

Estimation of Kinetic Parameters in Transition-Metal-Catalyzed Gas-Phase Olefin Copolymerization Processes

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The estimation of kinetic parameters is a critical part of developing a process model for industrial polymerization processes. In transition-metal-catalyzed gas-phase olefin copolymerization processes, polymer density is a strong function of the amount of higher α -olefin comonomers incorporated into the polymer. For the calculation of copolymer composition with a process model, propagation rate constants, which vary from one catalyst system to another, must be known. In this paper, several computational methods applicable to batch, semibatch, and continuous reactors are presented to estimate the propagation rate constants and reactivity ratios in gas-phase olefin copolymerization processes.

1. Introduction

In recent years, the polyolefin industry has experienced a revolutionary progress in catalyst and process technology. New and improved catalysts (e.g., single-site catalysts, metallocenes) are claimed to offer increased polymer productivity and more precise control of polymer properties. New end-use markets have also been developed to capitalize the development of new polyolefins that have distinct differences in their physical, mechanical, and rheological properties from conventional polyolefins. As the competition among polyolefin manufacturers becomes intense, it is crucial to shorten the new process development time for full commercialization of new process technology and to improve the existing polymerization processes.

In industrial polyolefin processes, many different types of catalysts are used in continuous liquid slurry, solution, and gas-phase polymerization reactors to diversify the product grade slate. Since polyolefins are produced in large quantities in continuous reactors, it is desirable to optimize the production schedule and effectively control the grade transition dynamics to minimize the production of off-specification products. One of the ways to improve the design and operation of a polymerization process is to develop an improved quantitative understanding of the process characteristics and use it to devise better operating strategies. A mathematical process model based on the fundamental reaction chemistry and physics of polymerization is a useful tool for such purposes.

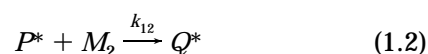
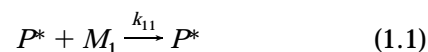
In developing a heterogeneous copolymerization process model, a kinetic scheme is first devised for a given catalyst and then modeling equations are derived. A typical polymerization process model consists of mass balances, energy balances, and a set of equations such as molecular weight moments to compute polymer molecular weight averages. The most important and often a very difficult task is to determine the relevant kinetic parameters for the process model. Given a specific polymerization catalyst, one may conduct laboratory experiments at different reaction conditions to obtain the kinetic data required for the process model. It is also not uncommon in practice that catalysts are tested directly on a large-scale pilot or a commercial plant. The main objective of this paper is to present analytical methods to estimate the copolymerization

propagation rate constants and reactivity ratios for transition-metal-catalyzed olefin copolymerization processes.

2. Estimation of Copolymerization Rate Constants

In gas-phase olefin polymerization processes, controlling the polymer property parameters such as copolymer composition and molecular weight averages is of particular importance. It is because copolymer density and melt index, which are two of the most important property measures used by polymer manufacturers, depend on these parameters. To control the comonomer content in the polymer, the reactivity of active transition-metal sites toward both monomer and comonomer should be known and gas-phase composition must also be controlled accordingly.

Let us consider the chain propagation reactions for a binary copolymerization system represented by



where P^* (Q^*) represents the growing polymer chain with M_1 (M_2) monomer linked to a transition-metal site. Although some transition-metal catalysts for olefin polymerization may have multiple active sites of different catalytic reactivity, let us assume that only one type of active site is present. To calculate the polymerization rate (or polymer productivity), copolymer composition, and polymer molecular weight averages, not only copolymerization reactivity ratios ($r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$) but also four propagation rate constants must be known.

The most commonly used method to determine the reactivity ratios in a homogeneous binary copolymerization system is to utilize the Mayo–Lewis equation:

$$\frac{dM_2}{dM_1} = \frac{M_2 [M_1 + r_2 M_2]}{M_1 [r_1 M_1 + M_2]} \quad (2)$$

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or

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (3)$$

where M_1 and M_2 are the bulk-phase concentrations of monomer and comonomer. f_1 and f_2 are the bulk-phase mole fractions of M_1 and M_2 , and F_1 is the mole fraction of M_1 in the polymer phase. Both eq 2 and eq 3 represent the instantaneous copolymer composition. To estimate the reactivity ratios using the above equations or in the form of the Fineman–Ross equation, the copolymer composition must be measured for different values of monomer/comonomer mole ratios. If the bulk-phase mole ratio is kept constant, the instantaneous copolymer composition becomes the final copolymer composition. If the comonomer/monomer mole ratio varies during polymerization, the copolymer composition will change with the reaction time. Experimentally, copolymerization experiments may be carried out to a low conversion to minimize the variation of bulk-phase composition. A continuous reactor can be used to keep the bulk-phase composition constant at its steady state.

In heterogeneous gas-phase olefin copolymerization processes, some care must be taken in determining the true reactivity ratios because the bulk-phase monomer concentration may not be identical to the monomer concentration at the catalytic active sites due to intraparticle mass-transfer resistance and monomer sorption effects (Hutchinson and Ray, 1990). In such a case, the monomer and comonomer concentrations at the catalytic sites should be used to determine the true reactivity ratios. In general, the kinetic parameters for a given catalyst system are measured or estimated by conducting laboratory polymerization experiments using either batch or semibatch reactors. To use the Mayo–Lewis equation to determine the reactivity ratios in gas-phase olefin copolymerization, a reactor must be operated to keep the comonomer/monomer mole ratio constant during the polymerization. However, in practice, keeping the comonomer/monomer mole ratio constant is not a trivial task because monomer and comonomer have different reactivities and, thus, they are consumed at different rates. The bulk-phase composition can be maintained constant by measuring the gas-phase composition on-line by, for example, gas chromatography and using it to regulate the feed rates of ethylene and comonomer with a sophisticated closed-loop control system (Chen, 1993). A similar method can also be used in liquid slurry copolymerization in which the gas-phase composition is controlled by on-line gas chromatography (Böhm, 1981, 1984). Another commonly used experimental method in studying the kinetics of olefin copolymerization is to charge the reactor with catalyst and comonomer to a desired initial pressure and then to add monomer (ethylene) to a desired total pressure. The reactor pressure is kept constant by adding ethylene to the reactor. The ethylene feed rate is used to approximately measure the polymerization rate. Since comonomer is not added during the reaction, it is inevitable that the comonomer/monomer ratio changes during the course of polymerization. If the catalyst exhibits a moderate activity toward the comonomer, the measured ethylene feed rate is not a true representation of the overall polymerization rate. The reactivity ratios in the olefin copolymerization processes can also be determined by means of a nonlinear regression to fit the experimentally measured copolymer composition data with the copolymer composition equation (e.g., eq 2) (Cozewith and Ver Strate, 1971).

