스틸렌 중합을 위한 충진 관류 흐름 반응기에서 실험연구 및 모델링

윤원중
경원대학교 화학공학과

Experimental Study and Model Simulation of Polymerization of Styrene in Continuous Filled Tubular Reactor

Won Jung Yoon
Dept. of Chem. Eng., Kyungwon University

Introduction

Free radical polymerization of vinyl monomers such as styrene, methyl methacrylate, and vinyl acetate in tubular reactors has been studied by many. The potential advantage of using empty tubular reactors as polymerization reactors are, for example, design simplicity, good heat transfer capability, and narrow molecular weight distribution of the product polymer. Although tubular reactors have been used for years in high pressure ethylene polymerization processes to produce low density polyethylene (LDPE), the use of tubular reactors for the polymerization of vinyl monomers has been quite limited. One of the major problems in using the empty tubular reactors for the polymerization of vinyl monomers is that the viscosity of the polymerizing liquid increases, leading to large radical axial temperature gradients and a significant distortions of velocity profiles. As a result, a buildup of slowly moving liquid layer occurs at the reactor walls, causing a large variation in residence time distribution, plugging problems, poor heat transfer, and poor product quality.

In this study, a solution polymerization of styrene is investigated using a filled tubular reactor packed with static mixing elements. The major reason for using the static mixing elements in the tube is to obtain a near plug flow profile and to avoid undesirable velocity distortions in the direction of liquid flow. In a tube filled with static mixers, each static mixer element divides the incoming flow and recombines it in a geometric sequence so that intensive radial mixing is obtained. A filled tubular reactor is used to polymerize styrene in ethylbenzene as a solvent with a binary mixture of symmetrical bifunctional initiators in the temperature range 90 to 120℃. The main objective of this work is to evaluate the performance of the filled tubular reactor for free radical solution polymerization of styrene with peroxy ester initiators and relatively low solvent volume fraction at low reaction temperatures, in which thermal polymerization effect is not significant. Both start-up transient and steady state behaviors of the reactor are investigated through laboratory experimentation and model simulations.

Experimental

A bench scale continuous filled tubular polymerization reactor facility has been built for styrene polymerization experiments. A schematic diagram of the experimental reactor system is illustrated in Fig. 1. The main reactor consists of two equal sized jacketed tubes made of stainless steel. The L/D ratio of each reactor segment is 28 and the tube diameter is 2.62cm (ID). Each tube has a cooling jacket (ID=5.25cm) through which cooling or heating fluid circulates to maintain constant jacket temperature. Each reactor segment is packed with 24 Sulzer SMX static mixers and the voidage of the packed tube is 0.91 Each static mixing element is turned around its main axis by 90° against its neighboring elements. The two reactor segments are connected by a short hollow connector unit (L=10.2cm) to which a ball valve has been attached for the sampling of small amounts of reaction fluids. There are three thermocouples (J-type) to measure the temperature at the reactor inlet, middle section, and outlet. A jacketed glass reactor, installed before the tubular reactor, can be used either as a monomer solution feeding tank or as a prepolymerizer. A pressure gauge has been installed at the bottom of the filled tubular reactor and the reactor outlet valve is fully open to atmosphere. The reactor is first fill with ethylbenzene and heated to a desired reaction temperature. Then the feed monomer solution containing a mixture of initiators is pumped to the bottom of the reactor. The polymer samples taken from the reactor are dissolved in toluene and precipitated by adding excess methanol. This procedure is repeated several time to ensure that unreacted monomer is completely removed. The samples are dried overnight in vacuo at 40℃. Then, the monomer conversion is determined by gravimetric method. The polymer molecular weight has been determined by gel permeation chromatography using four Ultrastyragel columns (Waters: 10^4, 10^3, 500Å, and linear) and tetrahydrofuran as a solvent.

Results and Discussion

The validity of proposed reactor model is first evaluated by comparing the experimental data and the model simulation results. The reactor variables that were varied are: jacket temperature in each reactor segment (T_{c1} and T_{c2}), feed initiator mixture composition (y_{Af}), residence time (θ), and feed initiator concentration(I_f). Recall that y_{Af} is the mole fraction of the slow initiator [Luperox 118] in the feed initiator mixture. In all these experiments, the solvent (ethyl benzene) volume fraction (f_s) was held constant at 0.3. In conducting the reaction experiments, a jacketed glass reactor was used as a feed tank and its temperature was maintained at 24℃ at which the polymerization of styrene was negligible.

A first set of experiments (Runs 1,2, and 3) was carried out at different reactor jacket temperatures with y_{Af}=0.5 and θ=160 min. Figure 2 show the polymer weight fraction profiles during the startup and steady state periods (Note: The polymer weight monomer.). Initially the reactor was filled with pure solvent. Here, ◆ represents the data for the samples taken from the middle of the reactor and ▲ represents the data for the samples taken from the reactor outlet. The solid line

are model simulation results. The experimental data during the startup transient period indicate that the concentration wave fronts are sharp but deviations from the plug flow are also apparent.

