

MODELLING AND OPTIMIZATION OF POLYMER SYSTEMS

Prasun Chatterjee

A Dissertation Submitted to
Indian Institute of Technology Hyderabad
In Partial Fulfillment of the Requirements for
The Degree of Master of Technology



भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemical Engineering

June, 2014

Declaration

I declare that this written submission represents my ideas in my own words, and where others' ideas or words have been included; I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

Prasun Chatterjee

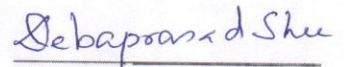
CH12M1009

Approval Sheet

This thesis entitled "Modeling and Optimization of Polymer Systems" by Mr. Prasun Chatterjee is approved for the degree of Master of Technology from Indian Institute of Technology Hyderabad.



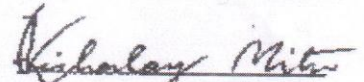
Dr. Chandra Shekhar Sharma; Asst. Professor
Examiner



Dr. Debaprasad Shee; Asst. Professor
Examiner



Dr. Saptarshi Majumdar; Asst. Professor
Co-Adviser



Dr. Kishalay Mitra; Asst. Professor
Adviser



Dr. Raja Banerjee; Asso. Professor
Chairman

Acknowledgements

It is a great pleasure for me to mention some of the key people in my life. Their support and encouragement helped me to cross any challenge during my M. Tech program at Indian Institute of Technology, Hyderabad.

First of all, I am very much grateful from core of my heart to my guide Dr. Kishalay Mitra. His constant support, trustworthy nature, care, and always uplifting any student remained very much inspiring for me. This project work was very challenging and very much innovative for chemical engineers. Due to his immense dedication and hard endeavor the project work was nicely completed. Once again, I am very much thankful to him for everything. I also would like to thank to my co-guide Dr. Saptarshi Majumdar for his countless support and inspiring words.

I am very much grateful to all the faculty members at Department of Chemical Engineering, IIT Hyderabad and my committee members: Dr. Chandra Sekhar Sharma, Dr. Debaprasad Shee, and Dr. Raja Banerjee.

At last, I want to dedicate all this work to the Supreme Personality of Lord Sri Krishna and Maa Saraswati for my spiritual guides.

Abstract

The modelling of linear Poly Lactic Acid (PLA) was carried out based on the study of the mechanism of Ring Opening Polymerization (ROP) of Poly Lactic Acid (PLA) on the basis of different sets of experimental data available in the literature. All possible mechanisms involving multiple steps such as initiation, propagation and chain transfer were considered and the model was build using these mechanisms. The approach was to formulate the model for the Multi Objective Optimization for Linear PLA. The formulation of the multi objective optimization problem for linear PLA was done with respect to two conflicting objective of maximizing conversion and minimizing time. The decision variables for this case were all the initial reactant concentrations for which the above mentioned objectives can be achieved. The model was run within the range of fixed ratios of catalyst to co catalyst concentrations to avoid going away from the experimental conditions using which the model has been built.

The Kinetic model for linear PLA was then extended to introduce branching by the addition of star polymers. The focus of the implementation is to develop a versatile and effective model that can simulate the actual procedure to prepare the long chain branched Poly Lactides. The approach of simultaneous scheme selection and parameter estimation has been proposed for selecting an appropriate scheme for a reaction mechanism which can describe the polymerization system. A part of the overall scheme in case of Polypropylene could be simulated, where significant success was found in terms of kinetic effects on molecular weights and PDI.

Nomenclature

B = Characteristic constant of PLA ring-chain equilibrium

C = Catalyst, $\text{Sn}(\text{Oct})_2$

$[C]$ = Concentration of catalyst

$[C_0]$ = Initial concentration of catalyst

OH = Dormant chains, OH-bearing species

$[\text{OH}]$ = Concentration of cocatalyst, 1-dodecanol

$[\text{OH}_0]$ = Initial concentration of cocatalyst, 1-dodecanol

E_a = Activation energy of reversible propagation

$[\text{IM}]$ = Concentration of OH-bearing impurities

k_{a1}, k_{a2} = Reversible catalyst activation rate coefficient

k_d = Depropagation rate coefficient

$K_{\text{eq},a}$ = Reversible catalyst activation equilibrium constant

$K_{\text{eq},c}$ = Equilibrium constant of PLA ring-chain equilibrium

k_p = Propagation rate coefficient

k_s = Reversible chain transfer rate coefficient

k_{te} = Intermolecular transesterification rate coefficient

M = Monomer

$[M]$ = Instantaneous monomer concentration

$[M_0]$ = Initial monomer concentration

$[M_{\text{eq}}]$ = Equilibrium monomer concentration

M_n = Number average molecular weight

M_w = Weight average molecular weight

MWD = Molecular weight distribution

N_c = Overall concentration of polymer chains

P_d = Dispersity

PLA = Poly(lactic acid)

P_n = Polymer chain with chain length n

R^* = Active chains

$[R^*]$ = Concentration of active chains

R_0 = Activated catalyst, tin alkoxide

R_n = Active chains with n repeating units

ROP = Ring-opening polymerization

t = Time

T = Temperature

X = Conversion

λ_i = i^{th} moments of active chains ($i = 0, 1, 2, 3$)

μ_i = i^{th} moments of dormant chains ($i = 0, 1, 2, 3$)

γ_i = i^{th} moments of dead chains ($i = 0, 1, 2, 3$)

Figures

Figure 2.1	Kinetic Scheme of Monomer Activation Mechanism	[7]
Figure 2.2	Schematic of Transesterfication Reaction	[8]
Figure 2.3	Kinetic Scheme of PLA	[9]
Figure 2.4	Species Balance equation for PLA	[10]
Figure 2.5	Differential order moment equations for PLA	[11]
Figure 2.6	Structure of Prepolymers	[12]
Figure 2.7	Kinetic Scheme of LCB Poly lactides	[13]
Figure 3.1	Schematic of Simultaneous Scheme Selection and Parameter Estimation	[16]
Figure 3.2	The Overall Scheme followed	[17]
Figure 4.1	Conversion Vs Time for PLA polymerization	[19]
Figure 4.2	Mw Vs Conversion for PLA polymerization	[19]
Figure 4.3	PDI Vs Conversion for PLA polymerization	[20]
Figure 4.4	Conversion Vs Time for PLA polymerization	[20]
Figure 4.5	Mw Vs Conversion for PLA polymerization	[21]
Figure 4.6	PDI Vs Conversion for PLA polymerization	[21]
Figure 4.7	Effect of Temperature on Mw	[22]
Figure 4.8	Effect of Temperature on Conversion	[23]
Figure 4.9	Effect of Temperature on Mn	[24]
Figure 4.10	Comparison of Mn values	[25]
Figure 4.11	The Modified Kinetic Scheme	[26]
Figure 4.12	Effect of K_{al} on Mw	[28]
Figure 4.13	Effect of $4 K_{LCB}$ on Mw	[28]
Figure 4.14	Effect of K_{d2} on Mw	[29]
Figure 4.15	Effect of K_{p2} on Mw	[30]

Tables

Table 4.1 Comparison of Experimental and Simulated Values
for Linear LCB Polylactides [24]

Table 4.2 Values of Kinetic Rate Constants [26]

Table 4.3 Comparison of Experimental and Model Values [27]

Contents

Declaration.....	ii
Approval Sheet.....	iii
Acknowledgement.....	iv
Abstract.....	v
Nomenclature.....	vi
Figures.....	viii
Tables.....	ix
Contents.....	x
[1] Introduction.....	1
1.1 Motivation.....	1
1.2 Literature Survey.....	1
1.3 Present Work.....	4
[2] Poly Lactic Acid (PLA) Modelling.....	4
2.1 PLA preparation.....	6
2.2 Model Formulation.....	6
2.3 Model Modification for Branching.....	11
[3] Simultaneous Scheme Selection.....	14

3.1 Model Description.....	14
3.2 Overall Reaction Scheme.....	16
[4] Results and Discussion	18
4.1 PLA Modelling.....	18
4.2 Simultaneous Scheme Selection.....	25
[5] Conclusion.....	31
5.1 Poly Lactic Acid.....	31
5.2 Polypropylene.....	32
References.....	33

Chapter 1

Introduction

1.1 Motivation

Branched polymers exhibit enhanced polymer processing properties as compared to their linear counterparts of similar molecular weight and this fact provides the former considerable edge over the latter for many practical applications. So a noteworthy amount of research has been going on in this direction while crossing the odds at the time of producing the cross linked equivalent of linear polymers. To honor the environmental issues, a number of experimental and theoretical studies are being conducted for various possible biodegradable routes of polymers at the same time. The effort is to replace some of the popular and useful polymers partially, if not completely, by biodegradable or biocompatible polymers of complementary properties. It would be ideal if one of such environmentally safe / clean polymers can show various enhanced properties in branched form or linear form. Poly Lactic Acid (PLA) is one of these polymers which meet several issues mentioned above.

1.2 Literature Survey

The most common route to PLA is the ring-opening polymerization of lactide with various metal catalysts (typically tin octoate) in solution, in the melt, or as a suspension. The metal-catalyzed

reaction tends to cause racemization of the PLA, reducing its stereo-regularity compared to the starting material. Polymerization of a racemic mixture of L and D lactides usually leads to the synthesis of poly-DL-lactide (PDLA) [1], which is amorphous in nature. Use of stereospecific catalysts can lead to heterotactic PLA, which has been found to show crystallinity. The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D to L enantiomers used, and to a lesser extent on the type of catalyst used. Due to the chiral nature of lactic acid, several distinct forms of polylactide exist: poly-L-lactide (PLLA) is the product resulting from polymerization of L, L-lactide (also known as L-lactide) [2]. PLLA has a crystallinity of around 37%, a glass transition temperature between 60-65°C, a melting temperature between 173-178°C and a tensile modulus between 2.7-16 GPa. Heat resistant PLA can withstand temperatures of 110°C. PLA is soluble in chlorinated solvents, hot benzene, tetrahydrofuran and dioxane. PLA has similar mechanical properties to PETE (Polyethylene Terephthalate) polymer, but has a significantly lower maximum continuous use temperature [3].

The synthesis of PLA by ring-opening polymerization (ROP) was first reported by Carothers et al. [4]. Low-molecular-weight polymer was produced, and the synthesis of high-molecular-weight materials was not possible until the development of effective lactide purification techniques in 1955. During the last half century, many different catalysts have been studied to increase the reaction productivity. They have been recently reviewed by Upadhyay et al. [5]. Among them, 2-ethylhexanoic acid tin(II) salt ($\text{Sn}(\text{Oct})_2$) is the most widely used in both scientific research and industrial production and is the only catalyst that has been accepted by the U.S. Food and Drug Administration. The first systematic kinetic analysis of ROP for PLA synthesis catalyzed by $\text{Sn}(\text{Oct})_2$ was reported by Eenink [6]. After his work, the influence of different process parameters on the polymer characteristics was elucidated and the corresponding “apparent” propagation rate coefficient, k_{eff} (defined as the pseudo-first-order propagation rate coefficient with respect to monomer, $k_{\text{eff}} = k_p \times R^*$, where R^* is the concentration of active chains and k_p is the propagation rate coefficient) was evaluated. However, the role of “natural” or environmental impurities, such as moisture and acidic species, on reaction behavior was not considered at all. In contrast, Zhang et al [7] found that hydroxyl and carboxylic acids strongly affect the reaction rate. Later on, Witzke et al. [8] reported a more comprehensive kinetic scheme of ROP of lactide in bulk. They introduced a “semi-living” behavior, meaning that

transesterification reactions are active along with reversible propagation. The values of the Arrhenius parameters for both reactions, propagation and transesterification, were reported. More recently, Puaux et al. [9] and Mehta et al. [10, 11] developed models based on the cationic mechanism; accordingly, the kinetic scheme involved irreversible initiation, irreversible propagation, and irreversible chain transfer to monomer and impurities.

