

# Dynamic Modeling of Solid-State Polymerization of Bisphenol A polycarbonate in a Moving Packed Bed Reactor

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## Abstract

A dynamic model has been developed for a continuous solid state step-growth polymerization of bisphenol A polycarbonate in a moving packed bed reactor (MPBR). In this process, low molecular weight polycarbonate prepolymer particles are supplied to the top of the reactor while a heated purge gas stream is supplied to the bottom of the reactor. For small prepolymer particles, intraparticle heat transfer and mass transfer effects are insignificant and a pseudo-continuum model is developed for the reactor. For large prepolymer particles in which intraparticle mass transport effect can be significant, both single particle and macroscopic reactor models are combined to calculate the temperature profiles, polymerization rate and polymer molecular weight along the reactor length. The model simulation results show that a temperature non-uniformity may develop in the reactor, particularly near the top portion of the reactor, and affects the performance of the solid state polymerization of polycarbonate.

## Key words

Solid-state polymerization (SSP), polycarbonate (PC), moving packed bed reactor, reactor modeling

## Introduction

Solid-state polymerization (SSP) is used industrially to manufacture high molecular weight condensation polymers such as polycarbonate (PC), poly(ethylene terephthalate) (PET) and nylons at a temperature above the polymer's glass transition temperature but below its melting point. For the successful polymerization of these condensation polymers to high molecular weight by SSP, a few conditions need to be satisfied. For example, in a solid state polycarbonate process, low molecular weight amorphous polycarbonate prepolymers prepared by melt polymerization are first partially crystallized before solid-state polymerization. Otherwise, polymer particles fuse and no solid state polymerization proceeds. Experimental and theoretical model simulations also show that the rate of SSP and polymer molecular weight are strongly dependent on the mole ratio of reactive end groups, reaction environment, and physical shape of the polymer particles. The polymer chain length distribution can also be quite broad even in the polymer that has a very high molecular weight average <sup>[1]</sup>.

Several different types of SSP reactors that are used in industry include fluidized bed reactors and packed bed reactors <sup>[2]</sup>. The previous SSP modeling work includes a CSTRs-in-series model by Mallon and Ray <sup>[2]</sup>, and plug flow models by Yao <sup>[3]</sup> and Algeri <sup>[4]</sup>. However, in these models potential temperature and concentration nonuniformities along the radial and axial directions in the reactor have not been considered. In this work, we develop a dynamic model of a moving packed bed reactor for the solid state polymerization of bisphenol A

polycarbonate. Through reactor simulations, we analyze the dynamic and steady state polymerization reactor performances.

### Modeling of Moving Packed Bed Reactor

In our previous work, we showed that for small prepolymer particles of low molecular weight, intraparticle heat transfer and mass transfer effects are insignificant and negligible. When such particles are used in a continuous moving packed bed reactor, we can treat the particle bed as a pseudo-continuum. The solid phase and gas phase energy balance equations are used to calculate the reactor temperature profile. For large particles, intraparticle temperature gradient might be negligible but the concentration gradient might not be negligible. Hence, both the concentration and temperature nonuniformities along the axial and radial directions in the reactor need to be considered to accurately calculate the polymerization rate. Since the reaction heat has little effect on the temperature profiles in the reactor level and the intraparticle temperature gradient is negligible, the reactor-level model and particle-level model are solved separately. For example, the reactor temperature profile is first calculated and then it is incorporated into the particle model to solve the mass balance equations.

For a moving packed bed reactor with relatively large polymer particles, the energy balance equations are derived as follows. Note that the major source of particle heating is the heated purge gas supplied to the bottom of the reactor. A heat loss through the reactor walls is also included in the model.

