

Polymerization of Butadiene with $\text{Co}(\text{acac})_3$ - $(i\text{-Bu})_3\text{Al-H}_2\text{O}$ Catalyst

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Synopsis

The polymerization of butadiene in toluene using $\text{Co}(\text{acac})_3$ - $(i\text{-Bu})_3\text{Al-H}_2\text{O}$ catalyst system was studied. Presented are the effects of the addition order, aging time, and composition of catalysts on rates, polymer microstructure, and molecular weights. The polymerization was found to be initiated by the $\text{Co}(\text{acac})_3$ -hydrolized aluminum alkyl complex. The chain propagation proceeds according to a first-order reaction with respect to monomer and active species and is a strong function of $\text{Al/H}_2\text{O}$ with an optimum ratio of 1.0, but independent of Al/Co . The nature of polymerization seems to change as $\text{Al/H}_2\text{O}$ increases from less than 1 to greater than 1. Transfer reaction is significant. From the kinetic data it was found that the termination reaction is most likely to be by combination.

INTRODUCTION

Polybutadiene (PB) with a configurational composition of 50% cis and 50% vinyl was obtained by Furukawa et al.¹ using a combination of $\text{Co}(\text{acac})_3$ with $(\text{Et})_3\text{Al}$ as catalyst. They qualitatively discussed the kinetics of the polymerization and the effects of catalyst composition on monomer conversion, polymer microstructure, and molecular weight.

In the present work, a detailed study of the polymerization of butadiene in toluene initiated with $\text{Co}(\text{acac})_3$ - $(i\text{-Bu})_3\text{Al-H}_2\text{O}$ is presented. The polymerization rates were determined under different catalyst compositions, giving particular attention to the water concentration. The kinetic data were analyzed in an attempt to develop a conversion model capable of describing the initiation, propagation, and termination steps of the polymerization. The results of the molecular weight of polymers and their microstructure under various polymerization conditions are also presented.

EXPERIMENTAL

Polymerization

A bench-scale batch reactor was used for the polymerization study. The detailed description of the reactor system and the procedures used were given elsewhere.^{2,3} The conversion of monomer at different time intervals was determined from the weight of polymer formed. GPC and IR were used, respectively, for the determination of the average molecular weights and the composition of microstructure.

Determination of Water Content

A Beckman GC-4 gas chromatograph equipped with Porapak Q, 50–80-mesh column was used for determining the water content in toluene and in butadiene monomer.

GC was first calibrated against dry toluene treated with molecular sieves with the addition of known quantities of water. A linear plot of peak area against the amount of water added was obtained. However, the extrapolation to zero water content does not pass through zero peak area. The calibration curve was corrected by forcing the curve to pass through the origin.

Due to the practical difficulties, the direct measurement of water content in the reaction mixture was not carried out. Instead, the water content of the solvent after treatment with molecular sieves (referred to as "dry solvent") and of the butadiene were first determined from the GC analysis. An amount of the water-saturated solvent was then added to bring the total water content to the predetermined level. Spot checks were made during the work to assure no appreciable changes of the water content in the dry solvent occurred. The water content so determined was estimated to be within ± 5 ppm.

Determination of Molecular Weight and Microstructure

Four styragel columns with pore sizes ranging from 3×10^3 to 1×10^6 Å were used. The calibration procedures followed the method described by Loo and Hsu.⁴ In brief, it was based on the universal calibration method using monodispersed standard polystyrene samples in conjunction with four broadly distributed standard PB samples. The intrinsic viscosities of the standard samples were measured at GPC operating temperature.

The signals from GPC were processed and corrected from the broadening effects by an on-line PDP 11/10 computer. The estimated error in averaged molecular weights is about $\pm 8\%$ at most.

Microstructure was determined using IR according to the method of Hsu and Ng.⁵ A KCl cell with path length of 1.0 mm was used coupled with a cell of adjustable path length. The sample solution was prepared in CS_2 with a concentration of 0.25–0.50 wt %. Absorption peaks at 10.3μ and 11.0μ of trans and vinyl configurations, respectively, and the area bounded between 12.0μ and 16.0μ for cis and vinyl were taken for the calculation of composition. A comparison of the results obtained from this experiment against the certified values of the standard PB samples shows a maximum deviation of 1%.