The mechanism of ROP of L, L-lactide catalyzed by $\text{Sn}(\text{Oct})_2$ has been investigated by many researchers, and different chain initiation mechanisms have been proposed, such as alkoxide initiation, monomer activation, and cationic initiation [12]. The most widely accepted one is the alkoxide mechanism, where stannous octoate reacts with OH-bearing species to form an alkoxide, which is the species initiating the polymerization. On the basis of such an initiation step, the same authors proposed a comprehensive kinetic scheme of the polymerization, involving reversible chain transfer and polymer interchange reactions, so-called “transesterifications” also. In previous modeling study at low temperature (i.e., 130°C) by Morbidelli et al. [4,12], it was shown that such reactions are in fact present and are responsible for the fast interchange of active end groups among the polymer chains and affect directly the molecular weight distribution (MWD) of the final polymer. The corresponding experimental data have been described quantitatively with a suitable kinetic model which included catalyst activation, propagation, reversible deactivation, and intermolecular transesterification [13]. On the other hand, the industrial production of PLA is usually run at higher temperatures (at least 180°C) to achieve faster reaction rates and avoid polymer crystallization and too high viscosity. Under such conditions, the role of other degradation reactions becomes important and, in some cases, dominant. With reference to ROP of L, L-lactide at high temperature, polymer degradation is a severe problem causing low molecular weight values. At temperatures as high as 400°C , McNeill and Leiper [14] proposed a comprehensive kinetic scheme for PLA pyrolytic elimination based on thermal volatile analysis (TVA) studies. Odian and Kopinke et al. [15,16] reduced the thermal pyrolysis kinetic scheme of PLA to five lumped reactions and concluded that polymer degradation follows two main mechanisms, radical and non-radical.

At lower temperatures ($180 - 230^\circ\text{C}$, i.e., close to the temperature values of interest in this study), Wachsen et al [17] proposed two possible degradation reactions: intramolecular transesterifications (back-biting) and non-radical random chain scission, which produce

macrocycles and acrylate-ended PLA, respectively. However, since the reactions producing the acrylate ended PLA chains require higher temperature values, one would expect that intramolecular transesterifications are the main mechanisms responsible for molecular weight decreasing with conversion in these conditions.

1.3 Present Work

In this study, modelling of linear PLA was carried out based on the study of the mechanism of ROP of Poly Lactic Acid (PLA) on the basis of different sets of experimental data available in the literature. All possible mechanisms involving multiple steps such as initiation, propagation and chain transfer were available and the model was build using these mechanisms. The aim was to fill the gap between experimental and the modelling efforts that are still present. The model developed was validated with the available experimental data in the literature. It is important to note that experimental values were available at specific ratios with which the correction of the model is tested.

The next approach was to formulate the model for the Multi Objective Optimization for Linear PLA. The formulation of the multi objective optimization problem for linear PLA was done with respect to two conflicting objective of maximizing conversion and minimizing time. The decision variables for this case were all the initial reactant concentrations for which the above mentioned objectives can be achieved. The model was run within the range of fixed ratios of catalyst to co catalyst concentrations to avoid going away from the experimental conditions using which the model has been built.

An attempt has been made to develop variable temperature model as it links the working range of the model. Analysis of various temperature affecting parameters like kinetic constants and activation energy were evaluated based on parameter estimation obeying Arrhenius law. Also the effects of temperature on reaction phenomenon were observed.

The Kinetic model for linear PLA was then extended to introduce branching by the addition of star polymers. The focus of the implementation is to develop a versatile and effective model that can simulate the actual procedure to prepare the long chain branched Poly Lactides [4]. The

approach is actually a technique of ROP of L-lactides where the LA monomer to initiator ratios were varied producing a series of pre polymers with different degrees of polymerization [12].

Next the approach of simultaneous scheme selection and parameter estimation has been proposed for selecting an appropriate scheme for a reaction mechanism which can describe the polymerization system. In this case, the optimizer is provided with all the possible combinations of different kinetic schemes, including reversible and irreversible reactions, available for a particular mechanism [4]. The job of the optimizer is to select intelligently the correct scheme out of finitely many possible schemes that describes the system in the best possible manner. It is assumed here if a mechanism can describe a set of data generated by a system well, it can describe the system. So, the error between the model predicted values, coming out of a scheme selected by the optimizer, and the experimental data becomes the objective function to drive the optimizer towards achieving the goal. For each of these schemes, the optimizer also provides us with the kinetic parameters used in the selected scheme. This scheme had hard time being integrated in the MATLAB framework and was not found working properly in case of branched PLA system for various reasons, lack of availability of experimental data being one of them. Hence, another more versatile system of Polypropylene has been approached for this purpose. The work in this direction is still being continued. A part of the overall scheme in case of Polypropylene could be simulated, where significant success was found in terms of kinetic effects on molecular weights and PDI.

Chapter 2

Poly Lactic Acid (PLA) Modelling

2.1 Poly Lactic Acid Preparation

L,L-Lactide (LA) was first dried overnight at 30°C under vacuum after recrystallization in toluene. It was melted at temperature < 100°C in a stirred flask in glove box; Sn(Oct)₂ and ROH were prepared next in glove box at a given molar ratio with respect to monomer in toluene (10 weight %). Anhydrous toluene was used to facilitate the transfer of catalyst and cocatalyst to the reaction vessels without contaminations. Namely, such mixtures were transferred to glass vials and sealed with T-type poly (tetrafluoroethylene) caps to prevent the loss of LA during the reaction by vaporization and recrystallization. All vials were finally transferred into a controlled heating block set at temperature of 130°C. PLA products in the different reaction vials were finally quenched in an ice bath at different times and kept for further characterizations. Reactions at constant amount of catalyst and different ratios catalyst / cocatalyst have been carried out in addition to the reactions at different catalyst amounts and constant ratio catalyst / cocatalyst.

2.2 Model Formulation

The approach of modelling presented in literature was based on the two most popular mechanisms available:

- Monomer Activation Mechanism
- Alkoxide Initiation Mechanism

In case of Monomer Activation Mechanism, the monomer, OH bearing species and catalyst forms a ternary complex all together. Accordingly, Sn atoms are not directly bonded to the active chains. This led the corresponding polymerization rate to follow first order kinetics with respect to the initial amount of catalyst and alcohol present [18]. The kinetic scheme is shown in the figure below:

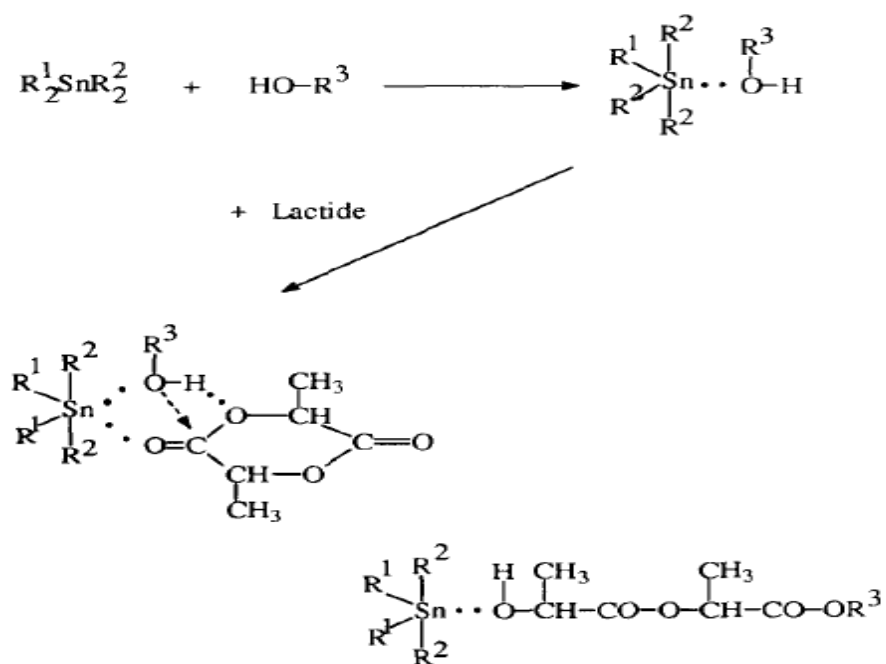


Figure 2.1: Kinetic scheme for Monomer Activation Mechanism

In the case of Alkoxide Initiation Mechanism [19], it involves reversible chain transfer and polymer interchange reactions called Trans-esterification reactions which are responsible for the fast interchange of active end groups among the polymer chains. The resulting polymerization mechanism is the most widely accepted and it has been used here for the model development.

Transesterification is the process of exchanging the organic group R'' of an ester with the organic group R' of an alcohol. These reactions are often catalysed by the addition of an acid or base

catalyst. The reaction can also be accomplished with the help of enzymes (biocatalysts) particularly lipases.

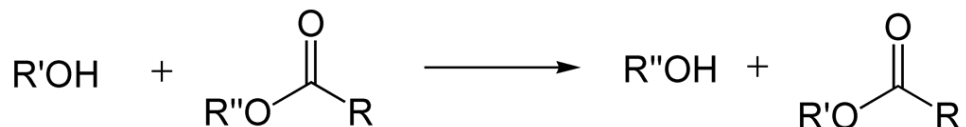


Figure 2.2: Schematic of Transesterification Reaction

In the transesterification mechanism, the carbonyl carbon of the starting ester (RCOOR^1) undergoes nucleophilic attack by the incoming alkoxide (R^2O^-) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the transesterified product (RCOOR^2). The various species exist in equilibrium, and the product distribution depends on the relative energies of the reactant and product.

Three types of reversible reactions can be identified: activations, propagations, and reversible deactivations. Reaction “a” is catalyst activation by alcohol, forming the truly active species - SnOR and octanoic acid, indicated by I and A, respectively. Note that each molecule of catalyst produces two active groups. So, the concentration of C should be twice the experimental concentration of the catalyst, $\text{Sn}(\text{Oct})_2$. Even though reaction “a” involves ROH, all OH-bearing species are able to reversibly activate the catalyst to form the active alkoxide groups. Accordingly, reaction “b” is also introduced. This is the reaction between the catalyst and a dormant chain D, the species indicated as $\text{HO}-(\text{LA})_n\text{-H}$ in the general scheme. Because of the similarity between the two reactions, the same rate coefficients are used just to keep the number of parameters in the final model as small as possible. Finally, it should be mentioned that according to the literature, the activation rate should be slower than deactivation; therefore, the value of the corresponding equilibrium constant, $K_{\text{eq,a}} = k_{\text{a1}} / k_{\text{a2}}$, is expected to be smaller than one.

