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Studies on propylene polymerization with a highly active $MgCl_2$ supported $TiCl_4$ catalyst system

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SUMMARY

Propylene polymerization was performed with a highly active $MgCl_2$ supported $TiCl_4$ in conjunction with Et_3Al and ethyl benzoate(EB). The obtained polypropylene sample was separated into four fractions by successive extraction with pentane, heptane and trichloroethylene(trichlene). Yield, Mn, Tm and microtacticity of each fraction were determined, and the effects of the concentration of EB on these items of results were investigated. It has been found that EB enhances yield, Mn and stereospecificity of trichlene insoluble(the most stereospecific) fraction, and in contrast, it decreases rapidly yields of other three fractions without changing the character of the polymers. From these findings, the functions of EB to the active centers were discussed.

INTRODUCTION

The $MgCl_2/TiCl_4/AlEt_3$/EB catalyst system shows high activity and high stereospecificity in propylene polymerization(1). The key roles, the structure and the chemical reaction of EB in the catalyst system have been investigated by the characterization of produced polypropylene(2,3,4,5,6,7,8,20), by kinetic studies(9,10,11,12) and by chemical analysis of catalysts (13,14,15,16,17,18,19). In this paper, several series of polypropylene samples were prepared with the subject catalyst system under the various EB concentrations, which were characterized by the analytical studies with NMR, DSC and GPC on each of the solvent-separated fractions. Then the effect of EB concentration on yield and stereoregularity of each fraction was examined to elucidate the function of EB to the active centers in the catalyst system.

EXPERIMENTAL

Preparation of the Catalyst: $MgCl_2$ alone was milled in a ball mill for 60 hr. Ten grams of the milled products were suspended in 100 ml of pure $TiCl_4$ for 2 hr at 80 °C. Solid product was isolated by filtration, which was washed with decane. The resulted product was found to contain 8 mg-Ti/g-catalyst.

Propylene Polymerization: After saturating 250 ml of n-decane in a 500 ml-glass flask with propylene, $AlEt_3$(3 mmol), predetermined amount of EB and $MgCl_2/TiCl_4$ catalyst(0.12 mg-atom, as Ti-atom) were added in this order at 50 °C, and polymerization was performed for 15 min at 50 °C under atmospheric pressure. After completion of polymerization, a small amount of ethanol was first added to the system to stop the polymerization, and the reaction mixture was poured into a large quantity of methanol. The resulting solid polymer was collected and dried under reduced pressure.

Characterization of polymer: Polypropylene sample was fractionated by successive Soxhlet extraction for 8hr each with boiling n-pentane, n-heptane and trichlene in this order into four fractions, i.e., pentane soluble (C5sol), pentane insoluble-heptane soluble(C5ins-C7sol), heptane insoluble-trichlene soluble (C7ins-T sol) and trichlene insoluble (T ins). Each fraction was characterized on molecular weight(Mn) by GPC(Waters Associates,Model ALC/GPC 150,mix polystyrene gel column, o-dichlorobenzene solvent,135 ℃), Tm by DSC(Perkin Elmer DSC 2,scan speed -10°C/min and +10 ℃/min) and the contents of methyl triads sequences(mm) by ^{13}C-NMR (JEOL,FX-100).

Reaction among catalyst components: $AlEt_3$(8.35 mmol), EB and $MgCl_2/TiCl_4$ catalyst(0.334 mg-atom,as Ti-atom) were added at 50°C under nitrogen into 700 ml of n-decane in this order, and were reacted for 15 min. After the reaction, the resulted solid was separated from the solvent, washed with hexane and dried under reduced pressure.

RESULTS AND DISCUSSION

Propylene polymerization was performed with a highly active $MgCl_2$ supported $TiCl_4$ catalyst (Ti 0.8 wt %) prepared by the reaction of pure $TiCl_4$ and mechanically pulverized $MgCl_2$ in conjunction with Et_3Al and ethyl benzoate(EB) by varying the concentration of EB in the range of EB/Ti=0-15 in decane at 50°C for 15 min under atmospheric pressure. The obtained polypropylene(PP) was fractionated by successive extraction into four fractions followed by the characterization.

All the results obtained are shown in Table 1.

