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Modeling and Simulation of Poly(L-Lactide) Polymerization in Batch Reactor

Davide Refinetti[a], Alessia Sonzogni[a], Flavio Manenti*[a], Nadson M. Nascimento Lima[b], Lamia Zuniga Linan[b], Rubens Maciel Filho[b]
[a] Politecnico di Milano, Dip. CMIC “Giulio Natta”, Piazza Leonardo da Vinci 32, 20133 Milano, Italy.
[b]Instituto de Biofabricação (BIOFABRIS), School of Chemical Engineering. State University of Campinas, UNICAMP, Campinas-SP, Brazil.
flavio.manenti@polimi.it

Poly(lactic acid) or Poly(Lactide) (PLA) has been extensively used both in food packaging and in biomedical applications. In fact this material is a thermoplastic polyester, which is compostable and so it can be used as an alternative to PET for food applications. Moreover it is a biocompatible and bio absorbable material and for this reason is used in biomedical area. It can be used with hydroxyl apatite for the production of composite materials used as scaffolds in bone tissue engineering, or as drug delivery system. In this work bulk melt ring-opening-polymerization (ROP) of L-Lactide (cyclic dimer of lactic acid) has been studied. Starting from the kinetic scheme developed by (Yu et al., 2011) an isothermal model has been developed and validated with experimental data obtained in laboratory. Once kinetic constants were evaluated, a complete model of a batch reactor for PLA production for biomedical applications has been developed. Finally a PI temperature control has been implemented on the reactor, in order to satisfy process targets (MW of 100[kDa] and conversion of 95%) in the shortest possible time period.

1. Introduction

PLA synthesis routes can be divided in two main groups. The first one regards the polycondensation of lactic acid. This route is the simplest one, but low molecular weights are achieved in bulk polymerization processes due to water formation that negatively influences esterification equilibrium. For this reason high vacuum must be applied in order to remove reaction water and achieve higher Mw. An alternative could be the adding of chain-coupling agents, or high boiling aprotic solvents which allow to perform azeotropic distillation of water and so reaching higher Mw. Although, both these solutions add complexity to the process and can negatively influence PLA biocompatibility. For this reason ROP of L-Lactide is a more interesting synthesis route if high Mw must be achieved and the final product must have a high purity. As can be seen in Figure 1 MW higher than 100[kDa] can be reached with bulk melt ROP.

2. Kinetic modelling

Starting from the kinetic scheme reported by (Yu et al., 2011) an isothermal model for ROP of L-Lactide has been developed. The catalytic system adopted comes from the work of (Yu, 2011) and is formed by Stannous Octoate (Tin(II) 2-ethylhexanoate) as catalyst and 1-dodecanol as cocatalyst. The reason of using an alcohol as cocatalyst is that the true initiator of the ROP of L-Lactide isn’t Stannous Octoate but tin(II) alkoxide, which is formed by the reaction of the catalyst with any OH-bearing specie. The kinetic scheme accounts for the reversible activation of catalyst into its active form. Furthermore it accounts for main reactions that influence ROP of L-Lactide, such as reversible propagation, reversible chain transfer between active chains (containing a stannous end group) and dormant or reversible terminated chains (containing an hydroxyl end group), intermolecular transesterifications and non-radical-random chain scission, which shortens polymer chain length and produce dead chains (containing an acrylic end group).

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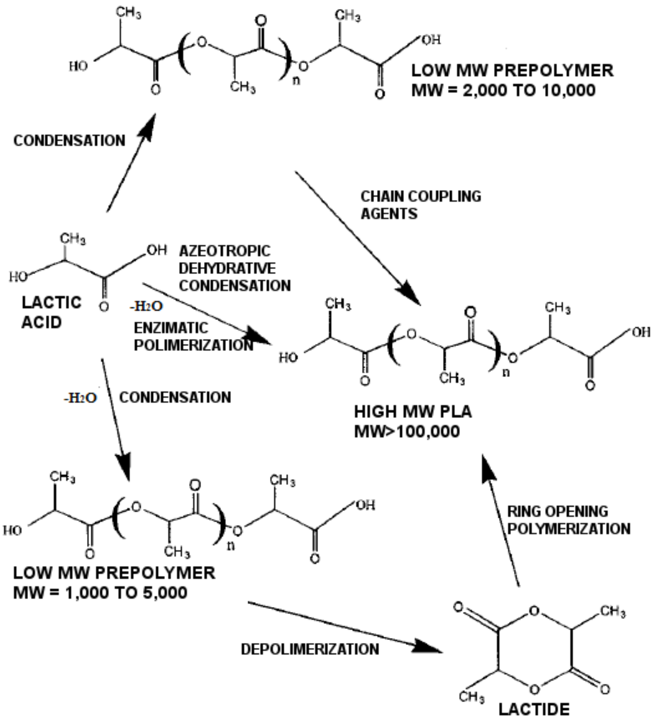


