

GRANTEE EXPERIENCE REPORT

Indo-German Centre for Sustainability (IGCS)
IGCS Research Exchange, Grant Period 2023

research brief

Darla Ashish Pradhan Joshi



Experience Report on IGCS Research Exchange, Grant Period 2023

IGCS School Participant

Darla Ashish Pradhan Joshi



Home Institute | Home Supervisor

Institute of Chemical Technology, Mumbai | Dr. Rambabu Dandela

Host Institute | Host Supervisor

AVT Fluid Process Engineering Lab, RWTH Aachen University,

Guided by: Prof. Dr.- Ing Andreas Jupke

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Research Topic

Copolymerization of Lactones (Polylactide and Polycaprolactone)

Starting/End date of the student exchange period

15.07.2023 – 15.10.2023

A promotional poster for IGCS grants. It features a smiling woman with long dark hair, wearing a yellow shirt and a backpack, standing in front of a white mandala pattern. The background is a dark red color. The text on the poster reads: 'IGCS INDO-GERMAN Centre for SUSTAINABILITY', 'Grants For Students and Researchers', 'Conduct Research on sustainability topics in India or Germany', 'APPLICATION OPEN', 'Floating deadline for the year 2024', and 'For more information: https://www.igcs-chennai.org/grants/'. At the bottom, there are logos for funding partners: DAAD, Department of Science and Technology, Federal Ministry of Education and Research, RWTH Aachen University, CIAU, and TU9.

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IGCS awards scholarships to students and researchers from India and Germany with excellent academic records, very good English, and intercultural communication skills. The scholarship consists of a mobility grant and an accommodation grant according to DAAD funding rates, as a rule. Learn more about the funding opportunities at IGCS [here](#).

Summary

Random and block copolymerization of lactones, such as L-lactide and ϵ -caprolactone, can be modelled using mathematical equations to describe the polymerization kinetics and the evolution of polymer composition over time. MATLAB is a powerful tool for such simulations due to its flexibility and numerical computing capabilities.

Here's a basic outline of how you could approach this in MATLAB:

Define Reaction Kinetics:

Define the rate equations for the polymerization of L-lactide and ϵ -caprolactone. These equations should include terms for initiation, propagation, and termination reactions.

Set Initial Conditions:

Specify the initial concentrations of monomers, initiators, and any other relevant species.

Numerical Integration:

Use MATLAB's ODE solvers (Ordinary Differential Equations) to numerically integrate the rate equations over time. The `ode45` function is commonly used for this purpose.

Plot Results:

Plot the evolution of monomer and polymer concentrations over time. You can use MATLAB's plotting functions to visualize the polymerization process.

Random Copolymerization:

If you are modelling random copolymerization, consider introducing random sequences of monomers during the propagation step.

Block Copolymerization:

For block copolymerization, you'll need to introduce a stepwise approach where one monomer is polymerized first, and then the second monomer is added in a subsequent step.

The effects of varying monomer compositions as well as polymer chain lengths on the copolymerization's were experimentally investigated. A mathematical model is developed considering reversible initiation, propagation, chain transfer, and transesterification reactions.

Here's a simplified example code snippet in MATLAB to give you an idea:

— — —

**** Polymerization Reaction Kinetics ****

The system of ordinary differential equations (ODEs) describing the polymerization reaction kinetics is given by :

$$\begin{aligned}\frac{dy_1}{dt} &= -k_1 \cdot y_1 \cdot y_3 \\ \frac{dy_2}{dt} &= -k_2 \cdot y_2 \cdot y_3 \\ \frac{dy_3}{dt} &= k_1 \cdot y_1 \cdot y_3 + k_2 \cdot y_2 \cdot y_3\end{aligned}$$

where:

Y1: concentration of L-lactide

Y2: concentration of ϵ -caprolactone

Y3: concentration of polymer

K1: rate constant for L-lactide polymerization

K2: rate constant for ϵ -caprolactone polymerization

**** Set Initial Conditions ****

The initial conditions are set as follows:

Initial concentrations: [1.0,1.0,0.0]

**** Solve ODEs Numerically ****

The ODEs are solved numerically over the time interval ([0, 10]).

**** Plot Results ****

The concentrations of L – lactide

ϵ – caprolactone, and the polymer are plotted over time.

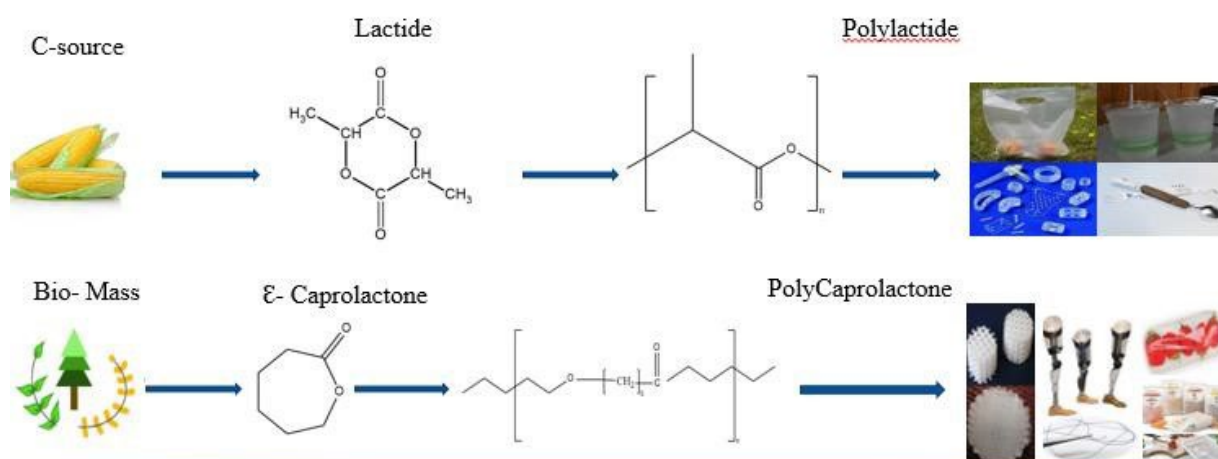
Moreover, it is demonstrated that the model can be utilized to elucidate comparable traits in the more rapid catalysts of the next generation, utilizing the "asme" catalyst archetype. This establishes the groundwork for expeditious catalyst development, catering to industrial requirements for swift and non-hazardous alternatives to the commonly employed toxic ROP catalyst, Sn octanoate, thereby bridging the divide between academic research and industrial applications.

