

Control of Molecular Weight Distribution of Polyethylene in Continuous Stirred Tank Reactors with High Activity Soluble Ziegler-type Catalysts

INTRODUCTION

Recently, it has been reported that some soluble organo-zirconium catalysts such as bis(cyclopentadienyl) dimethyl-zirconium [$\text{Cp}_2\text{Zr}(\text{CH}_3)_2$] show very high ethylene polymerization activity when cocatalyzed by aluminoxane, a reaction product of aluminum alkyl and water.¹⁻³ In various Ziegler-Natta olefin polymerization systems, catalyzed by either heterogeneous or soluble catalysts, hydrogen is an efficient chain transfer agent which regulates the molecular weight of polymers. Molecular weight distribution, represented by polydispersity ($Q = \overline{M}_w / \overline{M}_n$), is quite broad ($Q = 5-20$) when ethylene is polymerized over a solid catalyst. Since many polymer properties are strongly dependent on the MWD, controlling the MWD is of enormous industrial importance. Although several mechanisms have been proposed, our understanding of MWD broadening phenomena in heterogeneous polymerization is still incomplete.^{4,5}

In contrast to heterogeneous Ziegler catalysts which produce polymers of broad MWD, most of the soluble Ziegler catalysts produce polymers of narrow MWD. This is probably due either to the existence of a single or few active species or to the absence of mass transfer resistance in a growing polymer particle. With high-activity soluble catalysts such as $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ /aluminoxane, better control of MWD can be realized through the manipulation of reactor operating variables or through the alteration of reactor configuration.

In this paper, we shall demonstrate quantitatively how MWD can be broadened in consecutive continuous stirred tank reactors (CSTRs) operating at different chain transfer agent concentrations. The results reported here for two reactor systems can be extended to more general multireactor systems without significant computational difficulties.

MOMENT EQUATIONS

Let us consider two CSTRs of volume V_1 and V_2 , respectively. The unsteady state mass balances for the growing and dead polymer chains in reactors 1 and 2 take the form

$$\frac{dP_{n,1}}{dt} = k_{p1}M_1\left(P_{n-1,1} - \frac{1}{\alpha_1}P_{n,1}\right) - \frac{1}{\theta_1}P_{n,1} \quad (1)$$

$$\frac{dM_{n,1}}{dt} = k_{p1}M_1\left(\frac{1}{\alpha_1} - 1\right)P_{n,1} - \frac{1}{\theta_1}M_{n,1} \quad (2)$$

$$\frac{dP_{n,2}}{dt} = k_{p2}M_2\left(P_{n-1,2} - \frac{1}{\alpha_2}P_{n,2}\right) + \frac{1}{\theta_2}(P_{n,1} - P_{n,2}) \quad (3)$$

$$\frac{dM_{n,2}}{dt} = k_{p2}M_2\left(\frac{1}{\alpha_2} - 1\right)P_{n,2} + \frac{1}{\theta_2}(M_{n,1} - M_{n,2}) \quad (4)$$

where $P_{n,j}$ is the concentration of live polymer in reactor j , $M_{n,j}$ the concentration of dead polymer, k_{pj} the propagation rate constant, M_j the monomer concentration, θ_j the mean residence time, and α_j the probability of propagation. If only chain transfer to the chain transfer agent (e.g., H_2) is assumed to occur, α_j takes the form

$$\alpha_j = \frac{k_{pj}M_j}{k_{pj}M_j + k_{tr,j}X_j^\beta} \quad (5)$$

where X_j denotes the concentration of chain transfer agent. When hydrogen is used, $\beta \approx 0.5$ for the $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ -aluminoxane catalyst system.¹ Moment equations for live and dead polymers in each tank are as follows:

Tank 1:

$$\frac{d\lambda_{0,1}^l}{dt} = k_{p1}M_1P_{T1} - \left(\frac{k_{p1}M_1}{\alpha_1} + \frac{1}{\theta_1}\right)\lambda_{0,1}^l \quad (6)$$

$$\frac{d\lambda_{1,1}^l}{dt} = k_{p1}M_1P_{T1} - \left[k_{p1}M_1\left(\frac{1}{\alpha_1} - 1\right) + \frac{1}{\theta_1}\right]\lambda_{1,1}^l \quad (7)$$

$$\frac{d\lambda_{2,1}^l}{dt} = k_{p1}M_1(P_{T1} + 2\lambda_{1,1}^l) - \left[k_{p1}M_1\left(\frac{1}{\alpha_1} - 1\right) + \frac{1}{\theta_1}\right]\lambda_{2,1}^l \quad (8)$$