Figure 1: PLA synthesis routes

In order to evaluate weight average molecular weight and number average molecular weight of PLA during polymerization chain population balances have been solved, using a statistical method: the method of the moments. This method allows to evaluate dynamics of chain length distributions and so of molecular weight distributions.

$$Mn=\frac{\lambda_1+\mu_1+\gamma_1}{\lambda_0+\mu_0+\gamma_0}M_{mon} \qquad (1)$$

$$Mn=\frac{\lambda_2+\mu_2+\gamma_2}{\lambda_1+\mu_1+\gamma_1}M_{mon} \qquad (2)$$

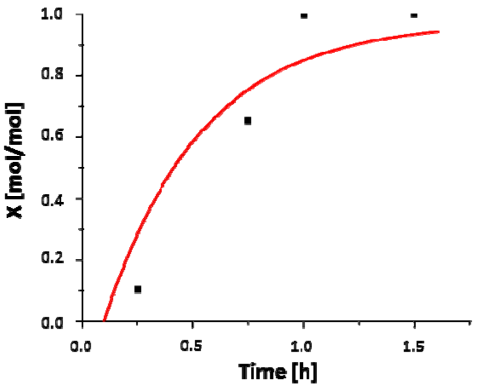
Since three chain populations are involved in the process (active, dormant and dead respectively indicated with λ, μ and γ) nine moments balances must be developed, three for each population (in order to evaluate zero, first and second order moments). These among with material balances on monomeric species (monomer, catalyst and octanoic acid formed as product of the activation reaction) form an ODE system which constitutes the ROP isothermal model.

2.1 Kinetic parameters estimation

Experimental data obtained for model validation have been taken in a temperature range from 140 °C up to 200 °C. Experiments were performed using molar ratios monomer on catalyst (M/C) and cocatalyst on catalyst (ROH/C) respectively of 1000 and 4. Mn and Mw were measured through Gel Permeation Chromatography(GPC), while monomer conversion (χ) was measured by gravimetric analysis of the samples (before and after monomer purification). These data have been used in an optimization procedure in which the objective function that had to be minimized was the sum of square errors (SSE).

$$SSE=\sum_{1}^{NE}\left[w_i^{Mn}\left(Mn(t_i)-Mn^{\exp}(t_i)\right)^2+w_i^{Mw}\left(Mw(t_i)-Mw^{\exp}(t_i)\right)^2+w_i^{\chi}\left(\chi(t_i)-\chi^{\exp}(t_i)\right)^2\right] \qquad (3)$$

Each term of the objective function has been properly weighted in order to make them of the same order of magnitude. The optimization of SSE is constrained to the mathematical model of the isothermal batch reactor. Model outputs at the various sampling time (t_i) have been taken for the evaluation of SSE. The degree of freedom that have to be optimized were the kinetic constants of the model. In order to reduce the number of variables that had to be optimized, equilibrium constants used for the evaluation of the reverse kinetic constants were taken from (Yu et al., 2011) and (Witzke et al., 1997) (e.g. ring-opening reaction and monomer-polymer equilibria).



