Simulation and Optimization of Polystyrene Free Radical Polymerization Process

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Abstract. A model for bulk polymerization of styrene was established by using the POLYMER module of ASPEN PLUS. The effects of the chain initiator (TBP), solvent (ethylbenzene) and the chain transfer agent (DDM) on the yield, number average degree of polymerization(DPN), weight average degree of polymerization(DPW), number average molecular weight(Mn), weight average molecular weight(Mw) and the polydispersity index(PDI) of polystyrene were investigated. Through the analysis, we can first consider the amount of styrene to obtain roughly the parameters of the polystyrene process. As the use of initiator in polymerization has the optimal value, we must strictly control the amount of TBP according to the amount of monomer styrene, and adjust the amount of chain transfer agent to control the product quality accurately.

1. Introduction

With the continuous development of computer technology, the simulation of the chemical process has become more and more mature and thus more and more widely used in chemical design. Using the chemical process simulation software-aspen plus (polymer module) to guide actual chemical process design can greatly shorten the time required for process design and lower related economic costs [1-2].

Polystyrene has excellent thermal stability and fluidity in the molten state, making polystyrene easy to process and its mass production available. Due to its rigid phenyl group, the product is a rigid plastic, coupled with certain thermal properties, excellent electrical insulation, and corrosion resistance, making polystyrene an important place in the field of packaging materials [3-4].

The styrene bulk polymerization method was adopted for this paper since it was widely used, that is, styrene was used as the monomer, tributyl phosphate as the initiator, ethylbenzene as the solvent, and mercaptan as the chain transfer agent. Polystyrene products having different comprehensive performance indexes (product flow rate, number average molecular weight, weight average molecular weight, polydispersity index, etc.) could be simulated by changing the feed ratio and feed amount of each raw material. By comparing the simulated results, we can obtain the correlation law of the polymerization reaction. It is of great significance to study the best production process for Polystyrene polymerization.
2. Results and Discussions of sensitivity analysis

2.1 Effect of styrene feed

The amount of variable in the sensitivity analysis was changed to the feed amount of monomer styrene, and the flow rate of styrene feed was set to 3400 kg/h, 5100 kg/h, 6860 kg/h, 8600 kg/h and 10300 kg/h with the other feed amount unchanged. The relationship between the polystyrene yield, PDI, DPN, DPW, Mn, Mw, and styrene feed was described in Figure 1.

As shown in Figure 1, with the increase in styrene amount, the yield of polystyrene increases rapidly, the PDI decreases significantly, the DPN/DPW decreases significantly, and the Mn/Mw reduces pronouncedly.

If the amount of styrene was increased to about 50% of the initial value (6860 → 10300 kg/h), the outlet flow rate of the polystyrene obtained was 2128 kg/h, compared with the previous value of 1185 kg/h, the outlet flow rate of the product increased by 80%; the number average polymerization degree was 909, 4.6% lower than the original DPN; the weight average polymerization degree was 1677, which was decreased by 5.4%; the Mn was 94643, which was 4.6% lower than the original one; the Mw was 174666, which was 5.4% lower than the previous one; the PDI was 1.85, which was 0.81% lower than the previous polydispersity index.

![Figure 1](image1.png)

Figure 1 Effect of styrene feed on yield (top left), PDI (top right), DPN/DPW (bottom left), Mn/Mw (bottom right)

2.2 Effect of initiator

The initiator is an important part of the feed with a significant effect on the quality of the product. When the amount of the initiator (Tributyl phosphate, TBP) ranged from 1 kg/h to 3 kg/h, the relationships between the polystyrene yield, PDI, DPN, DPW, Mn, Mw and TBP feed were plotted in Figure 2.
As shown in Figure 2, as the amount of TBP increases, the yield and PDI tend to decrease, and the DPN/DPW/Mn/Mw first increase and then decrease.

When the feed of TBP was 2.4 kg/h, the DPN/Mn reached a maximum value, and when the feed of TBP was 1.4 kg/h, the DPW/Mw reached a maximum.

When the feed of TBP increased from 2.1 kg/h to 3 kg/h, the yield had a decrease of 11%; the PDI was 1.86 with a decrease of 0.19%; the DPN/DPW decreased by 0.05%, and Mn/Mw was found to have a decrease of 0.24%.

