CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci
Copyright © 2007, AIDIC Servizi S.r.l., ISBN 978-88-95608-00-6

Investigation of Free Radical Polymerization of Using Bifunctional Initiators

Paula Machado[1], Cilene Franco[2], Liliane Lona[3],
[1,2,3] Dep. de Processos Químicos - Fac. de Engenharia Química – UNICAMP
Cidade Universitária "Zeferino Vaz"; Distrito Barão Geraldo – CEP: 13083-970
Campinas – SP – Brasil
pmachado@feq.unicamp.br, liliane@feq.unicamp.br

Peroxides monofunctional initiators are extensively used in industries. 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 are used. However both alternatives lead to lower molecular weights. Researches in the development and evaluation of bifunctional peroxides using styrene can be seen in open literature. The effect of bifunctional initiator to different monomers besides styrene, especially the ones that produce long chain branches, is an important issue to be researched. The objective of this work was to investigate free radical polymerization of monomers that produce linear and branched polymers using bifunctional initiators. Polyvinyl acetate was considered as branched polymer. Simulation results were compared with experimental data in order to validate the models proposed in this work.

1. Introduction

Nowadays, in the polymer industry, the advantage of using bifunctional initiators is to obtain at same time high molecular weight and high polymerization rate, which makes the utilization of bifunctional initiator a promising strategy of great industrial interest. In this study experimental and computational investigation of free radical polymerization of styrene (that produces a linear polymer) and vinyl acetate (that produces branched polymer) initiated by diperoxyester initiators has been performed. There is a few works reported in literature using bifunctional initiator to produce linear polymers. All of them use styrene as monomer, which presents termination only by combination and does not have chain transfer reactions in its mechanism. As long as we know, there is no research reported in literature using bifunctional initiators to produce branched polymers, as is the case of polymerization of vinyl acetate that presents transfer to monomer and transfer to polymer reactions, which can affect the behavior of bifunctional initiators during the polymerization.

In this work polymerization of vinyl acetate and styrene in ampoules were performed using the bifunctional initiator 1,4-di (t-butyl-carboperoxy) ciclohexane (Luperox 531). The effects of three parameters were analyzed: temperature, concentration and functionality of the initiator. The produced polymer was analyzed in terms of conversion, rate of polymerization, molecular weights and polydispersity.

The mathematical models also developed in this work (Machado 2004; Machado and Lona, 2004; Machado and Lona, 2005) provide simulation results that agree with experimental data obtained in this work.

2. Experimental Part

The mixture of purified monomer and the initiator is introduced in ampoules, where the bulk polymerization will occur. Then, the ampoules are placed in an oil bath at a chosen temperature. At chosen intervals of time one ampoule, at each interval of time, is removed from the oil bath and it is transferred immediately to a becker with ice cubes and then to a bottle with liquid nitrogen to stop the reaction. The content of the ampoule is removed using a solvent. The polymer is dissolved using ethanol and then precipitated using methylene chloride. After the solvent evaporation, the content of the ampoule is placed in a vacuum stove to full evaporation of the solvent and non-reacted monomer. Conversion values are obtained by the gravimetry method. The values of the average molecular weights were obtained through GPC (Gel Permeation Chromatography) analysis.

3. Reaction Mechanism

The reaction mechanisms for the free radical polymerization of styrene and vinyl acetate using bifunctional initiator are summarized below.

3.1 Bifunctional Initiator

Initiation

$$I \xrightarrow{2k_{d1}} R_{in}^* + \tilde{R}_{in}^* \tag{1}$$

$$R_{in}^* + M \xrightarrow{k_1} R_1^* \tag{2}$$

$$\tilde{R}_{in}^* + M \xrightarrow{k_2} \tilde{R}_1^* \tag{3}$$

$$\tilde{P}_r \xrightarrow{k_{d2}} R_{in}^* + R_r^* \tag{4}$$

$$\overset{\approx}{P}_r \xrightarrow{2k_{d2}} R_{in}^* + \tilde{R}_r^* \tag{5}$$

$$3M \xrightarrow{k_{ia}} 2R_1^* \tag{6}$$

Propagation

$$R_r^* + M \xrightarrow{k_p} R_{r+1}^* \tag{7}$$

$$\tilde{R}_r^* + M \xrightarrow{k_p} \tilde{R}_{r+1}^* \tag{8}$$

Termination

Combination

$$R_r^* + R_s^* \xrightarrow{k_{tc}} P_{r+s} \tag{9}$$

$$R_r^* + \widetilde{R}_s^* \xrightarrow{k_{tc}} \widetilde{P}_{r+s} \tag{10}$$

$$\widetilde{R}_r^* + \widetilde{R}_s^* \xrightarrow{k_{tc}} \widetilde{\widetilde{P}}_{r+s} \tag{11}$$

