

# An Analytic Approach in Kinetic Modeling of Ziegler–Natta Polymerization of Butadiene

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## SYNOPSIS

A kinetic modeling study was conducted for the Ziegler–Natta polymerization of butadiene with cobalt octoate/DEAC/water catalyst. The model equations for the single and dual active site models were analytically solved, and the closed-form expressions for conversion and both number and weight average molecular weights were obtained. The expressions for conversion and number average molecular weight are identical for both models. Also, the expressions of weight average molecular weight are similar for both models, but the expression for the dual active site model includes an additional scalar parameter. The parameter can be regarded as a “correction factor of weight average molecular weight,” which reflects the effect of dual active sites on the polydispersity. Using the expressions, a simple and noniterative kinetic modeling algorithm was established, and the parameter estimates were obtained. The estimated value of the correction factor ranges from 1.2 to 1.5 depending on the experimental data. The modeling results indicate the validity of the dual active site model. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Ziegler–Natta polymerization of butadiene has been studied by many researchers during the past few decades. Kinetic modeling has been one of the vital subjects in this field due to its importance in the design and control of reactors. The kinetics of the polymerization reaction has been extensively investigated<sup>1–4</sup> and various rate and molecular weight expressions were developed and used.<sup>5–14</sup> The kinetic studies were also carried out for the Ziegler–Natta polymerization of ethylene,<sup>15</sup> ethylene-propylene copolymer,<sup>16</sup> propylene,<sup>17</sup> and butene-1.<sup>18</sup> Honig<sup>19</sup> extensively investigated the Ziegler–Natta polymerization of butadiene using cobalt octoate with diethyl aluminum chloride (DEAC) and water as the catalyst, and Honig et al.<sup>20</sup> proposed a reaction scheme based on the investigation. However, their model consistently underestimates the weight-average molecular weight. Nitirahardjo et al.<sup>21</sup> modified the reaction scheme by assuming two active sites.

Vela Estrada et al.<sup>22,23</sup> suggested a reaction scheme with branching reaction.

Böhm<sup>12</sup> pointed out the analogy between the enzyme–substrate interaction of the Michaelis–Menten type enzyme reaction and the catalyst–monomer interaction of the Ziegler–Natta polymerization reaction. Heineken et al.<sup>24</sup> applied the singular perturbation theory to interpret the quasi-steady-state approximation in Michaelis–Menten kinetics using the enzyme to substrate ratio as the small parameter. In this study, the singular perturbation theory<sup>25</sup> is applied to the single active site (SAS) model proposed by Honig et al.<sup>20</sup> and the dual active site (DAS) model by Nitirahardjo et al.<sup>21</sup> to simplify the model equations.

The mathematical description of the polymerization reaction consists of conservation laws on the intermediate species, the monomer, and the quantities characterizing polymer chain distributions. Normally, they form a system of coupled, stiff, and nonlinear ordinary differential equations. The Bodenstein steady-state principle can be applied to the conservation equations of all intermediate species to assume quasi-steady states, and hence to turn the stiff differential equations into algebraic equations.

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**Table I** Reaction Scheme of Single Active Site Model

Reaction Step	Reaction	Rate Constant
Formation of active sites	$\text{Co} + \text{Al} + \text{H}_2\text{O} \rightarrow \text{C}^*$	$k_i$
Formation of byproducts	$\text{Co} + \text{Al} + \text{H}_2\text{O} \rightarrow \text{E}_b$	$k_s$
Initiation	$\text{C}^* + \text{M} \rightarrow \text{C}^*\text{P}_1$	$k_p$
Propagation	$\text{C}^*\text{P}_r + \text{M} \rightarrow \text{C}^*\text{P}_{r+1}$	$k_p$
Transfer to monomer	$\text{C}^*\text{P}_r + \text{M} \rightarrow \text{C}^*\text{P}_1 + \text{Q}_r$	$k_c$
Transfer to but-1-ene	$\text{C}^*\text{P}_r + \text{B} \rightarrow \text{C}^*\text{B} + \text{Q}_r$	$k_b$
Regeneration of active sites	$\text{C}^*\text{B} + \text{M} \rightarrow \text{C}^*\text{P}_1 + \text{B}$	$k_z$
Catalyst deactivation	$\text{C}^*\text{P}_r \rightarrow \text{Q}_r + \text{C}$	$k_t$

This assumption does not introduce any noticeable modeling error because the error associated with this simplification has a relative magnitude proportional to the ratio of the amount of catalyst to monomer. The typical value of the ratio is  $10^{-3}$  or less. Also, the differential expression for the rate of monomer consumption can be simplified by neglecting the terms other than the consumption by propagation reaction. This simplification introduces relatively the same magnitude of error as the quasi-steady-state approximation does. Both simplification processes share the unified theoretical basis that the terms that are much smaller than the leading order terms in the same equation can be neglected. This concept can be extended to the equations describing the change of the moments by precisely the same way. This study aims at developing a simple and practically applicable mathematical expression of weight-average molecular weight as well as that of conversion and number-average molecular weight for Ziegler-Natta polymerization of butadiene that uses cobalt octoate with DEAC and water as its catalyst.

