CHAPTER 4

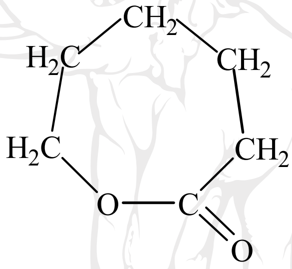
RING-OPENING POLYMERIZATIONS: KINETIC STUDIES

In this part of the research, the kinetics of the bulk ring-opening polymerization of a particular cyclic ester, ε-caprolactone, were studied in detail.

4.1 Design of Kinetic Experiments

4.1.1 Monomer

The cyclic ester monomer that was chosen for these kinetic studies was ε-caprolactone.



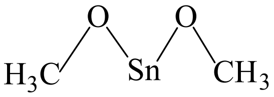
ε-caprolactone (CL)

ring size = 7

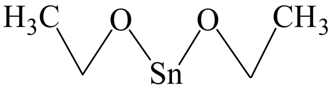
ε-Caprolactone (CL) was chosen mainly because of its easy polymerizability and the fact that not only ε-caprolactone monomer but also poly(ε-caprolactone) is a liquid at the polymerization temperatures used (90 and 140 °C). This avoided the complication of vitrification occurring during the course of the kinetic experiments since dilatometry was to be the main method used for following the progress of the reaction.

4.1.2 Initiators

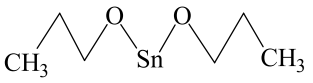
The initiators used for these studies were the series of tin(II) alkoxides described in the previous chapter, namely:



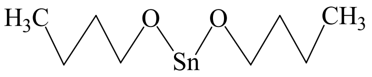
tin(II) methoxide
$Sn(OCH_3)_2$



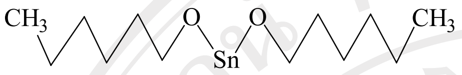
tin(II) ethoxide
$Sn(OC_2H_5)_2$



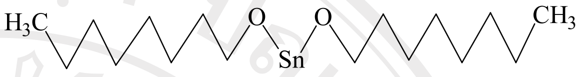
tin(II) propoxide
$Sn(OC_3H_7)_2$



tin(II) butoxide
$Sn(OC_4H_9)_2$



tin(II) hexoxide
$Sn(OC_6H_{13})_2$



tin(II) octoxide
$Sn(OC_8H_{17})_2$

In the past, tin(II) 2-ethylhexanoate (stannous octoate), $Sn(Oct)_2$, has been the most widely used initiator in the literature. However, it is now generally accepted that the $Sn(Oct)_2$ initiator and alcohol (ROH) coinitiator react together *in situ* at the polymerization temperature to form a tin(II) monoalkoxide, OctSnOR, and/or dialkoxide, $Sn(OR)_2$, which then become the 'true' initiator(s) of the polymerization reaction. The reaction between $Sn(Oct)_2$ and ROH can be represented as :

$$Sn(Oct)_2 + ROH \rightleftharpoons OctSnOR + OctH \qquad (4.1)$$

$$OctSnOR + ROH \rightleftharpoons Sn(OR)_2 + OctH \qquad (4.2)$$

where OctH is the octanoic acid by-product. These coupled reactions (4.1) and (4.2) are understood to be reversible although to what extent is still uncertain.

The coordination-insertion mechanism of the ROP of cyclic esters was described previously in Chapter 1. Since the tin(II) monoalkoxide and/or dialkoxide are generated *in situ* in unknown concentrations, and octanoic acid OctH is also formed as an unwanted by-product, it would seem logical to try to synthesize the $Sn(OR)_2$ dialkoxide separately first and then use it directly as the 'true' initiator in an accurately known concentration. This has been the rationale behind this project, especially since $Sn(OR)_2$ dialkoxides with $R > C_4H_9$, for example tin(II) hexoxide and tin(II) octoxide, have apparently not previously been reported as initiators in the ROP of cyclic esters. It is these novel initiators and the influence of the R group on initiator efficiency which are the novel aspects of this present research.

4.1.3 Temperature and Time

In this work, two different polymerization temperatures, 90 and 140 ^{o}C, were studied. These temperatures were chosen from the lower and upper ends of the range of 80-150 ^{o}C which has been commonly reported in the literature for the bulk ROP of ε-caprolactone. A higher temperature obviously has the advantage of increasing the rate because, as in any chemical reaction, the rate of polymerization is accelerated by an increase in temperature. On the other hand, a higher temperature also has the disadvantages of (a) increasing the equilibrium monomer concentration at the maximum conversion and (b) increasing the likelihood of transesterification reactions occurring, resulting in both a lowering of the average molecular weight and a broadening of the molecular weight distribution of the final polymer product. Consequently, in practice, the choice of polymerization temperature is usually aimed at finding an appropriate balance between maintaining a suitably fast reaction and keeping transesterification to within acceptable limits.

As far as the time of polymerization was concerned, this was determined by how much time was needed for the meniscus height in the dilatometer to become constant. Therefore, the polymerization time varied from run to run depending on the conditions used.

4.1.4 Analytical Techniques

The kinetics of the bulk ROP of ε-caprolactone were studied by a combination of two analytical techniques, namely:

- Dilatometry (for % conversion and R_p)

- Gravimetry (for % conversion)

These two techniques, previously described in Chapter 2, provide complementary information about the progress of a polymerization reaction.

4.2 Dilatometry

4.2.1 Dilatometer Design

For kinetic investigations of homogeneous polymerizations, a variety of methods and apparatus has been developed. The dilatometric method is especially useful on account of its simplicity and general applicability. This procedure is based on the measurement of the contraction in volume that results from the different densities of the monomer and polymer. The design and construction of small glass dilatometers depends on a number of considerations, such as the expected volume change and the accuracy with which it must be measured, the rate of polymerization, the corresponding rate of heat evolution and its effect on temperature uniformity, the viscosity of the polymerizing mixture, and the need for stirring. If, as is usual, a capillary is used to display the volume change, good temperature control throughout is essential, if possible to within ±0.1 ^{o}C, since the dilatometer is effectively also a very sensitive thermometer.

The dilatometer which was designed and constructed for use in this work is shown in Figure 4.1. It consisted of a 10 ml round-bottomed flask with a B10-sized 'Quickfit' neck into which a capillary column was inserted. The top of the capillary column was connected to a silica gel drying tube to prevent the ingress of atmospheric moisture into the system. A small magnetic bar (1 cm) was placed inside the round-bottomed flask for the dual purpose of (a) stirring the reaction mixture to maintain homogeneity and (b) maximizing the efficiency of heat transfer from the reaction mixture to ensure good temperature control.

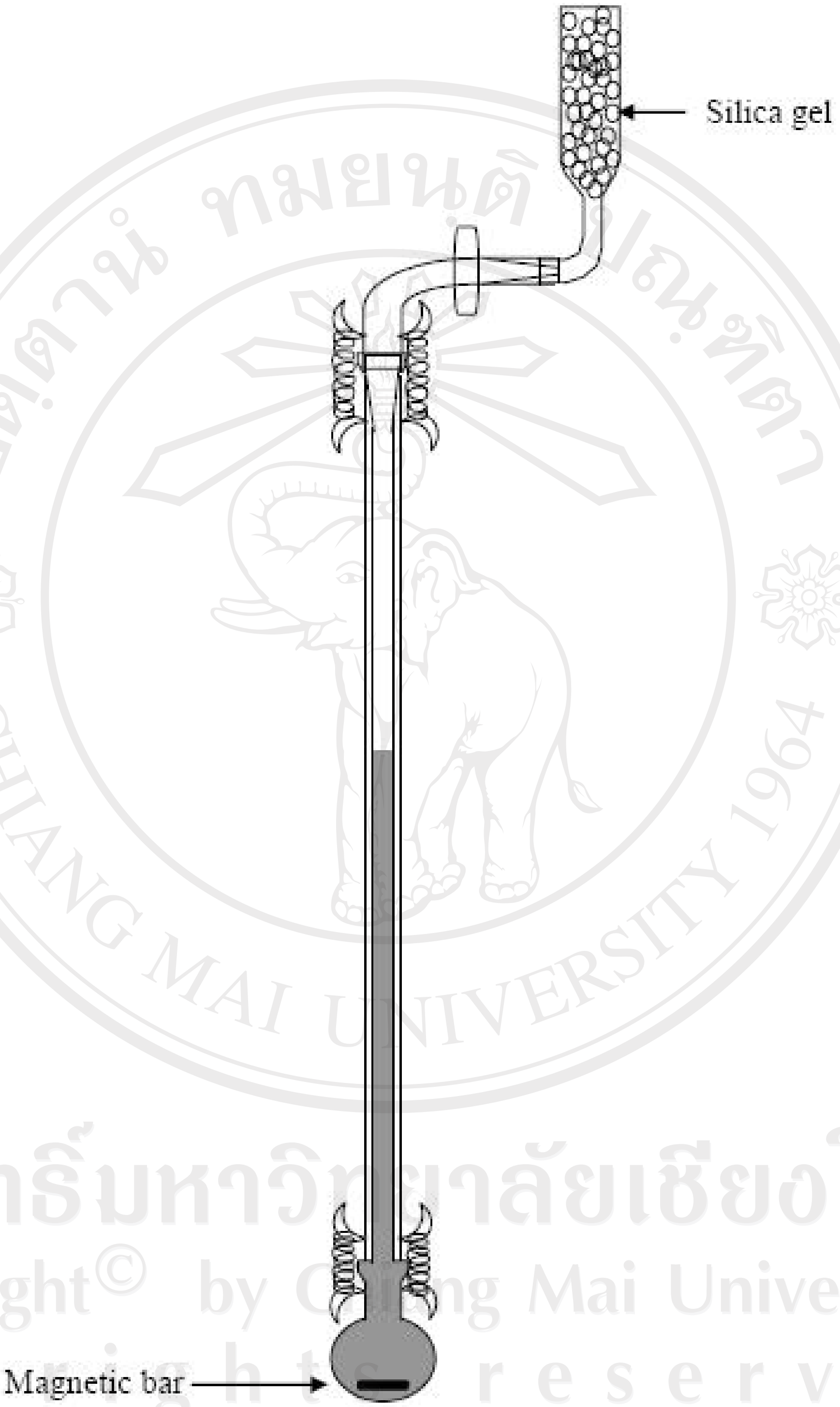


Figure 4.1 The glass capillary dilatometer which was designed for use in the kinetic experiments.

4.2.2 Dilatometer Calibration

Before use, it was first necessary to calibrate the dilatometer with respect to its volumetric dimensions. This was done by weighing the dilatometer empty and then filled with a known weight of monomer such that the meniscus level came within the capillary range at the temperature of the experiment. The density of the monomer at this temperature had already been determined in a density bottle equipped with a thermometer, while the capillary diameter was measured microscopically from a thinly-cut cross-section.

Before use, it was essential that the inside surfaces of the dilatometer were clean in order to minimize the effects of the reaction mixture adhering to the glass surface as the volume contracted and as the viscosity (and hence surface tension) increased. Thus, the dilatometer was cleaned thoroughly with a glassware cleaning solution followed by acetone and chloroform before use.

4.2.3 Dilatometry Apparatus

The dilatometry set-up employed depended on the polymerization temperature chosen. For the lower temperature of 90 ^{o}C, water could be used as the thermostat bath liquid with the apparatus set up as in Figure 4.2(a). However, for the higher temperature of 140 ^{o}C, the water bath had to be replaced by a silicone oil bath, as shown in Figure 4.2 (b). Temperature control was more difficult in this set-up because the silicone oil had to be heated with stirring from below by means of a hot plate and magnetic stirrer rather than immersion heated with circulation. Nevertheless, good temperature control was still achievable to within an acceptable ±0.2 ^{o}C. Cathetometer readings of the meniscus height in the capillary were accurate to ±0.001 cm.

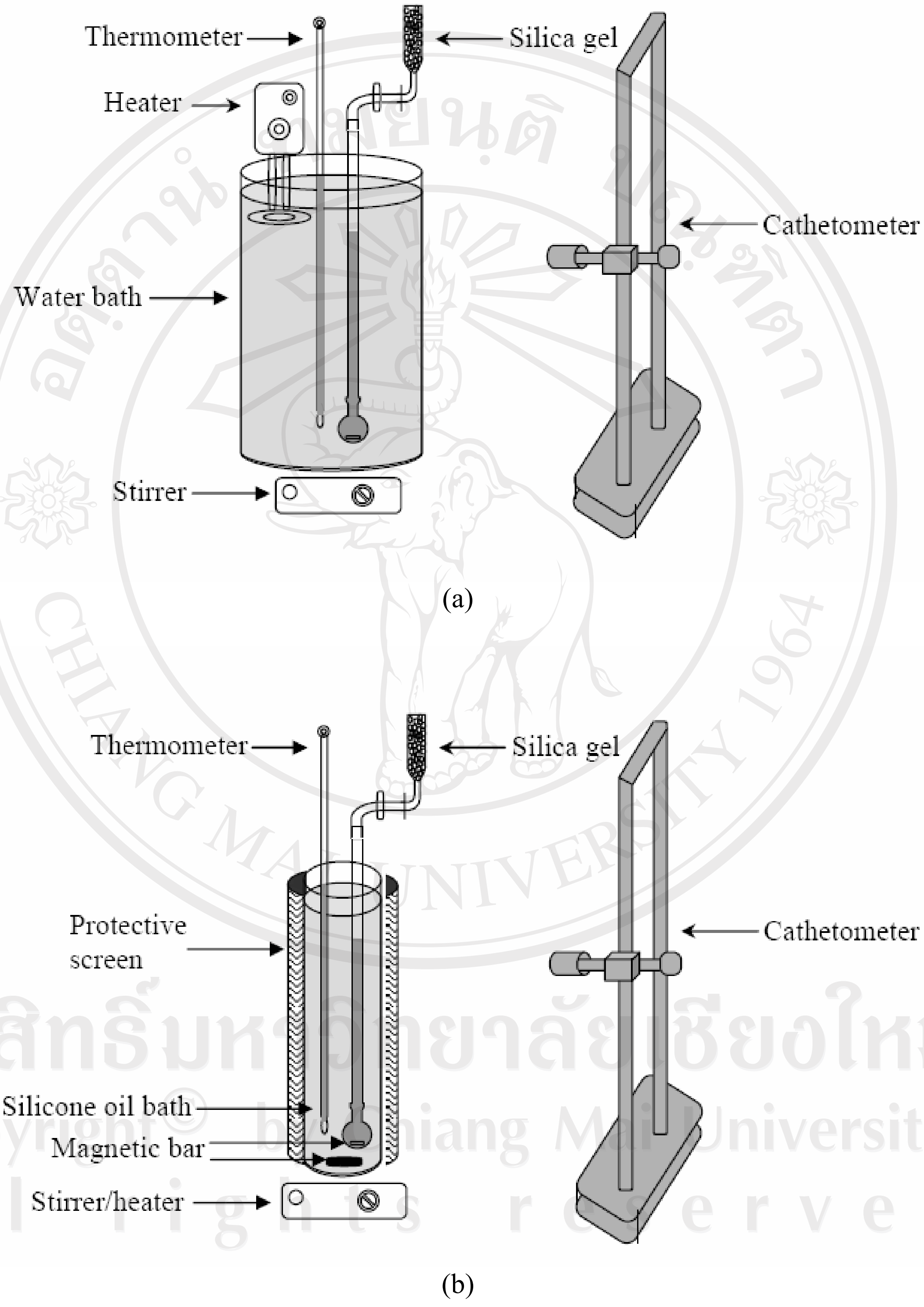


Figure 4.2 Dilatometry arrangements used in kinetic experiments (a) at the lower temperature of 90 ^{o}C and (b) at the higher temperature of 140 ^{o}C.

4.2.4 Dilatometric Data Analysis

Because the polymerization of a liquid monomer is generally accompanied by a decrease in volume, dilatometry is a convenient but indirect way to record the progress of monomer conversion. This method has been widely used for kinetic studies in polymer science since the equipment is relatively simple and inexpensive.

The application of conventional dilatometers to bulk polymerization reactions is limited by two main sources of error. Since the monomer itself is used as the recording liquid for the volume decrease, its increasing viscosity soon causes a distortion of the meniscus in the capillary, which makes accurate reading more difficult. In addition, the dissipation of the heat of reaction by either convection or conduction is increasingly hindered by the increasing viscosity of the polymerizing monomer/polymer mixture.

There are two methods of data analysis that are commonly used to calculate the % conversion and rate of polymerization:

Method 1: via the meniscus height at the final % conversion - referred to as the “Infinite Time Method”

Method 2: via the densities of monomer and polymer - referred to as the “Density Method”.

In this work, the Infinite Time Method (Method 1) was preferred since it avoided the uncertainty in determining the density of the polymer when solubilized in the monomer (Method 2).

The actual rate calculation in dilatometry is based on the proportionality of the change in volume, ΔV, to the change in height of the liquid meniscus, Δh, in the capillary, as given by

$$\Delta V = V_o - V = \pi r^2 \Delta h \qquad (4.3)$$

where V_0 is the initial volume of the system, V is the volume at time t, and r is the capillary radius.

This change in volume of the system, ΔV, may be related to the monomer concentration, reaction yield, and the rate of polymerization as follows. The total volume of the system, V, at any time t is given by

$$V = W_m\overline{V}_m + W_p\overline{V}_p + W_s\overline{V}_s \qquad (4.4)$$

where W_m, W_p and W_s are the weights and $\overline{V}_m$, $\overline{V}_p$ and $\overline{V}_s$ are the partial specific volumes of monomer, polymer and solvent (if used) respectively. To a very good approximation, $W_p = W^o_m - W_m$, where W^o_m is the initial weight of monomer. Combining this approximation with (4.4) and rearranging gives the weight of monomer at time t as

$$W_m = \frac{V - W^o{}_m\overline{V}_p - W_s\overline{V}_s}{\overline{V}_m - \overline{V}_p} \qquad (4.5)$$

Because no polymer is present initially, the initial volume V_0 is given by

$$V_o = W^o{}_m\overline{V}_m + W_s\overline{V}_s \qquad (4.6)$$

and, provided that all of the monomer is converted to polymer at the completion of the reaction, the final volume V_∞ is

$$V_\alpha = W^o{}_m\overline{V}_p + W_s\overline{V}_s \qquad (4.7)$$

Of course, this assumption of complete (100 %) monomer conversion can only be an approximation since it is a thermodynamic fact that there will inevitably be a certain "equilibrium monomer concentration", $[M]_{eq}$, remaining in the reaction mixture at the final (constant) volume V_∞. However, for ε-caprolactone bulk polymerization over the temperature range of 90-140 °C, this is believed to be a good approximation since the $[M]_{eq}$ for ε-caprolactone bulk polymerization, as observed experimentally at 100 °C, has been reported to be very small (≈0) [80].

