CHAPTER 5

CONCLUSIONS

5.1 EFFECT OF CATALYST STRUCTURE

It is well documented in the literature that L-lactide can be efficiently polymerized by $Sn(Oct)_2$ as catalyst. The advantages of $Sn(Oct)_2$ were described in Chapter 2. In this work, $Sn(Oct)_2$ was used in conjunction with diethylene glycol (DEG) as initiator and compared with SnOx under identical reaction conditions. From the results obtained, the effect of the catalyst structure has been observed in terms of the increases in % conversion and molecular weight of the polymer formed with time.

From Figures 5.1 and 5.2, both the % conversion and molecular weight increased more slowly with SnOx than with $Sn(Oct)_2$. Thus, the order of catalyst efficiency is clearly $Sn(Oct)_2$ > SnOx, even though they both have the same active Sn-O bond in their chemical structures. However, as mentioned in the previous chapter, the Sn-O bond in SnOx is contained within a 5-membered ring structure which possibly reduces its catalytic activity.

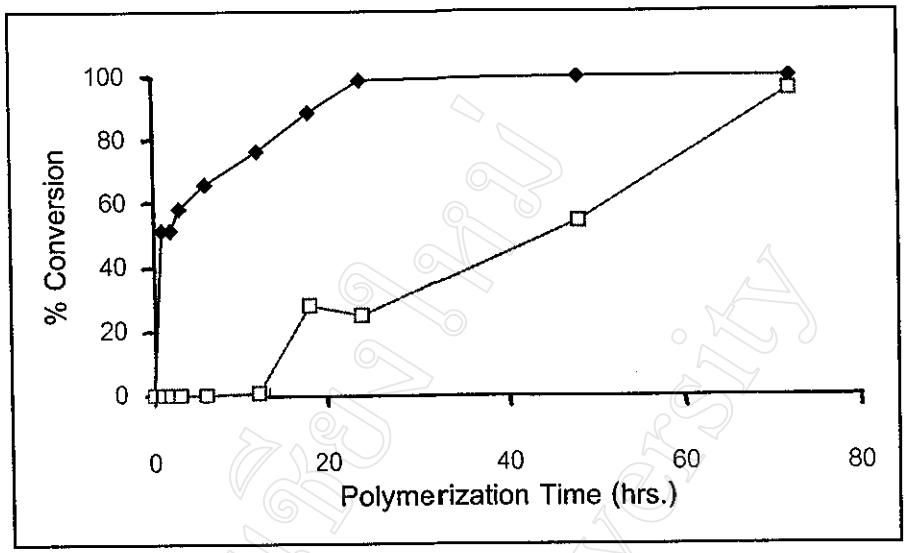


Figure 5.1 Comparison of the % conversion-time profiles (from gravimetry) using $Sn(Oct)_2$ and SnOx as catalysts at 140 °C.