Addition Procedure

It was found that the order of addition of monomer, $\text{Co}(\text{acac})_3$ and triisobutyl aluminum (TIBA) to the reactor greatly affected the catalyst reactivity. Figure 1 shows the results of the three different addition orders. The highest conversion was obtained when the TIBA solution was added first to the reactor filled with monomer solution and the predetermined amount of water, followed by the addition of $\text{Co}(\text{acac})_3$. No polymer was obtained over a period of more than 2 h as the order of addition was reversed. When TIBA solution and $\text{Co}(\text{acac})_3$ were premixed before they were added to the reactor, a reasonable conversion was

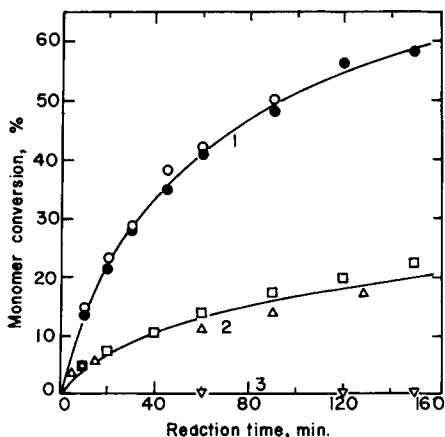


Fig. 1. Monomer conversion as a function of time with different addition orders (20°C). $[Co] = 1.26$ mmol/L; $[Al] = 16.4$ mmol/L; $[Al]/[H_2O] = 1.06$; $[M]_0 = 0.94$ mol/L. (1) TIBA added before $Co(acac)_3$; (2) TIBA and $Co(acac)_3$ premixed; (3) $Co(acac)_3$ added before TIBA.

reached after 2 h, but the conversion was substantially lower as compared to the first case.

As suggested by Medvedev,⁶ the cobalt catalyst reacts with water producing compounds which are no longer capable of forming active complexes with TIBA. When TIBA is added first, it reacts with water to form a hydrolyzed aluminum compound which is believed to be responsible for the formation of active complexes with $Co(acac)_3$.

In this work, the choice naturally follows the order of adding TIBA first before the addition of cobalt salt.

Aging of the Catalyst

With the addition procedure adopted as described in the previous section, the reactivity of the catalyst depends on how soon the cobalt solution is added after the addition of TIBA to the monomer solution. The delay of adding cobalt solution to the TIBA–monomer solution resulted in a serious reduction of catalyst activity. This aging effect is demonstrated in Figure 2 by plotting the conversion against the polymerization time. As shown, the conversion decreased as the aging time increased from 2 min to 60 min, but remained fairly constant after 60 min.

Obviously, the logical choice of aging time in view of data reproducibility should be either zero or more than 60 min. Zero time, in practice, is impossible; 2 min is the time needed to transfer the cobalt solution from the preparatory flask to the reactor. Therefore, data presented here were the results corresponding to the catalyst being aged for 2 min.

RESULTS AND DISCUSSION

Error Analysis on Monomer Conversion

Ziegler type catalysts have been known to be sensitive to any contamination. Precaution was then taken by careful experimental preparation and control. The

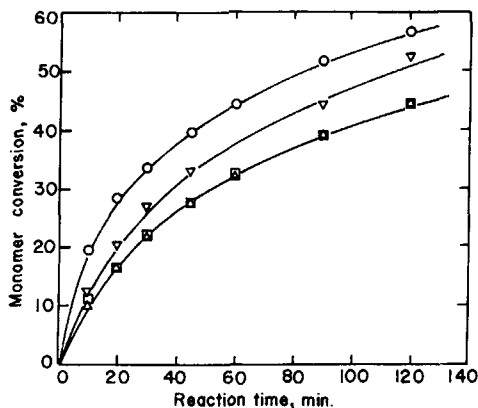


Fig. 2. Monomer conversion as a function of time with different aging times (20°C). $[Co] = 1.26$ mmol/L; $[Al] = 18.0$ mmol/L; $[Al]/[H_2O] = 1.17$; $[M]_0 = 0.94$ mol/L. Aging time: (○) 2 min; (▽) 30 min; (□) 60 min; (△) 120 min.

flask which was used to collect butadiene monomer was carefully calibrated and the estimated error in the volume measurement was less than 1.0%. The temperature of the reactor was continuously monitored and at no time did the fluctuation go beyond $\pm 0.5^\circ C$. The major source of error came from the measurement of polymer weight in the sample for the determination of conversion. The difficulty lies in the removal of catalyst from the reaction mixture. A complete removal of catalyst from a sample containing very little polymer is particularly a problem, often resulting in some loss of polymer. At low conversion, i.e., below 10%, the uncertainty of the conversion data was estimated to be in the range of 8–12%. The uncertainty was greatly reduced at higher conversions.

