

Polymerization of Butadiene in Toluene with Nickel(II) Stearate–Diethyl Aluminum Chloride Catalyst. II. Kinetic Study

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Synopsis

Based on the polymerization data presented in part I of this series, a kinetic mechanism for the polymerization of butadiene in toluene initiated with nickel(II) stearate–diethyl aluminum chloride was proposed. Expressions for the conversion, the degree of polymerization, and the cis content were derived. Those models were then used to correlate the experimental data from which the rate constants were estimated. A quantitative discussion of various aspects of the polymerization is also presented.

INTRODUCTION

In part I of this study,¹ the catalytic behavior of the nickel(II) stearate–diethyl aluminum chloride (DEAC) system in the polymerization of butadiene in toluene was discussed. The highlights of the findings are as follows: (1) The overall rate of polymerization decreases with time but approaches a constant rate after about 10–30 min of reaction time depending on the relative amounts of the catalyst components. (2) The propagation reaction appears to be first order with respect to monomer concentration. (3) No appreciable termination reaction was observed. (4) The transfer reaction to monomer dominates the chain-breaking step. And it has also been found that the cis-1,4 content of polybutadiene products decreases with reaction time, whereas the number- and weight-average molecular weights and the dispersity increase slightly with conversion.

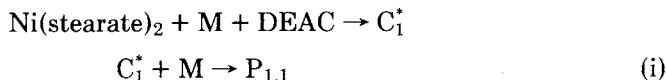
In this part of the study, an attempt was made to develop a kinetic model based on the experimental observations presented in part I. The expressions describing monomer conversion, the degree of polymerization, and the composition of microstructure were derived from the proposed kinetic scheme. The rate constants and the corresponding activation energies were estimated from the model fittings of the experimental data.

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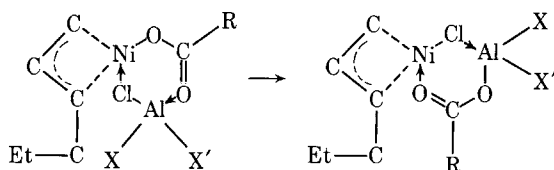
POLYMERIZATION MECHANISM

Formation of Active Species

Since no induction period was observed for all experiments, the initiation reactions are proposed as follows



and are assumed to be instantaneous. The reactions involve the complex formation of type I, C_1^* , and the engagement of the first butadiene monomer M onto the complex to form a living polymer, $\text{P}_{1,1}$, of chain length one of type I species. Of course, other reactions may also occur, leading to the compounds inactive in polymerization. As to be shown later, only a fraction of the added nickel is effective. As discussed in the previous publication,¹ the active complexes initially are in the form of type I but are converted to type II gradually, as shown below:



This transformation is likely to follow a first order reaction



where k_r is the rate constant. In view of the deacceleration of the rate during the initial stage of polymerization, it is then obvious that complex I is more reactive than complex II. Complex II, however, remains stable, leading to a constant polymerization rate after the completion of complex transformation.

Type I complex is also highly stereospecific which favors almost exclusively the cis-1,4 polymerization. On the other hand, the type II complexes, according to the molecular configuration, are believed to be less stereospecific. The buildup of type II complexes during polymerization is then responsible for the drop in cis content of polymer products as conversion increases.

Chain Propagation

It has been shown by numerous investigators that in the Ziegler polymerization the propagation reaction is first order with respect to the monomer and active species² with only a few exceptions reported other than first-order kinetics.

To examine the validity of the first-order assumption for this system, we write the overall polymerization rate in a first-order form:

$$R_p = -\frac{d[\text{M}]}{dt} = k_p[\text{C}^*][\text{M}] \quad (1)$$

where $[\text{C}^*]$ is the total concentration of active species. With the lack of termination, $[\text{C}^*]$ is the sum of $[\text{C}_1^*]$ and $[\text{C}_2^*]$ and can be considered as constant; k_p then is the overall propagation rate constant. Integration of eq. (1) gives

$$\ln \frac{[M_0]}{[M]} = k_p [C^*] t \quad (2)$$

where $[M_0]$ is the initial monomer concentration and t is the polymerization time.

According to eq. (2), for a first-order kinetics, a plot of $\ln [M_0]/[M]$ against t should give a straight line. Figure 2 represents such a typical plot. Obviously, from the plot only during the later stage of polymerization, the reaction truly follows first-order kinetics. However, as was pointed out, the falling rate is a result of the conversion of complexes I to complexes II rather than the invalidity of the first-order assumptions.

