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Kinetic Study on Propylene Polymerization by a High Activity Catalyst System: $MgCl_2/TiCl_4/PhCO_2Et$-$AlEt_3/PhCO_2Et$

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SUMMARY

Kinetic study was performed in short time propylene polymerization with a high activity-high stereospecificity catalyst system composed of $MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3/PhCO_2Et$. The concentration of the active centers, $[C^*]$, the propagation rate constant, k_p, and the chain transfer rate, r_{tr}, were determined. The change of these values by the change of polymerization conditions, the concentration of monomer, $AlEt_3$, and the temperature, were studied.

INTRODUCTION

It is well known(1) that the catalyst system consisting of the $MgCl_2$-supported titanium catalyst($MgCl_2/TiCl_4/PhCO_2Et$), triethylaluminium and ethyl benzoate($AlEt_3/PhCO_2Et$) exhibits a very high activity and high stereospecificity in propylene polymerization. In the previous paper(2) we have reported that high activity of the $MgCl_2$-supported titanium catalyst system is achieved by the increases both of the concentration of the active titanium centers, $[C^*]$, and the value of propagation rate constant, k_p. In this report, we have examined kinetically the short time propylene polymerization using the above catalyst system to obtain detailed information about this system.

EXPERIMENTAL

Preparation of the $MgCl_2$-supported titanium catalyst; In a 500ml stainless steel pot SUS-made balls(15$mm\phi$)(total 2.8kg), anhydrous $MgCl_2$(20g;0.21 mol) and $PhCO_2Et$(6ml;0.42mol) were co-ground for 5h under nitrogen. The solid ground product was heated with 200ml of $TiCl_4$ at 80°C for 2h in a glass flask. Then, the solid product was separated by filtration, and washed several times with decane. One gram of the obtained supported catalyst contained 21mg of Ti atoms.

Propylene polymerization; Slurry polymerization was carried out in a 1l glass-made flask using decane as solvent. Decane(500ml) was put into the flask, and it was filled with propylene or the mixed gas of propylene and nitrogen. $AlEt_3$, $PhCO_2Et$ and the solid catalyst were added, and then the polymerization was performed under atmospheric pressure for 5-600sec. at 50°C, 10°C and -10°C. After the completion of polymerization, a small amount of ethanol was added to the system to quench the polymerization, and then, the whole slurry was poured into a large amount of methanol. The obtained solid polymer was collected, washed with methanol containing HCl, and dried in vacuo.

Characterization of polymer; Isotactic index(I.I.) of polymer was given by the weight fraction insoluble in boiling heptane. Number average molecular weight, $\overline{M}_n$, of the polymer were measured by GPC(Waters Associ-

ates, Model ALC/GPC 150C), using a polystyrene gel columns(10^7, 10^6, 10^5, 10^4, and 10^3Å pore size) and *o*-dichlorobenzene as solvent at 135°C.

RESULTS AND DISCUSSION

Short time propylene polymerization(5-600*sec*.) by the catalyst system ($MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3/PhCO_2Et$) was performed under atmospheric pressure with the changes of the monomer concentration, polymerization temperature(50°C, 10°C, -10°C) and the $AlEt_3$ concentration. The results are listed in Table.1. The values of isotactic index of polymers were around 95%. Fig.1 shows the linear relation between the polymer yield, Y,(*mol*-C_3H_6/*mol*Ti) and polymerization time(*sec*.) in every condition from A to E. This result means that the polymerization rate, R, expressed as the slope remains constant during the polymerization. Therefore, the concentration of the active centers,$[C^*]$, may be regarded to be constant under the investigated conditions. The number of polymer molecules per Ti atom, $[N]$, is related with the polymer yield Y in Eq.[1],

$$[N] = [C^*] + (r_{tr}[C^*]/R)Y \qquad (1)$$

where r_{tr} is the rate of chain transfer and R is the polymerization rate.

