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STUDY OF KINETICS FOR BUTADIENE POLYMERIZATION IN THE PRESENCE OF ALKYL IRON CATALYST SYSTEM

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ABSTRACT

The kinetics of butadiene polymerization in hydrogenated gasoline was studied under $Fe(naph)_2-Al(i\text{-}Bu)_3-CH_2{=}CHCH_2Cl$ catalyst. The kinetic equation for the reaction was derived as

$$-\frac{d[M]}{dt} = k[Fe]_0[M]$$

its apparent activation energy, E_a, = 29.3 kJ/mol, and the preexponential factor $A = 3.04 \times 10^3$ min^{-1}. The experimental result showed that the reaction could be slowly initiated nonsteady-state polymerization, but at the early stage of polymerization it might well be regarded as quasi-steady state. The result also showed that the reaction had a relatively long period of constant rate polymerization. This suggests that slowly initiated constant-rate polymerization could also be nonsteady state. The conditions for the above reaction were clarified. Chain transfer was found in the reaction, and the main chain transfer reactions were determined to be in the quasi-steady-state stage by using graphical integration and equal ratio of rates methods. Identical results were obtained for the two different methods. It was found that the monomer and allyl chloride ($CH_2{=}CHCH_2Cl$) were the main transfer agents. Therefore, the number-average degree of polymerization could be expressed as

$$\bar{P}_n = \frac{\int_0^t R_p dt}{\int_0^t R_t dt + \int_0^t R_{trM} dt + \int_0^t R_{trCl} dt}$$

The effect of polymerization temperature on chain transfer to the monomer is discussed. Its apparent activation energy and preexponential factor were calculated to be $E_{trM} = 29.7$ kJ/mol and $A_{trM} = 6.3 \times 10^4\ \mathrm{dm^3 \cdot mol^{-1} \cdot min^{-1}}$.

INTRODUCTION

Systematic research on butadiene polymerization with iron catalyst systems has been reported [1, 2], but none has been concerned with reaction kinetics.

This paper first studies the kinetics of alkyl iron-catalyzed butadiene polymerization in hydrogenated gasoline as solvent, and obtains the reaction kinetic expression. The experimental results show that this reaction is slowly initiated and nonsteady state, but in the early stage it can be treated as quasi-steady state. The results also reveal that there exists a relatively long period of constant-rate polymerization. This immediately leads to the conclusion that the constant-rate polymerization could also be nonsteady state, which is different from Kagiya's viewpoint [3].

This paper also determines the main chain transfer reactions by considering only the steady-state stage. Both graphical integration and equal ratio of rates methods were used, with identical results. By calculating the rates of chain transfer reactions for various components, the chain transfer reactions to the monomer and allyl chloride were determined to be of primary importance. The transfers to others were secondary, and thus negligible.

EXPERIMENTAL

Material

Butadiene (Bd): Polygrade pure, provided by Qilu Petrochemical Corp., redistilled and dehydrated by Al_2O_3 for 2 weeks before use.

Catalyst: $Fe(naph)_2{-}Al(i\text{-}Bu)_3{-}CH_2{=}CHCH_2Cl$ (Fe-Al-Cl), self-made and diluted by hydrogenated gasoline to the desired concentration.

Polymerization

Test tubes (12 mL) were selected as the reactors. After being vacuumed and dried, they were purged by nitrogen in order to completely replace the air inside.

Bd hydrogenated gasoline solution was first placed under nitrogen protection and then various catalyst components were added while the reactor was kept in a water bath of the required temperature. When the end of the scheduled reaction time was reached, alcohol-containing anti-ager was added to stop the reaction. The raw product was then washed with alcohol to eradicate the remaining unreacted monomer and the solvent. Finally, the raw polymer was vacuumed until no further weight loss could be detected.

Analysis of the Polymer

The characteristic viscosity of the polymer was determined in toluene solvent by an Ubbelohde viscometer at 30 ± 0.2°C. The following equation [4] was used:

$$\eta = \sqrt{2(\eta_{sp} - \ln \eta_r)}/C$$

The molecular weight M_n was derived according to the following equation [5]:

$$[\eta] = 9.15 \times 10^{-5} M_n^{0.8}$$

The number-average molecular weight M_n was measured by the GPC procedure.

RESULTS AND DISCUSSION

The Kinetic Equation of the Polymerization

1. The Relationship between the Polymerization Rate and the Monomer Concentration

At a definite initial catalyst concentration and constant temperature, the conversion was measured against the reaction time. Plots of $-\ln(1 - x)$ against time t were drawn, as shown in Fig. 1. The linear relationship between $-\ln(1 - x)$ and t in the initial time range of polymerization indicates that the reaction rate is first order with respect to Bd concentration [M]. By measuring the tangent of the lines, the values of the first-order rate constant k' for various reaction temperatures were obtained, as listed in Table 1.

2. The Relationship between the Polymerization Rate and the Catalyst Concentration

At a definite initial Bd concentration and a constant Fe:Al:Cl ratio, k' was found to be linear with the initial Fe(naph)_2 concentration $[\text{Fe}]_0$; that is, the polymerization rate is also first-order with respect to the Fe(naph)_2 concentration. Thus, the kinetic equation can be expressed as

$$k' = k[\text{Fe}]_0$$

$$-d[\text{M}]/dt = k[\text{Fe}][\text{M}] \quad (1)$$

The result also revealed that k increases with an increase of $\text{Al}(i\text{-Bu})_3$ concentration when the other conditions are constant, but k reaches its maximum value at Al/Fe = 15 and begins to decline with a further increase of the Al/Fe ratio. The same is true for the relation of k and the $\text{CH}_2{=}\text{CHCH}_2\text{Cl}$ concentration, but the maximum value of Cl/Fe is only 3.

The active center concentrations in the quasi-steady-state stage were calculated, and they are listed in Table 2.