Third and fourth reactions, “c” and “d”, are the reversible propagation steps, those affecting the length of the active (or living) chains, R_n . The values of the corresponding rate coefficients are assumed to be independent of the chain length and applicable to both reactions. The corresponding equilibrium coefficient, $K_{\text{eq,p}} = k_p / k_d$, where k_d is the de-propagation rate

coefficient, is readily estimated, given the maximum achievable conversion. The last two reactions, “e” and “f”, are actually reversible chain transfer reactions. The reaction between an active chain and a molecule of alcohol results in a dormant chain with the same length and a new alkoxide group, which starts growing by the propagation reaction “c”. Because this transfer reaction is reversible, it is not affecting the system reactivity (the number of active chains remains the same) but strongly affects the molecular weight, that is, the total number of chains, N_c . Reaction “f” is a completely equivalent transfer involving a dormant chain as the OH bearing species; such reaction is not given in the original kinetic scheme [4, 21] because it does not affect the concentration of both active and dormant species. However, this reaction is accounted for in the model reported below to predict the evolution of the molecular weight reliably. Once more, the same rate coefficients are considered for both reactions “e” and “f” because of the complete equivalence of the reaction in both directions. In case of “f”, the same values are, therefore, expected for both forward and backward reactions, which means the corresponding equilibrium constant $K_{eq,s} = 1$.

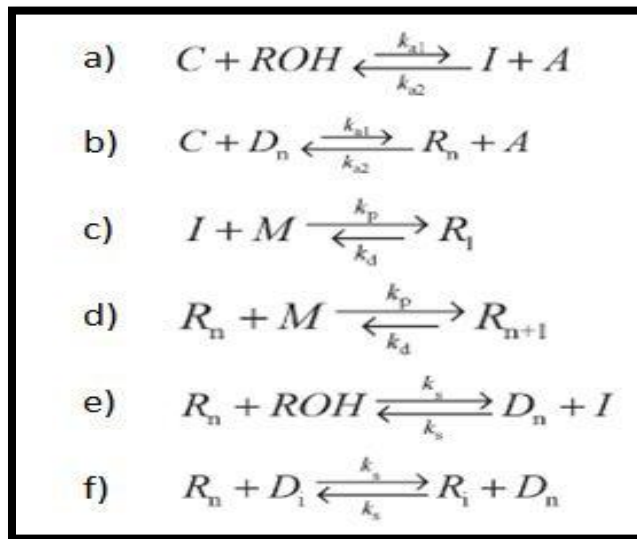


Figure 2.3: Kinetic Scheme for PLA

With reference to the simplified kinetic scheme in Figure 2.3, it is now useful to write down the corresponding set of material and population balance equations with reference to a well-stirred, homogeneous batch reactor (as given in Figure 2.4).

$$\begin{aligned}\frac{dC}{dt} &= -k_{a1}CROH + k_{a2}IA - k_{a1}C \sum_{n=1}^{\infty} D_n + k_{a2} \sum_{n=1}^{\infty} R_n A \\ \frac{dA}{dt} &= k_{a1}CROH - k_{a2}IA + k_{a1}C \sum_{n=1}^{\infty} D_n - k_{a2} \sum_{n=1}^{\infty} R_n A \\ \frac{dROH}{dt} &= -k_{a1}CROH + k_{a2}IA - k_s ROH \sum_{n=1}^{\infty} R_n + k_s I \sum_{n=1}^{\infty} D_n \\ \frac{dI}{dt} &= -k_p MI + k_d R_1 + k_{a1}CROH - k_{a2}IA + k_s ROH \sum_{n=1}^{\infty} R_n - k_s \sum_{n=1}^{\infty} D_n I \\ \frac{dM}{dt} &= -k_p MI - k_p M \sum_{n=1}^{\infty} R_n + k_d \sum_{n=1}^{\infty} R_n + k_s ROH \sum_{n=1}^{\infty} R_n - k_s \sum_{n=1}^{\infty} D_n I\end{aligned}$$

Figure 2.4: Species Balance Equations for PLA

The monomer equilibrium concentration (M_{eq}), defined as k_d / k_p and equal to the reciprocal of the more conventional equilibrium constant of the reaction, was found in the literature at 130°C. Such a value is consistent with a value of equilibrium conversion of 98.7%. Actually, the average value of the equilibrium conversion estimated by us from the experiments was slightly smaller and equals to 96.5%, corresponding to a M_{eq} value of 0.106 mol L⁻¹. The reason for such discrepancy is probably due to the limited accuracy of our experimental evaluation of the residual monomer amount by size exclusion chromatography (SEC). Because of the minor relevance of such peak, its area was arbitrarily attributed to the monomer, and thus the corresponding residual monomer amount was overestimated. Therefore, the M_{eq} value from the literature should be more reliable, and it has been used in all model simulations.

Side reactions, often mentioned as affecting the molecular weight of polyesters, are the molecular interchanges, known as transesterification reactions. Different interchange reactions

are possible, such as inter and intra-transesterification. However, it has been reported that inter-transesterification is the dominant mechanism in the bulk catalyzed ROP of lactide at 130°C. Finally, it should be noticed that such reactions are not affecting the number of both active and dormant chains in the system, but only the chain length of different chains produced by ROP reaction. Such reactions have been introduced in the kinetic scheme and the species balance equations are accordingly modified. The resulting species balance equations have been solved by the method of moments and the zeroth, first and second order moment equations for the live and the dead polymers have been derived. These equations are highly nonlinear ODEs, which are solved in MATLAB using the ODE toolbox.

Some of the moment equations contributing to the activation, propagation and reversible deactivation are as follows:

$$\frac{d\lambda_0}{dt} = k_{a1}\mu_0 C - k_{a2}\lambda_0 A + k_p MI - k_s \lambda_0 ROH + k_s \mu_0 I$$

$$\frac{d\lambda_1}{dt} = k_{a1}\mu_1 C - k_{a2}\lambda_1 A + k_p MI + k_p M\lambda_0 - k_d \lambda_0 - k_s \lambda_1 ROH + k_s \mu_1 I - k_s \lambda_1 \mu_0 + k_s \mu_1 \lambda_0$$

$$\frac{d\lambda_2}{dt} = k_{a1}\mu_2 C - k_{a2}\lambda_2 A + k_p MI + k_p M(2\lambda_1 + \lambda_0 + k_d(\lambda_0 - 2\lambda_1)) - k_s \lambda_2 ROH + k_s \mu_2 I - k_s \lambda_2 \mu_0 + k_s \mu_2 \lambda_0$$

$$\frac{d\mu_0}{dt} = -k_{a1}\mu_0 C + k_{a2}\lambda_0 A + k_s \lambda_0 ROH - k_s \mu_0 I$$

$$\frac{d\mu_1}{dt} = -k_{a1}\mu_1 C + k_{a2}\lambda_1 A + k_s \lambda_1 ROH - k_s \mu_1 I + k_s \lambda_1 \mu_0 - k_s \mu_1 \lambda_0$$

$$\frac{d\mu_2}{dt} = -k_{a1}\mu_2 C + k_{a2}\lambda_2 A + k_s \lambda_2 ROH - k_s \mu_2 I + k_s \lambda_2 \mu_0 - k_s \mu_2 \lambda_0$$

Figure 2.5: Different order moment equations for PLA

2.3 Model Modification for Branching

The linear PLA model has been extended to introduce branching by the addition of star polymers. The focus of the implementation is to develop a versatile and effective model that can

simulate the actual procedure to prepare the long chain branched Poly Lactides. [20] The approach is actually a technique of ring-opening polymerization (ROP) of L-lactides where the LA monomer to initiator ratios were varied producing a series of pre polymers with different degrees of polymerization [20, 22].

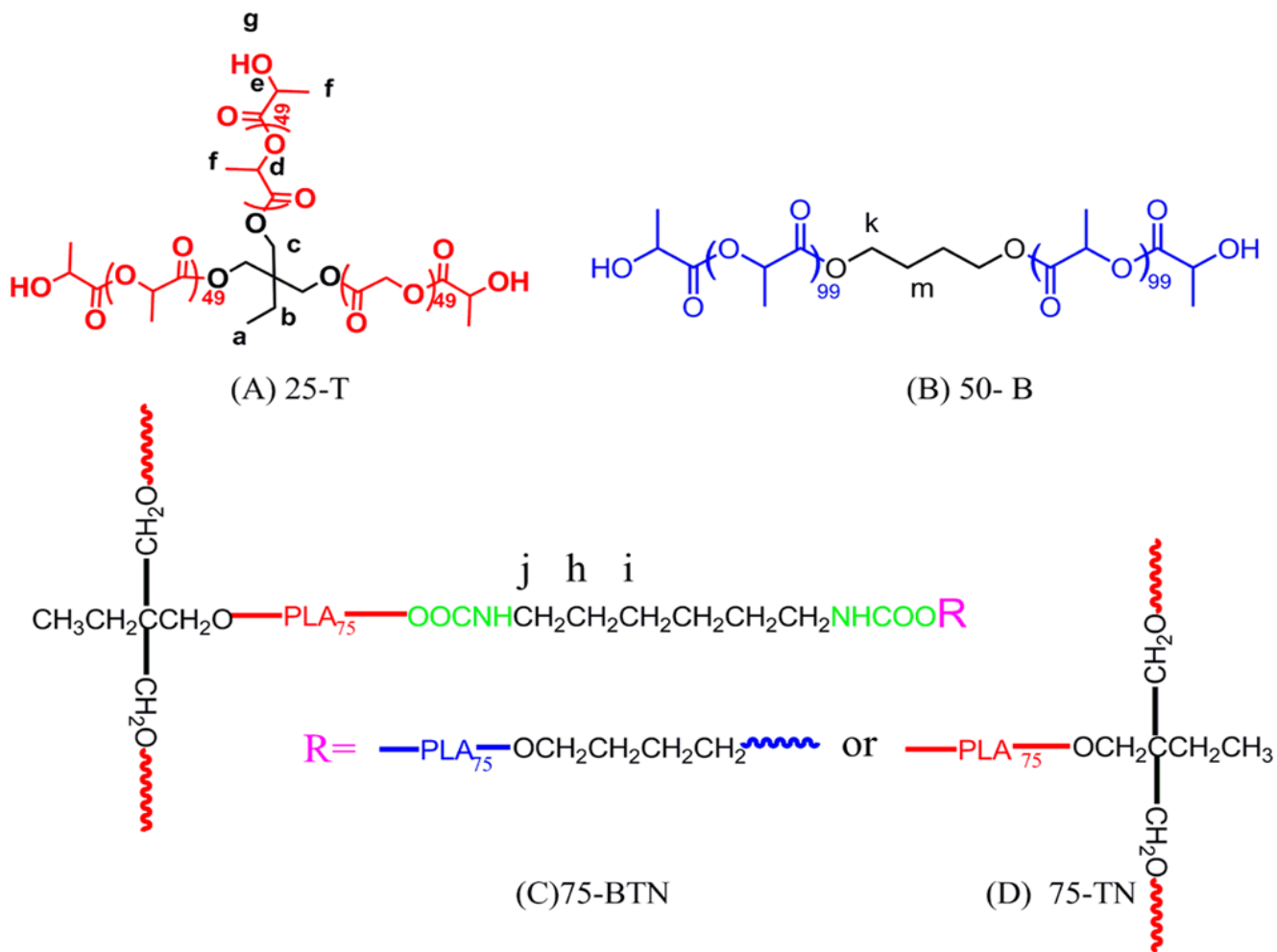


Figure 2.6: Structure of Pre polymers

The long chain branched Poly lactides were prepared by end-coupling of the terminal hydroxyl groups in PLA Pre-polymers with the NCO groups in HDI.

