

A Mathematical Model for the Ziegler-Natta Polymerization of Butadiene

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Synopsis

A mathematical model which describes conversion and molecular weight development in the homogeneous polymerization of butadiene has been developed. The reaction scheme and derivation of the model equations are included. It was found that a catalyst formation efficiency must be estimated for each polymerization. The correct trends were predicted, although weight-average molecular weight was often underestimated. The model could not fully account for the effect of water concentration.

INTRODUCTION

The mathematical model is becoming an invaluable tool for the development of effective design and control systems for polymerization reactors. Polymerization reactors are typically very complex in nature and so the efficacy of any model is dependent on a thorough understanding of the phenomena occurring in the process. Moreover, the widespread use of powerful computers has meant that sophisticated techniques can be used routinely.

Ziegler-Natta catalysts are characterized by sensitivity to changes in composition which can affect activity, stereoselectivity and molecular weight development. While this presents a considerable technical challenge, in that process control for uniform desired polymer production is arduous, in principle, wide flexibility allows a range of products to be prepared.^{1,2} Practical reaction control is complicated by the often complex effect of changes in operating parameters such as catalyst concentration, order of addition of reaction components, and temperature.

Despite the considerable experimental difficulties, and still imperfect knowledge of catalyst structure and polymerization mechanism, kinetic studies of a wide spectrum of Ziegler-Natta systems have appeared.³ There is, however, a relative paucity of literature describing process control and model development.⁴ In the case of olefins such as ethylene and propylene, for example, while a number of reaction models have been presented,⁵⁻¹¹ it is only in some recent publications that a variety of processes and polymerization catalyst systems have been revealed.¹²⁻¹⁶

A similar situation exists in the polymerization of butadiene. Information of a more technical nature is being released and operational factors for many

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TABLE I
 Rate Equations in Butadiene Polymerization

Author	Catalyst system	Rate equation	Ref.
Bawn	Co(acac) ₃ /Et ₂ AlCl/ H ₂ O	$\ln \frac{[M]_0}{[M]} = k_p t \quad (T < 25^\circ\text{C})$ $= \frac{k_p}{k_t} \ln(1 + k_t [C^*]_0 t) \quad (T > 25^\circ\text{C})$	18
Hsu and Ng	CoCl ₂ ·4C ₅ H ₅ N/ Et ₂ AlCl/H ₂ O	$\ln \frac{[M]_0}{[M]} = \frac{k_p k_c [Co]_i}{k_c - k_t}$ $\times \left[\frac{1}{k_t} (1 - e^{-k_t t}) - \frac{1}{k_c} (1 - e^{-k_c t}) \right]$	19
Yang and Hsu	Co(acac) ₃ / Al(i-Bu) ₃ /H ₂ O	$\ln \frac{[M]_0}{[M]} = \frac{k_p [C^*]}{k_c [C^*]_0} \ln(1 + k_c [C^*]_0 t)$	20
Curtis	CoF ₂ /Et ₃ Al ₂ Cl ₃	$R_p = k[Co][M]^2$	21
Lee and Hsu	Ni(II)stearate/ Et ₂ AlCl	$\ln \frac{[M]_0}{[M]} = k_{p2} [C^*]_t$ $+ \frac{[C^*]}{k_r} (k_{p1} - k_{p2})(1 - e^{-k_r t})$	22
Yoshimoto et al.	Ni(II)Carboxylate/ BF ₃ · Et ₂ O/AlEt ₃	$\frac{-d[M]}{dt} = \alpha k_p [C]_0 [M]$	23
Loo and Hsu	TiI ₄ /Al(i-Bu) ₃	$\ln \frac{[M]_0}{[M]} = \frac{k_p [C]_0}{k_d} (1 - e^{-k_d t})$	24
Bresler et al.	TiI ₂ Cl ₂ /Al(i-Bu) ₃	$R_{p0} = k_p [TiI_2Cl_2][M]$	25

 TABLE II
 Molecular Weight Equations in Butadiene Polymerization

Author	Catalyst system	Molecular weight equation	Ref.
Lee and Hsu	Ni(II)Stearate/ Et ₂ AlCl	$\bar{P}_N = \frac{\int_0^t R_p dt}{[C^*] + \int_0^t R_{fm} dt}$	22
		where $\int_0^t R_p dt = [M]_0 x$ $R_{fm} = [k_{fm1} [C^*] e^{-k_r t} + k_{fm2} [C^*] (1 - e^{-k_r t})] [M]$	
Yoshimoto et al.	Ni(II)carboxylate/ BF ₃ · Et ₂ O/AlEt ₃	$\frac{1}{P_N} = \frac{k_{tm}}{k_p} + \frac{\alpha [C]_0}{x [M]_0}$	23
Loo and Hsu	TiI ₄ /Al(i-Bu) ₃	$\bar{M}_N = m_0 [M]_0 \left[\frac{k_p x}{k_p [C]_0 - k_{ta} [A] \ln(1 - x)} \right]$	24

systems have been identified.^{4,17} Tables I and II show the expressions derived for rate and molecular weight. Curve-fitting techniques were used by several authors to model conversion versus time data^{19,20,22,24} but only Lee and Hsu²² and Loo and Hsu²⁴ attempted to model conversion and molecular weight. Their models, which adequately describe experimental data, have limited

applicability since only relatively low conversions and molecular weights were examined.