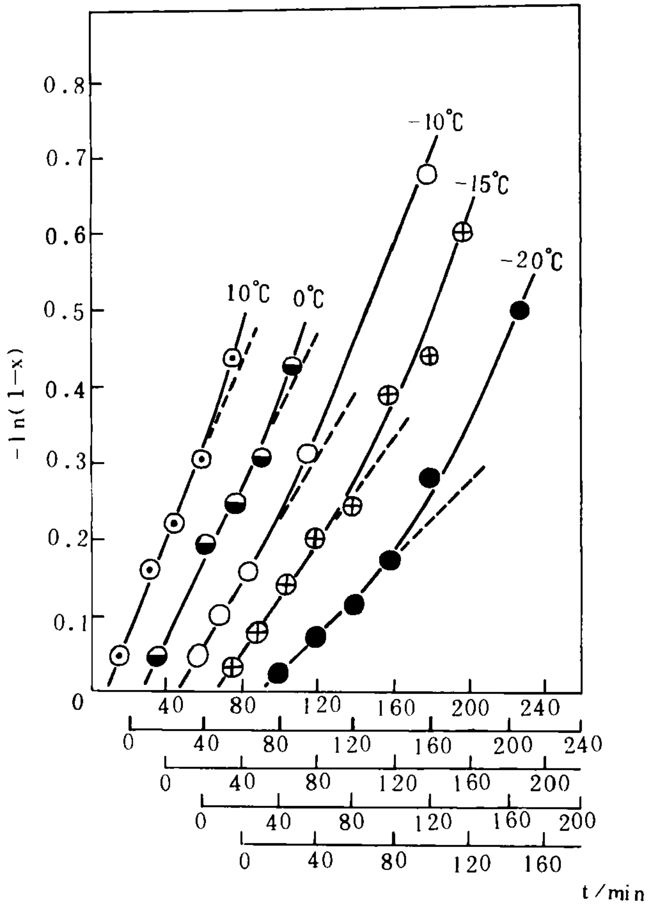

FIG. 1. Relationship between $-\ln(1-x)$ and t. Experimental conditions: $[M]_0 = 1.85$ mol/dm^3, Fe/M $= 4 \times 10^{-4}$, Al/Fe $= 10$, Cl/Fe $= 1.5$.

TABLE 1. Values of k' at Various Temperatures

Temperature, °C	−20	−15	−10	0	10
k', $\times 10^{-3}$ min^{-1}	2.75	3.85	5.20	7.80	12.80

TABLE 2. The Correspondence between $[P^*]_s$ and $[Fe]_0$

$[Fe]_0$, × 10^{-4} mol/dm^3	4.0	5.0	6.0	7.0	8.0
$[P^*]_s$, × 10^{-6} mol/dm^3	0.36	0.45	0.51	0.56	0.70

It is obvious that the active center concentration is approximately proportional to the Fe(naph)$_2$ concentration. Therefore, for the present system, Eq. (1) can also be expressed as

$$-d[M]/dt = R_p$$

$$R_p = k_p[P^*][M] \tag{2}$$

where k_p is the rate constant of the chain propagation and $[P^*]$ is the active center concentration.

3. The Dependence of the Polymerization Rate on the Reaction Temperature

Arrhenius parameters, the activation energy E_a, and preexponential factor were calculated from the data listed in Table 1 as follows:

$$E_a = 29.3 \text{ kJ/mol}, \qquad A = 3.04 \times 10^3 \text{ min}^{-1}$$

As E_a is relatively low, the polymerization could be considered to be a quick chain propagation reaction.

Determination of the Reaction Type

1. Constant Rate Polymerization

Figure 2 is a plot of the polymer content M_p versus the reaction time t at different temperatures.

It is known that

$$[M_p] = \int_0^t R_p\,dt \tag{3}$$

where $[M_p]$ is the polymer yield in terms of the monomer mole number. When R_p is independent of reaction time:

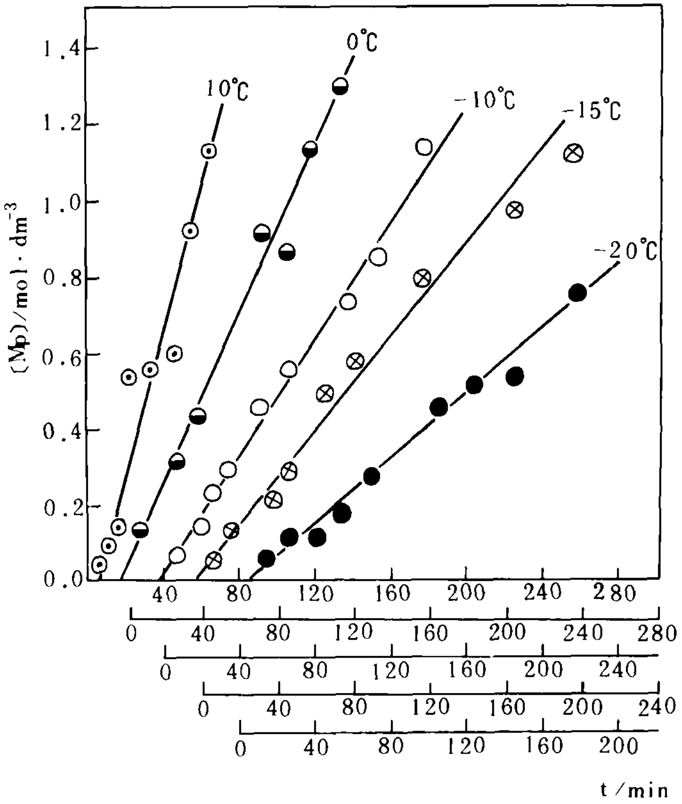

FIG. 2. Relationship between the polymer content and the polymerization time. Polymerization conditions as in Fig. 1.

$$[M_p] = R_p t \tag{4}$$

From the linear relationship between $[M_p]$ and t in Fig. 2, it is known that the polymerization rate remains roughly constant until conversion is up to 40%, i.e., the reaction has a relatively long period of constant-rate polymerization.