$$\frac{\partial \tilde{T}_s}{\partial t} = \frac{k_p}{\rho_p C_{p,p}} \left[ \frac{1}{R^2 \tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{T}_s}{\partial \tilde{r}} \right) + \frac{1}{H^2} \frac{\partial}{\partial \tilde{z}} \left( \frac{\partial \tilde{T}_s}{\partial \tilde{z}} \right) \right] - \frac{h_{gs} (\tilde{T}_s - \tilde{T}_g) 6}{\rho_p C_{p,p} d_p} - \frac{\dot{m}_p}{(1-\varepsilon) \rho_p S H} \frac{\partial \tilde{T}_s}{\partial \tilde{z}} \quad (1)$$

$$\frac{\partial \tilde{T}_g}{\partial t} = \frac{k_g}{\rho_g C_{p,g}} \left[ \frac{1}{R^2 \tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{T}_g}{\partial \tilde{r}} \right) + \frac{1}{H^2} \frac{\partial}{\partial \tilde{z}} \left( \frac{\partial \tilde{T}_g}{\partial \tilde{z}} \right) \right] + \frac{h_{gs} (\tilde{T}_s - \tilde{T}_g) 6(1-\varepsilon)}{\rho_p C_{p,p} d_p \varepsilon} + \frac{\dot{m}_g}{\varepsilon \rho_g S H} \frac{\partial \tilde{T}_g}{\partial \tilde{z}} \quad (2)$$

$$\frac{\partial x_c}{\partial t} = - \frac{\dot{m}_p}{(1-\varepsilon) \rho_p S H} \frac{\partial x_c}{\partial \tilde{z}} + k_c (x_{c,max} - x_c) \quad (3)$$

The initial conditions are given by,

$$\text{At } t = 0: \quad \tilde{T}_s = \tilde{T}_{s,0} = 1, \quad \tilde{T}_g = \tilde{T}_{g,0} = 1, \quad x_c = x_{c,0} \quad (4)$$

The boundary conditions are given by,

$$\frac{\partial \tilde{T}_s}{\partial \tilde{z}} = - \frac{\dot{m}_p C_{p,p} H}{k_p (1-\varepsilon) S} (\tilde{T}_{s,in} - \tilde{T}_s) \text{ at } \tilde{z} = 0 \quad (5a)$$

$$\frac{\partial \tilde{T}_s}{\partial \tilde{z}} = 0 \text{ at } \tilde{z} = 1 \quad (5b)$$

$$\frac{\partial \tilde{T}_s}{\partial \tilde{r}} = 0 \text{ at } \tilde{r} = 0 \quad (5c)$$

$$\frac{\partial \tilde{T}_s}{\partial \tilde{r}} = - \frac{h_{sw} R}{k_p} (\tilde{T}_s - \tilde{T}_w) \text{ at } \tilde{r} = 1 \quad (5d)$$

$$\frac{\partial \tilde{T}_g}{\partial \tilde{z}} = 0 \text{ at } \tilde{z} = 0 \quad (6a)$$