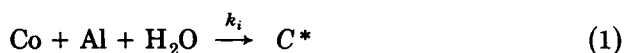
Therefore it would be of both scientific interest and technological importance that a model of greater practical relevance be presented. In this paper, a mathematical model which describes conversion versus time and molecular weight versus conversion profiles for the polymerization of butadiene by a cobalt-based Ziegler-Natta catalyst is derived. In addition to details of the derivation of the model equations, a description of the method of parameter estimation and model testing is provided.

MODEL DEVELOPMENT

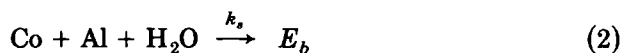
Reaction Scheme

The polymerization of butadiene initiated by a cobalt octoate/diethylaluminum chloride/water catalyst had been reported previously.²⁶ Polymerizations were conducted in a bench scale, stainless-steel batch reactor which was capable of reproducibly producing high molecular weight, high *cis*-polybutadiene in good yield. Two feedstock types were employed: a pure butadiene feed and a more complicated C-4 mixture, mainly 1,3-butadiene and but-1-ene, which is typical of that used for commercial production of polybutadiene. Kinetic and molecular weight data were presented and a reaction mechanism proposed. This mechanism forms the basis of the following reaction scheme, from which the model is derived.

Initiation (formation of active sites)



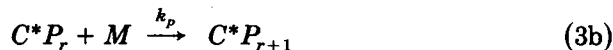
Formation of byproducts



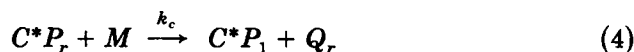
Propagation-first monomer molecule



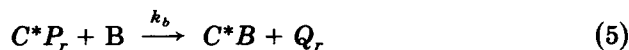
-subsequent monomer molecules



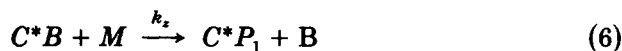
Transfer to cobalt



Transfer to But-1-ene



Regeneration of Active Sites



Catalyst Deactivation



- where
- Co = cobalt octoate
 - Al = diethylaluminium chloride
 - C^* = active catalyst site
 - E_b = catalyst byproduct
 - M = butadiene monomer
 - C^*P_1 = growing chain of unit length
 - C^*P_r = growing chain of chain length r
 - C^*B = short-lived but-1-ene/catalyst complex
 - Q_r = dead polymer chain of chain length r
 - B = but-1-ene
 - C = deactivated catalyst site

$k_i, k_s, k_p, k_c, k_b, k_z,$ and k_t are rate constants

The reactions describing formation of active sites are not fully understood and so eqs. (1) and (2) are written as overall reactions. Equation (2) is included because it can be shown from molecular weight data that not every cobalt atom forms an active site. In the propagation reaction, and all other reactions involving polymer chains, it was assumed that the rate constants were independent of chain length. For a more thorough discussion of the mechanistic aspects of the polymerization the reader should consult Ref. 26.

Model Equations for Rate of Polymerization

In order to derive an expression for the consumption of monomer a series of mass balances on the species present in the reactor must be performed. The first balance is on the amount of monomer:

$$\frac{1}{V} \frac{dM}{dt} = -k_p[C^*P][M] - k_p[C^*][M] - k_z[C^*B][M] \quad (8)$$

- where M = moles of butadiene monomer
 V = volume of the reaction mixture (liters)
 $[X]$ = concentration of species X (mole/liter)

$$C^*P = \sum_{r=1}^{\infty} C^*P_r = \text{total moles of growing chains}$$

If we assume that the amount of monomer consumed in reactions other than the propagation reaction is negligible Eq. (8) becomes

$$\frac{1}{V} \frac{dM}{dt} = -k_p[C^*P][M] \quad (9)$$

Equation (9) contains the amount of growing chains C^*P . The mass balance on this species is

$$\frac{1}{V} \frac{dC^*P}{dt} = k_p[C^*][M] - k_b[C^*P][B] + k_z[C^*B][M] - k_t[C^*P] \quad (10)$$

This equation contains the number of active sites that are not growing chains, C^* , and the number of but-1-ene/catalyst complexes, C^*B . The balance on the former is

$$\frac{1}{V} \frac{dC^*}{dt} = k_i[Co]^m[Al]^n[H_2O]^p - k_p[C^*][M] \quad (11)$$

It has been found that the concentrations of aluminum alkyl and water do not influence molecular weight.^{27,28} Thus we can say that the number of active sites is independent of aluminum alkyl, and water. Equation (11) can then be rewritten as:

$$\frac{1}{V} \frac{dC^*}{dt} = k_i[Co]^m - k_p[C^*][M] \quad (12)$$

The order of this reaction, m , was determined from experimental data.²⁶ The balance on the amount of but-1-ene/catalyst complexes C^*B is

$$\frac{1}{V} \frac{dC^*B}{dt} = k_b[C^*P][B] - k_z[C^*B][M] \quad (13)$$

The final balance required is for the amount of cobalt octoate

$$\frac{1}{V} \frac{dCo}{dt} = -k_i[Co]^m - k_s[Co]^w \quad (14)$$

The order of reaction for the formation of byproducts reaction, w , was assumed to be unity.