On the strength of this approximation, equations 4.6 and 4.7 may now be used to eliminate $\overline{V}_m - \overline{V}_p$ and $W_s\overline{V}_s$ from equation 4.5 and, when this is done, equation 4.8 is obtained.

$$W_m = \frac{V - V_\alpha}{V_o - V_\alpha} W^o{}_m \qquad (4.8)$$

The % conversion to polymer (or yield of the reaction) on a weight % basis, Y, may then be written as

$$\% \text{ Conversion} = Y = 100\frac{W^o{}_m - W_m}{W^o{}_m} = 100\ \frac{V_o - V}{V_o - V_\alpha} \qquad (4.9)$$

or

$$\% \text{ Conversion} = Y = \frac{100\Delta V}{V_o - V_\propto} = \frac{100\ \Delta h(t)}{\Delta h(\propto)} \qquad (4.10)$$

where $\Delta h(t) = h_0 - h$ = progressive change in meniscus height at any time t
$\Delta h(\infty) = h_0 - h_\infty$ = final change in meniscus height at time ∞ (i.e., at constant h)

This % conversion in equation 4.10 is obviously a cumulative parameter, meaning that it is the total % conversion of monomer to polymer over the time period from the start of the polymerization at time t=0 to any subsequent time t. Thus, the % conversion increases progressively from 0 % at the start to 100 % at the end.

Similarly, it is possible to proceed from equation 4.8 and utilize the definition of the rate of polymerization, R_p, in equation 4.11.

$$R_p = \frac{-d\,[M]}{dt} = \lim_{\Delta t \to o} \frac{\Delta[M]}{\Delta t} \qquad (4.11)$$

However, the rate of polymerization, R_p, in equation 4.11 is not a cumulative parameter. Instead, it can either be calculated as an **average** value over a long time period (usually starting from t=0) or as an **instantaneous** value over a very short (incremental) time period. Of these two, the instantaneous R_p is generally considered to be the more meaningful since it is an absolute value at a specific time rather than an average value over an ever-increasing time interval. Thus, combining this concept with the equation for the % conversion in equation 4.10 gives the instantaneous rate expression in equation 4.12.

$$R_p = \frac{\Delta Y}{100} \; \frac{[M]_o}{\Delta t} = \frac{\Delta h}{\Delta h(\propto)} \; \frac{[M]_o}{\Delta t} \qquad (4.12)$$

where Δh = incremental height change during Δt

$\Delta h_{(\infty)}$ = $h_0 - h_\infty$ = final change in meniscus height at time ∞ (i.e., at constant h)

Δt = incremental time interval between successive readings (mins)

$[M]_o$ = initial monomer concentration (mol l^{-1})

If two successive meniscus height readings h_1 and h_2, taken at times t_1 and t_2, gave % conversions of Y_1 and Y_2 from equation 4.10, then the value of R_p from equation 4.12 would be

$$R_p = \frac{\Delta Y}{100} \; \frac{[M]_o}{\Delta t} = \frac{Y_2 - Y_1}{100} \; \frac{[M]_o}{t_1 - t_2} \quad \text{mol } l^{-1} \text{min}^{-1}$$

This R_p is an “average” value over the time interval $t_1 \rightarrow t_2$ but, because this time interval is very small (i.e., incremental) compared to the total time $t_o \rightarrow t_\infty$ for the polymerization as a whole, it can be regarded to a good approximation as an **instantaneous** R_p at (as an average) the mid-point of the time interval, i.e.

$$R_p \text{ at time } = \frac{t_1 + t_2}{2} \quad \text{mins}$$

These equations 4.10 and 4.12 were used in this work for the calculation of the values of % conversion and R_p at various times t throughout the polymerization.

4.2.5 Experimental Procedure

An appropriate amount of distilled, degassed monomer together with 0.1 mol % of initiator were accurately weighed into a 10 ml ‘Quickfit’ round-bottomed flask. A small magnetic bar was added and the capillary carefully inserted into the neck of the flask so that the monomer meniscus level rose to a suitable height in the capillary, The complete dilatometer assembly was then clamped accurately vertical in the water or silicone oil bath at the polymerization temperature (zero time, t=0), a stop-watch started, and a cathetometer focused on the monomer meniscus level. After that, the meniscus level was read at regular intervals, short at the beginning and then lengthening as the time progressed.

From the cathetometer scale readings of meniscus height (h) obtained as a function of time (t), the % conversion and rate of polymerization (R_p) were calculated from the equations:

$$\%\ \text{Conversion} = \frac{100\Delta V}{V_o - V_\alpha} = \frac{100\ \Delta h(t)}{\Delta h(\alpha)}$$

$$R_p = \frac{\Delta h}{\Delta h(\propto)} \quad \frac{[M]_o}{\Delta t} \qquad \text{mol l}^{-1}\text{min}^{-1}$$

At the end of the polymerization, when the meniscus height had become constant (h_∞), the contents of the dilatometer were dissolved in chloroform and the polymer precipitated in n-hexane for gravimetric determination. The gravimetric final % conversion (at $t = \infty$) thus obtained provided a qualitative indication as to the validity of the approximation used in this Infinite Time Method of data analysis that $\Delta h(t = \infty)$ corresponded to 100 % conversion.

4.2.6 Experimental Results

The complete range of kinetic experiments by dilatometry is summarized in Table 4.1. In total, 12 kinetic runs were carried out using the 6 different tin(II) alkoxide initiators (0.1 mol %) at the 2 different temperatures of 90 °C and 140 °C. In each of the 6 runs conducted at 90 °C, it was found that the contraction in volume was extremely small, even at prolonged reaction times. Furthermore, the tin(II) alkoxide initiators appeared to remain largely if not completely undissolved in the ε-caprolactone monomer during this period, even with constant stirring. It was therefore concluded that a temperature of 90 °C was insufficient for initiator solubilization to take place irrespective of the increasing size of the OR groups in the $Sn(OR)_2$ initiator. Clearly, in the absence of solubilization, the aggregated forms of the initiators are essentially inactive at a temperature of 90 °C. The transition between the aggregated and non-aggregated forms is an equilibrium exchange which greatly influences the kinetics. Aggregation can either inhibit initiation at the start of the reaction or cause a temporary termination of the propagation species during the course of the reaction.

$$[\,Sn(OR)_2\,]_n \rightleftharpoons n\,Sn(OR)_2$$

aggregated form	non-aggregated form
insoluble	solubilizable
inactive	active

This equilibrium is clearly temperature as well as structure-dependent because, when the polymerization temperature was increased to 140 °C, polymerization occurred with each of the 6 initiators. At the same time, each initiator could be seen to gradually dissolve in the monomer with time. However, this dissolution process was slow and not always complete. As expected, initiator solubility tended to increase with the length of the OR groups and ranged from only sparingly soluble for the tin(II) methoxide, $Sn(OCH_3)_2$, to completely soluble for the tin(II) hexoxide, $Sn(OC_6H_{13})_2$, and tin(II) octoxide, $Sn(OC_8H_{17})_2$.

Table 4.1 Kinetic studies of the bulk ring-opening polymerization of ε-caprolactone: list of kinetic experiments carried out by dilatometry.

Run No.	Initiator *	Temperature °C	Raw Data	Data Analysis
1	$Sn(OCH_3)_2$	90	Table 4.2	Figure 4.3
2	$Sn(OC_2H_5)_2$	90	Table 4.3	Figure 4.4
3	$Sn(OC_3H_7)_2$	90	Table 4.4	Figure 4.5
4	$Sn(OC_4H_9)_2$	90	Table 4.5	Figure 4.6
5	$Sn(OC_6H_{13})_2$	90	Table 4.6	Figure 4.7
6	$Sn(OC_8H_{17})_2$	90	Table 4.7	Figure 4.8
7	$Sn(OCH_3)_2$	140	Table 4.8	Figures 4.9 – 4.11
8	$Sn(OC_2H_5)_2$	140	Table 4.9	Figures 4.12 – 4.13
9	$Sn(OC_3H_7)_2$	140	Table 4.10	Figures 4.14 – 4.15
10	$Sn(OC_4H_9)_2$	140	Table 4.11	Figures 4.16 – 4.17
11	$Sn(OC_6H_{13})_2$	140	Table 4.12	Figures 4.18 – 4.19
12	$Sn(OC_8H_{17})_2$	140	Table 4.13	Figures 4.20 – 4.21

* [Initiator] = 0.1 mol % (i.e., [M] : [I] = 1000 : 1)

The experimental results obtained from the 12 kinetic runs are given in Tables 4.2-4.13. The tables show the raw data values of meniscus height, h, at time, t, and the calculated values of % conversion and rate of polymerization, R_p, where applicable. Since it is clear from the results obtained at 90 ^{o}C (Runs 1-6, Tables 4.2-4.7) that the polymerization reactions only occurred to a very limited extent, only the values of h are plotted graphically as a function of time. This is because the % conversion requires knowing the value of h_∞ for a reaction that proceeds (as is assumed) to 100 % conversion. However, the results obtained at 140 ^{o}C (Runs 7-12, Tables 4.8-4.13), which show that the polymerizations went to completion, are plotted graphically for both % conversion and R_p (Figures 4.10-4.21).

At the beginning of each polymerization, there was a thermal equilibration period during which the meniscus level rose in the capillary due to thermal expansion. Consequently, the meniscus height at zero time, h_0, at the actual polymerization temperature, as required in the % conversion and rate calculations, could only be estimated by extrapolation back to time = 0 of the raw data plot between h and t. An example of this extrapolation is shown in Figure 4.9 for Run No. 7.

Run No. 1 : Caprolactone @ 90 ^{o}C / $Sn(OCH_3)_2$ (0.1 mol %)

Table 4.2 Dilatometric data from ε-caprolactone polymerization at 90 ^{o}C using 0.1 mol % tin(II) methoxide as initiator.

weight of ε-caprolactone = 8.9223 g
weight of $Sn(OCH_3)_2$ = 0.0141 g
capillary diameter = 0.18 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	11.495	Thermal equilibration	
4	11.499		
6	11.534		
8	11.558		
10	11.570		
12	11.569		
15	11.569		
20	11.569		
25	11.568		
30	11.568		
35	11.568		
40	11.568		
45	11.568		
50	11.567		
55	11.567		
60	11.567		
65	11.567		
70	11.567		
80	11.567		
90	11.567		
100	11.567		
110	11.567		
120	11.567		
130	11.567		
140	11.567		
150	11.567		
160	11.567		
170	11.567		
180	11.567		
190	11.567		
200	11.567		
220	11.567		
240	11.567		
260	11.567		
280	11.567		
300	11.567		
330	11.567		
360	11.567		

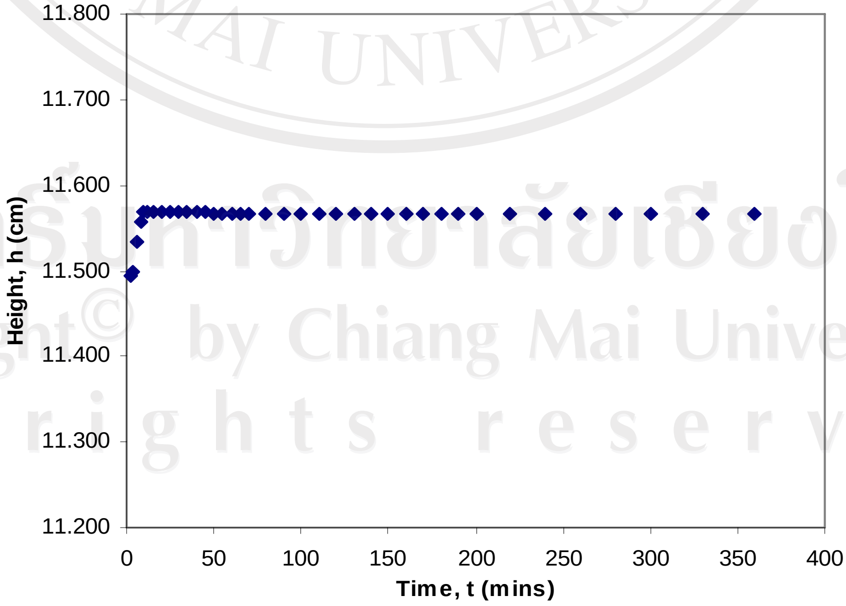


Figure 4.3 Cathetometer readings from dilatometry of meniscus height, h, against time for ε-caprolactone using tin(II) methoxide as initiator at 90 ^{o}C.

Run No. 2 : Caprolactone @ 90 ^{o}C / $Sn(OC_2H_5)_2$ (0.1 mol %)

Table 4.3 Dilatometric data from ε-caprolactone polymerization at 90 ^{o}C using 0.1 mol % tin(II) ethoxide as initiator.

weight of ε-caprolactone = 8.9221 g
weight of $Sn(OC_2H_5)_2$ = 0.0163 g
capillary diameter = 0.18 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	12.236	Thermal equilibration	
4	12.357		
7	12.432		
10	12.430		
12	12.426		
15	12.424		
20	12.420		
25	12.418		
30	12.416		
35	12.415		
40	12.413		
45	12.412		
50	12.411		
55	12.410		
60	12.410		
65	12.409		
70	12.408		
80	12.408		
90	12.408		

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
100	12.408		
110	12.408		
120	12.408		
130	12.408		
140	12.408		
150	12.408		
160	12.408		
170	12.408		
180	12.408		
190	12.408		
200	12.408		
220	12.408		
240	12.408		
260	12.408		
280	12.408		
300	12.408		
330	12.408		
360	12.408		

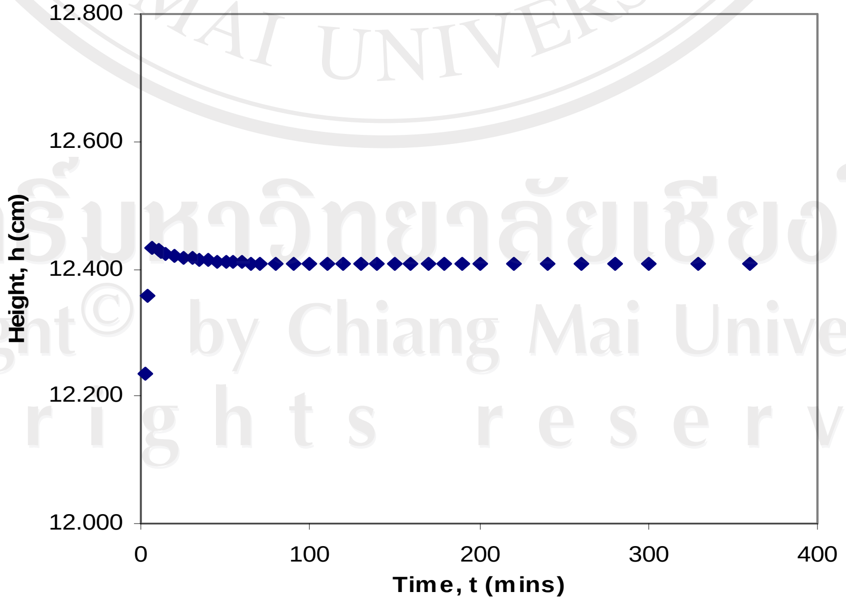


Figure 4.4 Cathetometer readings from dilatometry of meniscus height, h, against time for ε-caprolactone using tin(II) ethoxide as initiator at 90 ^{o}C.

Run No. 3 : Caprolactone @ 90 °C / $Sn(OC_3H_7)_2$ (0.1 mol %)

Table 4.4 Dilatometric data from ε-caprolactone polymerization at 90 °C using 0.1 mol % tin(II) propoxide as initiator.

weight of ε-caprolactone = 8.9224 g
weight of $Sn(OC_3H_7)_2$ = 0.0185 g
capillary diameter = 0.18 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	13.556	Thermal equilibration	
4	13.597		
6	13.602		
8	13.604		
12	13.583		
15	13.575		
20	13.568		
25	13.565		
30	13.560		
35	13.559		
40	13.558		
45	13.556		
50	13.555		
55	13.553		
60	13.553		
65	13.553		
70	13.552		
80	13.551		
90	13.551		
100	13.551		
110	13.551		
120	13.551		
130	13.551		
140	13.551		
150	13.551		
160	13.551		
170	13.551		
180	13.551		
190	13.551		
200	13.551		
220	13.551		
240	13.551		
260	13.551		
280	13.551		
300	13.551		
330	13.551		
360	13.551		

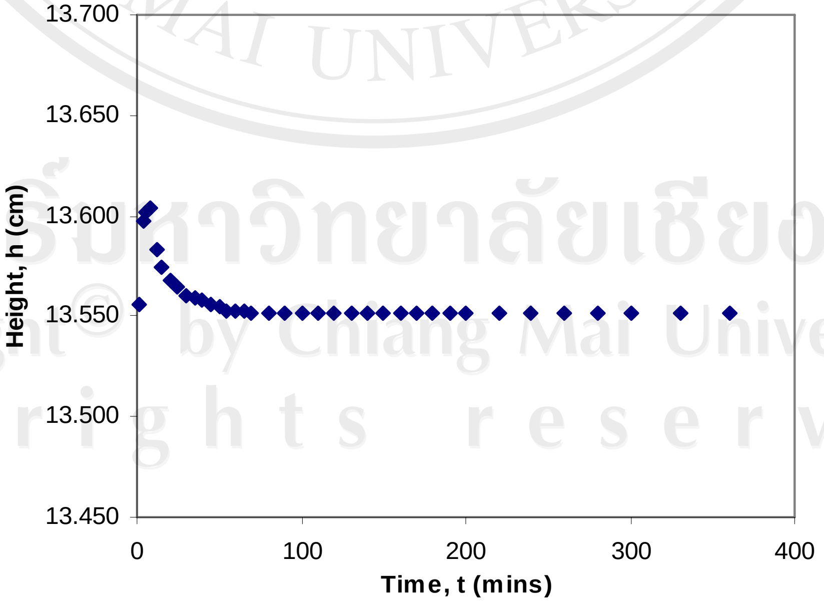


Figure 4.5 Cathetometer readings from dilatometry of meniscus height, h, against time for ε-caprolactone using tin(II) propoxide as initiator at 90 °C.