Since olefin polymers are produced industrially in continuous polymerization reactors, the ultimate application of a kinetic model is to predict the performance of a large-scale continuous reactor and design optimal polymerization conditions. Sometimes, a kinetic model developed in a laboratory may be inadequate in predicting the behavior of a large-scale reactor. In such a case, it is necessary to adjust the kinetic parameters to fit the plant data. Kinetic parameters can also be estimated on-line using stochastic filtering techniques in conjunction with a detailed process model and actual plant data (Sirohi and Choi, 1996).

In this paper, we shall discuss several methods for the estimation of copolymerization kinetic parameters using batch, semibatch, and continuous gas-phase olefin copolymerization data.

2.1. Estimation of Kinetic Parameters from Batch Copolymerization Data. Experimentally, conducting a batch gas-phase olefin copolymerization experiment is quite straightforward. The reactor is first charged with a known amount of catalyst. Then, monomer and comonomer are added to their desired partial pressures. As polymerization progresses, the reactor pressure decreases. The mass balance equations for M_1 (ethylene) and M_2 (comonomer) take the following form:

$$\frac{d}{dt}(V_g M_{1b}) = -W_{\text{cat}}(k_{11}P + k_{21}Q)M_{1s} \quad (4.1)$$

$$\frac{d}{dt}(V_g M_{2b}) = -W_{\text{cat}}(k_{12}P + k_{22}Q)M_{2s} \quad (4.2)$$

where P and Q [=moles of sites/g of catalyst] are the concentrations of the active catalytic sites, M_{1b} and M_{2b} are the bulk-phase monomer and comonomer concentrations, and M_{1s} and M_{2s} are the concentrations at the catalyst sites. W_{cat} is the mass of the catalyst charged in the reactor. The monomer concentrations at the catalyst sites can be correlated to the bulk-phase concentrations using the sorption factor, i.e., $M_{js} = \chi_j M_{jb}$ (Hutchinson and Ray, 1990). In deriving the above equations, the amounts of monomer and comonomer consumed by chain-transfer reactions are assumed negligibly small. It is also assumed that the catalyst is fully activated at the beginning of the polymerization and the reaction is isothermal.

As polymerization occurs, solid polymers are produced and, as a result, the free gas-phase volume decreases slightly. In actual laboratory experiments, one can charge the reactor with inert solid particles to promote uniform mixing and efficient heat transfer. The gas-phase volume (V_g) decreases according to the following equation:

$$\frac{dV_g}{dt} = -\frac{dV_s}{dt} = -\frac{W_{\text{cat}}}{\rho_p} [w_1(k_{11}P + k_{21}Q)M_{1s} + w_2(k_{12}P + k_{22}Q)M_{2s}] \quad (5)$$

where V_s is the solid-phase (polymer) volume, ρ_p is the density of the solid phase, w_1 and w_2 are the molecular weights of monomer M_1 and comonomer M_2 , respectively. In deriving the above mass balance equations, both intraparticle and interfacial mass transfer resistance effects are assumed negligible. If we assume that the concentration of vacant active sites is negligibly small once the polymerization starts, the following equation holds:

$$C^* = P + Q \quad (6)$$

where C^* is the total site concentration (moles of sites/g of catalyst).

Applying the quasi-steady-state assumption to the propagating sites, we obtain the following expressions for growing polymer chains:

$$P = \frac{C^*}{1 + \frac{k_{12} M_{2s}}{k_{21} M_{1s}}} \quad (7.1)$$

$$Q = \frac{k_{12} M_{2s}}{k_{21} M_{1s}} \left(\frac{C^*}{1 + \frac{k_{12} M_{1s}}{k_{21} M_{2s}}} \right) \quad (7.2)$$

Then, from eqs 4–7, we obtain

$$V_g \frac{dM_{1b}}{dt} = \left\{ \left(\frac{M_{1b} w_1}{\rho_p} - 1 \right) M_{1s} (r_1 + \phi_s) + \frac{M_{1b} M_{2s} w_2}{\rho_p} (1 + r_2 \phi_s) \right\} G^* \quad (8.1)$$

$$V_g \frac{dM_{2b}}{dt} = \left\{ \left(\frac{M_{2b} w_2}{\rho_p} - 1 \right) M_{2s} (1 + r_2 \phi_s) + \frac{M_{1s} M_{2b} w_1}{\rho_p} (r_1 + \phi_s) \right\} G^* \quad (8.2)$$

where $\phi_s \equiv M_{2s}/M_{1s}$ and $G^* = k_{12} W_{cat} C^*/(1 + k_{12} \phi_s/k_{21})$. From these equations, we get

$$\Phi = \frac{dM_{2b}/dt}{dM_{1b}/dt} = \frac{\left(\frac{M_{2b} w_2}{\rho_p} - 1 \right) M_{2s} (1 + r_2 \phi_s) + \frac{M_{1s} M_{2b} w_1}{\rho_p} (r_1 + \phi_s)}{\left(\frac{M_{1b} w_1}{\rho_p} - 1 \right) M_{1s} (r_1 + \phi_s) + \frac{M_{1b} M_{2s} w_2}{\rho_p} (1 + r_2 \phi_s)} \quad (9)$$

