Kinetic Parameters of Ring-Opening Polymerization of Poly (Lactic Acid) using Stannous Octoate With/ Without Triphenylphosphine as an Initiator

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Abstract: *The modeling of ring opening polymerization of L- lactide to poly (lactic acid) (PLA) has been carried out. Using a simple numerical technique, the individual rate constants are evaluated theoretically and are compared with the available experimental data. On comparing the rate constants for PLA polymerization synthesized using 2-ethylhexanoic acid tin(II) salt (stannous octoate) with and without triphenylphosphine (TPP), several interesting results are obtained. An attempt has also been made to quantify the kinetics of the polymerization when TPP is added to stannous octoate.*

Keywords: Modeling and simulation, Polylactide, Polymerization rate constants, Stannous octoate, Triphenylphosphine

1. Introduction

During the past 15 years, a number of aliphatic polyesters have aroused considerable interest due to their biodegradability and biocompatibility. Poly (lactic acid) (PLA) is the main biodegradable polyester of interest, primarily due to its biomedical and pharmacological applications. PLA has been produced commercially worldwide since the last decade. The catalyst currently used industrially is stannous octoate (zinc metal has been in use in France). Stannous octoate has been shown to be very effective as it causes a low degree of racemization at high temperature [1], has low toxicity, and is accepted by the US Food and Drug Administration. Although stannous octoate is known to initiate fast polymerization, it has been reported [2] that some bases, particularly TPP can increase the polymerization rate further, without any detrimental effect on the polylactide stability.

But, there is a lack of data for the rate constants for initiation, propagation and termination steps of PLA polymerization though some data about the apparent rate constant are available. Also, it is extremely difficult to find experimentally the absolute values of different rate constants. Thus, there is a need for mathematical modeling which when used with the readily available experimental data for the average molecular weights, can predict the polymerization rate constants with sufficient accuracy.

The addition of an equimolar amount of Lewis base, particularly TPP into stannous octoate, significantly enhances the lactide polymerization rate in bulk. TPP has two beneficial effects: it increases the polymerization rate and decrease the occurrence of the undesirable back biting reactions at least at monomer/initiator ratio greater or equal to 5000.[3] This kinetic effect has been accounted for by coordination of the Lewis base onto the metal atom of the initiator, making the insertion of the monomer in the growing chain end easier. However, the role of TPP and the favorable effect o the bulk lactide polymerization has to be cleared up, at a time when the polymerization catalysis by stannous octoate is still under debate.[2] So, we used TPP as co-initiator to enhance the polymerization rate and molecular weight of polylactide. Molecular weight increased from thousands to several ten thousands. This study is an attempt to find out quantitatively as to what happen when TPP is added to stannous octoate initiator.

2. Mathematical Model

In ring-opening polymerization, for both D- and L-lactides, initiation results in opening of the ring to form secondary initiator species P_1.[4] This can be generalized as:

$$M + I \xrightarrow{k_o} P_1 \qquad (1)$$
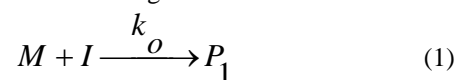
where, M is the monomer, I is the initiator and P_1 is the activated polymer of one unit (Figure 1). Initiation is characterized by a rate constant k_0. The initiator species grow by successive ring-opening additions of monomer molecules:

