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Effect of (s)-(+)-Ethyl-2-Phenylbutanoate and Poly(Ethylene Terephthalate) on the Polymerization of Propylene and 3-Methyl-1-Pentene over $TiCl_3$-$AlEt_3$

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Summary

(s)-(+)-Ethyl-2-phenylbutanoate was synthesized and polymerizations of propylene and racemic 3-methyl-1-pentene were conducted over $TiCl_3$-$AlEt_3$ combined with the compound. The addition of the compound caused a significant increase in the isotacticity of polypropylene as well as a substantial decrease in the activity. However, stereoelective polymerization of racemic 3-methyl-1-pentene didn't take place at all. Propylene polymerization was also carried out over $TiCl_3$-$AlEt_3$ by using poly(ethylene terephthalate) in place of the compound. The results obtained have led to the conclusion that these additives act mainly as reagents to reduce the concentration of $AlEt_3$ by the formation of the complexes between $AlEt_3$ and these additives.

Introduction

Recently numerous publications, particularly in the patent literature, have claimed a number of additives for Ziegler-Natta catalysts to improve the isotacticity of polypropylene (Montecatini Edison, 1972, Mitsui Petrochemical Industries, 1974). The precise role of such additives on the isotacticity is, however, left to be much studied.

On the other hand, it is well known that the stereochemical features of Ziegler-Natta catalysts are attributed to the chirality of the active species, the catalytic system having a substantially racemic structure, in the sence that centers with opposite chirality exist in equal amounts (PINO et al. 1961, MONTAGNOLI et al. 1969, ZAMBELLI et al. 1971, CARLIN et al. 1972, CIARDELLI et al. 1974).

To obtain a better insight into the above problem, (s)-(+)-ethyl-2-phenylbutanoate ((s)-(+)-EPB) was synthesized and racemic 3-methyl-1-pentene was polymerized over the $TiCl_3$-$AlEt_3$ system combined with the compound. Propylene polymerization was also conducted over the same catalytic system in the presence of either (s)-(+)-EPB or poly(ethylene terephthalate) (PET). From the results obtained, the role of these additives was discussed.

Experimental

Materials Commercial extra pure grade n-heptane was purified with the usual procedures. $TiCl_3$ (from Toho Titanium Co. Ltd., AA-grade) and triethylaluminum (TEA) were used without further purification. PET (from Toyobo Co. Ltd., $\bar{M}w$=10.000, obtained without using any catalyst) was used after being evacuated at 160 °C for 6 h. Research grade propylene (from Takachiho Chemical Co. Ltd.) and racemic 3-methyl-1-pentene (from Tokyo Kasei Co. Ltd., chirality; +0.003 in 10 % solution of cyclohexane) were purified according to the usual procedures. Nitrogen of ultra high purity (from Nihon Sanso Co. Ltd., 99.9995 % purity) was further purified by passing through the molecular sieve 3A colomn cooled at -196 °C.

Preparation of (s)-(+)-EPB. In a 500 ml glass reactor containing 300 ml of ethanol were added 40 mmol of (8,9R)-(-)-cinchonan-9-ol and 40 mmol of 2-phenyl butanoic acid (PBA) and the mixture was allowed to react at room temperature over night. After the reaction, most of ethanol was removed by evaporation to give solid products (salts). The salt of ((s)-(+)-PBA) with (8,9R)-(-)-cinchonan-9-ol was separated by repeated recrystallization from an aqueous solution of ethanol and hydrated by adding a dilute aqueous solution of HCl, followed by extraction with diethylether to give (s)-(+)-PBA [yield: 39 %, $[\alpha]_D^{26}$ (in benzene)=+91.0° (optical purity:99%)].

Then (s)-(+)-PBA was esterificated by ethanol according to the usual procedures to give (s)-(+)-EPB [yield:82%, $[\alpha]_D^{26}$ (in benzene):+66.2°(optical purity: 99%)].

