Determination of kinetic parameters for ethylene polymerization (with and without hydrogen) by Ziegler-Natta catalyst

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Appendix I

The aim of this section is to discuss the development of mathematical model for Ziegler-Natta catalyst ethylene polymerization and kinetic studies.

There are mathematical methods to calculate polymer properties. In these methods analytical, numerical and statistical approaches are proposed.
Usually, molecular weight average and other parameters in polymerization reactions can be calculated by numerical integration of the population balance equations and the method of molecular weight moments.
[Biesenberger JA, Sebastian DH (1983) Principles of polymerization Engineering, Wiley, New York]

For a simple substance, the abnormal molecular weight (λ) is the product of the molecular weight multiplied by the number of molecules in the substance:

$$\lambda = n \cdot M$$

This equation is called the non-normal first molecular weight moment, which the degree of moment increases with increasing the power of molecular weight as follows:

$$\lambda_j = n \cdot M^{\,j}$$

Due to the molecular weight diversity of different chains, the molecular weight moment of polymers is calculated as follows:

$$\lambda_j = \sum n_i M_i^{\,j}$$

For example, the zero to third moments of the molecular weight of polymers are expressed as follows:

$$\lambda_\circ = \sum n_i M_i^{\,\circ} = \sum n_i$$

$$\lambda_1 = \sum n_i M_i$$

$$\lambda_2 = \sum n_i M_i^{\,2}$$

$$\lambda_3 = \sum n_i M_i^3$$

Molecular weight moments can also be related to molecular weight averages:

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\lambda_1}{\lambda_\circ} \quad \Rightarrow \quad \lambda_1 = \lambda_\circ \overline{M}_n$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\lambda_2}{\lambda_1} \quad \Rightarrow \quad \lambda_2 = \lambda_1 \overline{M}_w = \lambda_\circ \overline{M}_n \overline{M}_w$$

$$\overline{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\lambda_3}{\lambda_2} \quad \Rightarrow \quad \lambda_3 = \lambda_2 \overline{M}_z = \lambda_\circ \overline{M}_n \overline{M}_w \overline{M}_z$$

Modeling by Using Moment Equations:

$$C_p + Al \xrightarrow{k_{aA}^j} P_{0,j}$$

$$C_p \xrightarrow{k_{aSp}^j} P_{o,j}$$

$$P_{0,j} + M \xrightarrow{k_i^j} P_{1,j}$$

$$P_{1,j} + M \xrightarrow{k_p^j} P_{2,j}$$

$$\vdots$$

$$P_{r,j} + M \xrightarrow{k_p^j} P_{r+1,j}$$

$$P_{r,j} + H_2 \xrightarrow{k_{trH}^j} P_{H,j} + D_{r,j}$$

$$P_{H,j} + M \xrightarrow{k_{iH}^j} P_{1,j}$$

$$P_{r,j} + M \xrightarrow{k_{trM}^j} P_{1,j} + D_{r,j}$$

$$P_{r,j} + Al \xrightarrow{k_{trAl}^j} P_{0,j} + D_{r,j}$$

$$P_{r,j} \xrightarrow{k_{t\beta}^j} P_{0,j} + D_{r,j}$$

$$P_{r,j} \xrightarrow{k_{dSp}^j} inactive\ specious + D_{r,j}$$

$$P_{r,j} + Al \xrightarrow{k_{dA}^j} inactive\ specious + D_{r,j}$$

Based on the above reactions, in semi-batch processes, mass balance equations for the reaction components are given by:

$$\frac{d\left[C_p\right]}{dt} = -\left[\sum_{j=1}^{5} k_{aA}^j \left[Al\right] + \sum_{j=1}^{5} k_{aSp}^j\right]\left[C_p\right]$$

$$\frac{d[Al]}{dt} = -\left(\sum_{j=1}^{5} k_{aA}^{j}\right)\left[C_p\right][Al] - \left(\sum_{j=1}^{5}\left[\left(k_{trA}^{j} + k_{dA}^{j}\right)\left(\sum_{r=1}^{\infty}\left[P_{r,j}\right]\right)\right]\right)[Al]$$

