Free Radical Polymerization of Methyl Methacrylate: MATLAB Modeling and Simulation

Abstract

This project involves modeling the batch bulk isothermal polymerization of methyl methacrylate (MMA) using the kinetic model described in the paper 'Free Radical Polymerization of Methyl Methacrylate: Modeling and Simulation by Moment Generating Function'. The simulation will incorporate the gel and glass effects and compare the results obtained by the generating function method and the moment method.

Introduction

Free radical polymerization is a fundamental process in polymer chemistry used to produce various polymeric materials. Methyl methacrylate (MMA) is a commonly used monomer in the production of polymethyl methacrylate (PMMA), a clear plastic used in various applications. This project aims to model the polymerization process of MMA using MATLAB, focusing on the kinetic aspects of the reaction and the effects of gel and glass phenomena.

Objectives

1. To develop a kinetic model for the batch bulk isothermal polymerization of MMA.
2. To implement the model in MATLAB and simulate the polymerization process.
3. To compare the results obtained from the generating function method and the moment method.
4. To analyze the impact of gel and glass effects on the polymerization kinetics and molecular weight distribution.

Methodology

Step 1: Defining the Kinetic Model

The kinetic model for the free radical polymerization of MMA is defined by the following reactions:

1. Initiation:

$$\mathbf{I} \rightarrow \mathbf{2R^*}$$

$$\mathbf{R^* + M} \overset{k_i}{\rightarrow} \mathbf{P_1^*}$$

2. Propagation:

$$\mathbf{P_n^* + M} \overset{k_p}{\rightarrow} \mathbf{P_{n+1}^*}$$

3. Termination by Disproportionation:

$$\mathbf{P_n^* + P_m^*} \overset{k_t}{\rightarrow} \boldsymbol{D_n + D_m}$$

Equations:

- Initiator decay:

$$\frac{\mathbf{d[I]}}{\mathbf{dt}} = \mathbf{-k_d[I]}$$

- Monomer consumption:

$$\frac{\mathbf{d[M]}}{\mathbf{dt}} = \mathbf{-k_i[M][R^*] - k_p[M]} \sum_{\boldsymbol{n=1}}^{\infty} \mathbf{P_n^*}$$

- Radical concentrations:

$$\frac{\mathbf{d[R^*]}}{\mathbf{dt}} = \mathbf{2fk_d[I] - k_i[R^*][M]}$$

$$\frac{\mathbf{d[P_1^*]}}{\mathbf{dt}} = \mathbf{k_i[M][R^*] - k_p[M]P_1^* - k_tP_1^*} \sum_{\boldsymbol{n=1}}^{\infty} \mathbf{P_n^*}$$

$$\frac{\mathbf{d[P_n^*]}}{\mathbf{dt}} = \mathbf{k_p[M][P_{n-1}^*] - k_p[M]P_n^* - k_tP_n^*} \sum_{\boldsymbol{n=1}}^{\infty} \mathbf{P_n^*}$$

Incorporate gel and glass effects using Chiu's relations:

$$\mathbf{k_t} = \mathbf{k_{t^0}} \frac{\mathbf{C}}{\mathbf{C} + \boldsymbol{\theta_t} \mathbf{k_{t^0}} \mathbf{H(1,t)}}$$

$$\mathbf{k_p} = \mathbf{k_{p^0}} \frac{\mathbf{C}}{\mathbf{C} + \boldsymbol{\theta_p} \mathbf{k_{p^0}} \mathbf{H(1,t)}}$$

$$\mathbf{H(1,t)} = \sum_{n=1}^{\infty} \mathbf{P_n}$$

Parameters Description

- **[I]**: Initiator concentration
- **[M]**: Monomer concentration
- **[R*]**: Radical concentration
- **[P_n]**: Concentration of polymer radicals with n units of monomer
- **[D_n]**: Concentration of dead polymer with n units of monomer
- **K_d**: Rate constant for initiator decay
- **K_p**: Rate constant for monomer propagation
- **K_t**: Rate constant for termination by disproportionation
- **f**: Initiator efficiency factor
- **H(1,t)**: Generating function of the polymer active species
- **C**: Constant related to monomer conversion
- **θ_t , θ_p**: Parameters related to gel and glass effects

Step 2: Developing the MATLAB Code

Develop MATLAB code to implement the differential equations using MATLAB's ODE solvers. The code should simulate the polymerization process and plot relevant parameters such as monomer conversion and molecular weight distribution.

Expected Plots:

1. Monomer concentration vs. Time
2. Instantaneous numeric and gravimetric molecular weights vs. Monomer conversion
3. Cumulative molecular weights vs. Monomer conversion

Step 3: Comparing Methods

Implement both the generating function method and the moment method in MATLAB. Compare the results obtained from both methods in terms of accuracy and computational efficiency.

Results and Discussion

1. Monomer Conversion:

- The monomer conversion curve should show how quickly the monomer is consumed during the polymerization process.

2. Molecular Weight Distribution:

- The molecular weight distribution plots should illustrate the impact of gel and glass effects on the growth of polymer chains.

3. Comparison of Methods:

- Discuss the similarities and differences in the results obtained from the generating function method and the moment method.

Conclusion

This project provides a comprehensive analysis of the free radical polymerization of MMA, highlighting the importance of kinetic modeling in understanding polymerization processes. The MATLAB implementation successfully simulates the polymerization process, allowing for a detailed comparison of different modeling methods.

References

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