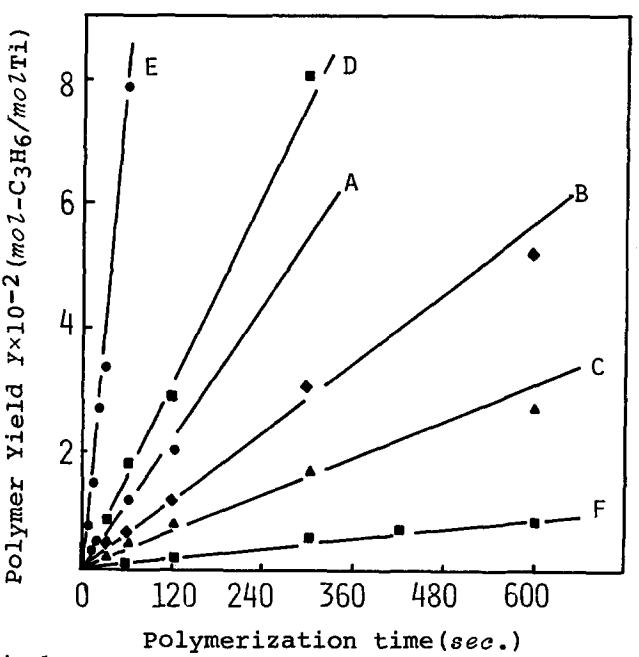

Fig.1
Time Dependence of the Polymer Yield vs Time. Polymerization conditions: [Ti]=0.55*mmol/l*,$AlEt_3/PhCO_2Et$=3*mol/mol*,
A: 10°C,[M]=0.71*mol/l*, [AlEt3]=13.8*mol/l*,
B: 10°C,[M]=0.37*mol/l*, [AlEt3]=13.8*mol/l*,
C: 10°C,[M]=0.21*mol/l*, [AlEt3]=13.8*mol/l*,
D: 10°C,[M]=0.71*mol/l*, [AlEt3]=27.5*mol/l*,
E: 50°C,[M]=0.28*mol/l*, [AlEt3]=13.8*mol/l*,
F:-10°C,[M]=0.38*mol/l*, [AlEt3]=13.8*mol/l*.

TABLE 1

Polymerization of propylene with $MgCl_2/TiCl_4/PhCO_2Et$-$AlEt_3/PhCO_2Et$ as catalyst system

Run No.	Polymerization conditions				Results			
	Temp. (°C)	Time (sec.)	[M] (mol/l)	[$AlEt_3$] (mmol/l)	Polymer yields (mol-C_3H_6/ molTi)	I.I. (%)	$\bar{M}_n \times 10^4$	$[N] \times 10^2$
A-1	10	5	0.71	13.8	23.8		5.33	1.88
2		10			34.8		7.37	1.98
3		15			43.8	95.4	7.53	2.44
4		60			117		11.6	4.23
5		120			197		14.8	5.60
6		300			874		16.8	21.8
7		600			1195		18.0	27.9
B-1	10	30	0.37	13.8	51.9		7.83	2.78
2		60			63.1		10.7	2.48
3		120			121		13.1	3.89
4		300			307		14.3	9.02
5		600			519		15.3	14.2
C-1	10	30	0.21	13.8	25.9		6.10	1.79
2		60			53.6		8.50	2.65
3		120			77.9		9.97	3.28
4		300			164		12.7	5.41
5		600			264		14.0	7.93
D-1	10	5	0.71	27.5	20.7		4.27	2.04
2		15			45.0		7.97	2.37
3		30			83.8		10.3	3.42
4		60			182	96.5	13.1	5.82
5		120			290		14.8	8.24
6		300			805		17.7	19.1
7		600			1380		18.2	31.9
E-1	50	5	0.28	13.8	73.6		5.72	5.40
2		10			143		6.06	9.90
3		15			216		5.97	15.2
4		20			269		6.38	17.7
5		25			295		5.65	21.9
6		30			338		5.51	25.8
7		60			788	94.5	6.04	54.8
F-1	-10	30	0.38	13.8	6.9		5.54	0.533
2		60			12.3		6.04	0.856
3		120			23.6		7.30	1.36
4		300			55.7		9.60	2.43
5		420			69.0		10.3	2.82
6		600			76.9	94.0	10.3	3.14