Run No. 4 : Caprolactone @ 90 ^{o}C / $Sn(OC_4H_9)_2$ (0.1 mol %)

Table 4.5 Dilatometric data from ε-caprolactone polymerization at 90 ^{o}C using 0.1 mol % tin(II) butoxide as initiator.

weight of ε-caprolactone = 8.9225 g
weight of $Sn(OC_4H_9)_2$ = 0.0207 g
capillary diameter = 0.18 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	14.140	Thermal equilibration	
5	14.147		
8	14.149		
10	14.150		
12	14.148		
15	14.147		
20	14.146		
25	14.145		
30	14.144		
35	14.140		
40	14.138		
45	14.138		
50	14.138		
55	14.137		
60	14.137		
65	14.137		
70	14.137		
80	14.136		
90	14.136		
100	14.136		
110	14.136		
120	14.136		
130	14.136		
140	14.136		
150	14.136		
160	14.136		
170	14.136		
180	14.136		
190	14.136		
200	14.136		
220	14.136		
240	14.136		
260	14.136		
280	14.136		
300	14.136		
330	14.136		
360	14.136		

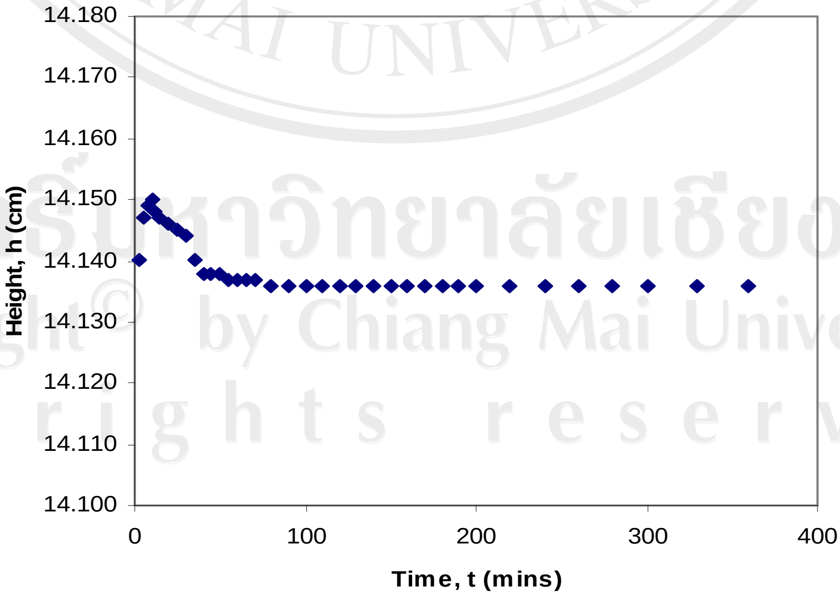


Figure 4.6 Cathetometer readings from dilatometry of meniscus height, h, against time for ε-caprolactone using tin(II) butoxide as initiator at 90 ^{o}C.

Run No. 5 : Caprolactone @ 90 °C / $Sn(OC_6H_{13})_2$ (0.1 mol %)

Table 4.6 Dilatometric data from ε-caprolactone polymerization at 90 °C using 0.1 mol % tin(II) hexoxide as initiator.

weight of ε-caprolactone = 8.9222 g
weight of $Sn(OC_6H_{13})_2$ = 0.0251 g
capillary diameter = 0.18 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
3	12.161	Thermal equilibration	
7	12.167		
10	12.167		
15	12.170		
20	12.175		
25	12.174		
30	12.173		
35	12.173		
40	12.165		
45	12.159		
50	12.159		
55	12.159		
60	12.159		
65	12.159		
70	12.159		
80	12.158		
90	12.158		
100	12.157		
110	12.157		
120	12.157		
130	12.157		
140	12.157		
150	12.157		
160	12.157		
170	12.157		
180	12.157		
190	12.157		
200	12.157		
220	12.157		
240	12.157		
260	12.157		
280	12.157		
300	12.157		
330	12.157		
360	12.157		

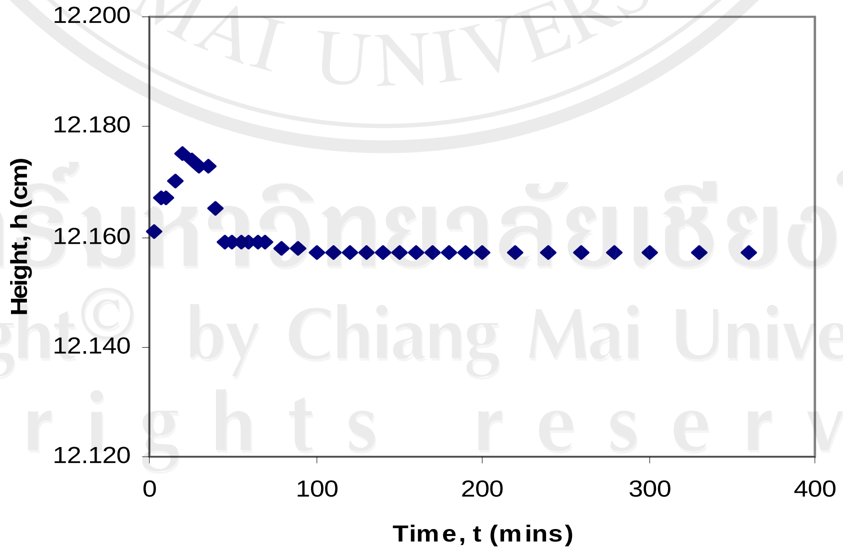


Figure 4.7 Cathetometer readings from dilatometry of meniscus height, h, against time for ε-caprolactone using tin(II) hexoxide as initiator at 90 °C.

Run No. 6 : Caprolactone @ 90 °C / $Sn(OC_8H_{17})_2$ (0.1 mol %)

Table 4.7 Dilatometric data from ε-caprolactone polymerization at 90 °C using 0.1 mol % tin(II) octoxide as initiator.

weight of ε-caprolactone = 8.9220 g
weight of $Sn(OC_8H_{17})_2$ = 0.0294 g
capillary diameter = 0.18 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	14.894	Thermal equilibration	
5	14.928		
8	14.928		
10	14.931		
12	14.940		
15	14.921		
20	14.830		
25	14.824		
30	14.824		
35	14.822		
40	14.822		
45	14.816		
50	14.814		
55	14.802		
60	14.740		
65	14.740		
70	14.740		
80	14.739		
90	14.739		
100	14.738		
110	14.738		
120	14.738		
130	14.738		
140	14.738		
150	14.738		
160	14.738		
170	14.738		
180	14.738		
190	14.738		
200	14.738		
220	14.738		
240	14.738		
260	14.738		
280	14.738		
300	14.738		
330	14.738		
360	14.738		

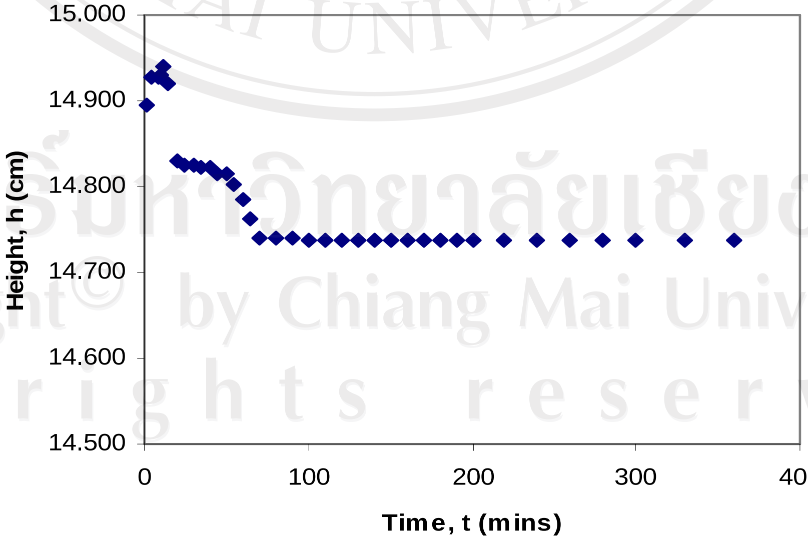


Figure 4.8 Cathetometer readings from dilatometry of meniscus height, h, against time for ε-caprolactone using tin(II) octoxide as initiator at 90 °C.

Run No. 7 : Caprolactone @ 140 ^{o}C / $Sn(OCH_3)_2$ (0.1 mol %)

Table 4.8 Dilatometric data from ε-caprolactone polymerization at 140 ^{o}C using 0.1 mol % tin(II) methoxide as initiator.

weight of ε-caprolactone = 8.9225 g
weight of $Sn(OCH_3)_2$ = 0.0141 g
capillary diameter = 0.18 cm
h_0 (from extrapolation - see Fig. 4.9) = 37.153 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	36.784	Thermal equilibration	
4	37.213		
6	37.482		
8	37.401		
10	37.381		
12	37.137	0.13	0.02507
14	37.064	0.70	0.01546
16	37.019	1.06	0.00172
18	37.014	1.10	0.00790
20	36.991	1.28	0.00790
22	36.968	1.47	0.00527
25	36.945	1.65	0.00527
28	36.922	1.83	0.00790
30	36.899	2.01	0.00527
33	36.876	2.19	0.00527
36	36.853	2.38	0.00395
40	36.830	2.56	0.00395
44	36.807	2.74	0.01614
48	36.713	3.49	0.00103
52	36.707	3.53	0.00189
56	36.696	3.62	0.00773
60	36.651	3.98	0.00527
63	36.628	4.16	0.00321
66	36.614	4.27	0.00206
70	36.602	4.36	0.00120
74	36.595	4.42	0.00086
78	36.590	4.46	0.00412
80	36.578	4.55	0.00807
84	36.531	4.93	0.00498
88	36.502	5.16	0.00756
92	36.458	5.50	0.00773
96	36.413	5.86	0.00670
100	36.374	6.17	0.00646
105	36.327	6.54	0.00495
110	36.291	6.83	0.00728
115	36.238	7.25	0.00673
120	36.189	7.64	0.01003
125	36.116	8.21	0.01003
130	36.043	8.79	0.00852
135	35.981	9.28	0.00522
140	35.943	9.58	0.00481
145	35.908	9.86	0.00646
150	35.861	10.23	0.00783
155	35.804	10.69	0.00302
160	35.782	10.86	0.00591
165	35.739	11.20	0.01127
170	35.657	11.85	0.00756
175	35.602	12.29	0.00714
180	35.550	12.70	0.00783
185	35.493	13.15	0.01058
190	35.416	13.76	0.00563
195	35.375	14.08	0.00646
200	35.328	14.46	0.00646
205	35.281	14.83	0.00701
210	35.230	15.23	0.00440
215	35.198	15.49	0.00756
220	35.143	15.92	0.00632
225	35.097	16.29	0.00756
230	35.042	16.72	0.00467
235	35.008	16.99	0.00508
240	34.971	17.28	0.00824
245	34.911	17.76	0.00481
250	34.876	18.04	0.00659
255	34.828	18.42	0.00714
260	34.776	18.83	0.00934
265	34.708	19.37	0.00605
270	34.664	19.71	0.00948
275	34.595	20.26	0.01127

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
280	34.513	20.91	0.00371
285	34.486	21.12	0.01058
290	34.409	21.73	0.00618
295	34.364	22.09	0.00948
300	34.295	22.64	0.02212
305	34.134	23.91	0.01827
310	34.001	24.97	0.02446
315	33.823	26.38	0.00467
320	33.789	26.65	0.02569
325	33.602	28.13	0.01017
330	33.528	28.71	0.00879
335	33.464	29.22	0.01030
340	33.389	29.81	0.02267
345	33.224	31.12	0.02185
350	33.065	32.38	0.02418
355	32.889	33.77	0.02528
360	32.705	35.23	0.00495
365	32.669	35.52	0.01209
370	32.581	36.21	0.02528
375	32.397	37.67	0.02679
380	32.202	39.22	0.01553
385	32.089	40.11	0.02542
390	31.904	41.58	0.02171
395	31.746	42.83	0.01566
400	31.632	43.73	0.01992
405	31.487	44.88	0.01498
410	31.378	45.74	0.01704
415	31.254	46.72	0.01896
420	31.116	47.82	0.01649
425	30.996	48.77	0.02253
430	30.832	50.07	0.00659
435	30.784	50.45	0.02143
440	30.628	51.68	0.01594
445	30.512	52.60	0.02624
450	30.321	54.11	0.02872
455	30.112	55.77	0.02858
460	29.904	57.42	0.01484
465	29.796	58.27	0.01978
470	29.652	59.41	0.02459
475	29.473	60.83	0.02075
480	29.322	62.03	0.02789
485	29.119	63.64	0.01539
490	29.007	64.52	0.01992
495	28.862	65.67	0.03270
500	28.624	67.56	0.01580
505	28.509	68.47	0.01539
510	28.397	69.35	0.03861
515	28.116	71.58	0.01539
520	28.004	72.47	0.01484
525	27.896	73.32	0.01814
530	27.764	74.37	0.03036
535	27.543	76.12	0.03311
540	27.302	78.03	0.02185
545	27.143	79.29	0.02404
550	26.968	80.67	0.02556
555	26.782	82.15	0.01800
560	26.651	83.18	0.02047
565	26.502	84.36	0.02130
570	26.347	85.59	0.01965
575	26.204	86.72	0.01814
580	26.072	87.77	0.02088
585	25.92	88.97	0.01566
590	25.806	89.88	0.00893
595	25.741	90.39	0.01827
600	25.608	91.45	0.01580
605	25.493	92.36	0.02459
610	25.314	93.77	0.01759
615	25.186	94.79	0.02212
620	25.025	96.06	0.00398
625	24.996	96.29	0.01539
630	24.884	97.18	0.01202
640	24.709	98.57	0.00302
650	24.665	98.91	0.00234
660	24.631	99.18	0.00392
670	24.574	99.64	0.00220
680	24.542	99.89	0.00096
690	24.528	100.00	0.00000
700	24.528	100.00	0.00000
710	24.528	100.00	0.00000
720	24.528	100.00	0.00000
730	24.528	100.00	0.00000
740	24.528	100.00	0.00000
750	24.528 = h_∞	100.00	0.00000

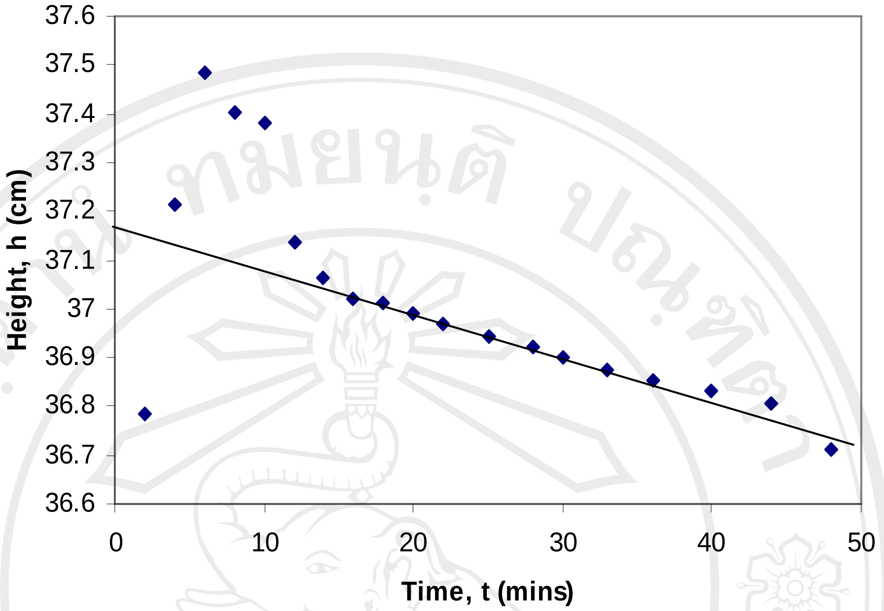


Figure 4.9 Extrapolation of h to zero time (h_0 at t = 0) for ε-caprolactone polymerization using 0.1 mol % tin(II) methoxide as initiator at 140 °C.

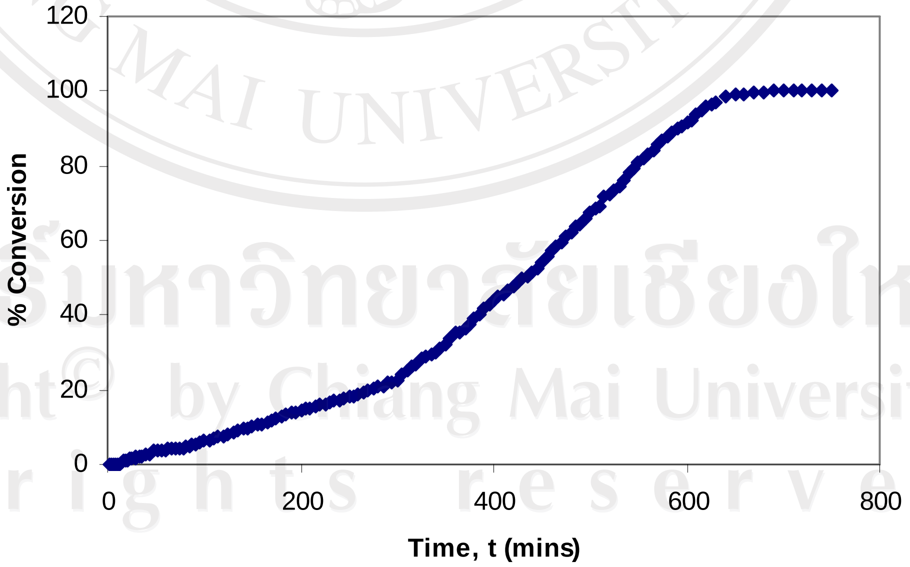


Figure 4.10 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using tin(II) methoxide as initiator at 140 °C.

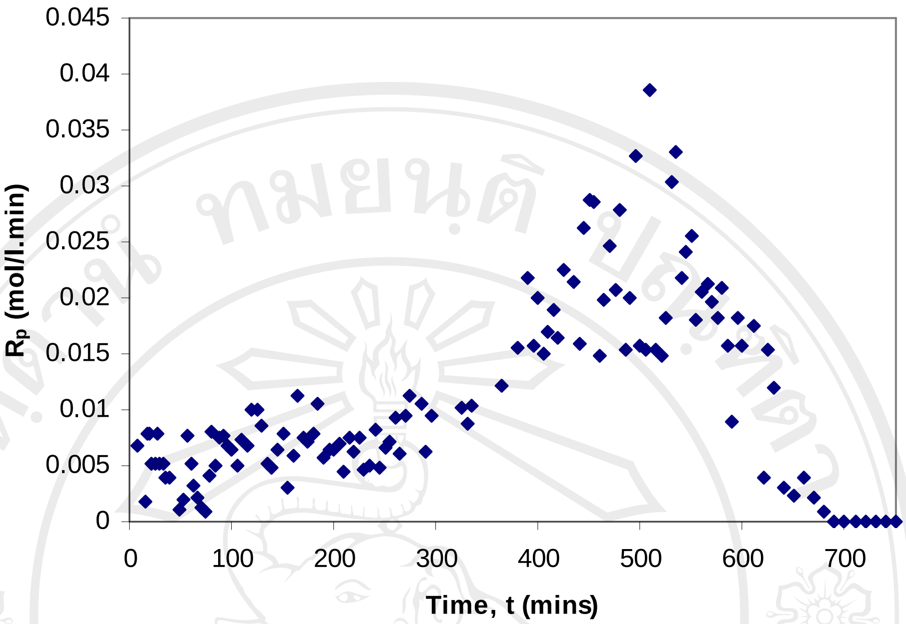


Figure 4.11 Kinetic profile from dilatometry of the rate of polymerization, R_p, against time for ε-caprolactone using tin(II) methoxide as initiator at 140 °C.