The overall precision may be measured from the data of duplicate runs. They are shown in Figure 1, curve 1, where the circles and dots are the monomer con-

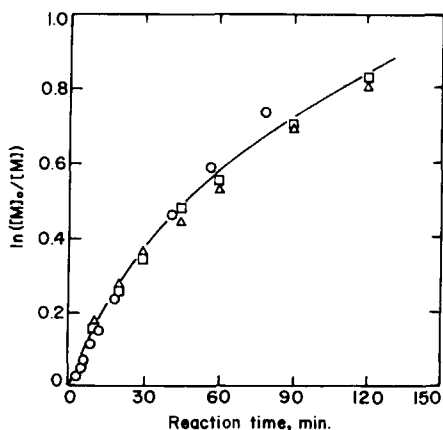


Fig. 3. Effect of initial monomer concentration on polymerization (20°C). $[Co] = 1.26$ mmol/L; $[Al] = 16.4$ mmol/L; $[Al]/[H_2O] = 1.06$. Monomer concentration: (○) 1.40 mol/L; (□, △) 0.94 mol/L (duplicate runs).

versions of two identical experiments. The data points through which the top curve in Figure 4 or 13 were drawn were also repeated runs.

Reaction Order with Respect to Monomer

Figure 3 shows plots of $\ln [M]_0/[M]$ vs time t at two different monomer concentrations. Clearly, the relation was independent of initial monomer concentration $[M]_0$, an indication of first-order polymerization with monomer. However, the first-order plots did not remain linear as conversion increased, as it should be if the reaction followed simple first-order kinetics.

There is no reason to believe the possible change of reaction order with monomer conversion. It is also highly unlikely that the propagation rate constant is dependent on the chain length. Even if it were so, with significant chain transfer reaction as to be shown later, the effect would be averaged out due to the distribution of chain length. Thus, the nonlinearity can only be attributed to the catalytic deactivation or termination leading to the observed reduction of polymerization rate. The nature of the termination will be discussed in the later section.

Dependence of Reaction Rate on Catalyst Composition

In both Figures 4 and 5, $\ln ([M]_0/[M])$ is plotted against time at different concentrations of $\text{Co}(\text{acac})_3$ ranging from 0.25 to 1.26 mmol/L at a fixed water concentration of 15.4 mmol/L. The difference between these two figures is the concentration of TIBA. Figure 4 shows the results where $[\text{Al}]$ is higher than $[\text{H}_2\text{O}]$, whereas, in Fig. 5, $[\text{Al}]$ is lower than $[\text{H}_2\text{O}]$. It is interesting to note that when $[\text{Al}]$ is higher than $[\text{H}_2\text{O}]$, the deactivation is relatively insignificant at lower $[\text{Co}]$, but becomes so at higher $[\text{Co}]$. The opposite effect of deactivation was observed when $[\text{Al}]$ is lower than $[\text{H}_2\text{O}]$.

In examining the effect of cobalt catalyst on polymerization, the initial poly-

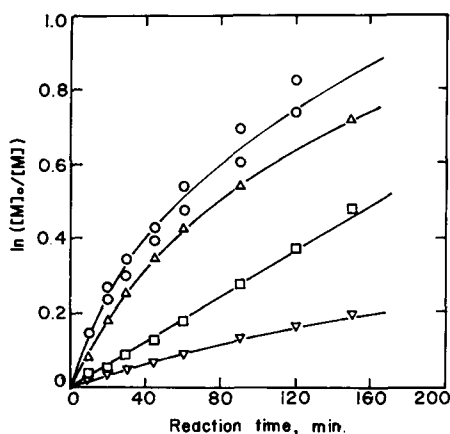


Fig. 4. Monomer conversion vs time at different cobalt concentrations (20°C). $[\text{Al}] = 16.4$ mmol/L; $[\text{Al}]/[\text{H}_2\text{O}] = 1.06$; $[\text{M}]_0 = 0.94$ mol/L. $[\text{Co}]$: (○) 1.26 mmol/L; (Δ) 0.67 mmol/L; (□) 0.42 mmol/L; (▽) 0.25 mmol/L.

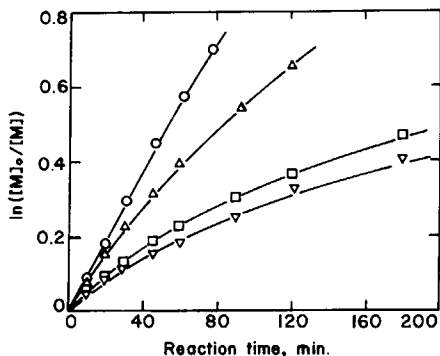


Fig. 5. Monomer conversion vs time at different cobalt concentrations (20°C). $[Al] = 13.3$ mmol/L; $[Al]/[H_2O] = 0.86$; $[M]_0 = 1.4$ mol/L. $[Co]$: (O) 1.26 mmol/L; (Δ) 1.01 mmol/L; (\square) 0.67 mmol/L; (∇) 0.42 mmol/L.