This equation can be rearranged into the following form:

$$Y = r_1 + r_2 X \quad (10)$$

where

$$Y \equiv \left(\Phi \left[\phi_s \left(\frac{M_{1b} w_1}{\rho_p} - 1 \right) M_{1s} + \frac{M_{1b} M_{2s} w_2}{\rho_p} \right] - \left[\left(\frac{M_{2b} w_2}{\rho_p} - 1 \right) M_{2s} - \phi_s \frac{M_{1s} M_{2b} w_1}{\rho_p} \right] \right) / \left(\frac{M_{1s} M_{2b} w_1}{\rho_p} - \Phi \left(\frac{M_{1b} w_1}{\rho_p} - 1 \right) M_{1s} \right) \quad (11.1)$$

$$X \equiv \frac{\phi_s \left(\frac{M_{2b} w_2}{\rho_p} - 1 \right) M_{2s} - \Phi \phi_s \left(\frac{M_{1b} M_{2s} w_2}{\rho_p} \right)}{\frac{M_{1s} M_{2b} w_1}{\rho_p} - \Phi \left(\frac{M_{1b} w_1}{\rho_p} - 1 \right) M_{1s}} \quad (11.2)$$

The reactivity ratios are determined by plotting Y vs X measured at different reaction times. To utilize eq 10, the concentrations of monomer and comonomer must be known during the reaction. Experimentally, it can be accomplished by taking gaseous samples from the reactor and measuring the gas-phase compositions using, for example, off-line or on-line gas chromatography. Recall that the concentrations of monomer and comonomer at the catalyst sites should be calculated from bulk-phase concentrations using appropriate sorp-

tion factors. At constant reaction temperature with the total pressure monitored continuously during the course of polymerization, one can determine the molar concentrations or partial pressures of monomer and comonomer and the values of dM_{1b}/dt and dM_{2b}/dt . It is also easy to show that eq 10 is valid even in the presence of catalyst deactivation during the course of polymerization.

Once r_1 and r_2 values are determined, the cross-propagation reaction rate constants can also be estimated. For example, eq 8.1 is rearranged to

$$F \equiv \left(\left[\left(\frac{M_{1b} w_1}{\rho_p} - 1 \right) M_{1s} (r_1 + \phi_s) + \frac{M_{1b} M_{2s} w_2}{\rho_p} (1 + r_2 \phi_s) \right] W_{cat} C^* \right) / (V_g (dM_{1b}/dt)) \quad (12.1)$$

$$= \frac{1}{k_{12}} + \frac{1}{k_{21}} \phi_s \quad (12.2)$$

where the gas-phase volume is calculated from the partial pressure measurements of monomer and comonomer:

$$V_g = \frac{V_t R T \rho_p - V_{g0} (P_{10} w_1 + P_{20} w_2)}{R T \rho_p - (P_1 w_1 + P_2 w_2)} \quad (13)$$

P_{10} is the initial partial pressure of monomer, P_{20} the initial partial pressure of comonomer, V_t the total reactor volume (excluding the volume of reactor internals), and V_{g0} the initial gas-phase volume. Thus, by plotting F vs M_2/M_1 (or P_2/P_1), the two cross-propagation rate constants, k_{12} and k_{21} , can be determined. If separate polymerization experiments are carried out with ethylene and comonomer, these homopolymerization rate constants can be estimated and the cross-propagation rate constants are determined from the reactivity ratio values. In the derivations presented, it was assumed that catalyst deactivation is negligible. Then, the active site concentration (C^* [moles of sites/g of catalyst]) must be presumed to be known. For single-site catalysts (e.g., metallocenes), every transition metal (e.g., Zr) is assumed to be catalytically active. Then, its concentration per unit mass of catalyst can be assumed to be the catalyst site concentration. If catalyst deactivation is not negligible, the site deactivation parameter must be estimated experimentally and used to calculate the actual site concentration during the polymerization.

It is also easy to show that the cumulative copolymer composition is expressed as follows:

$$\frac{\langle W_2 \rangle}{\langle W_1 \rangle} = \frac{(P_{20} V_{g0} - P_2 V_g) w_2}{(P_{10} V_{g0} - P_1 V_g) w_1} \quad (14)$$

where $\langle W_1 \rangle$ and $\langle W_2 \rangle$ represent the total masses of M_1 monomer and M_2 comonomer in the polymer phase, respectively. In using the above-described method with batch polymerization data, it is crucial to obtain the concentration derivatives (dM_{1b}/dt and dM_{2b}/dt) accurately. In practice, the amount of polymer produced in a batch copolymerization experiment is quite low because the density of the gas phase is very low. Thus, the volume change in the gas phase is usually only a few percent of the initial volume.

2.2. Estimation of Kinetic Parameters from Semibatch Copolymerization Data. Another method that is often used to estimate the kinetic parameters is

to charge the reactor with catalyst, cocatalyst, monomer, and comonomer. Then, make-up ethylene gas (M_1) is supplied to the reactor to keep the total pressure constant during polymerization. Since comonomer is not added, the comonomer/monomer mole ratio changes during polymerization. Thus, the Mayo–Lewis equation is not directly applicable.

For a semibatch copolymerization experiment, the monomer and comonomer mass balance equations take the following form:

$$\frac{d}{dt}(V_g M_{1b}) = q_1 - W_{\text{cat}}(k_{11}P + k_{21}Q)M_{1s} \quad (15.1)$$

$$\frac{d}{dt}(V_g M_{2b}) = -W_{\text{cat}}(k_{12}P + k_{22}Q)M_{2s} \quad (15.2)$$

where q_1 is the ethylene molar flow rate to the reactor operating at a constant total pressure. It is easy to show that the ethylene flow rate, which can be measured experimentally using a mass flowmeter, is related to the polymerization rates as follows:

$$q_1 = \left(1 - \frac{w_1 P_t}{\rho_p R T}\right) W_{\text{cat}} R_{p1} + \left(1 - \frac{w_2 P_t}{\rho_p R T}\right) W_{\text{cat}} R_{p2} \quad (16)$$

R_{p1} is the ethylene (M_1) polymerization rate, R_{p2} the comonomer polymerization rate, and P_t the total reactor pressure. Unlike in batch copolymerization experiments, there will be a significant increase in the solid-phase volume which is represented by

$$\frac{dV_s}{dt} = \frac{W_{\text{cat}}}{\rho_p} [w_1 R_{p1} + w_2 R_{p2}] \quad (17)$$