There is now an expression for each species of interest. These equations can be simplified by making some additional assumptions. The concentrations of C^* and C^*B must be very small and the rates of generation and consumption for each must be much larger than the rate of accumulation. Equation (12) becomes

$$k_p[C^*][M] = k_i[Co]^m \quad (15)$$

And so

$$[C^*] = \frac{k_i[Co]^m}{k_p[M]} \quad (16)$$

Similarly, we obtain from Eq. (13)

$$[C^*B] = \frac{k_b[C^*P][B]}{k_z[M]} \quad (17)$$

After substituting Eqs. (16) and (17) into Eq. (10) and rearranging we obtain

$$\frac{1}{V} \frac{dC^*P}{dt} = k_i[Co]^m - k_t[C^*P] \quad (18)$$

In summary, the equations needed to describe the rate of polymerization are

$$\frac{1}{V} \frac{dM}{dt} = -k_p[C^*P][M] \quad (9)$$

$$\frac{1}{V} \frac{dCo}{dt} = -k_i[Co]^m - k_s[Co] \quad (14)$$

$$\frac{1}{V} \frac{dC^*P}{dt} = k_i[Co]^m - k_t[C^*P] \quad (18)$$

The number of active sites is determined by the relative values of k_i and k_s , but since this varies in an unpredictable manner, it is necessary to define a catalyst formation efficiency f .

$$f = \frac{k_i - k_s}{k_i} \quad (19)$$

This rearranges to give

$$k_s = k_i(1 - f) \quad (20)$$

Calculation of the efficiency f involves use of initial rate and molecular weight data. This will be discussed further in a subsequent section.

Model Equations for Molecular Weight

The method of moments was used to derive the equations describing molecular weight development. This approach was taken because it was considered the most efficient way of calculating the molecular weight averages. No chain branching reactions have been included.

Polymer exists as growing chains and as dead polymer. The moments of the living polymer distribution are found first. Assuming constant volume, a balance on the growing chains of chain length r yields

$$\begin{aligned} \frac{d[C^*P_r]}{dt} = & k_p[C^*P_{r-1}][M] - k_p[C^*P_r][M] - k_c[C^*P_r][M] \\ & - k_b[C^*P_r][B] - k_t[C^*P_r] \end{aligned} \quad (21)$$

Similarly a balance on growing chains of unit length gives

$$\begin{aligned} \frac{d[C^*P_1]}{dt} = & k_p[C^*][M] - k_p[C^*P_1][M] - k_c[M]Y_0 + k_b[B]Y_0 \\ & - k_c[C^*P_1][M] - k_b[C^*P_1][B] - k_t[C^*P_1] \end{aligned} \quad (22)$$

Here Y_0 is the total growing chain concentration which is equivalent to the zeroth moment of the growing chain distribution.

According to the method of moments, Eq. (21) must be summed from $r = 2$ to $r = \infty$.

This gives

$$\begin{aligned} \frac{d \sum_{r=2}^{\infty} [C^*P_r]}{dt} &= k_p[M] \sum_{r=2}^{\infty} [C^*P_{r-1}] - k_p[M] \sum_{r=2}^{\infty} [C^*P_r] \\ &\quad - k_c[M] \sum_{r=2}^{\infty} [C^*P_r] - k_p[B] \sum_{r=2}^{\infty} [C^*P_r] \\ &\quad - k_t \sum_{r=2}^{\infty} [C^*P_r] \end{aligned} \quad (23)$$

The quantity Y_0 can be expressed simply as

$$Y_0 = \sum_{r=1}^{\infty} [C^*P_r] = \sum_{r=2}^{\infty} [C^*P_{r-1}] \quad (24)$$

and by adding Eqs. (23) and (22) we obtain

$$\frac{dY_0}{dt} = \frac{d[C^*P_1]}{dt} + \frac{d \sum_{r=2}^{\infty} [C^*P_r]}{dt} \quad (25)$$

After the appropriate substitutions are made and terms eliminated, the equation for the zeroth moment of the growing chain distribution is obtained

$$\frac{dY_0}{dt} = k_p[M][C^*] - k_t Y_0 \quad (26)$$

To obtain the first moment of the growing chain distribution, Y_1 , we multiply Eq. (21) by r , sum from $r = 2$ to $r = \infty$ and add this equation to Eq. (22). The resulting expression for Y_1 is

$$\begin{aligned} \frac{dY_1}{dt} &= k_p[M]Y_0 + k_p[C^*][M] + k_c[M](Y_0 - Y_1) \\ &\quad + k_b[B](Y_0 - Y_1) + k_t[Y_1] \end{aligned} \quad (27)$$