2. Slow Initiation and Nonsteady State of Polymerization

Because it is impossible for the monomer concentration to remain unchanged while the reaction conversion reaches 40%, [P*] has to gain with time in order to compensate for the loss of the monomer concentration if R_p is to remain approximately constant.

Let $[M]_0$ and $[P^*]_0$ be the initial monomer concentration and active center concentration, respectively. At reaction time t, their concentrations should be

$$[P^*] = [P^*]_0 + \Delta[P^*], \qquad [M] = [M]_0 - \Delta[M]$$

Substitution of the above expressions into Eq. (2) yields

$$R_p = k_p([P^*]_0[M]_0 + [M]_0\Delta[P^*] - [P^*]_0\Delta[M] - \Delta[P^*]\Delta[M]) \tag{5}$$

In the early stage of the reaction it is generally true that $\Delta[P^*] \rightarrow 0$, $\Delta[M] \rightarrow 0$. Then Eq. (5) immediately becomes

$$R_p = k_p[P^*]_0[M]_0 \tag{6}$$

This means that at the starting period of a reaction with very low conversion, the monomer and active center concentrations might be considered independent of time, and R_p is approximately constant.

This period is defined as quasi-steady-state polymerization. If $[P^*]_s$ is used to represent the mean concentration of the active center through this period,

$$[P^*]_s = \int_0^t R_i\,dt = \text{constant} \tag{7}$$

where R_i is the rate of chain initiation.

At appreciable conversion with noticeable changes of $[P^*]$ and $[M]$, the following equation is satisfied:

$$[M]_0\Delta[P^*] - [P^*]_0\Delta[M] - \Delta[P^*]\Delta[M] = 0$$

namely,

$$\frac{\Delta[M]}{[M]_0} = \frac{\Delta[P^*]}{[P^*]_0 + \Delta[P^*]} \tag{8}$$

that is, the percentage conversion of the monomer is equal to the ratio of the increase of active centers over the total number of active centers available at time t, and R_p will still be constant, i.e., the polymerization rate is still constant. Therefore, the active centers concentration in this system will increase from $[P^*]_0$ to $[P^*]_0 + \Delta[P^*]$ during the reaction from time 0 to t. According to Kagiya, this system is defined as slowly initiated and nonsteady-state polymerization. This suggests that the slowly initiated constant-rate polymerization can also be nonsteady state. This differs from Kagiya's viewpoint [3].

The Determination of the Active Center Concentration and Chain Propagation Rate Constant

At definite initial monomer concentration and catalyst dosage, plots of the number-average degree of polymerization $\bar{P}_n$ were drawn against reaction time t, as shown in Fig. 3. The transient linear relation at the start of every curve is proof of the existence of quasi-steady-state polymerization.

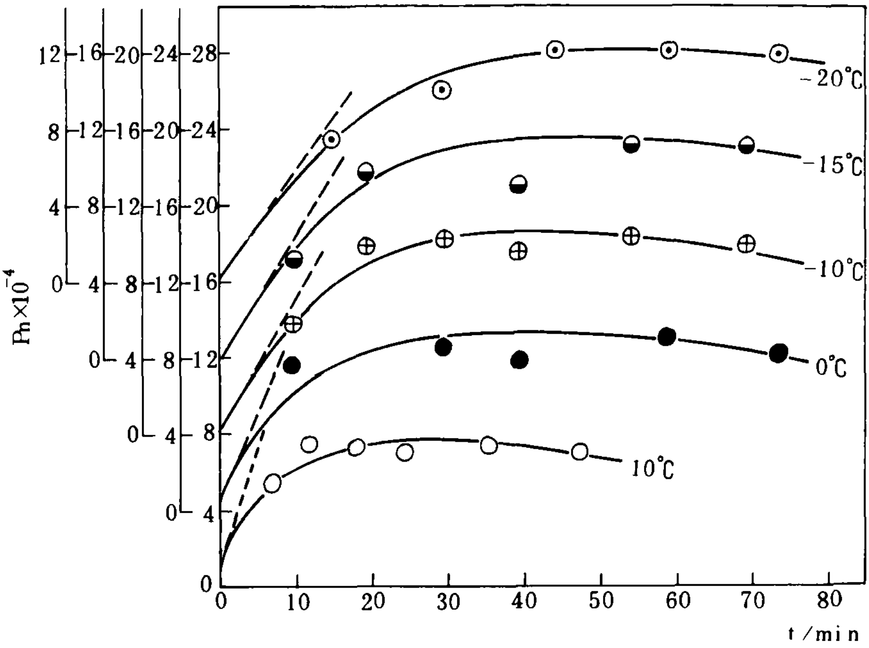

FIG. 3. Relationship between the number-average degree of polymerization and the polymerization time. Polymerization conditions as in Fig. 1.

It is known that for a nonbiradical terminal polymerization system, $\overline{P}_n$ is expressed as [6]

$$\overline{P}_n = \frac{\int_0^t R_p \, dt}{\int_0^t R_i \, dt + \sum_{Y} \int_0^t R_{trY} \, dt} \tag{9}$$

In quasi-steady state, the chain transfer rate R_{trY} can be negligible because of the very low value of $[P^*]_s$, that is,

$$\int_0^t R_{trY} = 0$$

Equation (9) can be written

$$\overline{P}_n = \frac{R_p}{[P^*]_s} t = k_p[M]_0 t \tag{10}$$

In Eq. (10), $\overline{P}_n$ is in linear proportion to t. So the transiency of the linear relation between $\overline{P}_n$ and t in Fig. 3 indicates that the quasi-steady state exists for only an extremely short time in actual polymerization. From the tangent of the straight lines shown in Fig. 3, $[P^*]_s$ and k_p were derived and are listed in Table 3, but these values are only approximate because of the inaccuracy in determining the tangents.

