

STUDIES ON THE KINETICS OF PROPYLENE POLYMERIZATION WITH THE COMPLEX- TYPE TiCl_3 CATALYST*

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ABSTRACT

The active center concentration C_p , the rate constant k_p , and the activation energy of chain propagation E_p in the polymerization of propylene with complex-type $\text{TiCl}_3-(\text{C}_2\text{H}_5)_2\text{AlCl}$ catalyst system were studied. The M_n was corrected by $\bar{M}_w/\bar{M}_n$ value determined by GPC. The values thus obtained for C_p , k_p , and E_p at 50°C were 3.01 mol/mol Ti, 6.27 1/mol $\cdot$ sec, and 5.10 Kcal/mol respectively.

The kinetic parameters were compared with those obtained from conventional $\text{TiCl}_3 \cdot \text{AlCl}_3$ catalyst, showing that the higher activity of the complex-type catalyst over the conventional catalyst is not only due to the higher C_p of the former, but to a greater extent due to the increase of the k_p value.

INTRODUCTION

In the study of the Ziegler-Natta polymerization kinetics, especially since the discovery of the high yield catalysts, there has been increasing interest in the investigation of C_p and k_p , because the catalytic activity obtained from the ordinary polymerization experiments is merely an overall relative comparison. The well-known complex-type (i.e. Solvay type) TiCl_3 catalyst system, which is characterized by its high stereospecificity and high activity, has already been employed in commercial production, but few works concerning its kinetic behaviour have been published^[1]. In the present paper, by comparing the kinetic parameters with those of the conventional $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ catalyst, we will elucidate the inherent nature of the high activity of the complex-type catalyst.

EXPERIMENTAL

Materials

Complex-type catalyst, a product of Beijing Research Institute of Chemical Industry, $\text{TiCl}_3 \sim 80\%$, $\text{TiCl}_4 \sim 8\%$, *n*-butyl ether 5–7%, specific area 98.9 M^2/g . Propylene, purity

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99.4%, CO 0.06 ppm, O₂ 2 ppm, H₂O 2 ppm (volume).

Polymerization apparatus and procedure

Polymerization of propylene was carried out in a 500 ml glass reactor at $50 \pm 0.3^\circ\text{C}$, under a constant pressure of $850\text{--}870 \pm 1$ mmHg, with the stirring speed of 600 rpm. The reactor was purged with N₂, and 300 ml hexane, (C₂H₅)₂AlCl and the catalyst (300–600 mg) were added subsequently. Al/Ti=4 (mole). The polymerization mass was quenched at a given time by ethanol, and the polymer was dried and weighed. Isotacticity of the polymer was determined by infrared or by extraction with heptane. The molecular weight distribution of the polymer was determined at 135°C with GPC Waters Model 200 using *o*-dichlorobenzene as solvent.

RESULTS AND DISCUSSION

1. Establishment of the kinetic control conditions

For the examination of the influence of external diffusion, tests of various stirring speed, from 200 to 750 rpm, and of various catalyst quantity, from 200 to 650 mg, under above specified conditions were carried out. The polymerization rate, R_p , was found to be constant. These results indicate that the external diffusion does not influence the polymerization rate. In order to examine the influence of the produced polymer on the internal diffusion which may be the controlling step in the polymerization process, we calculated the Thiele Modules α by the equation^[2] raised by Chien. The α value = 0.06, which is $\ll 1$, therefore the polymerization process could be considered to be kinetically controlled, and thus the following experiments were all conducted within the above range.