A mathematical framework has been constructed to account for reversible initiation, propagation, chain transfer, and transesterification reactions in the context of ring-opening copolymerization's involving l-lactide and ε-caprolactone. The model takes into consideration diffusion control associated with polymer chain length. Remarkably, the model provides accurate predictions for monomer conversions, number-average molecular weights, polydispersity index values, and cumulative copolymer compositions in the described copolymerization processes.

Report

During the project we have established a dynamic simulation model that can describe the copolymerization of lactide and ϵ -caprolactone catalysed with novel catalysts. This includes the setup of a suitable reaction network considering relevant side reactions, the description of the system with differential mass and population balances and consecutive algebraic equations, the discretization and solution of the resulting system of equations with suitable methods and the implementation of the developed methodology. Relevant chemical and thermodynamic material properties are to be determined experimentally in our laboratories.

The aim of the project is to develop a simulation model for the copolymerization of lactide and ϵ -caprolactone, through which the underlying physical effects can be understood in more detail. This model should also enable relevant quality characteristics of the product to be predicted based on the adjustable input variables, such as composition of the reactants and temperature, and thus ultimately enable optimization of the operating point of the polymerization and a model-based scale-up to be carried out.



➤ Copolymerization blends different monomers to enhance material properties and tailor glass transition temperatures.

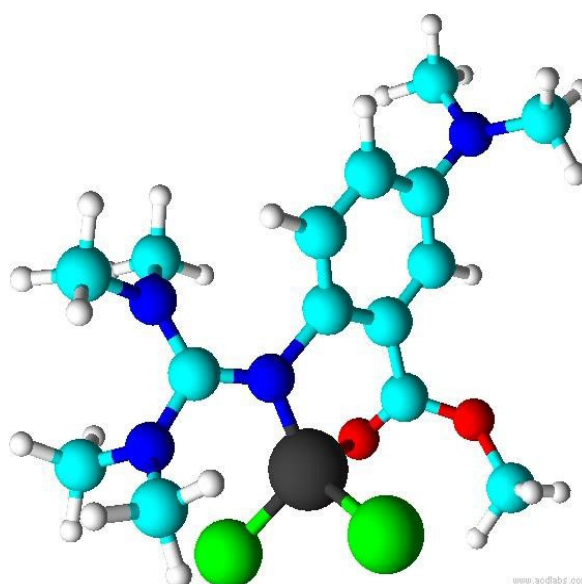
Introduction

Humankind has come to rely on fossil-derived plastics for many everyday uses. Up to 2015, it is estimated that a staggering 8.3 billion metric tons of plastics have been manufactured.

- (1) Given their incredible durability, synthetic polymers are predicted to persist in landfills for centuries to millennia.
- (2) Moreover, the leakage of plastics to the environment is a global pollution crisis, with an estimated 4.8 to 12.7 million metric tons of plastics entering the world's oceans each year.
- (3) One solution to these global challenges is the use of bioplastics. PLA and PCL are currently one of the most prominent and promising bio-based biodegradable polymers and can substitute polyethylene or polyethylene terephthalate in many applications.

The broad application range can even be extended by using a co-monomer like ϵ -caprolactone. However, the production of PLA and PCL based copolymers is not fully sustainable since the industrially used catalyst tin (II) octoate is toxic and remains inside the final product. Considering the biodegradable nature of lactide and ϵ -caprolactone based polymers, toxic tin remains after degradation of the polymer and accumulates in the environment. For this reason, the Department of Inorganic Chemistry at RWTH Aachen University develops robust and non-toxic zinc based. These catalysts not only enable polymerization to PLA and PCL, but also are highly active in copolymerization. In contrast to the industrially used catalyst, further relevant effects occur with these novel catalysts. In this work, a reaction model for the copolymerization of lactide and ϵ -caprolactone is to be implemented in MATLAB and Python.

