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# Copolymerization of Ethylene with Propylene over the Thermally-Reduced γ-$Al_2O_3$-Supported $TiCl_4$ Catalyst

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## Summary

Copolymerization of ethylene with propylene was conducted over the thermally-reduced γ-$Al_2O_3$-supported $TiCl_4$ catalyst both in the absence or presence of $AlEt_3$ (or $AlEt_2Cl$). It was found that the structure of the polymer drastically changed from a random copolymer to polyethylene with an increase in the concentration of $AlEt_3$. A plausible mechanism was proposed for the copolymerization.

## Introduction

Many patents and publications claim the synthesis of random and block copolymers from ethylene and propylene (BOOR 1979). The copolymer composition depends on the structure of the transition metal component and sometimes on the metal alkyl component. Carrick et al. first reported that the relative reactivities of ethylene and propylene were determined exclusively by the choice of the transition metal compound and were hardly dependent on the metal alkyl compound (CARRICK et al. 1960). When $Al(i\text{-}Bu)_3$ was used as the metal alkyl component, the reactivity of propylene increased in the order: $HfCl_4 < ZnCl_4 < TiCl_4 < VOCl_3 < VCl_4$. Junghanns et al. found a decrease in the relative reactivity of ethylene when $AlEt_3$ or $AlEt_2Cl$ was replaced by $AlEtCl_2$ or $Al_2Et_3Cl_3$ with the use of $VCl_4$ or $VOCl_3$ as the transition metal compound (JUNGHANNS et al. 1962). The relative reactivity of ethylene was also found to decrease with decreasing the valence of V or Ti (NATTA et al. 1958). Thus, variability in the active site plays an important role in determining the composition of the copolymer. Among the catalysts reported so far, such soluble catalysts as $VOCl_3$ and $VCl_4$ combined with $AlEt_2Cl$ are known to be most suitable for producing a random or moderately alternating copolymer. On the other hand, block copolymers have been prepared with heterogeneous catalysts which seem to contain multiple active sites.

The copolymers of ethylene with propylene are of very importance in the family of commercial products, and industrial efforts have been directed forward finding novel and more efficient catalysts for the synthesis of the desired copolymer. However, the nature of the active sites is still left to be much studied.

In the present paper was conducted the copolymerization of ethylene with propylene over the thermally-reduced $\gamma$-$Al_2O_3$-supported $TiCl_4$ catalyst, which had previously been proved to initiate isotactic polymerization of propylene without cocatalysts (SOGA et al. 1980).

## Experimental

Materials Research grade propylene, ethylene and n-heptane (from Takachiho Chemical Co.) were purified according to the same procedures reported earlier (SOGA et al. 1977). Nitrogen of ultra high purity (from Nihon Sanso Co., 99.9989 %) was further purified by passing through the molecular sieve 3A column cooled at -196 °C. $\gamma$-$Al_2O_3$ (from Nishio Co., 140 $m^2/g$) was evacuated at 300 °C for 4 h immediately before use. The other chemicals (research grade) were also commercially obtained and used without further purification.

Preparation of the catalyst. To a solution of $TiCl_4$ in n-heptane at room temperature was added a measured amount of $\gamma$-$Al_2O_3$ which had been heated i. vac. at 300 °C for 4 h. After raising the temperature to the boiling point, the mixture was kept standing for 6 h with vigorous stirring. Then, the precipitate was filtered under nitrogen, washed with plenty of n-heptane and heated i. vac. at 90 °C for 3 h. The supported catalyst, thus prepared, was used as polymerization catalyst by heating i. vac. at 800 °C for 4 h.

Copolymerization procedures. In a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed 5 ml of n-heptane and ca. 0.5 g of supported catalyst under nitrogen. The reaction vessel was cooled by liquid nitrogen, degassed i. vac. and then measured amounts of ethylene and propylene were introduced according to a similar procedure as described (SOGA et al. 1977). The polymerization was terminated by adding plenty of dilute hydrochloric acid solution in methanol. The polymer was extracted by hot o-dichlorobenzene under nitrogen, precipitated by adding plenty of methanol and dried i. vac. at room temperature overnight.

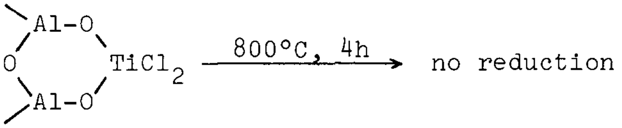
Analytical procedures. The amount of titanium contained in the catalyst was determined by atomic absorption spectrophotometry. The composition of the polymer was determined by the IR (WEI 1961) and $^{13}C$-NMR spectra (RANDALL 1978, CARMAN et al. 1977).

