MODEL-BASED REACTOR DESIGN TO CONTROL BRANCHED POLYMER ARCHITECTURE

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Abstract

The 3D structural control of branched polymer architecture is an important future trend in polymer production technology. The Monte Carlo simulation technique based on the random sampling technique is used to explore the effect of reactor types on the branched polymer structure, formed through free-radical polymerization that involves chain transfer to polymer, leading to simultaneous long-chain branching and scission, as in the case of low-density polyethylene synthesis. It was found that polymers with various types of branched architecture, from star-like globular structure to a more randomly branched structure, can be produced simply by changing the tank arrangement in a series of CSTRs having different sizes. Through the present investigation, I would like to emphasize the importance of stochastic approaches and the *active model use* aiming at creating new reactor design in which process engineers have the initiative.

Keywords

Branched polymer, Monte Carlo simulation, Radical polymerization, Reactor design.

Introduction

Pierre-Simon Laplace, sometimes referred to as Newton of France, was an earnest believer in differential equations and proposed the causal determinism hypothesis, known as Laplace's demon. We, chemical engineers, tend to think of ourselves as the descendants of Newton, and are very much accustomed to using differential equations. Laplace, on the other hand, knew that the differential equations describe only a single side of the moon and contributed significantly to the development of probability theory.

The objective function in the polymerization processes have evolved from the average properties, such as conversion and the average molecular weights, through the distributions, and now toward the 3D structural control of each product polymer. The stochastic approach, such as the Monte Carlo (MC) simulation method in which the 3D structure of each polymer molecule can be observed directly on the compute screen, is a powerful tool for such purpose. The usual MC method is a brute-force approach and requires an excess amount of calculation. About 20 years ago, when the computational speed was not very fast, I proposed the *random sampling technique* (Tobita, 1996), in which a polymer molecule is selected randomly from sea of product polymers, and the molecular structure is reconstructed by following the history of this particular polymer molecule. By sampling a large number of polymers, the statistical properties of the whole system are determined effectively. In this method, the system size considered is infinite, and therefore, the system boundary problem does not occur. The accuracy of the simulated results can be increased simply by sampling a larger number of polymer molecules.

This MC simulation method can be used to investigate the effects of various complex reactor systems, by taking advantage of small computational load. In this lecture, a series of N continuous stirred-tank reactors, consisting of one big tank and the same (N-1) small tanks is considered

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theoretically. It is shown that by simply changing the tank arrangement, various types of branched polymers, from star-like globular structure to a more randomly branched structure can be obtained, while keeping the following properties of the final products the same; the monomer conversion to polymer, the average branching and scission densities, and the relationship between the mean-square radius of gyration and molecular weight.

Method

In the random sampling technique, various probability functions that describe the chain connection statistics are required. In such a sense, this method needs "behind-the-scenes" work, compared with the usual MC methods. The concept is that both human beings and computers work collaboratively, taking full advantage of strengths of their own. The specific simulation method can be found in Tobita (2015a).

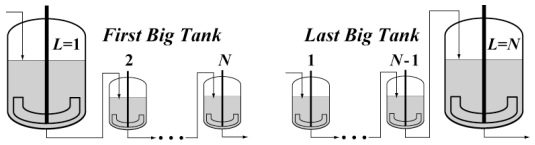

Figure 1. Examples of tank arrangement

Figure 1 shows two examples of tank arrangement, and L is the tank number of a large tank. Because every fluid element must flow through all tanks, the residence time distribution is kept the same irrespective of the tank arrangement. In the present CSTRs in series, when the final conversion is set to be the same, the average branching and scission densities of the final products do not change with the tank arrangement (Tobita, 2015a).

Results and Discussion

The MC simulation results for free-radical polymerization with simultaneous long-chain branching and minor contribution of scission, as in the case of low-density polyethylene production, are discussed here.

The weight-average molecular weight (MW) is the largest for the first big tank case (L=1), and decreases as the large tank moves backward, even though the average branching density is the same. The number-average MW does not change with the tank arrangement, and therefore, the molecular weight distribution (MWD) is the broadest for L=1.

The branching density of polymers having degree of polymerization, P reaches a constant value for large P. The limiting value, $\rho_{P\to\infty}$ is the smallest for L=1, and increases with a larger value of L. On the other hand, it was found that polymers with star-like globular structure are formed for L=1, and the branched structure approaches more random-like as L increases. As a result, the relationship between the mean-square radius of gyration $\langle s^2\rangle_0$ and P is essentially unchanged by the tank arrangement.

Table 1 summarizes the results obtained in this study. The qualitative reason why such behavior is observed is discussed in Tobita (2015b).

Table 1. Obtained results when the final conversion is set to be the same

Large tank number, L = 1, … , N	
Final average branch density	Unchanged
Final average scission density	Unchanged
Residence time distribution	Unchanged
Weight-average molecular weight	>
Branch density for large polymers, $\rho_{P\to\infty}$	<
Branched structure	Star-like ↔ Random
Relationship between $\langle s^2\rangle_0$ and P	Essentially the same

Conclusions

Branched polymers with various types of architecture can be produced simply by changing the tank arrangement. In the case of a tower-type multi-zone reactor, the branched structure could be controlled by changing the location of division plates.

Conventionally, most mathematical models have been used rather passively. The present type of positive model use may lead to propose novel reactor systems.

Table 2. Characteristics of positive model use

Passive model use	Positive model use
Aiming at improving the process already used in industry	Aiming at creating a new process
Emphasizing the quantitative agreement with experimental data	Emphasizing the novelty of the proposed process
Straightforward cause-and-effect logic	Divergence through try-and-error and convergence through reasoning
Initiative by chemists	Initiative by process engineers

References

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