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Computational and Experimental Investigation of Free Radical Polymerization of Styrene using a Multifunctional Initiator

[1]P.F.M.P.B. Machado, L. M. F. Lona
[1]School of Chemical Engineering, University of Campinas, UNICAMP, P.O. Box 6066, 13083-970, Campinas-SP, Brazil; tel.(fax) +55 19 35213914, e-mail: pmachado@feq.unicamp.br;
School of Chemical Engineering, State University of Campinas, UNICAMP, P.O. Box 6066, 13083-970, Campinas-SP, Brazil; tel. +55 19 35213954, e-mail: liliane@feq.unicamp.br

Lately, the study of peroxides multifunctional initiators has been explored in the scientific and industrial field. These initiators are able to increase the reaction rate in a free radical polymerization without decrease the molecular weight of the formed polymer. Besides that they can also generate branches in the polymeric chain, changing the polymer structure.

1. Introduction

Some works in literature show experimental and simulation studies related to free radical polymerization using bifunctional initiators. Machado and Lona (2005) present mathematical models to free radical polymerization of linear (polystyrene) and branched (polyvinyl acetate) polymer using bifunctional initiators.
The complexity of the kinetic mechanism increases as the functionality of the initiator increases. There are very few studies presenting models of free radical polymerization using initiators with functionality superior than two (Scorah, 2005 and Scorah et al., 2007).
To better understand the behavior of multifunctional initiators, trifunctional initiators were chosen to be studied as the next steps of a free radical polymerization using bifunctional initiator.
The trifunctional initiator selected was the TRIGONOX 301 (T301) from Akzo Nobel. It is a cyclic triperoxide and very unstable at temperatures greater than 40ºC. It must be kept at room temperature.
The objective of this study was to propose a kinetic mechanism and a mathematical model to free radical polymerization of styrene using a trifunctional initiator. Styrene was chosen because it is a very well known monomer and there are a lot of data about it. The mathematical model was built in Fortran 90 and predicts results as conversion, molecular weight and PDI. An experimental investigation was also explored to validate the simulations results. The experimental part followed the method of polymerization in ampoules. The validation was made to conversion and molecular weight.

1.1 Trifunctional Initiator

Figure 1 shows the structure of T301 and the first radical that is formed in the very beginning of the polymerization reaction.

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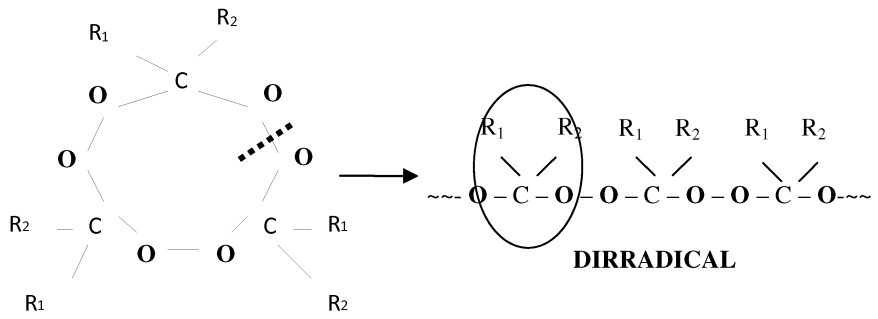

Figure 1: Structure of Trigonox 301 (Akzo Nobel).

2. Experiment Procedure

The experimental procedure followed the polymerization in ampoules.
Styrene was first washed with NaOH solution and deionized water. Then it was dried with $CaCl_2$.
The washed styrene was destilated using a vertical rotative evaporator equipped with vacuum compressor and a hot bath.
After that determined quantities of the solution initiator-monomer were transferred to ampoules. They were all sealed after the elimination of oxygen and put in a bath oil at a desirable temperature.
In determined intervals of time, each ampoule was removed from the bath, cooled and weighted. Then the ampoule was broken and the solution polymer + monomer + initiator was dissolved in tetrahydrofuran (THF) and then the polymer was precipitated with ethanol. After ethanol had evaporated, the sample of polymer went to a dryer to assure that all solvent evaporated. After this, the dried samples were weighted, and conversion was calculated based on differences of masses (gravimetry). Finally, the polymer was dissolved in THF and characterized by GPC ("Gel Permeation Chromatography") analysis, providing molecular weights data. These results brought elements to understand the behavior of trifunctional initiator in the production of polystyrene, once they have provided data to validate the mathematical model and to estimate parameters.

3. Modelling and Simulation

The mathematical model was based on the kinectic mechanism of the reaction presented below and was built using the Method of Moments.

$$I_3 \xrightarrow{3kd_1} \tilde{\tilde{R}}_{in}^{**} \xrightarrow{2kd_1} R_{in}^{**} + \tilde{R}_{in}^{**} \quad (1)$$

Initiation

$$\tilde{R}_{in}^{**} + M + M \xrightarrow{k_2} \tilde{R}_1^{**} \quad (2)$$
$$R_{in}^{**} + M + M \xrightarrow{K_1} R_1^{**}$$

$$\tilde{P}_r \xrightarrow{kd_2} R_r^{**} \quad (3)$$

$$\tilde{\tilde{P}}_r \xrightarrow{2kd_2} \tilde{R}_r^{**} \quad (4)$$

Propagation

$$\tilde{R}_r^{**} + M + M \xrightarrow{k_p} \tilde{R}_{r+1}^{**}$$
$$R_r^{**} + M + M \xrightarrow{K_p} R_{r+1}^{**} \quad (5)$$