$$\frac{d\lambda_{0,1}^d}{dt} = k_{p1}M_1\left(\frac{1}{\alpha_1} - 1\right)(P_{T1} - P_{1,1}) - \frac{1}{\theta_1}\lambda_{0,1}^d \quad (9)$$

$$\frac{d\lambda_{i,1}^d}{dt} = k_{p1}M_1\left(\frac{1}{\alpha_1} - 1\right)(\lambda_{i,1}^l - P_{1,1}) - \frac{1}{\theta_1}\lambda_{i,1}^d \quad (i = 1, 2) \quad (10)$$

Tank 2:

$$\frac{d\lambda_{0,2}^l}{dt} = k_{p2}M_2P_{T2} + \frac{1}{\theta_2}\lambda_{0,1}^l - \left(\frac{k_{p2}M_2}{\alpha_2} + \frac{1}{\theta_2}\right)\lambda_{0,2}^l \quad (11)$$

$$\frac{d\lambda_{1,2}^l}{dt} = k_{p2}M_2P_{T2} + \frac{1}{\theta_2}\lambda_{1,1}^l - \left[k_{p2}M_2\left(\frac{1}{\alpha_2} - 1\right) + \frac{1}{\theta_2}\right]\lambda_{1,2}^l \quad (12)$$

$$\frac{d\lambda_{2,2}^l}{dt} = k_{p2}M_2P_{T2} + \frac{1}{\theta_2}\lambda_{2,1}^l + 2k_{p2}M_2\lambda_{1,2}^l - \left[\left(\frac{1}{\alpha_2} - 1\right)k_{p2}M_2 + \frac{1}{\theta_2}\right]\lambda_{2,2}^l \quad (13)$$

$$\frac{d\lambda_{i,2}^d}{dt} = k_{p2}M_2\left(\frac{1}{\alpha_2} - 1\right)(\lambda_{i,2}^l - P_{1,2}) + \frac{1}{\theta_2}(\lambda_{i,1}^d - \lambda_{i,2}^d) \quad (i = 1, 2, 3) \quad (14)$$

where $\lambda_{i,j}^{l(d)}$ indicates the i th live (dead) moment in the j th reactor, and

$$P_{Tj} = \sum_{n=0}^{\infty} P_{n,j} \quad (15)$$

is a constant equal to the total active site concentration. $P_{1,j}$ must be determined from

$$\frac{dP_{1,1}}{dt} = k_{p1}M_1\left(P_{T1} - \lambda_{0,1}^l - \frac{1}{\alpha_1}P_{1,1}\right) - \frac{1}{\theta_1}P_{1,1} \quad (16)$$

$$\frac{dP_{1,2}}{dt} = k_{p2}M_2\left(P_{T2} - \lambda_{0,2}^l - \frac{1}{\alpha_2}P_{1,2}\right) + \frac{1}{\theta_2}(P_{1,1} - P_{1,2}) \quad (17)$$

Number average and weight average molecular weights in tank j are given by

$$\bar{M}_{n,j} = \frac{\lambda_{1,j}^l + \lambda_{1,j}^d}{\lambda_{0,j}^l + \lambda_{0,j}^d} \text{MW} \quad (18)$$

$$\bar{M}_{w,j} = \frac{\lambda_{2,j}^l + \lambda_{2,j}^d}{\lambda_{1,j}^l + \lambda_{1,j}^d} \text{MW} \quad (19)$$

and polydispersity by

$$Q_j = \overline{M}_{w,j} / \overline{M}_{n,j} \quad (20)$$

where MW is the molecular weight of the monomer.

RESULTS AND DISCUSSION

At steady state, the concentration of each species is constant, and the moment equations can be solved analytically. By controlling the polymerization temperature and partial pressure of ethylene and hydrogen, one can maintain constant reactant and catalyst concentrations in the liquid medium. Figure 1 represents the computer simulation result showing the MWD broadening in the second reactor as a function of α_2 . [see eq. (5)], which represents the relative concentration of chain transfer agent [i.e., if the concentration of chain transfer agent is high (low), α_2 is small (large)]. The numerical values of the kinetic parameters used in our model simulation are reported by Kaminsky et al.¹ for the bis (cyclopentadienyl) dimethyl-zirconium catalyst. Note that when the concentration of active species (P_T) in both reactors is identical (curve A) a significant broadening of MWD occurs if $\alpha_2 < \alpha_1$ (i.e., higher chain transfer agent concentration in tank 2). If $\alpha_2 = \alpha_1$, MWD in the second tank is the same as that in the first tank and $\overline{M}_w / \overline{M}_n = 2.0$. When $\alpha_2 > \alpha_1$ (i.e., lower chain transfer agent concentration in tank 2), MWD broadening occurs quite rapidly with an increase in α_2 . When the catalyst concentration in tank 2 is lower than that in tank 1 (curve B)—probably due to catalyst deactivation—MWD becomes slightly narrower but does not change considerably.