Polymerization procedures. In a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed a measured amount of catalyst, TEA, (s)-(+)-EPB or PET in situ, and n-heptane under nitrogen. The reactor was cooled by liquid nitrogen, degassed i. vac. and then purified propylene or racemic 3-methyl-1-pentene was introduced. The polymerization was terminated by adding dilute hydrochloric acid solution in methanol. The polymer obtained was thoroughly washed with methanol and dried i. vac. at room temperature.

Analytical procedures. The molecular weight distribution of polypropylene was measured at 135 °C by gel permeation chromatography (Waters Associates, Model 200) using four polystyrene gel columns [10^7, 10^6, 10^5, and 10^4 Å pore sizes] and o-dichlorobenzene as solvent. The flow rate of solvent was maintained at 1.0 ml/min. The calibration curve of the molecular weight was obtained on the basis of the universal calibration (GRUBISIC et al. 1967, OGAWA et al. 1972) with 10 standard samples of monodisperse polystyrene with molecular weights from 2,100 to 2,610,000. The number and weight average molecular weights ($\bar{M}n$, $\bar{M}w$) were obtained by the standard procedure by using data at 1/2 count (2.5 ml elution volume). The isotacticity of the polymer was determined by the method of LUONGO (1960) with IR, from 995 and 974 cm^{-1} bands, obtained with a Hitachi EPI-G3 spectrometer. Optical rotatory measurements on the solutions (cyclohexane and tetralin, 1/1 in volume) of the polymers were carried out at 20 °C by a Japan Spectroscopic Co. Ltd. DIP-4 digital polarimeter with sensitivity ± 0.002°.

Results and Discussion

Polymerization of propylene was first conducted at 65 °C for 15 min over the $TiCl_3$-$AlEt_3$ system either in the absence or presence of (s)-(+)-EPB. In Table 1 are shown the polymerization results together with some analytical data of the polymers produced. The addition of (s)-(+)-EPB to the catalytic system caused a significant increase in the isotacticity as well as a substantial decrease in the activity. This phenomenon is quite similar to that of the polymerization over the well-known $TiCl_3$-$AlEt_3$-ethylbenzoate (EB) system.

Table 1. Results of propylene polymerization over $TiCl_3$-$AlEt_3$ combined with (s)-(+)-EPB.

(s)-(+)-EPB (mmol)	yield[a] (g)	I.I.[b] (%)	$\bar{M}w$ ($x10^{-4}$)	$\bar{M}w/\bar{M}n$
0	9.47	70	41.3	8.86
0.05	9.29	72	-	-
0.25	4.57	87	-	-
0.50	0.69	95	71.0	4.07

a) Polymerization was conducted in a 100 ml stainless steel reactor at 65 °C by using 0.03 g of $TiCl_3$, 0.5 mmol of $AlEt_3$, 10 ml of n-heptane and 18 g of C_3H_6.

b) Isotacticity index of polymer (LUONGO, 1960)

As mentioned in the introduction, the polymerization of racemic α-olefins is known to be stereoelective due to the asymmetric structuure of the catalytic complex when transition metal halides combined with optically active organometallic compounds are used as catalyst. It might be expected, therefore, that optically active polymer is obtained from the polymerization of racemic 3-methyl-1-pentene over the $TiCl_3$-$AlEt_3$ catalyst combined with (s)-(+)-EPB, if (s)-(+)-EPB actually participate in the catalytic complex. From this point of view, polymerization of racemic 3-methyl-1-pentene was investigated in the presence of (s)-(+)-EPB. The results obtained are shown in Table 2. It should be noted that stereoelective polymerization could not be achieved at all even when (s)-(+)-EPB was used in a large amount. The result strongly indicates that the reaction between $TiCl_3$ and $AlEt_3$ in the presence of (s)-(+)-EPB does not yield active sites with a predominant absolute configuration. In other words, it may be said that (s)-(+)-EPB does not actually participate in the catalytic complex.

Table 2. Results of racemic 3-methyl-1-pentene polymerization over $TiCl_3$-$AlEt_3$ combined with (s)-(+)-EPB.