Catalyst: Ring-Opening-Polymerization with N, O Zinc Guanidine Catalysts,



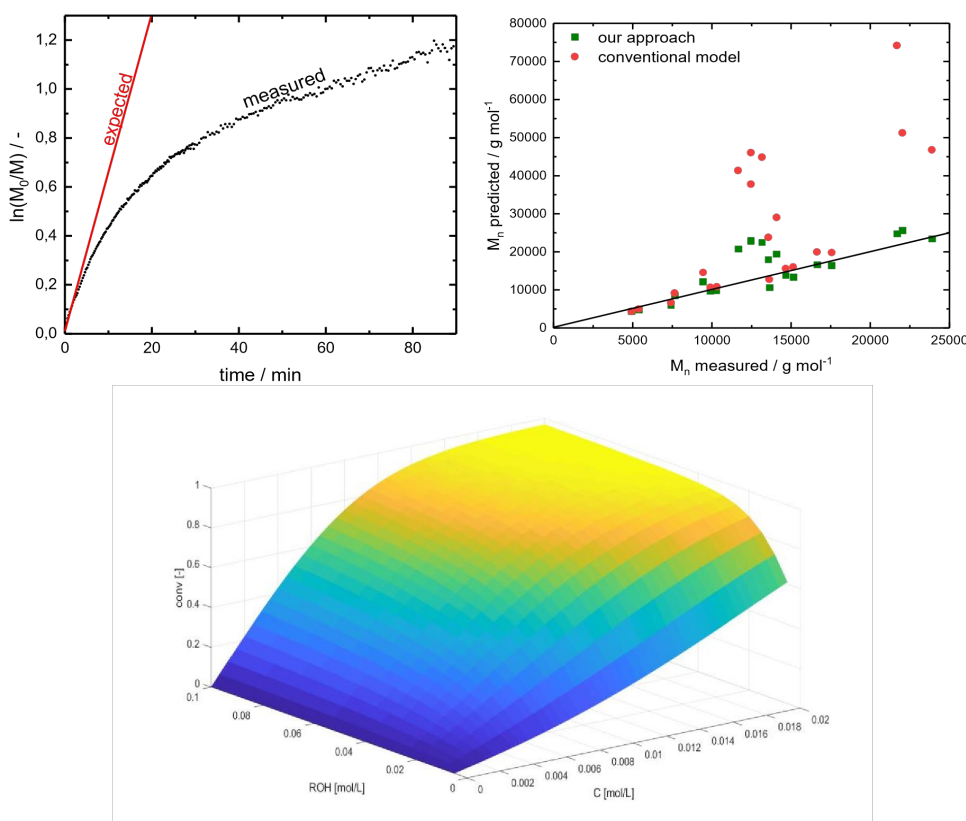
[ZnCl₂(TMGSNMe₂asme)]

General:

- Robust
 - Polymerization in polymer melt
 - Industrially relevant conditions
- Non-toxic
- Easy Synthesis
- High catalytic activity
- Proven performance in ring opening polymerization.

Hypothesis: Ligand of the catalyst acts as chain starter → catalyst concentration decreases

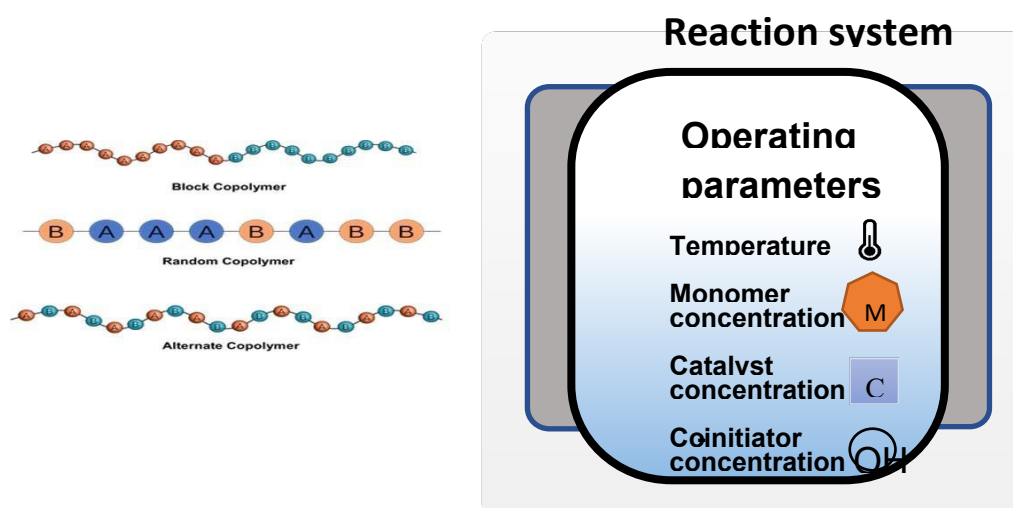
Molecular weight and end group analysis support hypothesis: The hypothesis suggests that in a catalytic reaction, the ligand of the catalyst serves as a chain starter, initiating the reaction. As the concentration of the catalyst decreases, there may be a proportional decrease in the initiation of reaction chains, potentially leading to a reduced overall reaction rate. This assumption is grounded in the idea that the catalyst, particularly its ligand, plays a crucial role in the initial steps of the reaction, and a decline in its concentration could hinder the efficiency of the catalytic process.



Conversion after 90 min of reaction at 150 °C

Copolymerisation Model for PLA and PCL:

A model is established for the bulk ring-opening copolymerization, assuming the catalytic mechanism involving $[ZnCl_2(TMG5NMe_2asme)]$. The copolymerization of lactic acid (LA) and ϵ -caprolactone (ϵ -CL) is investigated at 140°C using hydroxyethyl methyl acrylate (HEMA) as the alcohol initiator. HEMA is chosen to generate macromonomers for subsequent free-radical copolymerization. The model incorporates diffusion control arising from increased viscosity and monomer consumption in the reaction system. Model parameters are derived from experimental data in the literature. The resulting model is validated and employed to forecast the copolymerization outcomes of l-LA and ϵ -CL, enabling the production of copolymers with diverse compositions at fixed chain lengths and varied chain lengths at a constant composition. This model is valuable in designing and synthesizing biodegradable macromonomers, offering a strategy for tailoring chain structures through predicted monomer addition strategies based on the model.