The Kinetic Scheme for Long-Chain Branched Poly lactides (LCB-PLAs) is represented as follows:

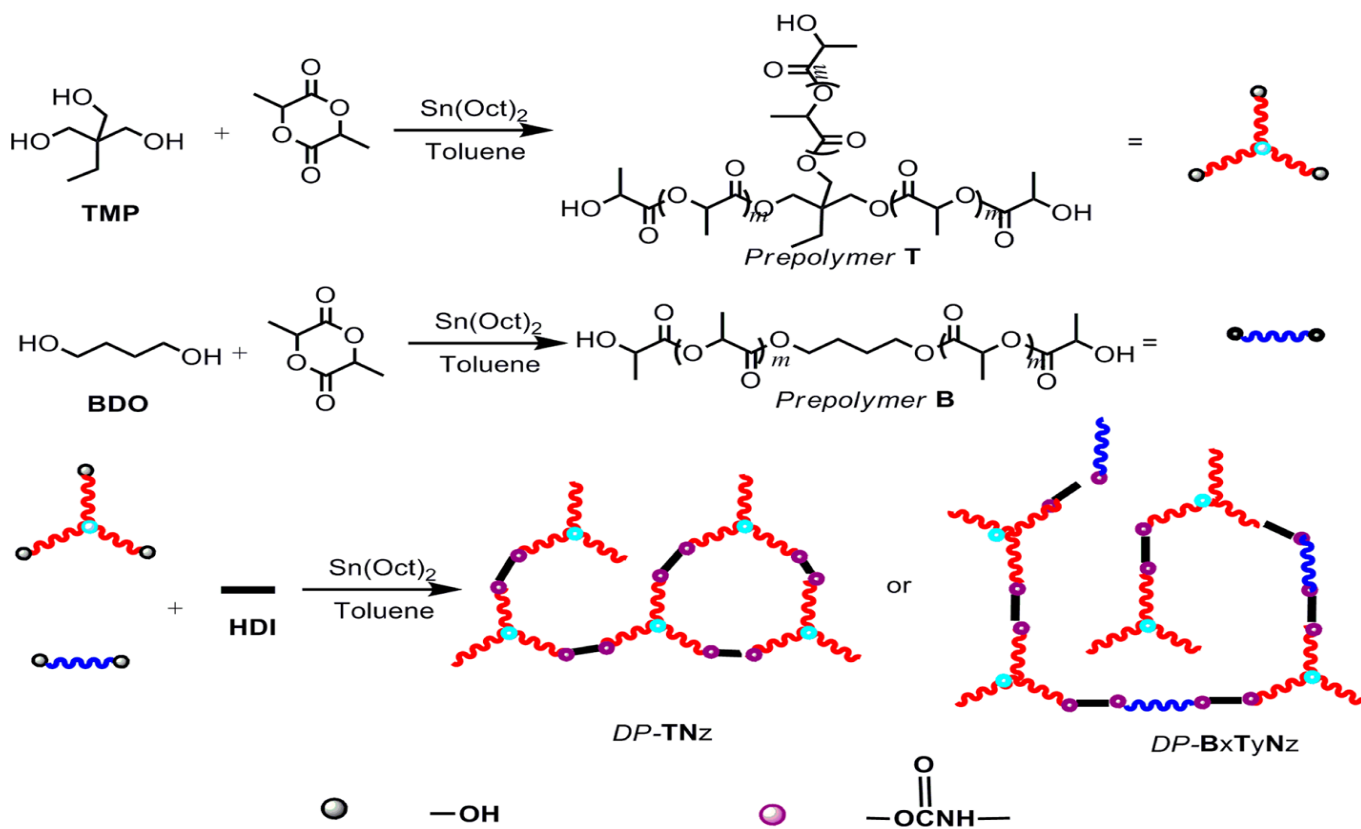


Figure 2.7: Kinetic Scheme for Long-Chain Branched Poly lactides

Chapter 3

Simultaneous Scheme Selection

3.1 Model Description

Generally, while modelling any polymerization system using the polymer reaction engineering approach, one needs to assume a possible occurrence of a particular reaction scheme, composed of several reaction steps. Once such scheme is assumed, model equations required to explain the process can be written and a model explaining different behavior of the process can be built upon. Many times the validity of such schemes can't be fully validated experimentally. Specially, if the numbers of possible reaction mechanisms are very large, it is not possible to validate each one of these steps involved in a reaction and come up with a model of correct reaction steps and thereby correct reaction schemes. However, thanks to the advancement of the modelling and optimization techniques, an effort can be made towards considering various possible steps before coming up with the correct steps while modeling a polymerization system. The approach we are going to adopt here is to assume a super set of various reaction steps possible for any kind of polymerization system and then choosing only the required number of steps from the super set that can explain the experimental behavior for such polymerization systems. Here we are going to explain this taking the poly propylene polymerization system into consideration. This could have applied for the PLA system as well. However, applying the

scheme selection approach for PLA was not helpful as in many cases the kinetic rate constants for forward and backward were identical leading to only few mechanisms to be considered. This approach is going to be most effective when number of schemes are going to be really large.

A kinetic model has been proposed to describe the propylene polymerization process with long chain branching for a twin catalyst system to fit the experimental evolution of molecular weights, PDI of Polypropylene. The Kinetic scheme of two catalyst system was considered for the development of the model.

The overall kinetic scheme followed consists of catalyst activation, initiation, propagation, chain transfer reactions and catalyst deactivation, in which, C_1 and C_2 represents the active sites of the first catalyst and second catalysts, respectively. The main chain transfer mechanism is B-hydride elimination and re-initiation occurs with the produced catalyst complex. Reversible chain transfer mechanism has been considered to achieve polymer with narrow molecular distribution. Second order deactivation has been considered for this which may be due to bimolecular deactivation. From this kinetic mechanism, one can derive the rate of formation of the live and the dead polymers to describe the molecular properties of the polymer. Also the steps of re-initiation have been considered in the kinetic scheme. Many of the schemes which are practically feasible have been considered to be reversible such as reversible B-Hydride elimination and reversible chain transfer to metal. Also chain transfer to co catalyst was considered to be reversible.

Given the various steps possible for branched Polypropylene polymerization system as above, the approach for simultaneous scheme selection and parameter estimation can be applied on it. In this case, the optimizer is provided with all possible combinations of different kinetic schemes available for a particular mechanism [21]. Many cases, both the reversible and irreversible routes for reactions are also provided. Now the optimizer is supposed to select different combinations of these schemes (by means of binary decision variables) and run each time with specific initial values (user defined) provided to integrate the generated ordinary differential equations from the selected scheme to minimize the objective function which is nothing but the error between the values predicted by the obtained model and the experimental data and estimate the associated kinetic parameters in the selected scheme. Thus we observe that the scheme selection is dynamic

in this case and the parameters are evaluated simultaneously. Hence it is called simultaneous scheme selection and parameter estimation.

As mentioned above, each backward kinetic constant is associated with a binary variable as shown in the figure 3.2. Since binary variables can take only 0 and 1 as possible value, the physical meaning of it is if the optimizer takes a value of 0 for a binary variable, it considers the reaction mechanism to be only a forward reaction thereby eliminating the backward terms. However, when it takes a value of 1, the optimizer assumes that the both forward and backward reactions are taking place and the kinetic scheme is suitably modified by the optimizer. Thus, the scheme is changing with each runs and the parameters are evaluated accordingly. One of the interesting observations is that the binary digits are not linked with the forward reactions. This is because it is assumed that the forward reactions must take place whereas the backward reaction might be optional (depending on the binary value chosen by the optimizer).



Figure 3.1 – Schematic of Simultaneous Scheme Selection and Parameter Estimation

3.2 Overall Reaction Scheme

The model was formulated in such a way that the overall scheme consisting of all possible reactions were given to the optimizer. The scheme has taken into consideration all combinations including initiation, propagation, b-hydride elimination, reversible chain transfer reactions. Many

of the reactions like long chain branching and chain transfer to co-catalysts were taken to be reversible. Only those reactions were taken irreversible where there is no certain way known for the backward reactions to take place. Hence we have assumed such reaction to be irreversible is not possible. Such an overall scheme is presented below in Figure 3.2.

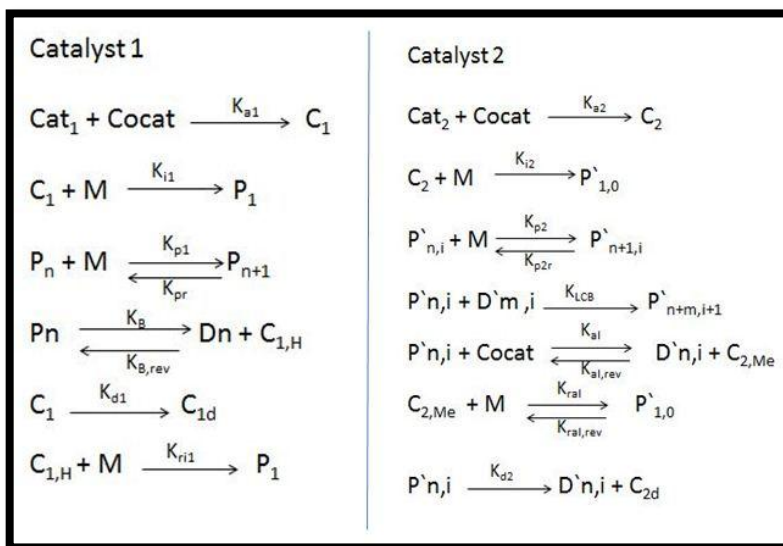


Figure 3.2: Overall scheme followed

Chapter 4

Results and Discussions

4.1 Poly Lactic Acid (PLA) Modelling

The PLA kinetic scheme presented in Figure 2.3 has been integrated using MATLAB integration routine for ordinary differential equations (ODE 45) and the model is validated using two main data sets available from the literature.

- With constant ROH/C ratio and different M/C ratio
- With constant M/C ratio and different ROH/C ratio

It is important to note that experimental values were available at these ratios with which the correctness of the model is tested. The results obtained in case of constant ROH/C ratio and different M/C ratio are as follows:

The conversion for PLA polymerization was plotted against time and the following results were observed.

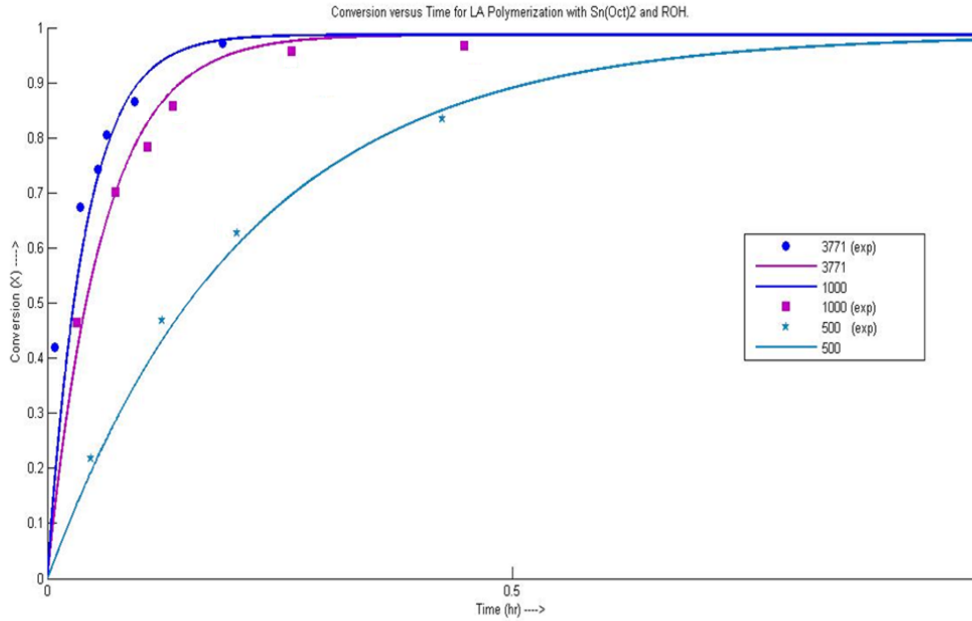


Figure 4.1: Conversion Vs Time for PLA polymerization

Also, variation of M_w with respect to conversion was observed and was found to increase at high conversion rates as can be seen in Figure 4.2.