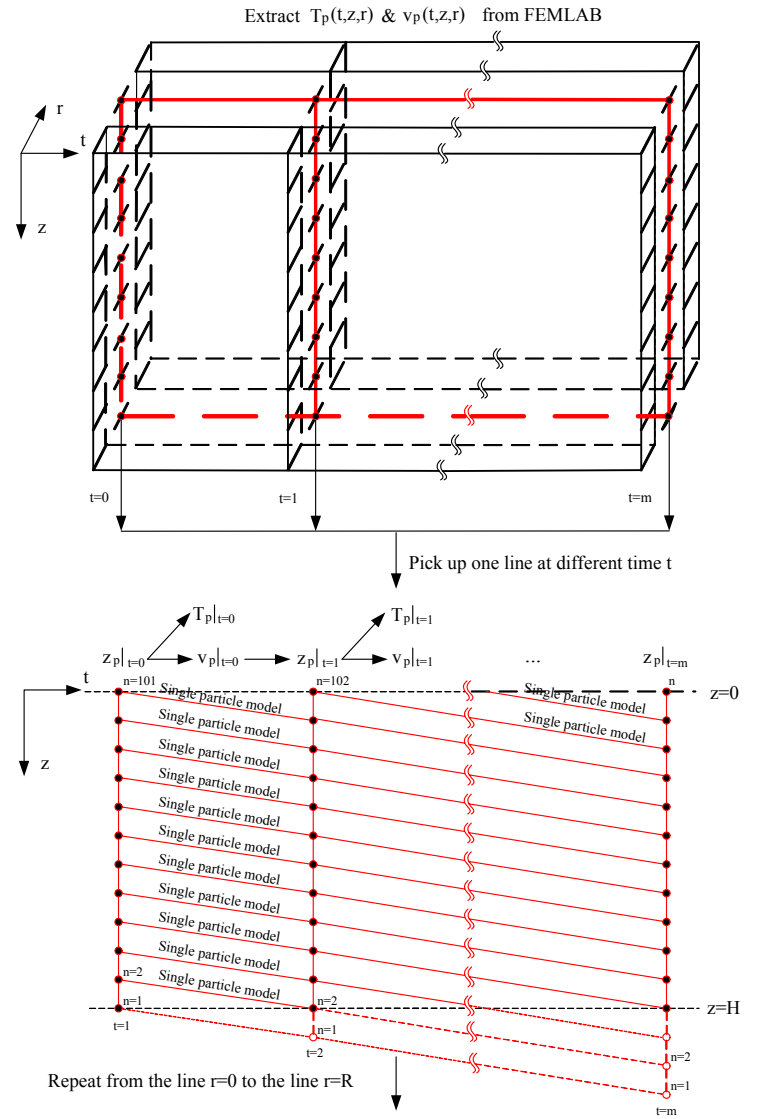
$$\frac{\partial \tilde{T}_g}{\partial \tilde{z}} = -\frac{\dot{m}_g C_{p,g} H}{k_g \varepsilon S} (\tilde{T}_g - \tilde{T}_{g,in}) \text{ at } \tilde{z} = 1 \quad (6b)$$

$$\frac{\partial \tilde{T}_g}{\partial \tilde{r}} = 0 \text{ at } \tilde{r} = 0 \quad (6c)$$

$$\frac{\partial \tilde{T}_g}{\partial \tilde{r}} = -\frac{h_{gw} R}{k_g} (\tilde{T}_g - \tilde{T}_w) \text{ at } \tilde{r} = 1 \quad (6d)$$

$$x_c = x_{c,in} \text{ at } \tilde{z} = 0 \quad (7)$$

The computational procedure is summarized as follows (See Figure 1): (i) we set uniform grid points for the reactor and divide the reactor into a mesh network. Since the plug flow pattern is assumed, we can consider the downward movement of particles line by line, i.e. we use the single particle model for each column (or vertical line); (ii) We choose one line at a time, and then discretize in the axial (z) direction, assign the number for each particle at  $t=t_0$ , and record the initial temperature for each particle; (iii) For a given small time increase, determine the new position of each particle in z direction; (iv) Find the temperature of each particle from the dynamic temperature profile in the solid phase at time  $t=t_1$ , and record it for each particle; (v) Find the amount of particles exiting the reactor during the time span from  $t_0$  to  $t_1$  if any, and add more particles at the entrance to make a constant number of particles in the reactor, and record both time  $t$  and temperature for those entering the reactor. For those particles exiting the reactor, we record time  $t$  leaving the reactor; (vi) Continue steps from (iii) to (v) for the given simulation time; (vii) Using the particle model, calculate the concentration and molecular weight profiles for each particle along the same line; (viii) Select another particle line in the reactor and repeat the calculations from step (ii) to (vii) until all the particle lines in the reactor are counted.



## Results and discussion

The reactor model equations (PDEs) have been solved by using FEMLAB®. A start-up process is used to simulate dynamic behavior in a moving packed bed reactor. We assume that initially the reactor is charged with prepolymer particles at ambient temperature. The prepolymer particles and heated purge gas flow countercurrently. The reactor operation conditions and prepolymer properties are given in Table 1.

The temperature profiles of the solid phase during the reactor startup are shown in Figure 2. It shows that temperature nonuniformity exists in both radial and axial directions, affecting the polymer molecular weight. Figure 2 also shows that it takes about 6 hours ( $0.5\bar{t}$ , residence time for solid particles  $\bar{t} \approx 11.5\text{hr}$ ) for the reactor temperature profile to reach a steady state. However, for molecular weight to reach its steady state profile, it takes much longer. Figures 3 and 4 show the profiles of weight-average molecular weight at 1 and 2 residence times, respectively.

