CHAPTER 4

Kinetic Studies by Dilatometry

The kinetics of the bulk ring-opening polymerisation of ε-caprolactone using tin(II) alkoxides were studied in detail using dilatometry as the analytical technique for following the progress of the reaction. Because the polymerisation of a liquid monomer is generally accompanied by a decrease in volume, dilatometry utilizes the volume change that occurs upon polymerisation to follow conversion versus time. Therefore, dilatometry is only 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.

In this experiment, the rate of polymerisation will be measured by the dilatometer developed as described in section 4.3. The dilatometer is placed in a constant temperature bath and the volume change in the capillary of the polymerising system, which is quantitatively related to the percent conversion, is followed with time. Dilatometry is not useful for most step polymerisations where there is a small molecule by-product and which results in no appreciable volume change upon polymerisation.

4.1 Homopolymer Polymerisation

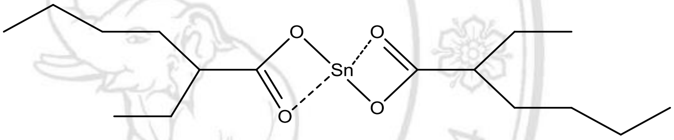
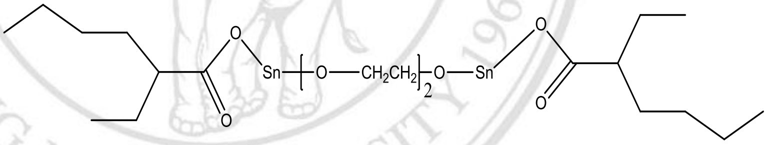
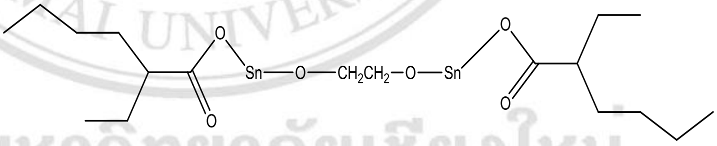
4.1.1 Monomer

ε-Caprolactone (ε-CL) is chosen for the kinetic studies of its polymerisation with the synthesised novel initiators due to its easy polymerisability. Most importantly, its polymer (poly(ε-caprolactone), PCL) is also liquid at the polymerisation temperature used (130 ^{o}C). This made it amenable to dilatometry study in bulk since there was avoidance of the complication of verification or solidification occurring during the course of the experiments. Moreover, PCL is becoming increasingly important commercially, especially in certain biomedical applications because of its biocompatibility and biodegradability and for polymer blends owing to its compatibility with a large range of polymers.

4.1.2 Initiators

The initiators used for these studies are the series of synthesised tin(II) alkoxides which are described in the chapter 3. Elementary work results showed that the solid initiators were hardly soluble in the monomer, while the liquid initiators were readily soluble. Therefore, the initiators used for kinetic studies by dilatometry were bis(tin(II) octoate) diethylene glycol ($[Sn(Oct)]_2DEG$), bis(tin(II) octoate) ethylene glycol ($[Sn(Oct)]_2EG$), and also commercially available tin(II) octoate and tin(II) octoate / HOROH mixtures. Their molecular formulae are shown in Table 4.1.

Table 4.1 The molecular formulae of initiators used for kinetic studies by dilatometry.

Initiator	Molecular formula
Tin(II) Octoate $Sn(Oct)_2$	
Bis(tin(II) octoate) diethylene glycol $[Sn(Oct)]_2DEG$	
Bis(tin(II) octoate) ethylene glycol $[Sn(Oct)]_2EG$	

4.2 Design of Kinetic Experiments

For the kinetic investigations of polymerisations, a variety of methods and apparatus has been developed [43, 105-107]. In this work, the technique used for kinetic studies of the ROP of ε-CL is dilatometry. The dilatometric method is especially useful on account of its simplicity and general application which provide complementary information about the progress of a polymerisation reaction in terms of % conversion and rate of polymerisation.

The design and construction of small glass dilatometers depend on a number of considerations as mentioned before, such as the expected volume change and the accuracy with which it must be measured, the rate of polymerisation, the corresponding rate of heat evolution and its effect on temperature uniformity, the viscosity of the polymerising 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.

Dilatometry Apparatus

In this work, the dilatometer was designed and constructed as shown in Figure 4.1. It consisted of a round-bottomed flask with a quickfit neck into which a capillary column was inserted. The top of the capillary column was connected to a $CaCl_2$ drying tube to prevent the ingrass of atmospheric moisture into the system. A small magnetic bar (1 cm) was placed inside the round-bottomed flask for the dual purpose of stirring the reaction mixture to maintain homogeneity and maximizing the efficiency of heat transfer to ensure good temperature control.

The dilatometer is placed in a thermostatically controlled oil bath maintained at the desired reaction temperature. As the polymerisation proceeds, liquid sample meniscus movement in the capillary is due to two factors:

1) Thermal expansion of the liquid sample.
2) Contraction due to polymerisation.

Initially, as the volume of liquid increases by thermal expansion, the liquid will rise up the capillary tube. As soon as the liquid has reached thermal equilibrium, the volume of the liquid will decrease with polymerisation. The change in height of the liquid in the capillary is measured periodically with a cathetometer. The rate of polymerisation can then be determined from the rate of change in the height of the liquid.

Good temperature control was achievable to within an acceptable ± 0.2 ^{o}C. Cathetometer readings of the meniscus height in the capillary were accurate to ± 0.001 cm.

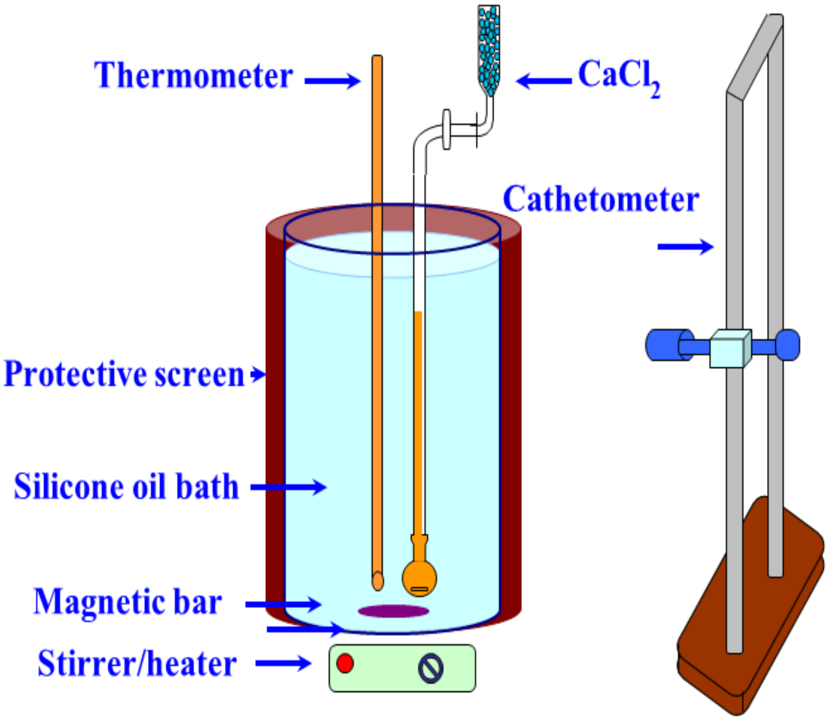


Figure 4.1 Dilatometry set-up used in kinetic studies of ROP of ε-CL.

4.3 Limitations of Dilatometry

It was shown that applications of this conventional dilatometer to bulk polymerisation reactions are limited by the following sources of error: a measurement of volume change is complicated if there are any gases dissolved in monomer which may be isolated as bubbles while the polymerisation occurs. The dilatometry technique will not be able to measure the volume contraction of a solid monomer: a problem of solvent evaporation at the polymerisation temperature could happen if the solid monomer is dissolved in a solvent. Since the monomer itself is used as a recording liquid for the volume decrease, its increasing viscosity soon causes a distortion of the meniscus in the capillary, resulting in a difficulty in reading. In addition, the dissipation of the heat of reaction by either convection or conduction is increasingly hindered by the increasing viscosity of the polymerising monomer/polymer mixture. A long period of thermal equilibration can occur as a result of using either too low an initiator concentration or too low a polymerisation temperature. Finally, when a high reactivity initiator or initiator concentration is used, measurement of the meniscus height can be difficult since the polymerisation rate under this condition is fast.

4.4 Dilatometric Data Analysis

In a dilatometry experiment, after reaching thermal equilibrium, as the polymerisation proceeds the volume of the polymerising mixture decreases. The data of volume change that occurs upon polymerisation are then used to follow conversion versus time. The change in volume of the system, ΔV, may be related to the monomer concentration, reaction yield, and the rate of polymerisation as follows. The total volume of the system, V, at any time t is given by

$$V = W_m \overline{V}_m + W_p \overline{V}_p + W_s \overline{V}_s \tag{4.1}$$

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 and rearranging gives the weight of monomer at time t as

$$W_m = \frac{V - W_m^{\circ} \overline{V}_p - W_s \overline{V}_s}{\overline{V}_m - \overline{V}_p} \tag{4.2}$$

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

$$V_0 = W_m^{\circ} \overline{V}_m + W_s \overline{V}_s \tag{4.3}$$

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

$$V_\infty = W_m^{\circ} \overline{V}_p + W_s \overline{V}_s \tag{4.4}$$

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 polymerisation over the temperature range of 110-140 ^{o}C, this is believed to be a good approximation since the $[M]_{eq}$ for ε-caprolactone bulk polymerisation, as observed experimentally at 100 ^{o}C, has been reported to be very small (≈ 0) [108].

On the strength of this approximation, equations 4.3 and 4.4 may now be used to eliminate $\overline{V}_m - \overline{V}_p$ and $W_s\overline{V}_s$ from equation 4.2 and, when this is done, equation 4.5 is obtained.

$$W_m = \frac{V - V_\infty}{V_0 - V_\infty}\, W^{o}_{m} \qquad (4.5)$$

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

$$\%\ \text{Conversion} = Y = 100\frac{W_m^{\circ} - W_m}{W_m^{\circ}} = 100\frac{V_0 - V}{V_0 - V_\infty} \qquad (4.6)$$

By using the dilatometry apparatus shown in Figure 4.1, change in volume, ΔV, is proportional to change in height of the liquid meniscus, Δh, in the capillary, as given by

$$\Delta V = V_o - V = \pi r^2\, \Delta h \qquad (4.7)$$

where V_0 is the initial volume of the system, V is the volume at time t, and r is the capillary radius. Therefore equation 4.6 can be written as

$$\%\text{Conversion} = Y = 100\frac{\Delta V}{V_0 - V_\infty} = 100\frac{\Delta h(t)}{\Delta h(\infty)} \qquad (4.8)$$

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 4.8 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 polymerisation 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 4.5 and utilize the definition of the rate of polymerisation, R_p, in equation 4.9.

$$R_p = \frac{-d[M]}{dt} = \lim_{\Delta t \to 0} \frac{\Delta[M]}{\Delta t} \qquad (4.9)$$

However, the rate of polymerisation, R_p, in equation 4.9 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 4.8 gives the instantaneous rate expression in equation 4.10.

$$R_p = \frac{\Delta Y}{100} \frac{[M]_0}{\Delta t} = \frac{\Delta h}{\Delta h(\infty)} \frac{[M]_0}{\Delta t} \qquad (4.10)$$

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 4.8, then the value of R_p from equation 4.10 would be

$$R_p = \frac{\Delta Y}{100} \frac{[M]_0}{\Delta t} = \frac{Y_2 - Y_1}{100} \frac{[M]_0}{t_2 - t_1} \qquad (4.11)$$

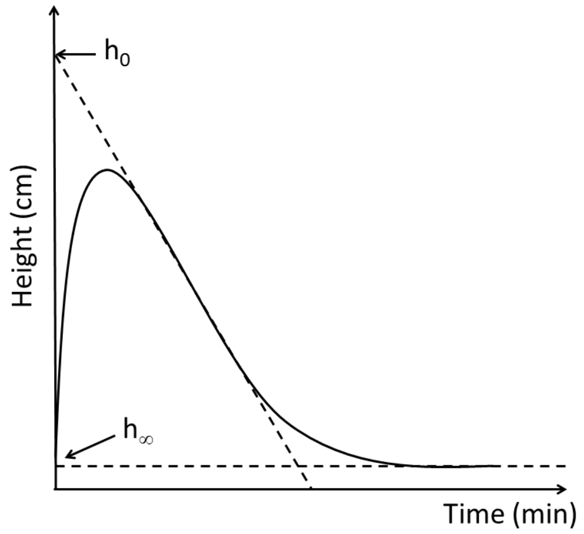
This R_p is an "average" value over the time interval $t_1 \rightarrow t_2$ but, because this time interval is very small (i.e., incremental) compared to the total time $t_o \rightarrow t_\infty$ for the polymerisation as a whole, it can be regarded to a good approximation as an **instantaneous** R_p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

$$R_p \text{ at time } = \frac{t_1 + t_2}{2} \qquad (4.12)$$

4.4.1 Initial Meniscus Height (h_0)

The true value of h_0, the initial meniscus height, cannot be measured directly since, when the dilatometer is first placed in the heating bath, there is a thermal equilibrium period during which the dilatometer and its contents increase in temperature up to the bath temperature. This equilibrium period may be take several minutes. During this period, the meniscus height h increase due to thermal expansion. However, this increase soon changes to be a decrease as the dilatometer approaches the bath temperature and contraction due to the onset of polymerisation takes over.

Thus, the value of h_0 need to be estimated from the initial part of the raw data curve as carefully and as accurately as possible. This is usually done by waiting for the thermal equilibration period to be complete and then extrapolating the subsequent data points back to zero time (t = 0) as shown below.



4.4.2 Kinetic Analysis

4.4.2.1. First-Order Kinetics Analysis

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

$$\frac{-d[M]}{dt} = k_1[M] \tag{4.13}$$

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:

$$\ln([M]_0/[M]_t) = k_1 t \qquad (4.14)$$

where k_1 is the first-order rate constant.