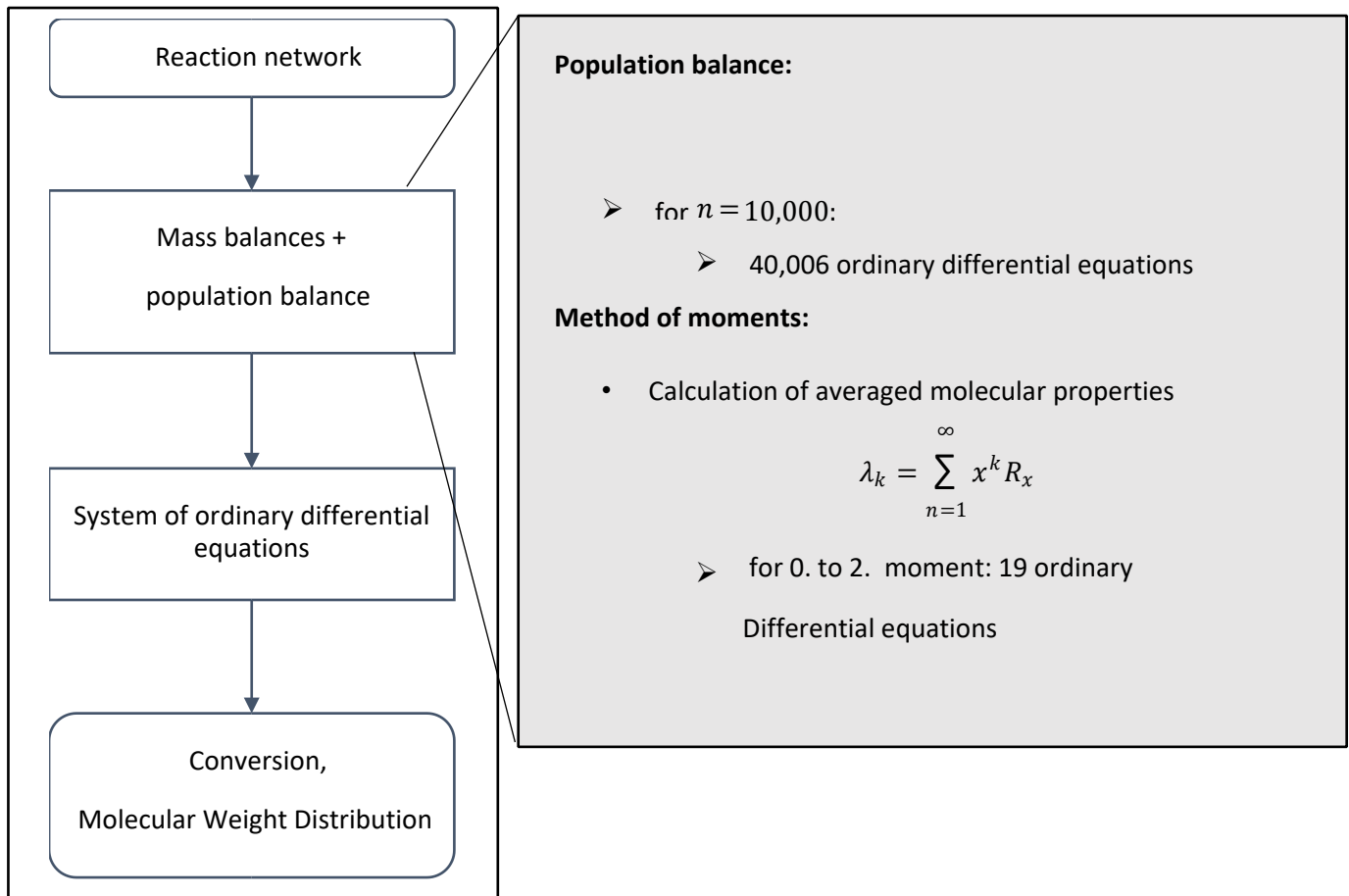
Output	Why Outputs are important?
Conversion	Influences composition and resulting polymer properties.
Molecular Weight Distribution	Influences the tailored properties, product consistency and stability.
	Influences the processing efficiency and end use applications.

Reaction network for the Copolymerization:

Catalyst Activation:	$C + ROH \leftrightarrow R_0 + A$	Small Molecules: M1: Monomer I-LA (i=1) M2: Monomer E-CL (i=2) C: Catalyst ROH: Alcohol (HEMA) R ₀ : Initiator (Oct-Sn-OR)
	$D_{n,i} + C \leftrightarrow R_{n,i} + A$	
Chain Initiation:	$R_0 + M_i \leftrightarrow R_1$	
Chain Initiation by Catalyst:	$C + M_i \leftrightarrow D_i$	
Chain Propagation:	$R_{n,i} + M_j \leftrightarrow R_{n+1,j}$	Large Molecules: $R_{n,i}$: Active polymer chain $D_{n,i}$: Dormant polymer chain
Intermolecular transesterification:	$R_{n,i} + R_{m,j} \leftrightarrow R_{n+m-p,i} + R_{p,j}$	
	$R_{n,i} + D_{m,j} \leftrightarrow R_{n+m-p,i} + D_{p,j}$	
Chain Transfer:	$R_{n,i} + ROH \leftrightarrow D_{n,i} + R_0$	
	$R_{n,i} + D_{m,j} \leftrightarrow D_{n,i} + R_{m,j}$	

→ 19 reactions were involved in the model.