merization rates were plotted against the concentrations of cobalt in Figure 6. In view of experimental errors and uncertainties associated with the determination of initial rate, the relationship may be considered linear. It seems to suggest that, at a given reaction condition, the number of active polymer chains is proportional to the initial concentration of cobalt, but requires a minimum concentration of cobalt to initiate polymerization as can be seen from the extrapolation of those lines to zero rate. Similar results have been obtained by Li and Hsu.⁷

Figure 6 also reveals that the slope of the initial rate varies with the ratio of $[Al]/[H_2O]$. Since each curve was plotted based on fixed concentrations of Al and H_2O , $[Al]/[H_2O]$ is varied along each curve with the exception of the upper curve (\square) where both $[Al]/[Co]$ and $[Al]/[H_2O]$ are fixed. The linear nature of the individual plots led to the conclusion that the polymerization rate is a function of $[Co]$ as well as $[Al]/[H_2O]$, but independent of $[Al]/[Co]$.

It has been known that the reaction of water with TIBA produces a variety of alkylaluminum derivatives; its composition depends on $[Al]/[H_2O]$ ratio. However, as suggested by Longiave and Castelli,⁸ not all alkylaluminum deriv-

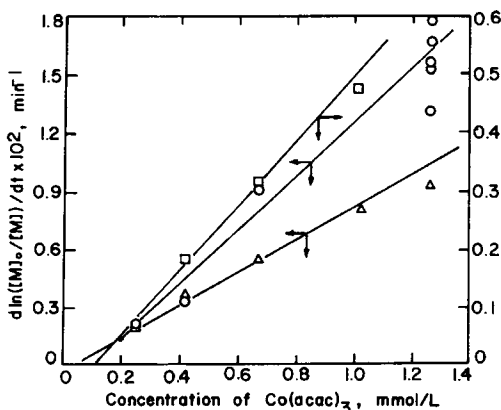


Fig. 6. Initial polymerization rate vs. the cobalt concentration (20°C). $[H_2O] = 15.4$ mmol/L; (O) $[Al]/[H_2O] = 1.06$; (Δ) $[Al]/[H_2O] = 0.86$; (\square) $[Co]/[Al]/[H_2O] = 0.044/1.15/1.00$.

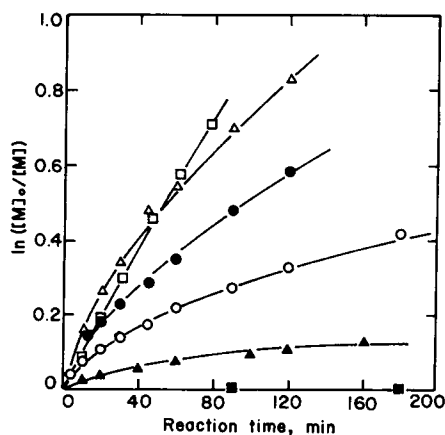


Fig. 7. Monomer conversion vs. time at different TIBA levels (20°C). $[Co] = 1.26$ mmol/L; $[H_2O] = 15.4$ mmol/L. $[Al]$ (mmol/L): (▲) 25.8; (○) 20.9; (△) 16.4; (●) 13.7; (□) 13.3; (■) 11.3.

atives containing Al—O can form active complexes with cobalt in polymerization. Furthermore, $[H_2O]$ and $[Al]$ are much higher than $[Co]$, a proportional change in $[H_2O]$ and $[Al]$ should not affect significantly the number of active complexes formed. This is confirmed indirectly from the results of the experimental series with fixed $[Co]/[Al]/[H_2O]$, which show that the initial polymerization rate is proportional to $[Co]$. The same results were also found by Medvedev et al.⁹

To study the effect of the $[Al]/[H_2O]$ ratio on polymerization rate, experiments were conducted with different concentrations of TIBA. The results are plotted with $\ln([M]_0/[M])$ vs time in Figure 7. As shown in the figure, when $[H_2O]$ is kept at 15.4 mmol/L and $[Co]$ at 1.26 mmol/L, the polymerization appears to increase drastically from zero at $[Al]$ equal to 11.3 mmol/L to a maximum and then drops rapidly thereafter.

Since the polymerization is directly proportional to the cobalt concentration, the initial rates divided by the cobalt concentration are plotted against the $[Al]/[H_2O]$ ratios. This is shown in Figure 8. The optimum ratio of $[Al]/[H_2O]$ occurs at the ratio of 1.0. Although the exact maximum rate is difficult to locate, it agrees quite well with the experimental results of Furukawa et al.¹ in their study of the polymerization of butadiene with $Co(acac)_3-AlEt_3-H_2O$. When the ratio drops to about 0.7, virtually no polymer is formed. When the ratio is above 1, the initial polymerization rate decreases quickly as the ratio increases.