Desproportionation

$$R_n^* + R_m^* \xrightarrow{k_{td}} P_n + P_m \tag{12}$$

$$R_n^* + \widetilde{R}_m^* \xrightarrow{k_{td}} P_n + \widetilde{P}_m \tag{13}$$

$$\widetilde{R}_n^* + R_m^* \xrightarrow{k_{td}} \widetilde{P}_n + P_m \tag{14}$$

$$\widetilde{R}_n^* + \widetilde{R}_m^* \xrightarrow{k_{td}} \widetilde{P}_n + \widetilde{P}_m \tag{15}$$

Chain Transfer to Small Molecules

$$R_n^* + T \xrightarrow{k_{fT}} P_r + T^* \tag{16}$$

$$\widetilde{R}_n^* + T \xrightarrow{k_{fT}} \widetilde{P}_r + T^* \tag{17}$$

T = initiator, solvent, CTA, inhibitor or impurity

Chain Transfer to Polymer

Long Chain Branch

$$R_r^* + P_s \xrightarrow{k_{fP}} P_r + R_s^* \tag{18}$$

$$\widetilde{R}_r^* + P \xrightarrow{k_{fP}} \widetilde{P}_r + R_s^* \tag{19}$$

$$R_r^* + P_s \xrightarrow{k^*} R_{r+s}^* \tag{20}$$

$$\widetilde{R}_r^* + P \xrightarrow{k^*} R_{r+s}^* \tag{21}$$

internal radical, LCB trifunctional

$$R_r^* + P_s \xrightarrow{k^{**}} R_{r+s}^* \tag{22}$$

$$\widetilde{R}_r^* + P \xrightarrow{k^{**}} R_{r+s}^* \tag{23}$$

crosslinking, tetrafunctional branch

4. Model

The model was built in Fortran 90. The equations of the model were developed based in the kinetic mechanism proposed in section 3.1. Mass balance for all species in the ampoules were considered (initiator, monomer, inhibitor, all kinds of radicals and dead polymers). The Method of Moments was used to predict the number average molecular weight ($\overline{Mn}$), the weight average molecular weight ($\overline{Mw}$) and the polydispersity index (PDI). Due to the complexity of the model and its stiffness, the Gear method was used to solve the equation system.

5. Results and Discussion

Figures 1 and 2 present the conversion curves to styrene at 115ºC and 125ºC, respectively. Comparing the results obtained from the modeling part with the experimental data, it is possible to verify the behavior of a bifunctional initiator with styrene. The model predictions showed good agreement with the experimental data. A good comparison between mono- and bi-functional initiators can be seen in Machado, 2004 ; Machado and Lona, 2004; Machado and Lona, 2005 and Franco, 2006.

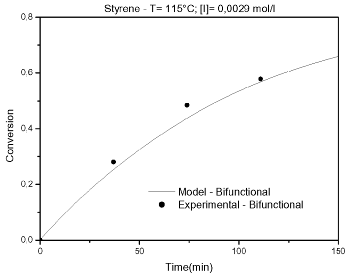

Figure 1 – Conversion x Time

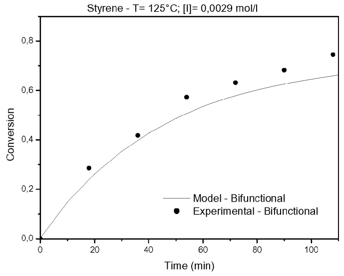

Figure 2 – Conversion x Time

Figure 3 presents the number average molecular weight ($\overline{Mn}$) profile to the same conditions used in figure 1. It was achieved an agreement between results from the model and experimental data, but an optimization work is being done to adjust all parameters, in order to improve them. Also the experimental part under these conditions is being repeated, in order to generate more experimental data.