## SAS MODEL

Based upon the experimental observations, Honig et al.<sup>20</sup> proposed a reaction scheme that contains catalyst formation, the initiation and propagation

of polymerization, transfer to monomer and but-1-ene, the regeneration of active sites, and catalyst deactivation. The reaction scheme is summarized in Table I. They derived the conservation equations to describe the kinetic behavior of a polymerization reactor. The detailed derivation procedures of conservation equations can be found in Honig et al.<sup>20</sup> and is not repeated here. In this study, the mathematical derivation is given to develop the expressions for the weight-average molecular weight.

The mathematical analysis of the polymerization reaction starts with the scaling analysis of each variable and parameter. For a well-designed polymerization system, the average chain length of polymer molecules can be approximately represented by the concentration ratio of monomer to catalyst, and it provides an important clue in determining the magnitudes of moments of chain distribution. For this reason, a small parameter  $\epsilon$  defined as the initial concentration ratio of cobalt octoate to butadiene monomer,  $[\text{Co}]_0/[\text{M}]_0$ , is introduced in the scaling analysis. The magnitude of kinetic parameters can also be properly represented by the small parameter  $\epsilon$ . The scaling analysis can be achieved with a rough experimental observations because a faulty analysis will produce self-contradictory results. The detailed results of scaling analysis for the present system are given in Table II for variables and Table III for parameters. They are relative magnitudes with respect to the initial monomer concentration  $[\text{M}]_0$  and the rate constant

**Table II** Magnitude of Variables

Variables	Magnitude
$X_2$	$\epsilon^{-1}[\text{M}]_0$
$[\text{M}], X_1, Y_1$	$[\text{M}]_0$
$Y_0, X_0, [\text{C}], [\text{C}^*], [\text{Co}]$	$\epsilon[\text{M}]_0$
$[\text{C}^*\text{P}_1], [\text{C}^*\text{B}]$	$\epsilon^2[\text{M}]_0$

**Table III** Magnitude of Parameters

Parameters	Magnitude
$k_i[\text{Co}]_0^{0.4}/[\text{M}]_0, k_s/[\text{M}]_0$	$\epsilon^{-1}k_p$
$k_z, k_t/[\text{Co}]_0$	$k_p$
$k_c, k_b$	$\epsilon k_p$

of the propagation reaction  $k_p$ , respectively. The overall time scale of the system must be determined from the consumption rate of monomer, and it is taken as  $(k_p[\text{Co}]_0)^{-1}$ , that is, the differential operator  $d/dt$  is treated as if it has the magnitude of  $k_p[\text{Co}]_0$ . In this article, the concentration of each species is denoted by the square bracket, for example,  $[\text{M}]$  for the concentration of butadiene monomer  $\text{M}$ , and the initial value of the concentration is denoted by the subscript 0. The  $n$ th moment of growing chain distribution is denoted by  $Y_n$ ,  $n = 0, 1, \dots$ , defined by

$$Y_n = \sum_{r=1}^{\infty} r^n [\text{C}^*\text{P}_r] \quad (1)$$

where  $\text{C}^*\text{P}_r$  is the growing chain with chain length  $r$ . The  $n$ th moments of total polymer  $X_n$ ,  $n = 0, 1, \dots$ , is defined by

$$X_n = Y_n + \sum_{r=2}^{\infty} r^n [\text{Q}_r] \quad (2)$$

where  $\text{Q}_r$  is the dead chain with chain length  $r$ . The overall conservation of key components are given, for the cobalt atom, as

$$Y_0 + [\text{C}] + [\text{E}_b] + [\text{Co}] + [\text{C}^*] + \underbrace{[\text{C}^*\text{B}]}_{O(\epsilon)} = [\text{Co}]_0, \quad (3)$$

for butadiene, as

$$X_1 + [\text{M}] = [\text{M}]_0, \quad (4)$$

and for but-1-ene, as

$$[\text{B}] + \underbrace{[\text{C}^*\text{B}]}_{O(\epsilon^2)} = [\text{B}]_0 \quad (5)$$

where  $\text{C}$  is the deactivated catalyst site;  $\text{E}_b$ , catalyst byproduct;  $\text{C}^*$ , active catalyst site; and  $\text{C}^*\text{B}$ , short-lived but-1-ene/catalyst complex. In Eqs. (3), (4), (5), and hereafter, the terms designated by  $O(\epsilon)$ ,  $O(\epsilon^2)$ , and  $O(\epsilon^3)$  have the relative magnitude of order of  $\epsilon$ ,  $\epsilon^2$ , and  $\epsilon^3$ , respectively, compared to the leading order terms. The leading order terms are unmarked. The conservation equation of cobalt octoate is

$$\frac{d[\text{Co}]}{dt} = -k_i[\text{Co}]^{1.4} - k_s[\text{Co}] \quad (6)$$

where  $k_i$  is the rate constant of the formation reaction of the active catalyst site;  $k_s$ , the rate constant of the formation reaction of the catalyst byproduct. The conservation of the active catalyst site can be described as

$$\frac{d[\text{C}^*]}{dt} = k_i[\text{Co}]^{1.4} - k_p[\text{C}^*][\text{M}], \quad (7)$$