♦ $Sn(Oct)_2$ □ SnOx

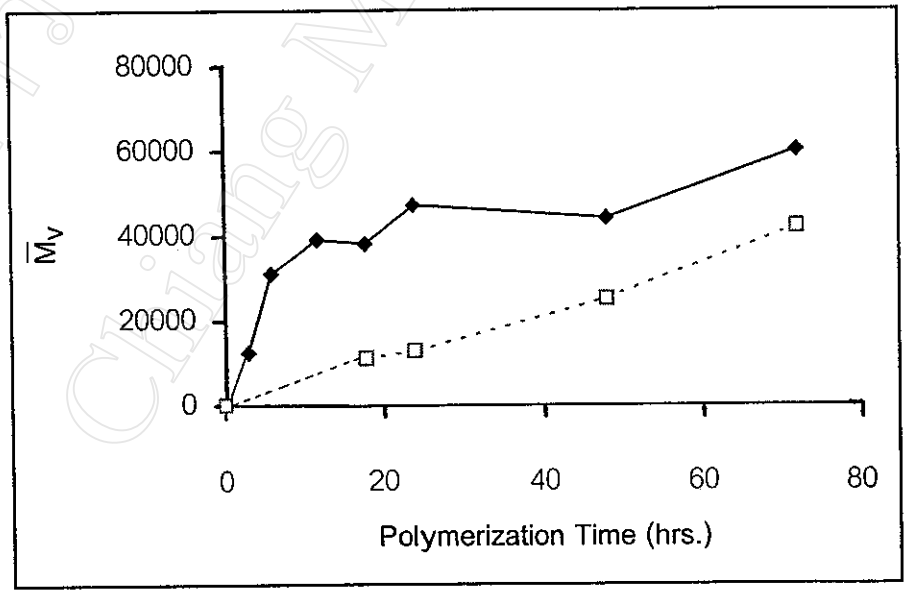
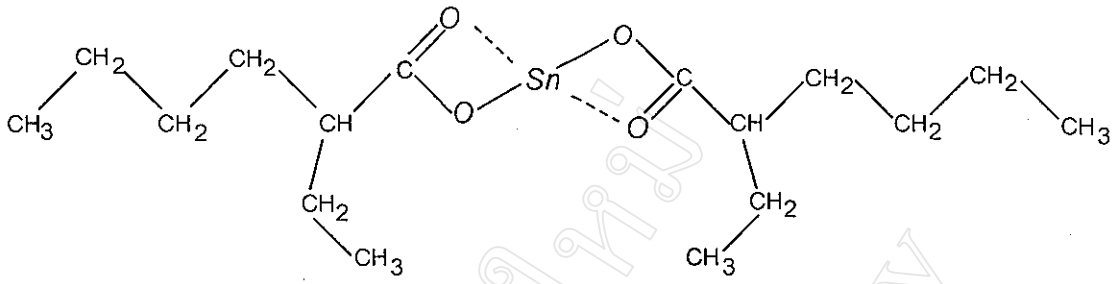
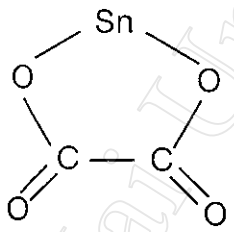


Figure 5.2 Comparison of the $\bar{M}_V$-time profiles (from dilute-solution viscometry) using $Sn(Oct)_2$ and SnOx as catalysts at 140 °C.

♦ $Sn(Oct)_2$ □ SnOx



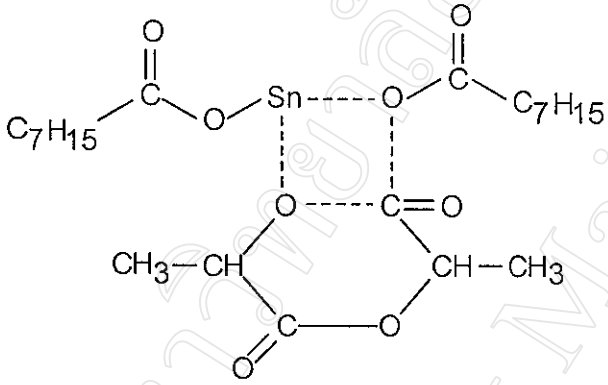
$Sn(Oct)_2$



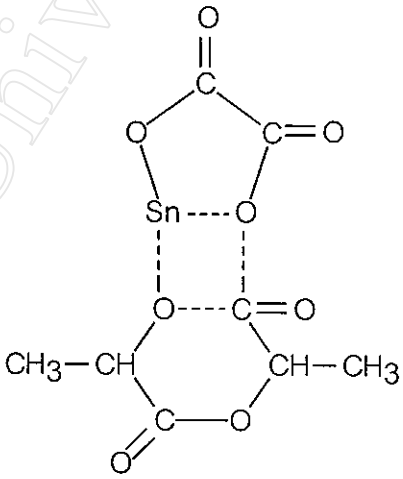
SnOx

In order to understand this effect more clearly, we must first consider the exact nature of the polymerization mechanism. It is generally accepted that the mechanism is of the so-called "coordination-insertion" type in which the Sn atom of the catalyst first coordinates through either a p-orbital or a d-orbital with the carbonyl oxygen atom of the L-lactide monomer. As a result of this coordination, the carbonyl carbon atom becomes more positive resulting in an increased susceptibility to nucleophilic attack by a hydroxyl group of the diethylene glycol initiator. This is then followed by ring-opening and monomer insertion into the O-H bond. This mechanism is shown in Scheme 5.1 for $Sn(Oct)_2$. The OH end-groups are retained so that propagation can continue. The reaction is, in effect, a type of "living" polymerization so long as the $Sn(Oct)_2$/SnOx catalyst and OH end-groups remain in the system.

Thus, the main conclusion to be drawn from the results of this work regarding the effect of catalyst structure is that the structural environment of the Sn-O bond affects its ability to coordinate with the monomer. This, in turn, affects the extent to which the catalyst can activate the monomer's acyl-oxygen C(=O)-O bond towards ring opening. In this respect, $Sn(Oct)_2$ is more effective than SnOx.