If the polymerization rates (R_{p1} and R_{p2}) are known, we obtain

$$\frac{R_{p2}}{R_{p1}} = \frac{M_{2s}}{M_{1s}} \frac{1 + r_2 \frac{M_{2s}}{M_{1s}}}{r_1 + \frac{M_{2s}}{M_{1s}}} \quad (18)$$

which is identical with eq 2. To use eq 18, the ratio of polymerization rates must be known. They can be estimated using eq 15 and 17:

$$\frac{R_{p2}}{R_{p1}} = \frac{g_1 w_1 - \left(\rho_p - \frac{P_t w_1}{RT}\right) \frac{dV_s}{dt}}{\left(\rho_p - \frac{P_t w_2}{RT}\right) \frac{dV_s}{dt} - w_2 q_1} \quad (19)$$

Notice that if dV_s/dt is measured or estimated, the right-hand side of eq 19 contains the known or measured quantities only. Then, the reactivity ratios can be determined from

$$\left(\frac{M_{2s}}{M_{1s}}\right) \left(\frac{R_{p1}}{R_{p2}} - 1\right) = r_1 - r_2 \frac{R_{p1}}{R_{p2}} \left(\frac{M_{2s}}{M_{1s}}\right)^2 \quad (20.1)$$

or

$$\left(\frac{\chi_2}{\chi_1}\right) \left(\frac{x_{1b}}{x_{2b}}\right) \left(\frac{R_{p1}}{R_{p2}} - 1\right) = r_1 - r_2 \frac{R_{p1}}{R_{p2}} \left(\frac{\chi_2}{\chi_1}\right)^2 \left(\frac{x_{1b}}{x_{2b}}\right)^2 \quad (20.2)$$

where x_{ib} is the mole fraction of monomer i in the bulk gas phase, which can be measured by gas chromatog-

raphy. Equation 20.1 or 20.2 is in the form of the well-known Fineman–Ross equation.

To use this method, it is necessary to measure the gas-phase composition and the rate of volume change of the solid phase (dV_s/dt). Although the gas-phase composition can be easily measured by gas chromatography, the solid-phase volume is rather difficult to measure on-line during the polymerization experiment. The values of dV_s/dt can be obtained by conducting several experiments under identical reaction conditions for different durations of reaction time. Of course, it is required that each experiment be reproducible. At the end of each experiment, the total weight or volume of the solid phase (V_s) is measured. Then, from the V_s vs time curve, dV_s/dt is estimated at different reaction times. In fact, it is not necessary to monitor the change in gas-phase composition during the entire reaction period. The composition needs to be measured only at the end of each semibatch polymerization experiment.

In olefin copolymerization with higher α -olefins, the r_2 value is usually much smaller than r_1 and the amount of comonomer units in the polymer phase is very small. It implies that estimating the value of r_2 may be very sensitive to measurement errors. For example, the numerator in eq 19 could be very close to zero, and then, as a result, the test equation (20.1) or (20.2) may be difficult to use. The fact that $r_1 \gg r_2$ implies that comonomers are incorporated to the polymer chain mostly via reaction 1.2 and the amount of ethylene consumed by reaction 1.3 is far smaller than the amount consumed by reaction 1.1.

It is easy to show that eq 20 is also valid for a deactivating catalyst system. However, if catalyst deactivation occurs, it is not possible to determine each propagation rate constant directly from the semibatch polymerization data. For example, consider the following equation which is obtained from eq 16:

$$\frac{W_{\text{cat}} C_0^*}{q_1} \left[\left(1 - \frac{w_1 P_t}{\rho_p R T}\right) \left(r_1 + \frac{M_{2s}}{M_{1s}}\right) M_{1s} + \left(1 - \frac{w_2 P_t}{\rho_p R T}\right) \left(1 + r_2 \frac{M_{2s}}{M_{1s}}\right) M_{2s} \right] = \frac{1}{\exp(-k_d t)} \left(\frac{1}{k_{12}} + \frac{1}{k_{21}} \frac{M_{2s}}{M_{1s}} \right) \quad (21)$$

where C_0^* is the initial concentration of active sites. In the above equation, a first-order irreversible catalyst deactivation is assumed. If there is no deactivation ($k_d \approx 0$), k_{12} and k_{21} can be determined by plotting the left-hand side (LHS) of eq 21 against M_{2s}/M_{1s} . For a deactivating catalyst, the catalyst deactivation rate constant must be known first.

If catalyst deactivation is not affected by the presence of comonomer, the deactivation rate constant can be determined by conducting a homopolymerization experiment in a semibatch reactor. For a semibatch homopolymerization reactor operating at a constant ethylene pressure, the ethylene feed rate (q_1') is expressed by

$$q_1' = \left(1 - \frac{w_1 P_t}{\rho_p R T}\right) \chi_1 \frac{P_t}{RT} W_{\text{cat}} C_0^* k_{11} \exp(-k_d t) \quad (22)$$

Equation 22 is rearranged to

$$\ln \left[\frac{q_1'}{\left(1 - \frac{w_1 P_t}{\rho_p R T}\right) \chi_1 \frac{P_t}{RT} W_{\text{cat}} C_0^*} \right] = \ln k_{11} - k_d t \quad (23)$$

By plotting the LHS of eq 23 against the polymerization time, k_d and k_{11} (ethylene homopolymerization rate constant) can be determined. With the catalyst deactivation rate constant determined, eq 21 is then used to estimate the cross-propagation rate constants. Of course, k_{12} can also be determined from the reactivity ratio (r_1) and the homopolymerization rate constant (k_{11}).

2.3. Estimation of Kinetic Parameters from Continuous Reactor Data. Quite often, the kinetic model developed based on the data obtained from a small-scale laboratory polymerization reactor may not be directly applicable to a large-scale continuous pilot plant or a commercial plant. It is possible that some unidentified impurities or catalyst poisons may mask the measured kinetic data in a small-scale laboratory reactor system. In a large continuous reactor process, the effect of impurities is relatively small and more reliable, and consistent process data can be obtained. In certain situations, the catalysts developed are directly tested in a pilot plant. Thus, it is desirable to have a method that can be used to estimate the kinetic parameters using pilot plant data. In this section, we shall discuss how steady-state continuous polymerization reactor data can be used to estimate copolymerization kinetic parameters.