2. Polymerization rate curves

For accurately measuring the change of the polymerization rate at the beginning of the reaction, an ampoule containing catalyst was put into the reactor and after equilibrium was reached in the reaction system, it was broken up. The curve obtained as shown in Fig. 1 is compared with that of the conventional catalyst. The steady state does not appear, even

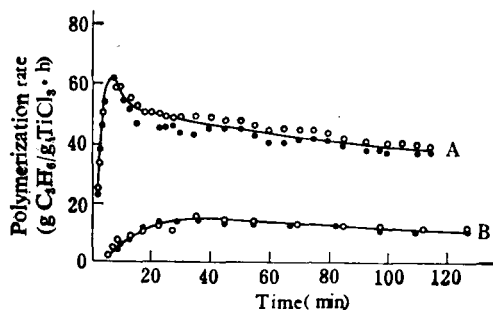


Fig. 1 Polymerization rate-time curves
A— Complex-type catalyst; B— Conventional TiCl₃ catalyst.

in a polymerization course of twelve hours. This is one of the characteristics of such complex-type catalyst.

By plotting $\ln R_p$ and $1/R_p$ against time (t) respectively and using least-squares fit method, the decay constant Kd_1 , Kd_2 and relative coefficients rc_1 and rc_2 were obtained. Comparing rc_1 with rc_2 , we found that the calculated decay constant Kd is mainly of the second order.

3. The isotacticity of the polymers

In our experiment, the isotacticity of the polymer is independent on polymerization time (Fig. 2), which is different from some literature results. We consider that the different results are owing to the use of different aluminum alkyls. It has been proved^[3] that the isotactic active centres polymerize propylene faster than the atactic ones do, therefore, it

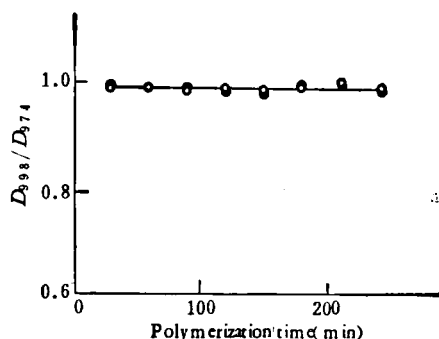


Fig. 2 The relationship between the ratio of intensity (D_{998}/D_{974}) of polymer and polymerization time

will be complicated to determine C_p and k_p if the isotacticity of the polymer varies in the polymerization course. Our result of constant isotacticity during polymerization is in favour of C_p and k_p determination.

4. The number-average molecular weight of the polymer

The number-average molecular weight $\bar{M}_n$ is an important parameter for determining C_p by the kinetic method. Owing to the fact that both the molecular weight and isotacticity of the polymer we obtained from the polymerization in the absence of hydrogen were too high to determine $\bar{M}_n$ by GPC method, we employed the viscometric method for doing that. Gardner^[3] used the equation $[\eta] = 0.917 \times 10^{-4} \bar{M}_n^{0.80}$ to obtain $\bar{M}_n$ value, but the influence of distribution of the molecular weight on the calculation of $\bar{M}_n$ was not taken into consideration. In our experiment the MWD's of polymers obtained in the presence of H_2 were examined to be log-normal distribution. Thus we can correct the $\bar{M}_n$ values obtained by viscometric method according to the equation^[4]

$$K_n = K (\bar{M}_w/\bar{M}_n)^{0.5a(a+1)} \quad (1)$$

Fig. 3 shows that the $\bar{M}_w/\bar{M}_n$ value of the polymer is substantially constant during the

polymerization. When the amount of H_2 increases, the molecular weight decreases, and the molecular weight distribution becomes wider. The MWD's of the polymers obtained in the presence of a small amount of H_2 , $\bar{M}_w/\bar{M}_n = 5.4$, is taken as an approximate value of MWD for correction of $\bar{M}_n'$ value. Thus $\bar{M}_n$ can be calculated as follows:

$$[\eta] = 5.4^{0.72} K \bar{M}_n^{0.80} = 1.205^{0.72} K \bar{M}_n'^{0.80}$$

$$\bar{M}_n = \sqrt[0.80]{\left(\frac{1.205}{5.4}\right)^{0.72}} \bar{M}_n' = 0.26 \bar{M}_n' \quad (2)$$

where $\bar{M}_n'$ is the number-average molecular weight obtained by viscometric method, $\bar{M}_n$ is the corrected value, and 1.205 is the value of $\bar{M}_w/\bar{M}_n$, which was originally used in establishing the equation.