To show that the falling rate period of polymerization also follows first-order kinetics, we rewrite eq. (2) in terms of fractional conversion x :

$$-\ln (1 - x) = k_p [C^*] t \quad (2')$$

Equation (2') now is independent of initial monomer concentration, and Figure 1 is a plot of x against t with different monomer concentrations. For the initial monomer concentration ranging from 0.57 to 2.29 mole/l., it is reasonable to say that within the experimental error all data points fall on a single curve. Consequently, the propagation reaction can be expressed by the following equation:



where k_{p_i} is the propagation rate constant of type i complexes and $P_{i,r}$ denotes the active polymer species with chain length r attached to a complex of type i .

Chain Termination

In part I we have demonstrated experimentally that even after 19 hr of polymerization, at which time the reaction has already reached a complete conversion, the reaction mixture remained active, as is shown by its capability of continuing

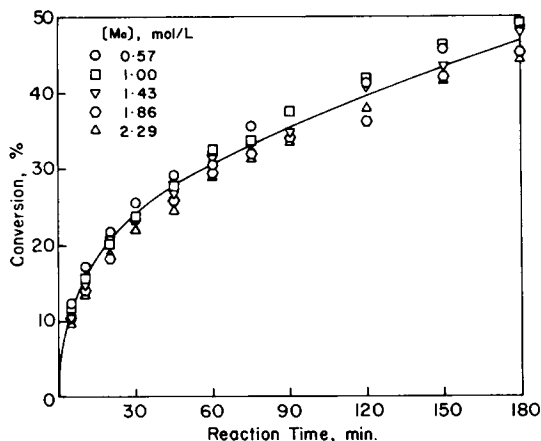


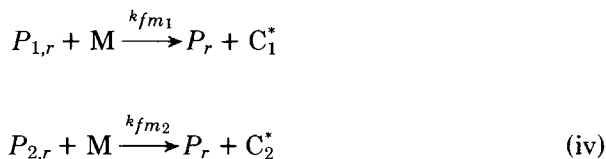
Fig. 1. Conversion curve at different initial monomer concentrations at 20°C. $[\text{Ni}(\text{stearate})_2] = 4.81$ mmole/l., $[\text{Al}]/[\text{Ni}] = 6.30$.

polymerization after a further addition of monomer solution. Furthermore, it has been shown that the polymerization after the second addition of monomer still maintained a constant rate. Without any doubt then, the termination reaction is definitely insignificant. On the other hand, we have found that the population of polymer, as measured by the total monomer conversion divided by the number-average molecular weight, increased steadily with reaction time, which clearly indicates the extensiveness of the chain-breaking reaction.

In the absence of termination reaction, the only possible chain-breaking reaction is undoubtedly the chain transfer reaction. For this system, three possible chain transfer reactions may be considered: transfer to solvent, to aluminum alkyl, and to monomer. It is unlikely that the chain transfer reaction to solvent is significant. With a large proportion of the reaction mixture being solvent, if the transfer to solvent were extensive, the rate of transfer to solvent would remain constant throughout the reaction. On the other hand, as the conversion advances, the rate of polymerization will fall because of the depletion of monomer; as a result the molecular weight should decrease rather than increase as is observed experimentally.

The effect of alkyl aluminum on molecular weight is given in Table I. Aluminum concentration varying from 0.01 to 0.12 mole/l. has little effect on the polydispersity. Thus, the possibility of the transfer to aluminum compound can also be discarded. Consequently, the only remaining possibility is the transfer to monomer.

Since there are two types of active species and we have no reason to assume equal reactivity, the transfer reactions can be represented by the following expressions:



where k_{fm_1} is the rate constant of chain transfer to monomer with respect to active species i , and P_r is the dead polymer with chain length r .

TABLE I
Average Molecular Weights of Polybutadiene Obtained at 20°C and at a Nickel Concentration of 4.81 mmole/l.^a

Experiment No.	[Al] × 10 ² , mole/l.	Conv., %	M_n	M_w	M_w/M_n
41	1.01	1.8	1310	1890	1.44
60	1.52	3.9	1300	1800	1.38
42	2.02	5.2	1460	2080	1.42
43	4.05	11.3	1550	2230	1.44
44	5.06	14.0	1530	2190	1.43
45	6.07	16.5	1510	2210	1.46
61	8.09	22.3	2200	3420	1.38
56	12.14	22.1	1500	2141	1.43

^a $[M_0] = 1.43$ mole/l.

DEVELOPMENT OF KINETIC MODEL

Based on the proposed polymerization mechanism, the expressions for conversion, the degree of polymerization, and the composition of microstructure can be derived accordingly.

