MODELING OF HIGH-CIS 1,3-BUTADIENE POLYMERIZATIONS WITH NEODYMIUM VERSATATE

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RESUMO – The present work addresses the modeling and simulation of the solution polymerization of 1,3-butadiene, initiated by neodymium versatate. A kinetic model was proposed to predict the pressure and temperature profiles, as well as cis-1,4 and trans-1,4 contents of the produced elastomer. The model fitted well the available experimental data within the experimental errors.

1. INTRODUCTION

The synthetic rubber industry has been developing and investing in the manufacture of new elastomers and vulcanized compounds. The production of high cis-polybutadiene has been the subject of several scientific studies throughout the last decades for the tire industry. Polybutadiene or butadiene rubber (BR) is the second most produced rubber worldwide and 70% of this production is for the tire industry (Friebe et al. 2006). Among the catalytic complexes, the majority of studies presented in literature were based on cobalt, nickel, titanium and neodymium (Friebe et al. 2002).

Ziegler-Natta catalysts for polymerization of conjugated dienes have been developed with lanthanide metals, since lanthanide atoms are bigger and less electronegative than other transition metals. Work in this field is concentrated on neodymium-based catalysts, because this element has the biggest catalyst activity among the lanthanide metals (Kobayashi et al. 1998; Fraga et al. 2003). However, to the best of our knowledge, there is scarce information about the mathematical modeling of polybutadiene reactions performed with neodymium catalysts. Based on this, the present study proposes a kinetic model for the polymerization of 1,3-butadiene, the simulation of reaction conditions and estimation of unknown model parameters using real experimental data.

2. MATERIALS AND METHODS

2.1. Catalyst Synthesis
The catalysts were prepared in sealed and dried glass bottles. Diisobutylaluminum hydride (DIBAH), neodymium versatate (NdV) and tert-butyl chloride were added under agitation. The catalyst was synthesized in the following conditions: Al/Nd=10, Cl/Nd=1 and temperature below 10°C. The synthesis was accomplished after 5 hours and then the catalyst was aged for 1 day.

2.2. Polymerization Experiments

Polymerization experiments were carried out in a 1 L stainless steel reactor for 90 minutes under 2 to 3 bar of pressure. The reactor was filled with dry solvent and 1,3-butadiene and heated to 70 °C. Then the catalyst based on neodymium was added and the polymerization was started. After that, the polymerization was poured into 100 mL ethanol containing antioxidant.

3. MODEL DEVELOPMENT

The kinetic mechanism proposed to describe polymerizations comprises the following fundamental steps: initiation, propagation, chain transfer and formation of long chain-branching. This mechanism was based in past works published by Cousteux et al. (2002), Ferreira Jr. et al. (2010), Mehdiabadi et al. (2008). According to the proposed kinetic mechanism, it is possible to write the molar balance equations for the components present in the polymerization process.

\[
\frac{dc_{\text{cat}}^*}{dt} = -\left(k_{\text{cis}} + k_{\text{trans}}\right)\left(\frac{M}{V}\right)\left(\frac{c_{\text{cat}}}{V}\right)V + k_d\left(\sum_{i=1}^{\infty} \frac{p_i^*}{V}\right)V
\]

\[
\frac{dM}{dt} = -\left[k_{\text{cis}} + k_{\text{trans}}\right]\left(\frac{c_{\text{cat}}}{V}\right) + \left[k_{p_{\text{cis}}} + k_{p_{\text{trans}}}\right]\left(\sum_{i=1}^{\infty} \frac{p_i^*}{V}\right)\left(\frac{M}{V}\right)V
\]

\[
\frac{dp_i^*}{dt} = \left[k_{p_{\text{cis}}} + k_{p_{\text{trans}}}\right]\left(\frac{c_{\text{cat}}}{V}\right) - \left[k_{p_{\text{cis}}} + k_{p_{\text{trans}}}\right]\left(\frac{p_i^*}{V}\right)\left(\frac{M}{V}\right)V - k_d\left(\frac{p_i^*}{V}\right)V - k_b\left(\frac{p_i^*}{V}\right)\left[\sum_{j=1}^{\infty} \frac{Q_j}{V}\right]V
\]

\[
\frac{dq_i^*}{dt} = k_d\left(\frac{p_i^*}{V}\right)V
\]

