)$  vs.  $1/T_m$ . The plots of  $\ln(\varphi/T_m^2)$  vs.  $1/T_m$  for different polymerization are shown in Figure 6, and the  $E_a$  obtained from the slope is presented in Table VI.

Using Doyle's approximation of expression of  $\log p(x) \cong -2.315 - 0.457E_a/RT$  for  $E_a/RT > 20$ , Flynn and Wall<sup>21</sup> obtained the following equation.

$$\log g(\alpha) = \log\left(\frac{k_0 f(\text{cat}) E_a}{R}\right) - \log \varphi - 2.315 - 0.457 \frac{E_a}{RT} \quad (26)$$

Equation (26) suggests that the  $E_a$  can be obtained from a plot of  $\log \varphi$  vs.  $1/T$  for a constant  $g(\alpha)$ . Therefore, to determine the  $E_a$  from dynamic DSC polymerization only requires the finding of the temperature at which a constant DPn is achieved at different heating rates. In this study,  $T_{50\%}$ , the temperatures at which 50% polymerization is achieved, were determined and used in the plot of  $\log \varphi$  vs.  $1/T_{50\%}$ , as shown in Figure 6. The values of the  $E_a$  obtained were summarized in Table VI.

The values of  $E_a$  are 75–82 KJ/mol from Kissinger method and 80–86 KJ/mol from Flynn–Wall method, respectively. Comparing with  $E_a$  determined by isothermal DSC polymerization, it shows that  $E_a$  determined by both Kissinger and Flynn–Wall methods from dynamic DSC polymerization is similar with the  $E_a$  derived from the isothermal DSC polymerization, which indicates that both isothermal and

dynamic DSC polymerization give similar kinetic results to describe the ROP polymerization process.

## CONCLUSIONS

Both isothermal and dynamic DSC experiments were performed to investigate the kinetics of Ti[O(CH<sub>2</sub>)<sub>4</sub>OCH=CH<sub>2</sub>]<sub>4</sub> initiated ROP of  $\epsilon$ -caprolactone. The  $E_a$  obtained from isothermal and dynamic DSC polymerization is 76–88 and 75–86 KJ/mol, respectively. The apparent polymerization rate constant was determined from the isothermal DSC experiments. The obtained kinetic parameters were used to develop a model for predicting the monomer conversion as a function of polymerization time, and the polymerization process can be well described by the model. The results of this study demonstrate that DSC is a convenient and reliable alternative to study the kinetics of ring-opening polymerization. The kinetic results also demonstrate that Ti[O(CH<sub>2</sub>)<sub>4</sub>OCH=CH<sub>2</sub>]<sub>4</sub> is an efficient initiator in the ring-opening polymerization of  $\epsilon$ -caprolactone, which can provide the possibility to synthesize double-bond functionalized PCL.

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