$Sn(Oct)_2$-L-lactide coordination



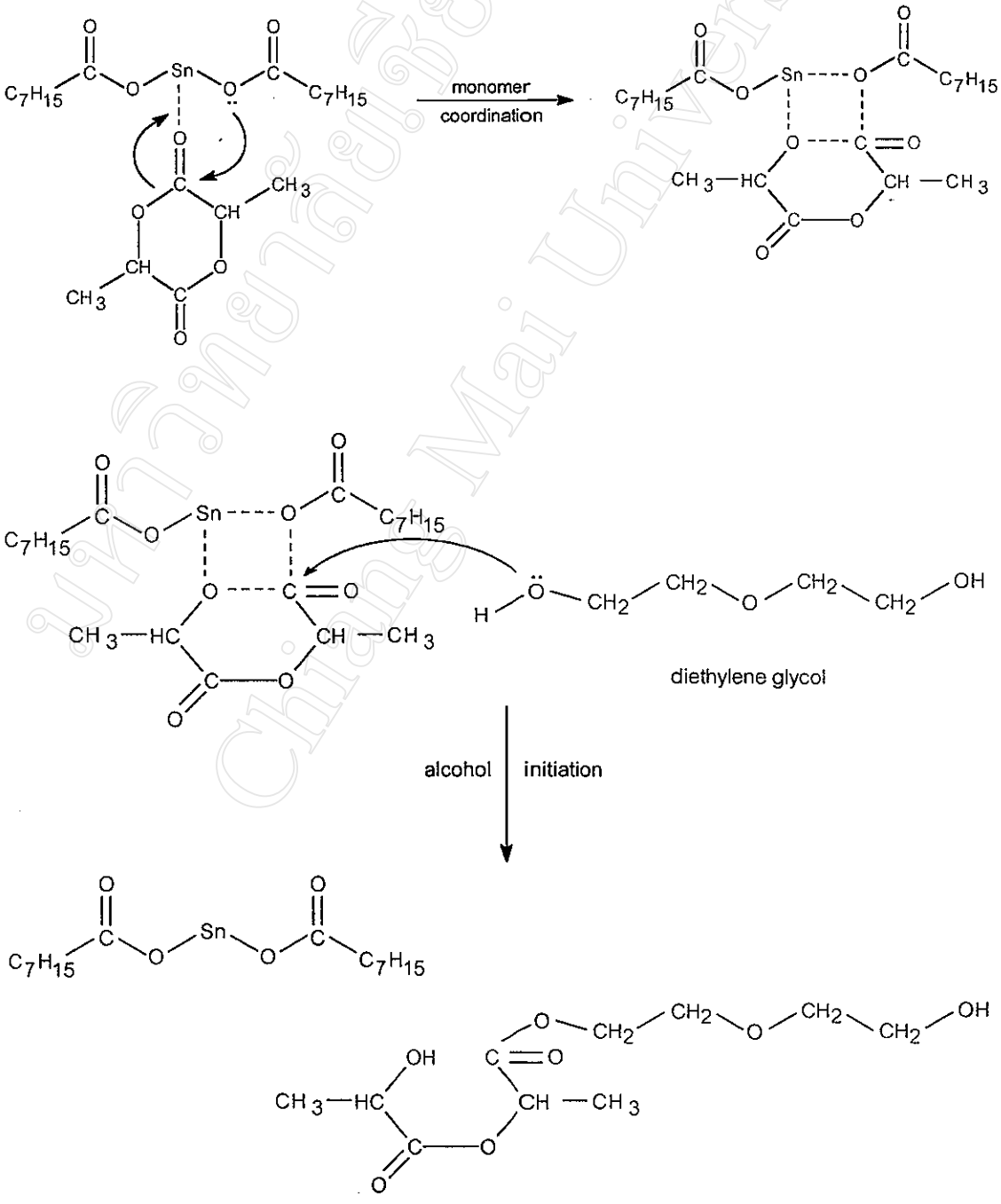
SnOx -L-lactide coordination

Another factor which needs to be taken into account is ***catalyst solubility*** in the monomer at the polymerization temperature. Although this project has not produced any specific data in this respect, it is quite likely that $Sn(Oct)_2$, being a liquid, is more easily soluble in L-lactide at 140 ^{o}C than SnOx which is a high melting point solid. This may also have been a contributing factor to the slower rate of reaction with SnOx.