Modelling of Reaction Network:



The linear ODE for the initial monomer concentrations are as follows,

For Monomer-1 (Polylactide),

$$\{dM1\}/\{dt\} = -k_{\{p11\}M1(R0+X_{\{LA_0\}}) - k_{\{p21\}X_{\{CL_0\}}M1} + k_{\{d1\}X_{\{LA_0\}}}$$

For Monomer-2 (Polycaprolactone),

$$\{dM2\}/\{dt\} = -k_{\{p22\}M2(R0+X_{\{CL_0\}}) - k_{\{p12\}X_{\{LA_0\}}M2} + k_{\{d2\}X_{\{CL_0\}}} - k_{\{CM2\}CM2}$$

For the Co-initiator of the reaction system i.e., (Oct-Sn-OR)

$$\{dRO\}/\{dt\} = -k_{\{p11\}R0M1} - k_{\{p22\}R0M2} + k_{\{a0\}CROH} - k_{\{da0\}R0A} + k_{\{tr11\}ROHX_{\{LA_0\}}} + k_{\{tr22\}ROHX_{\{CL_0\}}} - k_{\{tr11\}ROY_{\{LA_0\}}} - k_{\{tr22\}ROY_{\{CL_0\}}}$$

Similarly for the zeroth order of moments,

$$\begin{aligned} \frac{dX_{LA_0}}{dt} = & k_{p11}R0M1 + k_{p21}X_{CL_0}M1 - k_{p12}X_{LA_0}M2 - k_{da1}X_{LA_0}A + \\ & k_{a1}Y_{LA_0}C + F_{1c}(k_{d1}X_{LA_0} + k_{d2}X_{CL_0}) - k_{d1}X_{LA_0} - k_{tr11}X_{LA_0}ROH + \\ & k_{tr11}Y_{LA_0}R0 - k_{tr12}X_{LA_0}(Y_{LA_0} + Y_{CL_0}) + k_{tr21}Y_{LA_0}(X_{LA_0} + X_{CL_0}) - \\ & 2k_{x11}X_{LA_0}(X_{LA_1} - X_{LA_0}) - 2k_{x12}X_{LA_0}(X_{CL_1} - X_{CL_0}) + \\ & 2F_{1c}(k_{x11}X_{LA_0}(X_{LA_1} - X_{LA_0}) + k_{x12}X_{LA_0}(X_{CL_1} - X_{CL_0}) + \\ & k_{x21}X_{CL_0}(X_{LA_1} - X_{LA_0}) + k_{x22}X_{CL_0}(X_{CL_1} - X_{CL_0})) - \\ & (k_{x11}X_{LA_0}(Y_{LA_1} - Y_{LA_0}) + k_{x12}X_{LA_0}(Y_{CL_1} - Y_{CL_0})) + \\ & F_{1c}(k_{x11}X_{LA_0}(Y_{LA_1} - Y_{LA_0}) + k_{x12}X_{LA_0}(Y_{CL_1} - Y_{CL_0}) + \\ & k_{x21}X_{CL_0}(Y_{LA_1} - Y_{LA_0}) + k_{x22}X_{CL_0}(Y_{CL_1} - Y_{CL_0})) \end{aligned}$$

$$\begin{aligned} \frac{dX_{CL_0}}{dt} = & k_{p22}R0M2 + k_{p12}X_{LA_0}M2 - k_{p21}X_{CL_0}M1 + k_{a2}Y_{CL_0}C - \\ & k_{da2}X_{CL_0}A + F_{2c}(k_{d1}X_{LA_0} + k_{d2}X_{CL_0}) - k_{d2}X_{CL_0} - \\ & k_{tr22}X_{CL_0}ROH + k_{tr22}Y_{CL_0}R0 - k_{tr12}X_{CL_0}(Y_{LA_0} + Y_{CL_0}) + \\ & k_{tr21}Y_{CL_0}(X_{LA_0} + X_{CL_0}) - 2(k_{x21}X_{CL_0}(X_{LA_1} - X_{LA_0}) + \\ & k_{x22}X_{CL_0}(X_{CL_1} - X_{CL_0})) + 2F_{2c}(k_{x11}X_{LA_0}(X_{LA_1} - X_{LA_0}) + \\ & k_{x12}X_{LA_0}(X_{CL_1} - X_{CL_0}) + k_{x21}X_{CL_0}(X_{LA_1} - X_{LA_0}) + \\ & k_{x22}X_{CL_0}(X_{CL_1} - X_{CL_0})) - k_{x21}X_{CL_0}(Y_{LA_1} - Y_{LA_0}) - \\ & k_{x22}X_{CL_0}(Y_{CL_1} - Y_{CL_0}) + F_{2c}(k_{x11}X_{LA_0}(Y_{LA_1} - Y_{LA_0}) + \\ & k_{x12}X_{LA_0}(Y_{CL_1} - Y_{CL_0}) + k_{x21}X_{CL_0}(Y_{LA_1} - Y_{LA_0}) + \\ & k_{x22}X_{CL_0}(Y_{CL_1} - Y_{CL_0})) \end{aligned}$$

Modelling of Diffusion-Controlled Propagation and Transesterification:

We use an encounter-pair model with rate constants calculated via a semi-empirical approach based on free volume theory, considering two diffusion-controlled termination rate coefficient regimes.