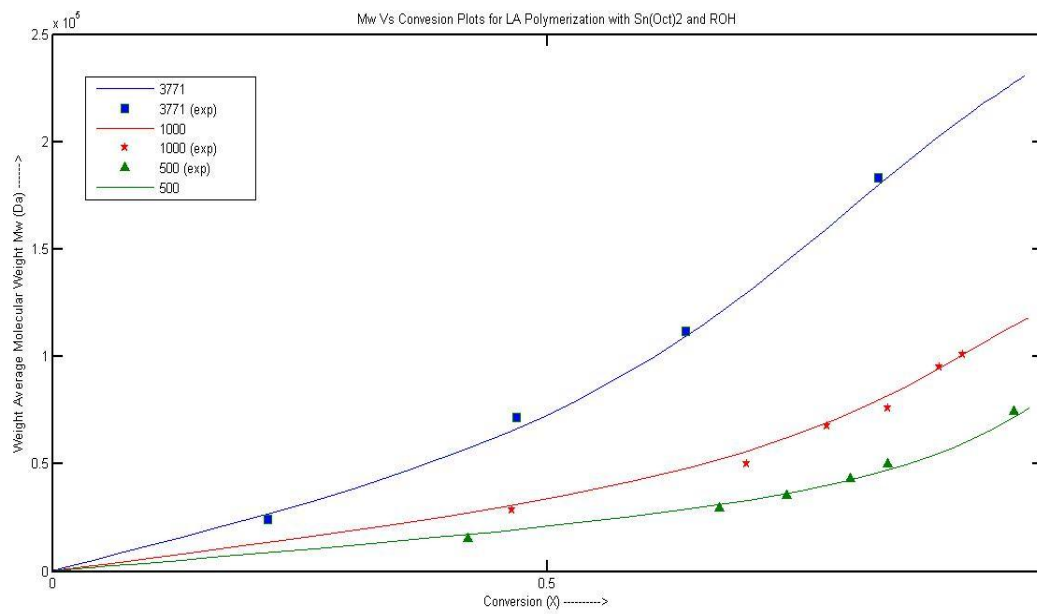


Figure 4.2: Mw Vs Conversion for PLA polymerization

PDI variation was plotted for different ratios of catalyst and co-catalyst with respect to the conversion of PLA obtained at known values (Figure 4.3).

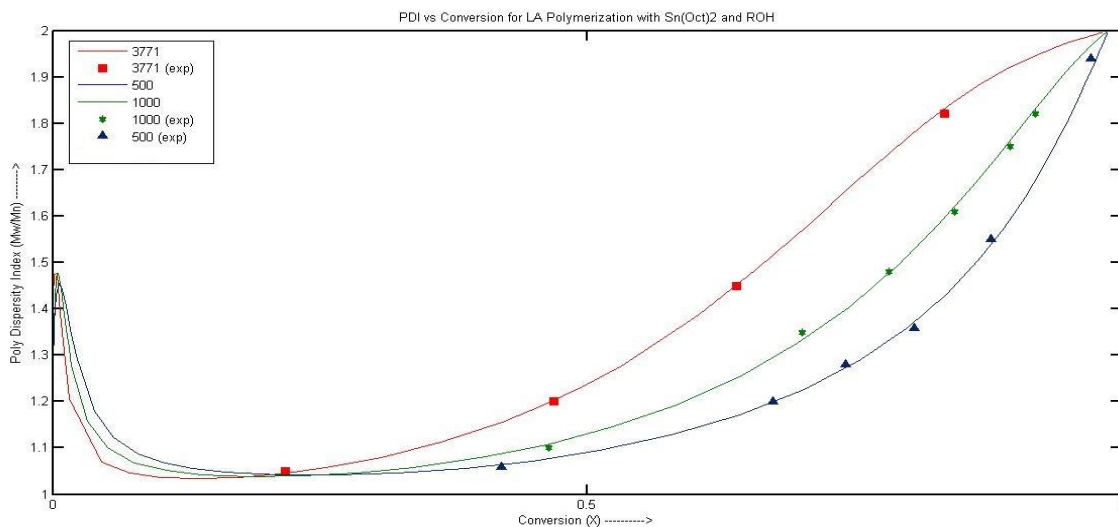


Figure 4.3: PDI Vs Conversion for PLA polymerization

The results obtained in case of constant M/C ratio and different ROH/C ratio in case of conversion in shown in Figure 4.4.

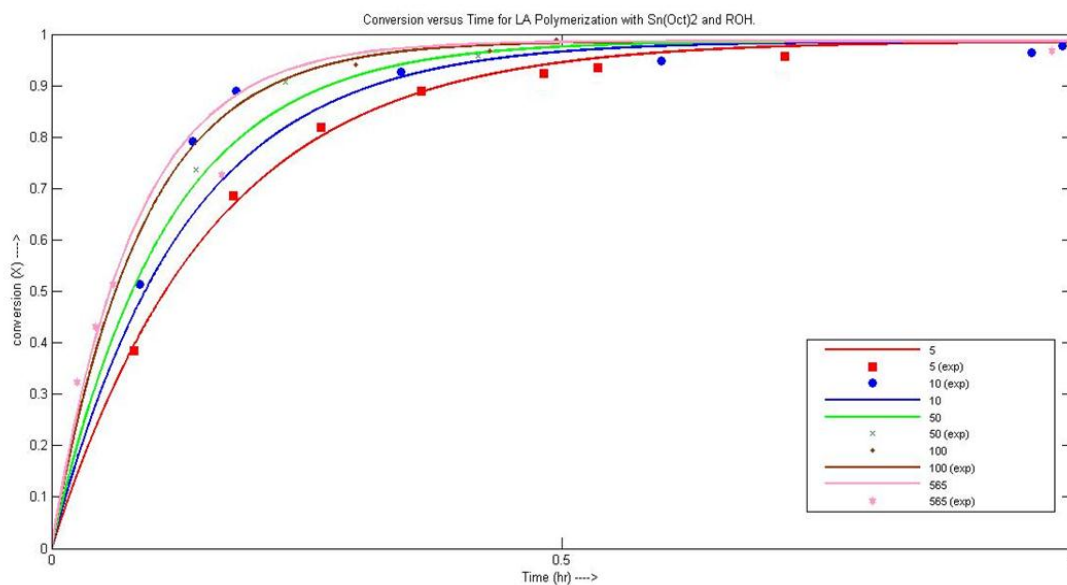


Figure 4.4: Conversion Vs Time for PLA polymerization

The effect of conversion on M_w was also observed and found to be in well agreement with the experimental data (Figure 4.5).

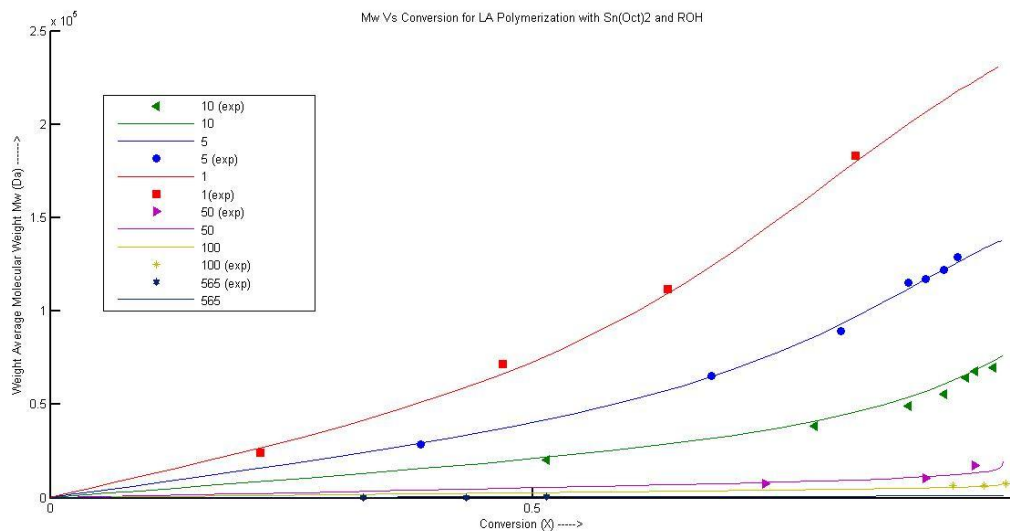


Figure 4.5: Mw Vs Conversion for PLA polymerization

Also the effect of PDI with conversion was observed and is in well agreement at the specific ratios of catalyst and co-catalyst concentrations (Figure 4.6).

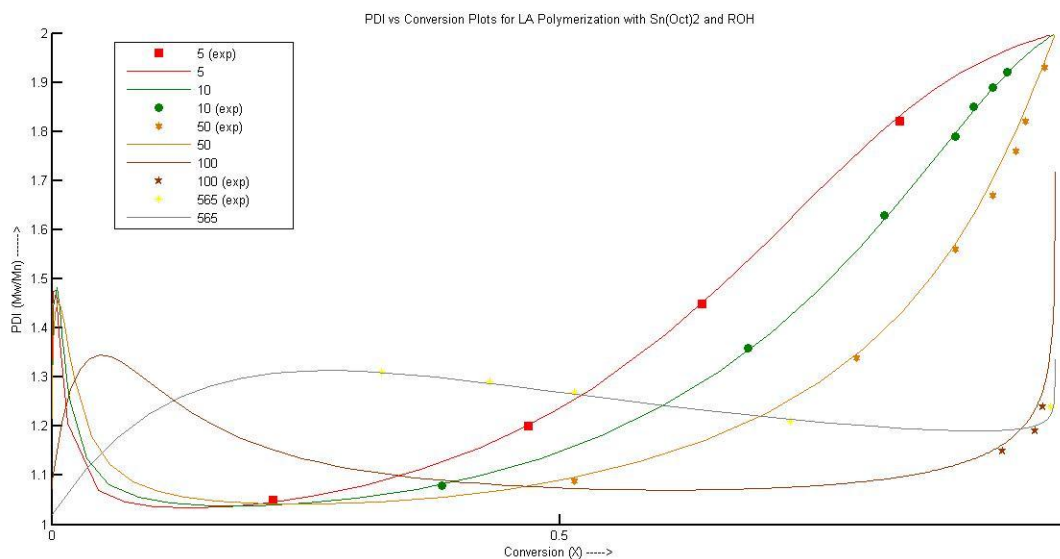


Figure 4.6: PDI Vs Conversion for PLA polymerization

An attempt has been made to develop variable temperature model as it links the working range of the model. Analysis of various temperature affecting parameters like kinetic constants and activation energy were evaluated based on parameter estimation obeying Arrhenius law. The model has been found successfully working in the temperature range $130^{\circ}\text{C} < T < 180^{\circ}\text{C}$. Also the effects of temperature on reaction phenomenon were observed (Figure 4.7).