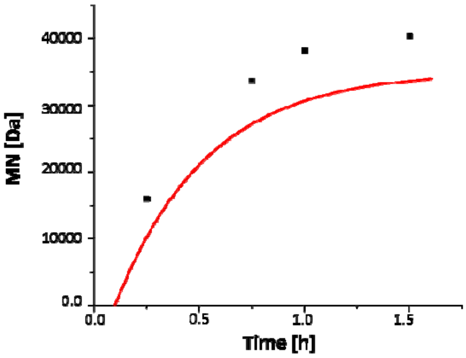


Figure 2: χ vs time 170°C (▪): Experimental data, Continuous line: model

Figure 3: Mn vs time 170°C (▪): Experimental data, Continuous line: model

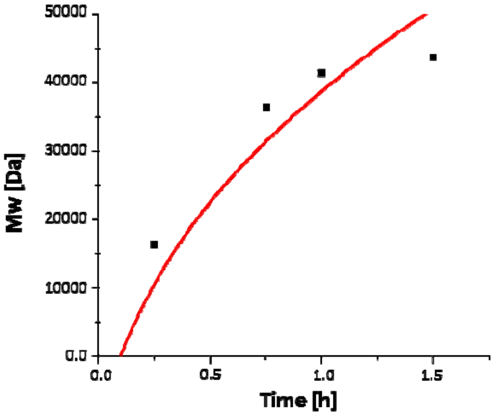


Figure 4: Mw vs time 170°C (▪): Experimental data, Continuous line: model

Table 1: estimation of the kinetic parameters

Reaction class	k_0	E_a [kJ/mol]
Activation	8.11E9[l/(mol h)]	29.5
Propagation	8.04E11[l/(mol h)]	77.7
Chain Transfer	6.33E7[l/(mol h)]	9.70
Transesterification	62.1[l/(mol h)]	14.5
Non-radical random chain scission	7.29E-5[h^{-1}]	96.0

As can be seen from Figure 2, 3 and 5 a delay time of 0.1 [h] has been taken. This value has been considered as the characteristic time necessary to the catalytic system to start the polymerization.

Pre-exponential factor of propagation constant is in good agreement with the value reported by (Yu, 2011) while its activation energy is almost equal to the values reported by (Witzke et al., 1997).

Although at 200 °C experimental data show that degradation of the polymer occurs in less than 2 hours, model previsions show that more time is needed before degradation starts. Thus the optimization procedure used in this work, led to underestimation of chain scission kinetic constant. This underestimation regards the value of pre-exponential factor while activation energy is in good agreement with literature values reported by (Yu, 2011) and (Witzke et al., 1997).

3. Batch reactor model

The model for the batch reactor is based on the pilot plant operating at the *Biofabris* of the University of Campinas (Zuniga-Linan et al., 2013). The model has been developed in MS Visual C++ and solved using BzzMath© library solvers (Buzzi-Ferraris and Manenti, 2012).

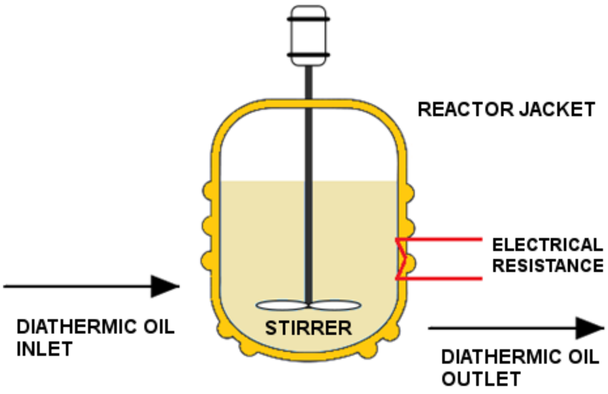


Figure 5: Reactor configuration

The reactor is a stirred reactor, which works at atmospheric pressure. This reactor has a cooling jacket at which is fed diathermic oil as cooling media. Since oil it's pumped to the reactor at room temperature (well above oil pour point, which is around -24 °C), an electrical resistance is installed in the jacket in order to rise oil temperature if needed.

Once geometrical features of the reactor have been defined an energy balance on the reactor and on the jacket were added to the isothermal model in order to develop the whole reactor model.

$$m_{TOT} C_p \frac{dT}{dt} = \left[\left(-\Delta H_{r,a} \right) r_a + \left(-\Delta H_{r,p} \right) r_p \right] V_r + UA\left(T_j - T \right) \tag{4}$$

$$\rho_{oil} V_j C_{p,oil} \frac{dT_j}{dt} = Q_{oil} \rho_{oil} C_{p,oil} \left(T_j^o - T_j \right) + UA\left(T - T_j \right) + pSP_e \tag{5}$$

In the energy balance on the reactor both endothermic heat of activation reaction and exothermic heat of propagation reaction have been considered. Although, adiabatic simulation of the reactor have showed that propagation heat of reaction is higher than the activation one. In the energy balance on the jacket heat power provided by the electrical resistance have been considered. P_e is the maximum power available from the resistance (20 kW), while pS is the normalized power value (from 0 to 1). The oil flux fed to the jacket is 130 L/h.