Given the correspondence from dilatometry (Infinite Time Method) that

$$\ln([M]_0/[M]_t) = \ln[(h_0-h_\infty)/(h-h_\infty)] \qquad (4.15)$$

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

$$\ln[(h_0-h_\infty)/(h-h_\infty)] = k_1 t \qquad (4.16)$$

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, this rather simplified approach fails to take into account the well known reversibility of ring-opening polymerisations and the thermodynamic nature of the equilibrium. In a reversible ring-opening polymerisation, the propagation-depropagation equilibrium can be expressed as

$$M_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^* \qquad (4.17)$$

where

M = monomer

M_n^* and M_{n+1}^* = propagation species

k_p = rate constant for propagation

k_{dp} = rate constant for depropagation

Therefore, the rate of propagation (polymerisation), R_p, is given by

$$R_p = -\frac{d[M]}{dt} = k_p[M_n^*][M] - k_{dp}[M_{n+1}^*] \qquad (4.18)$$

At equilibrium, $R_p = 0$ and the remaining monomer concentration is what is known as the equilibrium monomer concentration $[M]_e$. It also can be assumed that $[M_n^*] = [M_{n+1}^*] = [M^*]$ (for any value of n). Thus, equation 4.18 becomes

$$k_p[M^*][M]_e = k_{dp}[M^*]$$

$$k_p[M]_e = k_{dp} \qquad (4.19)$$

$$[M]_e = \frac{k_{dp}}{k_p} \qquad (4.20)$$

Combining eqs. (4.18) and (4.19) gives

$$-\frac{d[M]}{dt} = k_p[M^*][M] - k_p[M]_e[M^*]$$

$$-\frac{d[M]}{dt} = k_p[M^*]([M]-[M]_e) \qquad (4.21)$$

Integrating this rate equation 4.21 between the limits

initial monomer concentration = $[M]_0$ at time t = 0

intermediate monomer concentration = [M] at any time t gives

$$-\int_{[M]_0}^{[M]} \frac{d[M]}{[M^*]([M]-[M]_e)} = \int_0^t k_p dt$$

where, according to the Steady-State Approximation

$[M^*]$ = propagating (active) species concentration

= constant and therefore

$$\ln\left(\frac{[M]_0-[M]_e}{[M]-[M]_e}\right) = k_p[M^*]t \qquad (4.22)$$

Hence, if this rate equation is obeyed, a semi-log of

$$\ln\left(\frac{[M]_0-[M]_e}{[M]-[M]_e}\right) \quad \text{against} \quad t$$

should give a straight line of slope = $k_p[M^*]$

The equilibrium monomer concentration, $[M]_e$, can either be obtained experimentally or theoretically. In this chapter, $[M]_e$ was determined experimentally as described below.

Experimental determination of $[M]_e$ is considered as a preferred method because it is based on real experimental data. At the end of each polymerisation reaction, the polymer yield was determined as ***quantitatively*** as possible by dissolution and precipitation followed by careful filtering and drying under vacuum to constant weight. Below is an example for ε-caprolactone polymerisation at 130 ^{o}C using 0.1 mol % mixture initiator ($Sn(Oct)_2$ / EG) as initiator.

$$\%\text{ yield of polymer} = \left(\frac{\text{weight of the polymer obtained}}{\text{weight of the initial monomer}}\right) \times 100\ \%$$

$$= 99.71\ \%$$

% monomer remaining (at equilibrium) = 0.29 %

$$f = 0.0029$$

where f is the fraction of monomer remaining at equilibrium, i.e.

$$[M]_e = f\,[M]_0 \qquad (4.23)$$

Combining Equations 4.22 and 4.23, then the rate equation is modified as follows.

$$\ln\left(\frac{[M]_0 - f\,[M]_o}{[M] - f\,[M]_o}\right) = k_p[M^*]t \qquad (4.24)$$

When the kinetics of polymerisation is studied by dilatometry, the rate equation needs to be expressed in dilatometric terms.

$$\ln\left(\frac{(h_0 - h_\infty) - f\,(h_0 - h_\infty)}{(h - h_\infty) - f\,(h_0 - h_\infty)}\right) = k_p[M^*]t \qquad (4.25)$$

or

$$\ln\left(\frac{(1-f)(h_0 - h_\infty)}{(h - h_\infty) - f\,(h_0 - h_\infty)}\right) = k_p[M^*]t \qquad (4.26)$$

Where $[M]_0 \quad \alpha \quad h_0 - h_\alpha$

$[M] \quad \alpha \quad h - h_\alpha$

slope of linear part of the rate plot = $k_p[M^*] = k_{app}$

where k_{app} is the apparent first-order rate constant.

4.4.2.2. Zero-Order Kinetics Analysis

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 polymerisation reaction is a zero-order reaction, it is possible that the opposing rate effects of decreasing monomer concentration and increasing initiator solubilisation 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

$$[M]_0 - [M]_t = k_0 t$$

where k_0 is the zero-order rate constant.

This equation can be alternatively expressed as:

$$p = k_0 t / [M]_0 \qquad (4.27)$$

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)

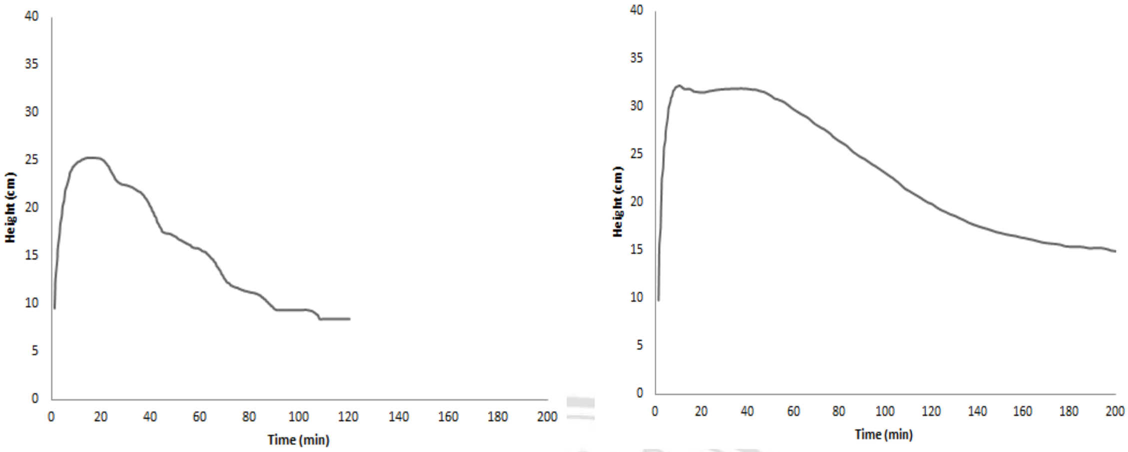
Given that $p = ([M]_0 - [M]_t) / [M]_0 = (h_0 - h)/(h_0-h_\infty)$ from dilatometry

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.

4.4.3 Preliminary Experimental Results

Dilatometry experiments for kinetic analysis were carried out initially by setting the temperature of the silicone oil bath at the desired reaction temperature. The dilatometer, filled with a sample mixture of ε-caprolactone and the chosen initiator and set as described in section 4.3.1, was then placed in a thermostatically controlled oil bath maintained at 130 ^{o}C. Upon immersion of the dilatometer, the temperature of the oil bath quickly dropped by up to 7 ^{o}C before gradually increasing back up to 130 ^{o}C over a period of about 10 minutes. This led to an initial period of non-isothermal thermal equilibration during which the meniscus movement in the capillary was due to both thermal expansion of the liquid sample and contraction due to polymerisation. Data taken during this equilibration period was used to estimate the meniscus height at zero time (h_o) as described in the following section.

One way of shortening the thermal equilibration period was to start at a slightly higher temperature of 140 ^{o}C. Immediately after immersing the dilatometer in the oil bath, the temperature was re-set to 130 ^{o}C, whereupon the oil bath temperature dropped to about 127 ^{o}C, only 3 ^{o}C below the required temperature. In this way, thermal equilibration was shortened by a half and the experimental data gave a smoother curve, as shown for example in Figure 4.2. Consequently, this technique was used in all kinetic experiments in order to shorten the thermal equilibration time and thus provide more valid data points during the initial period.



(a) (b)

Figure 4.2 Dilatometric data for ε-caprolactone polymerisation at 130 °C using 0.10 mol % $Sn(Oct)_2$; initial oil bath temperature set at (a) 130 °C and (b) 140 °C .

The data for all of the kinetic experiments are listed in Tables 4.3-4.7. These tables show the raw data values of meniscus height, h, at time, t, and the calculated values of % conversion using Equation 4.8. To calculate % conversion using Equation 4.8, h_0 and h_∞ needed to be determined as described in section 4.5.1. Figure 4.3 shows as an example how to determine h_0 and h_∞ for ε-caprolactone polymerisation using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C. The kinetic profile of % conversion against time calculated from data in Figure 4.3 is shown in Figure 4.4.

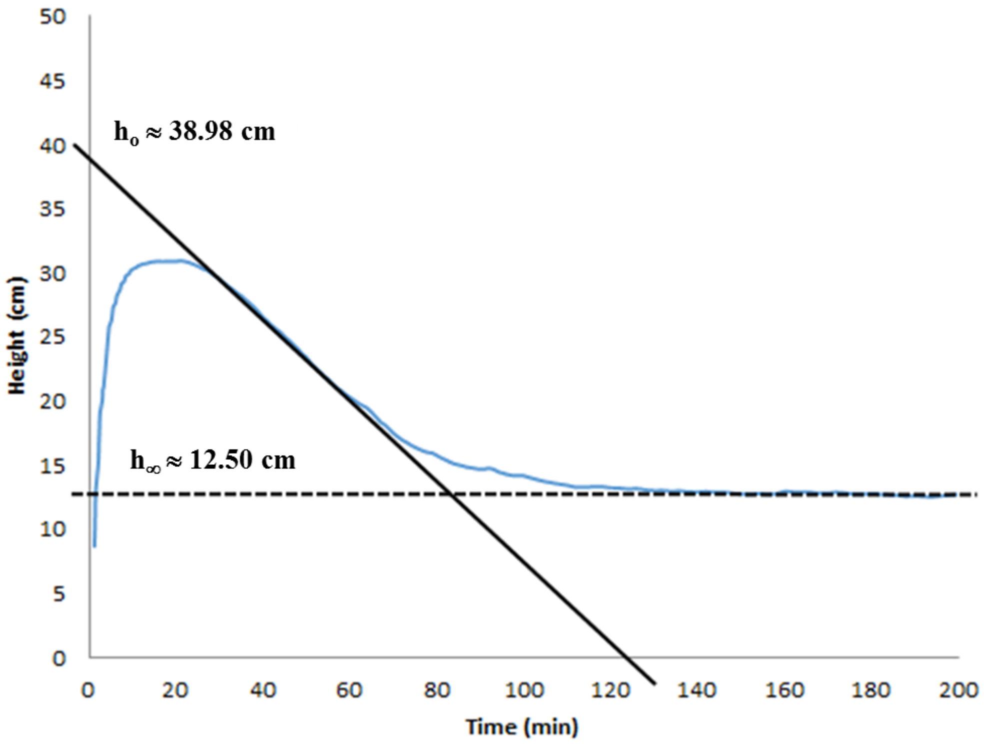


Figure 4.3 Extrapolation of h to zero time (h_0 at t = 0) and at constant height (h_∞) for ε-caprolactone polymerisation using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

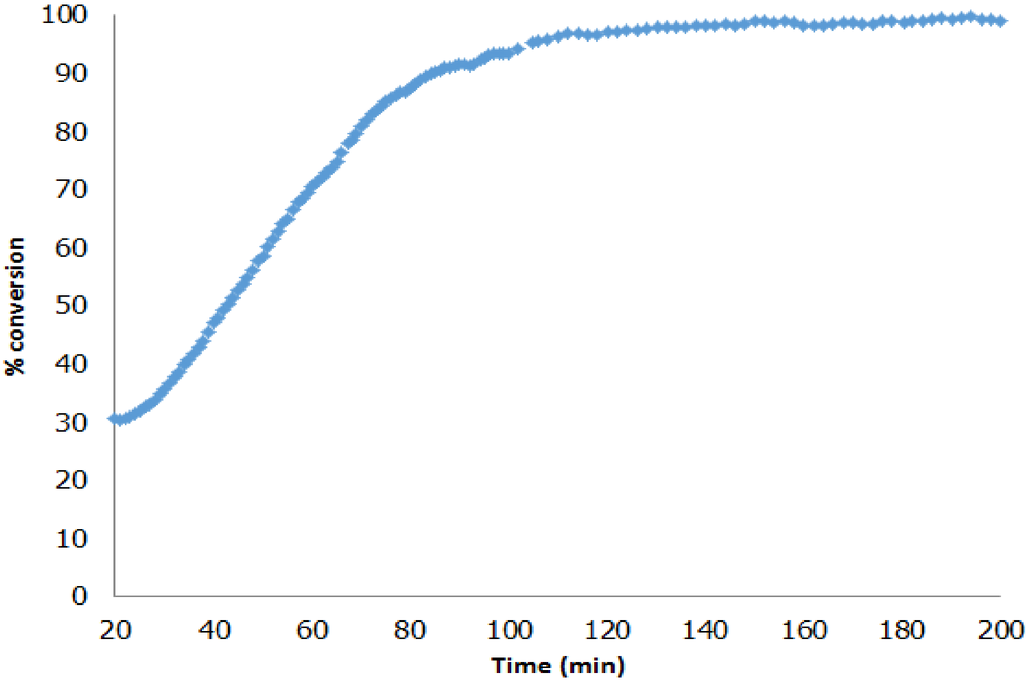


Figure 4.4 Kinetic profile of % conversion against time for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

First–Order and Zero-Order Rate Plots and Rate Constants

For most polymerisation reactions, a steady-state is usually reached within the first 20 % conversion. This steady-state then continues for the major part of the reaction (i.e. monomer conversion) until the monomer concentration becomes seriously depleted and/or the increase in viscosity of the system (especially in bulk) leads to diffusion-controlled processes becoming influential. Usually this occurs not later than about 80 % conversion. However, these limits (20-80 %) can very markedly from system to system and so each kinetic plot needs to be considered individually. In this work, conversion limit was also chosen in the range of 20-80 % for constructing a first-order rate plot according to equation 4.26 as shown in Figure 4.5. The apparent first-order rate constant, k_{app}, could then be determined from the slop of this rate plot.