Sample Calculations

In equation 4.12 for R_p, the value of $[M]_0$, the initial molar concentration of the ε-caprolactone monomer at the temperature of the polymerization (140°C) is given by:

$$[M]_o = \frac{\text{density of ε-caprolactone at 140 °C (see NOTE below)}}{\text{molecular weight of ε-caprolactone}}$$

$$[M]_o = \frac{0.990\ (\text{g cm}^{-3}) \times 1000\ (\text{cm}^3\ \text{l}^{-1})}{114.15\ (\text{g mol}^{-1})}$$

$$[M]_o = 8.673\ \text{mol l}^{-1}$$

NOTE : The monomer density at 140 °C was estimated by extrapolation of the linear graph between density (as determined experimentally at 30, 40, 50, 60 and 70 °C) and temperature.

Therefore, for example, at time t = 120 mins (in Table 4.8)

$$\% \text{ Conversion} = \frac{100\,\Delta h(t)}{\Delta h(\infty)} = \frac{100\,(h_o - h)}{h_o - h_\infty}$$

$$= \frac{100(37.153 - 36.189)}{37.153 - 24.528} \; \%$$

$$\boxed{\% \text{ Conversion} = 7.64\ \%}$$

$$R_p = \frac{\Delta h}{\Delta h(\infty)}\,\frac{[M]_o}{\Delta t} = \frac{\Delta h}{(h_o - h_\infty)}\,\frac{[M]_o}{\Delta t}$$

$$= \frac{(36.189 - 36.116)\quad 8.673}{(37.153 - 24.528)\,(125 - 120)} \quad \text{mol l}^{-1}\ \text{min}^{-1}$$

$$\boxed{R_p = 1.003 \times 10^{-3}\ \text{mol l}^{-1}\ \text{min}^{-1}}$$

Run No. 8 : Caprolactone @ 140 °C / $Sn(OC_2H_5)_2$ (0.1 mol %)

Table 4.9 Dilatometric data from ε-caprolactone polymerization at 140 °C using 0.1 mol % tin(II) ethoxide as initiator.

weight of ε-caprolactone = 8.9220 g
weight of $Sn(OC_2H_5)_2$ = 0.0163 g
capillary diameter = 0.18 cm
h_0 (from extrapolation) = 37.274 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	36.878	Thermal equilibration	
4	37.115		
6	37.192		
8	37.256		
10	37.249	0.19	0.00201
12	37.243	0.24	0.00134
14	37.239	0.27	0.00234
16	37.232	0.32	0.00837
18	37.207	0.52	0.00234
20	37.200	0.57	0.00301
22	37.191	0.64	0.00301
24	37.182	0.71	0.00268
26	37.174	0.77	0.00167
28	37.169	0.81	0.00167
30	37.164	0.85	0.00112
33	37.159	0.89	0.00134
36	37.153	0.93	0.00067
40	37.149	0.96	0.00223
43	37.139	1.04	0.00178
46	37.131	1.10	0.00424
49	37.112	1.25	0.00067
52	37.109	1.27	0.00987
56	37.050	1.73	0.00552
60	37.017	1.98	0.00753
64	36.972	2.33	0.00469
67	36.951	2.49	0.00178
70	36.943	2.55	0.00184
74	36.932	2.64	0.00201
78	36.920	2.73	0.03380
80	36.819	3.51	0.00954
84	36.762	3.95	0.02231
87	36.662	4.72	0.05176
90	36.430	6.51	0.00790
95	36.371	6.97	0.00469
100	36.336	7.24	0.00656
105	36.287	7.62	0.01299
110	36.190	8.37	0.02222
115	36.024	9.65	0.00428
120	35.992	9.89	0.01218
125	35.901	10.60	0.00576
130	35.858	10.93	0.00469
135	35.823	11.20	0.01513
140	35.710	12.07	0.00268
143	35.698	12.16	0.01473
145	35.654	12.50	0.00897
150	35.587	13.02	0.01125
155	35.503	13.67	0.00562
160	35.461	13.99	0.00964
165	35.389	14.55	0.00736
170	35.334	14.97	0.00776
175	35.276	15.42	0.00884
180	35.210	15.93	0.00254
185	35.191	16.08	0.00763
190	35.134	16.52	0.00643
195	35.086	16.89	0.01526
200	34.972	17.77	0.00924
205	34.903	18.30	0.00830
210	34.841	18.78	0.00870
215	34.776	19.28	0.00910
220	34.708	19.80	0.00763
225	34.651	20.24	0.00910
230	34.583	20.77	0.01098
235	34.501	21.40	0.00187
240	34.487	21.51	0.01098

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
245	34.405	22.14	0.00442
250	34.372	22.40	0.00402
255	34.342	22.63	0.00549
260	34.301	22.95	0.00054
265	34.297	22.98	0.02129
270	34.138	24.20	0.03173
275	33.901	26.03	0.01017
280	33.825	26.62	0.00817
285	33.764	27.09	0.02102
290	33.607	28.30	0.01245
295	33.514	29.02	0.00830
300	33.452	29.50	0.02209
305	33.287	30.77	0.03293
310	33.041	32.67	0.01928
315	32.897	33.78	0.02597
320	32.703	35.28	0.00723
325	32.649	35.69	0.01004
330	32.574	36.27	0.02383
335	32.396	37.65	0.02396
340	32.217	39.03	0.01874
345	32.077	40.11	0.02222
350	31.911	41.39	0.02182
355	31.748	42.65	0.01647
360	31.625	43.60	0.01981
365	31.477	44.74	0.01312
370	31.379	45.50	0.02289
375	31.208	46.82	0.02811
380	30.998	48.44	0.02222
385	30.832	49.72	0.00616
390	30.786	50.07	0.02262
395	30.617	51.38	0.01606
400	30.497	52.30	0.02477
405	30.312	53.73	0.02691
410	30.111	55.28	0.02798
415	29.902	56.90	0.01620
420	29.781	57.83	0.01807
425	29.646	58.87	0.02423
430	29.465	60.27	0.01941
435	29.320	61.39	0.02691
440	29.119	62.94	0.02825
445	28.908	64.57	0.02035
450	28.756	65.74	0.01821
455	28.620	66.79	0.01459
460	28.511	67.63	0.01673
465	28.386	68.60	0.03668
470	28.112	70.71	0.03829
475	27.826	72.92	0.01379
480	27.723	73.71	0.02436
485	27.541	75.12	0.03079
490	27.311	76.89	0.02450
495	27.128	78.31	0.01580
500	27.010	79.22	0.02209
505	26.845	80.49	0.00991
510	26.771	81.06	0.02316
515	26.598	82.40	0.03427
520	26.342	84.37	0.01888
525	26.201	85.46	0.01834
530	26.064	86.52	0.01955
535	25.918	87.64	0.01540
540	25.803	88.53	0.00683
545	25.752	88.92	0.01888
550	25.611	90.01	0.01526
555	25.497	90.89	0.02396
560	25.318	92.27	0.01821
565	25.182	93.32	0.02155
570	25.021	94.57	0.00522
575	24.982	94.87	0.01272
580	24.887	95.60	0.02490
585	24.701	97.04	0.00750
590	24.645	97.47	0.00977
595	24.572	98.03	0.00616
600	24.526	98.39	0.00576
605	24.483	98.72	0.00991
610	24.409	99.29	0.00321
615	24.385	99.48	0.00415
620	24.354	99.71	0.00214
625	24.338	99.84	0.00281
630	24.317	100.00	0.00000
635	24.317	100.00	0.00000
640	24.317	100.00	0.00000
650	24.317	100.00	0.00000
660	24.317	100.00	0.00000
670	24.317	100.00	0.00000
680	24.317	100.00	0.00000
690	24.317 = h_{∞}	100.00	0.00000

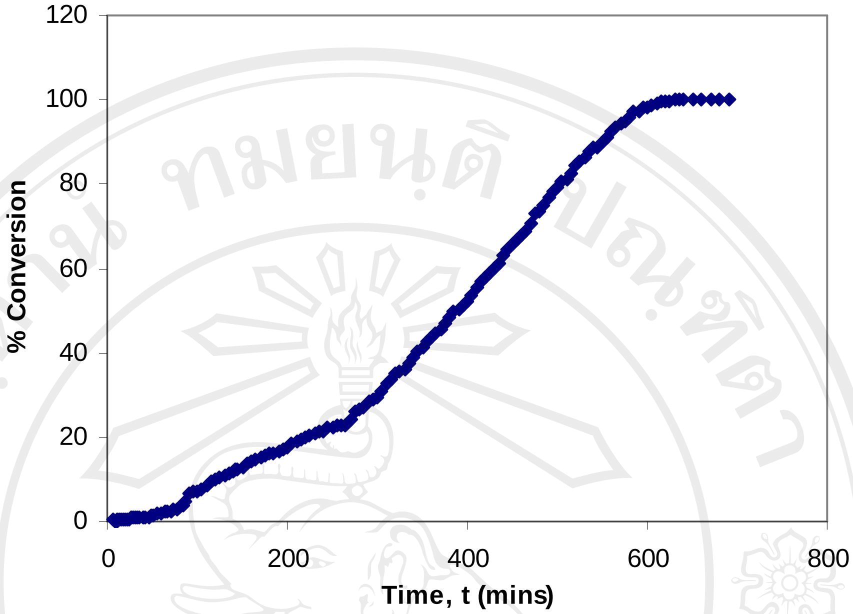


Figure 4.12 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using tin(II) ethoxide as initiator at 140 ^{o}C.

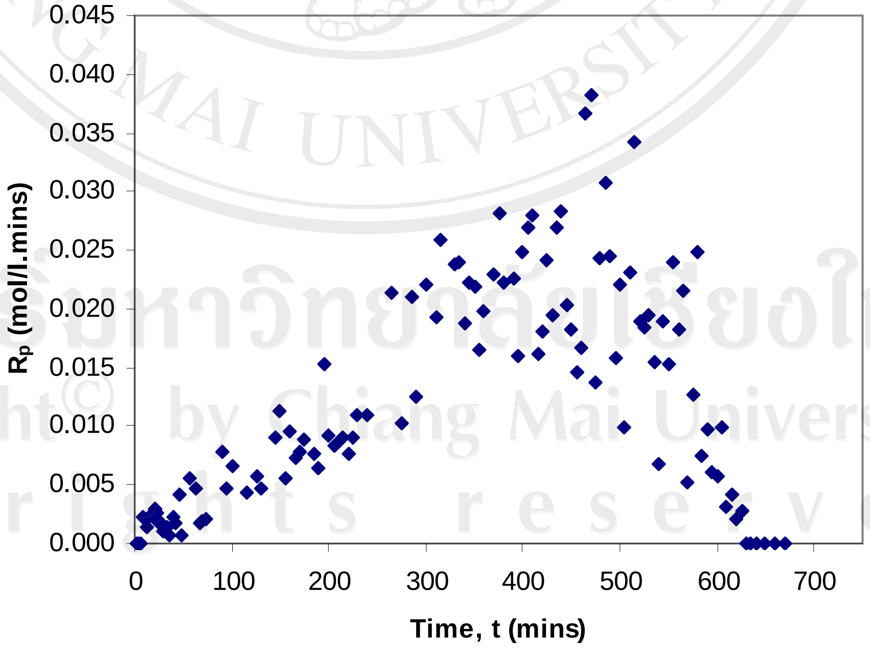


Figure 4.13 Kinetic profile from dilatometry of the rate of polymerization, R_p, against time for ε-caprolactone using tin(II) ethoxide as initiator at 140 ^{o}C.

Run No. 9 : Caprolactone @ 140 $^oC/Sn(OC_3H_7)_2$ (0.1 mol %)

Table 4.10 Dilatometric data from ε-caprolactone polymerization at 140 ^oC using 0.1 mol % tin(II) propoxide as initiator.

weight of ε-caprolactone = 8.9223 g
weight of $Sn(OC_3H_7)_2$ = 0.0185 g
capillary diameter = 0.18 cm
h_0 (from extrapolation) = 36.069 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	35.372	Thermal equilibration	
4	35.692		
6	35.711		
8	35.745		
10	35.760		
12	35.751	2.76	0.00376
14	35.741	2.85	0.00038
16	35.740	2.85	0.00201
19	35.732	2.92	0.00414
21	35.721	3.02	0.00339
23	35.721	3.02	0.00000
25	35.721	3.02	0.00602
27	35.705	3.16	0.00176
30	35.698	3.22	0.00326
33	35.685	3.33	0.01844
35	35.636	3.76	0.01505
37	35.596	4.10	0.01091
39	35.567	4.36	0.01405
42	35.511	4.84	0.00050
45	35.509	4.86	0.01605
48	35.445	5.41	0.01104
51	35.401	5.80	0.01906
54	35.325	6.46	0.00627
57	35.300	6.67	0.00226
60	35.291	6.75	0.00587
65	35.252	7.09	0.02985
68	35.133	8.12	0.00959
72	35.082	8.56	0.01072
76	35.025	9.06	0.01110
80	34.966	9.57	0.01069
85	34.895	10.19	0.02465
89	34.764	11.32	0.01731
93	34.672	12.12	0.01825
97	34.575	12.96	0.01580
100	34.512	13.51	0.01656
105	34.402	14.47	0.03161
110	34.192	16.29	0.01630
113	34.127	16.85	0.02389
117	34.000	17.95	0.02709
120	33.892	18.89	0.01787
124	33.797	19.72	0.02082
127	33.714	20.44	0.03462
130	33.576	21.63	0.01674
134	33.487	22.41	0.02157
137	33.401	23.15	0.02534
140	33.300	24.03	0.01599
144	33.215	24.77	0.03261
147	33.085	25.89	0.01279
150	33.034	26.34	0.02370
154	32.908	27.43	0.02885
157	32.793	28.43	0.01279
160	32.742	28.87	0.03060
163	32.620	29.93	0.02483
166	32.521	30.79	0.02483
170	32.389	31.93	0.01863
174	32.290	32.79	0.02408
177	32.194	33.63	0.04992
180	31.995	35.35	0.01008
185	31.928	35.93	0.02498
190	31.762	37.37	0.02137
195	31.620	38.61	0.03116
200	31.413	40.40	0.02182
205	31.268	41.66	0.03116
210	31.061	43.46	0.01430
215	30.966	44.28	0.01370
220	30.875	45.07	0.01430
225	30.780	45.90	0.00452
230	30.750	46.16	0.02152
235	30.607	47.40	0.02408
240	30.447	48.79	0.01460

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
245	30.350	49.63	0.01761
250	30.233	50.64	0.01084
255	30.161	51.27	0.02092
260	30.022	52.47	0.01550
265	29.919	53.37	0.02393
270	29.760	54.75	0.01264
275	29.676	55.48	0.02273
280	29.525	56.79	0.01580
285	29.420	57.70	0.01460
290	29.323	58.54	0.02228
295	29.175	59.82	0.01204
300	29.095	60.52	0.02182
305	28.950	61.78	0.02062
310	28.813	62.96	0.01926
315	28.685	64.07	0.01625
320	28.577	65.01	0.01460
325	28.480	65.85	0.02303
330	28.327	67.18	0.01686
335	28.215	68.15	0.01942
340	28.086	69.27	0.00978
345	28.021	69.84	0.02243
350	27.872	71.13	0.01610
355	27.765	72.06	0.02483
360	27.600	73.49	0.01731
365	27.485	74.49	0.01656
370	27.375	75.44	0.01656
375	27.265	76.40	0.01279
380	27.180	77.13	0.02137
385	27.038	78.37	0.01189
390	26.959	79.05	0.02107
418	26.371	84.15	0.02446
420	26.306	84.72	0.01505
425	26.206	85.59	0.01069
430	26.135	86.20	0.00527
435	26.100	86.51	0.01505
440	26.000	87.37	0.00436
395	26.819	80.27	0.01249
400	26.736	80.99	0.01294
405	26.650	81.73	0.02438
410	26.488	83.14	0.01101
450	25.942	87.88	0.02002
455	25.809	89.03	0.01535
460	25.707	89.92	0.02589
465	25.535	91.41	0.01279
470	25.450	92.15	0.02483
475	25.285	93.58	0.01957
480	25.155	94.71	0.01580
485	25.050	95.62	0.02378
490	24.892	96.99	0.02220
500	24.597	99.55	0.00783
505	24.545	100.00	0.00000
510	24.545	100.00	0.00000
515	24.545	100.00	0.00000
520	24.545	100.00	0.00000
530	24.545	100.00	0.00000
540	24.545	100.00	0.00000
550	24.545	100.00	0.00000
560	24.545	100.00	0.00000
570	24.545 $= h_\infty$	100.00	0.00000

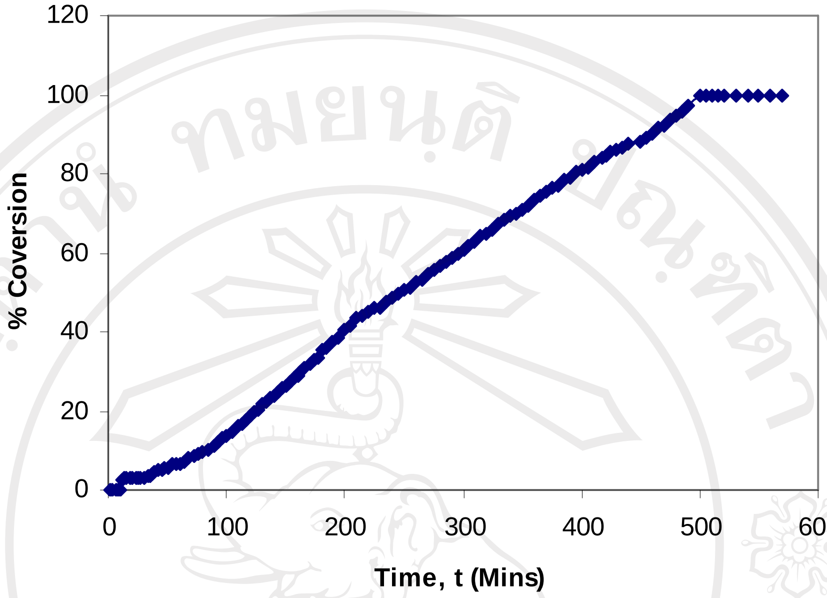


Figure 4.14 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using tin(II) propoxide as initiator at 140 °C.

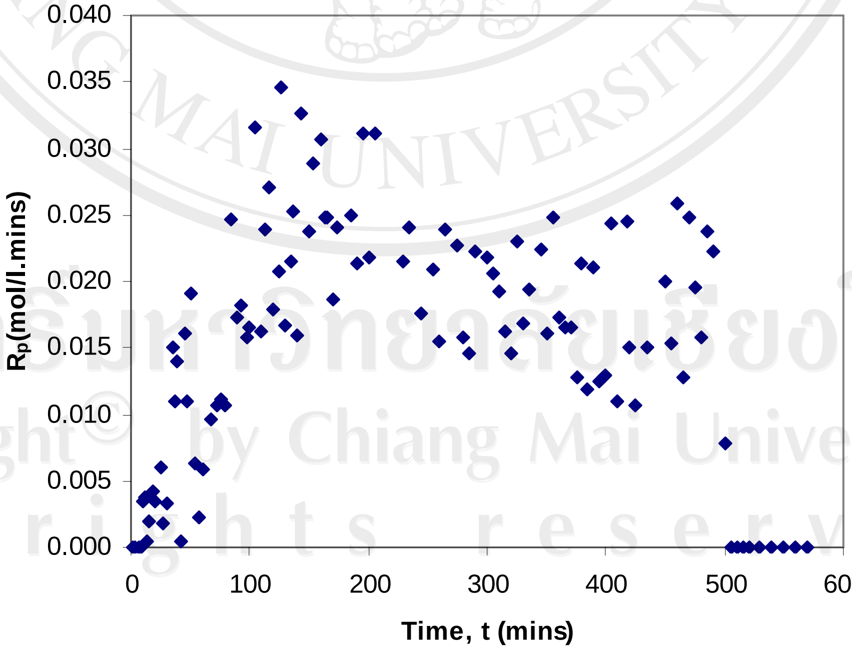


Figure 4.15 Kinetic profile from dilatometry of the rate of polymerization, R_p, against time for ε-caprolactone using tin(II) propoxide as initiator at 140 °C.

