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ON THE RATE LAW OF THE ZIEGLER-NATTA POLYMERIZATIONS

By

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Abstract

The rival rate laws, Rideal and Langmuir-Hinshelwood types, proposed for the heterogeneous Ziegler-Natta polymerizations were discussed in connection with recent experiments and proposed mechanisms. The Langmuir-Hinshelwood-type was appropriate for experiments and compatible with the concept of monomer coordination on which all mechanistic theories are based.

Introduction

To determine the rate law of a reaction is generally important in the discussion of reaction mechanism. This is especially true in the field of the Ziegler-Natta polymerizations where the rate law is closely related to the question of whether a monomer does coordinate on a polymerization center before its insertion into the polymer chain on the center or no. The coordination of monomers in an oriented form has been supposed necessarily in the all mechanistic theories proposed for propylene polymerizations with the heterogeneous Ziegler-Natta catalysts in order to explain the stereospecificity of the catalysts.¹⁾ Unfortunately, this important supposition has not been supported by any experimental evidence. If the rate law of the polymerizations is a Langmuir-Hinshelwood type, we can take this as a strong evidence of the monomer coordination. However, rate laws observed for propylene polymerizations are mostly Rideal type which is generally considered as an evidence of the direct insertion of solute monomers. As well-known, there are many difficulties in kinetic measurements of these very sensitive catalysis. In addition, polymerization rate itself changes with time during polymerization, which means that some observed rate laws are those of approximation. For this situation, the rate laws obtained for stationary polymerizations with the catalyst systems of a fixed sample of TiCl_3 combined

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with various alkylaluminums will be discussed in connection with the polymerization mechanism.

Rate Law obtained with TiCl_3 -Alkylaluminums

The reported rate laws are the Rideal type*

$$R_p = k[M] \frac{K_A[A]}{1 + K_A[A]} \quad (1)$$

and the Langmuir-Hinshelwood type

$$R_p = k[M] \frac{K_A[A]}{(1 + K_A[A])^2} \quad (2)$$

The values of K_A and of the highest rate $k[M]$ in (1) and of the maximum rate $k[M]/4$ in (2) obtained for the stationary polymerizations with TiCl_3 - AlR_2Y ($\text{R}=\text{Et}$, $n\text{-Dec}$; $\text{Y}=\text{R}$, H , Cl , Br)^{4,5,6)} are shown in Table 1 and they can be compared satisfactorily with each other. It should be noted here that the Langmuir-Hinshelwood equation (2) obtained with AlEt_2H , has K_A of ca 100 ℓ/mol that is almost the same with the values of K_A of the Rideal equation (1) obtained with another catalyst systems. Then, the rate equations seem to be further confirmed. However, the applicability of (2) for the case of AlEt_2H is fairly good and admitted of no dispute, because of clear appearance of a rate maximum at the region of low concentrations of AlEt_2H . On the other hand, there is room for discuss (1), even which was commonly obtained for many cases, as pointed out before by the author⁷⁾ who showed the experimental congruence of (2) with (1) in the region of low concentrations as

$$k[M] \frac{K_A[A]}{(1 + K_A[A])^2} \simeq \frac{k}{2} [M] \frac{(2K_A)[A]}{1 + (2K_A)[A]} \quad (3)$$

Here, the following more practical approximation can be taken when the maximum rate is judged as the highest rate.

$$k[M] \frac{K_A[A]}{(1 + K_A[A])^2} \simeq \frac{k}{4} [M] \frac{(fK_A)[A]}{1 + (fK_A)[A]} \quad (4)$$

with

$$f = \frac{4}{(1 - K_A[A])^2} \quad (5)$$

*) A type $R_p = k[M] K \sqrt{[A]'} / (1 + K \sqrt{[A]'})$ was proposed by Ingberman *et al.*²⁾ who used a correction $[A]' = [A] - a$. But it was shown that their original data were well expressed by (1)³⁾.

Rate law of the Ziegler-Natta Polymerization

On the basis of this consideration, the rate data, which were represented by (1), have been checked also by (2). As shown in the case with TiCl_3 - AlEt_2Cl , for example, the original data (Fig. 1) can be expressed by (1) (Fig. 2) as well as by (2) (Fig. 3). The revised results are summarized also in Tab. 1. From these results, we can take equation (2), which is a strong evidence of the monomer coordination, at least for the polymerizations with TiCl_3 - AlEt_2X ($\text{X}=\text{Cl}, \text{Br}$) and probably for all polymerizations with the heterogeneous Ziegler-Natta catalysts.

