

Catalysts

Kinetic Study on Propylene Polymerization with MgCl₂/TiCl₄-AlEt₃/PhCO₂Et System – The Role of Ethyl Benzoate

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SUMMARY

A kinetic study on propylene polymerization with the catalyst system of MgCl₂-supported TiCl₄ catalyst (MgCl₂/TiCl₄) in conjunction with AlEt₃ and PhCO₂Et (EB) has been made to elucidate the role of ethyl benzoate (EB) which is known to increase stereospecificity of produced polypropylene. It has been found that a part of added EB was fixed on the supported Ti catalyst and that EB modified the isotactic specific centers to increase the $k_p(\text{iso})$ value. Thus the productivity of isotactic polymer and the molecular weight of the isotactic polymer ($2 \cdot 10^4$ (\bar{M}_n) to $6 \cdot 10^4$ at 60°C) were increased.

INTRODUCTION

It is well known that the addition of ethyl benzoate (EB) to a highly active catalyst system, MgCl₂/TiCl₄-AlEt₃ (Cat.1), results in a remarkable increase of stereospecificity in propylene polymerization (1,2). Previously, we have reported (3) EB acts on the solid catalyst, killing selectively the active atactic centers, and that EB either increase the number of isotactic-specific centers (for example, transforms a part of atactic specific centers into isotactic-specific centers) or increase the propagation rate constant of the isotactic-specific centers. In the present work, we have made a kinetic study on the propylene polymerization with this catalyst system in order to examine the details of the effect of EB.

EXPERIMENTAL

Preparation of the catalyst: Preparation of the solid catalyst was carried out as described in the previous paper (3).

Polymerization and characterization: Propylene polymerization was carried out in 0.5 l of n-decane, which was first filled with propylene. AlEt₃ (5.0 mmol), PhCO₂Et (EB) (1.25 mmol), and the solid catalyst (0.2 mmol of Ti) were added in the said order, and then the polymerization was performed under atmospheric pressure at 60°C. After the designated time of polymerization, ethanol was first added to the system to stop the polymerization, and then a large amount of methanol was added to ensure the precipitation of all the polymer product. The resulting solid polymer was collected, washed with a methanol solution of hydrochloric acid, and dried in vacuo. Characterization of the produced polymer was carried out as described in the previous paper (4).

Reaction of the solid catalyst with AlEt₃ and EB: In a 0.4 l flask were placed 0.2 l of hexane under N₂, and [Ti]=13.4 mmol/l, [AlEt₃]=335 mmol/l, [PhCO₂Et]=83.8 mmol/l were added in the order of AlEt₃, PhCO₂Et, and finally MgCl₂/TiCl₄ catalyst. The reactant was stirred for 10-160 sec and the solid portion was separated by filtration (it took 15 sec for separation), and subjected to the G.C. determination of EB content.

RESULTS AND DISCUSSION

A short-time propylene polymerization was performed by using $\text{MgCl}_2/\text{TiCl}_4\text{-AlEt}_3/\text{PhCO}_2\text{Et}$ (EB) (Cat.2) at 60°C under atmospheric pressure for 7-60sec. Table 1 illustrates the time changes of the key data, i.e., the polymer yield, the isotactic index (I.I.), $[\eta]$, the number-average molecular weight (\bar{M}_n), the polydispersity (\bar{M}_w/\bar{M}_n), and the number of polymer chains produced per 1 mol of Ti ([N]) which has been calculated from the relation of polymer yield/ \bar{M}_n . The polymer obtained was separated into soluble (atactic polymer) and insoluble (isotactic polymer) fractions in boiling heptane.

Fig.1 shows the yields of isotactic and atactic polymers as a function of polymerization time, which are compared with the previously reported data (3) by $\text{MgCl}_2/\text{TiCl}_4\text{-AlEt}_3$ catalyst system (Cat.1, without EB). The yields of both of heptane-insoluble and soluble fractions were increased linearly with the polymerization time. These results mean that the propagation rate constants and the concentrations of the two active centers (isotactic-specific and atactic specific) remained constant. Comparison of the results of Cat.2 with those of Cat.1 indicates three effects of EB addition as follows:

- (1) the yield of isotactic polymer was increased about two times,
- (2) the yield of atactic polymer was decreased to one-sixth, and
- (3) \bar{M}_n of isotactic polymer was increased threefold (from $2.4 \cdot 10^4$ in ref. (3) to $6 \cdot 7 \cdot 10^4$) (see Fig.2).