Clearly, then, the reactivity of the catalyst is a strong function of water addition. Water must then participate in the formation of complexes. On the other hand, polymerization does not take place if the cobalt is added to the monomer solution before the addition of TIBA. These two observations provide the evidence that the water reacts first with TIBA and the product of this reaction then forms complexes with cobalt salt. Any water in excess will destroy the active complex as Timofeyva et al.¹⁰ have found that the number of active centers decreased as the concentration of water exceeded the optimum value. This is also consistent with the fact that the initial polymerization rate rises so drastically with the $[Al]/[H_2O]$ ratio when it is below the optimum value.

When the concentration of aluminum alkyl exceeds the water concentration, the excess aluminum might hinder the formation of active complex, which in turn

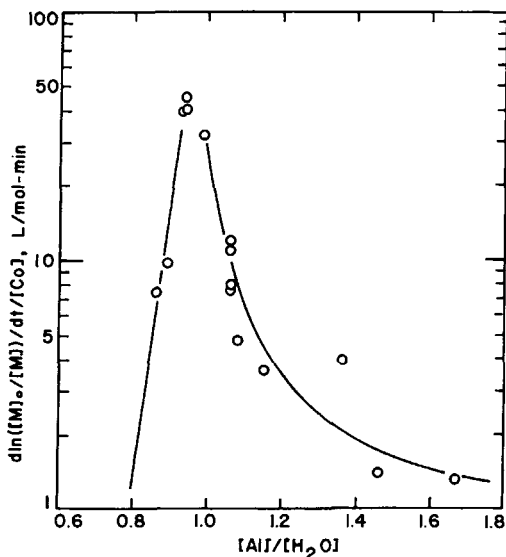


Fig. 8. Initial polymerization rate per mole of cobalt vs. $[Al]/[H_2O]$ ratio at $[H_2O] = 15.4$ mmol/L ($20^\circ C$).

results in an overall decrease in polymerization rate. This is a general phenomenon of polymerizations initiated by Ziegler-Natta catalysts.

Composition of Microstructure

The compositions of polymer microstructure were determined under different operating conditions. The variation of microstructure with conversion was also examined. It can be concluded that the composition is neither significantly changed during the course of polymerization nor affected by the catalyst composition. The average composition of all the samples measured was found to be: (*trans*-1,4) $2.7 \pm 1.1\%$; (*vinyl*-1,2) $33.1 \pm 3.1\%$; and (*cis*-1,4) $64.2 \pm 3.3\%$.

Since the microstructure composition remains constant during the course of

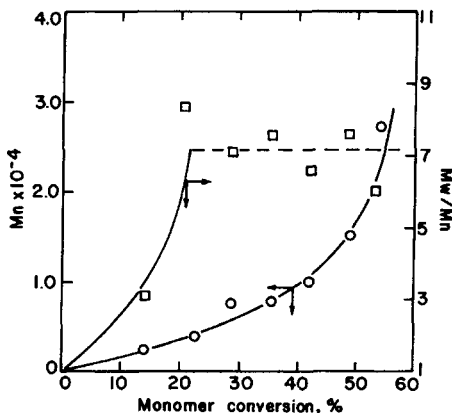


Fig. 9. \bar{M}_n and polydispersity of polymer products as a function of monomer conversion ($20^\circ C$). $[Co] = 0.42$ mmol/L; $[Al] = 14.5$ mmol/L; $[Al]/[H_2O] = 0.93$; $[M]_0 = 1.40$ mol/L.

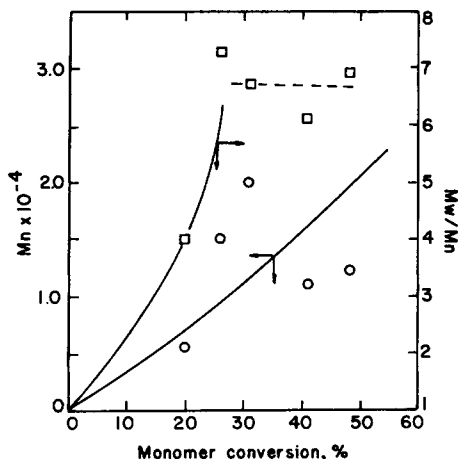


Fig. 10. \bar{M}_n and polydispersity of polymer products as a function of monomer conversion (20°C). $[\text{Co}] = 1.01 \text{ mmol/L}$; $[\text{Al}] = 13.3 \text{ mmol/L}$; $[\text{Al}]/[\text{H}_2\text{O}] = 0.86$; $[\text{M}]_0 = 1.40 \text{ mol/L}$.

polymerization, it is expected that the nature of the active centers should also remain unchanged. This is the additional evidence to reject the idea that the gradual decrease of polymerization rate is due to the change of reaction order.