Let us consider a continuous flow gas-phase olefin copolymerization reactor (e.g., fluidized bed or stirred bed) operating at a constant reaction temperature. Developing a comprehensive reactor model requires a good understanding of complex flow and mixing of gas and solid phases. In general, it is quite difficult to directly use a detailed gas-phase olefin polymerization reactor model for parameter estimation. The first step in the parameter estimation task is to obtain preliminary values of pertinent parameters which will eventually be adjusted or improved using additional plant data. For example, a continuous stirred bed reactor model can be used as an approximation to the detailed two-phase model for a gas-phase fluidized bed polymerization reactor (Choi and Ray, 1985). Of course, the kinetic parameters estimated using a simplified model may exhibit some discrepancies from the true values.

If the fluidized bed polyolefin reactor is modeled as a continuous stirred bed reactor, the mass balance equations are expressed in the following form:

$$V_g \frac{dM_{1b}}{dt} = Q_f M_{1f} - Q_o M_{1b} - W_b X_{cat} R_{p1} \quad (24.1)$$

$$V_g \frac{dM_{2b}}{dt} = Q_f M_{2f} - Q_o M_{2b} - W_b X_{cat} R_{p2} \quad (24.2)$$

$$W_b \frac{dX_{cat}}{dt} = q_{cat} - Q_s X_{cat} \quad (24.3)$$

$$W_b \frac{d(X_{cat} C^*)}{dt} = q_{cat} C_f^* - Q_s X_{cat} C^* - W_b X_{cat} k_d C^* \quad (24.4)$$

where W_b = solid bed weight, V_g = total gas phase volume, Q_f = input gas flow rate, Q_o = output gas flow rate, X_{cat} = mass fraction of catalyst in the solid phase, q_{cat} = catalyst mass flow rate, C^* = total active site concentration (moles of sites/g of catalyst), C_f^* = active site concentration in the catalyst feed stream (assumed known). In the above equations, perfect backmixing of the solid phase is assumed and the amount of unreacted monomer and comonomer in the product polymer phase

is assumed negligible. A first-order catalyst site deactivation reaction is also assumed. The polymerization rates are expressed as follows:

$$R_{p1} = (k_{11}P + k_{21}Q)\chi_1 M_{1b} \quad (25.1)$$

$$R_{p2} = (k_{12}P + k_{22}Q)\chi_2 M_{2b} \quad (25.2)$$

For a fluidized bed gas-phase polymerization process, a continuous stirred bed reactor model similar to the model represented by the above modeling equations can be used as an approximation (McAuley et al., 1990). From the rate expressions for M_1 and M_2 , the following equation is derived at steady state:

$$\frac{\chi_1 M_{1b}}{\chi_2 M_{2b}}(1 - \Phi) = \left(\frac{\chi_1 M_{1b}}{\chi_2 M_{2b}}\right)^2 \Phi r_1 - r_2 \quad (26)$$

where the copolymer composition ($\Phi = \langle M_2 \rangle / \langle M_1 \rangle$) can be measured experimentally. $\langle M_i \rangle$ is the number of moles of monomer i in the polymer. If the amount of unreacted monomers in the solid phase is negligible, Φ can be approximately estimated by the following equation at steady state:

$$\Phi \approx \frac{Q_f M_{2f} - Q_o M_{2b}}{Q_f M_{1f} - Q_o M_{1b}} = \frac{R_{p2}}{R_{p1}} \quad (27)$$

Notice that eq 26 is in the form of the Fineman–Ross equation. By plotting the left-hand side of eq 26 against $((\chi_1 M_{1b})/(\chi_2 M_{2b}))^2(1/\Phi)$, r_1 and r_2 can be determined. The steady-state comonomer polymerization rate (R_{p2}) can be calculated from the copolymer production rate once the product composition is known:

$$R_{p2} = \frac{Q_s^2(1 - x_1)}{W_b q_{cat}[w_1 x_1 + w_2(1 - x_1)]} \quad (28)$$

where x_1 is the mole fraction of monomer M_1 in the polymer phase. Equation 26 is also valid for deactivating catalyst systems. To use eq 26, several steady-state experiments must be carried out for different feed gas compositions.

From the steady-state mass balance equations for M_1 and M_2 , we obtain the following equations:

$$\frac{C_f^* \left(r_1 + \frac{\chi_2 M_{2b}}{\chi_1 M_{1b}} \right) \chi_1 M_{1b}}{R_{p1}} = (1 + \Theta k_d) \left(\frac{1}{k_{12}} + \frac{1}{k_{21}} \frac{\chi_2 M_{2b}}{\chi_1 M_{1b}} \right) \quad (29.1)$$

$$\frac{C_f^* \left(1 + r_2 \frac{\chi_2 M_{2b}}{\chi_1 M_{1b}} \right) \chi_2 M_{2b}}{R_{p2}} = (1 + \Theta k_d) \left(\frac{1}{k_{21}} + \frac{1}{k_{12}} \frac{\chi_2 M_{2b}}{\chi_1 M_{1b}} \right) \quad (29.2)$$

where $\Theta = W_b/Q_s$ (mass flow rate of the solid phase) is the mean residence time for the solid phase. If catalyst deactivation is negligible (i.e., $k_d \approx 0$) or the k_d value is known, k_{12} and k_{21} are determined by plotting the left-hand-side term of eq 29.1 or eq 29.2 vs M_{2b}/M_{1b} (steady-state values). However, if deactivation occurs, we need to know the deactivation rate constant to determine the cross-propagation rate constants. In a continuous gas-phase polymerization process, the deactivation rate constant can be estimated by performing the steady-state plant experiments at several different solid-phase residence times (Θ). For example, the catalyst inactivation

Table 1. Plant Model Parameters

$$\begin{aligned}
 k_{11} &= 1.616 \times 10^{14} \exp(-3523/T) \text{ (L/(mol}\cdot\text{h))} \\
 k_{12} &= 5.400 \times 10^{12} \exp(-3523/T) \text{ (L/(mol}\cdot\text{h))} \\
 k_{21} &= 1.616 \times 10^{13} \exp(-3523/T) \text{ (L/(mol}\cdot\text{h))} \\
 k_{22} &= 2.146 \times 10^{12} \exp(-3523/T) \text{ (L/(mol}\cdot\text{h))} \\
 k_d &= 0.5760 \exp(-503/T) \text{ (1/h)}
 \end{aligned}$$