From the values of k_p listed and the Arrhenius relation, the activation energy of chain propagation E_p and its preexponential factor A_p were also calculated:

TABLE 3. The Values of $[P^*]_s$ and k_p at Different Temperatures

	Temperature, °C				
	−20	−15	−10	0	10
$R_p/[P^*]$, × 10^{-4} min^{-1}	0.52	0.70	0.94	1.14	2.00
$[P^*]_s$, × 10^{-7} mol/dm^3	8.3	8.3	8.4	8.8	8.7
k_p, × 10^3 dm·mol^{-1}·min^{-1}	2.8	3.8	5.1	6.2	10.8

$$E_p = 18.1 \text{ kJ/mol}, \qquad A_p = 4.1 \times 10^7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$$

Determination of the Chain Transfer Reactions

1. The Presence of Chain Transfer Reaction

The active center concentration [P*] in this slowly initiated system increases gradually with time. Consequently, this might promote chain transfer and chain propagation. In Eq. (9) the increase of R_i and $R_{tr\mathrm{Y}}$ will reduce $\overline{P}_n$ while the increase of R_p enhances $\overline{P}_n$. This means that the decrease of $\overline{P}_n$ can only be caused by chain transfer and initiation. Therefore, the occurrence of a turning point, or the maximum point, in the $\overline{P}_n$-t curve shows that there is a chain transfer reaction in this system.

2. The Dependence of the Chain Transfer Reaction on the Monomer Concentration

The total chain transfer rate can be expressed as

$$R_{tr} = \sum_{\mathrm{Y}} R_{tr\mathrm{Y}} \tag{11}$$

$$R_{tr\mathrm{Y}} = k_{tr\mathrm{Y}}[\mathrm{P}^*][\mathrm{Y}]^{\beta} \tag{12}$$

where Y represents the chain transfer agents, which may be $\mathrm{Fe(naph)_2}$, $\mathrm{Al}(i\text{-Bu})_3$, $\mathrm{CH_2{=}CHCH_2Cl}$, the monomer, or the solvent; β is the order of the chain transfer reaction to the agent.

If Eq. (2) is substituted into Eq. (12), then

$$R_{tr\mathrm{Y}} = \frac{k_{tr\mathrm{Y}} R_p}{k_p[\mathrm{M}]} [\mathrm{Y}]^{\beta} \tag{13}$$

It has been proved that R_p remains approximately constant throughout the constant-rate polymerization period. Therefore, from Eq. (13), $R_{tr\mathrm{Y}}$ is in reverse proportion to the monomer concentration [M]. Because the monomer is consumed mostly by chain propagation, it is only after the polymer chain has reached a certain length and the monomer concentration is considerably reduced that an appreciable chain transfer reaction can begin to take place.

3. The Determination of the Main Chain Transfer Reaction

It is more convenient for this system to determine the main chain transfer reactions in the quasi-steady state and thereby infer the main chain transfer reactions in the nonsteady-state. Though the transfer rate in the quasi-steady state may be quantitatively small, it is still valid when comparing their relative values to each other. Here, two kinds of mathematical methods are applied for processing the experimental data.

(1). The Graphical Integration Method [7]. (a) Chain Transfer to the Monomer. Assume that chain transfer is mainly to the monomer, that is, [Y] = [M], and let $\beta = 1$. Then Eq. (13) becomes

$$R_{trM} = \frac{k_{trM}}{k_p} R_p \tag{14}$$

When Eq. (14) is substituted into Eq. (9), the following equation is derived for the constant-rate polymerization period:

$$\frac{1}{\overline{P}_n} = \frac{\int_0^t R_i \, dt}{[M_p]} + \frac{k_{trM}}{k_p} \tag{15}$$

For the quasi-steady-state period, the following equation is further derived:

$$\frac{1}{\overline{P}_n} = \frac{[P^*]_s}{[M_p]} + \frac{k_{trM}}{k_p} \tag{16}$$

Plots of $1/\overline{P}_n$ against $1/[M_p]$ at various temperatures were drawn, as shown in Fig. 4. If straight lines are obtained, the assumption that the chain transfer is mainly to the monomer is true. Otherwise, chain transfer to the monomer is secondary.

As Fig. 4 shows, the $1/[M_p]$ values selected fall within the range of corresponding to the quasi-steady state, and the lines are rather straight. Therefore, chain transfer to the monomer is the chief transfer reaction. k_{tr}/k_p was determined by measuring the intercept of the lines on the $1/\overline{P}_n$ ordinate. k_p is known and is listed in Table 3; k_{trM} was calculated and is listed in Table 4. As Table 4 indicates, k_{trM} values are so small that the chain transfer reaction can be neglected in the initial stage of polymerization. k_{trM} increases with an increase of the reaction temperature.

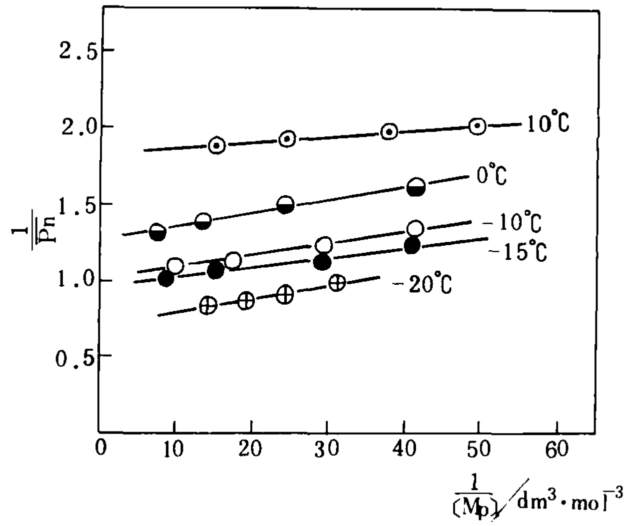

FIG. 4. Relationship between $1/\overline{P}_n$ and $1/[M_p]$. Polymerization conditions: Fe/M = 4 × 10^{-4}, Al/Fe = 10, Cl/Fe = 1.5, temperature 0°C.