Yields of the fractionated polymers

Fig.1 shows the changes of yields of each fraction with the EB/Ti molar ratio of the catalyst system. It is seen that the mode of variation of yield of T ins by the EB/Ti ratio is quite different from the variations of other three fractions. (Yields in Fig.1 are the relative values in which yield of C5 sol at EB/Ti=0 is defined as 100.)

T ins fraction : Yield of this fraction was the second highest at EB/Ti=0, which became the highest as the EB/Ti ratio was increased.

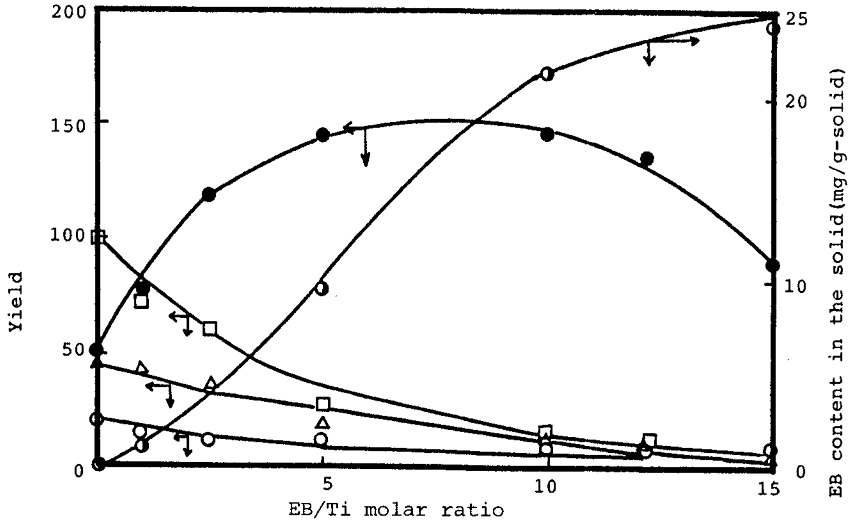

Fig.1 Effect of the EB/Ti molar ratio on yield of each fraction, and on the EB cntent in the solid catalyst
(● : T ins, ○ : C7ins-T sol, △ : C5ins-C7sol, □ : C5sol, ◐ : EB content)

In the range of higher EB/Ti ratios, yield was decreased gradually, but it was more than two times as high as that at EB/Ti=0.

C5 sol, C5 ins-C7 sol, C7 ins-T sol : Yields of these three fractions were higher in the following order ; C5 sol > C5 ins-C7 sol > C7 ins-T sol, and were decreased, at EB/Ti=15, to only 6/100, 1/9 and 3/10 of those at EB/Ti=0, respectively.

The characterization of the fractionated polymers (Table 1)

(1) C5 sol

Average-number molecular weight (Mn) of this fraction at EB/Ti=0 was 1.41×10^4 and meso/meso(mm) (the contents of methyl triads sequences) was 37 %. These values were hardly affected (or Mn seemed to be little decreased) by the introduction of EB into the catalyst system (Mn= $0.90-1.10 \times 10^4$, mm=33-37%) in spite of the remarkable decrease of yields. Moreover, no clear melting point(Tm) was found in DSC charts. Thus,this fraction was concluded to be of low molecular weight and non-stereospecific.

(2) C5 ins-C7 sol

Mn of this fraction at EB/Ti=0 was 1.62×10^4, almost similar to C5 sol, but mm was 77 %, significantly higher than that of C5 sol, indicating that this fraction was of low molecular weight and slightly stereospecific. These values were hardly affected by EB (Mn=$1.05-1.81 \times 10^4$,mm=71-79%) in spite of the considarable decrease of yields. These fractions showed two Tm peaks at 135-139°C and 147-150°C in DSC charts.

(3) C7 ins-T sol

Mn of this fraction was 4.98×10^4 and mm was 85% at EB/Ti=0. Also in this fraction, Mn($3.6-4.9 \times 10^4$) and mm(80-85%) were not affected by EB in spite of the decrease of yields. By DSC, two Tm peaks were determined at 151-155 °C(main) and 160°C. In comparison with the previous two fractions, this fraction was concluded to be of higher molecular weight and more stereospecific.