Molecular Weight Distribution

Three experiments at $[\text{Al}]/[\text{H}_2\text{O}]$ equal to 0.93, 0.86, and 1.15 were chosen for the study of molecular weight distribution. The results are shown in Figures 9, 10, and 11. By taking the 50% monomer conversion as a reference, the polydispersity of the polymer obtained with $[\text{Al}]/[\text{H}_2\text{O}]$ less than 1.0 is in the range of 6–8 (Figs. 9 and 10). At the same monomer conversion, for $[\text{Al}]/[\text{H}_2\text{O}]$ greater than 1.0, the polydispersity increases to about 17, which is unexpectedly high, much higher than the values of 2 or 3 reported^{5,7} for similar catalytic systems. A polydispersity of about 7.0 was reported in $\text{CoCl}_2\text{-4Py-(Et)}_2\text{AlCl}$ system, but it occurred only at a very high H_2O level.⁵

It has been well documented that the typical value for the polydispersity of polymers produced with homogeneous Ziegler–Natta catalyst is about 2–3.

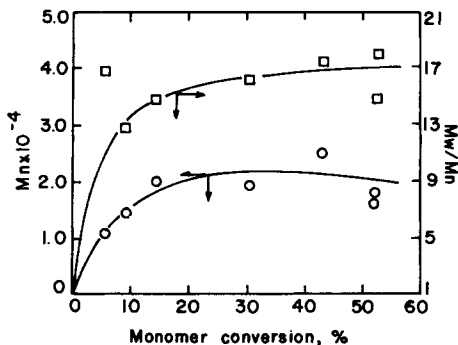


Fig. 11. \bar{M}_n and polydispersity of polymer products as a function of monomer conversion (20°C). $[\text{Co}] = 0.42 \text{ mmol/L}$; $[\text{Al}] = 17.7 \text{ mmol/L}$; $[\text{Al}]/[\text{H}_2\text{O}] = 1.15$; $[\text{M}]_0 = 1.40 \text{ mol/L}$.

Broad distribution is obtained only for the heterogeneous catalysts. Polydispersities of polypropylene, for example, of as high as 10 are common. This, however, is a result of having a distribution of activity of active centers for propagation for a heterogeneous surface.

In this work, the catalyst is soluble; thus the high polydispersities can only be explained by the possibility of branching in view of high vinyl content of the polymer products.

Figure 9 represents the case where both propagation and deactivation reaction rates are high ($[Al]/[H_2O] = 0.93$). The molecular weight maintains an upward increase with conversion, which agrees with Bawn's observation¹¹ in the system of $Co(acac)_3-AlEt_2Cl-H_2O$. The polydispersity also shows a fast increase up to 30% conversion, but then remains constant. As the concentration of $Co(acac)_3$ was raised to 1.01 from 0.42 mmol/L and the ratio of $[Al]/[H_2O]$ was lowered down to 0.86 (Fig. 11), similar results were obtained with respect to the variation of polydispersity even though the limiting polydispersity dropped from 8.3 to 6.3. The number average molecular weight (M_n), however, decreases after reaching a maximum at 30% conversion.

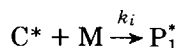
Figures 9, 10, and 11 also depict the variation of the number average molecular weight during the course of polymerization. Obviously, the characteristics of the curves depend on the ratio of $[Al]/[H_2O]$, whether it is greater or less than 1.0. Figure 11 shows the result of an experiment using high concentration of aluminum alkyl. The shape of the curve reflects the importance of chain transfer reaction, as seen from the rapid increase in the number average molecular weight in the first 20 min of polymerization followed by a slight decrease. Should the transfer reaction be absent, the M_n would continue to rise. With $[Al]/[H_2O]$ being 1.15, aluminum alkyl is in excess assuming a one-to-one reaction between aluminum alkyl and water. The free alkyl, as reported,^{2,5} is considered to be a good transfer agent.

In Figures 9 and 10 the number average molecular weight increases slowly at the early stage of polymerization. Here the ratio of $[Al]/[H_2O]$ is less than 1, and there is no free alkyl. The transfer reaction is then relatively unimportant as compared with the chain termination by combination. As a result, the molecular weight curves show a continuous increase with conversion.