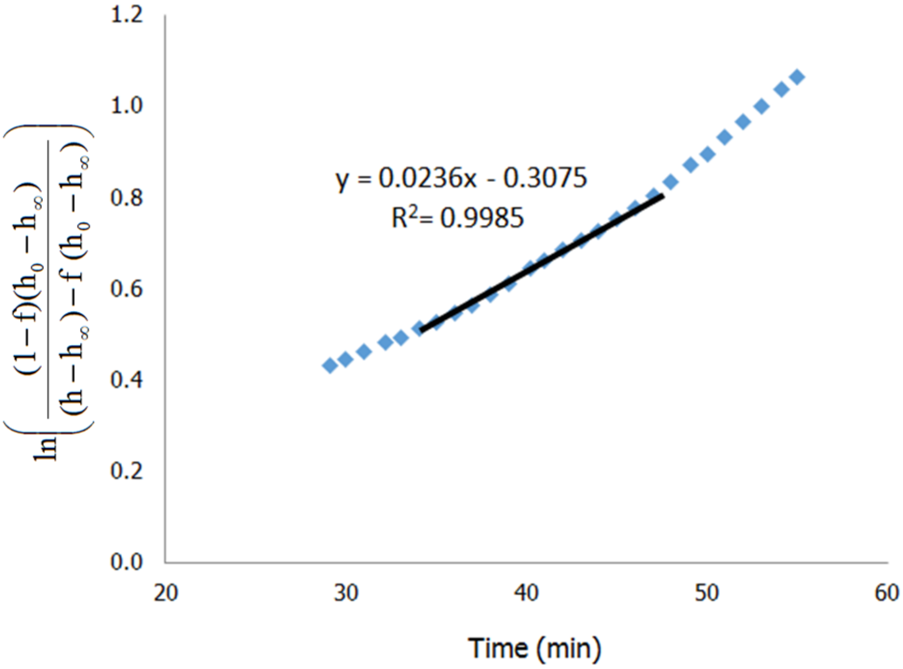


Figure 4.5 First-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 ^{o}C.

Figure 4.6 shows a zero-order plot in the same range (20-80 % conversion) according to equation 4.27. From the slope (= k_0 / $[M]_0$) of this linear portion, the zero-order rate constants, k_0, can be calculated, if $[M]_o$ is known.

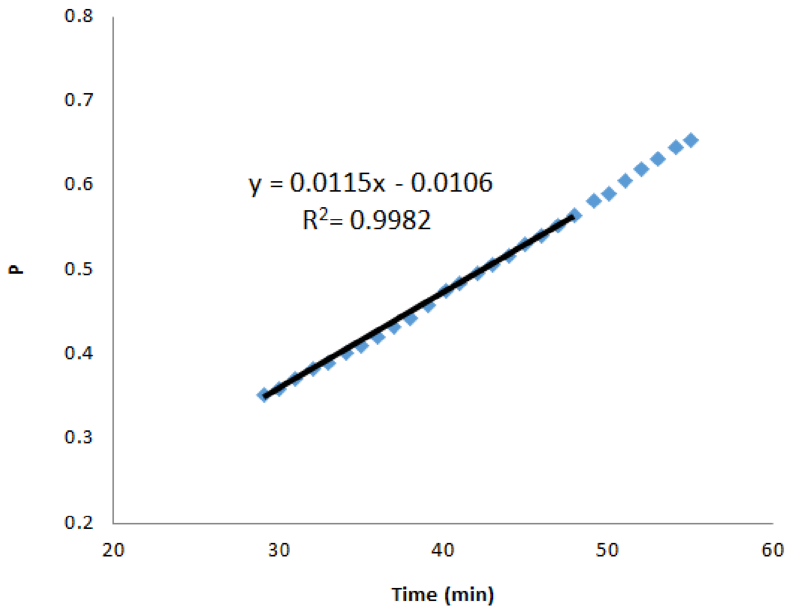


Figure 4.6 Zero-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

Evaluation of $[M]_o$

The value of $[M]_0$, the initial molar concentration of the pure ε-caprolactone, at the polymerisation temperature (130 °C) is given by:

$$[M]_0 = \frac{\text{Density of caprolactone at } 130\ ^{o}\text{C}}{\text{Molecular weight of } \varepsilon\text{- caprolactone}}$$

Densities of ε-caprolactone monomer at various temperatures are listed in Table 4.2 and Figure 4.7 [4]. From the extrapolated values in this Figure, density of ε-caprolactone at 130 °C is found to be 0.996 g /cm^3. Therefore, $[M]_0$ is calculated as below.

$$[M]_0 = \frac{0.996\ (\text{g}/\text{cm}^3) \times 1000\ (\text{cm}^3/\text{l})}{114.15\ (\text{g}/\text{mol})}$$

$$= 8.725\ \text{mol}/\text{l}$$

Table 4.2 Densities of ε-caprolactone monomer at various temperatures. [4]

Temperature (^{o}C)	Monomer Density ρ_m (g / cm^3)
Experimental Values	
40	1.0485
50	1.0427
60	1.0351
70	1.0309
Extrapolated Values	
90	1.018
120	1.002
130	0.996
140	0.990

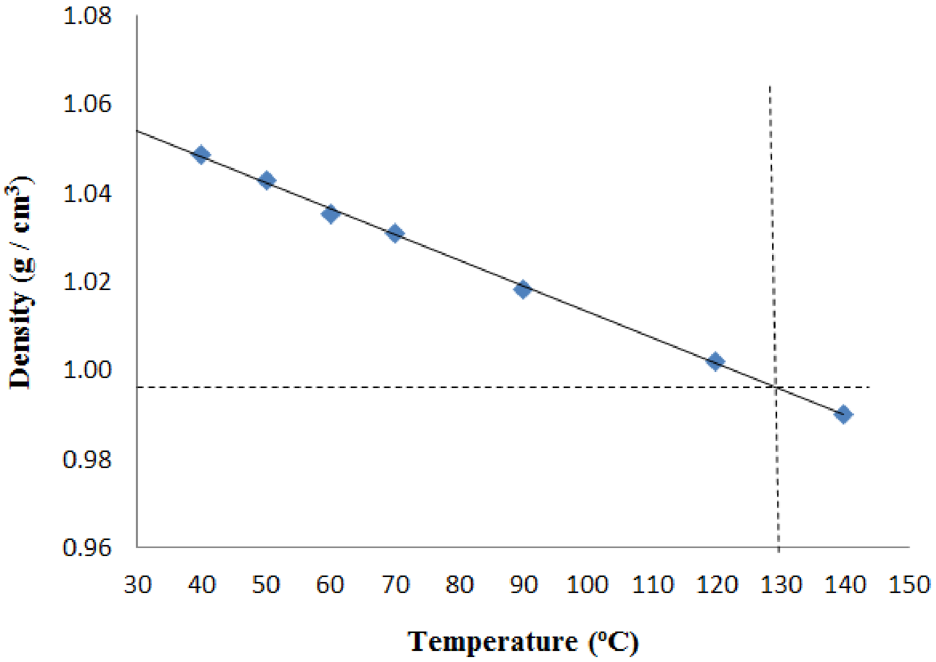


Figure 4.7 The linear decrease in density as a function of temperature for ε-caprolactone monomer.

4.4.4 Dilatometry Results

All raw data plots from the dilatometry experiments, kinetic profiles of % conversion against time, first-order rate plots and zero-order rate plots for ε-caprolactone using different initiator systems at 130 °C are shown in Figures 4.8-4.27.

Table 4.8 shows kinetic analysis results for all the dilatometry experiments explained above.

Table 4.3 Dilatometry data of ε-caprolactone polymerisation at 130 °C using 0.1 mol % $Sn(Oct)_2$ as initiator.

Weight of ε-caprolactone = 14.6140 g
h_0 (from extrapolation) = 39.98 cm
Weight of $Sn(Oct)_2$ = 0.0516 g
% Yield = 96.39
Capillary diameter = 0.180 cm
Residual monomer (f) = 0.036

Time (min)	Height (cm)	% Conversion
1.13	9.800	Thermal Equilibration
1.25	11.750	
1.40	14.175	
1.51	15.720	
2.05	17.370	
2.19	18.930	
2.36	20.500	
2.46	21.340	
2.58	22.500	
3.14	23.580	
3.30	24.550	
3.41	25.150	
3.51	25.770	
4.08	26.550	
4.18	26.975	
4.33	27.575	
5.11	28.860	
5.34	29.525	
5.53	29.925	
6.24	30.500	
6.39	30.720	
6.52	30.940	
7.06	31.170	
7.21	31.350	
7.37	31.520	
7.55	31.700	
8.05	31.800	
8.15	31.870	Thermal Equilibration
8.30	31.950	
8.41	32.015	
9.17	32.130	
10.01	32.220	
10.27	32.250	29.65
10.40	32.220	29.76
10.56	32.185	29.90
11.14	32.120	30.15
11.30	32.090	30.26
11.48	32.000	30.61
12.00	31.950	30.80
12.30	31.875	31.09
13.00	31.860	31.15
13.30	31.860	31.15
14.00	31.890	31.03
14.30	31.890	31.03
15.00	31.860	31.15
15.30	31.790	31.41
16.00	31.715	31.70
16.30	31.625	32.05
17.00	31.600	32.14
17.30	31.580	32.22
18.00	31.570	32.26
18.30	31.540	32.37
19.00	31.540	32.37
19.30	31.525	32.43
20.00	31.520	32.45
21.00	31.520	32.45
22.30	31.600	32.14
23.00	31.640	31.99
24.00	31.690	31.80
25.00	31.720	31.68
26.00	31.770	31.49
27.00	31.800	31.38
28.11	31.835	31.24
29.00	31.835	31.24
30.00	31.880	31.07
31.00	31.880	31.07
32.00	31.880	31.07
33.00	31.920	30.92
34.00	31.910	30.95
35.00	31.910	30.95
36.00	31.910	30.95
37.00	31.950	30.80
38.00	31.910	30.95
39.00	31.910	30.95
40.00	31.885	31.05
41.00	31.850	31.18
42.00	31.820	31.30
43.00	31.815	31.32
44.00	31.770	31.49
45.00	31.680	31.84
46.00	31.615	32.09

Table 4.3 (Continued).

Time (min)	Height (cm)	% Conversion
47.00	31.570	32.26
49.00	31.315	33.24
50.00	31.175	33.77
51.00	30.990	34.48
51.30	30.920	34.75
52.00	30.850	35.02
53.00	30.795	35.23
54.00	30.690	35.63
55.00	30.600	35.98
56.00	30.470	36.48
57.00	30.285	37.19
58.00	30.100	37.90
59.00	29.900	38.66
60.00	29.735	39.30
61.00	29.580	39.89
62.00	29.430	40.47
63.00	29.285	41.02
64.00	29.150	41.54
65.00	29.030	42.00
66.00	28.880	42.58
67.00	28.680	43.34
68.00	28.460	44.19
69.00	28.250	44.99
70.00	28.100	45.57
71.00	27.955	46.12
72.00	27.800	46.72
73.00	27.700	47.10
75.00	27.350	48.44
76.00	27.175	49.12
77.00	26.900	50.17
78.00	26.720	50.86
79.00	26.540	51.55
80.00	26.390	52.13
81.00	26.250	52.66
82.00	26.100	53.24
83.00	25.940	53.85
84.00	25.690	54.81
85.00	25.470	55.65
86.00	25.250	56.50
87.00	25.100	57.07
88.00	24.920	57.76
89.00	24.770	58.34
90.00	24.650	58.80
91.00	24.520	59.30
92.00	24.350	59.95
93.00	24.175	60.62
94.00	24.000	61.29
95.00	23.875	61.77
96.00	23.725	62.35
102.27	22.675	66.38
103.00	22.580	66.74
104.00	22.360	67.58
105.00	22.189	68.24
106.00	21.980	69.04
108.32	21.460	71.04
110.18	21.210	71.99
112.00	20.940	73.03
114.00	20.670	74.07
116.30	20.310	75.45
118.40	20.000	76.64
120.00	19.865	77.15
122.52	19.430	78.82
124.32	19.200	79.70
126.00	19.020	80.39
128.00	18.785	81.30
130.20	18.600	82.01
132.00	18.380	82.85
134.00	18.165	83.67
136.00	17.910	84.65
138.00	17.720	85.38
140.30	17.525	86.13
142.00	17.400	86.61
144.00	17.260	87.15
146.00	17.100	87.76
148.00	16.930	88.41
150.00	16.825	88.81
152.00	16.700	89.29
154.00	16.600	89.68
156.00	16.530	89.95
159.00	16.350	90.64
160.00	16.325	90.73
162.00	16.200	91.21
164.00	16.110	91.56
166.00	15.975	92.07
168.00	15.850	92.55
170.00	15.775	92.84
172.00	15.720	93.05
174.00	15.680	93.21
176.00	15.600	93.51
178.00	15.450	94.09
180.00	15.400	94.28
182.00	15.400	94.28
184.00	15.400	94.28
186.00	15.350	94.47
188.30	15.250	94.85
190.00	15.250	94.85
192.00	15.250	94.85
194.00	15.250	94.85
196.30	15.135	95.30
198.00	14.990	95.85
200.00	14.930	96.08
202.00	14.910	96.16
204.00	14.850	96.39
206.00	14.850	96.39
208.00	14.850	96.39
210.00	14.850	96.39

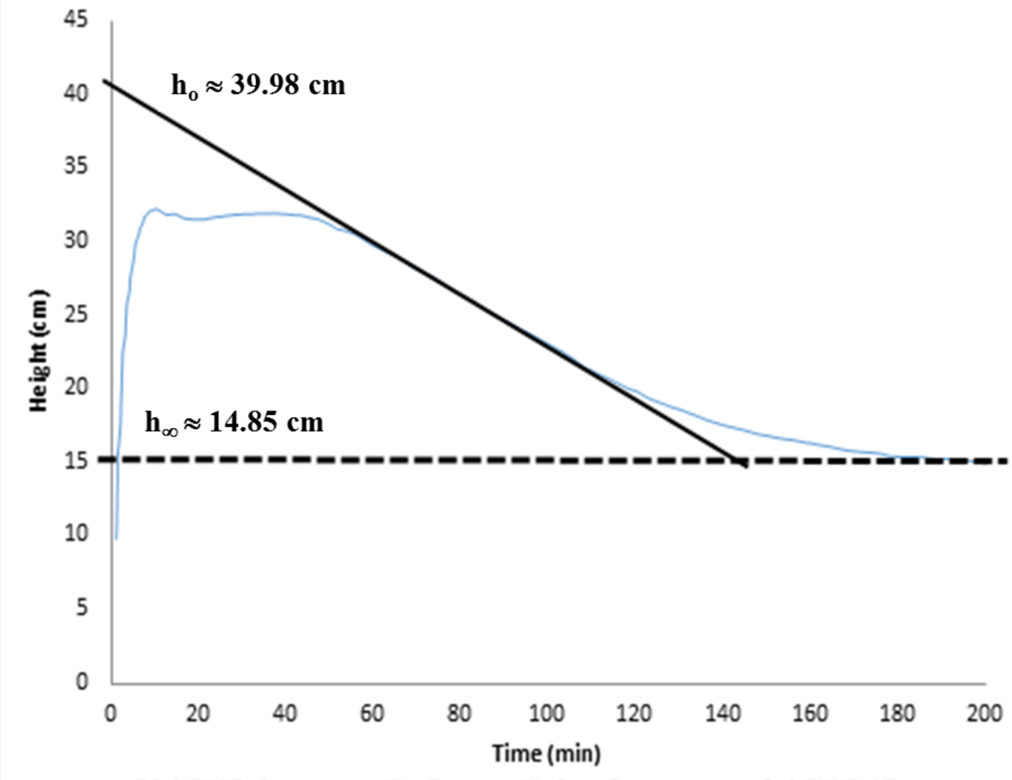


Figure 4.8 Extrapolation of h to zero time (h_0 at $t = 0$) for ε-caprolactone polymerisation using 0.1 mol % $Sn(Oct)_2$ as initiator at 130 ^oC.