The values of $[C^*]$ were determined from the intercepts of Fig.2, in which the linear relationship between $[N]$ and Y were obtained. Then, R can be expressed by Eq.(2)

$$R = k_p[M][C^*] \qquad (2)$$

where $[M]$ is the propylene concentration in medium(Table 1). R could be obtained from the slope of the straight lines in Fig.1, and concequently the values of k_p were determined from Eq.(2). r_{tr} could be obtained from the slope of the straight line in Fig.2. The average lifetime of polymer chain, t, was obtained from $t=1/r_{tr}$. All of the obtained values are listed in Table.2.

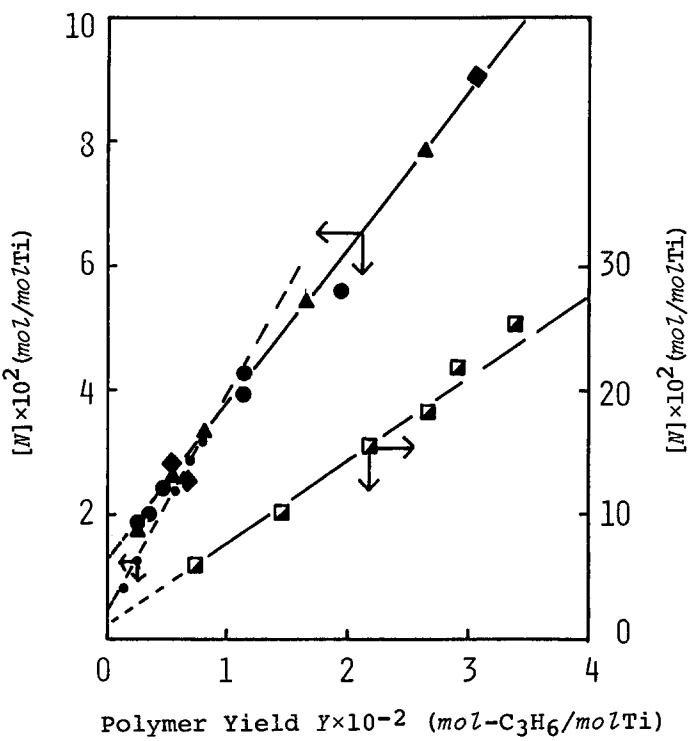

Fig.2 Relation between the polymer yield, Y, and the number of polymer chains produced per mol of Ti, $[N]$.
Polymerization conditions: (●): same with A in Fig.1 , (◆): same with B in Fig.1, (▲): same with C in Fig.1, (◪): same with E in Fig.1, (•): same with F in Fig.1.

TABLE 2
Data of Propylene Polymerization

Run	Polymerization conditions[a]							
	Temp. (°C)	[M] (mol/l)	[AlEt3] (mmol/l)	R (mol-C_3H_6/molTi·sec)	[C*]×10^2 (mol/molTi)	k_p (l/mol·sec)	r_{tr} (min^{-1})	t (min)
A	10	0.71	13.8	1.82	1.3	200	2.1	0.47
B	10	0.37	13.8	0.91	1.3	190	1.1	0.91
C	10	0.21	13.8	0.59	1.3	210	0.7	1.4
D	10	0.71	27.5	2.57	1.7	210	2.1	0.47
E	50	0.28	13.8	12.7	1.4	3200	26	0.038
F	-10	0.38	13.8	0.17	0.7	64	0.42	2.4

a) The concentration of the solid catalyst was 0.55mmolTi/l.
The molar ratio of $AlEt_3$ and $PhCO_2Et$ was kept as $AlEt_3/PhCO_2Et$=3mol/mol.