Termination

$$R_r^{**} + R_s^{**} \xrightarrow{k_{tc}} P_{r+s} \quad (6)$$

$$R_r^{**} + \tilde{R}_s^{**} \xrightarrow{k_{tc}} \tilde{P}_{r+s} \quad (7)$$

$$\tilde{R}_r^{**} + \tilde{R}_s^{**} \xrightarrow{k_{tc}} \tilde{\tilde{P}}_{r+s} \quad (8)$$

Transfer to Monomer

$$\tilde{R}_r^{**} + 2M \xrightarrow{k_{tfm}} \tilde{P}_r + R_1^{**} \quad (9)$$

$$R_r^{**} + 2M \xrightarrow{K_{tfm}} P_r + R_1^{**} \quad (10)$$

All species that are present in the polymerization reaction are present here in this mechanism.

4. Results and Discussion

The results from experimental part and computational part are shown below in Figures 2 to 3. The experimental data is used to validate predicted results from the model.

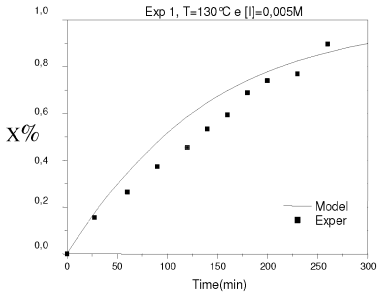

Figure 2. Conversion x Time.

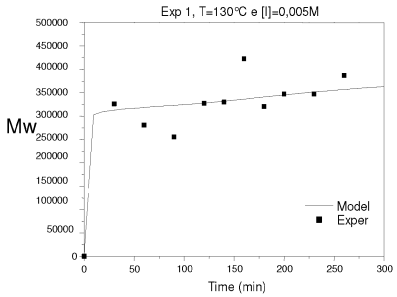

Figure 3. Weight Average Molecular Weight x Time.

The results above were obtained from Experiment 1, working in temperature of 130°C and initiator concentration of 0,005M.

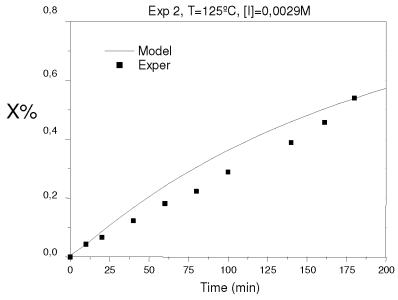

Figure 4. Conversion x Time.

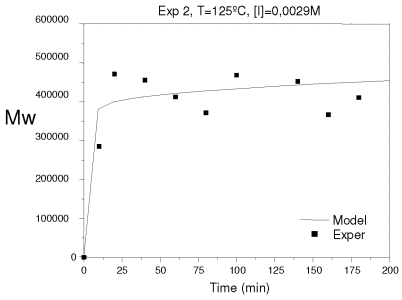

Figure 5. Weight Average Molecular Weight x Time.

The results above were obtained from Experiment 2, working in temperature of 125°C and initiator concentration of 0,0029M.

It is possible to verify from Figures 2 to 5 that the model predictions presented agreement with the experimental data. Since the model was validated, it was possible to explore it using different operating conditions providing a study of effects of temperature and initiator concentration on the reaction rate and proprieties of the polymer. Figures 6 and 7 show these effects.

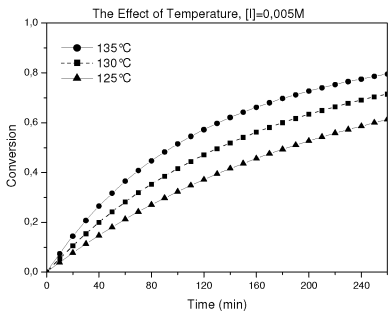

Figure 6. Conversion x Time.

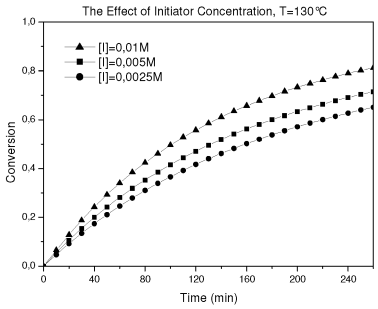

Figure 7. Conversion x Time.

It is possible to verify in Figure 6 that conversion increases as the temperature increases. That is expected since an increasing in temperature increases the reaction rate generating more radicals to consume the molecules of monomer. Figure 7 shows that an increasing in initiator concentration is also very important to achieve a faster conversion. And that was also expected, since a large quantity of initiator implies in a large quantity of consumed monomer. Another important analysis of these effects is related to Molecular Weights. They are not presented here yet because they are yet been studied.

5. Conclusion

Results from model simulation of styrene polymerization using trifunctional initiator TRIGONOX 301 showed agreement with experimental data. These results from simulation are new, since there are few researches published about this subject. The existent models are very few and they are not based in the Method of Moments. So far it was possible to verify some aspects of the behavior of a trifunctional initiator through the study of the effects of temperature and initiator concentration. This study will be explored also evaluating the behavior of the molecular weights in further analysis.

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