Model simulations have shown that M/C and ROH/C that allow to reach the process targets (Mw = 100 kDa, χ = 95 %) were respectively 6000 and 15, while the best operative temperature was 200 °C. Although characterization analyses performed on PLA synthesized on laboratory scale have shown that at this temperature degradation reactions play an important role at this temperature the highest polymerization rate is reached. For this reason polymerization time in the simulation was set lower than 3 h in order to avoid this problem.

4. Temperature control

In order to achieve process targets in the shortest time a control system has been developed on the system. In this process reactor temperature was the only controllable variable. This variable was controlled by manipulating heat power provided by the resistance. A conventional PI temperature control was developed and control parameters were chosen in order to minimize oscillations of both controlled and manipulated variables.

Table 2: tuning parameters

Control parameter	
pS_{bias} [-]	0.6
k_C [°C^{-1}]	0.05
T_I [h]	1

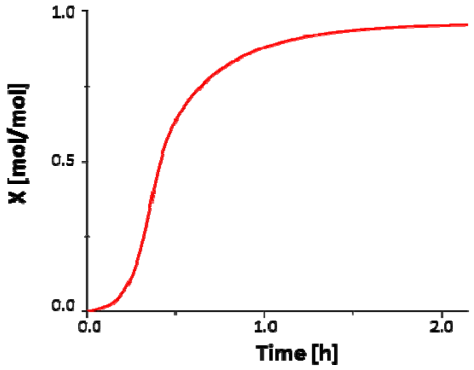


Figure 6: χ vs time

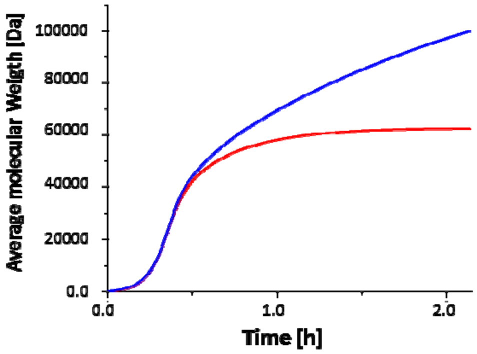


Figure 7: (-) Mn vs time, (-) Mw vs time

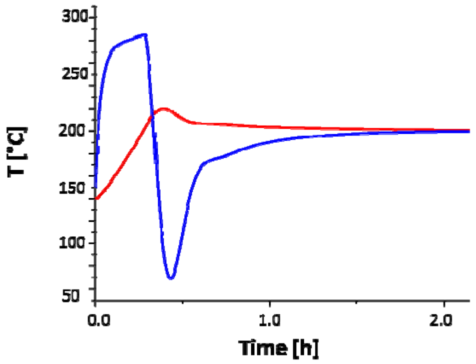


Figure 8: (-) T vs time, (-) Tj vs time

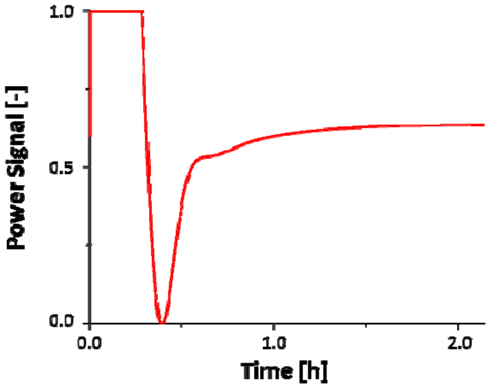


Figure 9: pS vs time

5. Conclusions

A comprehensive model for describing PLA bulk melt polymerization through ROP of L-Lactide is described. Dynamic evolution of PLA average properties (Mw and Mn), monomer conversion and reactor temperature is predicted with good accuracy, offering the possibility to deepen the understanding of the process and estimate PLA final properties (role of M/C and ROH/C ratios, role of acid impurities, role of polymerization temperature etc.). Furthermore, a temperature controller is implemented to preserve process conditions for the production of a polymer quality with applications in biomedical area (Mw = 100,000[Da] and 5% residual monomer content). Such a control system leads to a polymerization time of 2[h] without achieving any degradation phenomena that could occur during polymerization.

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