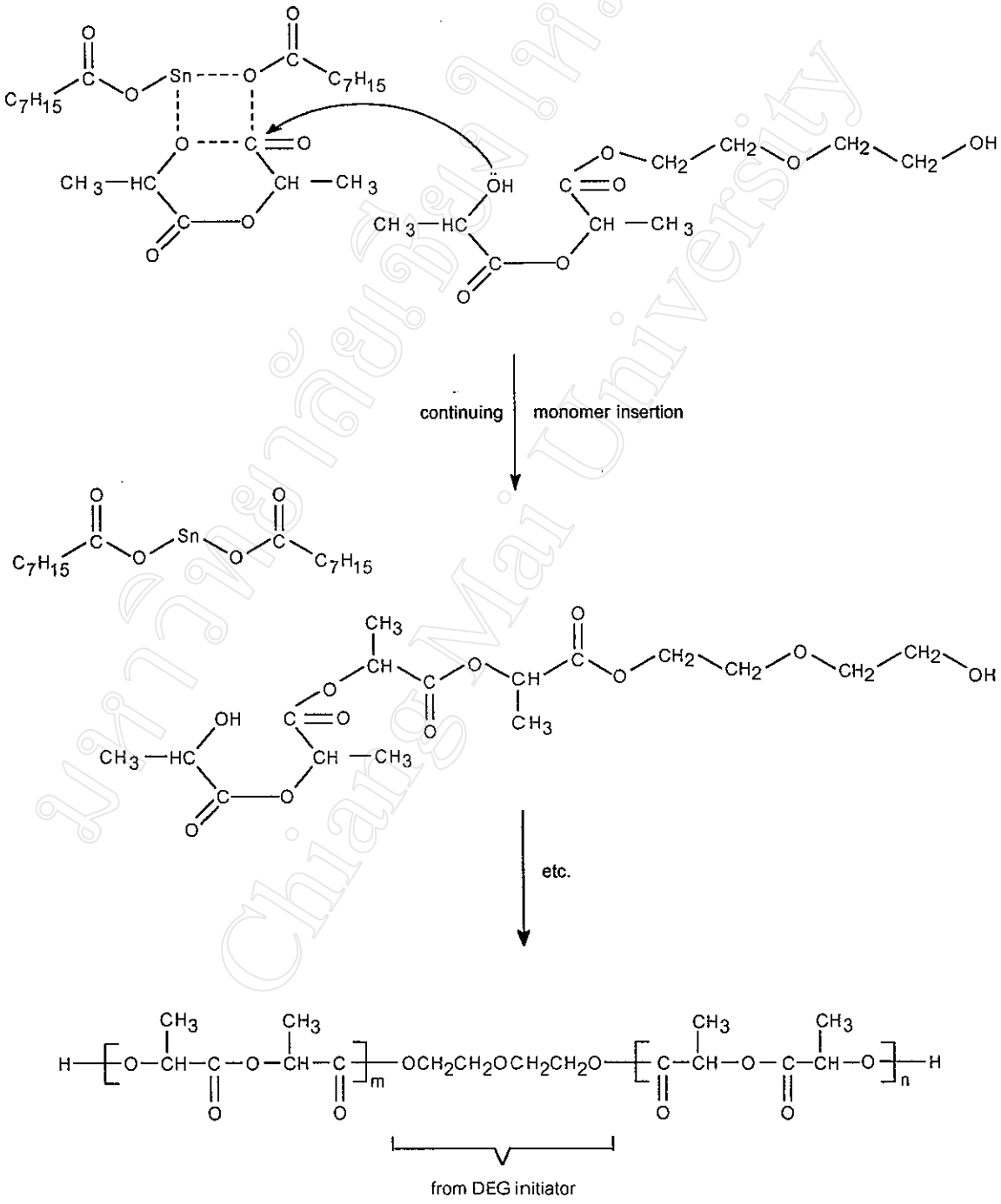
SCHEME 5.1

Proposed coordination-insertion mechanism for the ring-opening polymerization of L-lactide using stannous octoate as catalyst and diethylene glycol as initiator.