With the assumption of instantaneous initiation reaction, a fraction of nickel catalyst forms complexes I as soon as the catalyst components are mixed in the presence of monomer. Let $[C_1^*]_0$ be the amount of complexes I formed. Then, according to reaction (ii), the rate of disappearing of C_1^* or the formation of C_2^* owing to the complex transformation is given by

$$-\frac{d[C_1^*]}{dt} = \frac{d[C_2^*]}{dt} = k_r[C_1^*] \quad (3)$$

with the initial condition

$$[C_1^*] = [C_1^*]_0 \quad \text{at } t = 0$$

$[C_1^*]_0$ may be considered the effective concentration of nickel catalyst. In the absence of termination reaction,

$$[C_1^*]_0 = [C^*] \text{ (constant)} \quad (4)$$

where $[C^*]$ is the total concentration of active species or living polymer chains. At any time

$$[C^*] = [C_1^*] + [C_2^*] \quad (5a)$$

$$= \sum_{r=1}^{\infty} ([P_{1,r}] + [P_{2,r}]) \quad (5b)$$

Upon integration of eq. (3) and substitution of eq. (4),

$$[C_1^*] = [C^*] \exp(-k_r t) \quad (6)$$

The equation for $[C_2^*]$ according to eq. (5a) is then given by

$$\begin{aligned} [C_2^*] &= [C^*] - [C_1^*] \\ &= [C^*][1 - \exp(-k_r t)] \end{aligned} \quad (7)$$

The globe rate of polymerization according to reaction (iii) can be written as

$$R_p = -\frac{d[M]}{dt} = k_{p1}[C_1^*][M] + k_{p2}[C_2^*][M] \quad (8)$$

Substituting eqs. (6) and (7) into (8) and integrating, we obtain

$$\ln \frac{[M_0]}{[M]} = k_{p2}[C^*]t + \frac{[C^*]}{k_r} (k_{p1} - k_{p2})(1 - e^{-k_r t}) \quad (9)$$

As the time becomes large, $(1 - e^{-k_r t})$ approaches zero; thus, at long time t , the second term on the right-hand side of eq. (9) has no significant contribution, and $\ln [M_0]/[M]$ becomes linearly related with time t with a slope equal to $k_{p2}[C^*]$.

The number-average degree of polymerization, \bar{P}_n , can be derived according to Kagiya et al.³ When the growth of chain length is relatively slow and the concentration of the growing chain end is held constant, \bar{P}_n can be written as

$$\bar{P}_n = \frac{\int_0^t R_p dt}{[C^*] + \int_0^t R_{fm} dt} \quad (10)$$

where R_p and R_{fm} are the rates of polymerization and transfer to monomer, respectively. Equation (10) considers the transfer to monomer to be the only chain-terminating reaction. Since R_p is equal to $-d[M]/dt$,

$$\int_0^t R_p dt = M_0 - M$$

$$= M_0x \quad (11)$$

R_{fm} according to reaction (iv) is given by

$$R_{fm} = k_{fm1}[C_1^*][M] + k_{fm2}[C_2^*][M] \quad (12)$$

Substituting eqs. (6) and (7), respectively, for $[C_1^*]$ and $[C_2^*]$ in eq. (12) yields

$$R_{fm} = [k_{fm1}[C^*] e^{-krt} + k_{fm2}[C^*](1 - e^{-krt})][M] \quad (13)$$

After the inversion of Eq. (10) and the substitutions of eqs. (9), (11), and (13), we obtain

$$\frac{1}{\bar{P}_n} = \frac{[C^*]}{[M]_0x} + \frac{k_{fm1}[C^*]}{x} \int_0^t \exp \left\{ - \left(k_r t + k_{p2}[C^*]t + \frac{[C^*]}{k_r} (k_{p1} - k_{p2})(1 - e^{-krt}) \right) \right\} dt$$

$$+ \frac{k_{fm2}[C^*]}{x} \int_0^t (1 - e^{-krt}) \exp \left\{ - \left[k_{p2}[C^*]t + \frac{[C^*]}{k_r} (k_{p1} - k_{p2})(1 - e^{-krt}) \right] \right\} dt \quad (14)$$