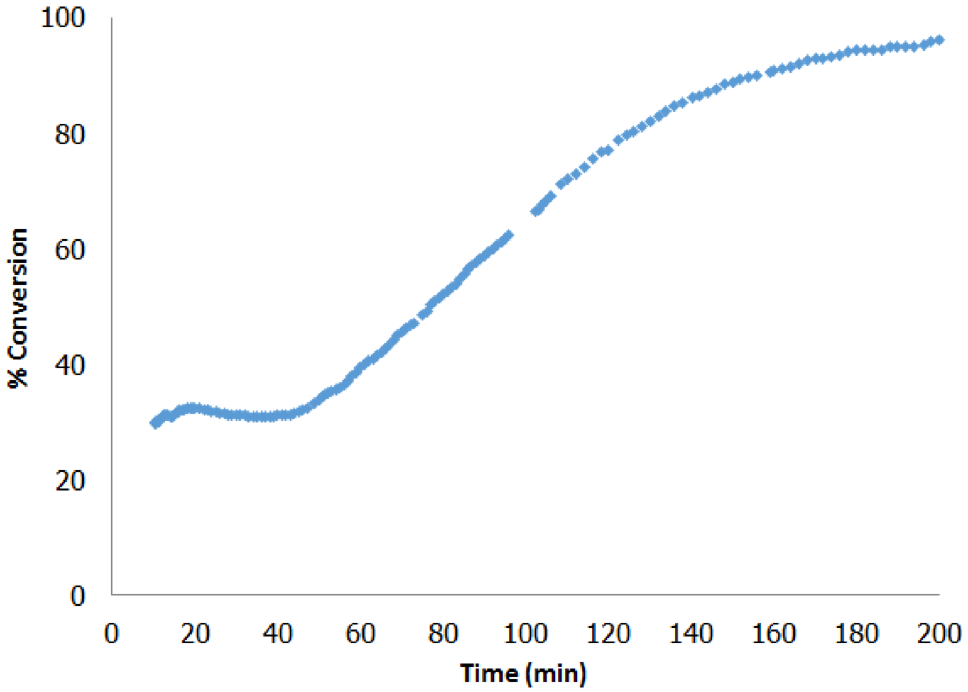


Figure 4.9 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ as initiator at 130 ^oC.

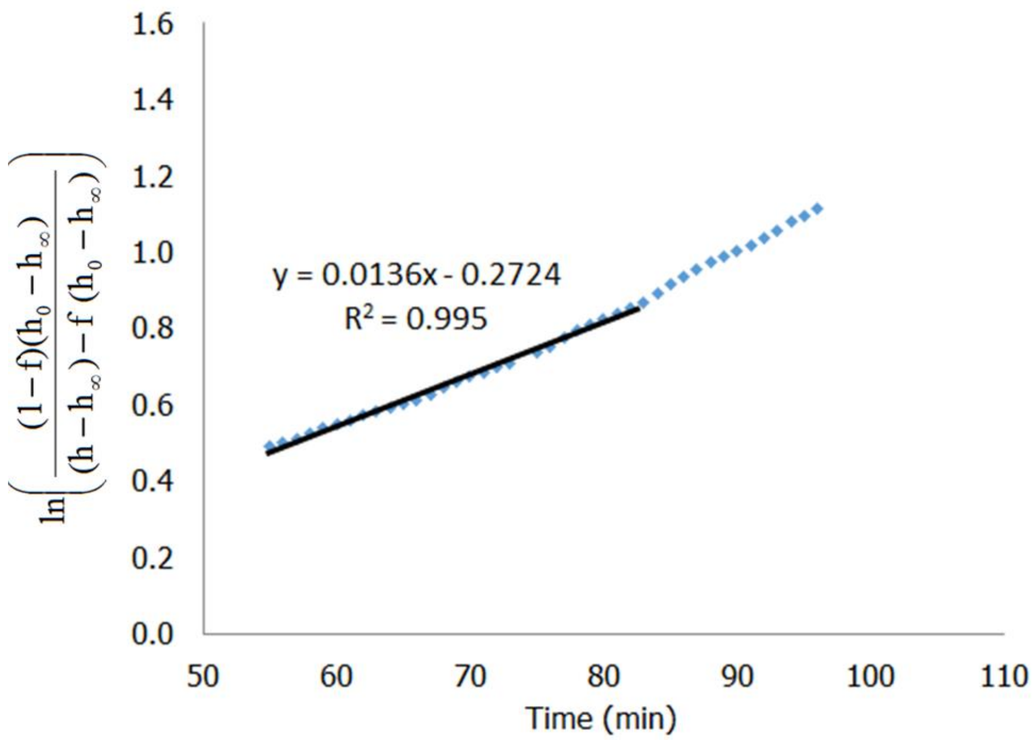


Figure 4.10 First-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ as initiator at 130 °C.

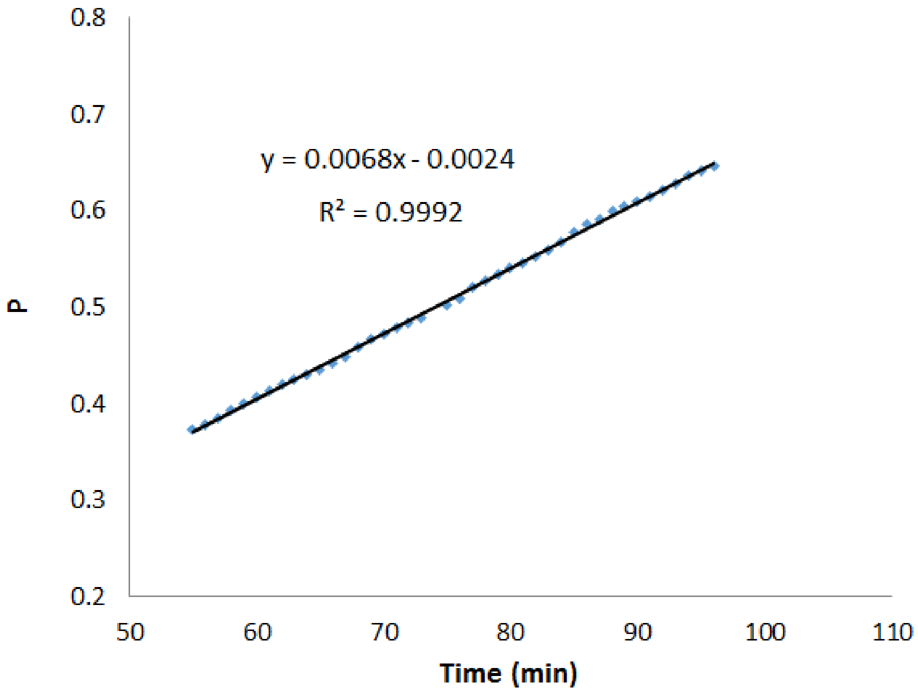


Figure 4.11 Zero-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ as initiator at 130 °C.

Table 4.4 Dilatometry data of *ε*-caprolactone polymerisation at 130 °C using 0.1 mol % mixture initiator ($Sn(Oct)_2$ / DEG) as initiator.

Weight of ε-caprolactone = 14.6081 g
h_0 (from extrapolation) = 33.73 cm
Weight of $Sn(Oct)_2$ / DEG = 0.0815 g
% Yield = 95.75
Capillary diameter = 0.180 cm
Residual monomer (f) = 0.042

Time (min)	Height (cm)	% Conversion
1.28	8.775	
1.35	9.000	
1.46	11.475	
1.59	13.300	
2.12	14.870	
2.24	16.280	
2.47	18.400	
3.11	20.300	
3.25	21.250	
3.38	22.150	
3.56	23.150	
4.07	23.720	Thermal Equilibration
4.21	24.440	
4.34	25.040	
4.58	25.900	
5.10	26.300	
5.25	26.720	
5.43	27.225	
6.00	27.600	
6.11	27.900	
6.24	28.180	
6.40	28.600	
6.53	28.900	
7.06	29.100	
7.28	29.500	
7.40	29.670	
7.56	29.910	
8.12	30.120	
8.25	30.285	
8.42	30.470	
9.00	30.635	
9.20	30.820	
9.40	30.930	
9.56	31.050	Thermal Equilibration
10.07	31.120	
10.30	31.240	
11.00	31.340	
11.30	31.420	
12.00	31.500	
12.30	31.550	
13.00	31.550	9.71
13.30	31.530	9.80
14.00	31.485	10.00
14.30	31.430	10.25
15.00	31.380	10.47
15.30	31.275	10.94
16.00	31.190	11.32
16.30	31.075	11.83
17.00	31.000	12.16
17.30	30.900	12.61
18.00	30.825	12.94
18.30	30.790	13.10
19.00	30.760	13.23
19.30	30.625	13.84
20.00	30.490	14.44
21.00	30.100	16.17
22.00	29.750	17.73
23.00	29.420	19.20
23.30	29.250	19.96
24.00	29.175	20.30
25.00	29.030	20.94
26.13	28.830	21.83
27.00	28.800	21.97
28.00	28.650	22.64
29.00	28.540	23.13
30.00	28.375	23.86
31.16	28.020	25.44
32.05	27.690	26.91
33.30	26.900	30.43
34.00	26.530	32.08
35.00	25.950	34.67
36.00	25.470	36.80
37.00	25.050	38.68
38.05	24.420	41.48
39.10	23.950	43.58
40.00	23.600	45.14
41.08	23.140	47.19
42.00	22.900	48.26
43.09	22.600	49.59
44.04	22.320	50.84
45.22	21.990	52.31
46.00	21.800	53.16
47.00	21.430	54.80
48.15	21.050	56.50

Table 4.4 (Continued).

Time (min)	**Height (cm)**	**% Conversion**
49.00	20.950	56.94
50.00	20.950	56.94
51.00	20.990	56.77
52.00	20.990	56.77
53.10	20.950	56.94
54.07	20.880	57.26
55.12	20.775	57.72
56.05	20.680	58.15
57.00	20.570	58.64
58.20	20.370	59.53
59.10	20.270	59.97
60.00	20.170	60.42
61.00	20.020	61.09
62.05	19.915	61.56
63.00	19.850	61.84
64.00	19.815	62.00
65.00	19.760	62.25
66.15	19.710	62.47
67.00	19.685	62.58
68.40	19.400	63.85
69.00	19.350	64.07
70.12	19.190	64.79
71.00	19.080	65.28
74.00	18.700	66.97
75.00	18.570	67.55
76.00	18.450	68.08
77.19	18.285	68.82
78.07	18.140	69.46
79.00	18.020	70.00
80.00	17.865	70.69
81.15	17.650	71.65
82.20	17.450	72.54
83.10	17.340	73.03
84.00	17.180	73.74
85.35	16.600	76.33
86.00	16.415	77.15
87.00	15.920	79.36
88.00	15.500	81.23
89.00	15.170	82.70
90.20	14.835	84.19
91.00	14.750	84.57
92.44	14.500	85.68
93.18	14.400	86.13
94.00	14.240	86.84
95.00	13.950	88.13
96.00	13.615	89.63
97.00	13.260	91.21
98.00	13.000	92.37
99.00	12.875	92.92
100.00	12.875	92.92
102.00	12.875	92.92
104.00	12.875	92.92
106.00	12.875	92.92
108.00	12.715	93.64
110.00	12.850	93.03
112.00	12.910	92.77
114.20	12.860	92.99
116.00	12.800	93.26
119.12	13.080	92.01
120.00	13.080	92.01
122.00	13.080	92.01
124.00	13.080	92.01
126.48	13.020	92.28
128.00	13.150	91.70
130.00	13.285	91.10
133.00	13.210	91.43
134.00	13.150	91.70
138.00	12.770	93.39
140.00	12.770	93.39
142.15	12.650	93.93
144.51	12.890	92.86
146.00	12.910	92.77
148.00	12.910	92.77
150.20	12.680	93.79
154.45	12.235	95.77
158.00	12.340	95.31
161.00	12.400	95.04
162.00	12.350	95.26
164.00	12.450	94.82
166.00	12.450	94.82
168.00	12.355	95.24
170.00	12.200	95.93
172.20	12.140	96.20
174.15	12.325	95.37
176.00	12.585	94.22
178.00	12.650	93.93
180.52	12.820	93.17
182.20	12.850	93.03
184.46	12.900	92.81
186.00	12.870	92.95
188.45	12.795	93.28
191.20	12.440	94.86
192.00	12.385	95.11
194.20	12.345	95.28
196.00	12.385	95.11
198.00	12.500	94.59
200.00	12.750	93.48
204.00	12.630	94.01
206.00	12.575	94.26
208.00	12.620	94.06
211.38	12.490	94.64
212.00	12.490	94.64
214.00	12.160	96.11
216.50	11.890	97.31
219.00	12.220	95.84
220.00	12.320	95.40

