



Modelling and determination of kinetic parameters for the free radical homopolymerization of α -Pinene

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Abstract

The process of homopolymerization of α -Pinene was studied. The main goal was to determine the kinetic data of the polymerization reaction utilizing the Method of Moments to model it as a free radical polymerization (FRP) process using AIBN as initiator. Experimental data obtained by another study was used to validate the model proposed by this research. As to replicate the same conditions of the laboratory experiment, this model reproduces conversion data as a function of time elapsed for the homopolymerization reaction of α -Pinene at 60 °C and 2% in weight of initiator. The kinetic constants obtained produce conversion values that vary from the experimental data up to a max of 5% for the first 10 h.

Key words:

α -Pinene, Homopolymerization, Kinetic simulation

Introduction

Pinene, a substance that can be found mostly in coniferous plants, such as the pine, can be used as a monomer for plastics and so can be a substitute for other plastics from fossil sources, diminishing the demand for oil in the plastic industry, and can be used for a variety of applications. Due to environmental concerns, the study of plastics made from renewable sources is vital for a more sustainable future.

The present work aims at modelling the process of polymerization of α -Pinene to further enrich the understanding of renewable sources plastics.

Results and Discussion

The reaction process was modeled as a Free Radical Polymerization, using the Method of Moments as a tool to determinate the kinetic constants. The equations used to simulate the reaction are the ones already proposed for FRP's (Mastan and Zhu, 2015).

The equations also rely on kinetic constants for each specific reaction, which were the aim of this work. This model is valid for the homopolymerization of α -Pinene at 60 °C at the initial concentration of 5 mol/L and Azobisisobutyronitrile (AIBN) as initiator at initial concentration of 2% in weight.

The first constant to be determined was the rate constant of initiator decomposition k_d . For this, the data available in the product sheet of a commercial seller of AIBN² was used. Plugging these data and temperature in the Arrhenius Equation the value obtained for the constant was $k_d=1.08E-5 \text{ s}^{-1}$.

In order to determinate the rate constant for monomer propagation k_p , for radical termination by combination k_{tc} and for radical termination by disproportionation k_{td} , experimental data obtained previously (Ramos et al., 1998) was used to verify the effectiveness of the model proposed. The value for the initiator efficiency f adopted was 0.5 as a typical value and the full termination constant k_t was determined by the sum of k_{td} and k_{tc} .

In order to best fit the model results to the experimental data a logarithmic trendline was generated to extrapolate conversion values.

With aid of Euler's method for solving the set of eight equations proposed simultaneously, multiple values for k_p , k_{tc} and k_{td} were tested in a smaller range of time

values to reduce computing usage and then compared to the trendline to verify the results compatibility. If the results did not fit, a new attempt was made, adjusting the values of the constants to improve the results by trial and error.

A model that followed the experimental reaction curve was obtained for $k_p=43 \text{ L/(mol.s)}$, $k_{tc}=1.02E+7 \text{ L/(mol.s)}$ and $k_{td}=1.02E+7 \text{ L/(mol.s)}$. These values were then used with aid of a Fourth Order Runge-Kutta numeric method to solve the set of equations simultaneously. The results of this simulation are presented in Image 1.

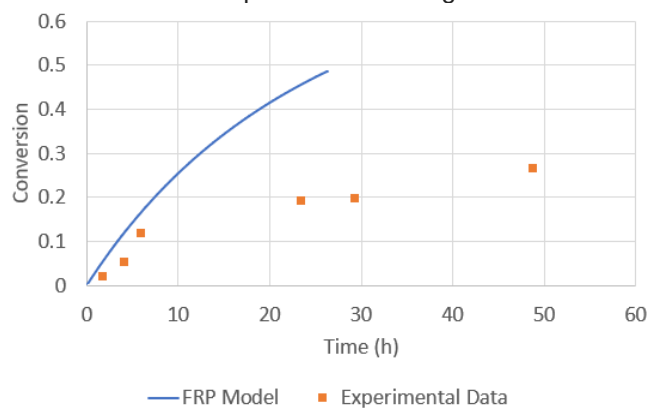


Image 1. Results of FRP modelling for the homopolymerization reaction compared to experimental data.

Conclusions

The model proposed fitted the experimental data obtained by Ramos³ for the same reaction with a margin of less than 5% for the conversion in the first 10 hours of reaction. This way, it is possible to assume that the values for the kinetic rate constants found can be used to describe the conversion behavior of the reaction with time not greater than 10 h in these same conditions.

¹ Mastan, M. e Zhu, S. Method of moments: A versatile tool for deterministic modeling of polymerization kinetics. Eur. Polym. J. **2015**, 68, 139-160.

² Perkadox® AIBN; Product Data Sheet; Akzo Nobel Polymer Chemistry, November, 2018.

³ Ramos, A. M., Lobo, L. S. e Bordado, J. M. Polymers from pine gum components: Radical and coordination homo and copolymerization of pinenes. Wiley Polym. Networks Group Rev. Ser. **1998**, 127, 43-50.