Since polybutadiene obtained in this experiment has a negligible content of vinyl-1,2 structure while the proportion of cis and trans configurations varies depending on the reaction time, the instantaneous cis content in the polymer produced at time t can be expressed by

$$S = \frac{\alpha k_{p1}[C_1^*] + \beta k_{p2}[C_2^*]}{k_{p1}[C_1^*] + k_{p2}[C_2^*]}$$

or

$$S = \frac{\alpha k_{p1}e^{-krt} + \beta k_{p2}(1 - e^{-krt})}{k_{p1}e^{-krt} + k_{p2}(1 - e^{-krt})} \quad (15)$$

where α and β are the probabilities for cis polymerization which result from the addition of a monomer to the active species I and II, respectively. The cumulative percentage of cis content will then be

$$\text{cis \%} = 100 \times \left(\frac{\int_0^t SR_p dt}{\int_0^t R_p dt} \right) \quad (16)$$

Equations (9), (14), and (16) can then be used to correlate the experimental data and from that, the rate constants, $[C^*]$, α , and β , can be estimated.

RESULTS AND DISCUSSION

Conversion Model

The experimental data of monomer conversion of each experimental run were fitted to eq. (9) with the least-squares method.⁴ The term

$$\sum_i \left\{ \left(\ln \frac{[M_0]}{[M]} \right)_{\text{exp}} - \left(\ln \frac{[M_0]}{[M]} \right)_{\text{calc}} \right\}_i^2$$

where subscript i denotes the data point at a given reaction time in each experimental run, was minimized to estimated three lumped parameters, $k_{p_2}[C^*]$, k_r , and $[C^*](k_{p_1} - k_{p_2})/k_r$ in eq. (9). The results are given in Table II. A graphic comparison for three experiments is presented in Figures 2 and 3, where the solid lines represent the calculated values from eq. (9) using the estimated values of the parameters, and the points are the data of direct experimental measurements.

In testing the adequacy of the conversion model, for each experimental run the residuals of the model fitting were examined, and no systematic trend was found. This ensures the validity of the assumption that the variance of all residuals is constant, a necessary condition for the use of the least-squares method with constant weighing factor.

Table II also shows that the rate constant k_r , for the transfer reaction of type I active species to type II remains fairly constant, and it is affected neither by the concentration of Ni nor by the Al/Ni ratio. The result is perceivable because the complex transformation probably involves no more than the structural rearrangement of the complex formation. A few exceptions, however, were observed. When the Al/Ni ratio is small, say below 5, the values of the estimated parameters become erroneous, even though the model still fits the individual experimental conversion data well. It was noted that the catalyst behaved quite differently at low Al/Ni ratio as compared to those whose ratio is greater than 6. The model proposed above may not provide an adequate description of the system at low Al/Ni ratio. In many Ziegler-Natta polymerizations, a minimum ratio of alkyl metal to transition metal is required for the initiation of polymerization. In this system, a low Al/Ni ratio gives very slow overall polymerization rate. Even though the initial polymerization rate is still high according to the initial slope of the $\ln [M_0]/[M]$ vs. t plot, it approaches a constant polymerization rate very rapidly. Because of the short falling rate period, the k_r estimation is naturally subject to greater uncertainties. The results of those experiments are represented by experiments 41 and 60 in Tables I and II.

Also from Table II, it can be seen that $k_{p_2}[C^*]$ increases with aluminum concentration at a constant Al/Ni ratio. The increase was also observed when either Ni or Al was kept constant as the concentration of the other catalyst component varied. This increase can be attributed to the increase in the population of active polymer species C^* rather than to the increase in the reactivity of the species as shown in Figure 4, where $(\{[C^*](k_{p_1} - k_{p_2})\}/k_r/k_{p_2}[C^*] = K)$ was plotted against nickel concentration for an Al/Ni ratio greater than 6.0. The ordinates of Figure 4 contain no $[C^*]$ because $[C^*]$ appears in both the numerator and denominator. Clearly, K remains at a constant value of 0.79 ± 0.05 over a nickel concentration range of 0.8–9.6 mmole/l.

After the elimination of $[C^*]$, the term K reduces to $(k_{p_1}/k_{p_2} - 1)/k_r$. Hence,