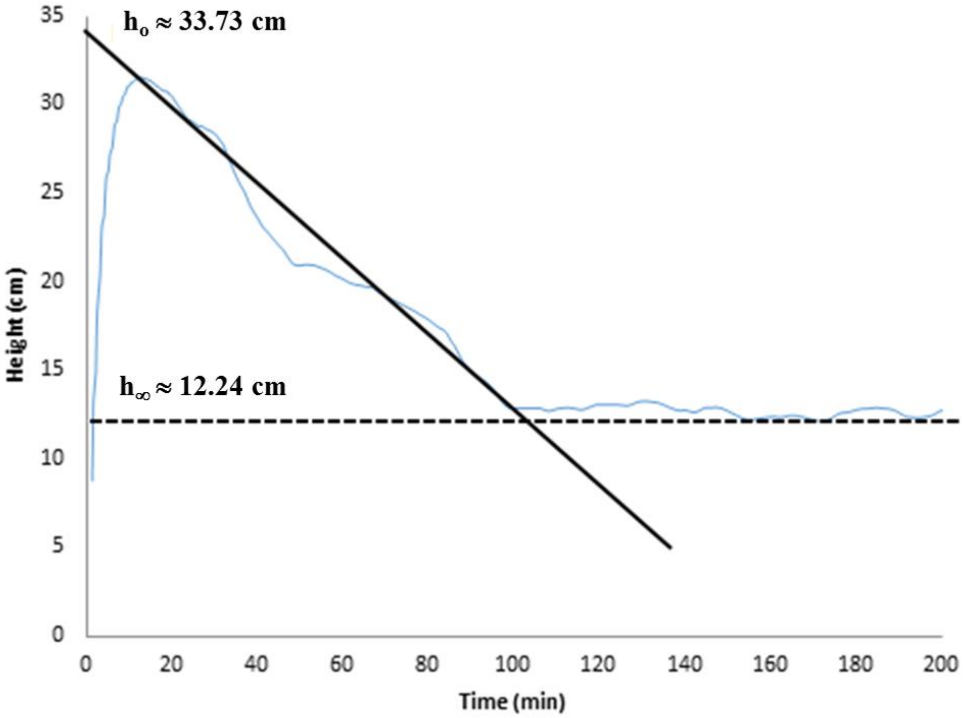


Figure 4.12 Extrapolation of h to zero time (h_0 at t = 0) for ε-caprolactone polymerisation using 0.1 mol % $Sn(Oct)_2$ / DEG as initiator at 130 °C.

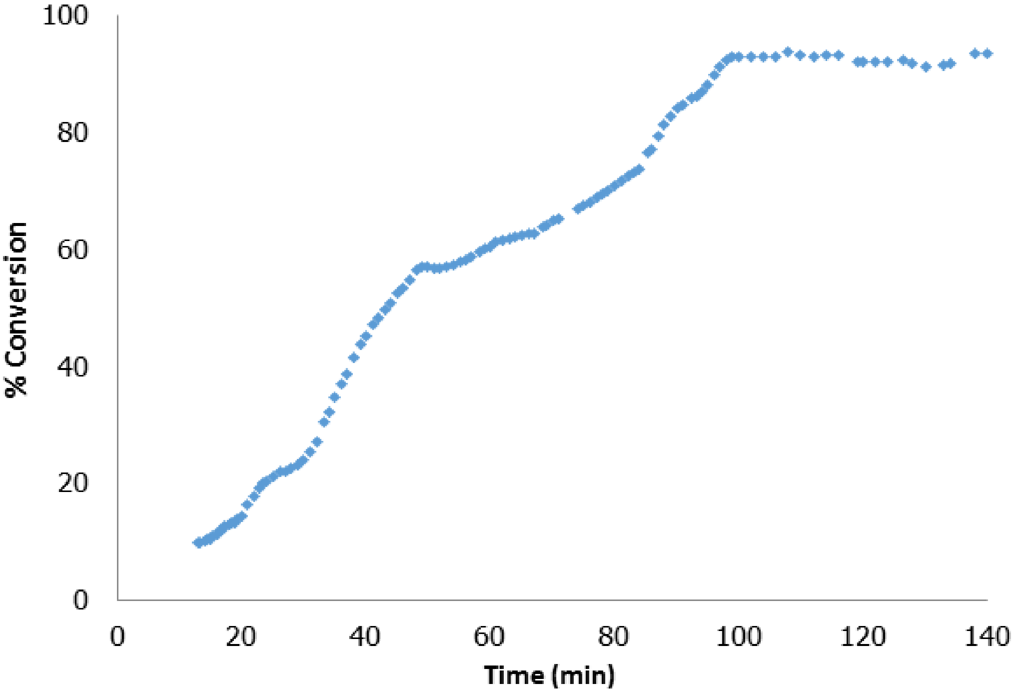


Figure 4.13 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / DEG as initiator at 130 °C.

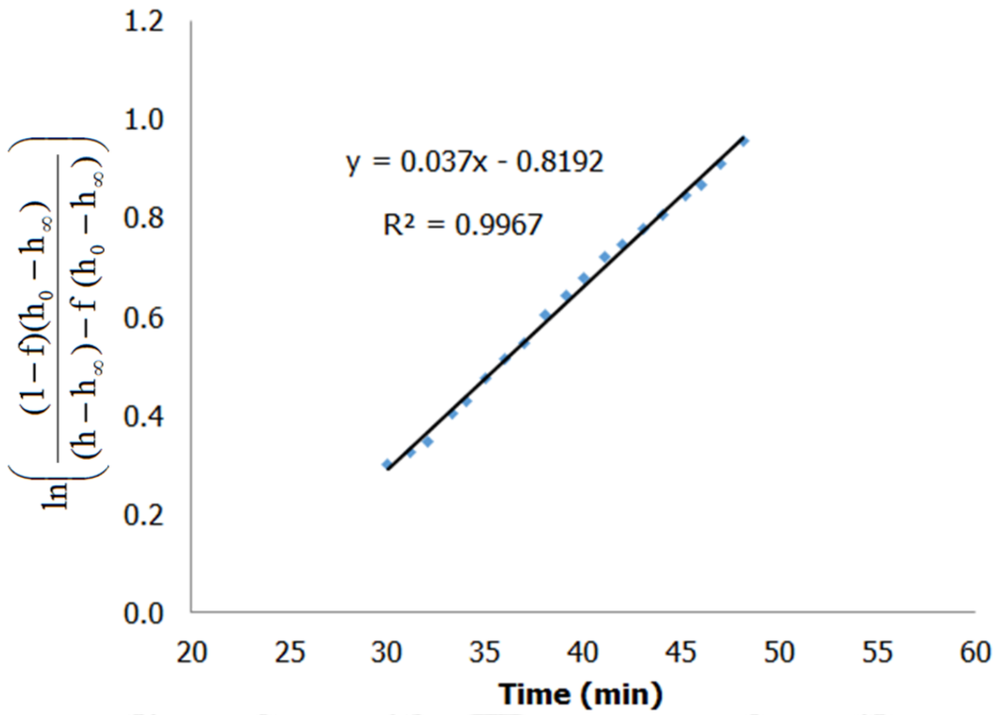


Figure 4.14 First-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / DEG as initiator at 130 °C.

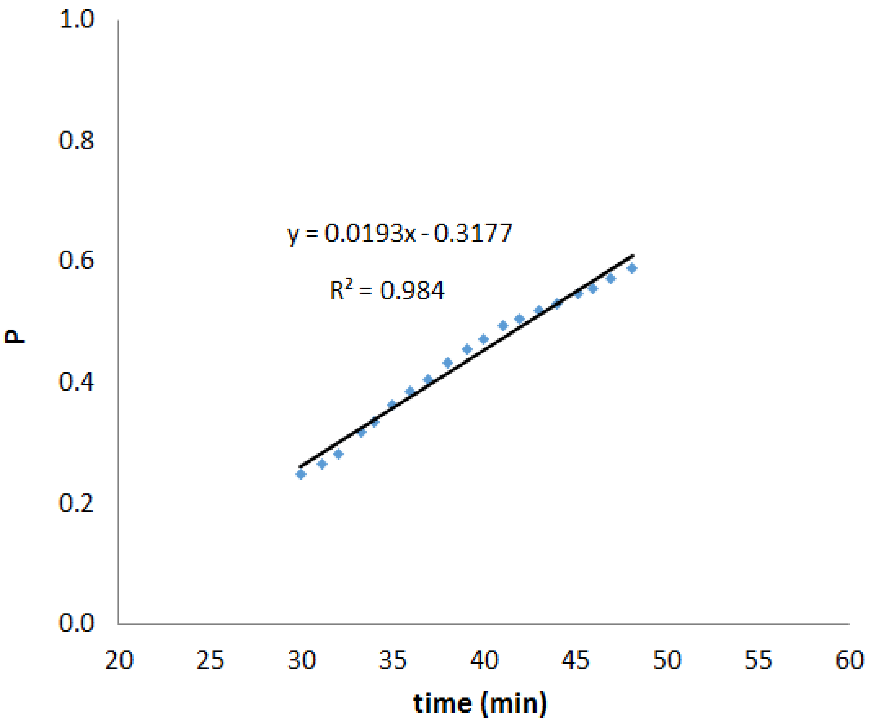


Figure 4.15 Zero-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / DEG as initiator at 130 °C.

Table 4.5 Dilatometry data of *ε*-caprolactone polymerisation at 130 °C using 0.1 mol % mixture initiator ($Sn(Oct)_2$ / EG) as initiator.

Weight of ε-caprolactone = 14.6008 g h_0 (from extrapolation) = 38.98 cm
Weight of $Sn(Oct)_2$ / EG = 0.0796 g   % Yield = 99.71
Capillary diameter = 0.180 cm   Residual monomer (f) = 0.003

Time (min)	**Height (cm)**	**% Conversion**
1.23	8.650	Thermal Equilibration
1.32	9.900	
1.41	11.360	
1.53	12.985	
2.12	15.250	
2.24	16.520	
2.38	17.770	
2.52	19.100	
3.04	20.030	
3.14	20.880	
3.34	21.065	
4.03	23.650	
4.15	24.190	
4.30	24.770	
4.43	25.300	
4.58	25.780	
5.12	26.250	
5.31	26.750	
5.44	27.070	
5.56	27.350	
6.09	27.625	
6.24	27.940	
6.40	28.190	
7.07	28.640	
7.26	28.900	
7.36	29.000	
7.46	29.130	
8.01	29.280	Thermal Equilibration
8.22	29.470	
8.36	29.640	
8.53	29.760	
9.12	29.883	
9.33	29.995	
9.56	30.150	
10.36	30.320	
11.00	30.420	
11.30	30.525	
12.00	30.600	
12.30	30.660	
13.00	30.690	
14.00	30.782	
14.30	30.820	
15.00	30.840	
15.30	30.860	
16.00	30.875	30.52
16.30	30.860	30.58
17.00	30.845	30.64
17.30	30.850	30.62
18.00	30.850	30.62
18.30	30.850	30.62
19.00	30.850	30.62
19.30	30.845	30.64
20.00	30.850	30.62
21.00	30.920	30.35
22.00	30.863	30.57
23.00	30.775	30.90
24.00	30.650	31.37
25.00	30.500	31.93
26.30	30.260	32.84
27.00	30.210	33.03
28.00	29.980	33.89
29.15	29.700	34.95
30.00	29.520	35.63
31.00	29.200	36.83
32.14	28.890	38.00
33.00	28.690	38.75
34.10	28.380	39.92
35.00	28.175	40.69
36.00	27.883	41.79
37.00	27.590	42.89
38.00	27.275	44.08
39.05	26.900	45.49
40.20	26.440	47.22
41.00	26.225	48.03
42.04	25.870	49.37
43.00	25.600	50.39
44.00	25.350	51.33
45.00	25.000	52.65
46.00	24.710	53.74
47.00	24.385	54.96
48.00	24.050	56.22

Table 4.5 (Continued).

Time (min)	Height (cm)	% Conversion
49.12	23.620	57.84
50.00	23.385	58.73
51.00	22.960	60.33
52.00	22.620	61.61
53.00	22.300	62.81
54.08	21.930	64.21
55.00	21.690	65.11
56.18	21.270	66.69
57.30	20.932	67.97
58.00	20.800	68.46
59.00	20.500	69.59
60.00	20.265	70.48
61.00	20.030	71.36
62.00	19.800	72.23
63.00	19.610	72.94
64.00	19.420	73.66
65.00	19.100	74.87
66.06	18.720	76.30
67.28	18.270	77.99
68.00	18.150	78.44
69.00	17.810	79.72
70.00	17.470	81.00
71.00	17.200	82.02
72.10	16.925	83.06
73.00	16.765	83.66
74.00	16.550	84.47
75.00	16.370	85.15
76.00	16.215	85.73
77.00	16.070	86.28
78.00	15.965	86.67
79.00	15.925	86.82
80.00	15.736	87.53
81.00	15.550	88.23
82.00	15.400	88.80
83.00	15.225	89.460
84.14	15.075	90.020
85.00	15.000	90.310
86.00	14.915	90.630
87.00	14.815	91.000
88.00	14.770	91.170
89.00	14.700	91.440
90.00	14.670	91.550
91.00	14.670	91.550
92.00	14.736	91.300
93.00	14.670	91.550
94.40	14.420	92.490
95.00	14.385	92.620
96.00	14.270	93.050
97.00	14.200	93.320
98.00	14.150	93.510
99.00	14.150	93.510
100.00	14.150	93.510
102.00	13.950	94.260
105.00	13.690	95.240
106.00	13.640	95.430
108.00	13.510	95.920
110.00	13.410	96.290
112.00	13.260	96.860
114.00	13.240	96.930
116.00	13.300	96.710
118.00	13.300	96.710
120.00	13.210	97.050
122.00	13.185	97.140
124.00	13.120	97.390
126.30	13.140	97.310
128.00	13.050	97.650
130.15	12.990	97.870
132.00	13.000	97.840
134.00	12.940	98.06
136.00	12.970	97.95
138.00	12.900	98.21
140.00	12.870	98.33
142.00	12.930	98.10
144.08	12.850	98.40
146.00	12.875	98.31
148.00	12.800	98.59
150.00	12.715	98.91
152.00	12.700	98.97
154.00	12.765	98.72
156.00	12.720	98.89
158.00	12.730	98.85
160.00	12.920	98.14
162.00	12.885	98.27
164.00	12.870	98.33
166.00	12.860	98.36
168.00	12.770	98.70
170.00	12.785	98.65
172.00	12.860	98.36
174.00	12.810	98.55
176.00	12.720	98.89
178.00	12.700	98.97
180.53	12.780	98.67
182.00	12.700	98.97
184.00	12.660	99.12
186.00	12.640	99.19
188.00	12.545	99.55
190.00	12.590	99.38
192.00	12.535	99.59
194.00	12.500	99.72
196.00	12.585	99.40
198.00	12.625	99.25
200.00	12.690	99.00