(s)-(+)-EPB (mmol)	yield[a] (mg)	chirality[b]
0	850	+ 0.001[c]
0.25	137	+ 0.002[c]
0.5	15	- 0.001[d]
0.5	17	

a) Polymerization was conducted in a 100 ml stainless steel reactor at 20 °C for 120 h over 0.03 g of $TiCl_3$ and 0.5 mmol of $AlEt_3$ by using 10 ml of *n*-heptane and 2 ml of racemic 3-methyl-1-pentene.
b) ℓ = 1 dm, c) 1.25 g/dl [mixed solution of cyclohexane and tetralin (1/1 in volume)],
d) 0.40 g/dl.

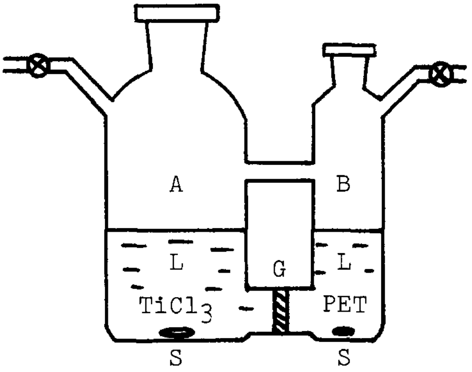
It is well established that EB, one of the typical additives reported so far for improving the isotacticity, easily reacts with $AlEt_3$ to give a complex of $EB \cdot 2AlEt_3$. It was also confirmed that a similar reaction easily proceeds between (s)-(+)-EPB and $AlEt_3$ to afford a complex of (s)-(+)-EPB$\cdot 2AlEt_3$.

We have reported in the previous paper (SOGA et al. 1967) that the isotacticity of polypropylene produced over the $TiCl_3$-$AlEt_3$ system strongly depends upon the concentration of $AlEt_3$; the lower the concentration of $AlEt_3$, the higher the isotacticity.

Therefore, it might be plausible to consider that the decrease in the concentration of $AlEt_3$ by complex formation with (s)-(+)-EPB caused the increase in the isotacticity. The remarkable increase in the molecular weight of the polymer obtained with the use of (s)-(+)-EPB (0.50 mmol) also supports this inference.

To obtain a better insight into this point of view, polymerization of propylene was conducted by using the following apparatus (Figure 1).

Figure 1.



Apparatus for propylene polymerization.
A, B : glass vessel (A:250 ml, B:100 ml),
G : glass filter (G-2), S : stirrer,
L : n-heptane solution of $AlEt_3$.

The vessel A (reactor) was separated from the vessel B by a glass filter (G). Measured amounts of $TiCl_3$ and PET were placed in the vessels A and B, respectively. Then an n-heptane solution of $AlEt_3$ was added into B, and polymerization was conducted at 65 °C for 3 h in A. Only $AlEt_3$ could pass freely through the glass filter (G), whereas PET which was insoluble in n-heptane couldn't. In Table 3 are shown the polymerization results.

Table 3. Polymerization results over $TiCl_3$-$AlEt_3$ combined with PET.

PET (g)	yield[a)] (g)	I.I. (%)	$\bar{M}w$ ($x10^{-4}$)	$\bar{M}w/\bar{M}n$
0	8.39	78	21.5	6.24
1	8.14	78	-	-
6	5.45	83	26.0	6.72
10	3.10	86	-	-

a) Polymerization was conducted in a glass reactor (Figure 1) at 65 °C by using 0.3 g of $TiCl_3$, 5 mmol of $AlEt_3$ and 125 ml of n-heptane at 1 atm of C_3H_6.

The addition of PET to the catalytic system caused a considerable increase in the isotacticity together with a substantial decrease in the activity. The results shown in Table 3 also strongly suggest that the decrease in the concentration of effective $AlEt_3$ by complex formation between $AlEt_3$ and the ester groups on the PET surface caused the increase in the isotacticity as well as the decrease in the activity.

These results may lead to the conclusion that the additives act mainly as reagents to reduce the concentration of $AlEt_3$ by complex formation. The question why does the isotacticity increase with decreasing the concentration of $AlEt_3$ is still left to be much studied.

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