

Development of a Software to Simulate Free Radical Polymerization of Linear and Branched Polymer Using Mono- and Bi- Functional Initiators

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Abstract

Monofunctional initiators are extensively utilized in free radical polymerization. In order to enhance productivity, usually higher temperature is used, however this leads to lower molecular weights. Bifunctional initiators increase the polymerization rate without decreasing the average molecular weight and this can be desirable. Bifunctional initiator is an important issue to be investigated and it is of great interest to industries. The objective of this work was to develop comprehensive mathematical models to simulate polymerization reactors with mono- and bi-functional initiators, using monomers that will produce linear and branched polymers. Polystyrene as linear polymer and poly(vinyl acetate) as branched polymer were considered. Models prediction showed good agreements with experimental data from literature and brought new information about vinyl acetate polymerization using bifunctional initiator.

Keywords: models, simulation, polymerization, bifunctional initiators

1. Introduction

Peroxides monofunctional initiators are extensively utilized in the production of various polymers as can be seen in Gao and Penlidis (1996) and industrial initiators catalogues. This kind of initiator produces two free radicals for each decomposed molecule of initiator. In order to enhance productivity, usually higher temperature or higher initiator concentration is used. However both alternatives lead to lower molecular weights. In order to obtain both high molecular weight and high productivity, bifunctional initiators can be used. Such initiators are decomposed into three fragments: one of them, called dirradical, has two free radicals (one at each end). It allows the chain to grow in both sides of the fragment, thus increasing the reaction rate with no decrease in molecular weight. Studies with polystyrene using mono- and bi-functional initiators are usually found, but studies with poly(vinyl acetate) do not exist. Researches in the development and evaluation of bifunctional peroxides using styrene can be seen in open literature. Polystyrene is usually utilized because it is a linear polymer with no branches (no chain transfer to polymer reaction), simplifying the kinetic mechanism. The effect of bi-

functional initiator to different monomers besides styrene, especially the ones that produce long chain branches, is an important issue to be researched due to their kinetic mechanism complexity.

The objective of this work was to develop comprehensive mathematical models to simulate polymerization reactors with mono- and bi-functional initiators, using monomers that produce linear and branched polymers. Simulation results were compared to experimental data in order to validate the models proposed.

2. Methods

The developed software is composed of four models: Program LINMONO, LINDIFUN, BRANMONO and BRANDIFUN. They simulate the production of linear and branched polymer using both mono- and bi-functional initiators. Fortran was used as environment and the integration methods used were Runge-Kutta for mono-functional initiators and Gear's method for bifunctional initiators. For this last case, Gear's method was used because a problem of stiffness was found using Runge-Kutta.

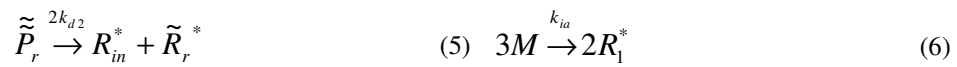
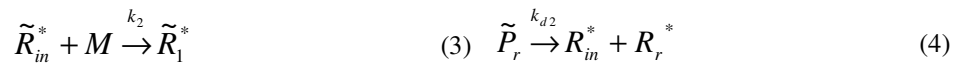
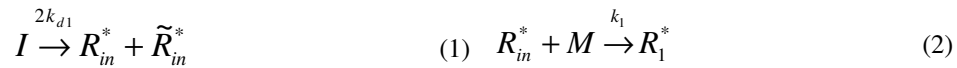
The software allows us to verify Molecular Weight and Conversion over polymerization time.

The mathematical models of these programs were based on mass balance equations for each specie in the reaction (monomer, initiator, solvent, CTA, etc) and method of Moments for live polymer and dead polymer that were developed through reaction mechanisms. These equations can be seen in Machado (2004).

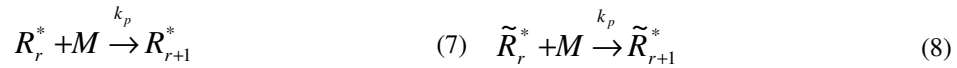
The reaction mechanism using monofunctional initiator is well known and it is found in many published articles and works (Benbachir and Benjelloun., 2001; Machado, 2004). Because of this, here it is presented just the reaction mechanism using bifunctional initiators.