INITIATION



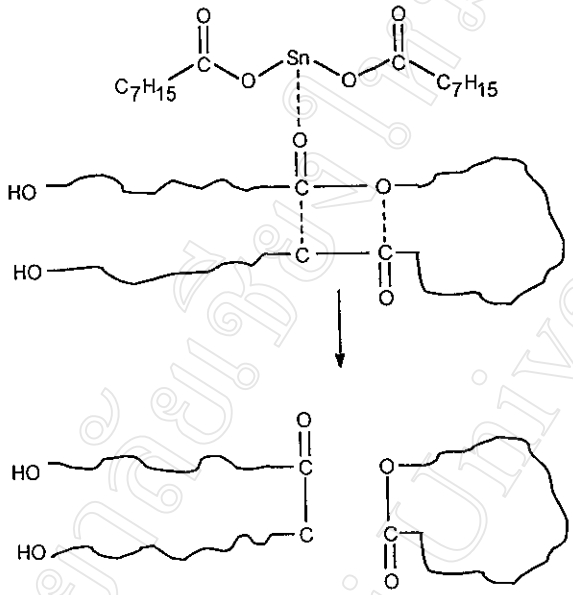
PROPAGATION



hydroxyl-terminated poly(L-lactide)

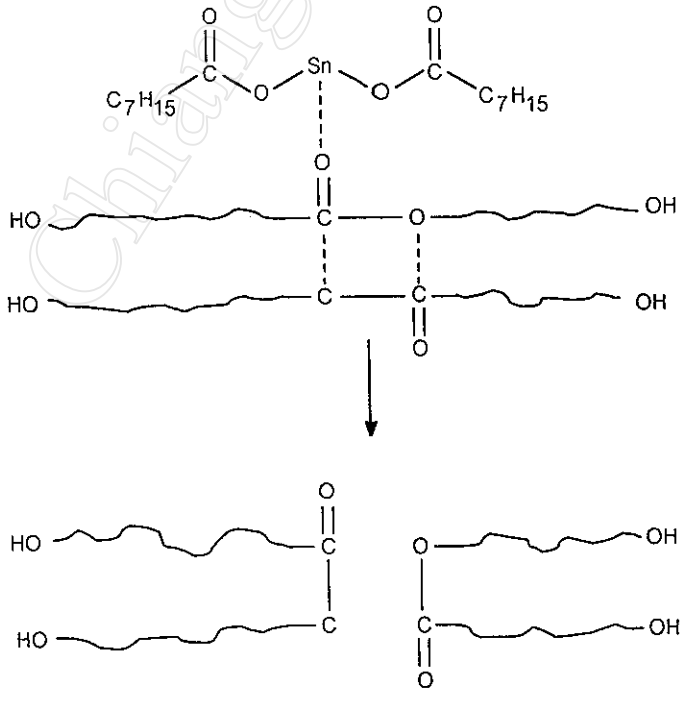
TERMINATION

(a) Intramolecular Transesterification

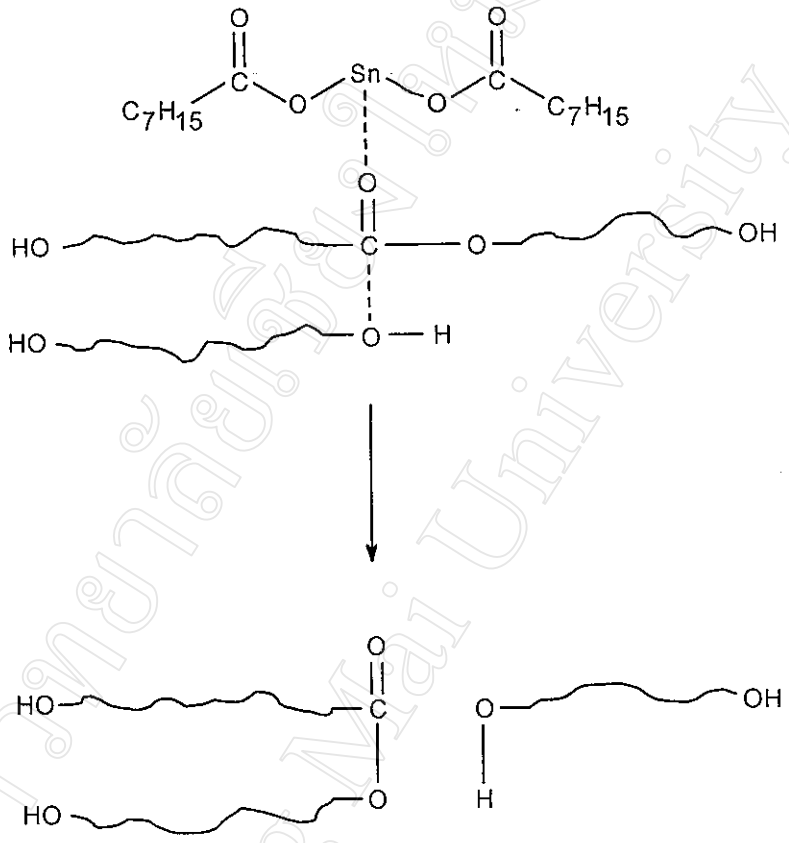


terminated polymer molecule

(b) Intermolecular Transesterification



(c) Hydrolysis / Alcoholysis by Moisture / Hydroxy-containing Compounds



5.2 EFFECT OF POLYMERIZATION TEMPERATURE

As expected, the effect of increasing the temperature is to increase the rate of polymerization. This is illustrated in the % conversion-time profiles in Figure 5.3 for the $Sn(Oct)_2$-catalysed reactions at the two temperatures of 140 °C and 180 °C. The corresponding $\overline{M}_V$-time profiles in Figure 5.4 also suggest a faster molecular weight

build-up at the higher temperature but the molecular weight then decreases with time due to what is believed to be thermal degradation via transesterification.

While these temperature/time effects are not new findings by any means, they do highlight the fact that each monomer-catalyst-initiator combination has its own unique set of temperature parameters which determine what the optimum polymerization temperature (or temperature profile) should be. These parameters include:

1. Monomer T_m – in the case that the monomer is a solid at room temperature, such as L-lactide, its T_m obviously determines the lower temperature limit for bulk polymerization in the melt.

2. Polymer T_m – if the polymer's T_m is higher than the polymerization temperature, the polymerizate will solidify after a certain molecular weight level has been attained whereupon the reaction rate will decrease considerably, as observed in this work.

3. Polymer T_g – in the event that the polymerizate does solidify during the course of the reaction, the polymerization temperature should be well above the polymer's T_g so that the highest possible % conversion can still be achieved in the solid state.