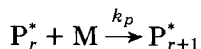
Monomer Conversion Model

Based on the experimental observations discussed, the following reaction model is proposed:

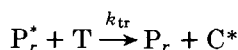
Initiation:



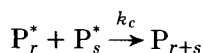
Propagation:



Chain transfer:



Termination by combination:



where C^* = active complex formed from the reduction of Co(III) to Co(II) with $(i\text{-Bu})_3\text{Al}$ and water, P_r^* = living polymers with chain length of r , P_r = inactive polymers with chain length of r , T = transfer agent, k_{tr} , k_i , k_p , k_c = rate constants for the reactions of initiation, propagation, chain transfer, and termination by combination, respectively.

If ΣP_r^* is replaced by P^* to simplify the notation, the kinetic rate expressions for the active polymers, and monomer consumption are given by

$$-\frac{d[P^*]}{dt} = k_c[P^*]^2 \quad (1)$$

$$-\frac{d[M]}{dt} = k_p[P^*][M] \quad (2)$$

with initial conditions

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

and

$$[M] = [M]_0 \quad \text{at } t = 0$$

$[C^*]_0$ is the initial concentration of active complex, which is a function of $[\text{Al}]/[\text{H}_2\text{O}]$ and the concentration of $\text{Co}(\text{acac})_3$. The relationship between $[C^*]_0$ and $[\text{Al}]/[\text{H}_2\text{O}]$ is complex, but $[C^*]_0$ is directly proportional to the $\text{Co}(\text{acac})_3$ initially added.

Integration of eq. (1) applying the initial conditions yields

$$[P^*] = -[C^*]_0/(k_c[C^*]_0t + 1) \quad (3)$$

Substituting $[P^*]$ from eq. (3) into eq. (2) and integrating, one obtains

$$\ln \frac{[M]_0}{[M]} = \frac{k_p[C^*]_0}{k_c[C^*]_0} \ln (1 + k_c[C^*]_0t) \quad (4)$$

The experimental data of monomer conversion of each experimental run were fitted to eq. (4) using the least square method. A typical comparison of the observed and calculated values of $\ln ([M]_0/[M])$ from the conversion model with estimated rate constants as shown in Figure 12, where the two sets of data points on the curve 1 represent the duplicate runs. The model appears to describe the experimental data well.

In testing the adequacy of the conversion model, the residuals were examined. In all runs no systematic trend was observed. Consequently, the results justify the use of the least square method with constant weighting. Further more, the ratio of the variance divided by the pure variance from replicate measurements were found to be always smaller than the values of corresponding F-distribution at a 95% confidence level. Hence there is no evidence from the tests to suggest any inadequacies of the model proposed. A model with first-order termination was also tested. The termination by combination fits the experimental data distinguishably better than the first-order termination, but more importantly

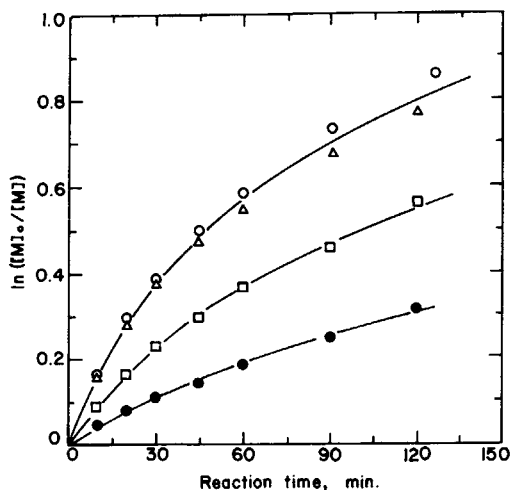


Fig. 12. A comparison of experimental and calculated values of monomer conversion as a function of time (20°C). (1) $[Co] = 0.42$ mmol/L, $[Al] = 14.5$ mmol/L, $[Al]/[H_2O] = 0.94$, $[M]_0 = 1.40$ mol/L; (2) $[Co] = 1.26$ mmol/L, $[Al] = 16.4$ mmol/L, $[Al]/[H_2O] = 1.06$, $[M]_0 = 0.94$ mol/L; (3) $[Co] = 0.42$ mmol/L, $[Al] = 13.3$ mmol/L, $[Al]/[H_2O] = 0.86$, $[M]_0 = 1.40$ mol/L. (Δ , \circ) are duplicate runs.

the first-order termination model failed the F-test. It is then believed that the termination reaction is bimolecular combination in nature.

The apparent rate constants for the propagation and combination (termination) reaction from curve fittings are given as $k_p [C^*]_0$ and $k_c [C^*]_0$, respectively in Table I. $[C^*]_0$ is the initial concentration of active complexes and the efficiency of the catalyst is taken as the ratio of $[C^*]_0/[Co]$, where $[Co]$ is the concentration of cobalt. Thus, the effective rate constants can be defined accordingly as the apparent rate constants divided by $[Co]$. Those values are presented in columns 7 and 9 of Table I.