To obtain the second moment, Y_2 , a similar procedure is adopted except that the first multiplication is by r^2 . The final form of the expression for Y_2 is

$$\begin{aligned} \frac{dY_2}{dt} &= k_p[M](Y_0 - 2Y_1) + k_p[C^*][M] - k_c[M](Y_0 - Y_2) \\ &\quad + k_b[B](Y_0 - Y_2) - k_t Y_2 \end{aligned} \quad (28)$$

Having found the first three moments of the growing chain distribution it is now necessary to derive the moments of the total distribution. The concentration of polymer chains of chain length r , P_r , is given by

$$[P_r] = [C^*P_r] + [Q_r] \quad (29)$$

where $[C^*P_r]$ = concentration of growing chains of chain length r

$[Q_r]$ = concentration of dead chains of chain length r

By definition, the i -th moment of the total distribution, X_i , is

$$X_i = \sum_{r=1}^{\infty} r^i [P_r] \quad (30)$$

Since $Q_1 = 0$ then

$$\frac{d[P_1]}{dt} = \frac{d[C^*P_1]}{dt} \quad (31)$$

and so

$$\frac{d[P_r]}{dt} = \frac{d[C^*P_r]}{dt} + \frac{d[Q_r]}{dt} \quad (32)$$

The balance on growing chains of chain length r , C^*P_r , was given earlier in Eq. (21). A balance on dead polymer chains of chain length r yields

$$\frac{d[Q_r]}{dt} = k_c[M][C^*P_r] + k_b[M][C^*P_r] + k_t[C^*P_r] \quad (33)$$

By adding Eqs. (21) and (33) we obtain

$$\frac{d[P_r]}{dt} = k_p[M][C^*P_{r-1}] - k_p[M][C^*P_r] \quad (34)$$

At this stage it is necessary to sum from $r = 2$ to $r = \infty$.

$$\begin{aligned} \frac{d \sum_{r=2}^{\infty} P_r}{dt} &= k_p[M] \sum_{r=2}^{\infty} [C^*P_{r-1}] - k_p[M] \sum_{r=2}^{\infty} [C^*P_r] \\ &= k_p[M] Y_0 - k_p[M] \sum_{r=2}^{\infty} [C^*P_r] \end{aligned} \quad (35)$$

Equation (22) is a balance on growing chains of unit length. The zeroth moment of the total chain distribution X_0 , is obtained by adding Eqs. (22)

and (35). The final form is

$$\frac{dX_0}{dt} = k_p[C^*][M] + k_c[M]Y_0 + k_b[B]Y_0 - k_c[M][C^*P_1] - k_b[B][C^*P_1] - k_t[C^*P_1] \quad (36)$$

Higher moments are again easily obtained. For the first moment of the total distribution, X_1 , we multiply Eq. (34) by r , sum from $r = 2$ to $r = \infty$ and then add this equation to Eq. (22). The resulting expression for X_1 is

$$\frac{dX_1}{dt} = k_p[M]Y_0 + k_p[C^*][M] + k_c[M]Y_0 + k_b[B]Y_0 - k_c[M][C^*P_1] - k_b[B][C^*P_1] - k_t[C^*P_1] \quad (37)$$

That is,

$$\frac{dX_1}{dt} = \frac{dX_0}{dt} + k_p[M]Y_0 \quad (38)$$

For the second moment, X_2 , the only difference is that the first multiplication is by r^2 . The expression obtained is

$$\frac{dX_2}{dt} = k_p[M](Y_0 + 2Y_1) + k_p[C^*][M] + k_c[M]Y_0 + k_b[B]Y_0 - k_c[M][C^*P_1] - k_b[B][C^*P_1] - k_t[C^*P_1] \quad (39)$$

That is,

$$\frac{dX_2}{dt} = \frac{dX_0}{dt} + k_p[M](Y_0 + 2Y_1) \quad (40)$$

The only equations that remain to be given are those for the number- and weight-average molecular weights. These are obtained from the expressions for number- and weight-average degrees of polymerization.

$$\bar{M}_N = M_m \bar{r}_N = M_m \frac{\sum_{r=1}^{\infty} rP(r)}{\sum_{r=1}^{\infty} P(r)} = M_m \frac{X_1}{X_0} \quad (41)$$

$$\bar{M}_W = M_m \bar{r}_W = M_m \frac{\sum_{r=1}^{\infty} r^2P(r)}{\sum_{r=1}^{\infty} rP(r)} = M_m \frac{X_2}{X_1} \quad (42)$$

where M_N , M_W are, respectively, cumulative number- and weight-average

molecular weights; r_N , r_W are number- and weight-average degrees of polymerization; M_m is the molecular weight of butadiene.