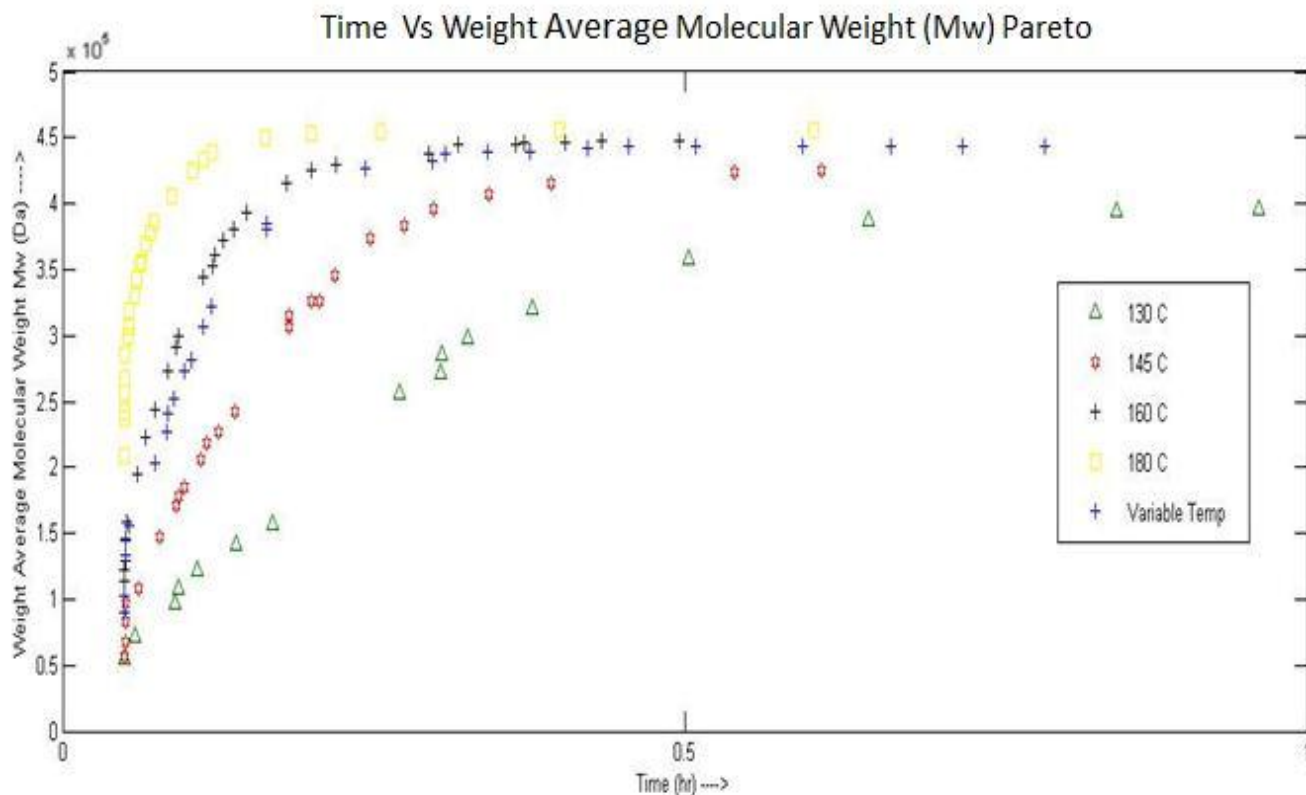


Figure 4.7: Effect of Temperature on M_w

The formulation of the multi objective optimization problem for linear PLA was done with respect to two conflicting objective of maximizing conversion and minimizing time. The decision variables for this case were all the initial reactant concentrations. The target for the optimizer is to find such initial reactant concentrations for which the conversion is maximized and time is minimized while honoring the experimental conditions. MATLAB optimization toolbox routine “gamultiobj” has been adopted for this purpose which is near replica of the well-established NSGA II [24] algorithm available in the literature. The optimizations run were both with and without constraints in the reaction ratios. General nature of these Pareto curves can be seen in Figure 4.8. Also the effect of temperature on the conversion was much significant. With

Increase in the temperature the conversion reaches to the maximum in a much lesser time as compared to that at a lower temperature (Figure 4.8).

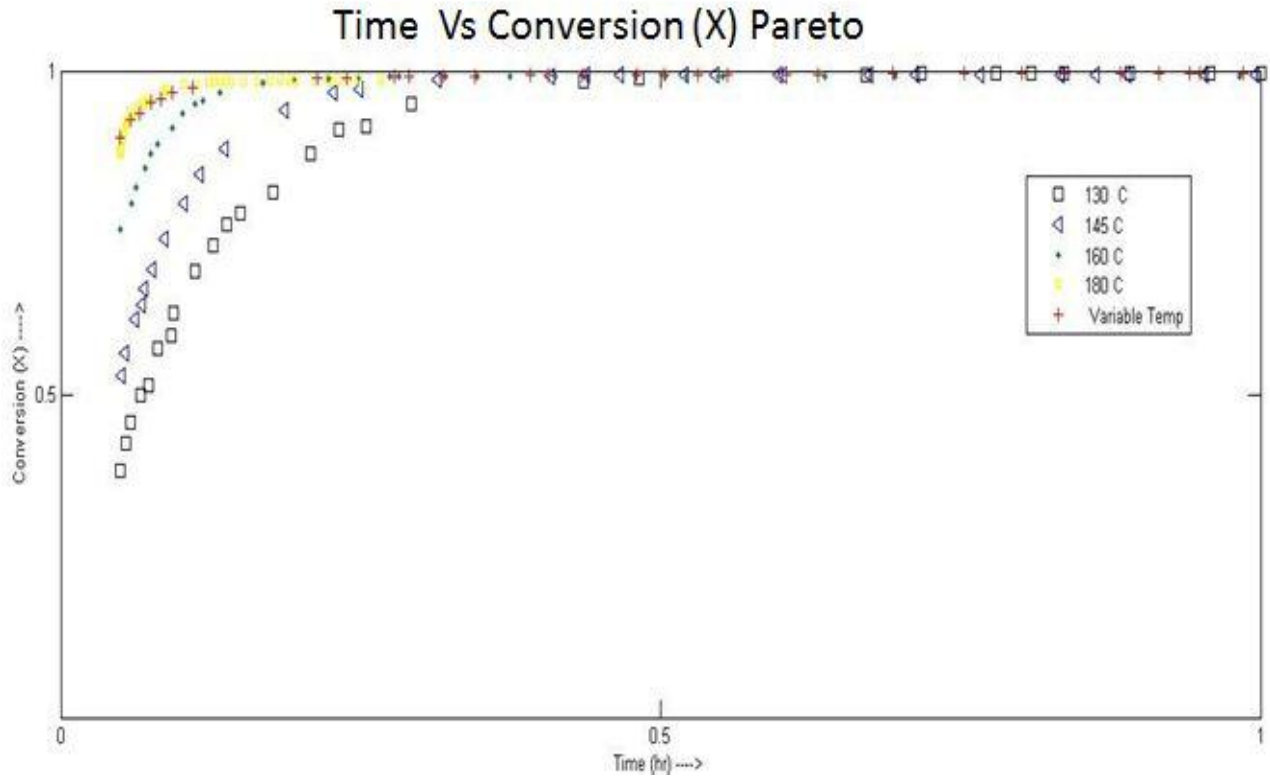


Figure 4.8: Effect of Temperature on Conversion

Increase in temperature causes a shift in Pareto to the left in case Number Average Molecular Weight vs Time Pareto. This is due to the value of high conversion rates at higher temperatures as compared to that in subsequent lower temperatures as shown in Figure 4.9.

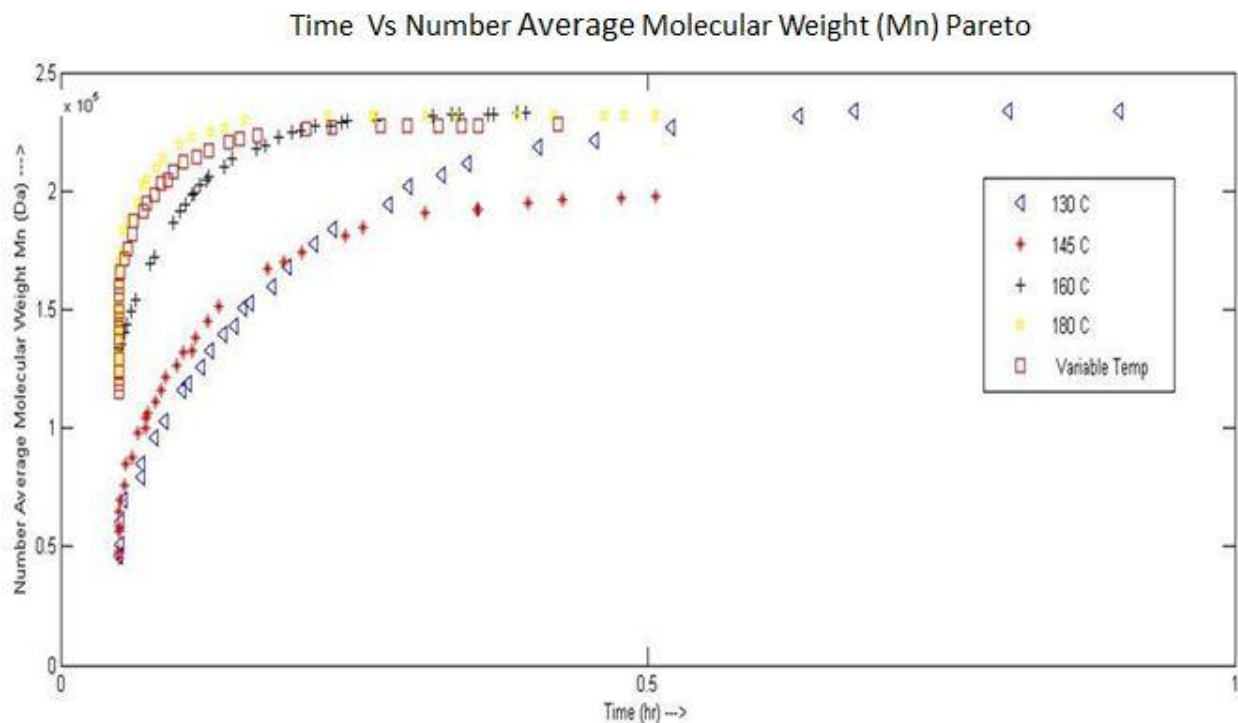


Figure 4.9: Effect of Temperature on M_n

The results obtained were quite satisfactory to the experimental data available for Linear Long Chain Polymer where calculation of forward and backward kinetic constants were done by parameter estimation. The comparison of the experimental and the simulated values were shown in the tabulated form below.

Table 4.1: Comparison of Experimental and Simulated Values for Linear LCB Polylactides

Sample	LA/OH	LA/Sn(Oct) ₂	Mn Exp (* 10 ⁴ g/mol)	PDI Exp	Yield Exp	Mn Model (* 10 ⁴ g/mol)	PDI Model	Yield Model
25-B	25	1000/1	0.69	1.44	0.85	0.71	1.39	0.99
50-B	50	1000/1	1.41	1.46	0.89	1.38	1.41	0.99
75-B	75	1000/1	2.10	1.32	0.92	1.998	1.45	0.99
100-B	100	1000/1	2.56	1.46	0.85	2.59	1.51	0.99

The comparisons between the M_n values were found to be of satisfactory range as shown in the Figure 4.10 which is found to be in good agreement with the experimental data available.