(4) T ins

This fraction at EB/Ti=0 was 8.11×10^4 of Mn and 92 % of mm, i.e.,it is of high molecular weight and highly stereospecific, indicating the presence of the active centers of high stereospecificity in this $MgCl_2/TiCl_4-Et_3Al$ catalyst system. The mode of variation of this fraction by the increasing of EB was considerably different from others. Mn was significantly increased to $9-11 \times 10^4$ and Tm value was increased with increase of EB/Ti molar ratio from two values at 155°C(main) and 160°C, via 155°C and 160 °C(main), to 160°C (single) at EB/Ti=12.2. This fact would mean that stereospecificity of T ins was enhanced by EB, although mm was only slightly increased to 93%. Consequently, EB increased yield, molecular weight and stereospecificity of only this fraction at the same time.

The results of the characterization can be summarized as follows.

As for stereospecificity,

(higher) T ins > C7 ins-T sol > C5 ins- C7 sol ≫ C5 sol

As for molecular weight,

(higher) T ins > C7 ins- T sol > C5 ins- C7 sol = C5 sol

The obtained facts suggest that in the subject $MgCl_2/TiCl_4-Et_3Al$ catalyst system, there is a broad distribution of the active centers having different stereospecificity, and EB would make the distinctive functions to those active centers as discussed below.

The action of EB to the active centers

As above mentioned, a suitable amount of EB increased yield and stereospecificity of T ins, which was the most stereospecific fraction, while, in contrast, decreased rapidly yields of other less or non-stereospecific fractions. (Of course, a large excess amount of EB would deactivates the catalyst activity, perhaps, due to the saturation of the

Table 1 Polymerization results and characterization of fractionated polypropylene prepared at various EB/Ti

Polymerization		T ins					C_7ins-T sol					C_5ins-C_7sol					C_5sol				
EB/Ti	PP	Yield[1] ( )[2]	Mn	Mw/Mn	mm	Tm	Yield ( )	Mn	Mw/Mn	mm	Tm	Yield ( )	Mn	Mw/Mn	mm	Tm	Yield ( )	Mn	Mw/Mn	mm	Tm
M/M	g		$x10^{-4}$			°C		$x10^{-4}$			°C		$x10^{-4}$			°C		$x10^{-4}$			°C
0	24.8	50 (23)	8.11	4.2	92	160 155.7*	20 (9)	4.94	3.7	85	160 155.8*	46 (21)	1.62	4.1	77		100 (46)	1.41	5.6	37	-
0.2	25.2							4.94	3.7												
1.0	23.7	77 (37)	11.6	4.0		160.3 155.4*	15 (7)	4.86	4.5		159.6 151	44 (21)	1.74	3.1		148 135.4	73 (35)	0.89	5.4		-
2.5	25.9	119 (52)	8.88	5.9		160 155.4*	11 (5)	3.61	5.7		160 155.2*	37 (16)	1.81	3.1	79	147 135	60 (26)	1.10	4.8	37	-
5.0	22.4	145 (73)	10.9	3.8	92	160.4 158.2	10 (5)			80		18 (9)	1.52	3.1	79	149.5 137.9	26 (13)	1.04	6.4		-
10	20.4	146 (81)			93		7 (4)					11 (6)	1.23	3.4	75		16 (9)			36	-
12.2	18.0	136 (85)	11.0	4.4	93	160.7	6 (4)					8 (5)	1.12	5.9		149.5 139.3	10 (6)	0.97	7.3		-
15	12.0	89 (84)			93		6 (6)					5 (5)	1.05	3.8	71		6 (6)			33	-

Polymerization condition ; n-decane 250 ml, 50 °C, 15 min, Et_3Al 3 mmol, Ti 0.12 mg-atom

1) Relative values in which the yield of C_5sol at "without EB" system is defined as 100

2) wt% of whole polymer

mm ; Contents of methyl triads sequences

* ; Main peak

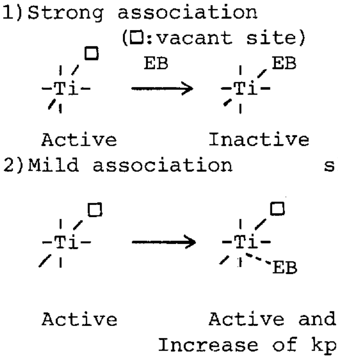

Fig.2 Function of EB
(Assumption (1))