Two more dynamic experiments were carried out by making step changes in the reactor residence time and the jacket temperature after the reactor had reached a steady state. Figure 3 show the polymer weight fraction and molecular weight profiles at the reactor outlet when the residence time was step increased from 80 to 160 min at t=240 min by reducing the feed flowrate. During the initial transient period at θ=80 min, the predicted values of polymer yield and molecular weight are slightly higher than the observed values but after the step change is made to θ=160 min (lower flow rate) an improved agreement between the experimental data and model predictions has been obtained. Figure 4 show the reactor response to a step change in the jacket temperature from 90 to 112℃ with θ=80 min. The dotted vertical line indicates the moment of step change and dashed lines indicate the reactor temperature profile. At 240 min, the bath temperature was raised by 2℃/min. First, it is seen that it takes more transition time to reach a new steady state than in the previous case shown in Figure 3. The polymer weight fraction increased from 18 to 35% as the jacket temperature was increased by 22℃. Again, the overall agreement between the model predictions and experimental data is quite reasonable. However, the measured polymer molecular weight values did not change as sensitively as the polymer weight fraction values.

Concluding Remarks

The feasibility of a filled tubular reactor packed with Sulzer SMX static mixers as a continuous styrene polymerization reactor has been investigated through laboratory experiments and model simulation. Although the L/D ratio of the filled tubular reactor used in our experimental work is significantly smaller than that of the empty tubular reactors studied in the past, styrene conversion up to about 70% has been obtained without operational problems during the experiments. We developed a dynamic axial dispersion model based on the experimental residence time distribution analysis for the reactor system. All the kinetic and physical parameters used in the model simulations were taken from the literature and considering some inconsistency in the reported values of kinetic parameters, quite satisfactory model predictions of polymer weight fraction and polymer molecular weight averages have been obtained for both steady state and transient operation conditions with out using any adjustable parameters. The experimental results suggest that the filled tubular reactor can be potentially a good continuous reactor for the polymerization of vinyl monomers. However, the model simulation results also indicate that when large diameter filled tubular reactors are used, a large temperature overshoot may take place, leading to deadend polymerization and low polymer molecular weight. In such case, the reactor operating conditions and reactor controls must be carefully designed in order to avoid these problems.

References

1. W. J. Yoon, Ph. D. Thesis, University of Maryland, College Park, Md. (1992).
2. W. J. Yoon, and K. Y. Choi, J. Appl. Polym. Sci., 46, 1353 (1992).

3. W. J. Yoon, and K. Y. Choi, polymer, 33, 4582 (1992).
4. W. J. Yoon, and K. Y. Choi, Polym. Eng. & Sci. in press (1996).

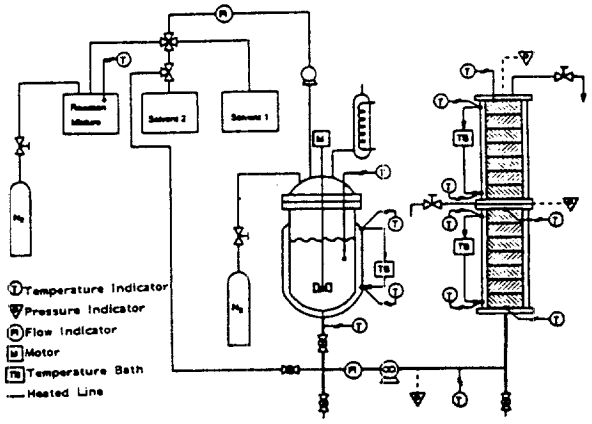

Fig. 1. Schematic diagram of continuous filled tubular polymerization reactor system.

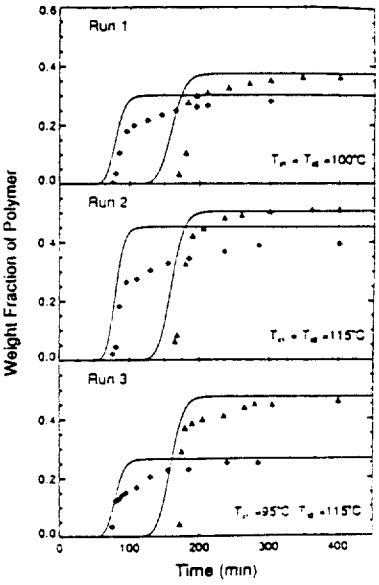

Fig. 2. Effect of reactor jacket temperature on polymer weight fraction profiles: θ=160 min, f_s=0.3, I_f=0.01 mol/L, y_M=0.5, T_f=298°K, γ=0.728, ◆ at z/L=0.5, ▲at z/L=1.0

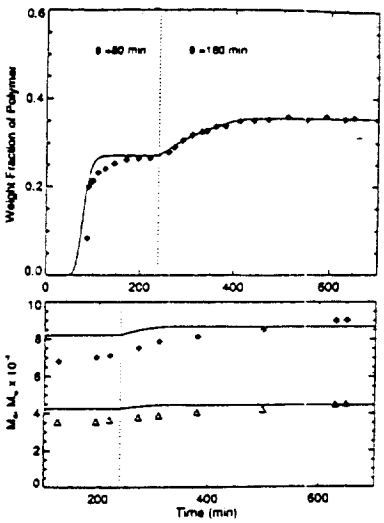

Fig. 3. The reactor transient response to a step change in residence time 80 to 160 min

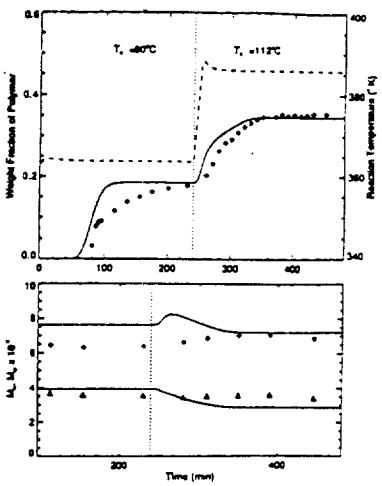

Fig. 4. The reactor transient response to a step change in coolant temperature from 90 to 112℃