(b) Chain Transfer to the Catalyst. Assume that chain transfer to one of the catalyst components is the main reaction and let $\beta = 1$. Combining Eqs. (13) and (9) leads to

$$\frac{[M_p]}{\overline{P}_n} = \int_0^t R_i\,dt + \frac{k_{trY}}{k_p}\int_0^t \frac{R_p}{M}[Y]dt \tag{17}$$

Applying the condition of constant-rate polymerization:

$$\frac{[M_p]}{\overline{P}_n} = \int_0^t R_i\,dt + \frac{k_{trY}R_p}{k_p}\int_0^t \frac{[Y]}{[M]}dt$$

TABLE 4. The Values of the Rate Constant of Chain Transfer to Monomer

	Temperature, °C				
	−20	−15	−10	0	10
k_{trM}/k_p, × 10^{-6}	6.6	6.9	8.0	9.8	11.4
k_{trM}, × 10^{-2} dm^3·mol^{-1}·min^{-1}	1.9	2.6	4.1	6.1	12.3

In the quasi-steady state it is practical to consider [Y] a constant because the chain transfer rate is very small. Then the equation becomes

$$\frac{[M_p]}{\overline{P}_n} = \int_0^t R_i\,dt + \frac{k_{trY}R_p[Y]}{k_p}\int_0^t \frac{1}{[M]}\,dt \tag{18}$$

With measured values of [M] and their corresponding times, $\int_0^t(1/[M])\,dt$ values are first calculated by the graphical integration method. Then plot $[M_p]/\overline{P}_n$ against $\int_0^t(1/[M])\,dt$. If straight lines are obtained, chain transfer to the concerned component of the catalyst is the most important reaction; curved lines mean they are secondary.

Figures 5, 6, and 7 are plots for chain transfer to $Fe(naph)_2$, $Al(i\text{-}Bu)_3$, and $CH_2{=}CHCH_2Cl$, respectively. The results shows that chain transfer to allyl chloride is primary while to others are secondary.

From Fig. 7, k_{trCl}/k_p was obtained by measuring the tangent of the line at 0°C, $k_{trCl}/k_p = 3.9 \times 10^{-3}$. From k_p as listed in Table 2, k_{trCl} was derived: $k_{trCl} = 24.2\ dm^3 \cdot mol^{-1} \cdot min^{-1}$.

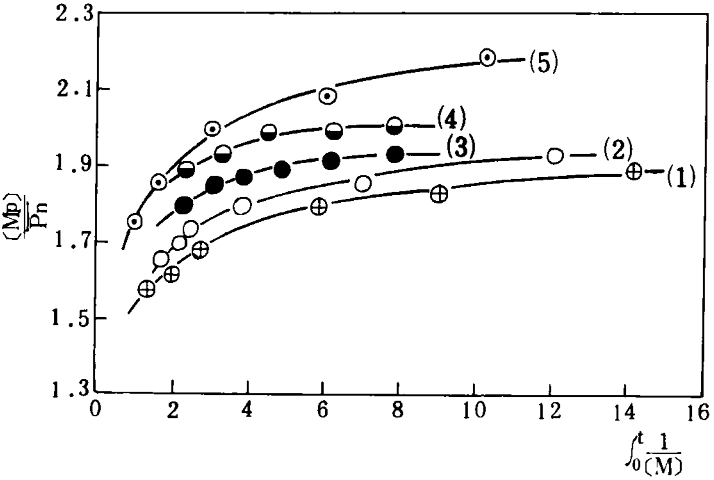

FIG. 5. Relationship between $[M_p]/\overline{P}_n$ and $\int_0^t \frac{1}{[M]}\,dt$ for $Fe(naph)_2$. Polymerization conditions: $Al/M = 4.0 \times 10^{-3}$, $Cl/M = 6.0 \times 10^{-3}$, $[M]_0 = 1.85$ mol/dm^3, temperature 0°C. (1) $[Fe]_0 = 4 \times 10^{-4}$ mol/dm^3. (2) $[Fe]_0 = 5 \times 10^{-4}$ mol/dm^3. (3) $[Fe]_0 = 6 \times 10^{-4}$ mol/dm^3. (4) $[Fe]_0 = 7 \times 10^{-4}$ mol/dm^3. (5) $[Fe]_0 = 7 \times 10^{-4}$ mol/dm^3.