4. Monomer-polymer T_c – as the polymerization temperature approaches the ceiling temperature, T_c, the likelihood of depolymerization back to the cyclic monomer via intramolecular transesterification increases. However, in the case of L-lactide, depolymerization is preceded by other thermal degradation mechanisms.

5. Polymer T_d – depolymerization at the T_c may be preceded by the onset of other polymer thermal degradation mechanisms at T_d such as intermolecular transesterification.

6. Catalyst / initiator efficiency range – each catalyst / initiator combination will have its own temperature range over which it is most effective with a given monomer.

Therefore, a temperature profile should be devised which can optimize conversion and molecular weight while keeping degradation to a minimum. Depending on the monomer, this may involve extended reaction times if the reaction needs to be concluded in the solid state. This is especially relevant to high melting point polyesters, such as polyglycolide (PG) and poly(L-lactide) (PLL) which have T_m values of about 220 ^{o}C and 170 ^{o}C respectively and are known to be thermally unstable if maintained in the melt state for long periods. However, the choice of temperature is also inextricably linked to the choice of catalyst and initiator, while the extent to which moisture can be excluded from the system is also vitally important.

Hence, although the ring-opening polymerization of cyclic esters is a relatively facile reaction, the attainment of both high conversion and high molecular weight requires knowledge and understanding of the underlying factors which control the reaction combined with practical expertise. Although it has not been within the scope of this thesis to optimize the reaction conditions, useful information as to how this can be achieved has been obtained which will be of benefit to future work.