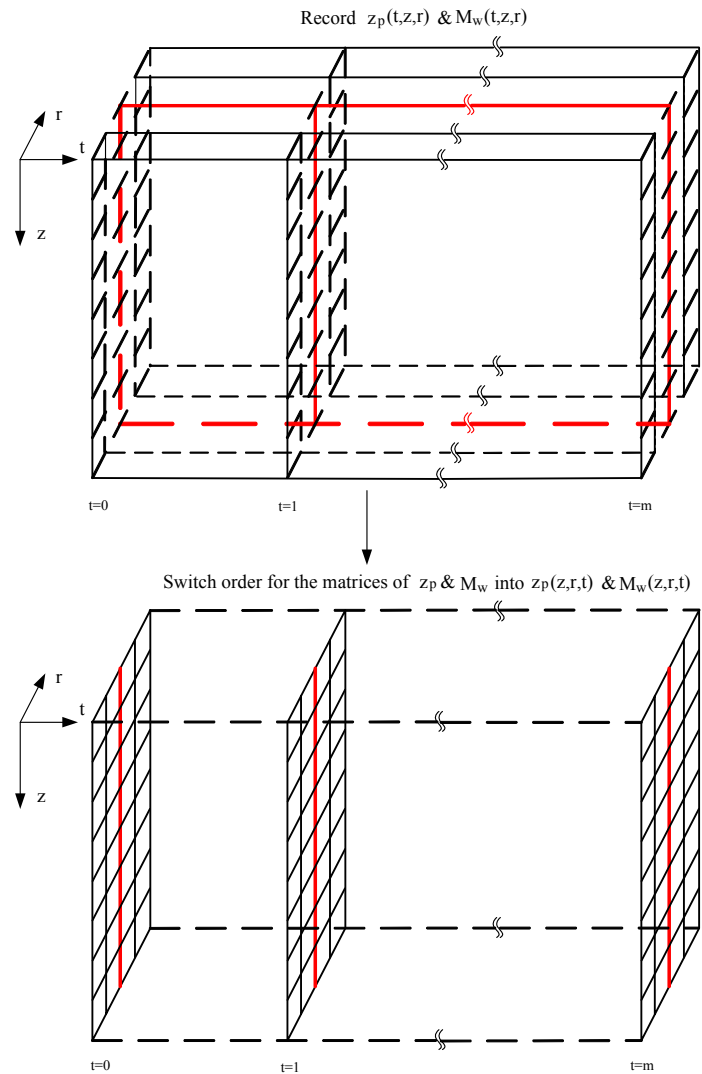


Fig. 1. Calculation scheme

Table 1. Operation conditions and prepolymer properties

$P$	Outlet pressure, 101325 (Pa)
$\varepsilon$	Voidage in the reactor, 0.4
$d_p$	Particle diameter, 0.01 (cm)
$T_{s,0}$	Initial temperature of solid phase, 298.15 (K), scaled value ( $\tilde{T}_{s,0} = 1$ )
$T_{g,0}$	Initial temperature of gas phase, 298.15 (K)
$T_w$	Reactor wall temperature, 298.15 (K)
$T_{s,in}$	Inlet temperature of solid phase, 298.15 (K)
$T_{g,in}$	Inlet temperature of gas phase, 469.15 (K)
$D$	Reactor diameter, 40 (cm)
$H$	Total reactor length, 400 (cm)
$\dot{m}_p$	Mass flow rate of solid particles, 500 (g/min)
$\dot{m}_g$	Mass flow rate of nitrogen gas, 3000 (g/min)
$x_{c,0}$	Initial crystallinity, 21.1%
$r'$	End group ratio in the prepolymer, 1.0
$C_{A,0}$	Initial concentration of phenyl carbonate group in the prepolymer, 0.0941 (mol/L)
$C_{B,0}$	Initial concentration of hydroxyl group in the prepolymer, 0.0941 (mol/L)
$C_{Z,0}$	Initial concentration of polymer repeating unit in the prepolymer, 8.6830 (mol/L)

