

## Kinetic Modeling of Non-Isothermal Anionic Styrene-Butadiene Block Copolymerization And Its Industrial Applications

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### Introduction

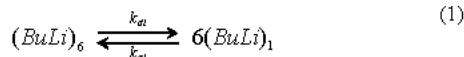
Styrene-butadiene (SB) diblock or styrene-butadiene-styrene (SBS) triblock copolymers (terpolymers) are industrially produced by anionic block copolymerization reaction. At LG Chem, about 50,000 metric tons of SBS a year are produced in Yeosu plant. Their major application areas include asphalt modification, shoe compounds, adhesives, and so on. Styrene block is first synthesized in a solution using alkyl lithium initiators such as butyl lithium. As the styrene monomer is completely consumed, the chain end active centers are still living and butadiene is further added to produce styrene-butadiene diblock copolymer. Coupling agents are then added to combine the two ends of different butadiene blocks to produce SBS triblock terpolymer. Some literature provides kinetic analysis on styrene and/or butadiene homo/ copolymerization with alkyllithium initiators [1, 2]. Their applications, however, are limited to isothermal operations only. In this study, we carry out kinetic modeling of anionic styrene-butadiene block copolymerization in non-isothermal operation so that the model developed can be directly used for quantitative analysis of a commercial-scale polymerization system. Particularly, the relation between the reaction temperature profile with conversion of monomers is presented in detail.

### Kinetic modeling

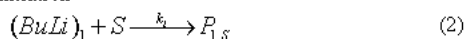
Butyl lithium (BuLi) is used as an initiator for SB diblock copolymerization. Usually n-hexane, cyclohexane, or a mixture of the two is used as solvent. Active BuLi initiator solution is injected into a batch reactor filled with styrene and solvent to synthesize the styrene block first. As all the styrene monomer is consumed completely, butadiene is fed into the reactor and the butadiene block begins to form from the active end of the styrene block. The reaction continues until all the butadiene monomer is consumed. After the reaction is finished, coupling agent is added to link active butadiene ends of different styrene-butadiene copolymer chains to form SBS triblock terpolymer. The whole reactions proceed in a near-adiabatic condition with a little cooling water flow through the reactor jacket. The reactor temperature increases dramatically during the reaction by the release of heat of polymerization of styrene and butadiene.

A kinetic scheme for anionic living styrene-butadiene block copolymerization reaction is shown in Eqs. (1)~(7). Here, the scheme assumes that the initiator is already activated in a solution. Also note that the coupling reaction is not included because it has little effect on the reaction temperature excursion.

Initiator dissociation/association

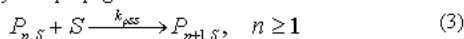


Chain initiation

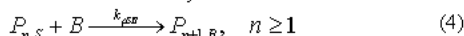


Propagation

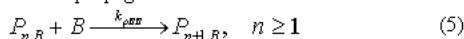
Styrene propagation:



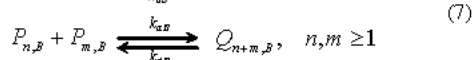
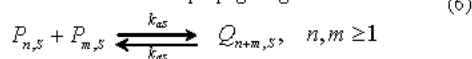
Butadiene addition to styrene block:



Butadiene propagation:



Association/dissociation of propagating ions:



An active BuLi molecule in nonpolar, aromatic solvents is known to associate with 5 others to form a 6-membered aggregate [2, 3]. The styrene polymerization is initiated by the dissociation of a BuLi molecule from the aggregate. For association/dissociation of living chain active centers, 2 living styrene or butadiene chains are known to form an association [2, 3]. Association with styrene and butadiene active centers is assumed to be negligible because of the sequential feeding of monomers. Note that  $P_{n,S}$  and  $P_{n,B}$  represent living chain

with styrene and butadiene at the active center, respectively. We used Aspen Polymers Plus™ 2004 to estimate the kinetic parameters and solve the rate equations.

### Results and discussion

The dotted line in Figure 1 shows the temperature profile of the real plant. The profile shows two different peaks: the first one appears during the styrene polymerization and the second one appears during the butadiene polymerization. These peaks give important measure for conversion of each monomer and the strategies for the butadiene feeding time and coupling agent are determined by these peak times. Therefore, it is very important for the model to accurately estimate the reactor temperature profiles. The model calculation result for the reaction temperature is shown as a solid line in Figure 1. Note that the peak temperatures of the model result give a little underestimation, while the overall trend is quite similar.

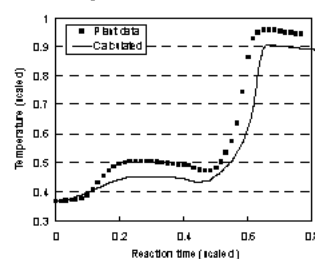


Figure 1. Comparison of reaction on temperature profiles.

Figure 2 shows the magnified reaction temperature profile compared with the calculated styrene conversion in styrene polymerization region. It is interesting to note that the complete consumption of styrene is not at the peak temperature, but after a certain period of time. This observation provides important information about when to charge butadiene.

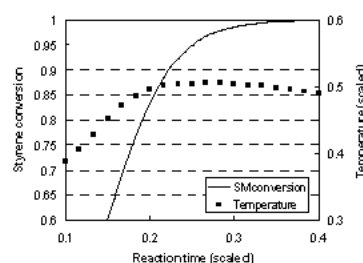


Figure 2. Temperature peak and styrene conversion.

### Conclusions

A kinetic modeling study on non-isothermal anionic styrene-butadiene block copolymerization is presented. Using the kinetic model it is possible to track important operation variables and analyze their relations including the reaction temperature and the conversion of monomers. It is also discovered that cooling water operation strategy plays a critical role in determining the temperature peaks, explaining the underestimation of reaction peak temperature by the model. With the knowledge gained through kinetic modeling better idea is obtained for more efficient operation in a commercial-scale SBS plant.

### References

- [1] Hsieh, H. L. and Quirk, R. P. Anionic Polymerization –Principles and Practical Applications, Marcel Dekker: New York, 1996.
- [2] Sirahi, A. and Ravindranath, K. *AIChE Meeting*, Houston, 1999.
- [3] Odian, G. Principles of Polymerization, 3<sup>rd</sup> Ed., John Wiley and Sons, 1991.