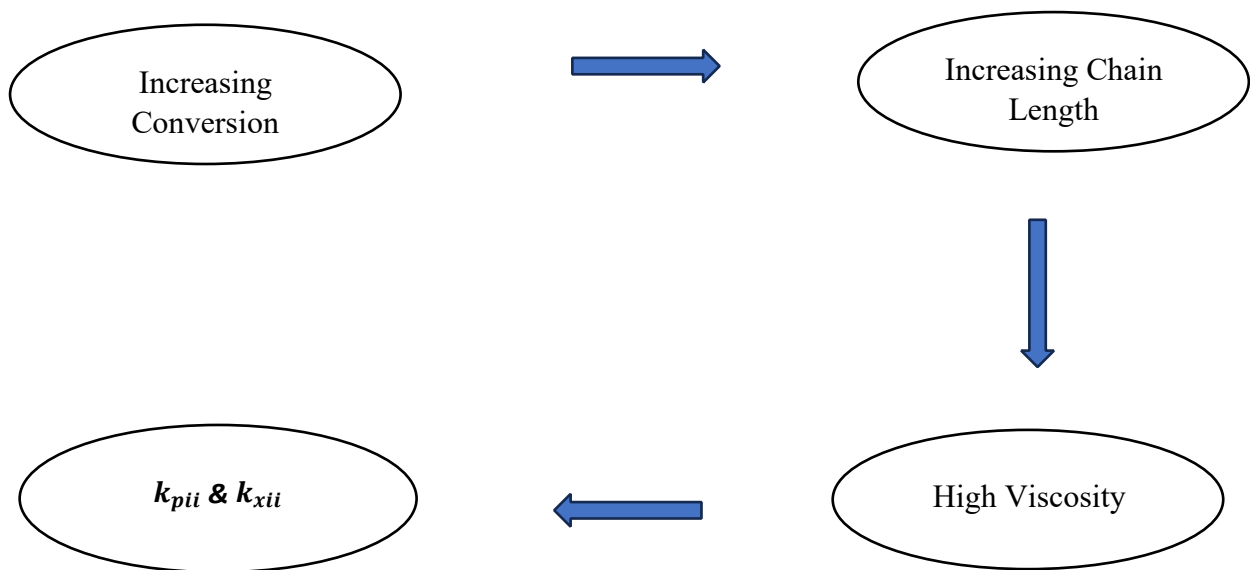
As the reaction progresses to high conversion and the chain length increases, the bulk reaction system tends to become more viscous. This viscosity hinders the rate of reaction by impeding the diffusion of the reacting species. In accordance with a classical encounter-pair model, the rate constants for propagation and transesterification can be expressed as follows.

The following are the equations used in our model:

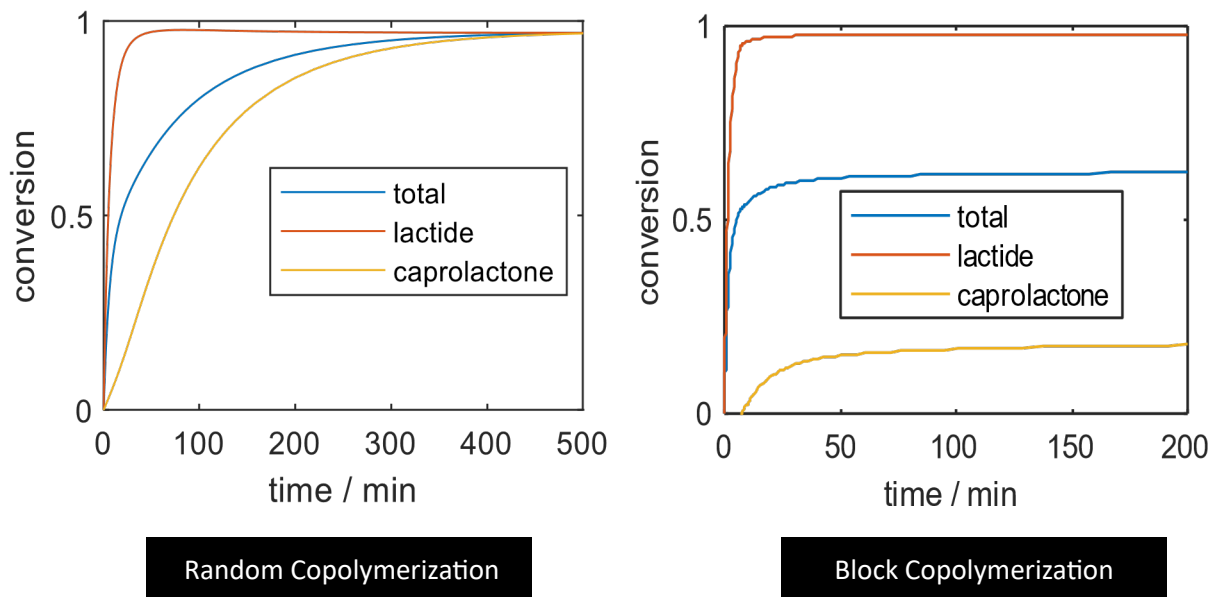
$$\frac{1}{k_{pii}} = \frac{1}{k_{pii,C}} + \frac{1}{k_{pii,D}}$$

$$\frac{1}{k_{xii}} = \frac{1}{k_{xii,C}} + \frac{1}{k_{xii,D}}$$

$$k_{pii} \propto \exp\left(\frac{-1}{v_f}\right), k_{xii} \propto \exp\left(\frac{-1}{v_f}\right)$$



Results and Discussion:



Conversion determines chemical reactivity, mechanical strength, and thermal stability.

In the context of copolymerization of lactones such as Polylactide (PLA) and Polycaprolactone (PCL), conversion refers to the extent to which monomer units have reacted to form the copolymer. The degree of conversion in copolymerization plays a crucial role in determining various properties of the resulting copolymer.

1. Chemical Reactivity:

High Conversion: A high degree of conversion implies that a significant portion of the monomer units have participated in the copolymerization reaction. This generally leads to a more chemically reactive copolymer with a well-defined structure.

Impact on Reactivity Ratios: The reactivity ratios of the monomers (PLA and PCL) influence the composition of the copolymer. High conversion allows for better control over the copolymer composition, affecting its overall chemical reactivity.