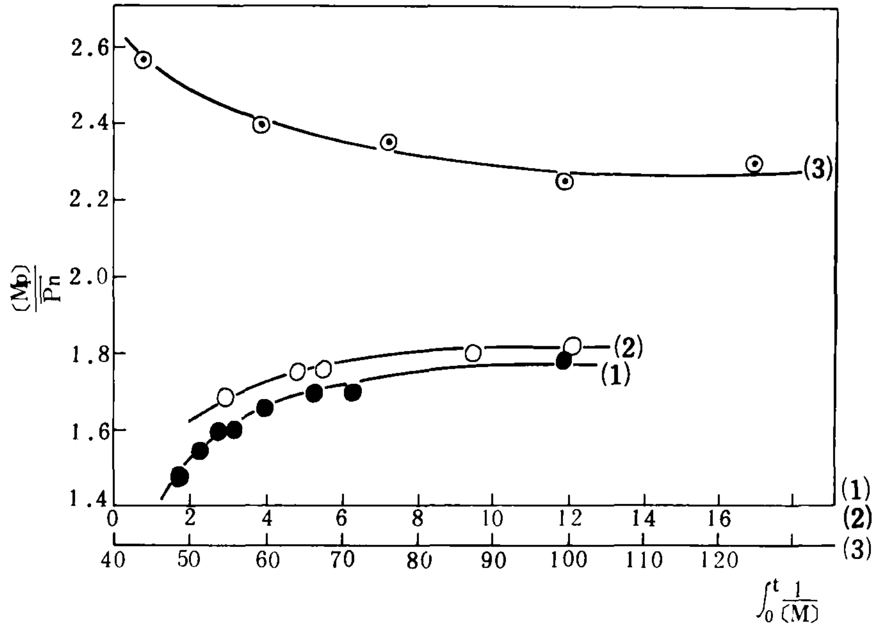

FIG. 6. Relationship between $[M_p]/\bar{P}_n$ and $\int_0^t \frac{1}{[M]}\,dt$ for Al(i-Bu)$_3$. Polymerization conditions: Fe/M = 4×10^{-4}, Cl/Fe = 1.5, $[M]_0 = 1.85$ mol/dm^3, temperature 0°C. (1) Al/Fe = 10. (2) Al/Fe = 15. (3) Al/Fe = 20.

(c) Chain Transfer to the Solvent. If chain transfer to the solvent is a chief reaction, it will be necessary in the constant-rate period that

$$\frac{[M_p]}{\bar{P}_n} = [P^*]_s + \frac{k_{trS}R_p[S]}{k_p}\int_0^t \frac{1}{[M]}\,dt \qquad (19)$$

where [S] is the concentration of hydrogenated gasoline. In the same way as described above, this reaction was determined to be secondary, which is obvious because of the impossibility for hydrogenated gasoline to be activated.

Note that $k_{tr\text{Cl}}$ is about an order of magnitude of 10^3 greater than $k_{tr\text{M}}$, while the monomer concentration is greater than the allyl chloride concentration of about the same order. Therefore, chain transfers to

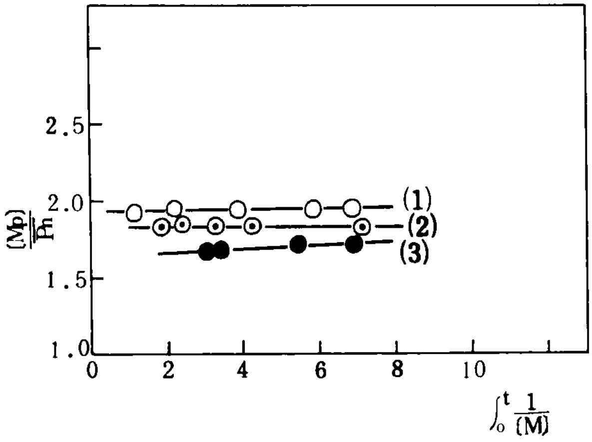

FIG. 7. Relationship between $[M_p]/\overline{P}_n$ and $\int_0^t \frac{1}{[M]} dt$ for $CH_2{=}CHCH_2Cl$. Polymerization conditions as in Fig. 4. (1) Cl/Fe = 2.0. (2) Cl/Fe = 1.5. (3) Cl/Fe = 1.0.

both monomer and allyl chloride are of similar rates, and both monomer and allyl chloride should be considered to be chief transfer agents.

(2). Equal Ratio of Rates Method. In the quasi-steady state, both monomer and active center concentrations change very little with time. Therefore, it is practical to assume that the ratio of the initial rates of chain transfer to chain propagation is approximately equal to the ratio of the rates of chain transfer to chain propagation at time *t*; that is, the two reactions increase at the same pace from time 0 to time *t*. This is expressed as

$$\frac{R_{trY,0}}{R_{p,0}} \doteq \frac{R_{trY,t}}{R_{p,t}} \tag{20}$$

This is called the equal ratio of rates method.

Substitute Eq. (2) and Eq. (12) into Eq. (20), and let $\beta = 1$:

$$\frac{[Y]_0}{[M]_0} \doteq \frac{[Y]}{[M]} \tag{21}$$

When every [Y] is summed up, Eq. (21) will be

$$\frac{\sum_{Y} [Y]_0}{[M]_0} \doteq \frac{\sum_{Y} [Y]}{[M]}$$

Equally, the following is written:

$$1 - \frac{[M]}{[M]_0} \doteq 1 - \frac{\sum_{Y} [Y]}{\sum_{Y} [Y]_0} \quad \text{and} \quad \frac{\sum_{Y} [Y]_0}{[M]_0} \doteq \frac{\sum_{Y} \Delta[Y]}{\Delta[M]}$$

where $\Delta[M] = [M]_0 - [M]$ is the concentration difference between the initial monomer concentration and the concentration at time t, and $\Delta[Y] = [Y]_0 - [Y]$ is the difference between the initial concentration of the chain transfer agent and the concentration at time t.

Accordingly, the following equations are derived:

$$\Delta[M] = [M_p] = \textstyle\int_0^t R_p \, \mathrm{dt}, \qquad \Delta[Y] = \int_0^t R_{trY} \, dt$$

$$\sum_{Y} \Delta[Y] = \sum_{Y} \int_0^t R_{trY} \, dt, \qquad \frac{\sum_{Y} [Y]_0}{[M]_0} \doteq \frac{\sum_{Y} \int_0^t R_{trY} \, dt}{\int_0^t R_p \, dt}$$