Table 2. Simulated Plant Data (Total Pressure = 35 bar)

run	W_b , ^a kg	T , °C	M_1 , mol %	M_2 , mol %	q_{cat} , ^a g/h	Q_s , ^a kg/h	$\langle M_2 \rangle / \langle M_1 + M_2 \rangle$ ^b	θ ^a = W_b / Q_s , h
1	100	70	42	8	5.70	25.0	5.29×10^{-2}	4.0
2	100	70	46	4	4.75	25.0	2.33×10^{-2}	4.0
3	100	70	49	1	4.00	25.0	5.30×10^{-3}	4.0
4	200	70	42	8	6.59	35.0	5.29×10^{-2}	5.71
5	200	70	46	4	5.36	35.0	2.33×10^{-2}	5.71
6	200	70	49	1	4.53	35.0	5.30×10^{-3}	5.71
7	300	70	42	8	7.79	45.0	5.29×10^{-2}	6.67
8	300	70	46	4	6.35	45.0	2.33×10^{-2}	6.67
9	300	70	49	1	5.41	45.0	5.30×10^{-3}	6.67
10	200	80	42	8	8.06	45.0	4.71×10^{-2}	4.4
11	200	80	46	4	6.62	45.0	2.07×10^{-2}	4.4
12	200	80	49	1	5.68	45.0	4.70×10^{-3}	4.4
13	200	80	42	8	5.40	35.0	4.70×10^{-2}	5.7
14	200	80	46	4	4.44	35.0	2.07×10^{-2}	5.7
15	200	80	49	1	3.81	35.0	4.70×10^{-3}	5.7
16	200	80	42	8	3.25	25.0	4.68×10^{-2}	8.0
17	200	80	46	4	2.67	25.0	2.08×10^{-2}	8.0
18	200	80	49	1	2.29	25.0	4.70×10^{-3}	8.0
19	200	90	42	8	6.68	45.0	4.22×10^{-2}	4.4
20	200	90	46	4	5.50	45.0	1.87×10^{-2}	4.4
21	200	90	49	1	4.80	45.0	4.30×10^{-3}	4.4
22	200	90	42	8	4.48	35.0	4.21×10^{-2}	5.7
23	200	90	46	4	3.71	35.0	1.86×10^{-2}	5.7
24	200	90	49	1	3.20	35.0	4.30×10^{-3}	5.7
25	200	90	42	8	2.70	25.0	4.20×10^{-2}	8.0
26	200	90	46	4	2.24	25.0	1.86×10^{-2}	8.0
27	200	90	49	1	1.93	25.0	4.30×10^{-3}	8.0

^a W_b = bed weight; q_{cat} = catalyst injection rate; Q_s = polymer production rate; θ = solid-phase residence time. ^b Mole fraction in the polymer.

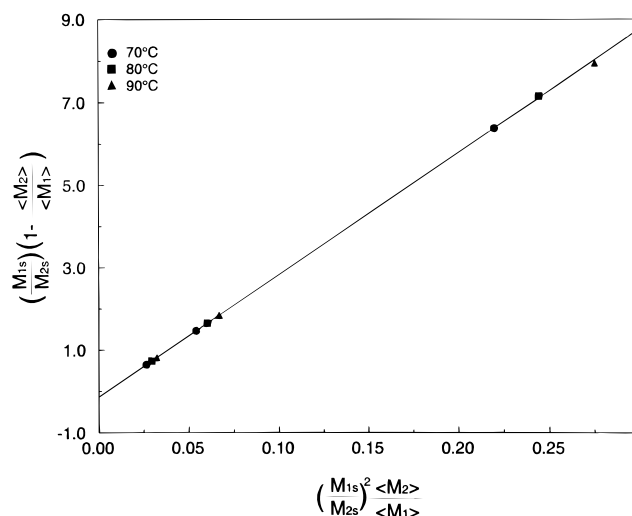
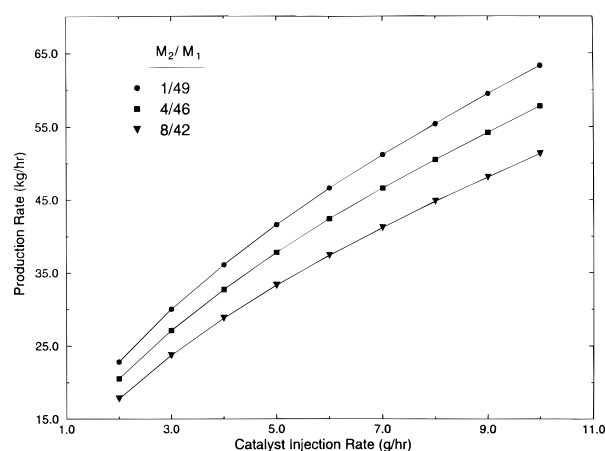
rate or bed weight may be varied. For a fixed solid-phase residence time, several steady-state tests are first carried out for different feed gas compositions to obtain the combined values of $(1 + \Theta k_d)/k_{12}$ and $(1 + \Theta k_d)/k_{21}$ by using eq 29.1. $(1 + \Theta k_d)/k_{21}$ and $(1 + \Theta k_d)/k_{12}$ can also be obtained by using eq 29.2. Then, similar experiments are conducted at different solid-phase residence times. These combined rate constant values are plotted against Θ . From the intercepts ($1/k_{21}$ or $1/k_{12}$) and slopes (k_d/k_{21} or k_d/k_{12}), the deactivation rate constant and cross-propagation rate constants are determined. **Note:** Since the amount of comonomer incorporated into the polymer phase is generally far smaller than the amount of ethylene polymerized, eq 29.2 yields more reliable values of the cross-propagation rate constants than eq 29.1.

If deactivation kinetics are little affected by the presence of comonomer, steady-state homopolymerization experiments can be carried out at several different residence times to determine the deactivation rate constant and the homopolymerization rate constant. It is straightforward to derive the following from the steady-state reactor model:

$$\frac{q_{cat} \chi_1 M_{1b} C_f^*}{Q_s} = \frac{1}{k_{11} \Theta} + \frac{k_d}{k_{11}} \quad (30)$$

By plotting the LHS of eq 30 vs Θ , the two rate constants are determined.