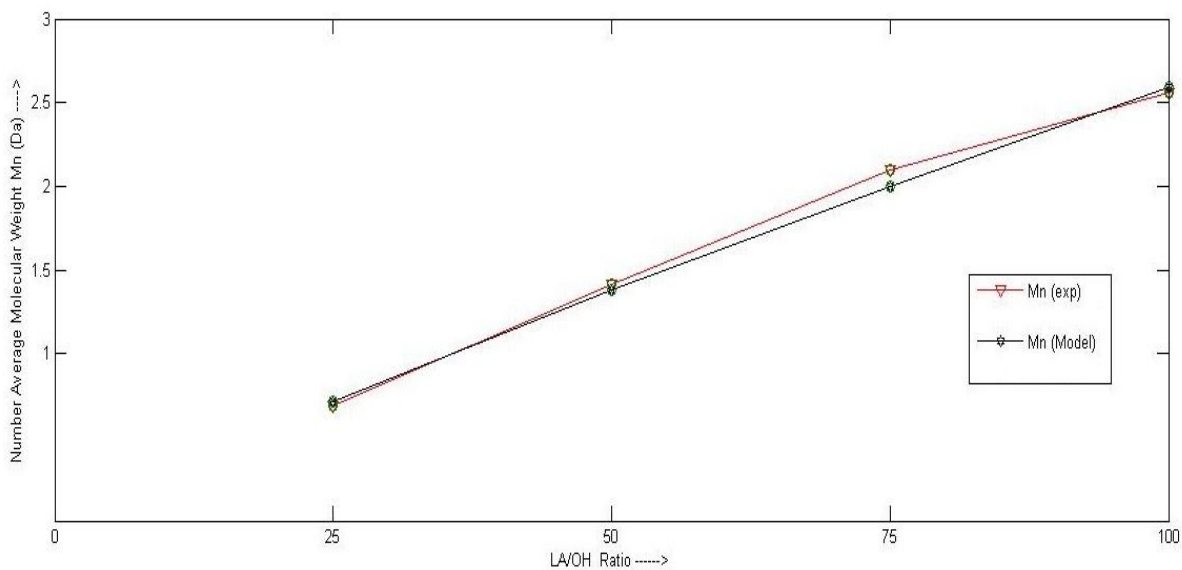


Figure 4.10: Comparison of M_n values

In case of branched PLA, the modelling has not been to a level of success and achievement as expected. This is due to the fact that there was limited literature available for a possible mechanism though some experimental data was available for model validation.

4.2 Simultaneous Scheme Selection

The simultaneous scheme selection procedure has been applied for the polypropylene system in which the overall scheme was modelled in MATLAB. This part of the work has been continuing. In the meanwhile, the overall scheme has been modified to a smaller scheme first as shown in Figure 4.11.

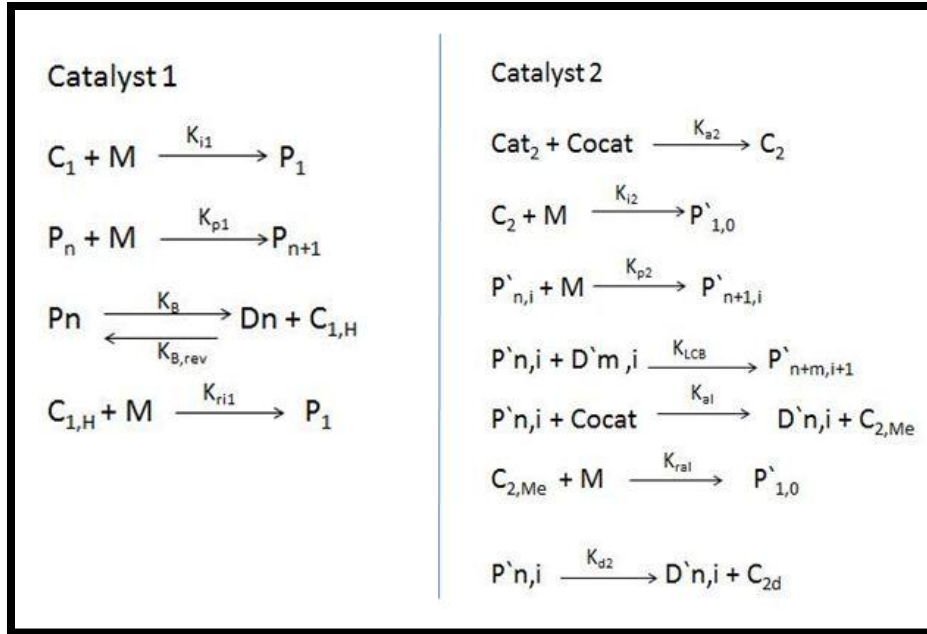


Figure 4.11: The Modified Kinetic scheme

With this modified scheme meaningful results were generated. This was just a validation to see if one of the schemes selected [19] by the optimizer makes technical meaning or not. The values of the kinetic parameters so evaluated for the model are represented in Table 4.2. Also the effects of various kinetic constants on the model parameters were evaluated simultaneously.

Table 4.2: Values of Kinetic Rate Constants

k_{i1}	4.7789×10^3 (L/(mol.min))
k_{p1}	1.0659×10^6 (L/(mol.min))
k_{β}	8.9738×10^7 (L/min)
$k_{\beta r}$	8.3145×10^6 (L/(mol.min))
k_{ri1}	1.4799 (L/(mol.min))
k_{a2}	8.8243×10^2 (L/(mol.min))

k_{i2}	6.5754×10^3 (L/(mol.min))
k_{p2}	9.4277×10^7 (L/(mol.min))
k_{lcb}	8.3375×10^8 (L/(mol.min))
k_{a1}	8.5325×10^4 (L/(mol.min))
k_{ral}	13.9312×10^4 (L/(mol.min))
k_{d2}	22.7379×10^{10} (L/(mol.min))

Comparison of the model parameters were done with the experimental values available in the literature. The comparison is shown in the Table 4.3.

Table 4.3: Comparison between Experimental and Model Values

Run N.o	M_w Exp (kg/mol)	PDI Exp	M_w Model (Kg/mol)	PDI Model
1	631.8	2.7	559.2	2.2
2	564.7	2.5	454.45	2.2
3	447.3	2.3	462.65	2.33
4	395.2	2.4	412.33	2.4
5	514.4	2.3	582.67	2.4

Some of the effects of Kinetic rate constants on the M_w were plotted and found in agreement with the experimental results available (as shown in Figure 4.11).

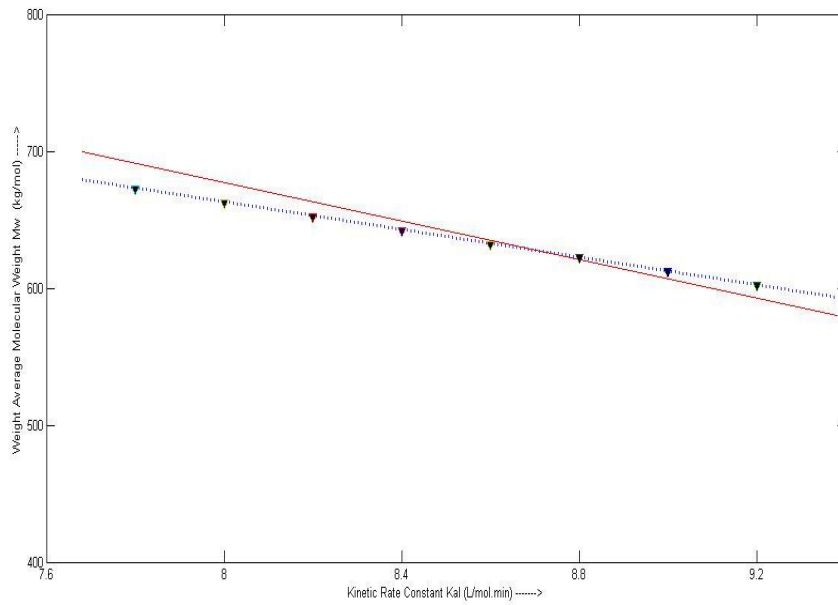


Figure 4.12: Effect of K_{al} on M_w

It is observed that with increase in the K_{LCB} , there is only a considerable amount of variation in M_w (see Figure 4.12). This is due to the reason that the molecular weight of the attacking monomer is very less as compared to the molecular weight of Polypropylene.

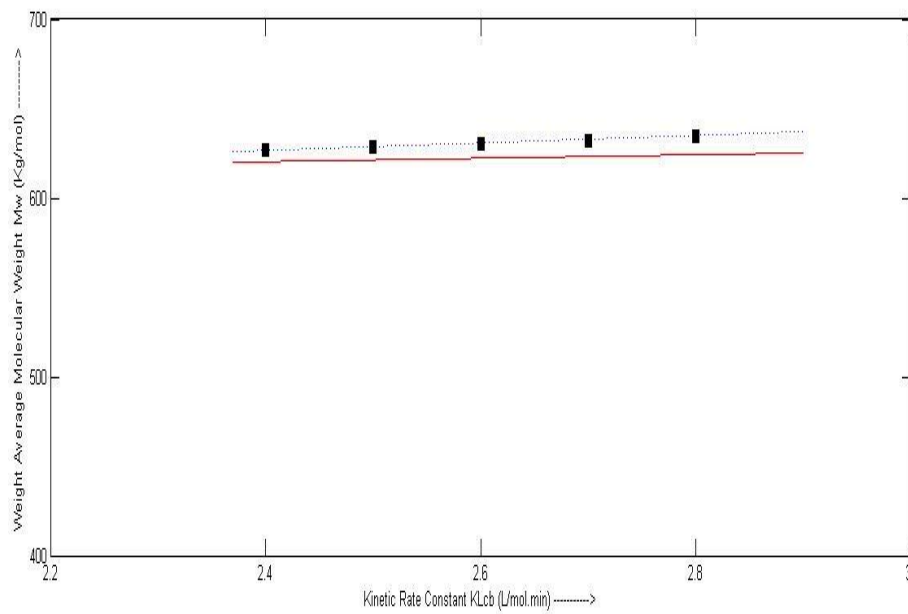


Figure 4.13 - Effect of K_{LCB} on M_w

Also in case of K_{d2} , there is hardly any variation observed in M_w due to increase in the value of K_{d2} (Figure 4.13).