2. Mechanical Strength:

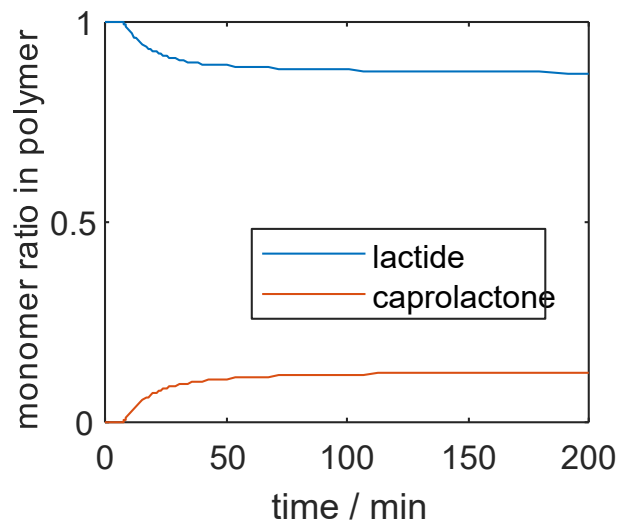
Effect on Molecular Weight and Chain Structure: The degree of conversion influences the molecular weight of the copolymer and the arrangement of polymer chains. Higher conversion often results in longer polymer chains, contributing to improved mechanical strength.

Interplay of PLA and PCL Units: Depending on the conversion, the copolymer will contain varying proportions of PLA and PCL units. The combination of these units in the polymer chain can affect mechanical properties.

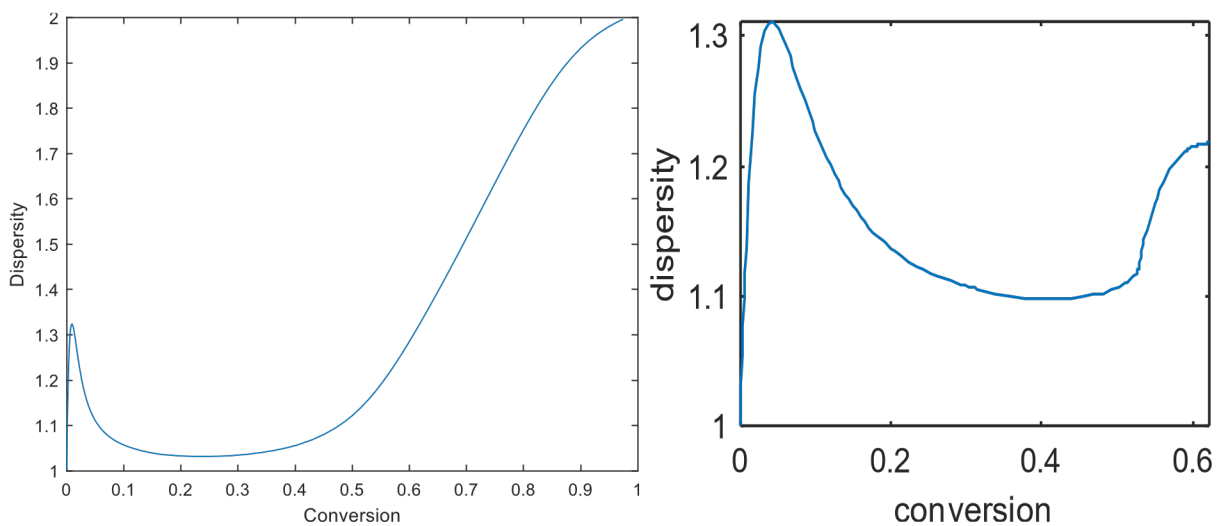
3. Thermal Stability:

Influence on Thermal Properties: The degree of conversion can impact the thermal stability of the copolymer. Higher conversion generally leads to copolymers with enhanced thermal stability due to the formation of a more interconnected and stable polymer network.

Melting and Glass Transition Temperatures: The thermal behavior, including melting and glass transition temperatures, is influenced by the copolymer composition, which is, in turn, influenced by the degree of conversion.



Monomer Ratio with Blocked Copolymerization



Dispersy determines the material consistency and performance.

In the context of copolymerization of lactones like Polylactide (PLA) and Polycaprolactone (PCL), dispersity is a critical parameter that significantly influences the material consistency and performance of the resulting copolymer.

Material Consistency:

Definition of Dispersity: Dispersity, often expressed as the polydispersity index (PDI), is a measure of the distribution of molecular weights within a polymer sample. A low dispersity indicates a narrow molecular weight distribution, suggesting a more consistent and uniform structure.

Impact on Material Homogeneity: In the copolymerization of PLA and PCL, maintaining low dispersity is essential for achieving a homogeneous distribution of monomer units along the polymer chains. This contributes to consistent material properties.

Performance Characteristics:

Polymer Chain Length and Performance: Dispersity directly affects the length of polymer chains in the copolymer. A low dispersity implies that most polymer chains have similar lengths, contributing to consistent and predictable performance characteristics.

Influence on Mechanical Properties: The mechanical properties of copolymers, including tensile strength and elasticity, are influenced by the dispersity. A narrow dispersity often results in copolymers with more predictable and reproducible mechanical performance.

Processing and Application Considerations:

Impact on Processing Stability: Consistent dispersity is crucial for stable processing conditions during the copolymerization reaction. It ensures uniform melting and flow behavior, which is essential for various processing techniques such as extrusion, injection molding, etc.

Predictable Application Performance: Copolymers with low dispersity exhibit more predictable and reliable performance in specific applications. Whether used in biomedical devices, packaging materials, or other applications, a consistent material is essential for meeting performance requirements.