TABLE II
Estimated Kinetic Parameters from Conversion Data

(A) [Ni] = 4.81 mmole/l., [Al]/[Ni] = 6.3, T = 20°C				
Experiment No.	[M ₀]	$k_{p2}[C^*] \times 10^2$, min ⁻¹	$[C^*](k_{p1} - k_{p2})/k_r$	k_r , min ⁻¹
52	0.57	0.15 ± 0.05	0.29 ± 0.06	0.08 ± 0.05
53	1.00	0.27 ± 0.01	0.21 ± 0.01	0.12 ± 0.02
27	1.43	0.25 ± 0.01	0.25 ± 0.01	0.11 ± 0.01
54	1.86	0.22 ± 0.01	0.21 ± 0.01	0.09 ± 0.02
55	2.29	0.22 ± 0.01	0.20 ± 0.01	0.10 ± 0.02
(B) [Al]/[Ni] = 6.3, T = 20°C				
Experiment No.	[Ni], mmole/l.	$k_{p2}[C^*] \times 10^2$, min ⁻¹	$[C^*](k_{p1} - k_{p2})/k_r$	k_r , min ⁻¹
58	2.41	0.10 ± 0.02	0.13 ± 0.03	0.04 ± 0.01
37	3.21	0.16 ± 0.01	0.12 ± 0.01	0.09 ± 0.02
27	4.81	0.25 ± 0.01	0.25 ± 0.01	0.11 ± 0.01
57	5.62	0.25 ± 0.02	0.22 ± 0.02	0.10 ± 0.02
38	6.42	0.32 ± 0.01	0.27 ± 0.01	0.09 ± 0.01
39	8.02	0.41 ± 0.01	0.30 ± 0.02	0.13 ± 0.02
35	9.63	0.54 ± 0.02	0.40 ± 0.02	0.12 ± 0.02
59	12.84	0.91 ± 0.01	0.43 ± 0.01	0.20 ± 0.02
(C) [Ni] = 4.81 mmole/l., T = 20°C				
Experiment No.	[Al]/[Ni]	$k_{p2}[C^*] \times 10^2$, min ⁻¹	$[C^*](k_{p1} - k_{p2})/k_r$	k_r , min ⁻¹
41	2.10	0.001 ± 0.001	0.01 ± 0.001	0.12 ± 0.02
60	3.16	0.02 ± 0.01	0.09 ± 0.01	0.62 ± 0.01
42	4.20	0.18 ± 0.01	0.06 ± 0.01	0.26 ± 0.13
43	8.42	0.27 ± 0.02	0.24 ± 0.02	0.08 ± 0.01
44	10.5	0.34 ± 0.01	0.27 ± 0.01	0.11 ± 0.02
45	12.6	0.38 ± 0.01	0.30 ± 0.01	0.11 ± 0.01
56	25.2	0.54 ± 0.01	0.34 ± 0.01	0.20 ± 0.02
(D) [Ni] = 4.81 mmole/l., [Al]/[Ni] = 6.3, T = 20°C				
Experiment No.	[H ₂ O], mmole/l.	$k_{p2}[C^*] \times 10^2$, min ⁻¹	$[C^*](k_{p1} - k_{p2})/k_r$	k_r , min ⁻¹
75	1.0	0.12 ± 0.02	0.11 ± 0.02	0.35 ± 0.12
76	1.4	0.16 ± 0.03	0.12 ± 0.02	0.38 ± 0.17
79	5.7	0.47 ± 0.01	0.11 ± 0.01	3.17 ± 0.89
74	7.8	0.63 ± 0.06	0.13 ± 0.03	3.51 ± 3.39
80	15.0	1.28 ± 0.09	0.14 ± 0.11	0.08 ± 0.01

K will also remain constant if the effects of catalyst composition on k_{p1} and k_{p2} are proportional. Though we do not have concrete experimental evidence to prove this, we believe the composition of catalyst has an insignificant influence on reactivity on the ground that it is highly unlikely that the quantitative dependence of k_{p1} and k_{p2} on the catalyst composition would be exactly the same.

The k_{p1}/k_{p2} ratio can be calculated from the estimated lumped parameters

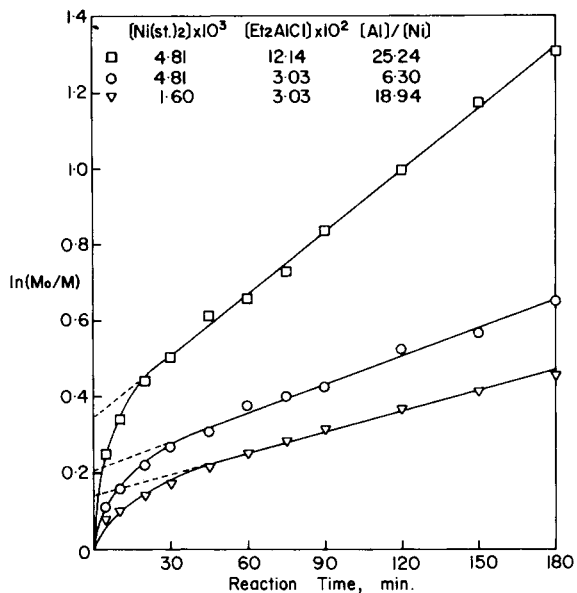


Fig. 2. Comparison of calculated $\ln(M_0/M)$ with experimental data at 20°C and $[M_0] = 1.43$ mole/l.