Run No. 10 : Caprolactone @ 140 ^{o}C/Sn(OC$_4$H$_9$)$_2$ (0.1 mol %)

Table 4.11 Dilatometric data from ε-caprolactone polymerization at 140 ^{o}C using 0.1 mol % tin(II) butoxide as initiator.

weight of ε-caprolactone = 8.9227 g
weight of Sn(OC$_4$H$_9$)$_2$ = 0.0207 g
capillary diameter = 0.18 cm
h$_0$ (from extrapolation) = 37.471 cm

Time (mins)	h (cm)	Conversion (%)	R$_P$ (mol/l.min)
2	36.650	Thermal equilibration	
4	37.321		
6	37.349		
8	37.279		
10	37.195	2.21	0.01736
12	37.145	2.61	0.03751
14	37.037	3.48	0.00069
16	37.035	3.49	0.02952
18	36.950	4.17	0.01736
20	36.900	4.57	0.00521
22	36.885	4.69	0.00382
24	36.874	4.78	0.01181
27	36.823	5.19	0.01690
30	36.750	5.77	0.02014
33	36.663	6.47	0.01158
36	36.613	6.87	0.01702
40	36.515	7.66	0.01615
44	36.422	8.40	0.00521
48	36.392	8.64	0.00747
52	36.349	8.99	0.00469
56	36.322	9.20	0.01250
60	36.250	9.78	0.01505
66	36.120	10.82	0.02084
70	36.000	11.78	0.01158
73	35.950	12.18	0.04897
75	35.809	13.31	0.01366
78	35.750	13.78	0.02674
80	35.673	14.40	0.00810
83	35.638	14.68	0.01962
87	35.525	15.58	0.02894
90	35.400	16.59	0.01563
94	35.310	17.31	0.01158
97	35.260	17.71	0.01389
100	35.200	18.19	0.01611
105	35.084	19.12	0.00722
110	35.032	19.53	0.01459
115	34.927	20.37	0.00375
120	34.900	20.59	0.00955
124	34.845	21.03	0.01875
127	34.764	21.68	0.00990
131	34.707	22.14	0.00469
135	34.680	22.35	0.00583
140	34.638	22.69	0.01431
145	34.535	23.51	0.01181
150	34.450	24.19	0.00528
155	34.412	24.50	0.00667
160	34.364	24.88	0.01441
164	34.281	25.55	0.01412
167	34.220	26.04	0.01042
170	34.175	26.40	0.01597
175	34.060	27.32	0.01361
180	33.962	28.10	0.01070
185	33.885	28.72	0.01000
190	33.813	29.29	0.01042
195	33.738	29.90	0.00458
200	33.705	30.16	0.01584
205	33.591	31.07	0.02362
210	33.421	32.43	0.00875
215	33.358	32.94	0.02403
220	33.185	34.32	0.03098
225	32.962	36.11	0.02612
230	32.774	37.62	0.00889
235	32.710	38.13	0.01875
240	32.575	39.21	0.05001
244	32.287	41.52	0.03380
247	32.141	42.68	0.01621
250	32.071	43.24	0.00708
255	32.020	43.65	0.00333

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
260	31.996	43.85	0.00222
265	31.980	43.97	0.00625
270	31.835	44.33	0.00306
275	31.913	44.51	0.01459
280	31.808	45.35	0.01848
285	31.675	46.42	0.01542
290	31.564	47.31	0.01584
295	31.450	48.22	0.02223
300	31.290	49.50	0.02264
305	31.127	50.80	0.01764
310	31.000	51.82	0.02209
315	30.841	53.10	0.01959
320	30.700	54.22	0.03917
325	30.418	56.48	0.01570
330	30.305	57.39	0.01806
335	30.175	58.43	0.01597
340	30.060	59.35	0.02195
345	29.902	60.62	0.01222
350	29.814	61.32	0.01973
355	29.672	62.46	0.02250
360	29.510	63.75	0.02167
365	29.354	65.00	0.01445
370	29.250	65.84	0.02139
375	29.096	67.07	0.02236
380	28.935	68.36	0.02570
385	28.750	69.84	0.01500
390	28.642	70.71	0.02473
395	28.464	72.13	0.02153
400	28.309	73.37	0.01861
405	28.175	74.45	0.02431
410	28.000	75.85	0.01986
415	27.857	76.99	0.03112
420	27.633	78.79	0.01917
425	27.495	79.89	0.02584
430	27.309	81.38	0.01736
435	27.184	82.38	0.01903
440	27.047	83.48	0.02042
445	26.900	84.66	0.01723
450	26.776	85.65	0.01986
455	26.633	86.79	0.01848
460	26.500	87.86	0.01236
465	26.411	88.57	0.02070
470	26.262	89.77	0.01903
475	26.125	90.86	0.00528
480	26.087	91.17	0.01292
485	25.994	91.91	0.01653
490	25.875	92.86	0.01528
495	25.765	93.75	0.01292
500	25.672	94.49	0.01000
505	25.600	95.07	0.00903
510	25.535	95.59	0.01181
515	25.450	96.27	0.00250
520	25.432	96.41	0.00653
525	25.385	96.79	0.00917
530	25.319	97.32	0.00472
535	25.285	97.59	0.01472
540	25.179	98.44	0.00201
550	25.150	98.67	0.01236
555	25.061	99.38	0.00424
565	25.000	99.87	0.00222
570	24.984	100.00	0.00000
580	24.984	100.00	0.00000
600	24.984	100.00	0.00000
610	24.984	100.00	0.00000
620	24.984	100.00	0.00000
630	24.984 = h_∞	100.00	0.00000

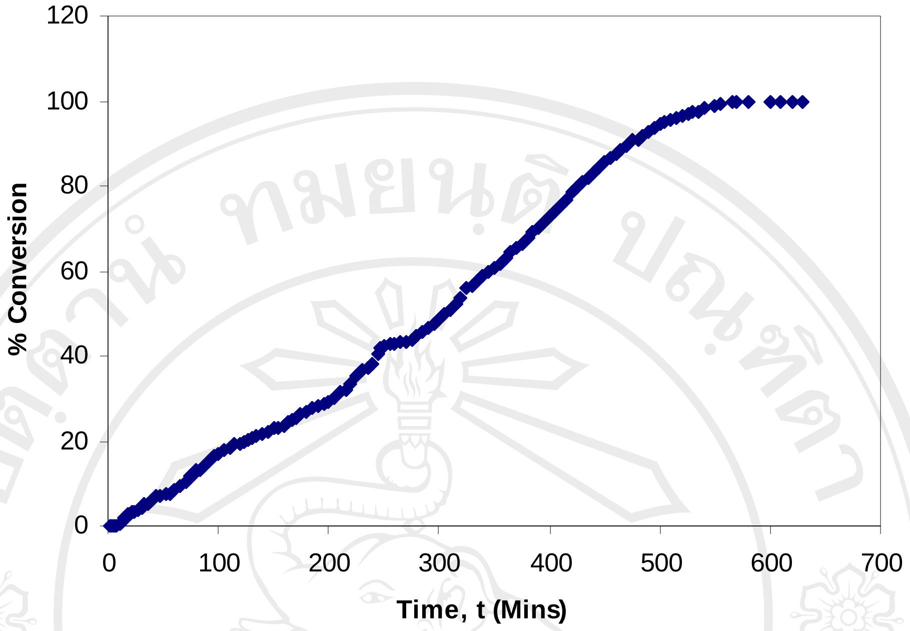


Figure 4.16 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using tin(II) butoxide as initiator at 140 ^{o}C.

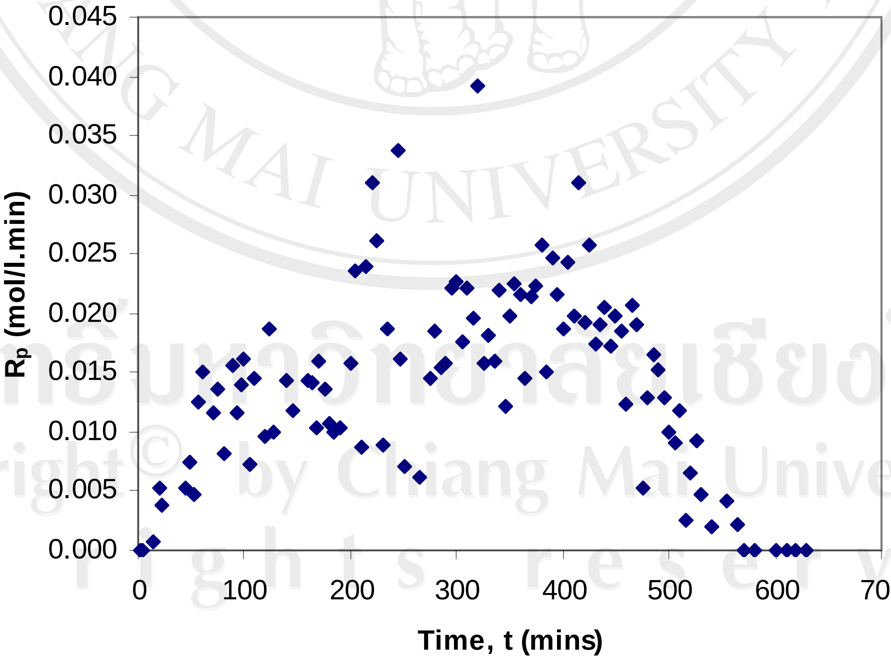


Figure 4.17 Kinetic profile from dilatometry of the rate of polymerization, R_p, against time for ε-caprolactone using tin(II) butoxide as initiator at 140 ^{o}C.

Run No. 11 : Caprolactone @ 140 ^{o}C/Sn(OC$_6$H$_{13}$)$_2$ (0.1 mol %)

Table 4.12 Dilatometric data from ε-caprolactone polymerization at 140 ^{o}C using 0.1 mol % tin(II) hexoxide as initiator.

weight of ε-caprolactone = 8.9222 g
weight of Sn(OC$_6$H$_{13}$)$_2$ = 0.0251 g
capillary diameter = 0.18 cm
h_0 (from extrapolation) = 34.398 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	33.552	Thermal equilibration	
4	33.786		
6	33.912		
8	33.950		
11	34.058		
13	34.062		
15	34.141		
17	34.138	2.32	0.00155
20	34.132	2.38	0.00116
22	34.129	2.40	0.00413
25	34.113	2.55	0.00233
27	34.107	2.60	0.02817
30	33.998	3.58	0.00103
33	33.994	3.61	0.00310
35	33.986	3.68	0.00186
40	33.974	3.79	0.00372
45	33.950	4.00	0.01227
51	33.855	4.85	0.02597
55	33.721	6.05	0.01969
60	33.594	7.19	0.03132
65	33.392	8.99	0.03818
69	33.195	10.75	0.03127
72	33.074	11.83	0.01256
77	32.993	12.56	0.01654
80	32.929	13.13	0.02264
85	32.783	14.44	0.03566
88	32.645	15.67	0.01957
92	32.544	16.57	0.00988
96	32.493	17.03	0.02849
100	32.346	18.34	0.01628
106	32.220	19.47	0.02733
110	32.079	20.73	0.02429
113	31.985	21.57	0.06473
115	31.818	23.06	0.03605
117	31.725	23.89	0.02687
120	31.621	24.82	0.02041
123	31.542	25.53	0.04083
126	31.384	26.94	0.03450
130	31.206	28.53	0.02093
134	31.098	29.50	0.00129
137	31.093	29.54	0.08476
140	30.765	32.47	0.04780
143	30.580	34.13	0.04625
146	30.401	35.73	0.04755
149	30.217	37.37	0.05310
151	30.080	38.59	0.03488
154	29.945	39.80	0.07184
157	29.667	42.29	0.05091
160	29.470	44.05	0.07184
163	29.192	46.53	0.06085
165	29.035	47.94	0.04910
168	28.845	49.63	0.06331
171	28.600	51.82	0.06318
175	28.274	54.74	0.07628
180	27.782	59.13	0.07132
185	27.322	63.25	0.06248
190	26.919	66.85	0.05209
195	26.583	69.85	0.05240
200	26.245	72.87	0.05830
205	25.869	76.23	0.04729
210	25.564	78.96	0.05923
215	25.182	82.37	0.04310
220	24.904	84.86	0.04372
225	24.622	87.38	0.03628
230	24.388	89.47	0.03674
235	24.151	91.59	0.02403
240	23.996	92.97	0.02031
245	23.865	94.15	0.01907
250	23.742	95.24	0.02264
255	23.596	96.55	0.00698

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
260	23.551	96.95	0.01093
270	23.410	98.21	0.00465
280	23.350	98.75	0.00519
290	23.283	99.35	0.00140
300	23.265	99.51	0.00116
310	23.250	99.64	0.00070
320	23.241	99.72	0.00085
330	23.230	99.82	0.00016
340	23.228	99.84	0.00023
350	23.225	99.87	0.00023
360	23.222	99.89	0.00016
370	23.220	99.91	0.00016
380	23.218	99.93	0.00000
390	23.218	99.93	0.00000
400	23.218	99.93	0.00023
410	23.215	99.96	0.00000
420	23.215	99.96	0.00000
430	23.215	99.96	0.00023
440	23.212	99.98	0.00000
450	23.212	99.98	0.00000
460	23.212	99.98	0.00016
470	23.210	100.00	0.00000
480	23.210	100.00	0.00000
490	23.210	100.00	0.00000
500	23.210	100.00	0.00000
510	23.210	100.00	0.00000
520	23.210	100.00	0.00000
530	23.210	100.00	0.00000
540	23.210	100.00	0.00000
550	23.210 $= h_\infty$	100.00	0.00000

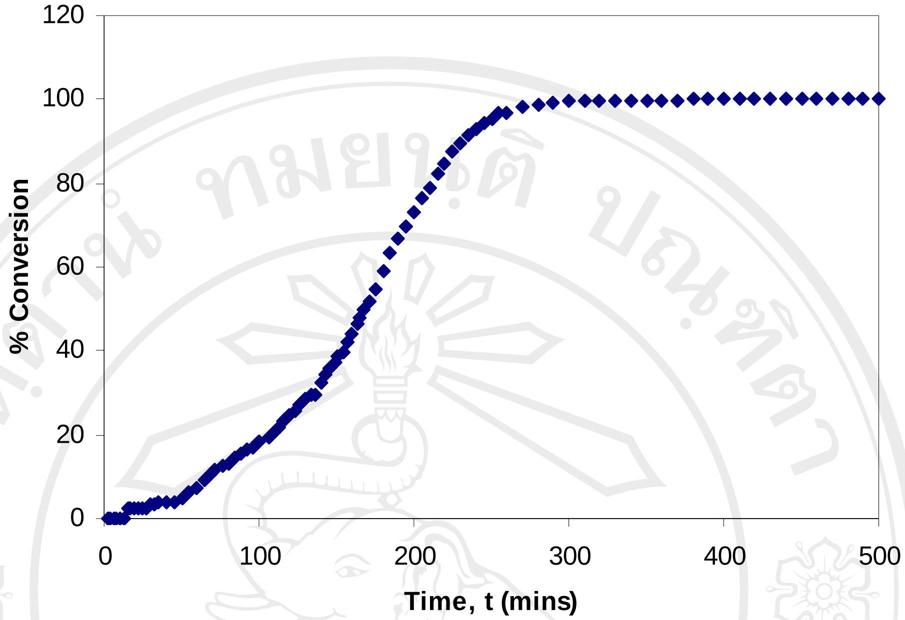


Figure 4.18 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using tin(II) hexoxide as initiator at 140 ^{o}C.

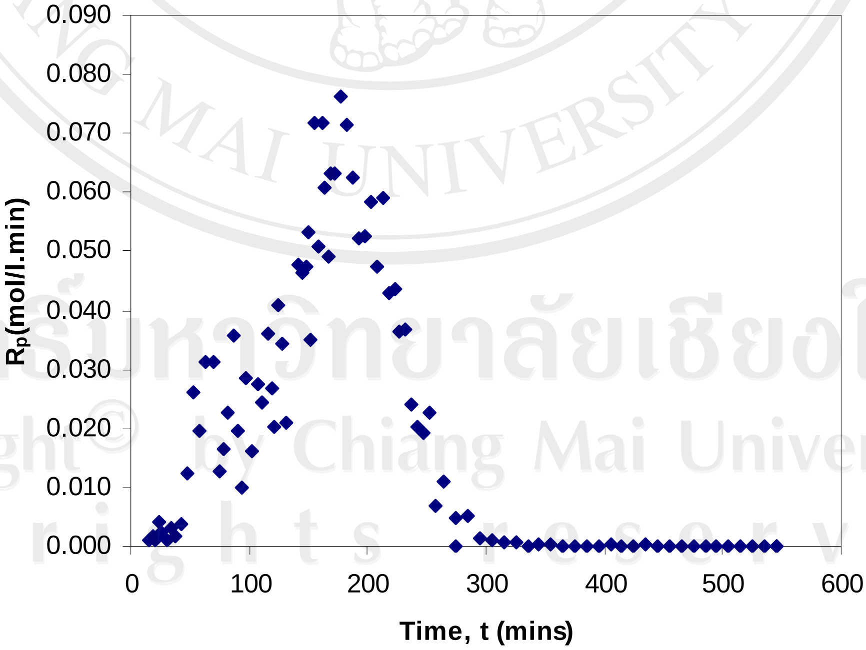


Figure 4.19 Kinetic profile from dilatometry of the rate of polymerization, R_p, against time for ε-caprolactone using tin(II) hexoxide as initiator at 140 ^{o}C.