Example. To illustrate the method just described, let us consider a fluidized bed ethylene copolymerization

**Figure 1.** Estimation of reactivity ratios.**Figure 2.** Polymer production rate vs catalyst injection rate (plant model): 80 °C, W_b = 200 kg, P = 35 bar.**Table 3. Reactivity Ratios**

T , °C	estd values		true values	
	r_1	r_2	r_1	r_2
70	29.71	0.136		
80	29.92	0.147	29.92	0.1328
90	29.34	0.121		

process with 1-butene as a comonomer. The fluidized bed reactor model used to generate simulated plant data is a two-phase bubbling bed model similar to the model reported by Choi and Ray (1985). First, at fixed reactor temperature and bed weight (W_b), several steady-state reactor simulations are carried out for different feed gas compositions and catalyst injection rates. Table 1 shows the numerical values of the kinetic constants (Hutchinson et al., 1992) used in the plant model simulations and Table 2 shows the simulated steady-state plant data. Then, at a given reaction temperature, eq 26 is applied to the plant data to determine the reactivity ratios. Figure 1 shows the test results, and both estimated and true values of the reactivity ratios are listed in Table 3. Notice that although the model used to derive eq 26 is different from the plant model, the estimated reactivity ratios are very close to the true values.

If homopolymerization rate constants (k_{11} and k_{22}) are known, the cross-propagation rate constants can be determined from these reactivity ratio values. Otherwise, the cross-propagation rate constants must be determined from the copolymerization data using eq 29.1 or 29.2. With all other reactor conditions kept

Table 4. Kinetic Constants Estimated^a

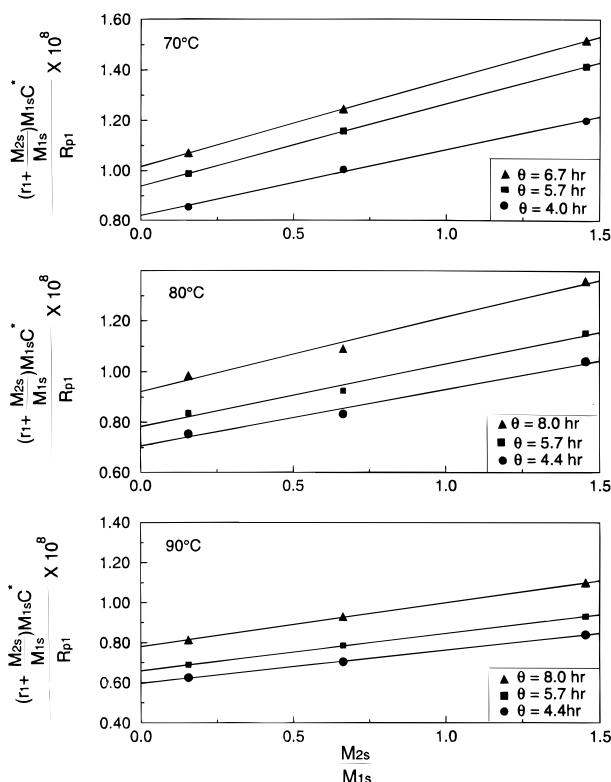
$T, ^\circ\text{C}$	$10^{-9}k_{11}$ L/(mol·h)	$10^{-8}k_{12}$ L/(mol·h)	$10^{-8}k_{21}$ L/(mol·h)	$10^{-8}k_{22}$ L/(mol·h)	k_d (1/h)
70	5.654 (5.619)	1.903 (1.878)	7.085 (5.619)	0.9663 (0.7462)	0.1389 (0.1330)
80	7.414 (7.515)	2.478 (2.511)	7.362 (7.515)	1.081 (0.9980)	0.1397 (0.1386)
90	9.633 (9.891)	3.283 (3.305)	10.02 (9.891)	1.209 (1.314)	0.1420 (0.1442)

$$k_{11} = 8.970 \times 10^{13} \exp(-3319/T) \text{ (L/(mol·h))}$$

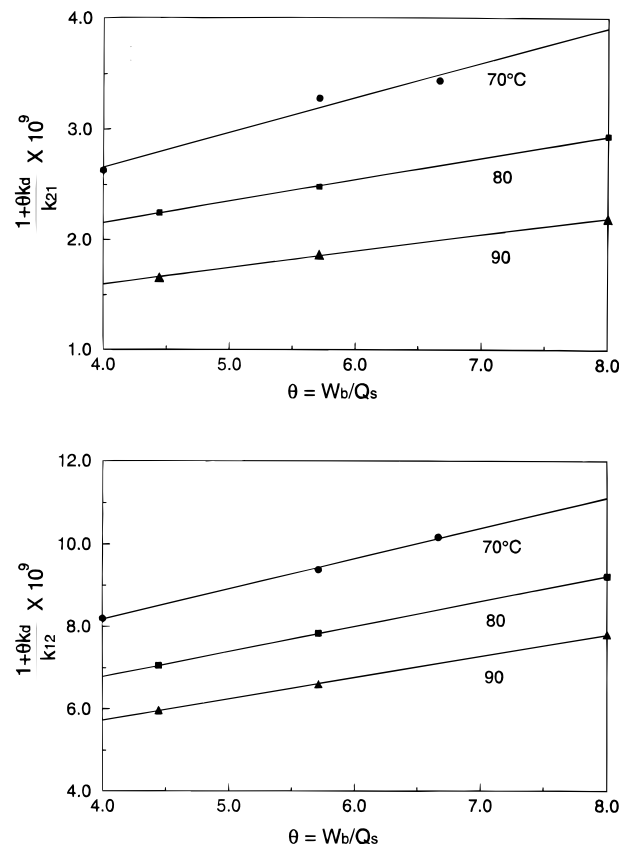
$$k_{12} = 3.757 \times 10^{12} \exp(-3396/T) \text{ (L/(mol·h))}$$

$$k_{21} = 3.496 \times 10^{11} \exp(-2143/T) \text{ (L/(mol·h))}$$

$$k_{22} = 5.659 \times 10^9 \exp(-1397/T) \text{ (L/(mol·h))}$$

$$k_d = 0.2058 \exp(-135/T) \text{ (1/h)}$$
^a Values in parentheses are true values.**Figure 3.** Determination of composite rate parameters.