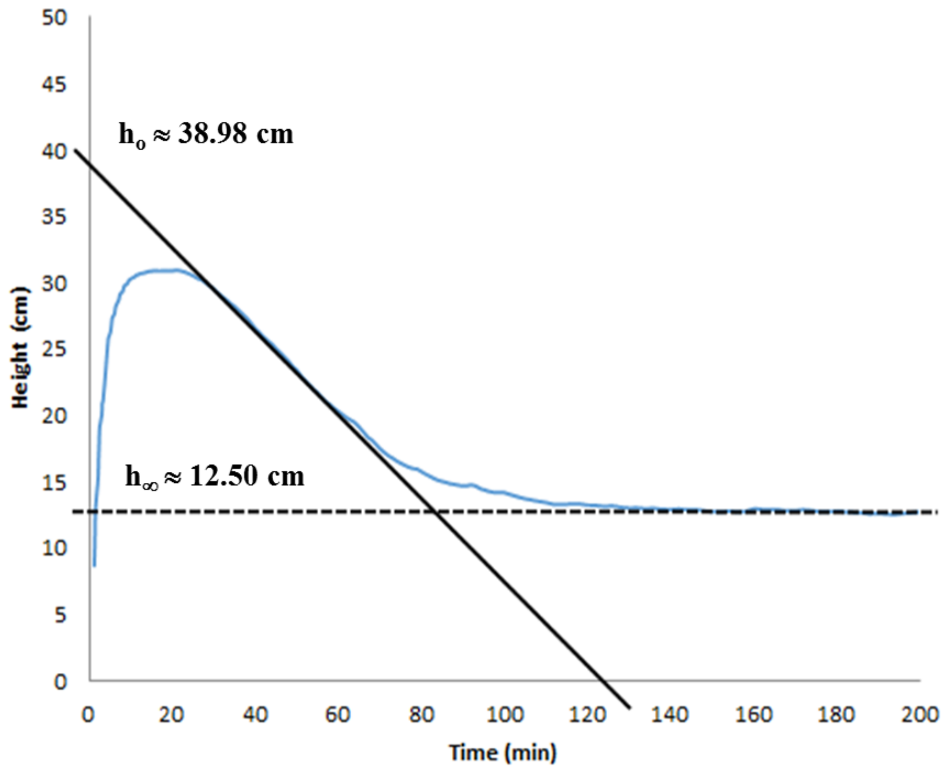


Figure 4.16 Extrapolation of h to zero time (h_0 at t = 0) and at constant height (h_∞) for ε-caprolactone polymerisation using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

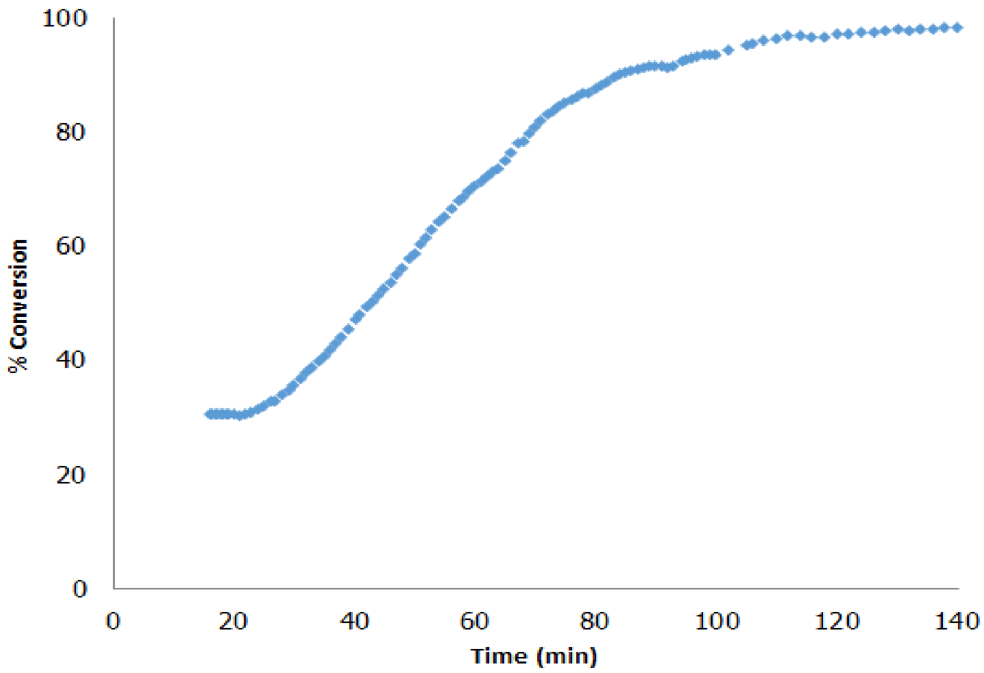


Figure 4.17 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

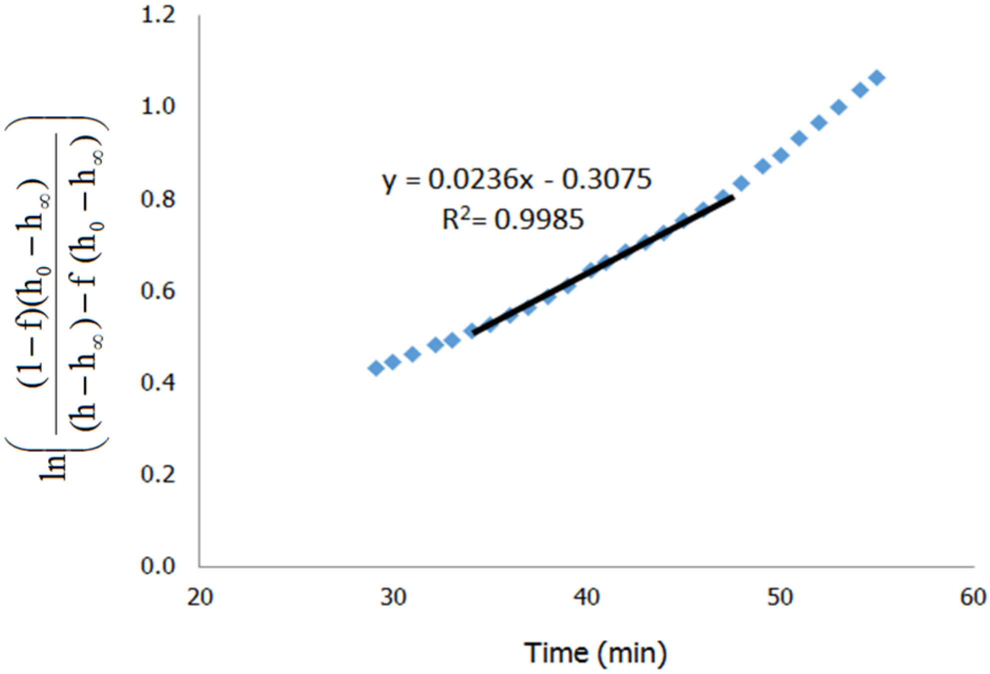


Figure 4.18 First-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

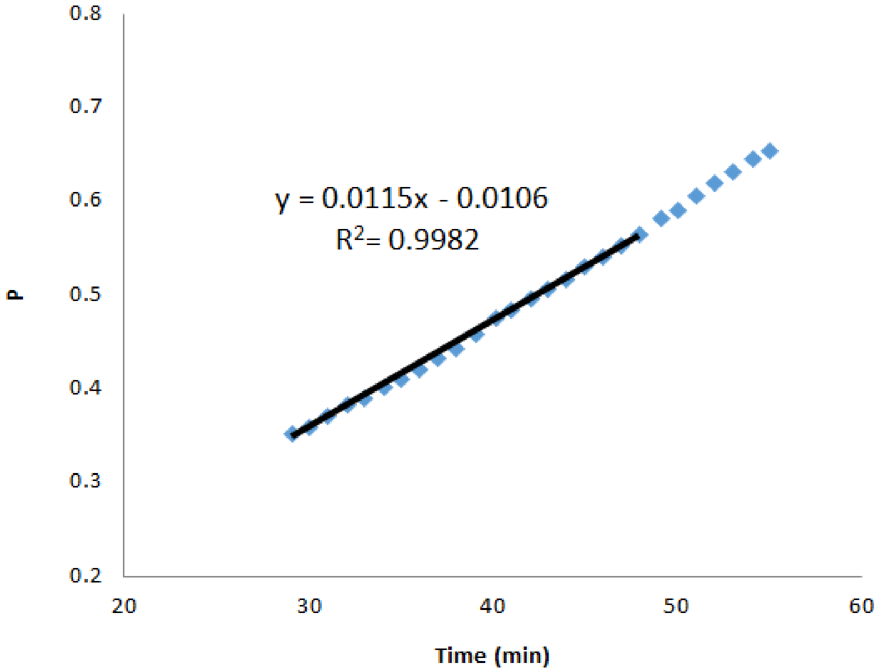


Figure 4.19 Zero-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $Sn(Oct)_2$ / EG as initiator at 130 °C.

Table 4.6 Dilatometry data of ε-caprolactone polymerisation at 130 ^{o}C using 0.1 mol % $[Sn(Oct)]_2DEG$ as initiator.

Weight of ε-caprolactone = 14.6070 g
Weight of $[Sn(Oct)]_2DEG$ = 0.0811 g
Capillary diameter = 0.180 cm
h_0 (from extrapolation) = 37.67 cm
% Yield = 90.75
Residual monomer (f) = 0.093

Time (min)	Height (cm)	% Conversion
1.47	8.640	Thermal Equilibration
1.54	9.550	
2.06	11.175	
2.20	13.100	
2.35	14.500	
2.48	15.650	
3.02	16.950	
3.18	18.175	
3.30	19.100	
3.40	19.720	
3.50	19.410	
4.04	21.140	
4.14	21.780	
4.30	21.500	
5.00	23.800	
5.15	24.300	
5.30	24.810	
5.47	25.300	
6.00	25.800	
6.32	26.450	
6.46	26.700	
7.06	27.100	
7.20	27.300	
7.33	27.570	
7.46	27.730	
8.06	27.980	
8.25	28.215	
8.42	28.415	Thermal Equilibration
9.10	28.700	
9.25	28.823	
9.44	28.990	
10.06	29.150	
10.19	29.260	
10.35	29.335	
10.52	29.417	
11.10	29.545	
11.58	29.765	
12.17	29.830	
12.38	29.860	
13.16	29.925	
13.55	29.990	
14.16	30.040	
14.50	30.112	
15.13	30.180	
15.35	30.235	
16.00	30.295	
16.48	30.395	25.71
18.16	30.300	26.04
18.56	30.235	26.27
19.17	30.215	26.34
19.35	30.115	26.70
19.51	30.075	26.84
20.09	29.975	27.19
20.27	29.890	27.49
20.52	29.715	28.11
21.10	29.585	28.57
21.30	29.465	28.99
21.50	29.310	29.54
22.06	29.227	29.84
22.26	29.150	30.11
22.41	29.100	30.28
23.05	29.100	30.28
23.37	29.145	30.13
24.00	29.200	29.93
24.30	29.250	29.75
25.00	29.300	29.58
25.30	29.375	29.31
26.00	29.430	29.12
26.30	29.465	28.99
27.00	29.520	28.80
27.30	29.520	28.80
28.00	29.510	28.84
28.30	29.500	28.87
29.00	29.485	28.92
29.30	29.465	28.99
30.00	29.415	29.17
31.00	29.200	29.93
32.00	28.873	31.09
33.00	28.430	32.65
34.00	27.900	34.52
35.00	27.400	36.29

Table 4.6 (Continued).

Time (min)	**Height (cm)**	**% Conversion**	**Time (min)**	**Height (cm)**	**% Conversion**	**Time (min)**	**Height (cm)**	**% Conversion**
36.00	27.040	37.56	72.00	18.020	69.44	76.00	16.960	73.18
37.00	26.910	38.02	73.00	17.770	70.32	77.00	16.810	73.71
38.00	26.870	38.17	74.00	17.500	71.28	78.00	16.720	74.03
39.00	26.850	38.24	75.00	17.180	72.41	79.00	16.630	74.35
40.00	26.780	38.48	76.00	16.960	73.18	80.00	16.530	74.70
41.15	26.550	39.30	77.00	16.810	73.71	81.00	16.450	74.99
42.00	26.320	40.11	78.00	16.720	74.03	82.00	16.390	75.20
43.00	25.900	41.59	79.00	16.630	74.35	83.00	16.300	75.52
44.00	25.400	43.36	80.00	16.530	74.70	84.00	16.200	75.87
45.00	24.870	45.23	81.00	16.450	74.99	85.14	16.000	76.58
46.00	24.490	46.58	82.00	16.390	75.20	86.00	15.870	77.04
47.00	24.250	47.42	83.00	16.300	75.52	87.00	15.675	77.73
48.00	24.120	47.88	84.00	16.200	75.87	88.00	15.340	78.91
49.00	24.000	48.31	85.14	16.000	76.58	89.00	15.025	80.02
50.00	23.820	48.94	86.00	15.870	77.04	90.00	14.750	80.99
51.00	23.500	50.07	55.00	22.160	54.81	91.00	14.650	81.35
52.00	23.120	51.42	56.00	21.920	55.66	92.00	14.600	81.52
53.00	22.710	52.87	57.00	21.620	56.72	93.00	14.600	81.52
54.00	22.385	54.01	58.00	21.260	57.99	94.00	14.590	81.56
55.00	22.160	54.81	59.00	20.870	59.37	95.00	14.590	81.56
56.00	21.920	55.66	60.00	20.525	60.59	96.00	14.590	81.56
57.00	21.620	56.72	61.00	20.270	61.49	97.00	14.590	81.56
58.00	21.260	57.99	62.00	20.050	62.27	98.09	14.470	81.98
59.00	20.870	59.37	63.00	19.850	62.97	99.00	14.400	82.23
60.00	20.525	60.59	64.00	19.660	63.64	100.00	14.250	82.76
61.00	20.270	61.49	65.00	19.450	64.39	101.00	14.065	83.41
62.00	20.050	62.27	66.00	19.200	65.27	102.00	13.835	84.23
63.00	19.850	62.97	67.35	18.835	66.56	103.00	13.565	85.18
64.00	19.660	63.64	68.00	18.750	66.86	104.00	13.390	85.80
65.00	19.450	64.39	69.00	18.530	67.64	105.00	13.370	85.87
66.00	19.200	65.27	70.00	18.400	68.10	106.00	13.370	85.87
67.35	18.835	66.56	71.00	18.225	68.71	107.00	13.425	85.68
68.00	18.750	66.86	72.00	18.020	69.44	108.00	13.490	85.45
69.00	18.530	67.64	73.00	17.770	70.32	109.00	13.530	85.31
70.00	18.400	68.10	74.00	17.500	71.28	110.00	13.600	85.06
71.00	18.225	68.71	75.00	17.180	72.41	111.00	13.600	85.06

Table 4.6 (Continued).