The use of a chain transfer agent also results in the reduction of the molecular weight of polymer. Figure 2 shows the variation of the number average molecular weight in the second tank as a function of α_2 . Note that \overline{M}_n decreases significantly for $\alpha_2 < \alpha_1$, while \overline{M}_n increases for $\alpha_2 > \alpha_1$. Thus, polymers from the second reactor have broader MWD and shorter chain lengths for $\alpha_2 > \alpha_1$ compared to those from the first reactor. This implies that polymer molecular weight and MWD can be controlled by maintaining different chain transfer agent concentrations in the two reactors. The mean residence times (θ_1 and θ_2) have been found to have negligible impact on the MWD in both reactors. The result of our simulation work shows quantitatively how the controlling of MWD broadening can be accomplished using highly active soluble Ziegler-catalyst systems.

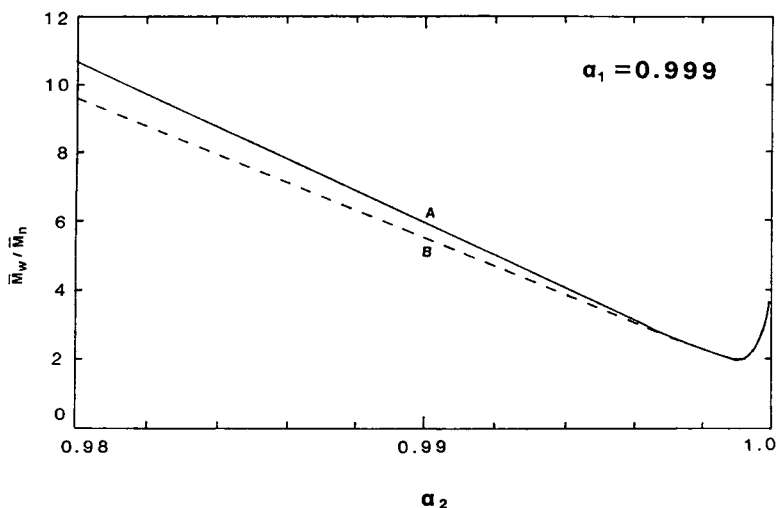


Fig. 1. The effect of α_2 on the polydispersity of polymers in the second tank; $k_{p1} = k_{p2} = 1.43 \times 10^4$ L/mol s, $M_1 = M_2 = 0.3$ mol/L, $P_{T1} = 3.0 \times 10^{-8}$ mol/L, $P_{T2} = 3.0 \times 10^{-8}$ mol/L (curve A), $P_{T2} = 1.5 \times 10^{-8}$ mol/L (curve B), $\theta_1 = \theta_2 = 2$ h.¹

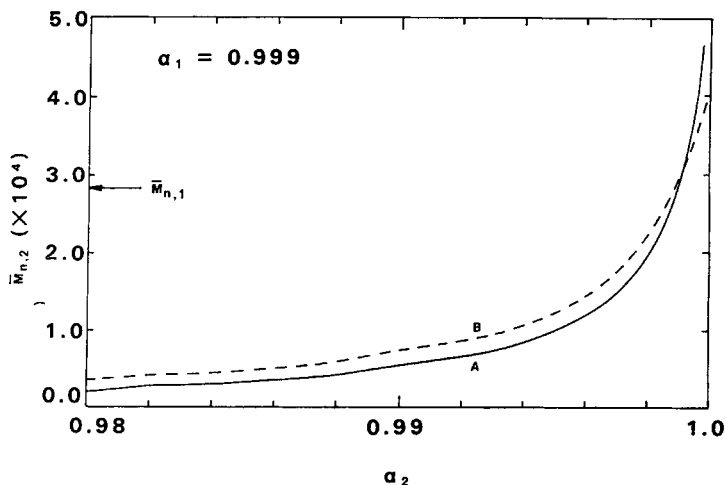


Fig. 2. The effect of α_2 on the molecular weight of polymers in the second tank.

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