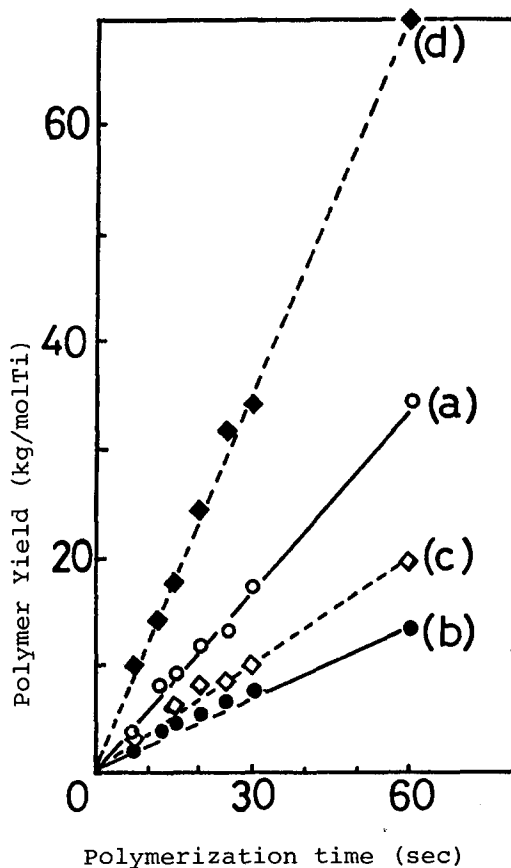


Fig.1 Time dependences of polymer yield in the polymerization of propylene with $\text{MgCl}_2/\text{TiCl}_4\text{-AlEt}_3$ catalyst system (Cat.1) and $\text{MgCl}_2/\text{TiCl}_4\text{-AlEt}_3/\text{PhCO}_2\text{Et}$ catalyst system (Cat.2). Polymerization conditions: temp. 60°C ; $[\text{propylene}] = 0.24 \text{ mol/l}$, mol ratio $\text{Al/Ti} = 25$. (a): Insoluble fraction in boiling heptane, produced with Cat.2 (with EB). (b): Soluble fraction in boiling heptane, produced with Cat.2 (with EB). (c): Insoluble fraction in boiling heptane, produced with Cat.1 (without EB). (d): Soluble fraction in boiling heptane, produced with Cat.1 (without EB).

TABLE 1
 Polymerization of propylene with $MgCl_2/TiCl_4-AlEt_3/PhCO_2Et$ (Cat.2) as catalyst^{a)}

Polymerization times (sec)	Polymer yields (kg/molTi)	I. I. (wt. %)	[η] c)			$\bar{M}_n \cdot 10^{-4}$ (g/mol)			\bar{M}_w/\bar{M}_n			$10^2 \cdot [N]$ g)	
			whole	d)	iso. e)	ata. f)	whole	d)	iso. e)	ata. f)	whole	d)	iso. e)
7	5.6	63.0	0.91	1.28	0.43	2.93	5.76	1.50	3.77	2.64	2.66	6.10	14.0
12	12.3	68.3	1.07	1.46	0.47	3.51	6.52	1.48	3.94	2.74	2.90	12.9	26.4
15	13.8	67.2	1.12	1.50	0.50	2.62	6.49	1.51	4.38	2.87	3.04	14.3	30.0
20	17.4	68.9	1.14	1.53	0.47	3.61	6.79	1.42	4.10	2.80	3.02	17.7	38.0
25	20.0	66.9	1.10	1.46	0.46	3.32	6.52	1.43	4.06	2.74	2.88	20.4	46.8
30	24.2	71.4	1.03	1.45	0.44	3.01	6.54	1.51	3.63	2.82	2.55	26.5	45.7
60	48.0	71.6	1.30	1.81	0.49	3.32	7.43	1.56	4.39	3.24	3.07	46.2	87.2

a) Polymerization conditions are given in Fig.1.

b) I. I. represents the weight fraction of polymers insoluble in boiling heptane.

c) [η] was measured viscometrically in decalin at 135°C.

d) Whole polymer.

e) Isotactic polymer (insoluble fraction in boiling heptane).

f) Atactic polymer (soluble fraction in boiling heptane).

g) [N] represents the number of polymer chains produced per titanium atom.