Run No. 12 : Caprolactone @ 140 ^{o}C/Sn(OC$_8$H$_{17}$)$_2$ (0.1 mol %)

Table 4.13 Dilatometric data from ε-caprolactone polymerization at 140 ^{o}C using 0.1 mol % tin(II) octoxide as initiator.

weight of ε-caprolactone = 8.9220 g
weight of Sn(OC$_8$H$_{17}$)$_2$ = 0.0294 g
capillary diameter = 0.18 cm
h_0 (from extrapolation) = 36.897 cm

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
2	36.125	Thermal equilibration	
4	36.395		
6	36.437		
8	36.440		
10	36.450		
12	36.464		
14	36.572		
16	36.592		
18	36.595		
20	36.591	2.65	0.00075
22	36.589	2.66	0.00175
25	36.582	2.72	0.00075
29	36.578	2.76	0.00131
33	36.571	2.82	0.00037
37	36.569	2.84	0.00100
40	36.565	2.87	0.00075
45	36.560	2.91	0.00090
50	36.554	2.97	0.00060
55	36.550	3.00	0.00045
60	36.547	3.03	0.00240
65	36.531	3.17	0.00262
67	36.524	3.23	0.00225
69	36.518	3.28	0.00675
72	36.491	3.51	0.00275
75	36.480	3.61	0.01260
80	36.396	4.33	0.00600
85	36.356	4.68	0.01875
90	36.231	5.76	0.03500
93	36.091	6.97	0.02150
96	36.005	7.71	0.02475
100	35.873	8.86	0.03075
103	35.750	9.92	0.01000
106	35.710	10.27	0.03450
109	35.572	11.46	0.02250
112	35.482	12.24	0.02975
115	35.363	13.27	0.02575
118	35.260	14.16	0.02437
120	35.195	14.72	0.03125
123	35.070	15.80	0.02350
126	34.976	16.61	0.03075
130	34.812	18.03	0.04125
133	34.647	19.46	0.02800
136	34.535	20.43	0.03131
140	34.368	21.87	0.04300
143	34.196	23.36	0.03050
146	34.074	24.42	0.00881
150	34.027	24.82	0.06124
153	33.782	26.94	0.01725
156	33.713	27.54	0.03412
160	33.531	29.11	0.02225
163	33.442	29.88	0.03050
166	33.320	30.94	0.04200
168	33.208	31.91	0.02737
170	33.135	32.54	0.02750
173	33.025	33.49	0.03500
176	32.885	34.70	0.03562
178	32.790	35.52	0.04050
180	32.682	36.46	0.03725
183	32.533	37.74	0.04537
185	32.412	38.79	0.03800
188	32.260	40.11	0.03787
190	32.159	40.98	0.03825

Time (mins)	h (cm)	Conversion (%)	R_P (mol/l.min)
192	32.057	41.86	0.03775
195	31.906	43.17	0.03700
198	31.758	44.45	0.04050
200	31.650	45.38	0.03937
202	31.545	46.29	0.04350
204	31.429	47.29	0.04837
206	31.300	48.41	0.05924
208	31.142	49.78	0.04162
210	31.031	50.74	0.03900
212	30.927	51.63	0.04275
214	30.813	52.62	0.04950
216	30.681	53.76	0.04762
218	30.554	54.86	0.03900
220	30.450	55.76	0.03475
223	30.311	56.96	0.04237
225	30.198	57.94	0.04050
227	30.090	58.87	0.04350
230	29.916	60.38	0.03775
233	29.765	61.68	0.06524
235	29.591	63.19	0.04025
238	29.430	64.58	0.05437
240	29.285	65.84	0.04312
242	29.170	66.83	0.03600
244	29.074	67.66	0.04912
246	28.943	68.79	0.03825
248	28.841	69.68	0.03975
250	28.735	70.59	0.04275
253	28.564	72.07	0.04825
256	28.371	73.74	0.05100
258	28.235	74.92	0.03787
260	28.134	75.79	0.04175
263	27.967	77.24	0.02925
266	27.850	78.25	0.04425
268	27.732	79.27	0.03975
270	27.626	80.19	0.04150
273	27.460	81.62	0.03375
276	27.325	82.79	0.03806
280	27.122	84.54	0.03425
283	26.985	85.73	0.02925
285	26.907	86.40	0.02640
290	26.731	87.93	0.02875
293	26.616	88.92	0.02156
297	26.501	89.92	0.02100
300	26.417	90.64	0.02355
305	26.260	92.00	0.01875
310	26.135	93.08	0.02310
315	25.981	94.41	0.01590
320	25.875	95.33	0.01875
325	25.750	96.41	0.00975
330	25.685	96.97	0.01365
335	25.594	97.76	0.00660
340	25.550	98.14	0.01050
345	25.480	98.75	0.00735
350	25.431	99.17	0.01140
355	25.355	99.83	0.00300
360	25.335	100.00	0.00000
370	25.335	100.00	0.00000
380	25.335	100.00	0.00000
390	25.335	100.00	0.00000
400	25.335	100.00	0.00000
410	25.335	100.00	0.00000
420	25.335 $= h_\infty$	100.00	0.00000

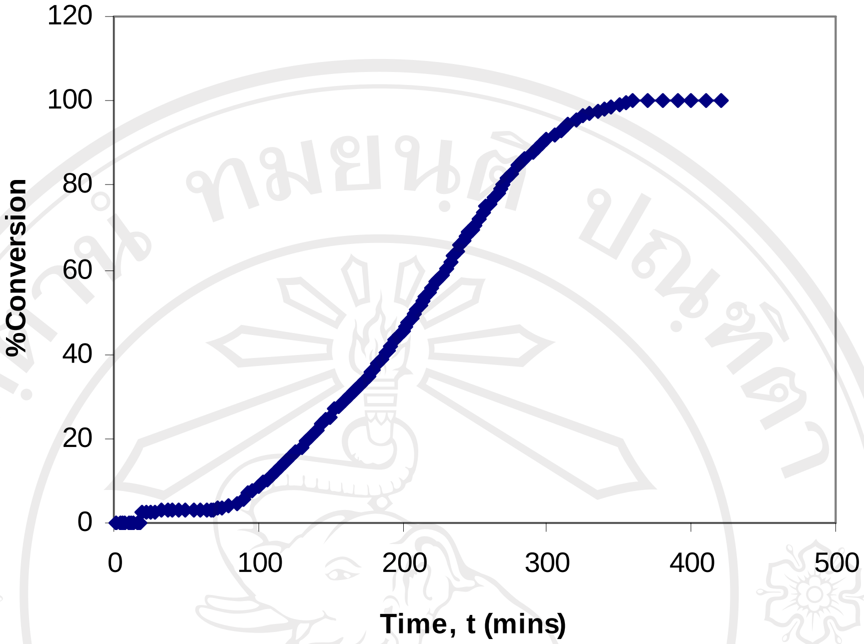


Figure 4.20 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using tin(II) octoxide as initiator at 140 °C.

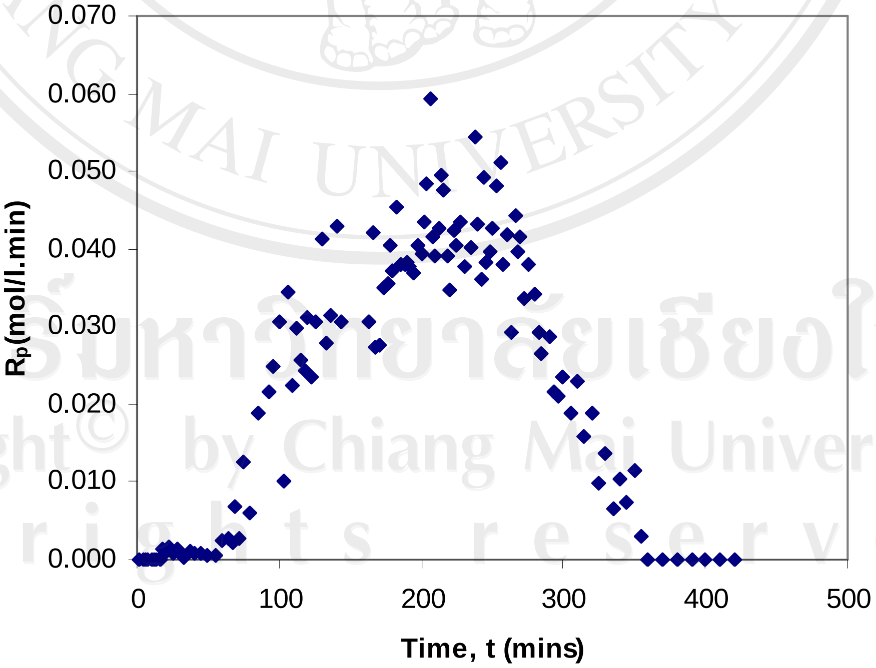


Figure 4.21 Kinetic profile from dilatometry of the rate of polymerization, R_p, against time for ε-caprolactone using tin(II) octoxide as initiator at 140 °C.

4.2.7 Kinetic Analysis

4.2.7.1 First-Order Kinetics

It has been widely reported in the research literature that the bulk polymerization of ε-caprolactone using coordination-insertion-type initiating systems is kinetically first-order (n=1) with respect to monomer, i.e.

$$-\frac{d[M]}{dt} = k_1[M]$$

which, when integrated between the limits of $[M]_0$ at time t=0 and $[M]_t$ at time t=t, gives the first-order rate equation of:

$$\ln([M]_0/[M]_t) = k_1 t$$

where k_1 is the first-order rate constant.

Given the correspondence from dilatometry (Infinite Time Method) that

$$\ln([M]_0/[M]_t) = \ln[(h_0-h_\infty)/(h-h_\infty)]$$

the first-order rate equation can be expressed in terms of the primary dilatometric data (h,t) as

$$\ln[(h_0-h_\infty)/(h-h_\infty)] = k_1 t$$

Therefore, for a first-order reaction, a semi-log plot of $\ln[(h_0-h_\infty)/(h-h_\infty)]$ or $\ln([M]_0/[M]_t)$ against time t should yield a straight line graph of slope = k_1 = the first-order rate constant.

However, as the first-order rate plots in Figures 4.22-4.27 show, there is little or no adherence to first-order kinetics in any of the plots. This is undoubtedly a consequence of the time taken for initiator solubilization to occur. Since initiator solubilization is taking place over a large part if not the whole of the polymerization reaction, the kinetics of monomer consumption are complicated accordingly. Instead of the tin(II) alkoxide initiator providing a steady-state concentration of active sites throughout the course of the reaction, as would be the case if it was instantly soluble in the monomer, it provides a constantly changing (increasing) concentration as it gradually solubilizes. Moreover, the fact that active site (Sn-O) deaggregation is believed to be in equilibrium with reaggregation complicates the situation even further. Thus we have a situation where, even though the coordination-insertion mechanism of polymerization is known to be first-order, the kinetics are distorted by other extraneous factors peculiar to the system, hence the marked deviation from what would otherwise be first-order kinetics.

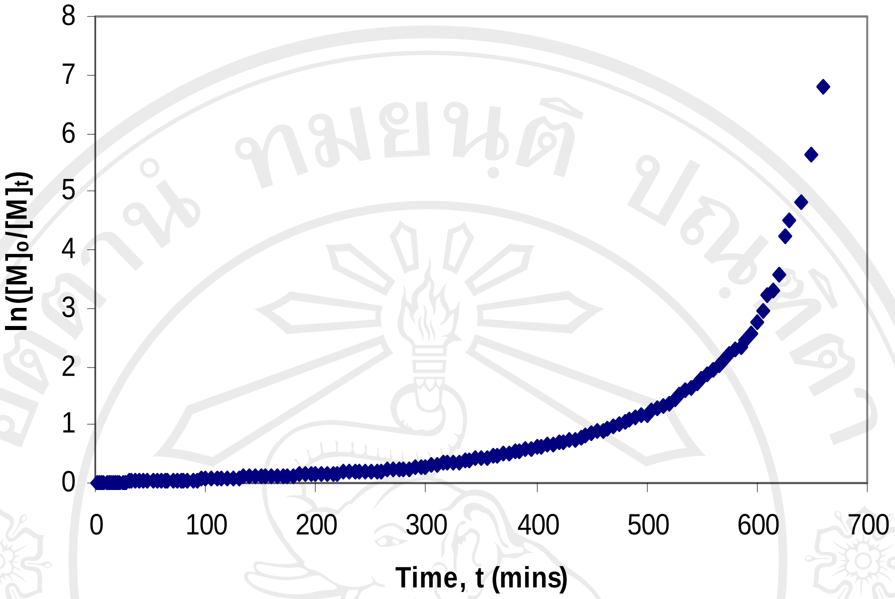


Figure 4.22 First-order rate plot from dilatometry for ε-caprolactone polymerization at 140 °C using tin(II) methoxide as initiator.

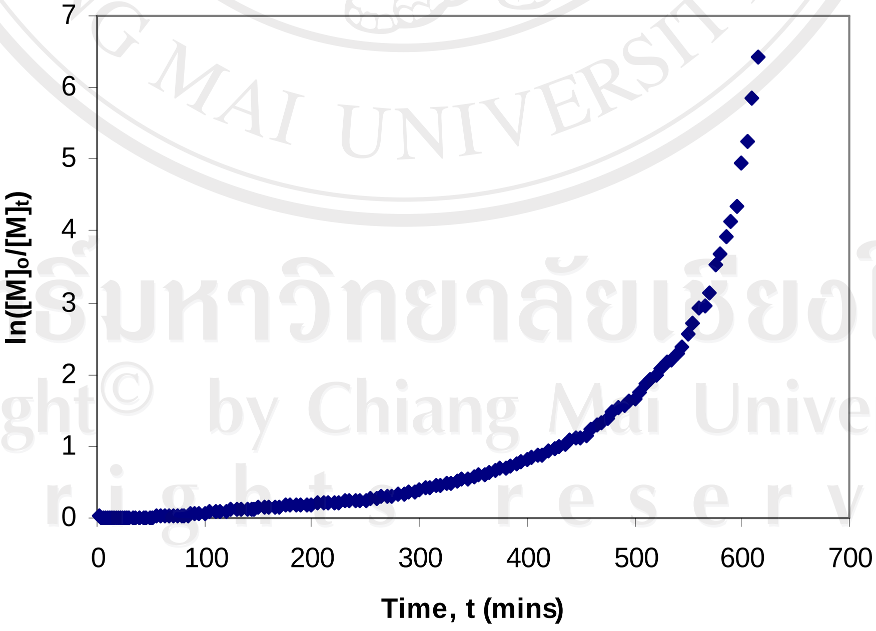


Figure 4.23 First-order rate plot from dilatometry for ε-caprolactone polymerization at 140 °C using tin(II) ethoxide as initiator.

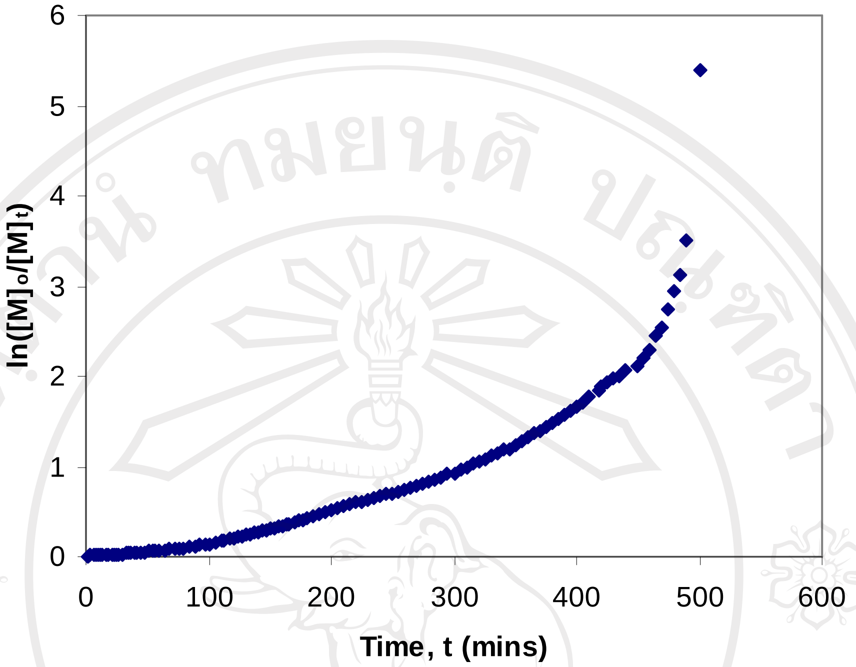


Figure 4.24 First-order rate plot from dilatometry for ε-caprolactone polymerization at 140 °C using tin(II)propoxide as initiator.

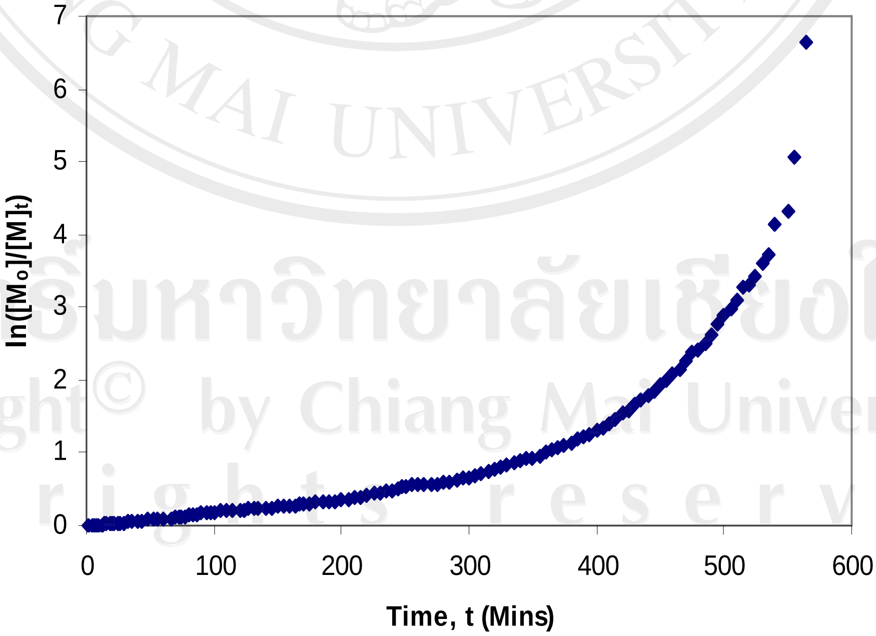


Figure 4.25 First-order rate plot from dilatometry for ε-caprolactone polymerization at 140 °C using tin(II) butoxide as initiator.

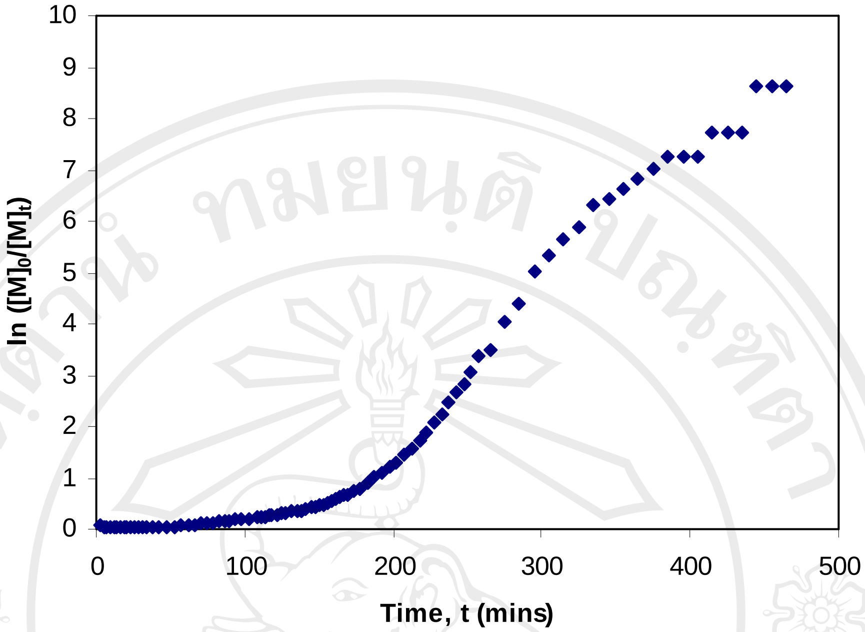


Figure 4.26 First-order rate plot from dilatometry for ε-caprolactone polymerization at 140 °C using tin(II) hexoxide as initiator.