Time (min)	Height (cm)	% Conversion
112.00	13.600	85.06
113.00	13.540	85.27
114.00	13.450	85.59
115.00	13.325	86.03
116.00	13.100	86.82
117.00	12.850	87.71
118.00	12.670	88.34
119.00	12.650	88.42
120.00	12.730	88.13
121.00	12.780	87.96
122.00	12.860	87.67
123.00	12.920	87.46
124.00	12.920	87.46
125.00	12.990	87.21
126.00	13.050	87.00
127.00	13.070	86.93
128.00	13.095	86.84
129.00	13.095	86.84
130.28	12.920	87.46
131.10	12.820	87.81
132.18	12.590	88.63
133.00	12.350	89.48
134.15	12.190	90.04
135.00	12.240	89.86
136.00	12.300	89.65
137.00	12.420	89.23
138.00	12.500	88.95
139.00	12.590	88.63
140.22	12.620	88.52
141.35	12.670	88.34
142.00	12.670	88.34
143.00	12.670	88.34
144.18	12.420	89.23
145.38	12.370	89.40
146.00	12.300	89.65
148.00	11.985	90.77
150.00	12.150	90.18
153.00	12.420	89.23
156.00	12.630	88.49
159.00	12.630	88.49
162.00	12.600	88.59
165.00	11.900	91.07
168.00	12.150	90.18
170.00	12.320	89.58
172.00	12.480	89.02
174.00	12.480	89.02
176.00	12.330	89.55
178.00	11.860	91.21
180.00	11.970	90.82
182.00	12.100	90.36
184.00	12.320	89.58
186.00	12.340	89.51
188.00	12.250	89.83
190.00	11.760	91.56
192.00	11.600	92.13
194.00	11.730	91.67
196.00	11.910	91.03
198.00	12.090	90.39
200.00	12.250	89.83

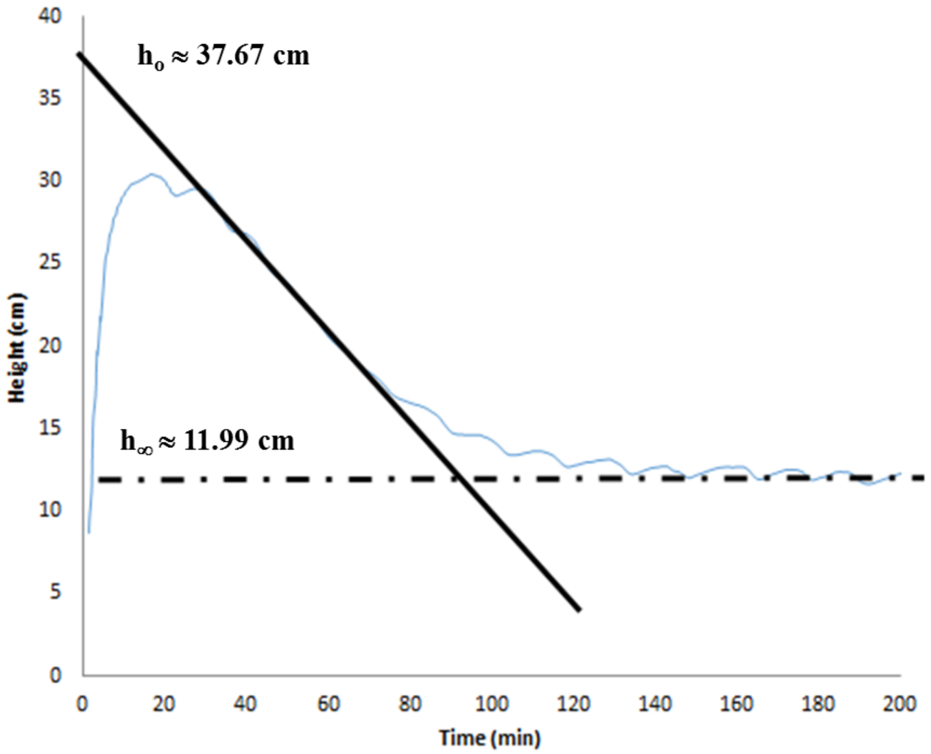


Figure 4.20 Extrapolation of h to zero time (h_0 at t = 0) for ε-caprolactone polymerisation using 0.1 mol % $[Sn(Oct)]_2$ DEG as initiator at 130 ^{o}C.

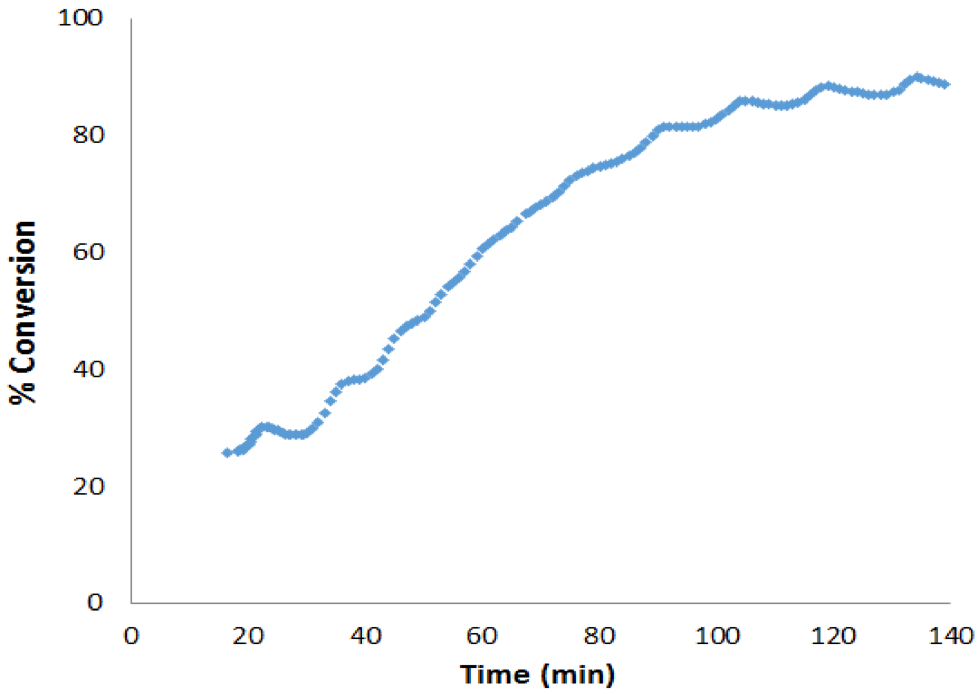


Figure 4.21 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using 0.1 mol % $[Sn(Oct)]_2$ DEG as initiator at 130 ^{o}C.

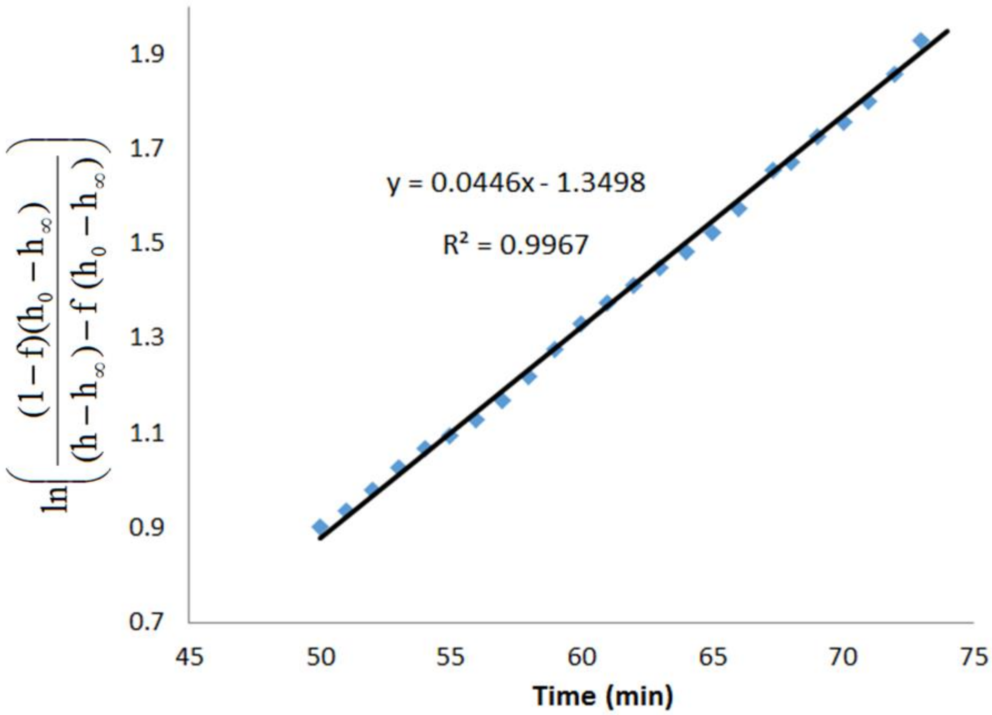


Figure 4.22 First-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $[Sn(Oct)]_2$ DEG as initiator at 130 °C.

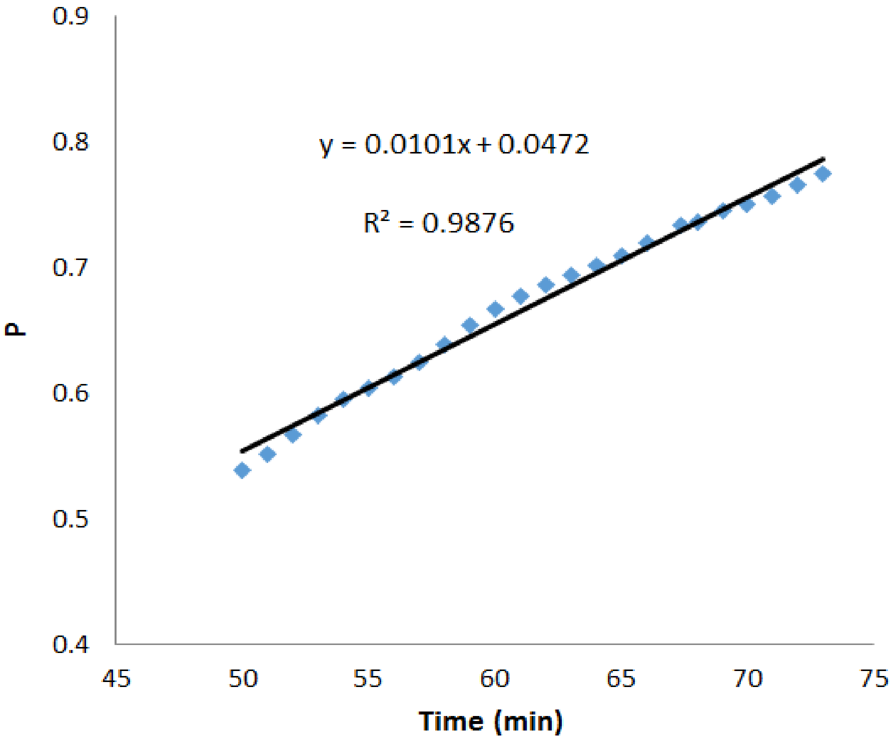


Figure 4.23 Zero-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $[Sn(Oct)]_2$ DEG as initiator at 130 °C.

Table 4.7 Dilatometry data of ε-caprolactone polymerisation at 130 ^{o}C using 0.1 mol % $[Sn(Oct)]_2EG$ as initiator.

Weight of ε-caprolactone = 14.6150 g h_0 (from extrapolation) = 35.78 cm
Weight of $[Sn(Oct)]_2EG$ = 0.0751 g % Yield = 99.68
Capillary diameter = 0.180 cm Residual monomer (f) = 0.003

Time (min)	Height (cm)	% Conversion
1.09	10.200	Thermal Equilibration
1.20	11.900	
1.30	13.325	
1.45	15.450	
1.55	16.670	
2.10	18.250	
2.22	19.450	
2.32	20.220	
2.43	21.050	
2.53	21.800	
3.03	22.530	
3.15	23.220	
3.29	24.050	
3.40	24.550	
3.50	24.975	
4.01	25.420	
4.14	25.875	
4.27	26.310	
4.40	26.700	
4.53	27.025	
5.07	27.350	
5.36	28.090	
5.52	28.320	
6.23	28.750	
6.36	28.900	
6.47	28.950	
6.58	29.020	
7.33	29.020	Thermal Equilibration
7.52	29.150	
8.04	29.200	
8.18	29.300	
8.50	29.410	
9.08	29.470	
9.30	29.540	
9.48	29.610	
10.05	29.650	
10.30	29.650	
11.00	29.710	
11.30	29.770	
12.00	29.810	
12.30	29.810	
13.00	29.870	24.28
13.30	29.850	24.37
14.00	29.870	24.28
14.30	29.920	24.08
15.00	29.920	24.08
15.30	29.970	23.87
16.00	30.000	23.75
17.00	30.070	23.46
17.30	30.700	20.87
18.44	29.990	23.79
19.10	30.040	23.58
19.30	30.040	23.58
20.00	29.970	23.87
21.00	29.810	24.53
22.00	29.635	25.25
23.00	29.333	26.49
24.00	29.070	27.57
25.00	28.850	28.47
26.00	28.660	29.25
27.00	28.585	29.56
28.30	28.500	29.91
29.00	28.500	29.91
30.00	28.570	29.62
31.00	28.660	29.25
32.00	28.645	29.32
33.00	28.560	29.67
34.00	28.450	30.12
35.42	28.240	30.98
36.00	28.170	31.27
37.23	27.900	32.38
38.00	27.775	32.89
39.00	27.300	34.84
40.00	26.850	36.69
41.00	26.400	38.54
42.20	25.670	41.54
43.00	25.400	42.65
44.00	25.120	43.80
45.00	24.800	45.11
46.00	24.620	45.85
47.00	24.425	46.66

Table 4.7 (Continued).