The equations needed to describe the molecular weight are

$$\frac{d[C^*P_1]}{dt} = k_p[C^*][M] - k_p[C^*P_1][M] + k_c[M]Y_0 + k_b[B]Y_0 - k_c[C^*P_1][M] - k_b[C^*P_1][B] - k_t[C^*P_1] \quad (22)$$

$$\frac{dY_0}{dt} = k_p[C^*][M] - k_tY_0 \quad (26)$$

$$\frac{dY_1}{dt} = k_p[M]Y_0 + k_p[C^*][M] + k_c[M](Y_0 - Y_1) + k_b[B](Y_0 - Y_1) + k_tY_1 \quad (27)$$

$$\frac{dX_0}{dt} = k_p[C^*][M] + k_c[M]Y_0 + k_b[B]Y_0 - k_c[M][C^*P_1] - k_b[B][C^*P_1] - k_t[C^*P_1] \quad (36)$$

$$\frac{dX_1}{dt} = \frac{dX_0}{dt} + k_p[M]Y_0 \quad (38)$$

$$\frac{dX_2}{dt} = \frac{dX_0}{dt} + k_p[M](Y_0 + 2Y_1) \quad (40)$$

$$\bar{M}_N = Mm \frac{X_1}{X_0} \quad (41)$$

$$\bar{M}_W = Mm \frac{X_2}{X_1} \quad (42)$$

RESULTS AND DISCUSSION

Model Parameters

The parameters were estimated using data obtained from widely varying reaction conditions. They were then used in all the model predictions which follow. In contrast to the approach taken by other workers,^{20,22,24} a least-squares method was not used. Most likely, due to the number of highly correlated parameters attempts to use this method proved very difficult and gave estimates that were often physically unrealistic. Instead, a trial and error

method was adopted to fit the model to the experimental data by eye and the following values for the parameters were obtained.

$$\begin{aligned}
 k_i &= 1.0 \times 10^9 && \left(\frac{1}{\text{min}} \right) \left(\frac{\text{mol}}{\text{liter}} \right)^{1-m} \\
 k_p &= 1.95 \times 10^9 \exp \left[\frac{-4570.6}{T(\text{K})} \right] && \text{liter/mol min} \\
 k_c &= 2.82 \times 10^6 \exp \left[\frac{-5117.1}{T(\text{K})} \right] && \text{liter/mol min} \\
 k_b &= 1.0 \times 10^{-4} \text{ (at } 15^\circ \text{C)} && \text{liter/mol min} \\
 k_t &= 0.002 \text{ (at } 15^\circ \text{C)} && \text{liter/mol min} \\
 m &= 1.4
 \end{aligned}$$

All parameters were estimated from previously published experimental data,²⁶ except the initiation rate constant (k_i) which was arbitrarily set to a very large number. In the system under study, no induction or acceleration periods were observed and so it was concluded that initiation was instantaneous.

The order of reaction (m) and the Arrhenius equations for the propagation rate constant (k_p) and transfer to cobalt rate constant (k_c) were determined from experiments using pure butadiene feedstock. Rate constants for the catalyst regeneration and catalyst deactivation reactions (k_b and k_t , respectively) were found from experiments using the "mixed-C4" feed, but since these were conducted at 15°C , only the value for that temperature is given.

Conversion and Molecular Weight Profiles

The catalyst formation efficiency (f) was estimated for each case as it was not possible to accurately predict the number of active sites. Lee and Hsu²² and Loo and Hsu²⁴ attempted to calculate the concentration of active centers but their values exhibited a large degree of scatter. Unsatisfactory and conflicting results have also been obtained when radioactive labelling techniques were used.³

Conversion versus time plots for both feedstock systems are shown in Figures 1 and 2. The solid lines represent the calculated values and the points are the experimental data. It is clear that the model fits the data well. The model also adequately describes conversion versus time profiles with changing reaction conditions. For example, the effect of changing cobalt octoate concentration is shown in Figure 3 and that of temperature in Figure 4.

A more important indication of the adequacy of the model is a comparison between calculated and measured molecular weight. In the latter case, it was found that irrespective of feedstock composition, both number-average and weight-average molecular weights increased rapidly during the initial stages of the polymerization, but as conversion increased, the number-average curve approached a constant value.²⁶

The calculated molecular weight as a function of conversion for both types of feedstock is shown in Figures 5 and 6. The correct trend is obtained,