$k_{p2}[C^*]$, k_r , and $[C^*](k_{p1} - k_{p2})/k_r$ and was found to be 10.0 ± 1.0 for all experiments with no water added. On the other hand, when water was added, the values obtained from curve fitting are drastically different from those without

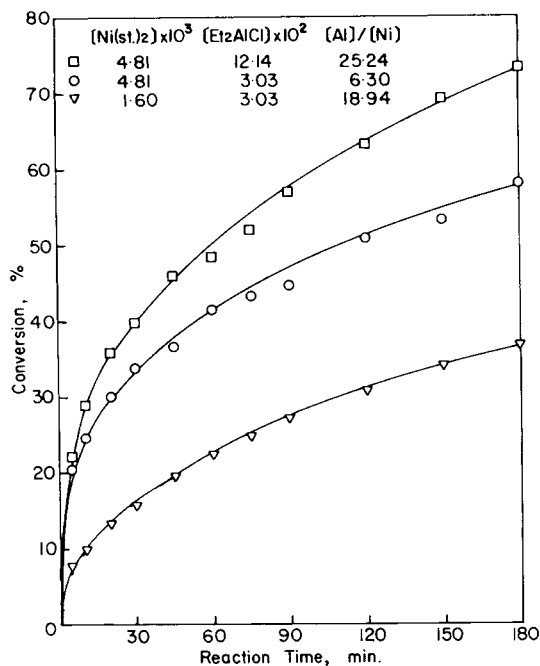


Fig. 3. Comparison of calculated conversion with experimental data at 20°C and $[M_0] = 1.43$ mole/l.

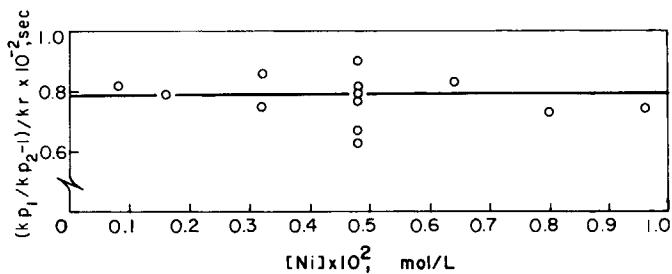


Fig. 4. Plot of $(k_{p1}/k_{p2} - 1)/k_r$ vs. nickel concentration at different $[Al]/[Ni]$ ratios at 20°C. $[M_0] = 1.43$ mole/l.

water. In fact, with the limited data available, no systematic trend can be detected. Thus, because the K value is insensitive to the reactivity of the active species, any effects of catalyst composition on reactivity, if significant, should be reflected in k_{p1}/k_{p2} .

With the understanding that k_{p1} is independent of the concentration of aluminum compound, the effectiveness of the nickel catalyst under different aluminum concentrations can then be studied through the term $k_{p2}[C^*]/[Ni]$. Figure 5 depicts the relationship of the effectiveness factor to the free aluminum compound in the mixture, which is given as $([Al] - 2[Ni])^{1/2}$ by assuming that 2 mole DEAC are needed to react with 1 mole $Ni(stearate)_2$. DEAC is believed to be present in the form of dimers. With some scattering, as would be expected, the effectiveness of the catalyst is linearly related to the square root of the free aluminum compound. The plot excludes those experiments where the Al/Ni ratio is below 5.0. At low Al/Ni ratio, the data points fall outside the linear region.

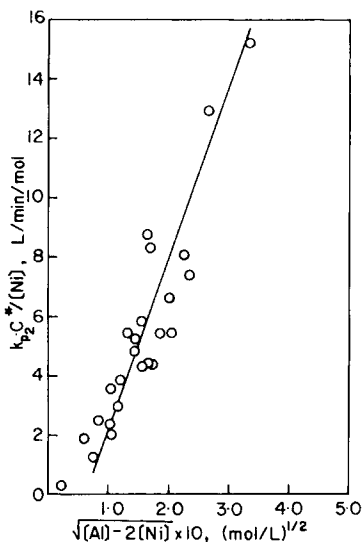


Fig. 5. Correlation of the effectiveness of nickel catalyst with free alkyl concentration at 20°C. $[M_0] = 1.43$ mole/l.