where  $k_p$  is the rate constant of the initiation and propagation reactions. Both reactions are instantaneous without an induction period, so we can assume that

$$[\text{Co}] = 0 \quad (8)$$

and

$$[\text{C}^*] = 0 \quad (9)$$

immediately after the initiation. The Bodenstein steady-state principle is applied to the two intermediate species, namely  $\text{C}^*\text{B}$  and  $\text{C}^*\text{P}_1$  as

$$\underbrace{\frac{d[\text{C}^*\text{B}]}{dt}}_{O(\epsilon)} = k_b Y_0 [\text{B}] - k_z [\text{C}^*\text{B}] [\text{M}] \quad (10)$$

and

$$\underbrace{\frac{d[\text{C}^*\text{P}_1]}{dt}}_{O(\epsilon)} = \underbrace{k_p [\text{C}^*] [\text{M}]}_0 - k_p [\text{C}^*\text{P}_1] [\text{M}] + k_c Y_0 [\text{M}] + k_z [\text{C}^*\text{B}] [\text{M}] - \underbrace{k_c [\text{C}^*\text{P}_1] [\text{M}] - k_b [\text{C}^*\text{P}_1] [\text{B}] - k_t [\text{C}^*\text{P}_1]}_{O(\epsilon)} \quad (11)$$

where  $k_b$  is the rate constant of the transfer reaction to but-1-ene;  $k_z$ , the rate constant of the regeneration reaction of active site;  $k_c$ , the rate constant of the transfer reaction to monomer; and  $k_t$ , the rate constant of the catalyst deactivation reaction. The rate of monomer consumption can be simplified by the following scaling rule

$$\frac{d[\text{M}]}{dt} = -\underbrace{k_p [\text{C}^*] [\text{M}]}_0 - k_p Y_0 [\text{M}] - \underbrace{k_c Y_0 [\text{M}] - k_z [\text{C}^*\text{B}] [\text{M}]}_{O(\epsilon)}. \quad (12)$$

The zeros in Eq. (12) and hereafter denote the assumption given in Eq. (9) regardless of the magnitude of  $[C^*]$ . The equation for zeroth moment of growing chain distribution can be simplified by adopting Eq. (9) and the quasi-steady-state approximation described by Eq. (10) as follows

$$\frac{dY_0}{dt} = \underbrace{k_p[C^*][M]}_0 - \underbrace{k_b Y_0[B] + k_z[C^*B][M] - k_t Y_0}_{\text{QSSA}} \quad (13)$$

The first moment for the growing chain distribution can be simplified as

$$\frac{dY_1}{dt} = \underbrace{k_p[C^*][M]}_0 + k_p Y_0[M] - k_c Y_1[M] - k_b Y_1[B] - k_t Y_1 + \underbrace{k_c Y_0[M] + k_z[C^*B][M]}_{O(\epsilon)} \quad (14)$$

The zeroth moment for the total chain distribution is described by

$$\frac{dX_0}{dt} = \underbrace{k_p[C^*][M]}_0 + k_c Y_0[M] + k_z[C^*B][M] - \underbrace{k_b[C^*P_1][B] - k_c[C^*P_1][M] - k_t[C^*P_1]}_{O(\epsilon)} \quad (15)$$

From Eqs. (4) and (12), the first moment for the total chain distribution is

$$\frac{dX_1}{dt} = k_p Y_0[M] \quad (16)$$

The second moment for the total chain distribution is also greatly simplified as follows

$$\frac{dX_2}{dt} = \underbrace{k_p[C^*][M]}_0 + 2k_p Y_1[M] + \underbrace{k_p Y_0[M]}_{O(\epsilon)} + \underbrace{k_c Y_0[M] + k_z[C^*B][M]}_{O(\epsilon^2)} - \underbrace{k_c[C^*P_1][M] - k_b[C^*P_1][B] - k_t[C^*P_1]}_{O(\epsilon^3)} \quad (17)$$

The number-average molecular weight,  $M_n$ , and weight-average molecular weight,  $M_w$ , are defined, respectively, as

$$M_n = M_m \frac{X_1}{X_0} \quad (18)$$

and

$$M_w = M_m \frac{X_2}{X_1} \quad (19)$$

where  $M_m$  is the molecular weight of butadiene monomer.

After omitting the terms with magnitude of  $O(\epsilon)$  or smaller, Eqs. (12)–(17) are much simplified, and the closed-form solution can be partially or fully obtained. Integrating (13) yields