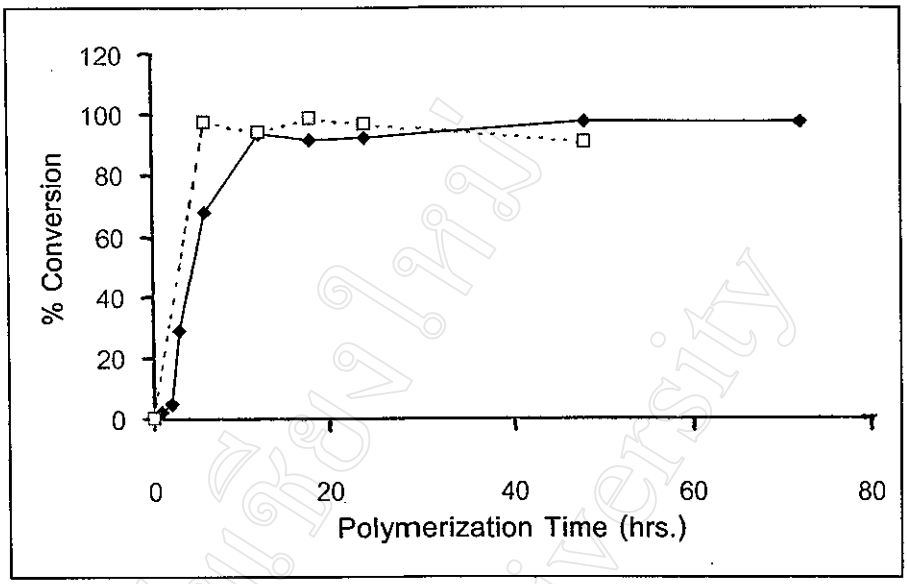


Figure 5.3 Comparison of the % conversion-time profiles using $Sn(Oct)_2$ as catalyst at 140 °C and 180 °C.

♦ 140 °C □ 180 °C

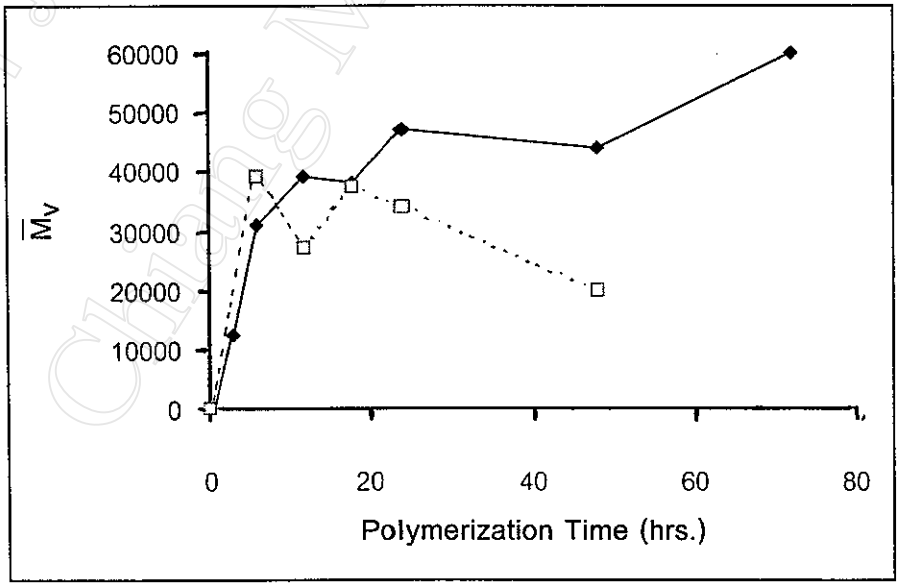


Figure 5.4 Comparison of the $\bar{M}_V$-time profiles using $Sn(Oct)_2$ as catalyst at 140 °C and 180 °C.

♦ 140 °C □ 180 °C

5.3 EFFECT OF OTHER REACTION CONDITIONS

In addition to temperature, time and reactant concentrations, other reaction conditions need to be chosen carefully if the kinetics of polymerization, % conversion and the molecular weight of the polymer formed are to be optimized. Amongst these other reaction conditions are:

1. Monomer Purity

The monomer must be rigorously purified before use. In the case of L-lactide, it should be purified by recrystallization with ethyl acetate about 2-3 times until its mole % purity (DSC) reaches at least 99.9 %. It should be stored in a vacuum desiccator and used as soon as possible after purification.

2. Catalyst and Initiator Purity

The catalysts, $Sn(Oct)_2$ and SnOx, and the initiator, DEG, may also contain impurities which can affect both the rate of polymerization and the molecular weight of the polymer obtained. For example, $Sn(Oct)_2$ typically contains octanoic acid and trace amounts of moisture which are very difficult to remove completely. Therefore, like the monomer, they too may need to be rigorously purified before use, either by vacuum distillation (liquids) or recrystallization (solids) in order to maximize polymer yield and molecular weight.

3. Practical Method

The practical method of polymerization used throughout this work was bulk polymerization (pure monomer + catalyst / initiator only), thus eliminating from consideration any complications from solvent / medium effects. The monomer and initiator were mixed together at room temperature in a controlled atmosphere glove box, under a dry N_2 atmosphere, to avoid contact with moisture before transferring to the heating bath at the reaction temperature.