Effects of the propylene monomer concentration

The concentration of propylene monomer in the polymerization medium was varied in the range from 0.71 to 0.21mol/l at 10°C by diluting propylene with nitrogen introduced to the polymerization system. As shown in Fig.1 and Table 2, R increased in proportion to the increase of the monomer concentration (Run A-C in Table 2) whereas [C*] and k_p were considered to be almost constant, independent from [M]. On one hand, the chain transfer rate, r_{tr}, increased linearly with the monomer concentration, [M] (Fig.3). The fact that the intercept in Fig.3 is almost zero is taken to suggest that the chain transfer reaction caused by the other transfer agent, for instance $AlEt_3$, was almost negligible. Thus, the chain transfer reaction was caused almost exclusively by the propylene monomer.

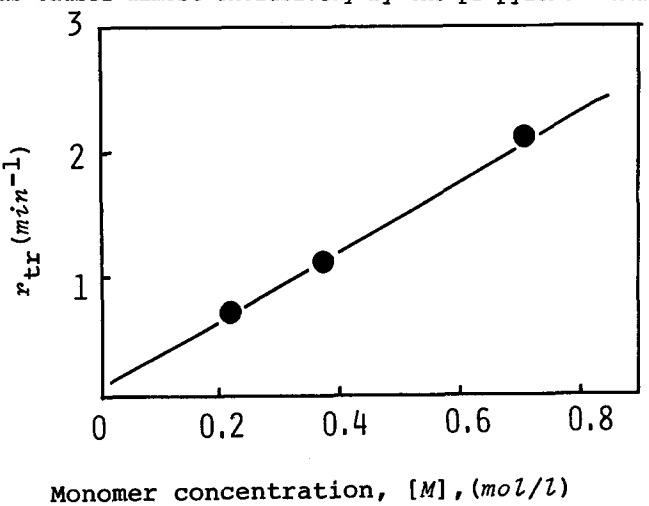

Fig.3 Relation Between Chain Transfer Rate, r_{tr}, and Monomer Concentration, [M]

Effect of concentration of $AlEt_3$

Polymerization rate, R, increased about 1.5 times by varying the concentration of $AlEt_3$, (molar ratio of $AlEt_3$ and $PhCO_2Et$ was kept as $AlEt_3/PhCO_2Et=3mol/mol$) from 13.8 to 27.5$mmol/l$. The values of k_p were considered to be unchanged (Run A, D in Table 2), therefore, the increase of R seemed to be due to the increase of $[C^*]$.

Effects of polymerization temperature

The polymerization rate, R, increased with the increase of polymerization temperature (Run B, E, F in Table 2) in spite of the decreased of monomer concentration, and the values of k_p increased very much from 64 (at -10 °C) to 3200$l/mol \cdot sec.$ (at 50°C). In consideration of a small change of $[C^*]$ in Table 2, the increase of R depends mostly on the increase of the k_p value.

Average lifetime of growing polymer chain

The average lifetime of the growing polymer chains, t (given by $t=1/r_{tr}$) in Table 2 is in the range of 0.04-2.4min. The time for example, t=2-3sec at 50°C polymerization, is very short compared with 4-10min. at 60-70°C polymerization in the conventional $TiCl_3$ catalyst system (4) (5).

CONCLUSIONS

The results of this study are summaried as follows.

i) The concentration of active centers, $[C^*]$, was 1-2% of the used Ti atoms, which did not depend on the monomer concentration, but increased a little according to the increase of $AlEt_3$ concentration and that of polymerization temperature. The values of k_p changed very widely, from 64 to 3200$l/mol \cdot sec.$, according to the change of polymerization temperature from -10°C to 50°C.

ii) The chain transfer rate was proportional to the monomer concentration, and the chain transfer reaction was considered to be mostly caused by the propylene monomer.

iii) The average lifetime of the growing polymer chain was in a range of 0.04-2.4$min.$, these values being very short compared with 4-10min of classical $TiCl_3$ catalyst system.

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