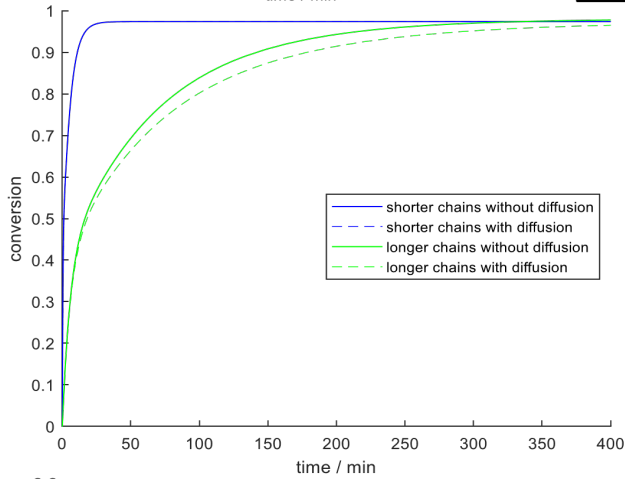
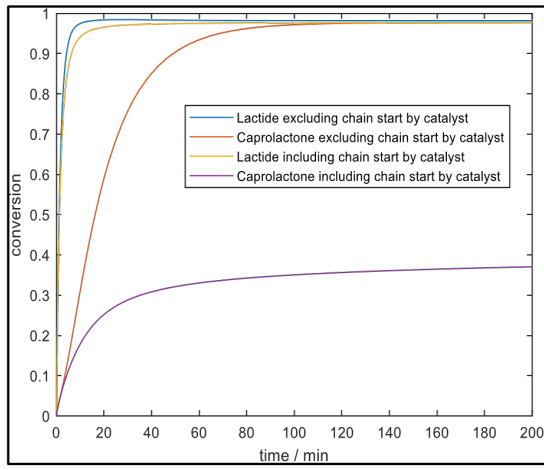
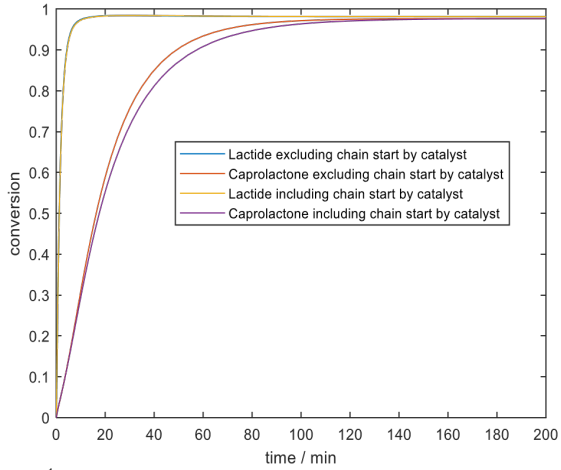
Control over Copolymer Composition:

Influence on Monomer Distribution: Dispersity plays a role in determining the distribution of PLA and PCL units within the copolymer. Low dispersity aids in achieving a well-controlled and defined composition, enabling the tailoring of material properties to meet specific needs. In summary, dispersity is a crucial factor in the copolymerization of PLA and PCL, influencing material consistency and performance. Maintaining low dispersity is key to achieving a uniform structure, predictable mechanical properties, and ensuring that the copolymer meets the desired specifications for various applications. Control over dispersity enhances the reproducibility and reliability of copolymer performance.

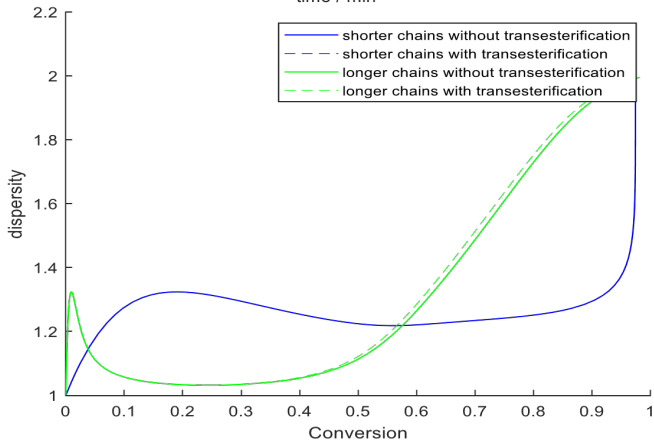
kCM influences the conversion of the Lactide much than that of the Caprolactone

**[50;50;5;1]; % molar ratio of M1:M2:
ROH:C, [kCM1, kCM2 = 1e⁻⁴, 1 e⁻⁴]**

**[50;50;5;1];% molar ratio of M1:M2:
ROH:C, [kCM1, kCM2 = 1e⁻³, 1 e⁻³]**



**Higher Chain Length → Higher
rate of Conversion and Dispersy**



**Ratio 1 = [5;5;1;1]; % molar ratio of
M1:M2:ROH:C**
**Ratio 2 = [100;100;1;1]; % molar ratio of
M1:M2:ROH:C**

Conclusion

A dynamic model is developed to describe the Sn(Oct)₂-catalyzed ring-opening copolymerization of lactic acid (l-LA) and epsilon-caprolactone (e-CL). This model considers monomer conversions and polymer chain characteristics such as molecular weight (M_n), polydispersity index (PDI), and cumulative copolymer composition. The influence of polymer chain length on diffusion control is incorporated into the model. The validity of the model is confirmed through comparison with experimental kinetics data from the literature, specifically for the bulk ring-opening homopolymerization of l-LA or e-CL. The model is employed to simulate the ring-opening copolymerization of l-LA and e-CL at 140°C, considering variations in monomer compositions and chain lengths. Furthermore, the model demonstrates accurate predictions for the kinetics of the ring opening copolymerization of l-LA and e-CL.

The particular results were achievable with the help of Mr. Niclas Conen, Mr. Christoph Kabatnaik and Dr. Andreas Jupke, Chair of Fluid Process Engineering, AVT.FVT RWTH Aachen University.

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