5.4 EVALUATION OF KINETIC METHODS

The main objective of this project has been to study the reaction profile in the bulk polymerization of L-lactide. This kinetic study has involved selecting and comparing 3 different experimental methods, namely:

(1) gravimetry

(2) Fourier-transform infrared spectroscopy (FT-IR)

(3) proton nuclear magnetic resonance spectroscopy (^{1}H-NMR)

A fourth method, dilatometry, perhaps the most common method for studying polymerization kinetics, could not be used because it depends on the polymerization system remaining in the liquid state throughout. In the case of L-lactide, the system solidifies after a while so that the reaction has to be completed in the solid state.

Of the 3 methods studied, ***gravimetry*** is the most obvious and direct method since it involves physically separating the polymer formed and then weighing it to calculate the % conversion. In doing so, it also provides polymer samples for molecular weight determination. However, as mentioned in the previous chapter, gravimetry suffers from the disadvantage that the low molecular weight fraction in any given sample taken at any given time may not precipitate completely from solution during the separation process. This is especially true during the initial part of the reaction when the molecular weight is still low. Despite this, gravimetry is still widely used in kinetic studies.

The second method used, ***FT-IR***, was taken from a literature report [11] which was specifically about L-lactide polymerization. While it is not an absolute method in the same way that gravimetry is, it has the advantage that the data obtained (peak absorbance) is sensitive to the disappearance of monomer / appearance of polymer

right from the beginning of the reaction. Consequently, % conversions from FT-IR tended to be higher than from gravimetry, especially at the beginning of the reaction. However, FT-IR also has its uncertainties, for example: (1) uncertainties in constructing an accurate baseline to the spectrum, and (2) uncertainties in the correlation between peak absorbance ratio and % conversion. Nevertheless, this FT-IR method is an interesting alternative to gravimetry and should be studied further, especially if improvements in spectral resolution can be made.

The third and final method studied was *^{1}H-NMR*. Again, this method was taken from the literature [11] but, as it turned out, could not be applied in this work because the corresponding monomer/polymer peaks overlapped. Consequently, the % conversion could not be calculated as intended from the peak area intergration. Possibly, higher resolution combined with scale expansion may overcome this problem and so this is another method which should be studied further rather than be discarded.

In conclusion, these 3 methods combined have provided much useful information regarding the reaction profile, both in terms of polymer conversion and molecular weight build-up (from dilute-solution viscometry). While some questions still remain, the basic methodology for deciding upon what the various reaction conditions/parameters should be is now well understood. It is hoped that the results of this work will benefit future researchers working in this field.

SUGGESTIONS FOR FURTHER WORK

Continuing on from the work described in this thesis, the following suggestions for further work are made:

1. Polymer Purification/Gravimetry

Polymer purification by re-precipitation from solution has been carried out in this work in order to separate the polymer formed from the residual monomer. For this purpose, chloroform was used as the solvent and methanol as the non-solvent. However, it is possible that other solvent/non-solvent combinations could be more efficient than chloroform/methanol in precipitating the polymer from solution, especially the lowest molecular weight fractions. This would help to reduce the error in the % conversions obtained from gravimetry and provide more representative samples for molecular weight determination.

2. FT-IR

FT-IR has been shown to be a promising alternative to gravimetry but is heavily dependent on spectral quality. Higher peak resolution combined with scale expansion would improve the accuracy of the peak absorbance ratio calculations considerably. However, it should be remembered that this is not an absolute method, since it requires calibration, and so it would be better if it could be correlated more closely with improved gravimetry data.

3. ^{1}H-NMR

The ^{1}H-NMR results showed that the monomer and polymer peaks overlapped too closely for the peak area intergration to be used for calculating the % conversion. However, it was possible to observe the hydroxyl-terminated chain end units during the initial part of the reaction. This provides useful information about the way in which the reaction starts, including the existence, if any, of an "induction period".

4. Molecular Weight Determination

Dilute-solution viscometry was used in this work for polymer molecular weight determination. While it is a convenient and uncomplicated method, it is not particular reliable for low molecular weights ($\bar{M}_V < 10^4$). An alternative method which can be used over a wide range of molecular weight ($\bar{M}_V = 10^3 - 10^6$), such as gel permeation chromatography (GPC), would be better. GPC would also be able to provide useful information about the molecular weight distribution.

5. Catalyst / Initiator Concentrations

In this project, the catalyst ($Sn(Oct)_2$ or SnOx) and initiator (DEG) concentrations were kept constant at 0.02 and 0.04 mole % (relative to the monomer) respectively. These concentrations and their ratio should be varied in order to determine their effects on both the rate of reaction and the molecular weight of the final polymer product. This should also include "baseline" experiments using both the catalyst and the initiator alone for comparison.