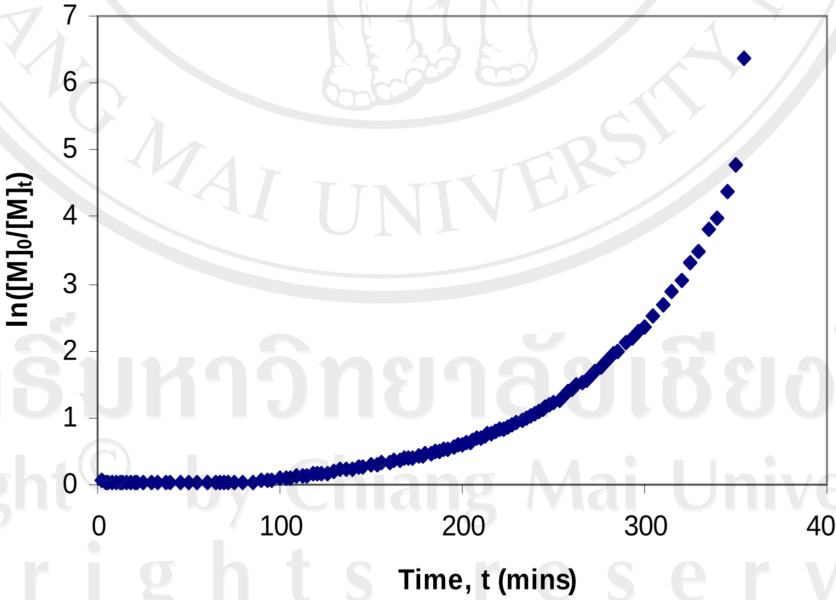


Figure 4.27 First-order rate plot from dilatometry for ε-caprolactone polymerization at 140 °C using tin(II) octoxide as initiator.

4.2.7.2 Zero-Order Kinetics

It is noticeable from the earlier % conversion-time profiles that they all have linear or near-linear portions from about 30 % conversion onwards. The % conversion-time plots are essentially zero-order kinetic plots. While this is not meant to imply that the polymerization reaction is a zero-order reaction, it is possible that the opposing rate effects of decreasing monomer concentration and increasing initiator solubilization could approximately balance each other resulting in pseudo-zero-order kinetics.

The zero-order rate equation is given by

$$-\frac{d[M]}{dt} = k_0$$

which when integrated gives

$$[M]_0 - [M]_t = k_0t$$

where k_0 is the zero-order rate constant.

This equation can be alternatively expressed as:

$$p = k_0t / [M]_0$$

where $[M]_0$ = initial monomer concentration (mol l^{-1}) at time t = 0
$[M]_t$ = remaining monomer concentration (mol l^{-1}) at time t
k_0 = zero-order rate constant (mol l^{-1} min^{-1})
p = extent of reaction (or fraction of conversion)

Given that $p = ([M]_0 – [M]_t) / [M]_0 = (h_0 – h)/(h_0-h_\infty)$ from dilatometry

a zero-order plot of p against time t should yield a (partial) straight line graph of slope = $k_0/[M]_0$. Knowing $[M]_0$, the value of k_0, the zero-order rate constant, can be calculated.

The zero-order plots of extent of reaction, p, against time, t, are shown in Figs. 4.28-4.33. All of the plots show reasonable straight line portions over a range of p ≈ 0.3-0.9 (% conversion ≈ 30-90 %) which represents a significantly large part of the reaction. From the slopes (= $k_0/[M]_0$) of these linear portions, the zero-order rate constants, k_0, can be calculated. These values of k_0, together with other related kinetic parameters which can be derived from the zero-order plots, are compared in Table 4.14 below.

Table 4.14 Zero-order rate constants, k_0, and related parameters for the tin(II) alkoxide-initiated polymerizations of ε-caprolactone at 140 °C.

Initiator	k_0 * (mol l^{-1} min $^{-1}$)	Linear Range for k_0 (% Conversion)	Time to 100 % Conv. t_∞ (min)
$Sn(OCH_3)_2$	2.11×10^{-2}	30-90 %	690
$Sn(OC_2H_5)_2$	2.18×10^{-2}	30-90 %	630
$Sn(OC_3H_7)_2$	1.77×10^{-2}	40-90 %	505
$Sn(OC_4H_9)_2$	2.01×10^{-2}	45-90 %	570
$Sn(OC_6H_{13})_2$	6.58×10^{-2}	35-80 %	470
$Sn(OC_8H_{17})_2$	4.63×10^{-2}	30-85 %	360

* k_0 calculated from the slope = $k_0/[M]_0$ where $[M]_0 = 8.673$ mol l^{-1}

The values for k_0 in the above table suggest that there is little to choose between the first four initiators ($R \leq C_4H_9$). The only clear conclusion that can be drawn from these results is that the hexoxide and octoxide give significantly faster reactions by a factor of 2-3. This is consistent with the visual observation that these were the only 2 initiators which completely dissolved within the timescale of the polymerization (i.e., within the time to h_∞). Their times to 100 % conversion, t_∞, are also significantly shorter.

As mentioned previously, these k_0 values are only pseudo (or apparent) zero-order rate constants, not true rate constants in the mechanistic sense. The propagation mechanism is certainly first-order with respect to monomer but the observed kinetics are complicated (a) by the slow solubilization of the initiator and (b) by the deaggregation-reaggregation equilibrium in solution. That the observed kinetics appear to be zero-order over a large part (≈ 50 %) of the reaction is probably just a fortuitous consequence of the increasing initiator solubilization counterbalancing the decreasing monomer concentration as far as their respective effects on the rate is concerned. Nevertheless, the apparent adherence to zero-order kinetics, fortuitous though it may be, is useful insofar that it allows the rate constants k_0 in Table 4.14 to be determined and compared.

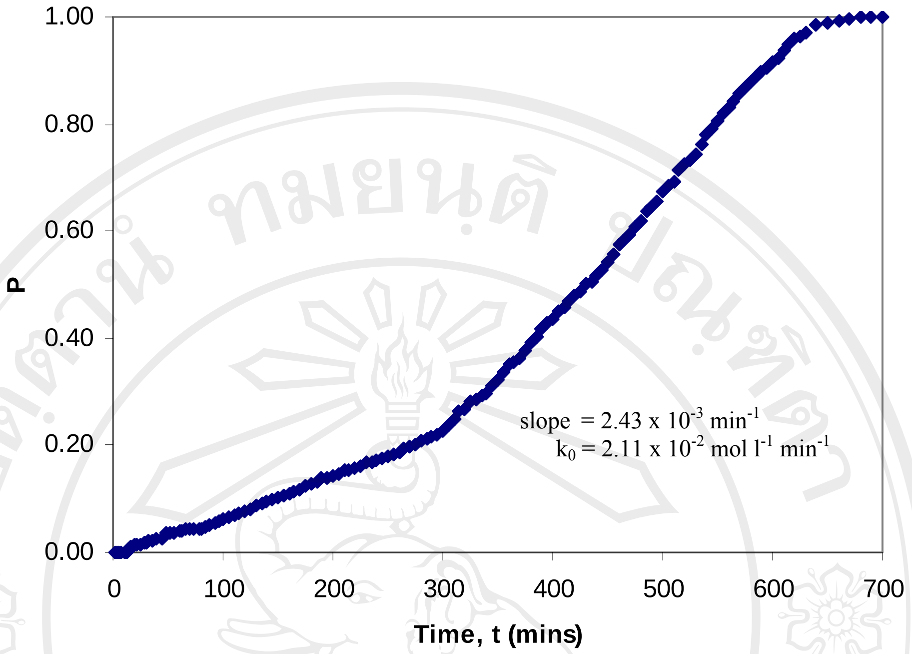


Figure 4.28 Zero-order rate plot of extent of reaction, p, against time, t, for the polymerization of ε-caprolactone at 140 °C using 0.1 mol % tin(II) methoxide, $Sn(OCH_3)_2$, as initiator.

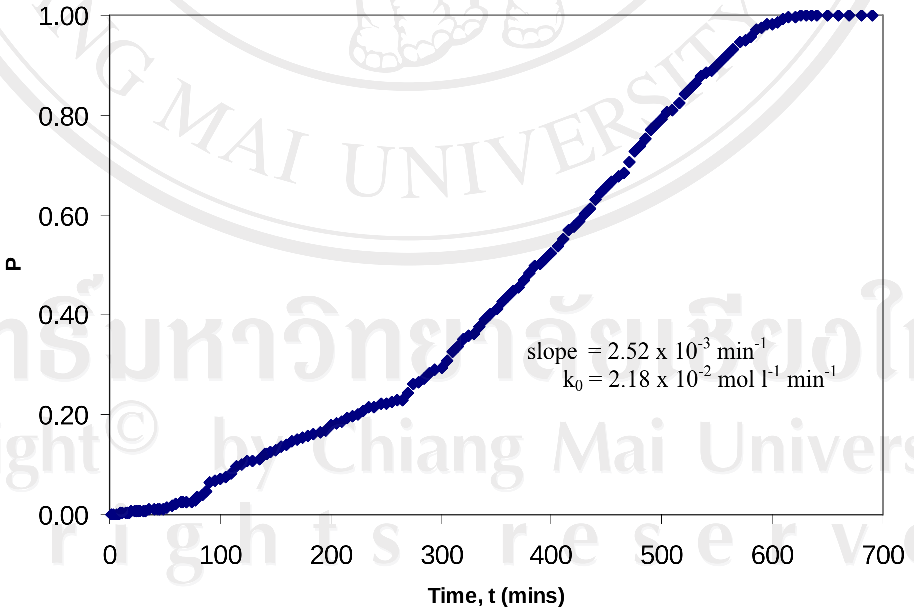


Figure 4.29 Zero-order rate plot of extent of reaction, p, against time, t, for the polymerization of ε-caprolactone at 140 °C using 0.1 mol % tin(II) ethoxide, $Sn(OC_2H_5)_2$, as initiator.

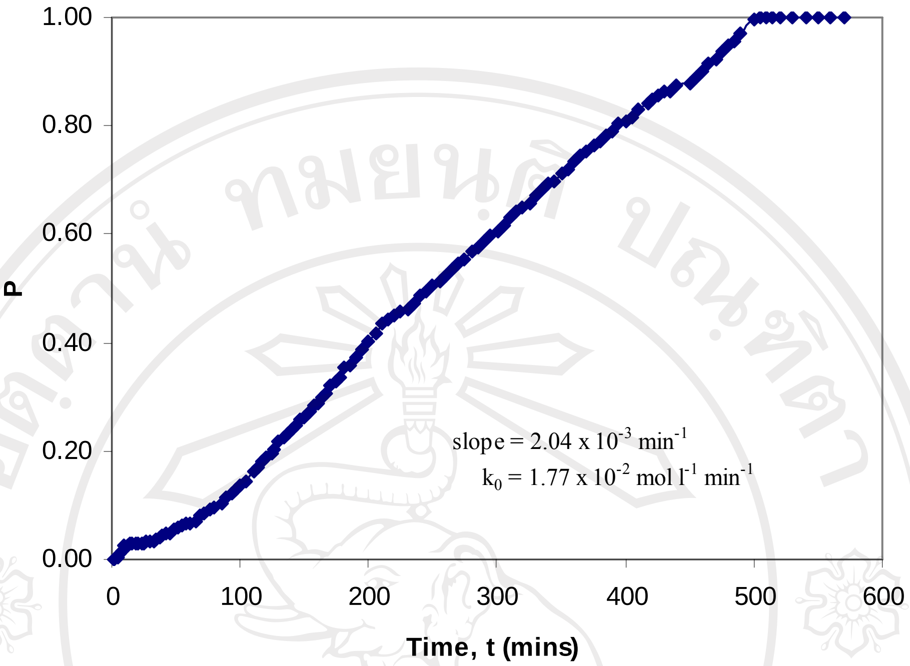


Figure 4.30 Zero-order rate plot of extent of reaction, p, against time, t, for the polymerization of ε-caprolactone at 140 °C using 0.1 mol % tin(II) propoxide, $Sn(OC_3H_7)_2$, as initiator.

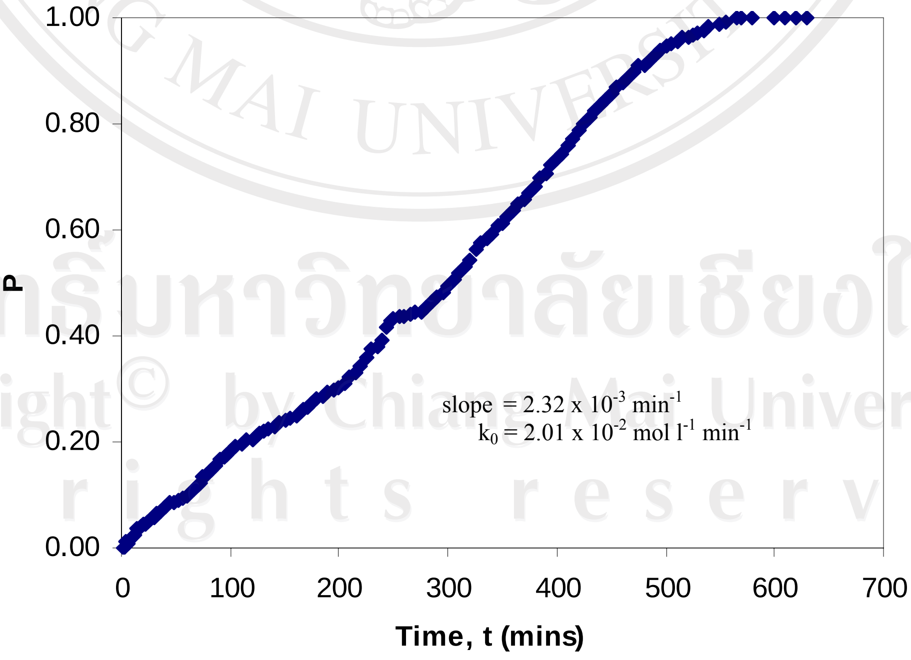


Figure 4.31 Zero-order rate plot of extent of reaction, p, against time, t, for the polymerization of ε-caprolactone at 140 °C using 0.1 mol % tin(II) butoxide, $Sn(OC_4H_9)_2$, as initiator.

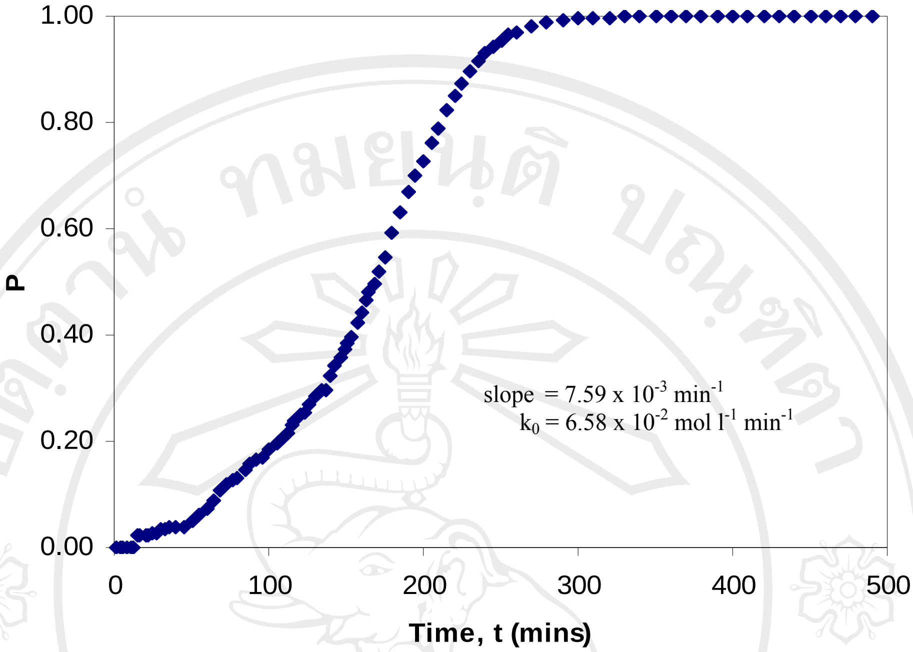


Figure 4.32 Zero-order rate plot of extent of reaction, p, against time, t, for the polymerization of ε-caprolactone at 140 °C using 0.1 mol % tin(II) hexoxide, $Sn(OC_6H_{13})_2$, as initiator.

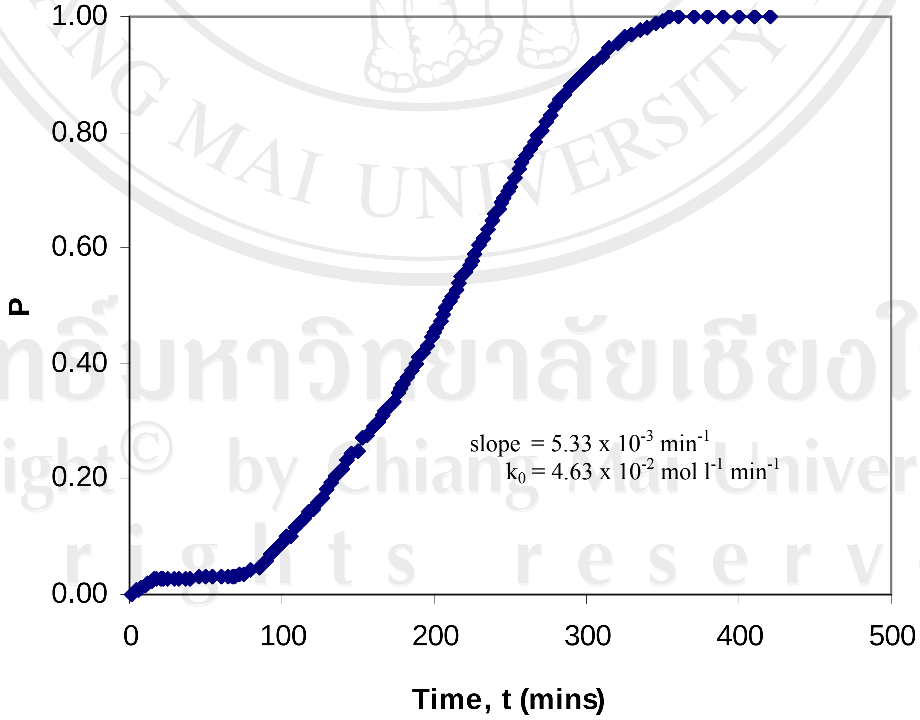


Figure 4.33 Zero-order rate plot of extent of reaction, p, against time, t, for the polymerization of ε-caprolactone at 140 °C using 0.1 mol % tin(II) octoxide, $Sn(OC_8H_{17})_2$, as initiator.