2.1 Bifunctional Initiators

2.1.1 Initiation

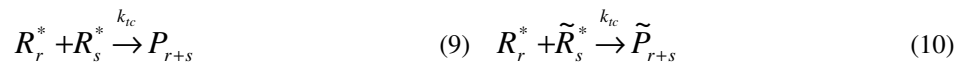


2.1.2 Propagation



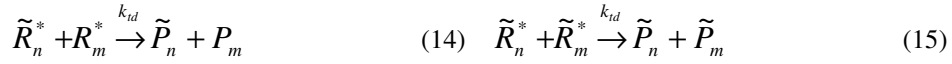
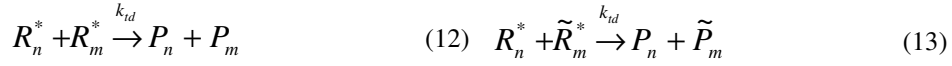
2.1.3 Termination

Combination

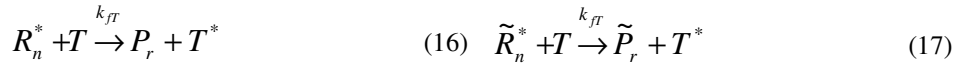




Desproportionation



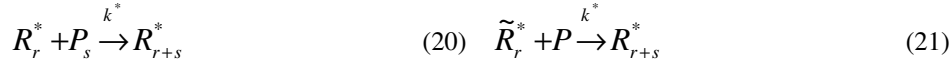
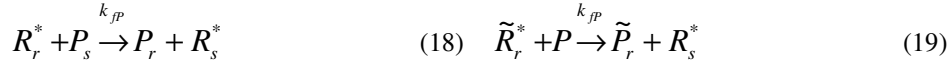
2.1.4 Chain Transfer to Small Molecules



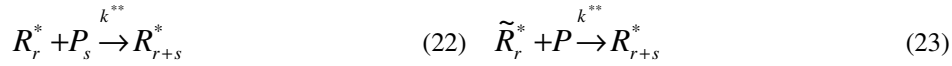
T = initiator, solvent, CTA, inhibitor or impurity

2.1.5 Chain Transfer to Polymer

Long Chain Branch



internal radical, LCB trifunctional



crosslinking, tetrafunctional branch

3. Research Results

3.1 Linear Polymer Simulation

Figures 1 to 5 show the results from the simulation of styrene polymerization using BPO as monofunctional initiator and D162 and L256 as bifunctional initiators. BPO was chosen because it is well known and studied initiator as can be seen in Dhib et al. (2000) and usually utilized in styrene polymerization. Figures 4 and 5 show some validation plots to the model. These results show that models prediction presented good agreements with experimental data from literature (Dhib et al, 2000).

D162 and L256 were chosen because first D162 is the most suited as a substitute for BPO and second L256 and BPO have similar half life, but L256 has the advantage to accelerate the reaction and obtain high molecular weights (Dhib et al., 2000). Figure 1 presents the profiles of the three initiators dissociation constant rate (kd) versus temperature. L256 dissociates faster than BPO and D162. Figure 2 presents the monomer conversions profiles using the three initiators. Comparing the BPO and L256 profiles, it is observed that L256 conversion is faster than BPO conversion, as observed

also in Dhib et al. (2000). This can be explained by the fact that L256 generates more free radicals compared to BPO. Comparing the D162 and BPO profiles, it is observed that they are very similar. Despite of D162 generates four primary radicals (one dirradical and two monorradicals and BPO generates two primary radicals (two monorradicals), BPO has higher dissociation constant rate (higher k_d) at 90°C (see Figure 1). This promotes a higher propagation rate and, as result, similar profiles.

Figure 3 presents the weight average molecular weight profiles obtained using the three initiators: BPO, D162 and L256. BPO and D162 profiles are very close. This behavior was observed in Dhib et al. (2000), as well in their experimental data.

Comparing BPO and L256 profiles, it is observed that L256 presents the highest molecular weight despite of the fact of having the highest conversions (see Figure 2), Here it is observed clearly the effect of two radicals in the same initiator fragment (chain growth in both sides of the fragment, increasing simultaneously the molecular weight and the reaction rate).