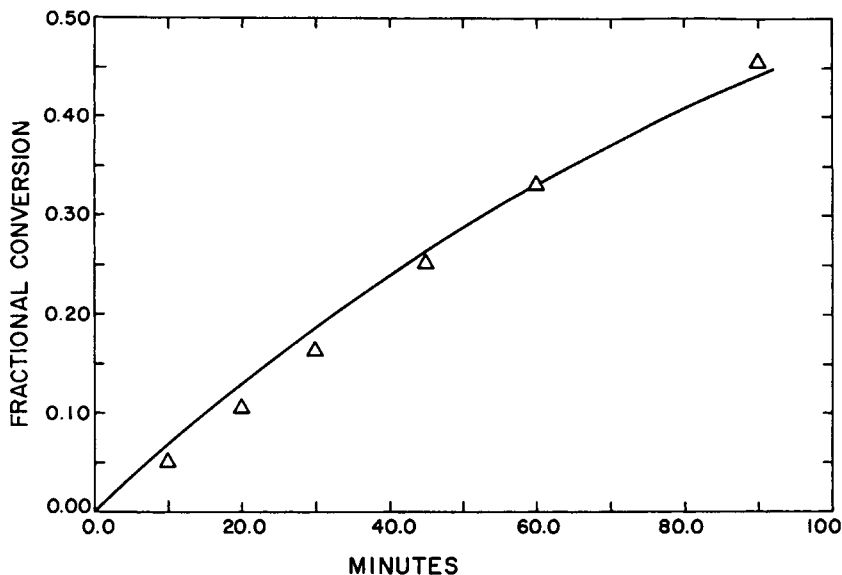


Fig. 1. Conversion versus time: $[Co] = 1.25 \times 10^{-4} M$; $[Al] = 2.51 \times 10^{-2} M$; $[H_2O] = 7.47 \times 10^{-3} M$; $[M]_0 = 1.85 M$ $T = 15^\circ C$. Pure butadiene feedstock.

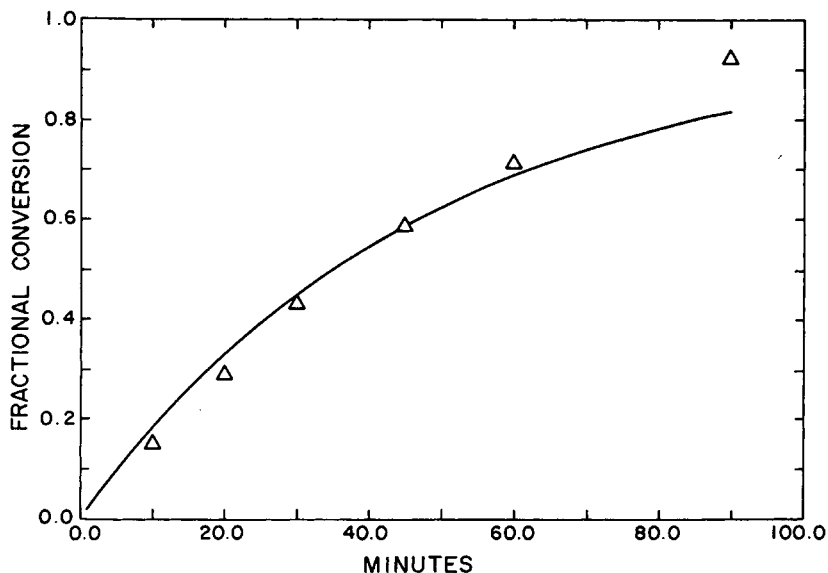


Fig. 2. Conversion versus time: $[Co] = 1.24 \times 10^{-4} M$; $[Al] = 2.51 \times 10^{-2} M$; $[H_2O] = 7.5 \times 10^{-3} M$; $[M]_0 = 1.42 M$ $T = 15^\circ C$. "Mixed-C4" feedstock.

although the fit is not as good as for conversion versus time. The majority of molecular weight versus conversion profiles predicted by the model were unable to fully reproduce the increase in polydispersity with conversion. While the number-average molecular weight curves followed the expected pattern, the weight-average molecular weight was often underestimated, particularly at high conversion.

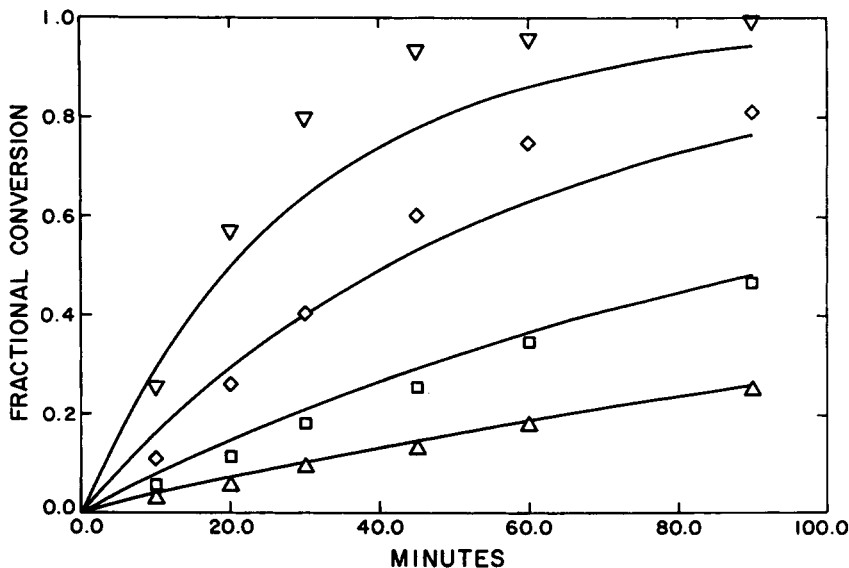


Fig. 3. Conversion versus time: $[Al] = 2.51 \times 10^{-2} M$; $[H_2O] = 7.47 \times 10^{-3} M$; $[M]_0 = 1.45 M$; $T = 15^\circ C$. Pure butadiene feedstock. $[Co] \times 10^4$, M: (Δ) 0.62; (\square) 1.25; (\diamond) 2.5; (∇) 5.0.