$$Y_0 = \alpha[Co]_0 e^{-k_t t} \quad (20)$$

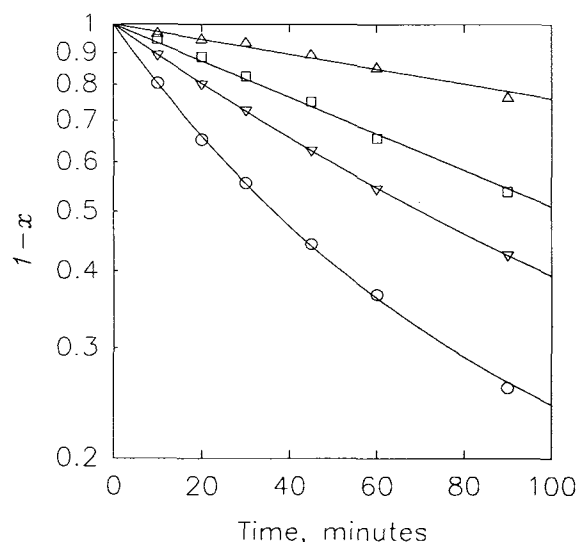
where  $\alpha$  is the efficiency of formation of active catalyst site defined by  $1 - [E_b]/[Co]_0$ . Because  $[C] = 0$  at the beginning, the initial value of  $Y_0$  can be taken as  $\alpha[Co]_0$ . It is extremely difficult to measure the efficiency,  $\alpha$ , directly from experiments, and  $\alpha$  is treated as another parameter to be estimated. For this reason, the rate constants  $k_i$  and  $k_s$  are not evaluated. Using this expression, monomer consumption can be described as

$$[M] = [M]_0 \exp\left(-k_p \alpha [Co]_0 \frac{1 - e^{-k_t t}}{k_t}\right), \quad (21)$$

which was obtained by Hsu and coworkers<sup>10,11,13,14</sup> for the butadiene polymerization with various Ziegler–Natta catalysts. The zeroth moment of the total chain distribution can be obtained by integrating Eq. (15) with  $X_0 = \alpha[Co]_0$  at  $t = 0$  as

$$X_0 = \alpha[Co]_0 + \frac{k_c}{k_p} ([M]_0 - [M]) + \frac{k_b}{k_p} [B]_0 \log \frac{[M]_0}{[M]} \quad (22)$$

In the cobalt based Ziegler–Natta polymerization of butadiene, although the catalyst deactivation reaction is assumed in the reaction mechanism, the reaction does not significantly affect the kinetic behavior, especially when the reaction temperature is not too high. Bawn<sup>6</sup> reported that the deactivation reaction can be neglected when the reaction temperature is below 25°C for  $Co(acac)_3/DEAC/water$



**Figure 1** Fractional conversion versus time for  $[M]_0 = 1.42M$ . ( $\Delta$ )  $T = 5^\circ\text{C}$ ; ( $\square$ )  $15^\circ\text{C}$ ; ( $\nabla$ )  $25^\circ\text{C}$ ; and ( $\circ$ )  $35^\circ\text{C}$ .

catalyst, which is also pointed out by Honig<sup>19</sup> for the present catalyst. Figure 1 shows the effect of temperature on the fractional conversion  $x$ , which is defined as  $x = ([M]_0 - [M])/[M]_0$ . The estimated values of kinetic parameters  $k_p\alpha$  and  $k_t$  are summarized in Table IV, and are obtained by regression analysis of  $-\log(1-x)$  versus time with the constraint  $k_t \geq 0$  explicitly specified. The relatively large values of root mean square error (RMSE) for the lower temperatures (5 and  $15^\circ\text{C}$ ) indicate that the constraint is active for these cases. When the deactivation reaction can be neglected, that is,  $k_t = 0$ , Eqs. (20) and (21) can be further simplified as

$$Y_0 = \alpha[\text{Co}]_0 \quad (23)$$

which is constant and

$$[M] = [M]_0 e^{-k_p\alpha[\text{Co}]_0 t}, \quad (24)$$

**Table IV** Temperature Effect on Conversion

Temperature ( $^\circ\text{C}$ )	$k_p\alpha$ ( $M^{-1} \text{min}^{-1}$ )	$k_t \times 10^2$ ( $\text{min}^{-1}$ )	RMSE ( $\times 10^2$ )
5	22	0.00	1.0
15	54	0.00	1.1
25	91	0.41	0.4
35	184	1.07	0.5

RMSE, root mean square error of regression.

respectively. The first moment of the total chain distribution is

$$X_1 = x[M]_0 = [M]_0(1 - e^{-k_p\alpha[\text{Co}]_0 t}). \quad (25)$$

The initial value of the moments of  $X_1$ ,  $Y_1$ , and  $X_2$  can be set to zero according to the results of scaling analysis.<sup>25</sup> In this study, we do not consider the polymerization with mixed  $C_4$  feedstock so that  $[B]_0 = 0$ . The first moment of growing chain distribution has the expression

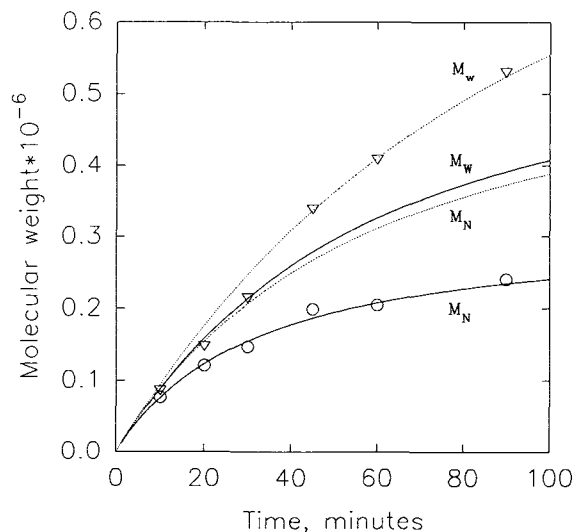
$$Y_1 = \frac{k_p}{k_c} Y_0 \left[ 1 - \exp\left(-\frac{k_c X_1}{k_p Y_0}\right) \right]. \quad (26)$$