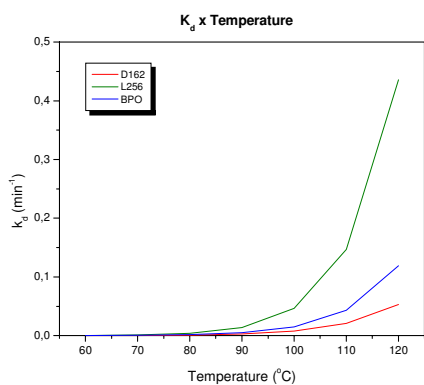


Figure 1. $k_d \times T$

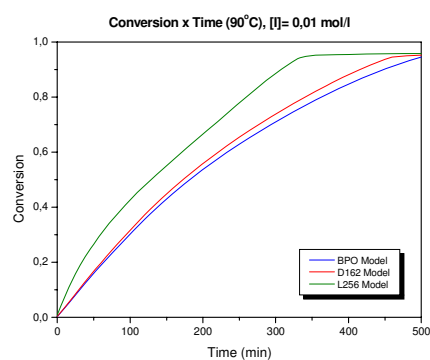


Figure 2. Conversion x Time

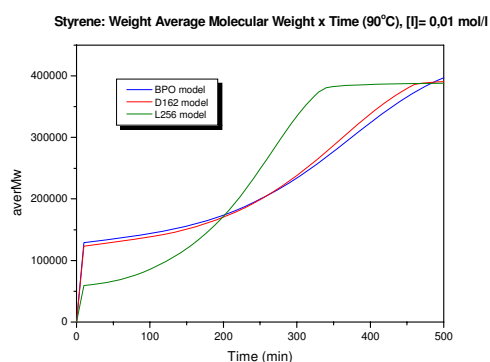


Figure 3. $averMw \times Time$

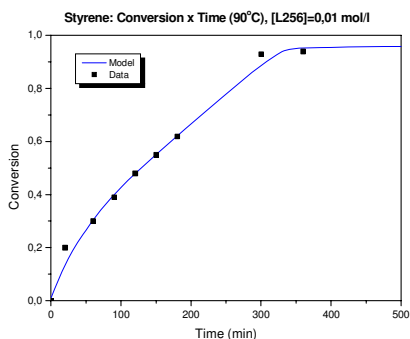


Figure 4. Mn and Mw x T

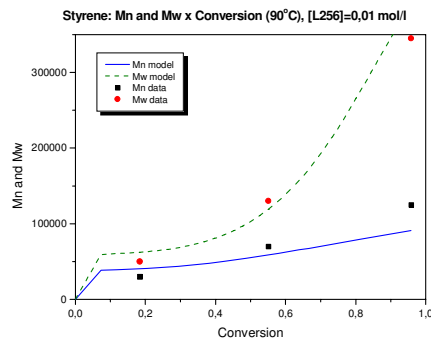


Figure 5. Conversion x Time

3.2 Branched Polymer Simulation

Figures 6 and 7 show the results from the simulation of vinyl acetate polymerization using BPO as monofunctional initiator and, D162 and L256 as bifunctional initiators. The results of this section are very new and there is no data in literature to validate the models. The discussions will be done based on the results obtained from styrene polymerization (section 3.1). Figure 6 presents the monomer conversions profiles using the three initiators. Comparing the BPO and L256 profiles, it is observed that L256 conversion is faster than BPO conversion. Comparing the D162 and BPO profiles, it is observed that they are very similar. The same behavior was observed in styrene polymerization, however the time of polymerization to vinyl acetate is smaller. Figure 7 presents molecular weight profiles obtained using the three initiators: BPO, D162 and L256. BPO and D162 profiles are very close. This behavior was observed also in styrene polymerization (section 3.1)

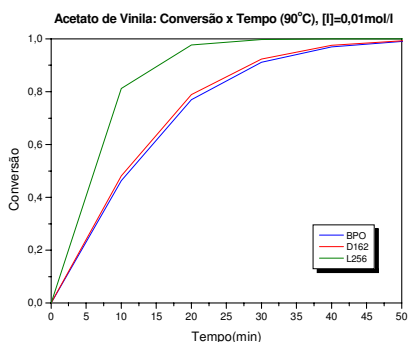


Figure 6. Conversion x Time

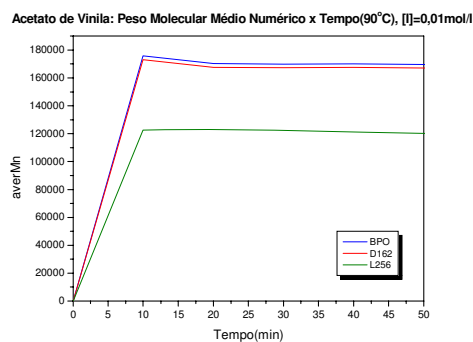


Figure 7. averMn x Time

Comparing BPO and L256 profiles, curiously it is observed that BPO presents the highest number average molecular weight. This behavior was obtained in styrene polymerization as well (not shown), in which the results could be validate with Dhib et al. (2000) experimental data. The average Mn is given by the polymer mass divided by

the number of initiated chains. So, to bifunctional initiator the number of chains is higher (three chains, one of them being a dirradical, compared to two chains for the monofunctional initiator), so average M_n will be smaller. This is also accentuated to L256, because it presents a higher k_d compared to BPO and D162, at 90°C.

4. New Aspects

This is a very important study using modeling and simulation, since studies with bifunctional initiators and branched polymers are a new issue and there is neither model nor experimental data that could provide a good understanding of their behavior.

5. Conclusion

Results from simulation of styrene polymerization using monofunctional initiator, BPO, and bifunctional initiators, D162 and L256, showed good agreement with experimental data from literature, showing that the models are good tools to estimate the behavior of this polymerization using these types of initiators.

Results from simulation of vinyl acetate polymerization using the three initiators are new, since there is no research nor published articles about this subject. There is no data to validate or to compare models results. In this work, it was just presented a discussion based on data obtained in styrene polymerization. In the future, an experimental research will be done to complement this work, to better understand these polymerization reactions and to validate the results obtained from styrene and vinyl acetate polymerization using mono and bifunctional initiators.

References

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