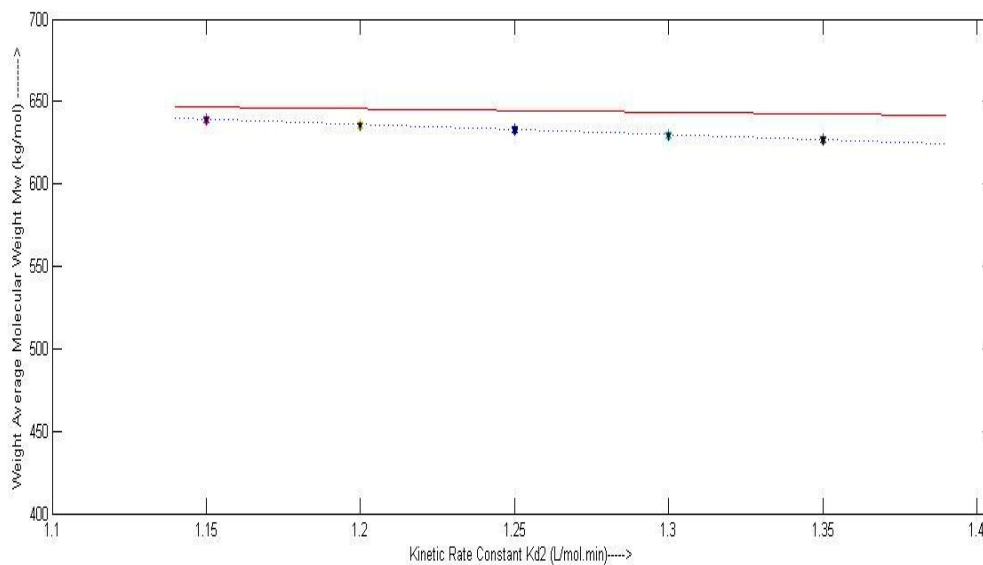


Figure 4.14 Effect of K_{d2} on M_w

With increase in the value of K_{p2} , there is a significant increase in the propagation rate, which leads to the subsequent increase in the M_w of the species (Figure 4.14).

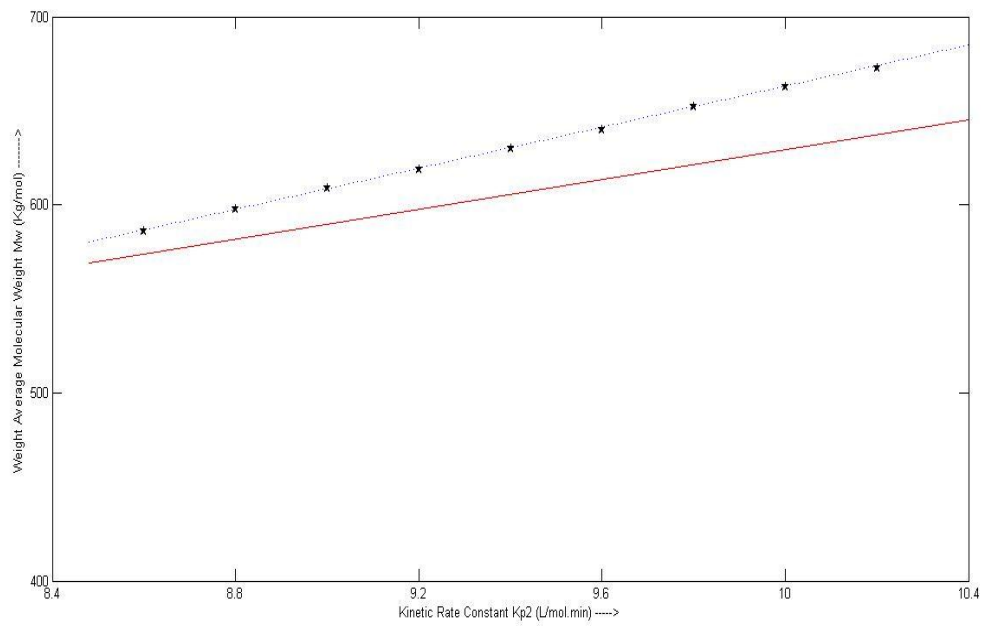


Figure 4.15: Effect of K_{p2} on M_w

Chapter 5

Conclusion

5.1 Poly Lactic Acid (PLA) Modelling

A mathematical model has been developed based on the Alkoxide Initiation Mechanism where all the kinetic mechanisms were taken into consideration while modelling PLA polymerization system [38]. The model was found to be working in the given temperature range. For the multi objective optimization, the Pareto trade-off is observed for conversion, polymerization time and M_w and M_n . The importance of temperature was investigated in case of finding the optimal Pareto fronts.

Also a model for L,L-lactide polymerization at temperatures ranging from 130 - 180°C in bulk, with $\text{Sn}(\text{Oct})_2$ as the catalyst and 1-dodecanol as co-catalyst, has been developed, including inter and intramolecular trans esterification reactions. In this approach the basic linear PLA scheme was extended for linear long chain branched polymer system and the scheme and associated parameters were estimated simultaneously. From the results, we could differentiate that the values of M_n and PDI gave satisfactory match with the available experimental data.

In case of branched PLA the modelling has not been to a level of success and achievement as expected. This is due to the fact that there was limited literature available for a possible mechanism though some experimental data was available for model validation.

This idea of simultaneous scheme selection could have been applied for the PLA system as well. However, applying the scheme selection approach for PLA was not helpful as for many schemes, the kinetic rate constants for forward and backward were identical leading to only few mechanisms to be considered. This approach is supposed to be most effective when number of schemes are going to be really large.

5.2 Polypropylene Modelling

A novel idea of simultaneous scheme selection and parameter estimation has been presented in this work with a goal of developing a model for a polymerization system. LCB PP polymerization model has been considered for this purpose. As this work is being continued, a part of the overall scheme has been considered to see if such a scheme is selected by the optimizer, it contains physical meaning or not. In this manner, a mathematical model with a newly proposed chemical mechanism for a LCB PP system with twin catalysts has been presented in this work which can validate the available experimental results. The proposed model can predict the molecular properties such as molecular weight, PDI.

The molecular weight of the PP copolymer is found to depend on the co-catalyst concentration (due to chain transfer reaction) and the co-catalyst/catalyst ratio (due to the bimolecular deactivation). Also if more time is allowed before the catalyst (C_2) addition, long chain branching content is increased in the copolymer due to accumulation of more amounts of PP macromonomers in the reactor;

The Kinetic rate constant k_{al} affects the molecular weight and the long chain branching content. Molecular weight of the polymer is decreased due to the high chain transfer rate to co-catalyst. However, grafting density of Polypropylene macromonomers is almost constant. This may be due to the fact that the rate of macromonomer insertion and the rate of propagation are not affected by the co-catalyst. However, higher molecular weight polymers can be produced with the decrease of bimolecular deactivation.

References

- [1] Wang, L.; Jing, X.; Cheng, H.; Hu, X.; Yang, L.; Huang, Y. Rheology and Crystallization of Long-Chain Branched Poly (L-lactide)s with Controlled Branch Length. *I&EC Research* 2012, 51, 10731–10741.
- [2] Kricheldorf, H. R.; Saunders, I.; Stricker, A. Polylactones 48. Sn(Oct)₂-initiated polymerizations of lactide: A mechanistic study. *Macromolecules* 2000, 33, 702–709.
- [3] Kowalski, A.; Duda, A.; Penczek, S. Kinetics and mechanism of cyclic esters polymerization initiated with tin(II) octoate. 3. Polymerization of L,L-dilactide. *Macromolecules* 2000, 33, 7359–7370.
- [4] Yu, Y. C.; Storti, G.; Morbidelli, M. Ring-opening polymerization of L,L-lactide: Kinetic and modelling study. *I&EC Research* 2009, 42, 8187–8197.
- [5] Upadhyay; S. N, Mehta, R.; Kumar, V.; Bhunia, H.; Synthesis of poly (lactic acid). *Macromolecules* 2005, 45, 325–349
- [6] Eenink, M. Synthesis of Biodegradable Polymers and Development of Biodegradable Hollow Fibers for the Controlled Release of Drugs. Ph.D. Thesis, Technische Hogeschool Twente Enschede, Enschede, The Netherlands, 1987.
- [7] Zhang, X.; Macdonald, D. A.; Goosen, M. F. A.; Mcauley, K. Role of environmental impurities on Long Chain Branched Polylactic acid . *Journal of Polymer Science, Part A: Polymer Chemistry*. 1994, 32, 2965–2970.
- [8] Witzke, D. R.; Narayan, R.; Kolstad, J. J. Reversible kinetics and thermodynamics of the homopolymerization of L-lactide with 2-ethylhexanoic acid tin(II) salt. *Macromolecules* 1997, 30, 7075–7085.
- [9] Puaux, J. P.; Banu, I.; Nagy, I.; Bozga, G. Study of catalyzed polymer initiated systems *Macromolecules*; 2007, 259, 318–326.

- [10] Mehta, R.; Kumar, Upadhyay, S. N. Kinetic Modelling of poly (lactic acid) based on cationic mechanism. *Macromolecules* 2007, 40, 425–432.
- [11] Mehta, R.; Kumar, V.; Upadhyay, S. N. Modelling of Poly (lactic acid) at high temperatures initiated by cationic mechanisms. *Journal of Polymer. Technology.* 2007, 46, 257–264.
- [12] Yu, Y. C.; Storti, G.; Morbidelli, M. Ring-opening polymerization of L,L-lactide: Kinetic and modelling study. *Macromolecules* 2011, 44, 7927–7940.
- [13] Lundberg, R. D.; Cox, E. F. In *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Edition.; Dekker: New York, 1969; pp 247-302.
- [14] Mcneill, I.; Leiper, H. A. Degradation studies of some polyesters and polycarbonates. 1. Polylactide—General features of the degradation under programmed heating conditions. *Polymer Degradation and Stability* 1985, 11, 267–285.
- [15] Odian, G. G., *Principles of Polymerization*, 4th ed.; Wiley- Interscience: Hoboken, N.J., 2004.
- [16] Kopinke, F. D.; Remmler, M.; Mackenzie, K.; Moder, M.; Wachsen, O. Thermal decomposition of biodegradable polyesters. 2. Poly(lactic acid). *Polymer Degradation and Stability* 1996, 53, 329–342.
- [17] Wachsen, O.; Reichert, K.; Kruger, R. P.; Much, H.; Schulz, G. Thermal decomposition of biodegradable polyesters. 3. Studies on the mechanisms of thermal degradation of oligo-L-lactide. *Polymer Degradation and Stability* 1997, 55, 225–231.
- [18] S. Zhu, D. Li, Molecular weight distribution of metallocene polymerization with long chain branching using a binary catalyst system, *Macromolecules Theory Simulation*, 1997, 793.
- [19] Mogilicharla, A.; Mitra, K.; Majumdar, S, Modelling of Propylene Polymerization with Long Chain Branching. *Chemical Engineering Journal* 2014, 246, 175-183.
- [20] Dorgan, J. R.; Janzen, J.; Knauss, D. M.; Hait, S. B.; Limoges, B. R.; Hutchinson, M. H. Fundamental solution and single-chain properties of polylactides. *Journal of Polymer. Science., Part B: Polymer. Physics.* 2005, 43, 3100–3111.

[21] S.T. Babik, G. Fink, Propylene polymerization and activation with $\text{Ph}_3\text{C} [\text{B}(\text{C}_6\text{F}_5)_4]$ and; iron hydride species in the catalytic cycle in the bimetallic complex, *Journal of Polymer Science*. 200 (2006) 254.

[22] Moon, S. I.; Lee, C.W.; Taniguchi, I.; Miyamoto, M.; Kimura, Y. Melt & solid polycondensation of L-lactic acid: an alternative route to poly (lactic acid) with high molecular weight. *Macromolecules* 2001, 42, 5059–5062.

[23] Montaudo, G. Mass-spectral determination of cyclic oligomer distributions in polymerization and degradation reactions. *Macromolecules* 1991, 24, 5829–5833.

[24] K. Deb, *Multi-Objective Optimization Using Evolutionary Algorithms*, Wiley, Chichester, 2001.