Because  $k_t = 0$ ,  $Y_0$  and  $\alpha[\text{Co}]_0$  are interchangeably used. The second moment of the total chain distribution is

$$X_2^{(\text{SAS})} = 2 \frac{k_p}{k_c} (X_1 - Y_1) \quad (27)$$

where the superscript SAS denotes the single active site model. The expression for  $M_n$  and  $M_w$  are obtained as

$$\frac{M_w}{M_n} = \frac{k_c}{k_p} + \frac{Y_0}{X_1} \quad (28)$$



**Figure 2** Molecular weight curves calculated using the SAS model for  $[M]_0 = 1.43M$ . ( $\circ$ ) denotes number-average molecular weight ( $M_n$ ); ( $\nabla$ ) weight-average molecular weight ( $M_w$ ). Solid lines denote calculated molecular weights from  $M_n$  data and dotted lines calculated molecular weights from  $M_w$  data.

**Table V** Effect of Different Data on Regression Results

Data	$k_p\alpha^a$ ( $M^{-1} \text{ min}^{-1}$ )	$k_c/k_p$ ( $\times 10^4$ )	$\alpha$
$M_n$	58.2	1.49	0.448
$M_w$	58.2	0.64	0.441

<sup>a</sup> Estimated from conversion data.

and

$$M_w^{(\text{SAS})} = 2M_m \times \frac{k_p}{k_c} \left( 1 - \frac{1 - \exp(-k_c X_1/k_p Y_0)}{k_c X_1/k_p Y_0} \right). \quad (29)$$

Equation (28) was derived by Kagiya et al.<sup>5</sup> and used by Yoshimoto et al.<sup>9</sup> and Böhm<sup>12</sup> for the regression analysis of  $M_n$ . As shown in Eqs. (28) and (29), both  $M_n$  and  $M_w$  are expressed by the same parameters, namely  $k_c/k_p$  and  $\alpha$ . If  $k_p\alpha$  is determined from the conversion data and  $k_c/k_p$  and  $\alpha$  are determined from  $M_n$  data, then each of  $k_p$ ,  $k_c$ , and  $\alpha$  is decided and there is no adjustable parameter to fit the  $M_w$  data. Figure 2 shows the regression results of molecular weights for  $[\text{Co}]_0 = 1.25 \times 10^{-4} M$  and  $[\text{M}]_0 = 1.43 M$ . The estimated parameter values are summarized in Table V. The solid lines are for the calculated  $M_w$  and  $M_n$  with the parameters estimated from the conversion and  $M_n$  data. As shown in the figure,  $M_w$  is clearly underestimated. On the other hand,  $k_p$ ,  $k_c$ , and  $\alpha$  can be estimated from the conversion and  $M_w$  data. The dotted lines in Figure 2 show the results. In the latter case,  $M_w$  is correctly predicted and  $M_n$  is overestimated. From Figure 2 it can be deduced that the SAS model can correctly predict the trends of both  $M_w$  and  $M_n$ , but it incorrectly estimates the magnitudes of molecular weights.

## DAS MODEL

A more complicated reaction scheme, namely a dual active site model, has been proposed by Nitirahardjo et al.<sup>21</sup> that is capable of predicting  $M_w$  as well as conversion and  $M_n$ . The DAS model contains basically the same reaction steps as the single active site counterpart of Honig et al.<sup>20</sup> does, but each reaction step consists of two parallel reactions as a consequence of DAS assumption. The detailed reaction scheme and full kinetic model equations can

be found in Nitirahardjo et al.<sup>21</sup> and are omitted here. Precisely the same scaling rule as that of the SAS model is applied to the DAS model. The concentrations  $[\text{Co}]$ ,  $[\text{C}_1^*]$ ,  $[\text{C}_2^*]$  are assumed to be zero immediately after the instantaneous initiation. The quasi-steady-state approximation is applied to the concentration of  $[\text{C}_j^* \text{B}]$  and  $[\text{C}_j^* \text{P}_1]$ ,  $j = 1$  and  $2$ . For the case of  $k_t = 0$ , the following expressions can be obtained analogously to the SAS model:

$$Y_{0j} = \alpha_j [\text{Co}]_0 \quad (30)$$

where  $Y_{0j}$  is the zeroth moment of the growing chain distribution for active site  $j$ ,  $j = 1$  and  $2$ ,

$$[\text{M}] = [\text{M}]_0 e^{-(k_{p1}\alpha_1 + k_{p2}\alpha_2)[\text{Co}]_0 t}, \quad (31)$$

and

$$X_0 = (\alpha_1 + \alpha_2)[\text{Co}]_0 + \frac{k_{c1}\alpha_1 + k_{c2}\alpha_2}{k_{p1}\alpha_1 + k_{p2}\alpha_2} ([\text{M}]_0 - [\text{M}]). \quad (32)$$