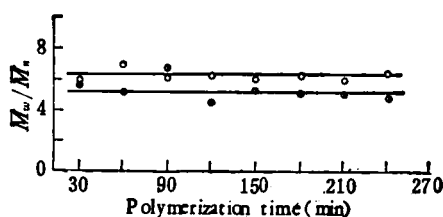


Fig. 3 The relationship between MWD of polypropylene obtained in the presence of H_2 and polymerization time. H_2 quantity
○—4.23 mmol; ●—3.38 mmol.

5. Determination of active centre concentration C_p and rate constant k_p

For determining C_p , Canova^[5] and Doi^[6] have developed various methods, but they are not suitable for our case.

It has been shown^[3] that

$$Y_t/\bar{M}_{n,t} = C_p (1 + k_{tr} [x] t) = C_p \text{ (when } t = 0) \quad (3)$$

where Y_t is the yield of polymerization, $[x]$ is the concentration of the chain transfer regulator. We plot $Y_t/\bar{M}_{n,t}$ against Y_t and work out C_p value by using least-squares fit method and extrapolating the line to zero yield (Fig. 4, Table 1).

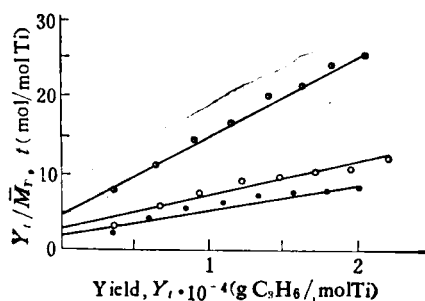


Fig. 4 The relationship between $Y_t/\bar{M}_{n,t}$ and Y_t at various polymerization temperatures
●—60°C; ○—50°C; ●—40°C.

Table 1 Determination of C_p and k_p for different catalyst systems

No.	Catalyst type	Polymn. temp. ($^{\circ}\text{C}$)	[M] (mol/l)	R_p max. ($\frac{\text{g propylene}}{\text{g TiCl}_3 \cdot \text{hr}}$)	Calculated value	
					$C_p \cdot 10^3$ (mol/mol Ti)	R_p (1/mol · sec)
15	Complex-type	40	0.4333	53.5	2.62	4.84
					2.43	5.00
16				49.2	2.24	5.16
8		50	0.2835	60.0	3.36	6.42
9				52.4	2.91 3.01	6.45 6.27
10				45.6	2.75	5.95
11		60	0.1457	58.8	5.01	8.19
					5.17	8.18
31			0.1530	65.4	5.32	8.18
20	Conventional	50	0.2835	13.9	1.73	2.88
					2.06	2.55
21				14.8	2.39	2.22

$$\frac{C_p \text{ complex}}{C_p \text{ conventional}} \cong 1.5$$

$$\frac{k_p \text{ complex}}{k_p \text{ conventional}} \cong 2.5$$

Tait^[1] et al. have determined both the C_p and k_p for two batches of Solvay catalysts by his newly developed allen adsorption method. Our results are close to theirs.

Table 1 shows that the value of C_p increases with polymerization temperature. Similar or contrary results were obtained by other workers with various catalyst systems.

Both C_p and k_p of complex-type TiCl_3 catalyst system are higher than that of $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ catalyst system. This can be explained as follows:

1) The higher C_p values for complex-type TiCl_3 catalyst can be attributed to its porous structure along with higher specific area and there could be more exposed Ti atoms on the surface of catalyst particles.

2) The atactic active centres are complexed with added ether during the catalyst preparation, so the ratio of the isotactic active centres to the atactic active centres is raised. As already mentioned above^[3] that k_p value of isotactic active centre is much higher than that of atactic active centre, so that the k_p value as a whole is increased.

Different explanations of the high activity for high efficiency catalyst have been proposed. Some attribute it to the increase of C_p , others to the increase of k_p . We can draw a conclusion from our results that the higher catalytic activity of the complex-type TiCl_3 catalyst over the conventional $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$ catalyst is not only due to its higher C_p value,

but also to a great extent due to its higher k_p value.