C* and the Effects of Transfer Reaction on Molecular Weight

Fitting of the conversion model gives only what is known as the lumped parameter $k_{p2}[C^*]$, a product of the propagation rate constant in the region of constant polymerization and the total concentration of active species. Also, no information on transfer reaction can be extracted from the monomer conversion since it is independent of transfer reaction. On the other hand, if we follow the molecular weight of the polymer during the batch polymerization, eq. (14) may be used to estimate $[C^*]$ as well as the transfer rate constants k_{fm1} and k_{fm2} . Some results of the model fitting of eq. (14) are presented in Table III. The integrals in eq. (14) were evaluated using the parameter values of k_r , $k_{p2}[C^*]$, and $[C^*](k_{p1} - k_{p2})/k_r$ obtained from the conversion model. The trapezoidal rule was employed for the numerical integration.

Unfortunately, the precision of the estimate $[C^*]$ is extremely sensitive to experimental errors. The level of uncertainty in $[C^*]$ at a 95% confidence level could be as high as $\pm 150\%$ for some experiments. Because of the poor precision, the analysis of $[C^*]$ reveals very little that can be of any help to substantiate the arguments used in the previous section.

However, qualitatively it is clear that only a fraction of the nickel added is effective in polymerization. It is interesting to note that from experiments 74, 75, 76, 79, and 80, in which water was added, the $k_{p2}[C^*]$ values increase steadily with the $[H_2O]/[Al]$ ratio, but $[C^*]/[Ni]$ shown in Table III of experiment 80 is not much different from those with no water addition. So, the primary effect of water is the enhancement of the catalytic reactivity.

The transfer rate constants k_{fm1} and k_{fm2} , obtained from fitting the molecular weight model, give reasonable confidence intervals, as given in Table III. As expected, the k_{fm1}/k_{fm2} ratio is close to the k_{p1}/k_{p2} ratio in view of the experimental results on the polydispersity of the products. In all experiments, the polydispersity of polybutadiene only varies slightly with conversion. The magnitude of k_{fm1} is not influenced by the Al/Ni ratio. The model describes the molecular weight well, and a few examples are shown in Table IV which verify the assumption that the transfer to monomer dominates the chain termination reaction.

In the study of water effect, we can see that the addition of water increases the transfer rate constants, but not as drastically as its effect on k_p . This explains the fact that in the presence of water, the molecular weights of the polybutadiene, on the average, are doubled, but the polydispersity remains fairly constant.

TABLE III
Results from the Curve Fitting of Equation (14)

Experiment No.	[Ni], mmole/l.	[Al]/[Ni]	[C*], mmole/l.	k_{fm1} , mole/l./min	k_{fm2} , mole/l./min	[C*]/[Ni]
51	9.63	3.15	2.5	0.14	0.01	0.26
33	4.81	6.30	0.59	1.3	0.09	0.12
35	9.63	6.30	6.4	0.24	0.01	0.66
36	1.60	6.30	0.50	0.18	0.02	0.31
61	4.81	16.80	0.53	2.9	0.17	0.11
46	0.80	37.90	0.38	0.50	0.06	0.48
80 ^a	4.81	6.30	3.22	0.39	0.15	0.67

^a Water was added.

TABLE IV
Comparison of Calculated M_n with Experimental Data

Time, min	Experiment 33		Experiment 36		Experiment 80	
	M_n exp.	M_n calc.	M_n exp.	M_n calc.	M_n exp.	M_n calc.
5	1540	1480	1630	1820	4040	4090
10	1560	1570	1820	1900	3720	3660
20	1660	1650	1920	1880	3470	3470
30	1630	1700	2100	1890	3370	3410
45	1700	1770	2080	1940	—	—
60	1800	1830	1950	2010	—	—
75	1880	1870	2000	2100	3190	3180
90	1920	1900	2060	2160	—	—
120	1990	1970	2080	2140	—	—
150	1970	2020	2100	1930	—	—
180	2040	2060	2070	2130	—	—

Microstructure of Polybutadiene

The cis content of polybutadiene is given by eq. (16). With the k_{p1}/k_{p2} values obtained from the conversion model, the values of α and β are selected for the best fit of the experimental data of cis-1,4 content. Figure 6 shows the comparison of cis content plotted against time between the experimental data and calculated data from eq. (16). For three experiments the values of α , which is a measure of the stereoregularity of species I, are all above 0.9, much higher than the corresponding β of species II; β has a value around 0.6. Experiment 36 does not give a good fit, and the value of β is unreasonably low. This discrepancy could be caused by the large standard deviation ($\sim 30\%$) observed in the estimated lumped parameters of $k_{p2}[C^*]$ and $[C^*](k_{p1} - k_{p2})/k_r$, particularly the latter. This is always the case when the amounts of catalyst components are at extremes.