Comparison of Eqs. (30), (31), and (32) yields the following relations between the parameters:

$$\alpha_1 + \alpha_2 = \alpha \quad (33)$$

$$k_{p1}\alpha_1 + k_{p2}\alpha_2 = k_p\alpha \quad (34)$$

$$k_{c1}\alpha_1 + k_{c2}\alpha_2 = k_c\alpha. \quad (35)$$

Again, the first moment of the total chain distribution is

$$X_1 = x[\text{M}]_0 = [\text{M}]_0 (1 - e^{-k_p\alpha[\text{Co}]_0 t}) \quad (36)$$

where  $k_p\alpha$  satisfies Eq. (34). The first moment for the growing chain distribution for active site  $j$  can be expressed as

$$Y_{1j} = \frac{k_{pj}}{k_{cj}} Y_{0j} \left[ 1 - \exp\left(-\frac{k_{cj} X_1}{k_p Y_0}\right) \right] \quad (37)$$

for  $j = 1$  and  $2$ . The second moment for the total chain distribution is

$$X_2 = 2 \frac{k_{p1}}{k_{c1}} \left( \frac{k_{p1} Y_{01}}{k_p Y_0} X_1 - Y_{11} \right) + 2 \frac{k_{p2}}{k_{c2}} \left( \frac{k_{p2} Y_{02}}{k_p Y_0} X_1 - Y_{12} \right). \quad (38)$$

The termination mechanism of the Ziegler-Natta polymerization is generally much simpler than that of free radical polymerization. The experimental results show that the polydispersity is slightly larger than 2. Based upon these observations, a simple termination step (the chain transfer to monomer in this study) is assumed; that is, the two active sites have different reactivities of propagation but the same reactivity of chain transfer to monomer. When  $k_{c1} = k_{c2} [=k_c$  by Eqs. (33) and (35)], Eq. (38) can be simplified to yield

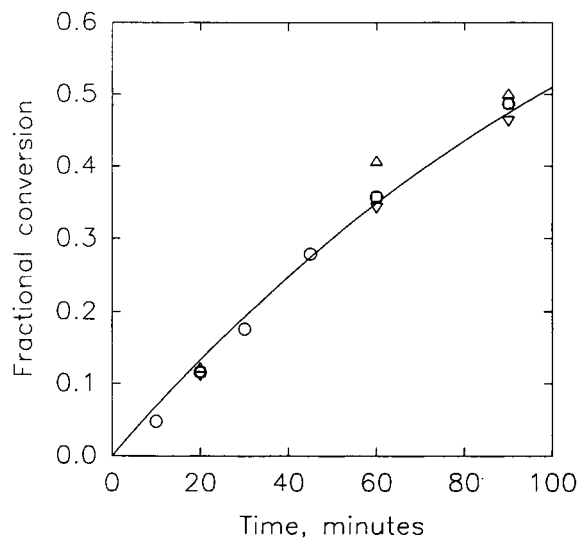
$$X_2 = 2\beta_2 \frac{k_p}{k_c} (X_1 - Y_1) \quad (39)$$

where  $Y_1$  is given in Eq. (26) and  $\beta_2$  is constant satisfying the following relation

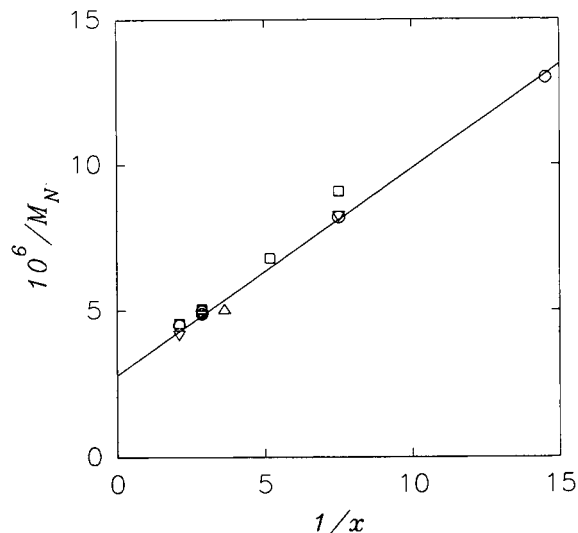
$$k_{p1}^2 \alpha_1 + k_{p2}^2 \alpha_2 = k_p^2 \alpha \beta_2. \quad (40)$$

It is noteworthy that the second moment of the total chain distribution for the DAS model is similar to that of the SAS model except that it has another adjustable scalar multiplier  $\beta_2$ , and, consequently, it satisfies the desired property of  $X_2$  mentioned earlier. Finally, the  $M_w$  for the DAS model can be expressed as

$$M_w = 2\beta_2 M_n \times \frac{k_p}{k_c} \left( 1 - \frac{1 - \exp(-k_c X_1 / k_p Y_0)}{k_c X_1 / k_p Y_0} \right). \quad (41)$$



**Figure 3** Fractional conversion versus time for  $[M]_0 = 1.43M$ . (○) data set I; (▽) data set II; (□) data set III; and (△) data set IV.