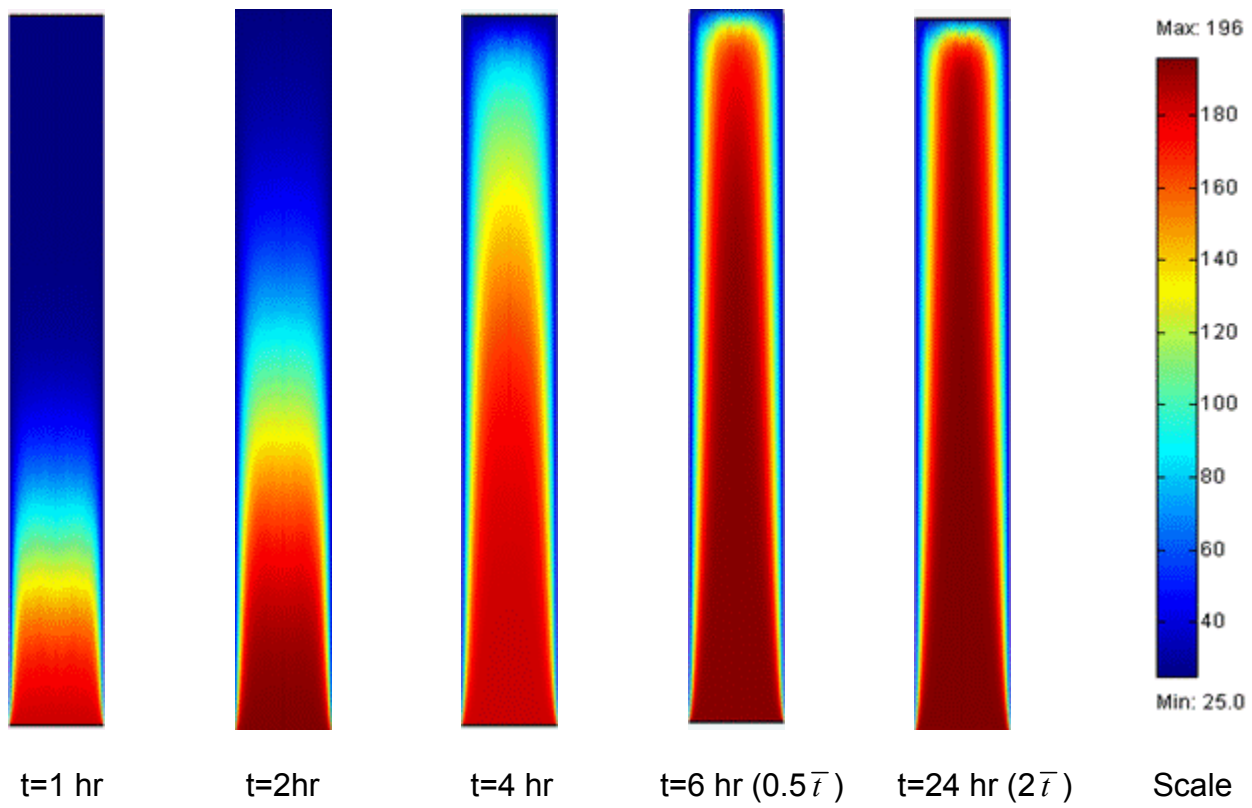


Figure 2. Reactor temperature profiles.

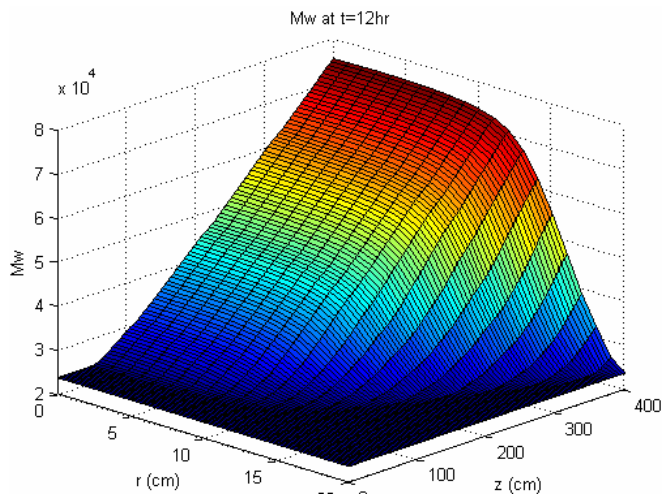


Figure 3. 3-D  $M_w$  @  $t=12$  hr ( $1\bar{t}$ ).