$$\frac{d\left[P_{0,j}\right]}{dt} = \left(k_{aA}^{j}\left[Al\right] + k_{aSp}^{j}\right)\left[C_P\right] - k_i^{j}\left[P_{0,\mathrm{j}}\right][M] + \left(k_{trAl}^{j}\left[Al\right] + k_{t\beta}^{j}\right)\sum_{r=1}^{\infty} P_{\mathrm{r},j}$$

$$\frac{d\left[P_{1,\mathrm{j}}\right]}{dt} = \left[k_i^{j}\left[P_{0,\mathrm{j}}\right] - k_p^{j}\left[P_{1,\mathrm{j}}\right] + k_{trM}^{j}\sum_{r=1}^{\infty}\left[P_{r,j}\right] + k_{iH}^{j}\left[P_{H,j}\right]\right][M]$$

$$\frac{d\left[P_{H,j}\right]}{dt} = k_{trH}^{j}\sum_{r=1}^{\infty}\left[P_{r,j}\right]\left[H_2\right] - k_{iH}^{j}\left[P_{H,j}\right][M]$$

$$\frac{d\left[H_2\right]}{dt} = -\left[\sum_{j=1}^{5}\left(k_{trH}^{j}\sum_{r=1}^{\infty}\left[P_r^{j}\right]\right)\right]\left[H_2\right]$$

$$\frac{d\left[P_{r,j}\right]}{dt} = k_p^{j}\left[P_{r-1,j}\right][M] - \left(k_p^{j}[M] + k_{trH}^{j}\left[H_2\right] + k_{trM}^{j}[M] + k_{trAl}^{j}[Al] + k_{t\beta}^{j} + k_d\right)\left[P_{r,j}\right]$$

$$\frac{d\left[D_{r,j}\right]}{dt} = \left(k_{trH}^{j}\left[H_2\right] + k_{trM}^{j}[M] + k_{trAl}^{j}[Al] + k_{t\beta}^{j} + k_d^{j}\right)\left[P_{r,j}\right]$$

$$k_d^{j} = k_{dSp}^{j} + k_{dA}^{j}[Al]$$

α^j, The probability of a propagation reaction to the sum of propagation and termination reactions in center j, is defined as follows:

$$\alpha^{j} = \frac{k_p^{j}[M]}{k_p^{j}[M] + k_{trH}^{j}\left[H_2\right] + k_{trM}^{j}[M] + k_{trAl}^{j}[Al] + k_{t\beta}^{j} + k_d^{j}}$$

number- and weight-average molecular weight (M_n and M_w), molecular weight distribution, and polydispersity index, moment equations are used herein. For growing polymer chains in active center j, kth moment is defined by:

$$\lambda_k^{j} = \sum_{r=1}^{\infty}\left(r^{k}\left[P_{r,\mathrm{j}}\right]\right)$$

Also, for dead polymer chains in active center j, k^{th} moment is defined by:

$$\mu_k^{j} = \sum_{r=1}^{\infty} r^{k}\left[D_{r,j}\right]$$

Substituting the moments in mass balance equations, one may rearrange the equations to the following ones:

$$\frac{d[Al]}{dt} = -\left(\sum_{j=1}^{5} k_{aA}^{j}[Al] + \sum_{j=1}^{5} k_{aSp}^{j}\right)\left[C_p\right] - \left(\sum_{j=1}^{5}\left[\left(k_{trAl}^{j} + k_{dA}^{j}\right)\lambda_0^{j}\right]\right)[Al]$$

$$\frac{d\left[P_{0,j}\right]}{dt} = \left(k_{aA}^{j}[Al] + k_{aSp}^{j}\right)\left[C_p\right] - k_i^{j}\left[P_{0,\mathrm{j}}\right][M] + \left(k_{trAl}^{j}[Al] + k_{t\beta}^{j}\right)\lambda_o^{j}$$

$$\frac{d\left[P_{1,\mathrm{j}}\right]}{dt} = \left[k_i^{j}\left[P_{0,\mathrm{j}}\right] - k_p^{j}\left[P_{1,\mathrm{j}}\right] + k_{iH}^{j}\left[P_{H,j}\right] + k_{trM}^{j}\lambda_0^{j}\right][M]$$