**Figure 4**  $1/M_n$  versus  $1/x$  for  $[M]_0 = 1.43M$ . (○) data set I; (▽) data set II; (□) data set III; and (△) data set IV.

The individual values of  $k_{p1}$ ,  $k_{p2}$ ,  $\alpha_1$ , and  $\alpha_2$  cannot be estimated from the conversion,  $M_n$ , and  $M_w$  data because there are only three constraints, Eqs. (33), (34), and (40), to relate them; the microstructure of the two active catalyst sites cannot be identified from the conversion  $M_n$  and  $M_w$  data only. In spite of the indeterminacy of the individual parameters, the kinetic model capable of predicting the conversion,  $M_n$  and  $M_w$  can be identified. It is possible by employing the lumped parameters:  $\alpha$ , the total efficiency of formation of active sites;  $k_p$ , average rate constant of propagation reaction;  $k_c$ , rate constant of transfer reaction to monomer;  $\beta_2$ , the "correction factor of weight-average molecular weight" for a DAS. It can be easily shown from Eqs. (33), (34), and (40) that  $\beta_2 \geq 1$ .

## KINETIC MODELING

Thanks to the aid of simple expressions for the moments of chain distribution, the following kinetic modeling algorithm has been established and used.

**Step 1.** Estimate  $k_p \alpha$  from  $-\log(1 - x_i)$  versus  $t_i$ , for  $i = 1, \dots, m$ . The subscript  $i$  denotes the  $i$ th experimentally measured data, and  $m$ , the number of measurements.

**Step 2.** Calculate  $x(t_i)$ . Estimate  $k_c/k_p$  and  $\alpha$  from  $1/M_n$  versus  $1/x(t_i)$  using Eq. (28).

**Step 3.** Calculate  $k_p$  and  $k_c$  from  $k_p \alpha$ ,  $k_c/k_p$ , and  $\alpha$ .

**Table VI** Parameter Estimates

Data Set	$k_p$ ( $M^{-1} \text{ min}^{-1}$ )	$k_c \times 10^2$ ( $M^{-1} \text{ min}^{-1}$ )	$\alpha$	$\beta_2$
I	130	1.94	0.448	1.24
II	134	2.19	0.412	1.19
III	124	1.76	0.476	1.30
IV	108	1.54	0.586	1.49
V	128	1.43	0.512	1.39
$\sigma^a$	9	0.27	0.059	0.11

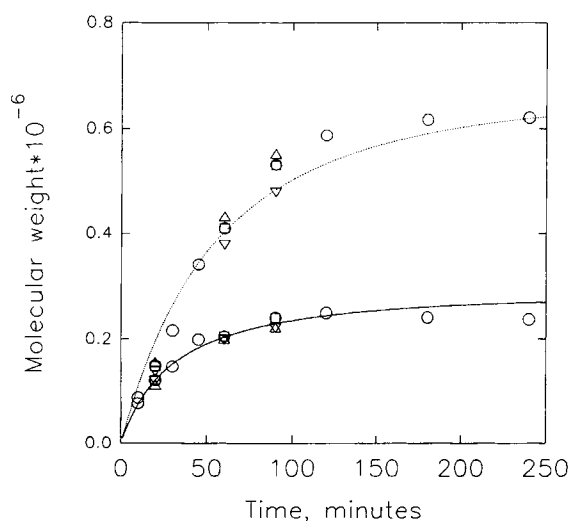
<sup>a</sup> The standard deviation of parameter estimates.

**Step 4.** Calculate  $X_2^{(\text{SAS})}$  using Eq. (27). Estimate  $\beta_2$  from  $M_{wi}$  versus  $X_2^{(\text{SAS})}(t_i)/X_1(t_i)$  using Eq. (39).

In this algorithm, all regression problems are linear with one or two parameters, which can be achieved by the standard least-squares method.

## RESULTS AND DISCUSSION

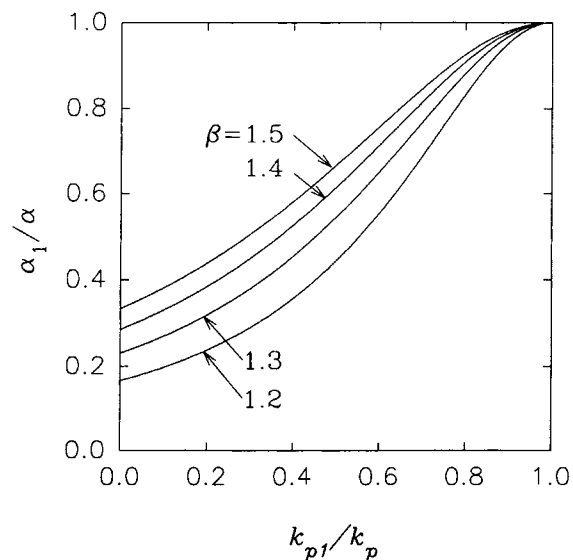
Using the proposed algorithm, kinetic modeling has been carried out with the conversion and molecular weight data adopted from Honig.<sup>19</sup> All the data used here have the same catalyst condition: the concentration of cobalt octoate is  $1.25 \times 10^{-4} M$ ; DEAC,  $2.51 \times 10^{-2} M$ ; water,  $7.47 \times 10^{-3} M$ . The algorithm was first tested for the data with  $[M]_0 = 1.43 M$  and  $T = 15^\circ\text{C}$ , which is referred to as data set I. The



**Figure 5** Molecular weight versus time for  $[M]_0 = 1.43 M$ . (○) data set I; (▽) data set II; (□) data set III; (△) data set IV; solid line,  $M_n$ ; and dotted line,  $M_w$ .