$$P_j + M \xrightarrow{k_j} P_{j+1} \quad , j=1, 2, 3, \dots \qquad (2)$$
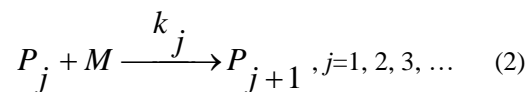
Where, P_j is the active polymer chain of j units. The rate constant k_j refers to the jth propagation step on a chain. The nature of the chain-growth process in ring-opening polymerization bears a superficial resemblance to chain polymerization. Only monomer adds to the growing chain in the propagation step. Species larger than monomer do not react with the growing chains. However, ring-opening polymerizations can have the characteristics of either chain or step polymerization or both. [4]
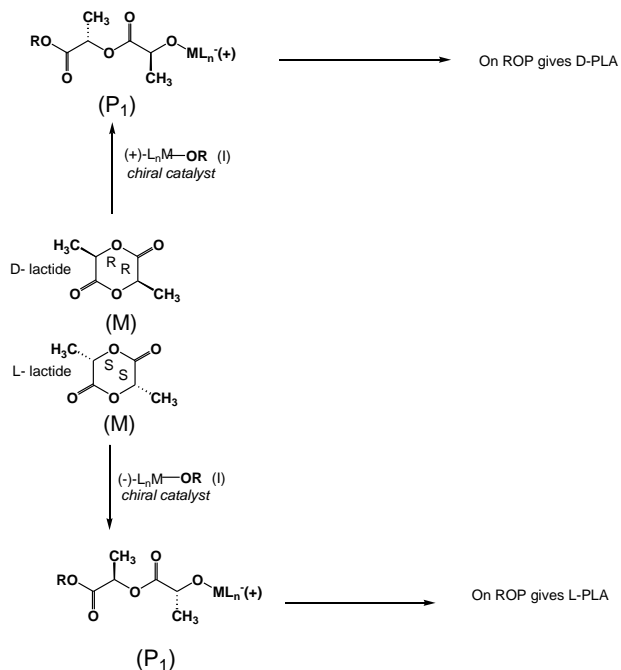
Figure 1: Initiation of L- lactide and D- lactide

The growth of polymer chain continues till its termination or till the monomer is completely consumed. The termination may occur in several different ways. Termination by transfer to monomer can take place in ring-opening cationic [5] as well as anionic [6] polymerization. The anionic polymerization of lactide proceeds via alkoxide anions, and these anions are basic enough to deprotonate the monomer [6] (Figure 2).
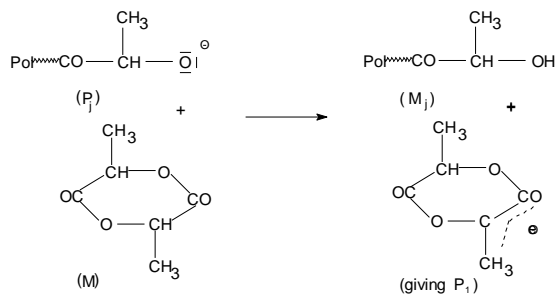

Figure 2: Deprotonation of the monomer in anionic polymerization of PLA

This deprotonation involves racemization and represents a chain transfer to the monomer with the consequence of reduced molecular weights. Odian [4] has discussed in detail the mechanism of chain transfer to monomer in the anionic ring-opening polymerization. In the present case, the termination mechanism has been assumed to be the chain transfer to monomer, giving:

$$P_j + M \xrightarrow{k_t} M_j + P_1 \qquad (3)$$
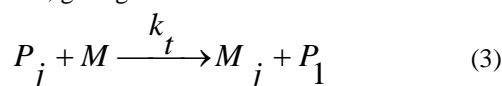
In equation (3), it is assumed that the charged ring spontaneously forms P_1. Here M_j is the deactivated polymer of j repeat units, which will not participate in any reaction and

the rate constant k_t refers to the termination by transfer to the monomer.

Mass balance equations for a batch reactor may be written for the above kinetic scheme as:

$$\frac{d[M]}{dt} = -[M]\{k_0[I] + \sum_{j=1}^{n} k_j[P_j] + \sum_{j=1}^{n} k_{tj}[P_j]\}$$
(4)

$$\frac{d[I]}{dt} = -k_0[I][M] \quad (5)$$

$$\frac{d[P_1]}{dt} = k_0[I][M] - k_1[P_1][M] + \sum_{j=2}^{n} k_{tj}[P_j][M]$$
(6)

$$\frac{d[P_j]}{dt} = [M]\{k_{(j-1)}[P_{j-1}] - k_j[P_j] - k_{tj}[P_j]\}, j > 1 \quad (7)$$

and

$$\frac{d[M_j]}{dt} = k_{tj}[P_j][M], j \geq 1 \quad (8)$$

with initial conditions, at $t=0$

$$[M_j]=0 \text{ and } [P_j]=0, j \geq 1 \qquad (9)$$

$$[M]=[M_o] \qquad (10)$$

$$[I]=[I_o] \times s \qquad (11)$$

Here, the symbols in square brackets represent respective molar concentrations and subscripts of rate constants (ks) indicate chain length dependent values. In equation (11), s represents number of chains initiated by an initiator molecule.