\[
\frac{dq_i}{dt} = -k_b\left(\frac{Q_i}{V}\right)\left(\sum_{j=1}^{\infty} \frac{p_j^*}{V}\right)V
\]

\[
\frac{db}{dt} = 2k_b\left[\sum_{j=1}^{\infty} j \left(\frac{Q_j}{V}\right)\right]\left(\sum_{i=1}^{\infty} \frac{p_i^*}{V}\right)V
\]

\[
\frac{dc_{\text{cis}}}{dt} = k_{p_{\text{cis}}}\left(\sum_{i=1}^{\infty} \frac{p_i^*}{V}\right)\left(\frac{M}{V}\right)V + k_{1_{\text{cis}}}\left(\frac{c_{\text{cat}}}{V}\right)\left(\frac{M}{V}\right)V
\]
\[
\frac{d\text{trans}}{dt} = k_{p\text{trans}} \left( \sum_{i=1}^{\infty} \frac{P_i^*}{V} \right) \left( \frac{M}{V} \right) V + k_{1\text{trans}} \left( \frac{\text{Cat}^*}{V} \right) \left( \frac{M}{V} \right) V
\]

where \( M \) is monomer 1,4-butadiene, \( \text{Cat}^* \) is the activated catalyst, \( b \) is the number of pendant double bonds, \( \text{cis} \) and \( \text{trans} \) are the amount of \( \text{cis} \) and \( \text{trans} \) content respectively, \( V \) is the medium volume, \( P_i^* \) is the living polymer chain with length \( i \), \( Q_j \) is a dead polymer chain with length \( i \) and, finally, \( Q_i^\ominus \) is a dead polymer chain with length \( i \) and with a terminal unsaturation, \( k_{1\text{cis}} \) is the kinetic constant for the formation of the \( \text{cis} \) content, \( k_{1\text{trans}} \) is the kinetic constant for the formation of the \( \text{trans} \) content, \( k_{p\text{cis}} \) is the kinetic constant for propagation of the \( \text{cis} \) content, \( k_{p\text{trans}} \) is the kinetic constant for the propagation of the \( \text{trans} \) content, \( k_b \) is the kinetic constant for the reincorporation by internal unsaturation and \( k_d \) is the kinetic constant for the spontaneous transfer. Since the number of differential equation for living and dead polymer chains is extremely high, the numerical resolution becomes unfeasible without the use of appropriate numerical approximations. For this reason, the method of moments was adopted (Hulburt et al. 1964) to simplify the ODE system, reducing the final number of ODE’s to less than twenty.

4. RESULTS AND DISCUSSION

The 1,3-butadiene reactions attained yields above 80% (m/m) and produced high \( \text{cis} \)-polybutadiene, with more than 96% of \( \text{cis} \)-1,4 content, which is in good agreement with literature (Mello et al. 2008). Polymerization model equations were implemented in FORTRAN. All balance equations were solved numerically using backward differentiation formula (BDF) as available in the DASSL code with relative and absolute tolerances of \( 10^{-4} \) (Petzold 1982). Figure 1 shows the simulation results and experimental data used for butadiene system. Monomer conversions and average molecular weights are not shown for lack of space, but calculated and experimental results agreed fairly well, as expected from available temperature and pressure profiles.

![Figure 1 – Pressure (1.A) and Temperature (1.B) profiles (ED: Experimental Data; MD: Model Data)](image)

Table 1 – Model Parameters Used in the Simulation

| Parameter | Value | Parameter | Value | Parameter | Value |
|-----------|-------|-----------|-------|-----------|-------|
| \( k_{1\text{cis}} \) | 0.0641 | \( k_{p\text{cis}} \) | 369.6 | \( k_d \) | 0.035 |
4. CONCLUSION

The performed 1,3-butadiene polymerizations achieved high cis-polybutadienes, with more than 96% of cis-1,4 content, which is in good agreement with literature. A kinetic model was proposed for the 1,3-butadiene polymerization and the simulated temperature and pressure profiles were very close to the available experimental data. Therefore, it was shown that pressure and temperature profiles can be simulated confidently by using the proposed model. Average molecular weights and monomer conversions can also be predicted with the current model after parameter estimation.

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