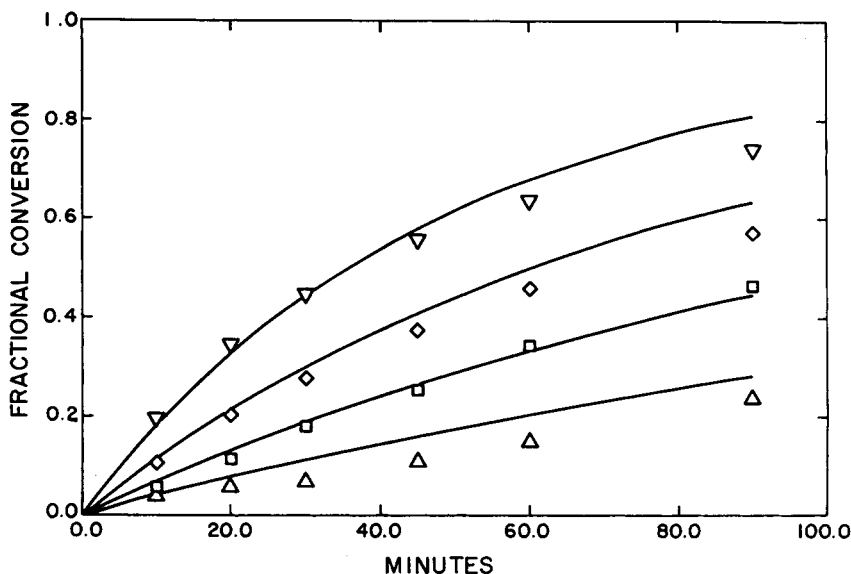


Fig. 4. Conversion versus time: $[Co] = 1.25 \times 10^{-4} M$; $[Al] = 2.51 \times 10^{-2} M$; $[H_2O] = 7.47 \times 10^{-3} M$; $[M]_0 = 1.42 M$. Pure butadiene feedstock. T , $^\circ C$: (Δ) 5; (\square) 15; (\diamond) 25; (∇) 35.

Loo and Hsu²⁴ also observed a discrepancy between calculated and measured molecular weights and attributed this to the assumption that the aluminum alkyl concentration was independent of conversion. Improved fit was obtained when it was proposed that aluminum alkyl participated in chain transfer reactions to give inert derivatives. This approach is not appropriate in the present system as both molecular weight values and size exclusion

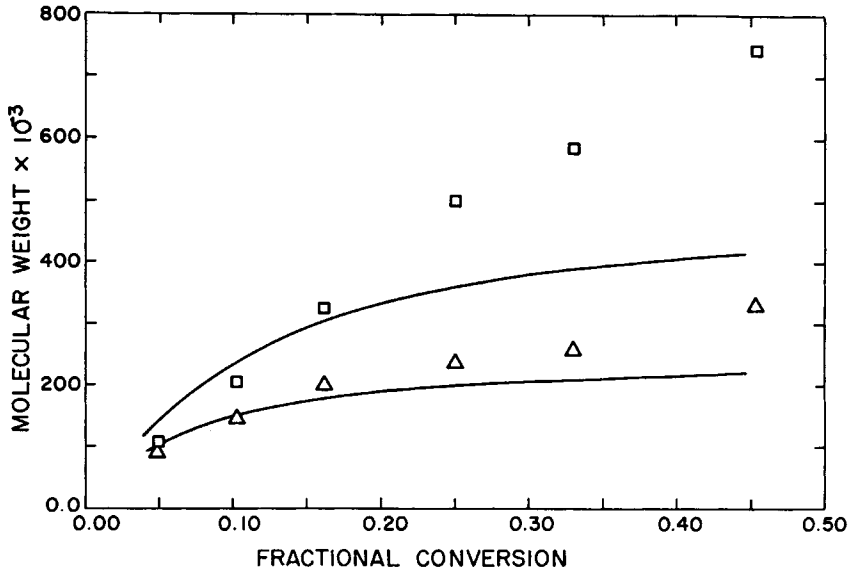


Fig. 5. Molecular weight versus conversion. Conditions as for Figure 1: (Δ) \bar{M}_N ; (\square) \bar{M}_W .