Time (min)	**Height (cm)**	**% Conversion**
48.00	24.200	47.58
49.00	23.950	48.61
50.00	23.750	49.43
51.00	23.590	50.09
52.00	23.270	51.40
53.00	23.050	52.30
54.15	22.840	53.17
55.00	22.610	54.11
56.00	22.330	55.26
57.00	22.140	56.04
58.00	21.930	56.91
59.22	21.580	58.34
60.00	21.450	58.88
61.00	21.185	59.97
62.00	20.900	61.14
63.00	20.500	62.78
64.00	20.130	64.30
65.00	19.700	66.07
66.00	19.280	67.79
67.30	18.800	69.77
68.00	18.650	70.38
69.00	18.380	71.49
70.00	18.180	72.31
71.00	17.960	73.22
72.00	17.720	74.20
73.00	17.550	74.90
74.00	17.340	75.77
75.00	17.140	76.59
76.00	16.971	77.28
77.00	16.820	77.90
78.30	16.650	78.60
79.00	16.480	79.30
80.00	16.335	79.90
81.00	16.220	80.37
82.00	16.040	81.11
83.45	15.785	82.16
84.00	15.735	82.36
85.30	15.470	83.45
86.00	15.340	83.98
87.00	15.080	85.05
88.00	14.835	86.06
89.00	14.580	87.11
90.00	14.420	87.76
91.00	14.280	88.34
92.00	14.110	89.04
93.00	14.040	89.32
94.00	13.930	89.78
95.00	13.830	90.19
96.00	13.750	90.52
97.00	13.700	90.72
98.00	13.670	90.85
99.00	13.550	91.34
100.00	13.520	91.46
102.00	13.490	91.58
104.00	13.420	91.87
106.00	13.375	92.06
108.00	13.250	92.57
110.00	13.000	93.60
112.00	12.680	94.91
114.24	12.480	95.73
116.00	12.350	96.27
118.00	12.330	96.35
120.00	12.260	96.64
122.00	12.260	96.64
124.00	12.260	96.64
126.47	12.330	96.35
128.00	12.340	96.31
130.00	12.350	96.27
132.30	12.330	96.35
134.17	12.200	96.89
136.00	12.000	97.71
138.00	11.650	99.14
140.00	11.590	99.39
143.00	11.520	99.68
144.00	11.520	99.68
146.00	11.520	99.68
148.00	11.550	99.56
150.00	11.600	99.35
155.00	11.835	98.38
160.00	11.870	98.24
171.49	11.490	99.80
178.44	11.680	99.02
180.00	11.740	98.78
185.00	11.500	99.76
190.00	11.470	99.88
195.00	11.550	99.56
200.00	11.710	98.90

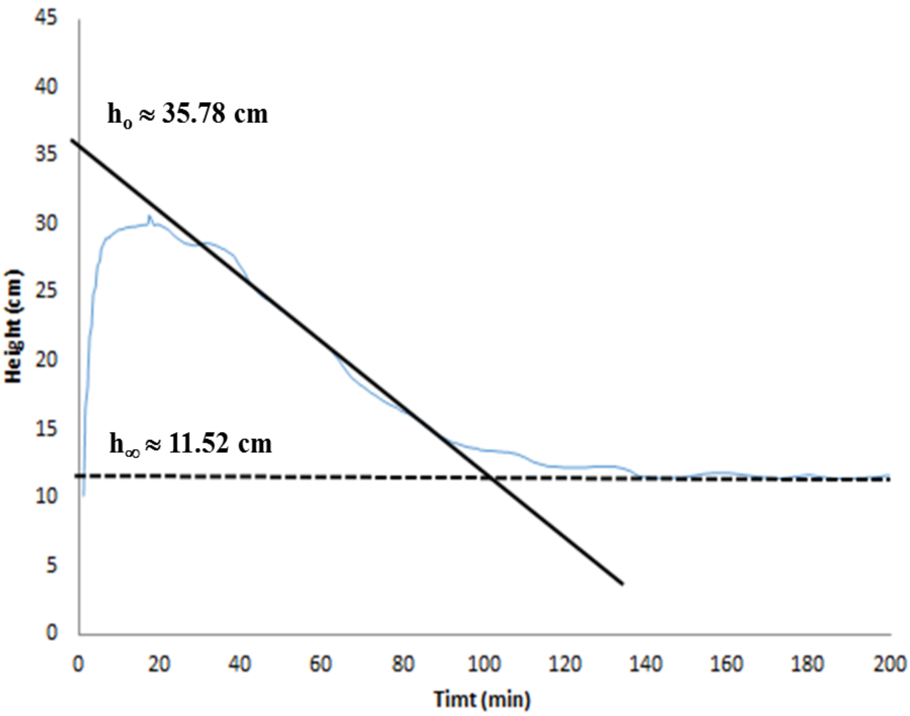


Figure 4.24 Extrapolation of h to zero time (h_0 at t = 0) for ε-caprolactone polymerisation using 0.1 mol % $[Sn(Oct)]_2EG$ as initiator at 130 °C.

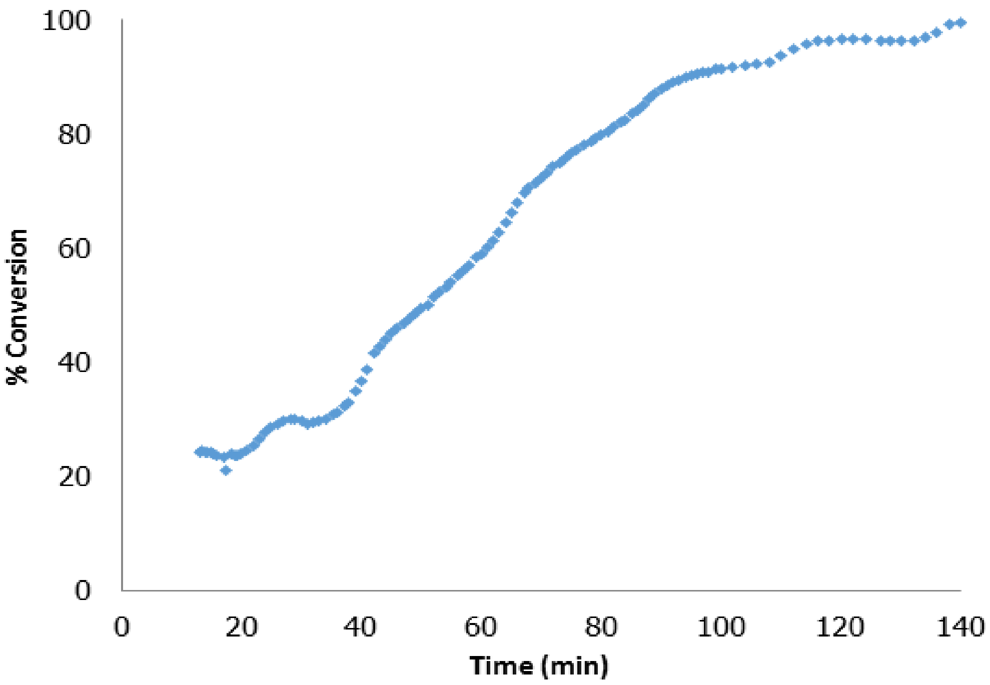


Figure 4.25 Kinetic profile from dilatometry of % conversion against time for ε-caprolactone using 0.1 mol % $[Sn(Oct)]_2EG$ as initiator at 130 °C.

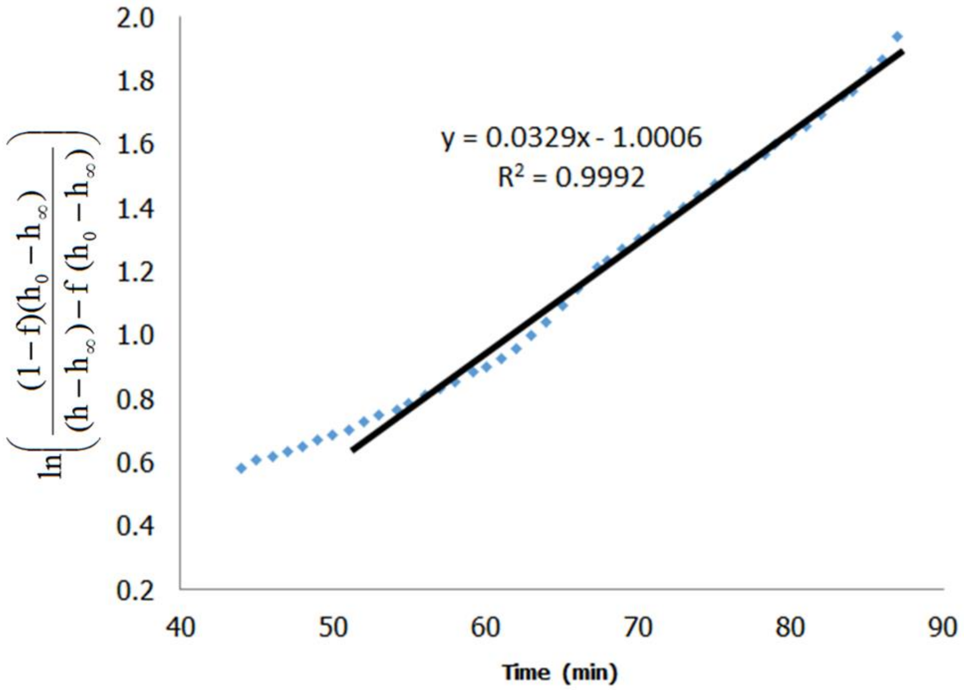


Figure 4.26 First-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $[Sn(Oct)]_2EG$ as initiator at 130 ^oC.

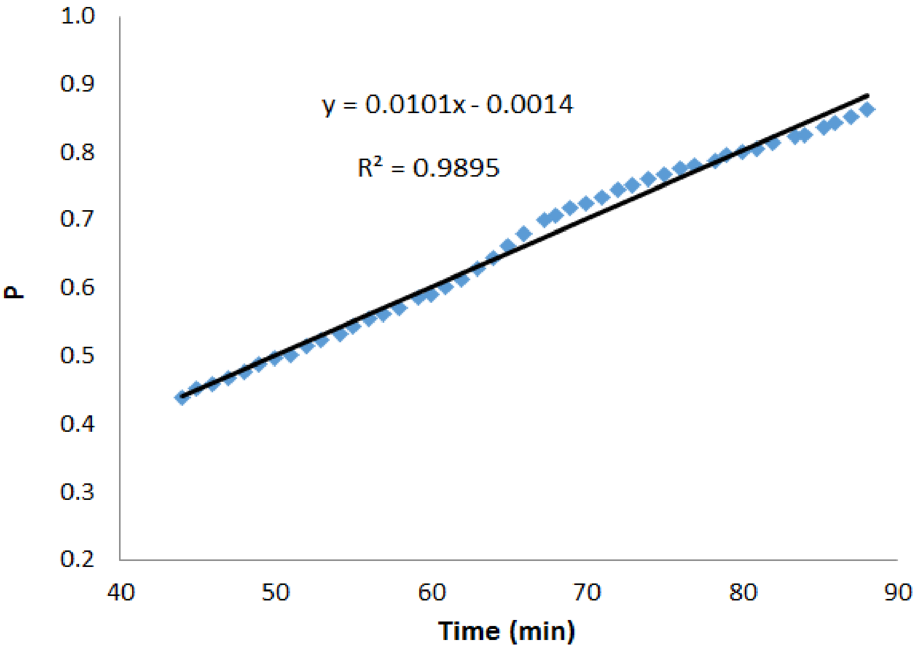


Figure 4.27 Zero-order rate plot from dilatometry for ε-caprolactone using 0.1 mol % $[Sn(Oct)]_2EG$ as initiator at 130 ^oC.

Table 4.8 Summary of kinetic results for ε-caprolactone polymerisation using different liquid initiating systems at 130 °C.

Initiator	Concentration (mol %)	% Yield	First-order Rate Constant		Zero-order Rate Constant	
			k_1 (min^{-1})	R^2	k_0 ($mol\ l^{-1} min^{-1}$)	R^2
$Sn(Oct)_2$	0.1	96.4	0.014	0.995	0.059	0.999
$Sn(Oct)_2$ / DEG *	0.2 / 0.1	95.8	0.037	0.997	0.168	0.984
$Sn(Oct)_2$ / EG *	0.2 / 0.1	99.7	0.024	0.999	0.100	0.998
$[Sn(Oct)]_2DEG$ **	0.1	90.7	0.045	0.997	0.088	0.988
$[Sn(Oct)]_2EG$ **	0.1	99.7	0.033	0.999	0.088	0.990

The experimental data used for the kinetic calculation was taken from the 20-70 %

* Mixed initiators (tin(II) octoate / HOROH) with mol ratio = 2:1 → generates $[Sn(Oct)]_2ORO$ *in situ*

** Initiators pre-prepared separately and used directly rather than generated *in situ*

The % yields, first-order rate constants, zero-order rate constants, and conversion ranges for the rate plots are summarized in Table 4.8. According to the literature, the polymerisation reaction in bulk is consistently described as being kinetically first-order with respect to the monomer concentration. However, as the results here have shown, the kinetic data in some cases fits a zero-order rate plot more closely than a first-order rate plot. The reasons for this are unclear but one possibility is that the deviation from first-order kinetics could be due to diffusion-controlled effects (e.g., Trommsdorf effect) as the viscosity of the system increases with % conversion. Increased viscosity also increases the viscous drag of the liquid meniscus on the glass surface of the dilatometer's capillary. Thus, there are both internal and external factors which may contribute towards a deviation from the expected first-order kinetics. Despite this, the first-order rate constants k_1 in Table 4.8 are still considered to be more reliable than the zero-order rate constants k_0 from a mechanistic point of view.

It is also significant to note in Table 4.8 that the first-order rate constants (k_1, min^{-1}) for the pre-prepared liquid initiators tended to be higher than for the corresponding $Sn(Oct)_2$ / diol mixtures. This is as would be expected and shows the advantage of preparing the true initiator separately and using it directly rather than generating it *in situ* in an uncertain concentration.