constant, the solid bed weight (W_b) is changed and the resulting copolymer composition and the outlet gas-phase composition are measured. It is important that the bulk-phase comonomer/monomer mole ratio is varied while the reactor residence time is kept constant. Since the polymer production rate is affected by the catalyst injection rate, bed weight, and feed gas composition, it is necessary to find the reactor operating conditions that give a desired residence time. As we change the bed weight, the amount of catalyst in the reactor changes, and as a result, the monomer conversion and the polymer production rate change. Figure 2 shows the steady state polymer production rate as a function of catalyst injection rate for different comonomer/monomer mole ratios. From these plant data, one can determine the reactor operating conditions that will give the desired residence time at different bulk gas compositions. Figure 3 shows the plots of eq 29.1 for three different polymerization temperatures and residence times. From this figure, the combined values of the rate constants are obtained. Then, the slopes and intercepts obtained are plotted against the residence time as shown in Figure 4 to determine the deactivation rate constant and cross-propagation rate constants. The estimated values of the kinetic parameters are compared with the true values in Table 4. Some discrepancies exist; however, the predicted polymer production

**Figure 4.** Determination of k_{12} and k_{21} .**Table 5. Simulation Comparison^a**

$\phi = M_2/M_1$	Q_s , kg/h		$C_x = \langle M_2 \rangle / (\langle M_1 \rangle + \langle M_2 \rangle)$	
	pred	plant data	pred	plant data
1/49	54.9	55.4	0.47	0.48
4/46	50.4	50.5	2.07	2.08
8/42	45.0	44.8	4.69	4.71

^a $W_b = 200$ kg, $P = 35$ bar, $T = 80$ °C, $q_{cat} = 8$ g/h.

rate and copolymer composition, as shown in Table 5, are in good agreement with the simulated plant data.

3. Concluding Remarks

In this paper, we have presented three different methods to estimate the copolymerization kinetic parameters using batch, semibatch, and continuous copolymerization data. In industrial olefin polymerization processes, a large number of high-activity catalysts is frequently used to tailor polymer properties. Unlike in other polymerization systems such as free-radical polymerizations, the kinetic parameters in the olefin polymerization are strongly dependent on the nature of the catalyst. If a process model is to be developed, relevant kinetic parameters must be determined for each catalyst system. Obviously, it is a quite costly, time consuming, and difficult task.

In this paper, we have presented three analytical parameter estimation methods that can be used for laboratory and plant scale olefin copolymerization reactor systems. It is possible that the use of different experimental methods may yield different values of kinetic parameters to some extent. For example, some unidentifiable reactive impurities may affect the observed reaction kinetics and small-scale laboratory reactors may be more sensitive to impurities than large-plant-scale reactors. The efficiency of mixing of solid particles can also be an important factor. Therefore, it is suggested that the kinetic measurements be carried out using different methods and the results be carefully evaluated. If the main usage of the process model is to design process control systems or optimal reactor operations for a continuous process, it may be preferable to use the steady-state pilot plant data for parameter estimation.

In the mathematical derivations presented in this paper, the main objectives are to derive the analytical equations, albeit with some simplifying assumptions, that can be directly used for the estimation of major kinetic parameters. In reality, there are some issues to consider in using the equations presented in this paper. They are, for example, the availability of accurate monomer sorption factors, the effects of intra-particle mass- and heat-transfer resistances, and the effect of some reactions that are not considered in the kinetic model used in this work. One may expect that the numerical values of the estimated kinetic parameters may depend on the accuracy of these factors. It should also be pointed out that single-site polymerization kinetics have been assumed in our kinetic modeling. If the proposed methods are applied to multisite catalyst systems, estimated kinetic parameters will be the approximate or effective values. Unfortunately, little is known or published about what experimental techniques can be used to estimate a large number of kinetic parameters in multi-site catalyst systems for olefin copolymerization.

Finally, it is worth noting that the parameter estimation should be carried out in several steps. First, the order of magnitude estimates of major kinetic parameters such as propagation rate constants must be known using the methods presented in this paper. Then, the accuracy of these kinetic parameters can be improved using a more advanced and, thus perhaps, more complex process model together with additional plant data and appropriate parameter optimization techniques that are readily available.

Nomenclature

C^* = total active site concentration, mol/g of catalyst
 f_j = mole fraction of monomer j in the bulk phase
 F_j = mole fraction of monomer j in the polymer phase
 k_d = catalyst deactivation rate constant, h^{-1}
 k_{ik} = propagation rate constant, $\text{m}^3/(\text{mol}\cdot\text{h})$
 M_{jb} = concentration of monomer j in the bulk phase, mol/ cm^3
 P = concentration of the active site with M_1 monomer linked, mol/g of catalyst

P_j = partial pressure of monomer j , atm
 P_t = total pressure, atm
 q_{cat} = catalyst injection rate, g of catalyst/h
 q_j = molar flow rate of monomer j , mol/h
 Q = concentration of active site with M_2 monomer linked, mol/g of catalyst
 Q_t = input gas flow rate, cm^3/h
 Q_o = output gas flow rate, cm^3/h
 Q_s = polymer production rate, g/h
 r_1 = reactivity ratio (k_{11}/k_{12})
 r_2 = reactivity ratio (k_{22}/k_{21})
 R = gas constant, cal/(mol·K)
 R_{pj} = polymerization rate of monomer j , mol/(g of catalyst·h)
 T = temperature, K
 V_g = gas-phase volume, cm^3
 V_s = solid-phase volume, cm^3
 V_t = total reactor volume, cm^3
 w_j = molecular weight of monomer j , g/mol
 W_b = bed weight, g
 W_{cat} = mass of catalyst, g
 $\langle W_j \rangle$ = total mass of monomer j in the polymer phase, g
 X_{cat} = mass fraction of catalyst in the polymer phase

Greek Letters

ρ_p = polymer density, g/ cm^3
 $\phi_s = M_{2s}/M_{1s}$
 χ_j = sorption factor for monomer j

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