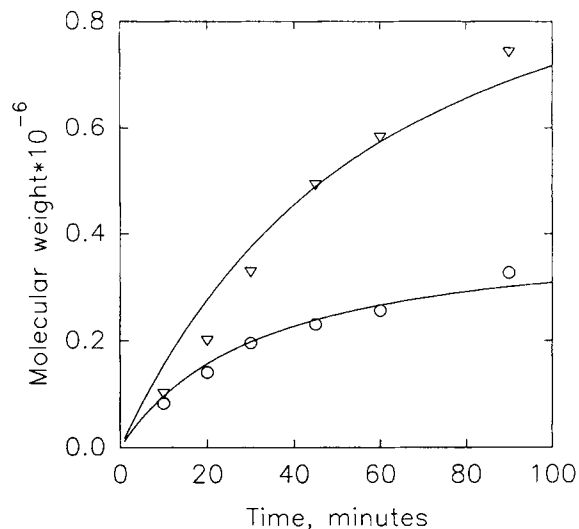
small parameter  $\epsilon$  is  $0.87 \times 10^{-4}$  for this data. Figure 3 shows the conversion versus time data for  $t \leq 90$  min. The value of  $k_p \alpha$  estimated from this data is  $58.2 M^{-1} \text{ min}^{-1}$ . In Figure 4, a plot of  $1/M_n$  versus  $1/x$  shows the linear relation predicted by Eq. (28). The estimated value of  $k_c/k_p$  is  $1.49 \times 10^{-4}$  and that of  $\alpha$  is 0.448. Finally, the correction factor  $\beta_2$ , which is 1.24, was estimated from the  $M_w$  data. The resultant parameter values are summarized in Table VI. Figure 5 shows calculated  $M_n$  and  $M_w$  curves with the estimated parameter values. In Figure 5, the last three data measured at time  $t > 90$  min were not used during the estimation, but they show good agreement with the predicted curves. Three different data sets with the same conditions were used to check the consistency of the parameter estimation. They are referred to as data sets II, III, and IV, and each data set contains only three measurements at  $t = 20, 60,$  and  $90$  min. The data are also shown in Figures 3, 4, and 5 and the resultant parameter estimates are shown in Table VI, which agree well with the previous results from data set I. Finally, the kinetic modeling procedures were repeated for the data with a different initial monomer concentration,  $[M]_0 = 1.83 M$  and the resultant parameter values are also reported in Table VI as data set V. Figure 6 shows that again the calculated molecular weights agree well with the experimental data.

From the basic assumption, the parameter estimates of each column in Table VI should have the same value, and it turns out to be true within a rea-



**Figure 6** Molecular weight versus time for  $[M]_0 = 1.83 M$ . (○) number-average molecular weight and (▽) weight-average molecular weight.





**Figure 7**  $\alpha_1/\alpha$  versus  $k_{p1}/k_p$  for various values of  $\beta_2$ .

sonable amount of deviation. If we consider the fact that data sets II, III, and IV each contains only three measurements, the consistency of the parameter estimates indicates the significance of the kinetic model, especially the correction factor  $\beta_2$ , and the stability of the kinetic modeling procedure together with the reproducibility of the experiments. Although the individual value of the parameters  $k_{p1}$ ,  $k_{p2}$ ,  $\alpha_1$ , and  $\alpha_2$  cannot be decided, they somehow depend on the correction factor  $\beta_2$ . The dependency of  $k_{p1}$  and  $\alpha_1$  are graphically illustrated in Figure 7 for various values of  $\beta_2$ . Figure 7 also shows the feasible range of  $\alpha_1$  for a given  $\beta_2$ . Because the estimated value of  $\beta_2$  ranges from 1.2 to 1.5, it can be said that the active site 1, which is relatively less active, accounts for at least 20% of the total active sites.

## CONCLUSION

The kinetic behavior of the Ziegler-Natta polymerization of butadiene can be qualitatively predicted using the single active site model, but the  $M_w$  is consistently underestimated because the chain distribution calculated by this model is narrower than the actual distribution. The chain distribution, and the  $M_w$ , can be correctly predicted by our DAS model. The most important feature of the dual active model is that the two different active sites have different reactivity of propagation but equal reactivity of chain transfer to monomer. The scaling analysis technique is applied to the model equations, and the closed-form expressions are derived for the conversion,  $M_n$ , and  $M_w$ . A simple kinetic modeling algo-

rithm was developed and used to obtain the optimal parameter estimates. The kinetic modeling results show the validity of the DAS model.

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