Let

$$A = \frac{\sum_{Y} [Y]_0}{[M]_0} \tag{22}$$

Thus, A is a constant and is called the constant of equal ratio of rates. Hence, from the above equations, A is also

$$A \doteq \frac{\sum_{Y} \int_0^t R_{trY} \, dt}{\int_0^t R_p \, dt} \tag{23}$$

By considering that Y may be either one of the catalyst components or the monomer or the solvent, A can be further expressed as

$$A = C_M + C_{Fe}\frac{\int_0^t [\mathrm{Fe}]\,dt}{\int_0^t [\mathrm{M}]\,dt} + C_{Al}\frac{\int_0^t [\mathrm{Al}]\,dt}{\int_0^t [\mathrm{M}]\,dt}$$

$$+ C_{Cl}\frac{\int_0^t [\mathrm{Cl}]\,dt}{\int_0^t [\mathrm{M}]\,dt} + C_S\frac{\int_0^t [\mathrm{S}]\,dt}{\int_0^t [\mathrm{M}]\,dt}$$

where $C_Y = k_{trY}/k_p$ is called the constant of the chain transfer to agent Y. In the quasi-steady state, since both R_p and R_{trY} are very small, it is feasible to consider the concentration of every component to be a constant, i.e., $[Y] = [Y]_0$. Thus, the expression of A is greatly simplified to [8, 9]

$$A = C_M + C_{Fe}\frac{[\mathrm{Fe}]_0}{[\mathrm{M}]_0} + C_{Al}\frac{[\mathrm{Al}]_0}{[\mathrm{M}]_0} + C_{Cl}\frac{[\mathrm{Cl}]_0}{[\mathrm{M}]_0} + C_S\frac{[\mathrm{S}]}{[\mathrm{M}]_0} \qquad (24)$$

By substituting Eq. (23) into Eq. (9), in the quasi-steady state we derive

$$\frac{1}{\overline{P}_n} = \frac{[\mathrm{P}^*]_s}{[\mathrm{M}_p]} + A \qquad (25)$$

A can be easily obtained from Eq. (25) by drawing a plot of $1/\overline{P}_n$–$1/[\mathrm{M}_p]$ and measuring its intercept on $1/\overline{P}_n$. From the values of A thus obtained and the corresponding values of $[\mathrm{M}]_0$, an A–$1/[\mathrm{M}]_0$ plot can be drawn. Similarly, C_M can be derived from Eq. (24).

Let $[\mathrm{Al}]_0/[\mathrm{M}]_0$, $[\mathrm{Cl}]_0/[\mathrm{M}]_0$, and $[\mathrm{S}]/[\mathrm{M}]_0$ ratios be fixed. Then Eq. (24) can also be written as

$$A = B + \frac{C_{Fe}}{[\mathrm{M}]_0}[\mathrm{Fe}]_0$$

where

$$B = C_M + C_{Al}\frac{[\mathrm{Al}]_0}{[\mathrm{M}]_0} + C_{Cl}\frac{[\mathrm{Cl}]_0}{[\mathrm{M}]_0} + C_S\frac{[\mathrm{S}]}{[\mathrm{M}]_0}$$

and B is a constant.

After A is determined at various $[\mathrm{Fe}]_0$ values, C_{Fe} is determined. In the same way, C_{Al}, C_{Cl}, and C_{S} are determined successively.

(a) Chain Transfer to the Monomer. At different initial monomer concentrations, the relations between $1/\overline{P}_n$ and $1/[\mathrm{M}_p]$ were derived at various temperatures as indicated in Fig. 4. The relation between A and $1/[\mathrm{M}]_0$ at 0°C is shown in Fig. 8. The linear relationship indicates that the rate of chain transfer to the monomer is first order with respect to the monomer concentration, i.e., it proves the assumption that $\beta = 1$. From the intercept of the line in Fig. 8, C_{M} was determined: $C_{\mathrm{M}} = 7.1 \times 10^{-6}$. Since k_p is already known to be 6.2×10^3 $\mathrm{dm^3 \cdot mol^{-1} \cdot min^{-1}}$, $k_{tr\mathrm{M}}$ can be immediately calculated: $k_{tr\mathrm{M}} = 4.4 \times 10^{-2}$. This is very close to the value of $k_{tr\mathrm{M}}$ at 0°C as derived by the graphical integration method and listed in Table 4.

(b) Chain Transfer to the Catalyst. The relation between A and $[\mathrm{Fe}]_0$ is shown in Fig. 9. The straight line is roughly parallel to the abscissa; that is, $C_{\mathrm{Fe}} = 0$. This is in accordance with the previous result that chain transfer to the $\mathrm{Fe(naph)_2}$ component is negligible.

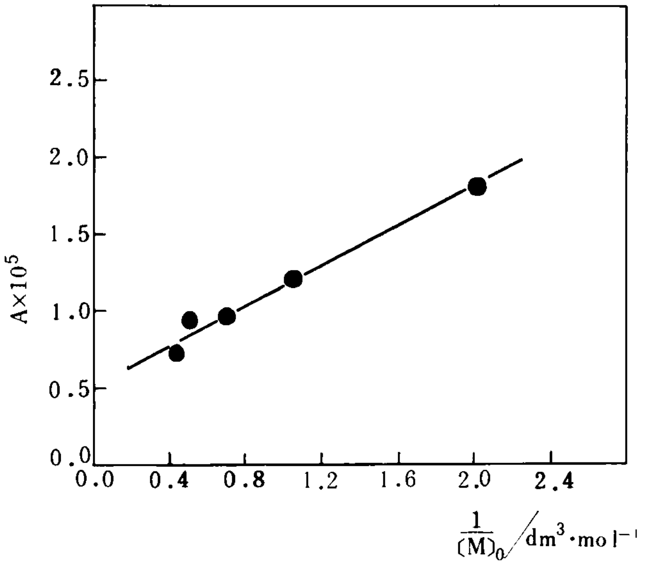

FIG. 8. Relationship between A and $1/[\mathrm{M}]_0$. Polymerization conditions as in Fig. 4.