$$\frac{d\left[P_{H,j}\right]}{dt} = k_{trH}^{j}\lambda_0^{j}\left[H_2\right] - k_{iH}^{j}\left[P_{H,j}\right][M]$$

$$\frac{d\left[H_2\right]}{dt} = -\left[\sum_{j=1}^{5}\left(k_{trH}^{j}\lambda_0^{j}\right)\right]\left[H_2\right]$$

$$\frac{d\left[P_{r,j}\right]}{dt} = k_p^{j}\left[P_{r-1,j}\right][M] - \left(\frac{1}{\alpha^{j}}\right)k_p^{j}[M]\left[P_{r,j}\right]$$

$$\frac{d\left[D_{r,j}\right]}{dt} = k_p^{j}[M]\left(\frac{1}{\alpha^{j}} - 1\right)\left[P_{r,j}\right]$$

The zero moment, the first, and the second moment equations were used to calculate number- and weight-average molecular weight and polydispersity index. If polymer molecular weight, at each moment of the reaction, stems from dead and growing chains, equations related to number- and weight-average molecular weight and polydispersity index are given by:

$$\bar{M}_n^{\,j} = \frac{\mu_1^{j} + \lambda_1^{j}}{\mu_0^{j} + \lambda_0^{j}} \times M_0$$

$$\bar{M}_w^{\,j} = \frac{\mu_2^{j} + \lambda_2^{j}}{\mu_1^{j} + \lambda_1^{j}} \times M_0$$

$$PDI = \frac{\bar{M}_w^{\,j}}{\bar{M}_n^{\,j}} = \frac{\left(\mu_2^{j} + \lambda_2^{j}\right)\left(\mu_0^{j} + \lambda_0^{j}\right)}{\left(\mu_1^{j} + \lambda_1^{j}\right)^2}$$

where, M_0 is monomer molecular weight.

To calculate $\bar{M}_n^{\,j}$, $\bar{M}_w$ and *PDI* one needs to numerically compute moment equations used. Rearranging the above equations, the following equations can be derived for the zero moment, the first, and the second moment of growing and dead chains:

$$\frac{d\lambda_0^j}{dt} = \left[k_i^j \left[P_{0,j} \right] + k_{iH}^j \left[P_{H,j} \right] + k_p^j \left[P_{1,j} \right] \left(\frac{1}{\alpha^j} - 1 \right) + \left(k_{trM}^j + k_p^j \left(1 - \frac{1}{\alpha^j} \right) \right) \lambda_0^j \right] [M]$$

$$\frac{d\lambda_1^j}{dt} = \left[k_i^j \left[P_{0,j} \right] + k_{iH}^j \left[P_{H,j} \right] + k_p^j \left[P_{1,j} \right] \left(\frac{1}{\alpha^j} - 1 \right) + \left(\left(k_{trM}^j + k_p^j \right) \lambda_0^j + k_p^j \left(1 - \frac{1}{\alpha^j} \right) \right) \lambda_1^j \right] [M]$$

$$\frac{d\lambda_2^j}{dt} = \left[k_i^j \left[P_{0,j} \right] + k_{iH}^j \left[P_{H,j} \right] + k_p^j \left[P_{1,j} \right] \left(\frac{1}{\alpha^j} - 1 \right) + \left(\left(k_{trM}^j + k_p^j \right) \lambda_0^j + 2k_p^j \lambda_1^j + k_p^j \left(1 - \frac{1}{\alpha^j} \right) \right) \lambda_2^j \right] [M]$$

$$\frac{d\mu_0^j}{dt} = k_p^j [M] \left(\frac{1}{\alpha^j} - 1 \right) \lambda_0^j$$

$$\frac{d\mu_1^j}{dt} = k_p^j [M] \left(\frac{1}{\alpha^j} - 1 \right) \lambda_1^j$$

$$\frac{d\mu_2^j}{dt} = k_p^j [M] \left(\frac{1}{\alpha^j} - 1 \right) \lambda_2^j$$