Ethylene Homopolymerization Kinetics with a Constrained Geometry Catalyst in a Solution Reactor

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Appendix A

The concentration of complexed active sites given by Equation (6) is rewritten below as Equation (A-1),

$$[P^{*} \cdot M] = \frac{k_f [M] C_t}{k_r + k_f [M]} \tag{A-1}$$

or,

$$[P^{*} \cdot M] = \frac{K [M] C_t}{1 + K [M]} \tag{A-2}$$

The propagation rate is given by,

$$R_p = k_p [P^{*}.M][M] \tag{A-3}$$

Substituting Equation (A-2) in (A-3) gives,

$$R_p = \frac{k_p C_t K[M]^2}{1 + K[M]} \tag{A-4}$$

Catalyst sites are assumed to decay according to the second order model given below,

$$\frac{\mathrm{d}C_t}{\mathrm{d}t} = -k_d C_t^{\,2} \tag{A-5}$$

Integration of Equation (A-5) yields,

$$\frac{1}{C_t} = \frac{1}{C_0} + k_d t \tag{A-6}$$

Rearranging,

$$C_t = \frac{C_0}{1 + k_d C_0 t} \tag{A-7}$$

Substituting Equation (A-7) in (A-4), we get,

$$R_p = \frac{k_p C_0 K[M]^2}{(1 + K[M])(1 + k_d C_0 t)} \tag{A-8}$$

The molar balance for monomer in a semi-batch reactor is given by,

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = \frac{F_{M,in}}{V_R} - R_p \tag{A-9}$$

Since monomer concentration is kept constant, it can be concluded that,

$$F_{M,in} = R_p V_R \tag{A-10}$$

Substituting Equation (A-8) in (A-10) leads to the final equation for monomer uptake rate,

$$F_{M,in} = \frac{k_p K V_R C_0 [M]^2}{(1 + K[M])(1 + k_d C_0 t)} \tag{A-11}$$

Appendix B

Taking Laplace transform of Equations (19) and (20) gives

$$sC_t(s) - C_0 = -(k_{dth} + k_d^{'})C_t(s) + k_a^{'}C_d(s) \tag{B-1}$$

$$sC_d(s) = -k_a^{'}C_d(s) + k_d^{'}C_t(s) \tag{B-2}$$

Rearranging Equation (B-2),

$$C_d(s) = \frac{k_d^{'}C_t(s)}{(s + k_a^{'})} \tag{B-3}$$

and then substituting Equation (B-3) into Equation (B-1) yields,

$$C_t(s) = \frac{C_0(s + k_a^{'})}{(s + k_{dth} + k_d^{'})(s + k_a^{'}) - k_d^{'}k_a^{'}} \tag{B-4}$$

The theory of partial fractions enables us to write Equation (B-4) as,

$$C_t(s) = \frac{C_0(s_1 + k_a^{'})}{(s_1 - s_2)(s - s_1)} - \frac{C_0(s_2 + k_a^{'})}{(s_1 - s_2)(s - s_2)} \tag{B-5}$$

where s_1 and s_2 are constants defined, previously, in Equations (22) and (23),

Taking the inverse Laplace transform of Equation (B-5) gives the solution for the concentration of active sites in the time domain,

$$C_t = \frac{C_0}{(s_1 - s_2)}\left[(s_1 + k_a^{'})e^{s_1 t} - (s_2 + k_a^{'})e^{s_2 t}\right] \tag{B-6}$$