If the feed of TBP was reduced from 2.1 kg/h to 1 kg/h, the yield increased from 1185 kg/h to 1380 kg/h, with an increase of 17%; the PDI was 1.86, with an increase of 0.33%; the DPN/DPW had a decrease of 0.22%; Mn/Mw showed a decrease of 0.04%.

2.3 Effect of solvent

The solvent (ethylbenzene, EB) has a function of dissolving monomer, dispersing the heat of reaction, and taking up a part of a chain transfer agent in the polymerization reaction.

The flow rate of ethylbenzene feed was set to 65 kg/h, 98 kg/h, 133 kg/h, 166 kg/h and 199 kg/h with the other feeds unchanged. The relationships between the polystyrene yield, PDI, DPN, DPW, Mn, Mw, and ethylbenzene amount were obtained and shown in Figure 3.

With the increase in ethylbenzene, the polystyrene yield and PDI increased slightly; the DPN/DPW/Mn/Mw decreased in a small range.

For example, when the feed of EB increased from 133 kg/h to 199 kg/h, the yield increased from 1185 kg/h to 1190 kg/h, with an increase of 0.4%; the PDI was 1.86, showing an increase of 0.065%; the DPN had a decrease of 0.44%; Mn showed a decrease of 0.053%; the DPW has a decrease of 0.24%; Mw decreased by 0.24%.
2.4 Effect of the chain transfer agent

Chain transfer agent (n-Dodecyl Mercaptan, DDM) has the effect of promoting the initiation of a reaction in a hydrocarbon solvent and controlling the length of the polymer chain. With the chain transfer agent DDM, the molecular weight and degree of polymerization of the polymer can be adjusted within a certain range to achieve the desired properties of the target grade.

The feed flow rate was set to 2.5 kg/h, 3.75 kg/h, 4.9 kg/h, 6.25 kg/h, and 7.5 kg/h with the other feed amount unchanged. The relationships between the polystyrene yield, PDI, DPN, DPW, Mn, Mw and DDM amount were obtained and shown in Figure 4.

When the feed amount of DDM increased, the yield increased a little, the PDI was basically unchanged, and the DPN/DPW/Mn/Mw values were slightly reduced.

According to Figure 4, when the feed of DDM increased from 4.9 kg/h to 7.5 kg/h, the yield increased from 1184.8 kg/h to 1185.0 kg/h; the PDI remained unchanged; the DPN/DPW/Mn/Mw showed a decrease of about 0.01%.
Figure 4 Effect of DDM feed on yield (top left), PDI (top right), DPN/DPW (bottom left), Mn/Mw (bottom right)

3. Conclusions
(1) The monomer styrene flow has a great influence on the physical property data of the product. The polystyrene yield, the PDI, DPN, DPW, Mn, and Mw are initially controlled by the flow rate of monomer styrene.

(2) The change in the flow rate of the initiator can further control the yield of polystyrene, the PDI, the DPN, DPW, Mn, and Mw. A suitable flow rate of initiator can improve the quality of the polymer product.

(3) Compared with the styrene flow rate and initiator, the chain initiator has less influence on the product. Thus, we can finely adjust the quality of the obtained product by adjusting the flow rate of the chain initiator to meet the requirements.

(4) According to the data on the styrene bulk polymerization in the polymer module of Aspen plus, the result is basically in line with the actual situation. Therefore, we could use it to guide the actual chemical process design and greatly shorten the process design, the time required and lower the associated economic costs.

4. Experiment model
The polymerization process is shown in Figure 5, the definition of the polymerization equation and the related parameters are in the supporting information.
Acknowledgments
This work is financially supported by the Talent Scientific Research Fund of LSHU (No.2016XJJ-010), the 2016 General Project of Education Department of Liaoning Province (No.L2016003), the Doctoral Research Fund of Liaoning Science and Technology Department (No. 20170520158), the Opening Funds of Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, Jiangnan University (JDSJ2018-05) and the Opening Project of State Key Laboratory of Polymer Materials Engineering (Sichuan University) (Grant No.sklpme2019-4-24).

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