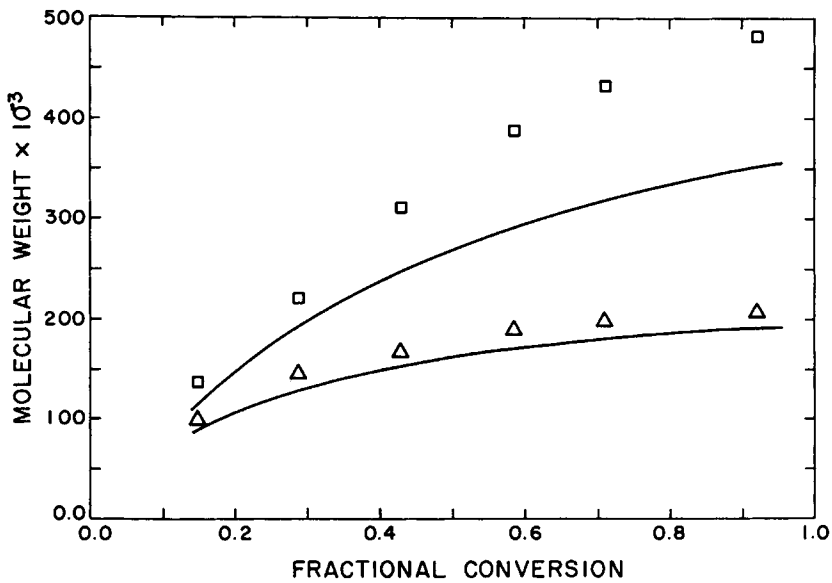


Fig. 6. Molecular weight versus conversion. Conditions as for Figure 2: (Δ) \bar{M}_N ; (\square) \bar{M}_W .

chromatograms indicated quite conclusively that aluminum alkyl was not a chain transfer agent.²⁶

The most serious limitation of the model, however, was its inability to properly reproduce the experimental findings with respect to the effect of water concentration. Since rate but not molecular weight was dependent on water concentration, it was concluded that the activity of each site rather than the number of sites was affected by water concentration. Further, there

TABLE III
 Effect of Water Concentration on Molecular Weight

$[\text{H}_2\text{O}] \times 10^2$, M	M_N Meas.	M_N Calcd.	M_W Meas.	M_W Calcd.
Approximately 15% conversion				
0.5	91,000	110,000	139,000	160,000
0.75	98,000	85,000	136,000	115,000
1.0	86,000	150,000	105,000	239,000
1.25	100,000	160,000	134,000	249,000
Approximately 50% conversion				
0.5	223,000	185,000	476,000	345,000
1.0	219,000	200,000	426,000	389,000
1.25	214,000	205,000	431,000	400,000

$[\text{Co}] = 1.24 \times 10^{-4} \text{ M}$

$[\text{Al}] = 2.51 \times 10^{-2} \text{ M}$

$[M]_0 = 1.4 \text{ M}$

$T = 15^\circ \text{ C}$

"Mixed-C4" Feed.

was no evidence to suggest that water was involved in any chain transfer or deactivation reactions.²⁶

The conversion versus time profiles for each water concentration could only be predicted by manipulating the catalyst formation efficiency (f). This procedure changed the number of active sites and so it was not possible to predict the molecular weights. As shown in Table III, the calculated molecular weights do not compare favorably with the measured values and also exhibit considerably more scatter.

It is apparent that refinements to the model are necessary. Comparison with other published work, though, provides little benefit. In the system under study, a number of the more common proposals, including chain transfer to monomer^{22,23} or aluminum alkyl,^{19,20,24} were found to be inappropriate.²⁶ Similarly, there was no reason to assume that either different types of active site²² or different stereoregulating mechanisms²¹ were present. Nonetheless, there is uncertainty regarding the nature and concentration of active sites, as reflected by the need for the parameter f . Clarifying the situation will considerably increase the knowledge of the reaction mechanisms and hence the utility of mathematical models.

CONCLUSIONS

A mathematical model based on a polymerization mechanism involving re-use of active centers, combined with termination, has been derived. The model describes polymerization to high conversion with respect to both kinetics and molecular weight. Adequate agreement with measured data was obtained, except in those polymerizations in which water concentration was varied. Despite the need for a catalyst formation efficiency, which limits the model's applicability in areas such as process simulation, it is considered that the model will be of greater practical importance than those hitherto presented.

NOMENCLATURE

- Al = diethylaluminium chloride
 B = but-1-ene
 C = deactivated catalyst site
 Co = cobalt octoate
 C* = active catalyst site
 C*B = short-lived but-1-ene/catalyst complex
 C*P₁ = growing chain of unit length
 C*P_r = growing chain of chain length r
 E_b = catalyst byproduct
 f = catalyst formation efficiency
 k_i = initiation rate constant
 k_p = propagation rate constant
 k_c = transfer to cobalt rate constant
 k_b = transfer to but-1-ene rate constant
 k_z = regeneration of active sites rate constant
 k_d = catalyst deactivation rate constant
 k_s = formation of by-products rate constant
 M = moles of butadiene monomer
 M_N = cumulative number-average molecular weight
 M_w = cumulative weight-average molecular weight
 Q_r = dead polymer chain of chain length r
 r_N = number-average degree of polymerization
 r_w = weight-average degree of polymerization
 V = volume of reaction mixture (liters)
 X_i = i-th moment of the total chain distribution
 Y_i = i-th moment of the growing chain distribution

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