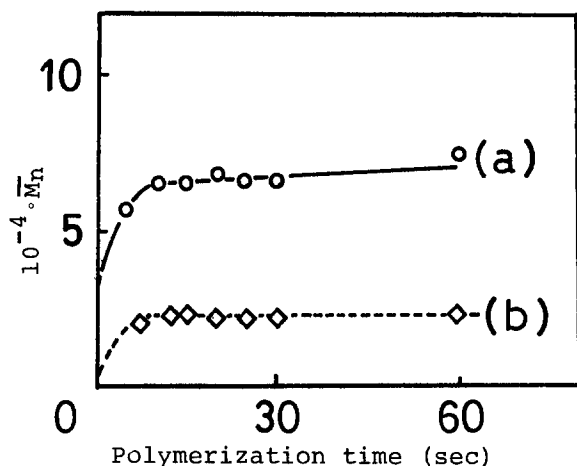


Fig.2 The change of molecular weight, M_n , of the insoluble fraction in boiling heptane (isotactic polymer) by polymerization time in the polymerization of propylene.

(a): Produced with Cat.2 (with EB). (b): Produced with Cat. 1 (without EB).

Consequently, EB increased the I.I. value of the polymer from 20% to 70%.

On the other hand, the relation between the number of polymer chain, $[N]$, and the polymer yield, Y can be expressed by Eq. (1).

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

where $[C^*]$ is the concentration of the active titanium centers, k_{tr} is chain transfer rate constant, and R is the polymerization rate. Fig.3 shows the relation between $[N]$ and Y . $[C^*]_{iso}$ and $[C^*]_{ata}$, the concentration of the isotactic-specific and the atactic-specific centers, respectively, were determined from the intercept of Fig.3 according to Eq. (1). R can be expressed by Eq. (2).

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

where $[M]$ is the propylene concentration in the solvent ($[M]=0.24 \text{ mol/l}$ under the present experimental condition). R was obtained from the slope of the straight line in Fig.1, and k_p was determined from Eq. (2). k_{tr} could be obtained from the slope of the straight line in Fig.3 and Eq. (1). τ is the mean life time of a polymer chain which has been obtained from $\tau=1/k_{tr}$. All of these kinetic parameters are listed in Table 2, which are compared with the corresponding data of Cat.1(3). From the comparison of Cat.2 (with EB) with Cat.1 (without EB) in Table 2, it can be said that by the addition of EB to the catalyst system, the concentration of the isotactic-specific active center, $[C^*]_{iso}$ was changed a little, but $k_p(iso)$ increased very much from 500-1500 ($\text{l/mol}\cdot\text{sec}$) to 2100-6300, on the other hand, the concentration of the atactic-specific active centers, $[C^*]_{ata}$, was dramatically decreased from 14-58 mol% to 2-6 mol%, but $k_p(ata)$ remained unchanged.

In order to understand the behavior of EB in the polymerizations of the present study, the supported Ti catalyst ($\text{MgCl}_2/\text{TiCl}_4$), AlEt_3 , and EB were reacted in hexane in the absence of propylene for 10-160 sec at room temperature (mol ratios of these catalyst component were same with those in polymerization condition), and the solid portion was separated by filtration and washed with hexane and dried in vacuo. GC analysis for EB on the treated solid catalyst was performed (Fig.4). As shown in Fig.4, about 8 mg of EB (7 mol% of EB added to the polymerization system) were immediately fixed on 1 g of the supported Ti catalyst and the fixed amount of EB remained almost constant during the investigated period. This fact suggests that in the poly-