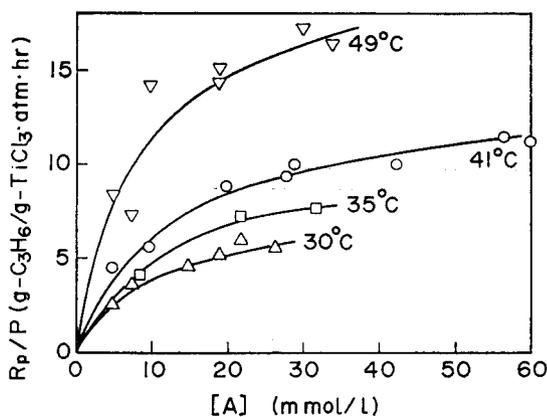


Fig. 1. Dependence of stationary rate on the concentration of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ at various temperatures, $[\text{TiCl}_3] = 16 \text{ mmol/l}$.

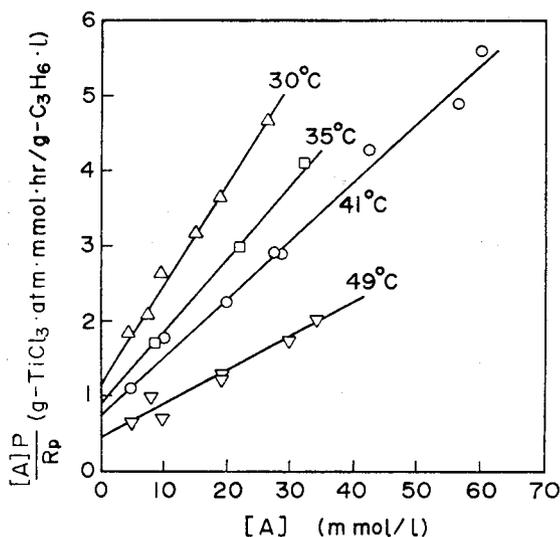


Fig. 2. Plots of $[\text{A}]P/R_\infty$ versus $[\text{A}]$ for TiCl_3 - $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ system. (Linear plots of Rideal type rate law for the data of Fig. 1)

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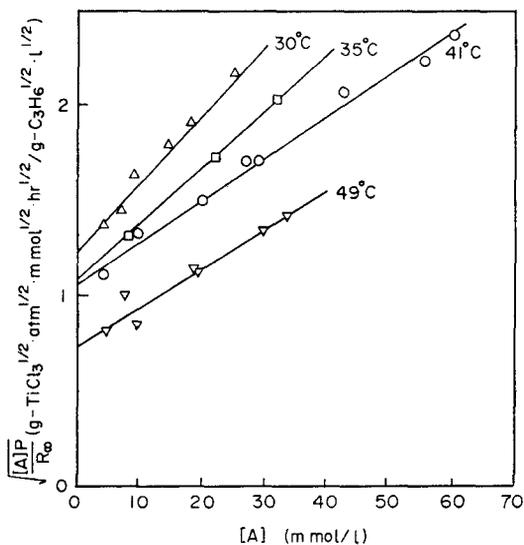


Fig. 3. Plots of $\sqrt{[A]P/R_{\infty}}$ versus $[A]$ for $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ system. (Linear plots of Langmuir-Hinshelwood type rate law for the data of Fig. 1)

TABLE 1. Rate Laws for Stationary Propylene Polymerization with TiCl_3^*

Catalyst	T °C	Rideal Type		Langmuir-Hinshelwood Type			
		highest rate**	K_A (ℓ/mol)	maximum rate**	K_A (ℓ/mol)		
$\text{AlEt}_2\text{Cl}^{(5)}$	49	22.2	105	revised 17.0	27.0		
	41	12.9	97			10.8	21.0
	35	9.9	125			7.8	29.1
	30	7.8	100			5.6	29.6
$\text{AlEt}_2\text{Br}^{(5)}$	49	13.0	115	10.7	21.6		
	41	9.3	145	8.2	24.7		
	35	5.6	110	4.4	25.1		
	30	4.6	75	3.4	20.5		
$\text{AlEt}_2\text{H}^{(6)}$	41			34.3	100		
	30			25.3	50		
$\text{AlEt}_3^{(4)}$	44	32	120		(25~30)		
	32		220				
$\text{AlEt}_3^{(10)}$	50			($K_M=0.163$)	21.2		
$\text{Al}(\text{n-Dec})_3^{(5)}$	41	33	160				

* The used catalysts are Toho Titanium-TAC^{5,6)} and Stauffer-AA^{4,10)} and all are γ or δ form, $3\text{TiCl}_3 \cdot \text{AlCl}_3$.