Bresler et al.¹² in their study of butadiene polymerization catalyzed by $Ti_2Cl_2-Al(iso-C_4H_9)$ proposed a reversible bimolecular termination and reported a value of 1068 L/mol·min for the effective combination rate constant at 20°C. Their value is substantially higher than the corresponding rate constant obtained in this work. It is not surprising, however, in view of much higher reactivity of the catalyst used in their study. The propagation rate constant given by them is larger by a factor of some proportion. Zgonnik,¹³ Bawn,¹¹ and Chien¹⁴ also observed the termination reaction by bimolecular combination for their studies of Ziegler-Natta catalyst, but only Chien attempted to correlate the rate data of ethylene polymerization and gave the effective rate constant of combination a value of 29.4 L/mol·min at 0°C and 544 L/mol·min at 30°C. These values are comparable to the values obtained in this study at 20°C.

It is interesting to note that both $k_p [C^*]_0$ and $k_c [C^*]_0$ are very sensitive to the concentrations of aluminum alkyl and water, but the ratio of k_c/k_p remains constant at an average value of 0.025, which implies that the concentrations of aluminum alkyl and water greatly influence the effectiveness of the cobalt catalyst but have little effect on the rate constants.

Since it has been found that the ratio $[Al]/[H_2O]$ has a great influence on the polymerization rate, as shown in Figure 8, one would expect the same dependence

TABLE I
Rate Constants Used in Calculating the Conversion Curves in Figure 12

Expt. no.	$[M]_0$ (mol/L)	$[Co]$ (mmol/L)	$[Al]$ (mmol/L)	$[Al]/[H_2O]$	$k_p[C^*]_0$ (min^{-1})	$k_p[C^*]_0/[Co]$ (L/mol·min)	$k_c[C^*]_0$ (min^{-1})	$k_c[C^*]_0/[Co]$ (L/mol·min)	k_c/k_p
32.33	1.4	0.42	14.5	0.94	2.0	4.760	0.047	112.	0.024
14	0.94	1.26	16.4	1.06	0.97	770	0.024	19.0	0.025
26	1.4	0.42	13.3	0.86	0.41	976	0.011	26.2	0.027

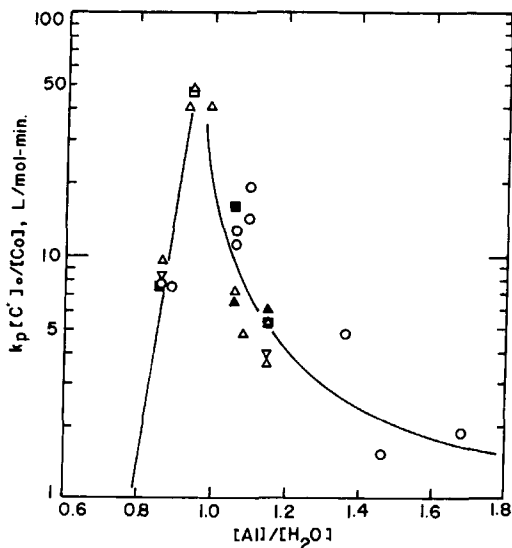


Fig. 13. Correlation of apparent propagation rate constant with the ratio of $[Al]/[H_2O]$ ($20^\circ C$). $[Co]$ (mmol/L): (O) 1.26; (∇) 1.01; (\blacksquare) 0.67; (\square) 0.51; (Δ) 0.42; (\blacktriangle) 0.25.

of the lumped parameter $k_p [C^*]_0$ obtained from the curve fitting. This dependence is shown in Figure 13, where $k_p [C^*]_0 / [Co]$ is plotted against $[Al]/[H_2O]$. The similarity between Figures 8 and 13 is quite obvious. In Figure 8, the plot is, however, based on a fixed water concentration whereas, in Figure 13, additional data are included at different water levels.

Although the relative quantities of $[Al]$ and $[H_2O]$ determine largely the number of active complexes formed initially, it is reasonable to believe that it affects on the activity of the catalyst as well. The curve fitting gives only the product of k_p and $[C^*]_0$; nevertheless, $[C^*]_0$ should be in the same order of magnitude of cobalt added. $k_p [C^*]_0 / [Co]$ then should also have the order of magnitude of k_p . If this is compared with k_p found in the homogeneous $CoCl_2$ system,^{5,7,15,16,17} the k_p obtained in this work is much lower.

Even though the data fit the model well with the termination reaction by combination, the understanding of the termination reaction is still minimal. No obvious correlation of $k_c [C^*]_0$ can be found with any reaction variable. The data seem to vary greatly from experiment to experiment. The partial explanation to the lack of correlation is the complex nature of the termination reaction and sensitivity to impurities.

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