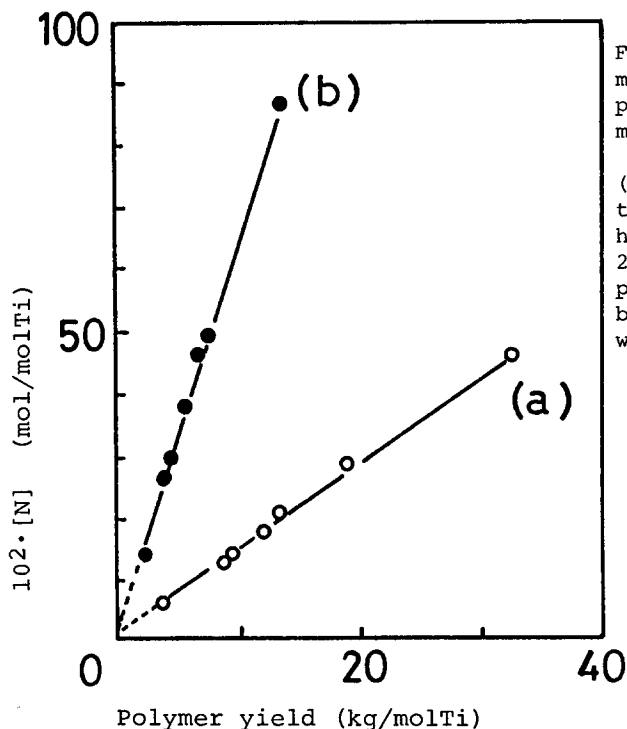


Fig.3 Relation between polymer yield and the number of polymer chains produced per mol of Ti, [N].

(a): Isotactic polymer (fractions insoluble in boiling heptane) produced with Cat. 2 (EB used). (b): Atactic polymer (fractions soluble in boiling heptane) produced with Cat.2 (EB used)

TABLE 2

Kinetic parameters of propylene polymerizations with Cat.1 and Cat.2

Cat.No.	Catalyst systems	Fractions	Polymn. rate a) (mol/molTi·sec)	I.I. (wt.%)	[C*] (mol%)	k_p (l/mol·sec)	τ (sec)
Cat.1	MgCl ₂ /TiCl ₄ - AlEt ₃	whole ^{b)}	35	21-26	20-60	240-730	
		iso. ^{c)}	8		2-6	500-1500	2-5
		ata. ^{d)}	27		14-58	200-800	
Cat.2	MgCl ₂ /TiCl ₄ - AlEt ₃ /EB ^{e)}	whole ^{b)}	20	63-76	4-7	1200-2100	3
		iso. ^{c)}	15		1-3	2100-6300	3
		ata. ^{d)}	5		2-6	350-1000	3

a) mole of propylene/mole of Ti/sec

b) Whole polymer

c) Isotactic polymer (insoluble fraction in boiling heptane).

d) Atactic polymer (soluble fraction in boiling heptane).

e) EB represents PhCO₂Et.

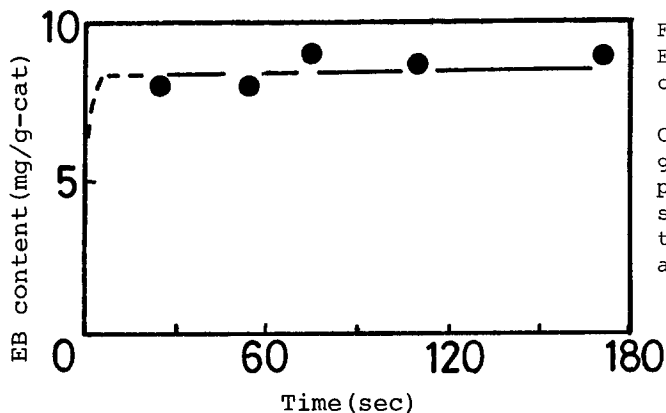


Fig.4 Time dependence of EB content in the solid catalyst.

Catalyst preparation is given in experimental part. Time in the abscissa represents the total time for reaction and separation.

merization a part of added EB is fixed on the solid catalyst quickly and maintained at least during the investigated polymerization time.

Three kinetic effects of EB which have been elucidated here can be best explained as follows. The increase of the yield of isotactic polymer was mainly due to the increase of $k_p(\text{iso})$ value, not by increase of $[\text{C}^*]_{\text{iso}}$, and the increase of M_n of isotactic polymer may be attributable to the increase of $k_p(\text{iso})$ value. On the contrary, the large decrease of the yield of atactic polymer was due to the large decrease of $[\text{C}^*]_{\text{ata}}$, but not to the decrease of $k_p(\text{ata})$ value.

From these facts, it is concluded that EB poisons preferentially the atactic-specific active centers with high selectivity, perhaps by being fixed on the coordination site and blocking the monomer coordination, and moreover it modifies the isotactic-specific active centers in the manner to increase the $k_p(\text{iso})$ value. To clarify the mechanism of the increase of $k_p(\text{iso})$ by the fixation of EB requires further studies.

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