4.3 Gravimetry

4.3.1 Experimental Procedure and Results

In contrast to the previous method of dilatometry which only provides indirect measurements of monomer conversion, gravimetry is the most direct way of obtaining conversion data. In gravimetry, the polymer which is produced is physically separated for quantitative determination. However, it does suffer from the drawback that, in the course of separating the polymer formed from the residual monomer by dissolution and reprecipitation, the lowest molecular weight (oligomeric) fractions may not be able to precipitate as a filterable solid, leading to an erroneously low experimental value for the % conversion.

The polymerization procedure used was the same as that described previously for dilatometry except that the 10 ml round-bottomed flasks were tightly sealed. At various time intervals during the polymerization, a round-bottomed flask was removed from the silicone oil bath, cooled quickly to room temperature, and its contents dissolved in chloroform. The polymer was then separated out from solution by dropwise addition into ice-cooled hexane with efficient stirring followed by prolonged standing to ensure the maximum amount of precipitation possible. Finally, the polymer precipitate was carefully filtered off under gentle suction in a sintered glass crucible (porosity 4 or 5), washed with more hexane, and dried to constant weight in a vacuum oven at 40 ^{o}C.

The % conversion was calculated from the equation below:

$$\%\ \text{Conversion} = \frac{\text{Dry weight of polymer}}{\text{Initial weight of monomer}} \times 100\ \%$$

From the dry weights of polymer obtained for each of the ε-caprolactone polymerizations, the % conversions were calculated as given in Tables 4.15-4.20. In each case, the final % conversion, as calculated gravimetrically from the dilatometer contents at h_∞, is also shown for comparison.

Table 4.15 Gravimetric % conversions from ε-caprolactone polymerization at 140 ^{o}C using tin(II) methoxide as initiator.

Initial Monomer Weight (g)	Polymer Yield (g)	Time (mins)	Conversion (%)
3.0018 3.0007 3.0015 3.0011 3.0008	1.315 1.713 2.215 2.683 2.803	420 480 540 600 720	43.8 57.1 73.8 89.4 93.4
8.9225	8.102	750	90.8 *

* final % conversion, as determined from the dilatometer contents at h_∞

Table 4.16 Gravimetric % conversions from ε-caprolactone polymerization at 140 ^{o}C using tin(II) ethoxide as initiator.

Initial Monomer Weight (g)	Polymer Yield (g)	Time (mins)	Conversion (%)
3.0004 3.0010 3.0008 3.0014 3.0011	1.203 1.570 2.155 2.569 2.851	360 420 480 540 600	40.1 52.3 71.8 85.6 95.0
8.9220	8.137	690	91.2 *

* final % conversion, as determined from the dilatometer contents at h_∞

Table 4.17 Gravimetric % conversions from ε-caprolactone polymerization at 140 °C using tin(II) propoxide as initiator.

Initial Monomer Weight (g)	Polymer Yield (g)	Time (mins)	Conversion (%)
3.0011	1.221	240	40.7
3.0017	1.669	300	55.6
3.0005	2.136	360	71.2
3.0012	2.395	420	79.8
3.0015	2.779	480	92.6
8.9223	8.110	570	90.9 *

* final % conversion, as determined from the dilatometer contents at h_∞

Table 4.18 Gravimetric % conversions from ε-caprolactone polymerization at 140 °C using tin(II) butoxide as initiator.

Initial Monomer Weight (g)	Polymer Yield (g)	Time (mins)	Conversion (%)
3.0003	1.311	300	43.7
3.0010	1.798	360	59.9
3.0011	2.284	420	76.1
3.0005	2.652	480	88.4
3.0007	2.830	540	94.3
8.9227	8.155	630	91.4 *

* final % conversion, as determined from the dilatometer contents at h_∞

Table 4.19 Gravimetric % conversions from ε-caprolactone polymerization at 140 ^{o}C using tin(II) hexoxide as initiator.

Initial Monomer Weight (g)	Polymer Yield (g)	Time (mins)	Conversion (%)
3.0012	1.582	180	52.7
3.0007	2.230	210	74.3
3.0015	2.638	240	87.9
3.0013	2.914	300	97.1
3.0005	2.869	420	95.6
8.9222	8.280	550	92.8 *

* final % conversion, as determined from the dilatometer contents at h_∞

Table 4.20 Gravimetric % conversions from ε-caprolactone polymerization at 140 ^{o}C using tin(II) octoxide as initiator.

Initial Monomer Weight (g)	Polymer Yield (g)	Time (mins)	Conversion (%)
3.0009	1.251	150	41.7
3.0011	1.549	210	51.6
3.0006	2.587	300	86.2
3.0012	2.860	330	95.3
3.0007	2.803	360	93.4
8.9220	8.173	420	91.6 *

* final % conversion, as determined from the dilatometer contents at h_∞

4.3.2 Kinetic Analysis

The gravimetric % conversions in Tables 4.15-4.20 are plotted against time in Figures 4.34-4.39 alongside the corresponding dilatometric data for comparison. On the whole, the two types of data show good agreement with the % conversions from gravimetry being generally only slightly lower than those from dilatometry. The main reason for this disparity between the two techniques is, as mentioned previously, the likelihood of incomplete precipitation of the polymer in this gravimetric method. Another source of error which, conversely, causes the dilatometric % conversions to be slightly higher than their true values is the assumption of complete 100 % conversion at $\Delta h(\infty)$. However, this latter error is believed to be less serious than the former.

However, the overall kinetic profiles in Figures 4.28-4.33 are similar in appearance for both methods. Even though gravimetry has the advantage of being the more direct method, it suffers from the disadvantage of being unresponsive during the initial build-up of molecular weight until such time that a critical molecular weight for precipitation is attained. Thereafter, it continues to underestimate the true % conversion due to the non-precipitation of the lowest molecular weight fractions. Consequently, from the experiments carried out here, the gravimetric data is considered to be less amenable to kinetic analysis than the dilatometric data.

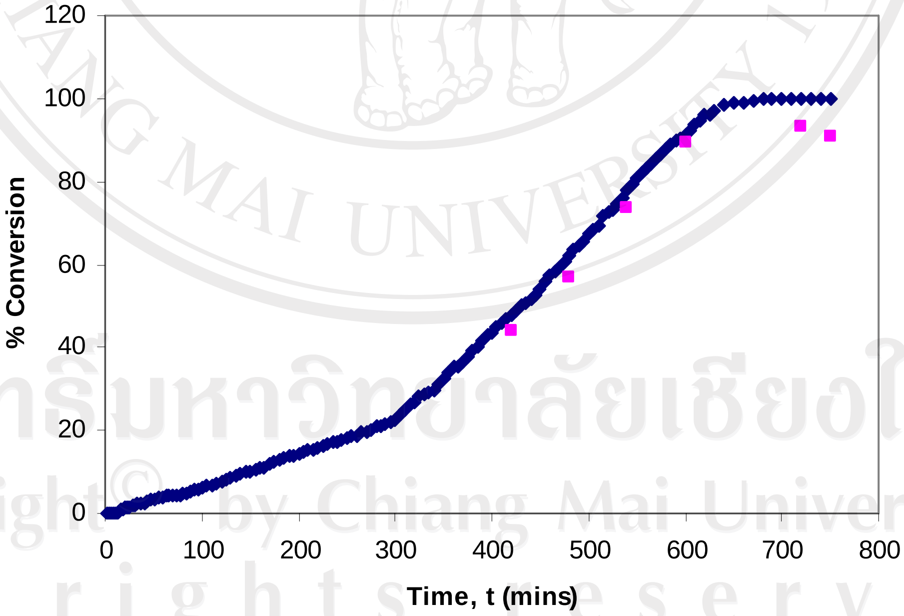


Figure 4.34 Comparison of gravimetric (■) and dilatometric (♦) % conversion-time profiles for ε-caprolactone polymerization at 140 °C using tin(II) methoxide as initiator.

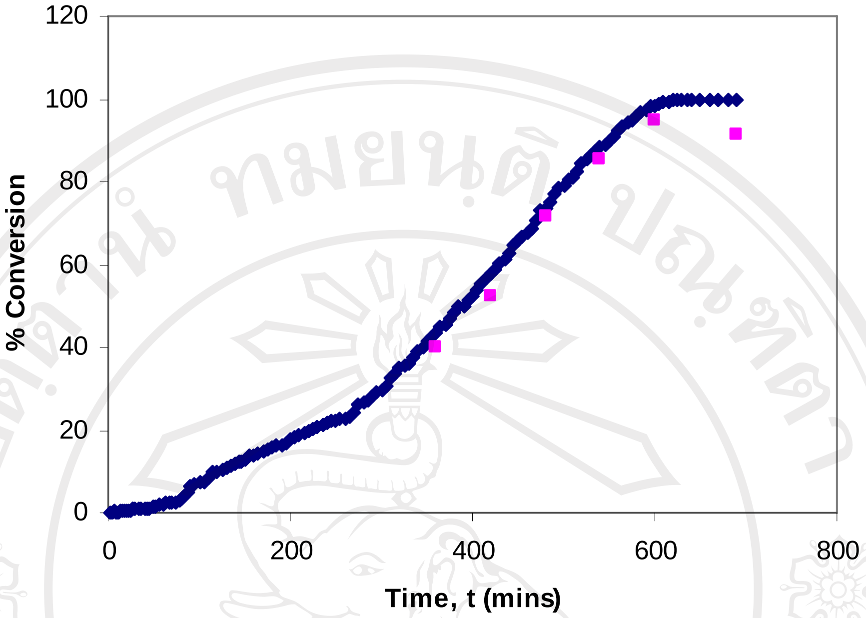


Figure 4.35 Comparison of gravimetric (■) and dilatometric (♦) % conversion-time profiles for ε-caprolactone polymerization at 140 ^{o}C using tin(II) ethoxide as initiator.

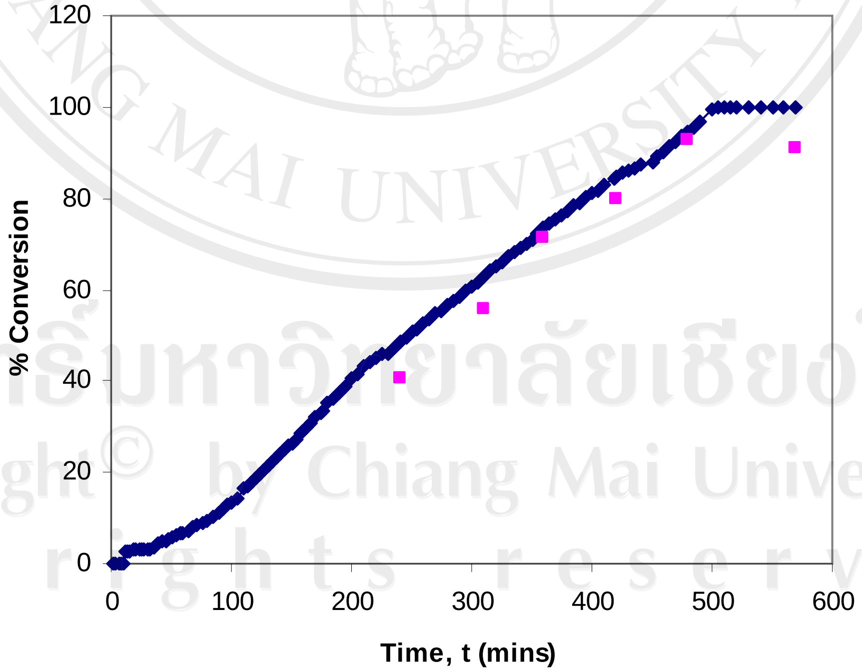


Figure 4.36 Comparison of gravimetric (■) and dilatometric (♦) % conversion-time profiles for ε-caprolactone polymerization at 140 ^{o}C using tin(II) propoxide as initiator.

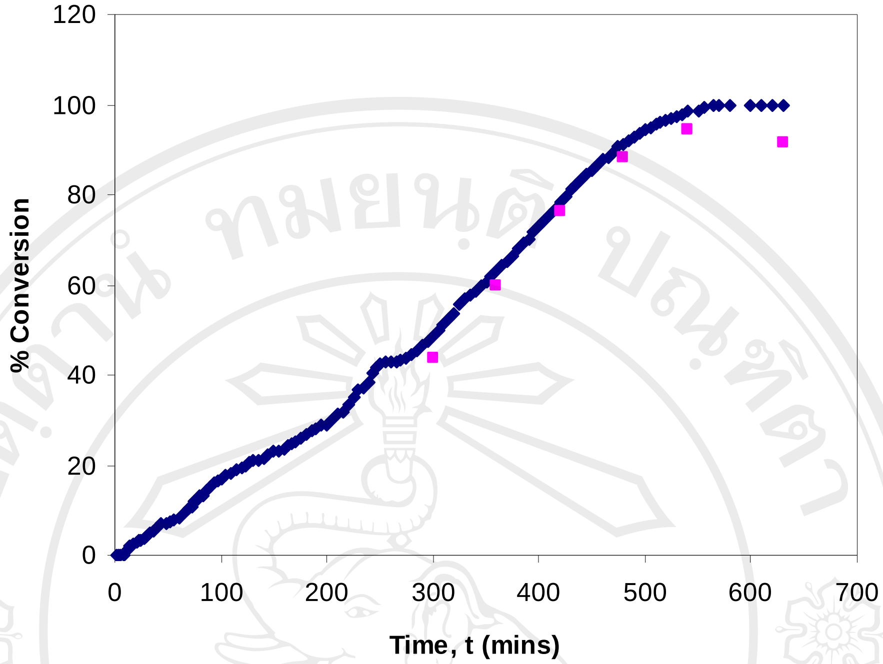


Figure 4.37 Comparison of gravimetric (■) and dilatometric (♦) % conversion-time profiles for ε-caprolactone polymerization at 140 °C using tin(II) butoxide as initiator.

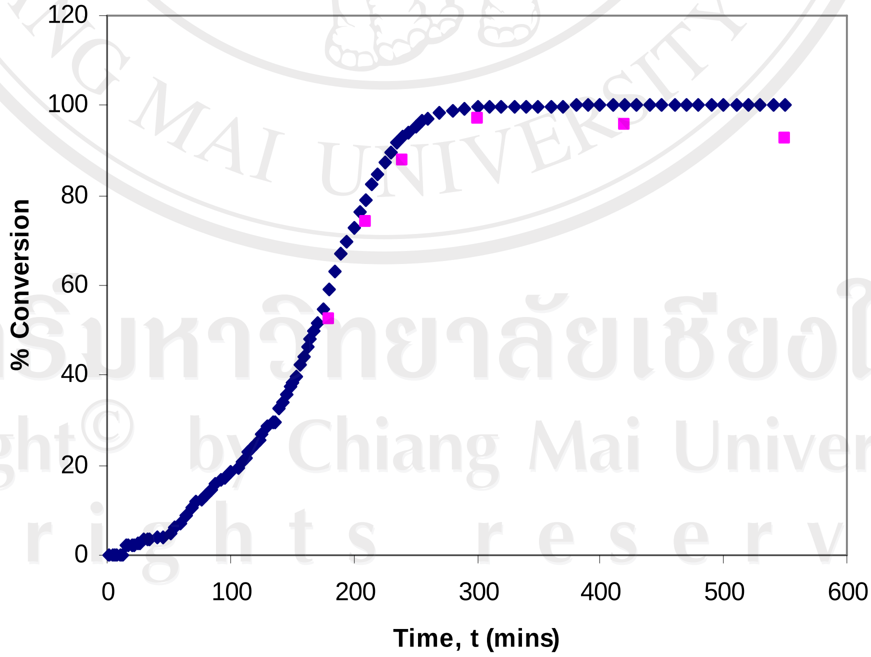


Figure 4.38 Comparison of gravimetric (■) and dilatometric (♦) % conversion-time profiles for ε-caprolactone polymerization at 140 °C using tin(II) hexoxide as initiator.

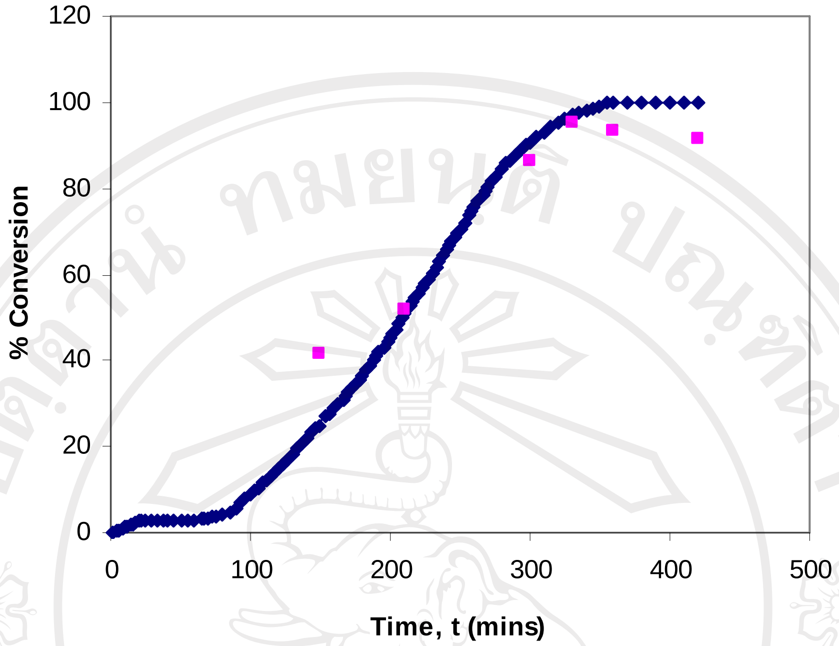


Figure 4.39 Comparison of gravimetric (■) and dilatometric (♦) % conversion-time profiles for ε-caprolactone polymerization at 140 ^{o}C using tin(II) octoxide as initiator.

The main conclusions to be drawn from these combined gravimetric-dilatometric results are:

(1) Generally, the gravimetric % conversions show good agreement with those from dilatometry. As expected, the % conversions from gravimetry tend to be slightly less than from dilatometry.

(2) If the thermodynamic predictions are to be believed that ε-caprolactone polymerization in bulk goes to near-quantitative conversion (i.e., minimal residual monomer concentration), then the final % conversions from gravimetry (including from the dilatometer contents at h_∞) of 90-95 % indicate that gravimetry does indeed underestimate the % conversion by around 5-10 %.

Clearly, both techniques have their different advantages and disadvantages and, if only for this reason alone, it has been useful to compare the results from these two techniques side by side. Dilatometry is the preferred technique as far as kinetic analysis and rate measurements are concerned but gravimetry is still very useful for providing absolute snapshots of the reaction's progress at various times and, in doing so, for providing valuable quantitative support for the dilatometry results.