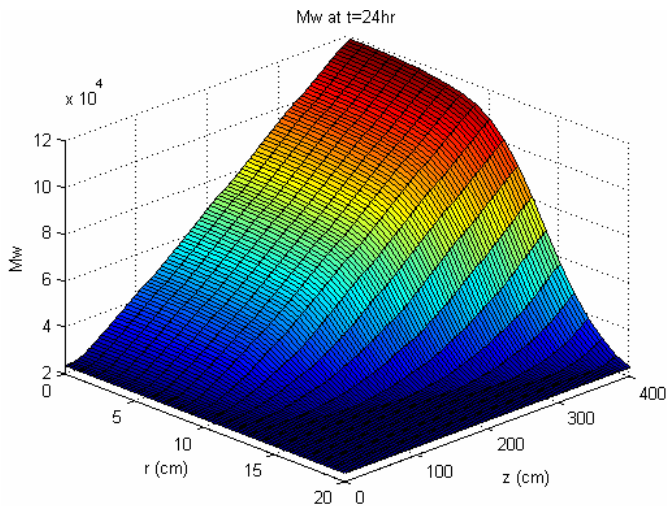


Figure 4. 3-D  $M_w$  @  $t=24$  hr ( $2\bar{t}$ ).

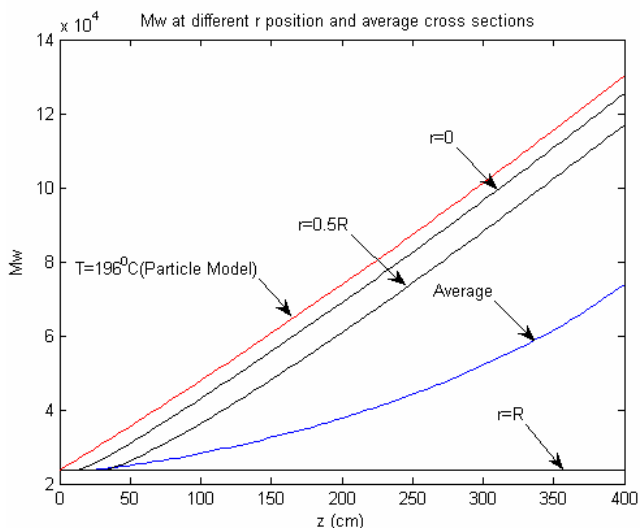


Figure 5. Radial molecular weight profiles.

Figure 5 shows the radial profiles of polymer molecular weight. Notice that there is a significant heterogeneity in the  $M_w$  values. Near the reactor walls where the reaction temperature is low because of heat loss to the reactor walls, the polymer molecular weight does not increase. Near the center of the reactor, highest molecular weight is obtained. Also shown in Figure 5 is the polymer weight profile in a single polymer particle with reaction time equivalent to the reactor length at steady state. Since the particle is at the reaction temperature for the entire reaction period, its molecular weight is larger than those obtained from the continuous reactor. In other words, this simulation results show that reactor heat transfer effects need to be analyzed when scaling up the single particle simulation results.

The sensitivity of the continuous solid state polymerization reactor model to a few selected reactor parameters (mass flow rates of solid phase and gas phase) are shown in Figures 6 and 7.

Figures 6 and 7 show that higher flow rate of gas phase or lower flow rate of solid phase leads to a higher molecular weight average at the reactor outlet.