The summation over j in equation (4) and (6) should continue to infinity, however, it is practically impossible to do so in numerical techniques. In the present case, $n=5000$, which is well above the experimentally reported values for PLA, was taken. It was observed that a value more than this has no significant effect on the results. These equations were solved on a PC using a simple numerical technique with a very small step size, has been reported by the authors. [7-10]

It should be mentioned that steady state assumption has not been made in the present analysis. It was observed during the simulations that the molecular weight of polymer formed is more sensitive to k_p than k_t for shorter reaction time whereas effect of k_t is pronounced for prolonged reaction time. The number average molecular weight, M_n, however, is not very sensitive to k_o. It is known that ratio of rate of initiation to sum of the rates of initiation, propagation and termination, affects

the molecular weight distribution. Thus, k_o values were fine-tuned using the dispersity (M_w/M_n) data, where M_w is the weight average molecular weight.

The parameters k_o, k_p and k_t were selected from M_n and M_w vs polymerization time curves for different values of rate constant parameters by comparing the simulated and experimental curves. The values giving a close fit were chosen. Thus the curve fitting was optimized by trial and error and model comparison was done by visual assessment. An average simulation took about 30 minutes for simulating polymerization on a 1.9 GHz Pentium 4 PC.

3. Result and Discussion

Table 1: Summary of rate constants determined for various initiators.

S.No.	Initiator	k_o (l/mol.min)	k_p (l/mol.min)	k_t (l/mol.min)
1.	Stannous Octoate	0.003	15	0.060
2.	Stannous Octoate and Triphenylphosphine	0.200	15	0.023

The termination rate constant, k_t, for pure stannous octoate initiator is about 2.6 times that for stannous octoate with Triphenylphosphine (TPP) initiator. This could be the major reason for the difference in the average molecular weights achieved in PLA synthesis in the two cases. In the case of stannous octoate with TPP initiator there is an induction time up to about 2.5 hr. Table 1 lists the kinetic rate constants for both cases. Comparing the kinetic rate constants for the two catalysts: stannous octoate and stannous octoate with TPP, a few interesting conclusion can be made:

The propagation rate constant, k_p, is same for both the initiators. This means that the polymer chain once initiated will grow at the same rate in both cases (also, there is an assumption in the analysis that the propagation rate constant is independent of the chain length).

The initiation rate constant, k_o, is comparatively very low for pure stannous octoate initiator. This would also explain the high experimental values of dispersity (implying a very broad molecular weight distribution). The growing polymer chains will start and terminate at different time leading to a broad MWD. In contrast, for stannous octoate with TPP initiator, the experimental dispersity is very low which would be a desirable attribute of this system.

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In the case of stannous octoate with TPP initiator there is an induction time up to about 2.5 hr. It is interesting to note that initially it was not possible to curve fit the data for any value of k_p and k_t. However, once the time axis was shifted by 2.5 hr, an excellent fit was obtained for particular k_p and k_t. This induction time is possibly due to the fact that the catalyst has to be thermally activated in the beginning of the polymerization in order to be effective. It would be interesting to know as to what would happen if the catalyst were activated before it is added into polymerization system?

In both cases, the average molecular weights exhibit a maximum at an initial monomer to initiator ratio of 2568. The increase in molecular weight with increasing initial monomer to initiator ratio is because as this ratio increases, there will be fewer initiating sites for same number of monomer molecules and thus will lead to longer polymer chains. However, it is observed that at initial monomer to initiator ratio of 5068, the average molecular weights values fall dramatically. This could be because the number of initiating sites is reduced to such a level that chain termination by impurities becomes significant and thus results in a smaller chain length.

4. Conclusion

A simple and reliable model has been presented for the polymerization of lactide to PLA. The model enables numerical solution of rate equations for initiation, propagation, and termination steps. The simulation can be done in conjunction with the experimental data to yield individual rate constants. This methodology offers greater opportunity for capturing high, non-equilibrium polymer yield through appropriately timed termination of the polymerization reaction.

A comparison of polymerization kinetics has been done when the initiator used is stannous octoate with and without TPP (triphenylphosphine). It is interesting that even though higher molecular weight product is obtained in a shorter time period with the latter, the propagation rate constant is same for both cases. The termination rate constant is higher for stannous octoate as compared to the case when TPP is also added to the polymerization kettle. This would lead to lower molecular weights. Also, the initiation rate constant is much lower in stannous octoate case which is responsible for a higher polydispersity value, and hence a broader molecular weight distribution.

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