** The unit of rate = g-propylene/g-TiCl₃·hr·atm.

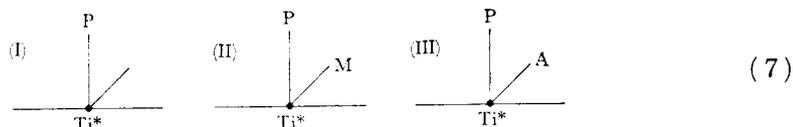
Rate law of the Ziegler-Natta Polymerization

Langmuir-Hinshelwood Mechanism

The experimental formula (2) can be considered as an approximate form, in the case where $K_M[M] \ll 1$, of the general form (6).

$$R_p = k_L C_0^* \frac{K_M[M] K_A[A]}{(1 + K_A[A] + K_M[M])^2} \quad (6)$$

where k_L is the rate constant of the insertion of a coordinated monomer into the polymer chain on a polymerization center, C_0^* the total number of "active centers". Here, the three states of "active centers" can be supposed as,



The active center must be active titanium atom Ti^* on the surface and its total number is C_0^* , (I) is the active center with a polymer chain P and one vacancy \square and its total number $C_0^* \theta_A \theta_0$, (II) that with a chain with a coordinated monomer and its total number $C_0^* \theta_A \theta_M$ and (III) is that with a chain with a coordinated organometallic compound and its number $C_0^* \theta_A^2$, providing that $\theta_A = K_A[A]/(1 + K_A[A])$, $\theta_M = K_M[M]/(1 + K_A[A])$ and $\theta_0 = 1/(1 + K_A[A])$. The structures (7) coincide with those supposed commonly in almost the proposed mechanistic theories. The rate equation (6) or (2) can be represented by

$$R_p = k_L K_M[M] C_0^* \theta_A \theta_0 \quad (8)$$

which is the same form with the general rate law of polymerizations (9)

$$R_p = k_p [M] C^* \quad (9)$$

where k_p and C^* have been called as "a rate constant of polymerization" and "the number of polymerization centers". There are the two methods to determine the values of k_p and C^* . One is the quenching method to determine C^* with the use of radio active agents of transfer or termination of growing polymer chains and the other is the method to obtain $k_p [M]$ from the relation between number average molecular weight and polymerization time. It is obvious that these methods give us the total number of the three states, (I)+(II)+(III), as C^* and then $k_L K_M \theta_0$ as k_p . The quenching method with the use of ^{14}CO proposed recently by Zakharov *et al.*⁹⁾ gives smaller values for C^* and larger but constant values for k_p . Here, the author

propose an explanation for the discrepancy as bellow. Since that a carbon monooxide coordinates to a vacant site and then is inserted into metal-carbon bond, it should be considered that the new method gives $C_0^* \theta_A \theta_0$ for C^* and $k_L K_M$ for k_p . Using the quenching method with BuO^3H , Schnecko *et al.*⁹⁾ obtained that $C^* = 5 \times 10^{-3}$ (mol/mol-Ti) and $k_p = 18$ (ℓ /mol.s) for the propylene polymerization with TiCl_3 (Stauffer AA)- AlEt_2Cl at 60°C , $[\text{A}] = 100$ mmol/ ℓ , while Zakharov *et al.*⁸⁾ reported that $C^* = 1.7 \times 10^{-3}$ (mol/mol-Ti) and $k_p = 90$ (ℓ /mol.s) at 70°C . The value of the activation energy in this case is 14 kcal/mol, independent of temperature, and then 90 (ℓ /mol.s) at 70°C corresponds to 50 (ℓ /mol.s) at 60°C . So, if the value of θ_0 was $1/3$ when $K_A [\text{A}] = 2$ the discrepancy between the two sets of data can be understood. Next, it will be shown that the Langmuir-Hinshelwood rate law can explain succesfully observed k_p values, which are within $1 \sim 10^2$ ℓ /mol.s at $40^\circ \sim 70^\circ$. Using the activation energy 14 kcal/mol, we obtain $5 \times 10^9 \sim 7 \times 10^{10}$ ℓ /mol.s for the frequency factor k_p^0 . In the case of this rate low, the rate constant k_L should be $(kT/h) \exp(-E_L/RT) = 6 \times 10^{12} \exp(-E_L/RT)$, which requires that $K_M = 10^{-2} \exp(E_M/RT)$ and $(E_L - E_M) = 14$ kcal/mol.

If the data of Vessely,¹⁰⁾ $K_M = 0.163$ ℓ /mol at 50°C was correct, the heat of coordination of propylene monomer E_M is 2 kcal/mol. Then, the Langmuir-Hinshelwood rate law seems, so for, to be fit for the Ziegler-Natta polymerizations.

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