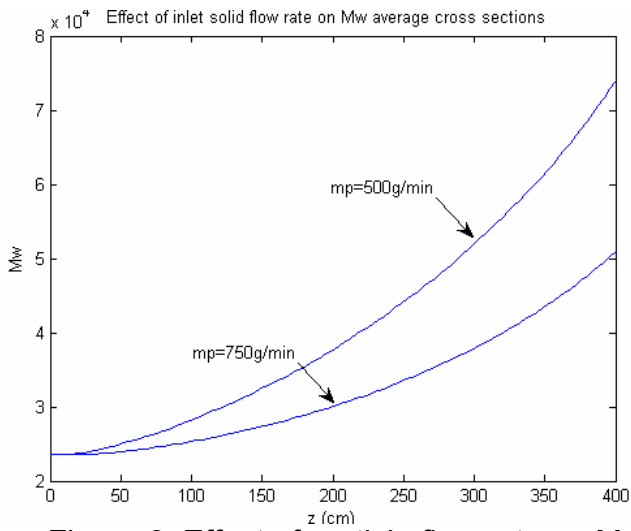


Figure 6. Effect of particle flow rate on  $M_w$ .

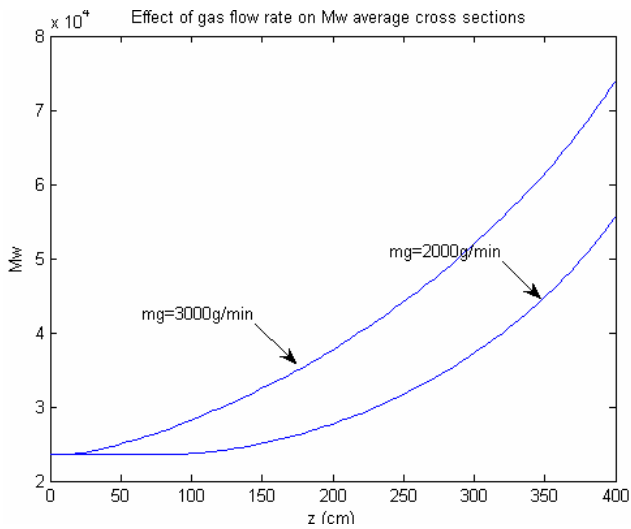


Figure 7. Effect of gas flow rate on  $M_w$ .

Figure 8 shows the effects of prepolymer particle size on the molecular weight average. As expected, prepolymer particle size has a significant effect on the molecular weight. The smaller the particle size is, the faster the polymer molecular weight increases.



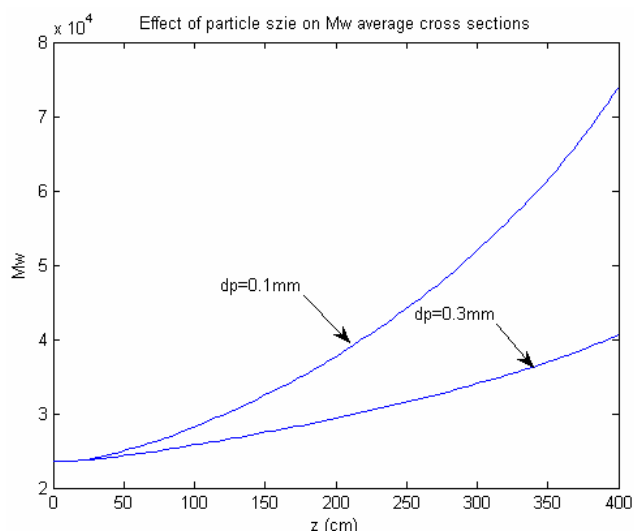


Figure 8. Effect of particle size on  $M_w$ .

### Concluding Remarks

Mathematical models of small and large prepolymer particles have been developed and incorporated into a dynamic continuous solid state polymerization reactor model. The reactor modeled in this work is a packed moving bed reactor in which prepolymer particles of low molecular weight are supplied to the top of a vertical and cylindrical reactor. A hot nitrogen gas is supplied to the bottom of the reactor to heat up the prepolymer particles. This countercurrent flow system of gas and solid phases is effective for the solid state polymerization, but due to some heat loss through the reactor walls, temperature nonuniformity develops in the reactor. The dynamic model has been solved using the finite element method. The reactor simulation results indicate that both radial and axial temperature nonuniformities exist and they have a strong effect on the polymer molecular weight. More results will be presented at the meeting.

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