Figure 4 presents the weight average molecular weight ($\overline{Mw}$) profile to the same conditions used in figure 3. The experimental data showed good agreement with the model predictions. As expected, the values of $\overline{Mw}$ are greater than $\overline{Mn}$ (Dhib et al.; 2000; Machado, 2004 and Franco, 2006).

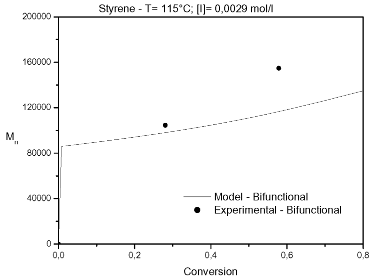

Figure 3 – $\overline{Mn}$ x Conversion

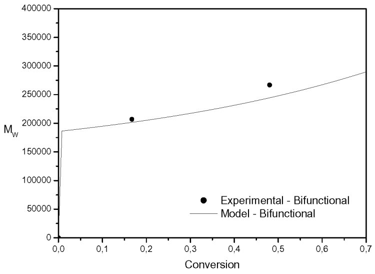

Figure 4 – $\overline{Mw}$ x Conversion

Figure 5 presents the conversion curve to vinyl acetate at 115ºC. Comparing the obtained results from the modeling part with the experimental data, it is possible to verify the behavior of the bifunctional initiator with the vinyl acetate: the conversion is faster (in relation to styrene). This was expected since the polymerization of vinyl acetate generates more radicals than the polymerization of styrene. The model predictions showed good agreement with the experimental data. A good comparison between mono- and bi-functional initiators with vinyl acetate can be seen in Machado, 2004 ; Machado and Lona, 2004; Machado and Lona, 2005 and Franco, 2006.

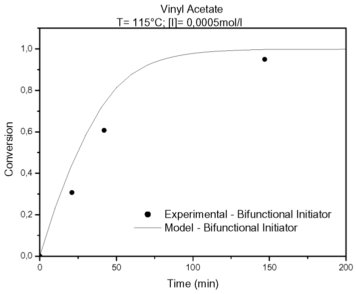

Figure 5 – Conversion x Time

Figure 6 and 7 present the number average molecular weight ($\overline{Mn}$) profile and the weight average molecular weight ($\overline{Mw}$) profile to the same conditions used in figure 5. The experimental data showed good agreement with the model predictions. It is very important to notice here that the $\overline{Mw}$ and $\overline{Mn}$ obtained with vinyl acetate are higher than the ones obtained with styrene despite using just less than ¼ of the concentration of initiator. This can be explained by the presence of branched chains for polyvinyl acetate. Also the effect of a bifunctional initiator clearly intensified the increasing in the molecular weights values as can be seen in Machado, 2004.

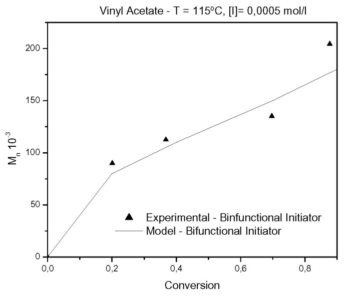

Figure 6 – $\overline{Mn}$ x Conversion

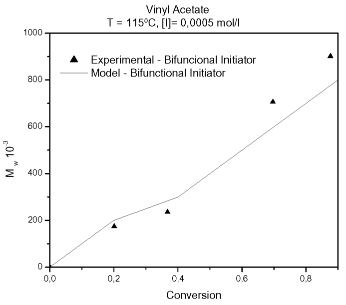

Figure 7 – $\overline{Mw}$ x Conversion

6. Conclusion

This work shows the advantages in using bi-functional initiators in the free radical polymerization of styrene (generating a linear polymer) and vinyl acetate (generating a branched polymer). It can be concluded based on the conditions of this study that this type of initiator allows to reach high conversions and high molecular weighs simultaneously.

7. References

Dhib, R.; Gao, J.; Penlidis, A.; Polymer Reaction Engineering, 8(4), p.299-464, 2000.

Franco, C.M.; MSc Thesis, Feq/Unicamp, 2006

Machado, P.F.M.P.B.; MSc Thesis, Feq/Unicamp, 2004.

Machado, P.F.M.P.B.; Lona, L.M.F.; Historical Records Cobeq 2004 (CD)

Machado, P.F.M.P.B.; Lona, L.M.F.; E. Symp. on Comp. Aided Proc. Eng.-15, 2005, 20 A, 445-450.