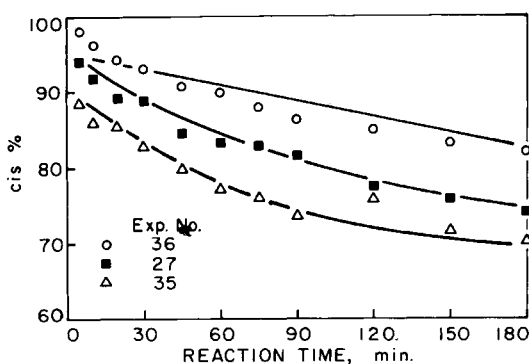


Fig. 6. Comparison of calculated cis content with experimental data (20°C):

Experiment No.	[Ni] $\times 10^3$, mole/l.	[Al] $\times 10^2$, mole/l.	α	β
36	1.60	1.01	0.95	0.35
27	4.81	3.03	0.95	0.60
35	9.63	6.07	0.90	0.50

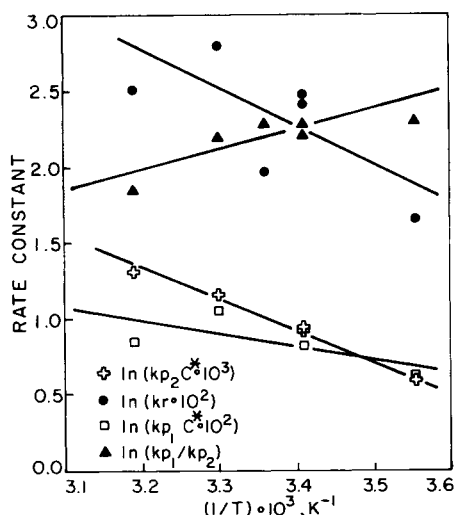


Fig. 7. Arrhenius plot of rate constants. $[\text{Ni}(\text{stearate})_2] = 4.81 \times 10^{-3}$ mole/l., $[\text{DEAC}] = 3.03 \times 10^{-2}$ mole/l., $[\text{M}_0] = 1.43$ mole/l.

Activation Energy

To study the activation energy for the butadiene polymerization, experiments were conducted at five different temperatures at a given composition of catalyst. An $[\text{Al}]/[\text{Ni}]$ ratio of 6.3 and a concentration of 4.81 mmole/l. for $[\text{Ni}]$ were chosen for convenience. Because the rate constants are independent of catalyst composition as previously discussed, only one catalyst composition was studied. The Arrhenius plot of the rate constants is given in Figure 7, and the activation energies are listed in Table V.

It is well known that the activation energy of many Ziegler-Natta catalysts is in the range of 42–63 kJ/mole.² For the polymerization of butadiene, Jolly and Wilke⁵ summarized that the activation energy is 42–63 kJ/mole for π -allyl nickel complex catalysts and 33.5–42 kJ/mole for nickel-based Ziegler-Natta catalysts. Azizov and co-workers⁶ reported that the activation energy for π -allyl complex is decreased to ~ 25 kJ/mole in the presence of some electron acceptors. And recently, Munoz-Escalona⁷ obtained different activation energies for different stages of ethylene polymerization using $\text{TiCl}_3\text{-Et}_3\text{Al}$ catalyst. Their reported values are 35 kJ/mole for the overall activation energy at the maximum polymerization rate, 14 kJ/mole for that during the decay period, and 21 kJ/mole for that of the stationary polymerization rate. Activation energies obtained in this work are relatively low, and further study is needed to confirm these values.

TABLE V
Activation Energies of Polymerization

Parameter	Activation energy, kJ/mole
k_r	21
$k_{p_1}C^*$	6.8
$k_{p_2}C^*$	17
k_{p_1}/k_{p_2}	-2.6

CONCLUSIONS

The proposed models give adequate descriptions of the polymerization reactions initiated with $\text{Ni}(\text{stearate})_2\text{-Et}_2\text{AlCl}$ catalyst. The analysis of the kinetic data using those models helps a great deal in the quantitative understanding of the system. It confirms the formation of two types of complexes active in polymerization with a relative reactivity ratio of 10. Unfortunately, the model is very sensitive to experimental errors in the study of the concentration of complexes, and more data are required to draw conclusive results. Water seems to have drastic effects on the polymerization rate, the molecular weights, and the microstructure. This has not been studied in depth and will be the subject for future study.

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