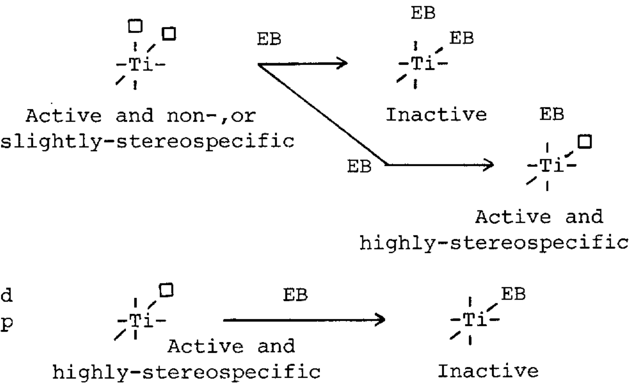

Fig.3 Function of EB
(Assumption (2))

vacant coordination sites in active centers.) The observed mode of variation of the fractions would be possibly interpreted in two different ways by assuming the following two kinds of the functions of EB to the active centers.

Assumption(1);The change of the propagation rate constant by EB. EB would associate with the active centers mildly or strongly depending on the concentration of EB and stereospecificity of the active centers having the different acidity (the more stereospecific would be the less acidic). The mild association would result in the increase of both the propagation rate constant by the unknown effects and the steric hindrance at the subject active center, while the strong one would result in the deactivation by the saturation of the coordination sites.(Fig.2) Thus the increase of T ins would be explained by the mild association of EB to the highly stereospecific active centers.

Assumption(2);The change of the number of the active centers by EB. A part of EB would transform the less or non-stereospecific active centers into the highly stereospecific active centers to result in the increase of T ins, for example, by the partial saturation of the plural vacant coordination sites, increasing the steric hindrance at the active centers. Another part of EB would lower the number of the active centers by the complete saturation.(Fig.3) The observed profiles in Fig.1 can be explained as the results of the competition of the positive and negative effects of EB on the number of the active centers.

In summary, EB directly takes part in the formation of a part of the highly stereospecific active centers to increase yield and stereospecificity and at the same time to modify k_p or k_{tr} value in the manner to increase the molecular weight of T ins. On the other hand, EB would deactivates the less or non-stereospecific active centers with high efficiency without changing the distribution of the nature of the active centers, because EB made the rapid decrease of yield without changing the character of the subject polymers.

Interaction between $MgCl_2/TiCl_4$ catalyst,Et_3Al and EB

The interaction among the catalyst components was investigated by analyzing the solid part after the reaction of them under the polymerization conditions except that propylene was not supplied. From the results shown in Tab.2 and Fig.1, a part of EB introduced into the catalyst system

Table 2 Content of EB and Ti in the solid recovered after the reaction among $MgCl_2/TiCl_4$,Et_3Al and EB

Added amount of EB	Content of EB and Ti in the solid		
EB/Ti	EB	Ti	EB/Ti
M/M	wt%		M/M
0	0	0.8	0
1	0.11	0.8	0.04
5	0.98	0.8	0.39
10	2.16	0.7	0.98
15	2.41	0.7	1.10

was fixed on the solid catalyst. The amount of fixed EB was increased rapidly, when EB was added in a small amount, then was gradually increased by the further addition and attained to EB/Ti= 1.10 at the addition of EB/Ti=15, in which all of Ti atoms would be apparently associated with EB in the solid catalyst.

In Fig.1, there is observed a rough correlation between the amounts of fixed EB on the solid catalysts and yields of the fractions. Thus, the rapid increase of fixed EB would correspond to the rapid increase of T ins and the rapid decrease of other three fractions, and the gradual increase of fixed EB by further EB addition would correspond to the gradual decrease of T ins via maximum peak due to the poisonous effects by excess EB and to the gradual decrease of other fractions.

Although these experiments were carried out in the absence of propylene monomer, the observed behavior of EB would support the proposed ideas about the function of EB to Ti atoms in the previous part of this paper.

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