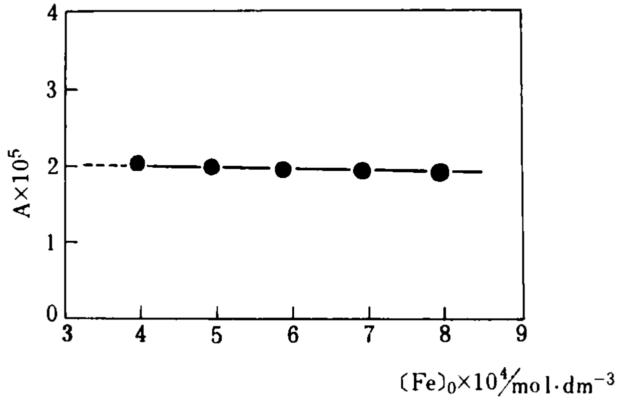

FIG. 9. Relationship between A and $[Fe]_0$. Polymerization conditions: Al/M = 4.0×10^{-3}, Cl/M = 6.0×10^{-4}, $[M]_0 = 1.85$ mol/dm³, temperature 0°C.

In the same way, the relation between A and $[Cl]_0$ was determined as shown in Fig. 10. Since $k_p = 6.2 \times 10^3$ dm^3·mol^{-1}·min^{-1} and C_{Cl} was measured to be 7.7×10^{-3}, k_{trCl} was determined to be 47.7 dm^3·mol^{-1}·min^{-1} at 0°C.

The rate constants of chain transfer to Al(i-Bu)$_3$, C_{Al}, and to the solvent C_S were also determined. The results are identical with those obtained by the graphical integration method; that is, chain transfer to both of them is negligible.

Therefore, the expression of the degree of polymerization for this system can be written as

$$\bar{P}_n = \frac{\int_0^t R_p\,dt}{\int_0^t R_i\,dt + \left(\int_0^t R_{trM}\,dt + \int_0^t R_{trCl}\,dt\right)} \qquad (26)$$

4. The Dependence of Chain Transfer on the Polymerization Temperature

As Fig. 3 shows, the higher the polymerization temperature, the sooner the number-average degree of polymerization begins to decline. This suggests that the chain transfer constant k_{tr} increases remarkably with an increase of temperature, and this also suggests that the activation

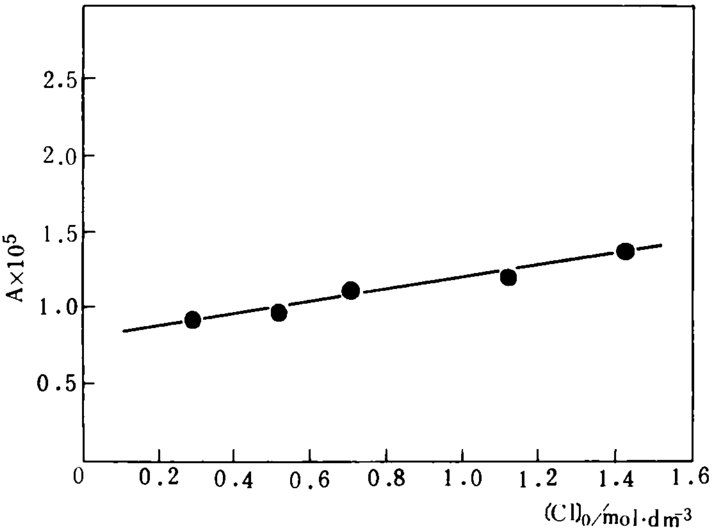

FIG. 10. Relationship between A and $[Cl]_0$. Polymerization conditions as in Fig. 4.

energy of chain transfer, E_{tr}, is greater than that of propagation, E_p. The following is a discussion on the temperature dependence of chain transfer to the monomer.

From the k_{trM} values at various temperatures listed in Table 4, and the Arrhenius relation, the apparent activation energy of chain transfer to the monomer, E_{trM}, was calculated to be 2.9 kJ/mol, greater than the propagation counterpart $E_p = 18.1$ kJ/mol; the preexponential factor $A_{trM} = 6.3 \times 10^4$ is less than that of propagation $A_p = 4.1 \times 10^7$. By considering that the preexponential factor can be treated as the collision frequency between the reactants, then the frequency of collisions between the activated chain and the monomer that leads to chain propagation is about an order of magnitude of 10^3 larger than the frequency of collisions which lead to chain transfer. This fact makes us believe that though both chain transfer and propagation result from the reaction between activated chain and monomer, there exist two different mechanisms for the same reaction, and that the difference should not be ignored.

On the contrary, if the difference be ignored and we let A_{trM} and A_p be equal, the following equation would be derived:

$$\frac{k_{trM}}{k_p} = \frac{A_{trM}}{A_p} e^{-\frac{(E_{trM} - E_p)}{RT}} = e^{-\frac{(E_{trM} - E_p)}{RT}} \tag{27}$$

By applying the data listed in Table 4, this would lead to $E_{trM} = 44.0$ kJ/mol, 14.3 kJ/mol greater than the experimental value. This wide gap again tells us that it is unreasonable to arbitrarily assume $A_{trM}/A_p = 1$ and to consider the two mechanisms to be identical [8].

CONCLUSIONS

1. The polymerization rate is first-order with respect to the monomer concentration and to the Fe(naph)$_2$ concentration under the conditions specified.

2. Butadiene polymerization in this system is of slow initiation and nonsteady state. The initial stage could be considered quasi-steady state.

3. A constant rate at appreciable conversion in this system is also possible, although it is nonsteady state.

4. For a slowly initiated system, the occurrence of a maximum value of the number-average degree of polymerization with time is an indication of the existence of a chain transfer reaction. It is convenient to determine the chain transfer reaction by both graphical integration and the ratio of equal rates methods in the quasi-steady-state stage.

5. Chain transfers to the third catalyst component, allyl chloride, and the monomer predominate over chain transfers to the other components.

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