6. The activation energy for polymerization

The apparent activation energy E_a obtained by plotting $\ln(R_p/[M])$ against T is 11.3 Kcal/mol. And the activation energy for chain propagation, E_p , obtained by plotting $\ln k_p$ against T is 5.10 Kcal/mol (Fig. 5). The frequency factor A_p is 1.8×10^4 1/mol · sec. The difference between E_a and E_p (ΔE) is 6.2 Kcal/mol. ΔE in fact indicates the extent of dependence of C_p value on the polymerization temperature. Zakharov^[7] calculated E_a for the polymerization with $\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3 - (\text{C}_2\text{H}_5)_2\text{AlCl}$ system. They are quite close to our results.

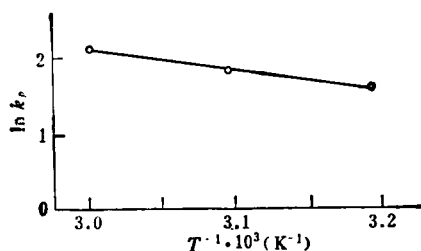


Fig. 5 Determination of activation energy of chain propagation E_p for complex-type catalyst

7. Polymerization in the presence of H_2

From equation^[3] it might be expected that the determination of C_p would not be influenced by the addition of hydrogen during the polymerization. The comparison of the results is shown in Fig. 6. In the case of adding hydrogen, the obtained $Y_t/\bar{M}_{n,t} - Y_t$ relationship is not linear. The extrapolated C_p value from the first several data of the curve coincides with those obtained without adding H_2 , but the later data of the curve drops evidently, therefore it is impossible to obtain any reasonable C_p value at all. The reason for this is not clear yet. It might be predicted as follows: because all the H_2 is added at the

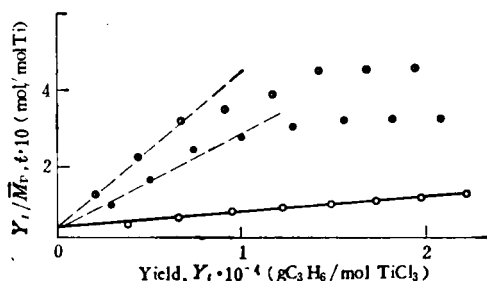


Fig. 6 The comparison of $Y_t/\bar{M}_{n,t} - Y_t$ relationship for propylene polymerization in the absence and presence of H_2

H_2 quantity ○—Zero mmol; ●—3.38 mmol; ◐—4.23 mmol.

beginning of the polymerization, the H_2 concentration is gradually decreased due to the consumption of H_2 during polymerization. Thus the decrease of the $k_{tr} [x]$ value leads to a decrease of $Y_i/\overline{M}_{n,i}$, which in turn causes the curve in the plot to bend downward.

REFERENCES

- [1] Tait, P. J. T., Kinetic Consideration and Active Center Determination in Ziegler-Natta Polymerization, "Preparation and Properties of Stereoregular Polymers" (Lenz R. W. Editor), Reidel Publishing Co., 1978.
- [2] Chien, J. C. W., *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *8*, 2555.
- [3] Gardner, K., Parsons, I. W., Haward, R. N., *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1683.
- [4] Kurata, M., Tsunashima, Y., Iwama, M., Kamada, K., "Polymer Handbook", Brandrup Ed. 2nd ed. Wiley Interscience, 1974.
- [5] Canova, L., Mazzulo, S., Giannini, U., IUPAC Intern. Symp. on Macromolecules, Florence, Sept. 1980, Preprints Vol. 2. *Makromol. Chem. Suppl.* **1981**, *5*, 216—229.
- [6] Doi, Y., Keij, T., *Makromol. Chem.*, **1979**, *180*, 2235.
- [7] Zakharov, V. A., IUPAC Intern. Symp. on Macromolecules, Florence, Sept. 1980, Preprints Vol. 1.