$^{13}$C-NMR spectra were measured at 120 °C using a JEOL JNM PS-100 spectrometer equipped with the PFT-100 Fourier transform system operating at 25.14 MHz. The pulse interval was 11 s and the number of transients accumulated were 1000 - 2000. Solutions were made up in trichlorobenzene to 3.0 weight percent. The chemical sift was represented in ppm downfield from internal tetramethylsilane (TMS).

## Results and Discussion

We have previously measured the ESR spectrum of the $\gamma$-$Al_2O_3$-supported $TiCl_4$ catalyst (composed of ca. 75 % of [1] and ca. 25 % of [2]) (SOGA et al. 1980). A considerable amount of $Ti^{4+}$ was reduced to $Ti^{3+}$ by heating the catalyst at 800 °C for 4 h (eq. 1),

$$\underset{[1],\ (\mathrm{ca.}\ 75\%)}{>\mathrm{Al\text{-}O\text{-}TiCl_3}} \xrightarrow{800^\circ\mathrm{C},\ 4\mathrm{h}} \underset{[2]}{>\mathrm{Al\text{-}O\text{-}TiCl_2}} \qquad (1)$$


[3], (ca. 25%)

(2)

and the thermally-reduced catalyst [2] initiated isotactic polymerization of propylene without cocatalysts ([1] was inactive).

[1] was completely reduced to [2] (eq. 1) when the catalyst was treated with $AlEt_2Cl$ (10 mmol/ℓ-n-heptane) at 75 °C. The reduction of [2] didn't proceed at all under the condition, while no reduction took place in case of [3] (eq. 2) as reported by Chien et al. (CHIEN et al. 1976).

On the other hand, when the catalyst was treated with $AlEt_3$ (10 mmol/ℓ-n-heptane) at 75 °C, [1] was rapidly reduced to give the mixture of [2] and further reduced titanium species ($Ti^{2+}$ and $Ti^{0}$).

Taking these results into consideration, the copolymerization of ethylene with propylene was conducted over the thermally-reduced $\gamma$-$Al_2O_3$-supported $TiCl_4$ catalyst in the absence or presence of $AlEt_3$ (or $AlEt_2Cl$). The homopolymerizations of ethylene and propylene over the catalyst without cocatalyst were first examined. As shown in runs no. 1 and 7 in Tab. I, the relative reactivities of ethylene and propylene over the present catalyst were much closer as compared with those over the conventional

TABLE I

Results of Copolymerization of Ethylene with Propylene[a)]

| Run No. | Ethylene (ℓ) | Propylene (ℓ) | Ti-supported (matom/g-cat.) | Polymer Yield (g/matom-Ti·h) | Propylene in Copolymer (mol %) | |
|---|---|---|---|---|---|---|
| | | | | | IR[b)] | $^{13}$C-NMR[c)] |
| 1 | 5.0 | 0 | 0.36 | 9.2 | - | - |
| 2 | 3.5 | 3.5 | 0.36 | 9.6 | 15 | - |
| 3 | 2.0 | 5.0 | 0.36 | 5.7 | 24 | - |
| 4 | 1.0 | 6.0 | 0.36 | 3.7 | 38 | 37 |
| 5[d)] | 1.0 | 6.0 | 0.36 | 18 | 34 | 36 |
| 6 | 0.5 | 6.5 | 0.36 | 1.4 | 51 | - |
| 7 | 0 | 7.0 | 0.36 | 0.74 | - | - |

a) Copolymerization was conducted at 65 °C for 15 min over the thermally-reduced (evacuated at 800 °C for 4 h) $\gamma$-$Al_2O_3$-supported $TiCl_4$ catalyst by using 5 ml of n-heptane in a 100 ml stainless steel reactor.
b) Ref. (WEI 1961)
c) Ref. (RANDALL 1978, CARMAN et al. 1977)
d) 0.4 mmol of $AlEt_2Cl$ was added.

titanium based catalysts (BOOR 1979). Then the copolymerization was conducted at various molar ratios of ethylene/propylene in the absence of cocatalyst.

The $^{13}$C-NMR spectrum of a typical copolymer [Fig. 2(a)] indicates that the present catalyst gives selectively a random copolymer. The addition of $AlEt_2Cl$ to the catalyst (run no. 5 in Tab. I) improved the activity, keeping the copolymer composition unchanged. This may be attributed to an increase in the concentration of [2] as mentioned above. Then the copolymerization as well as the homopolymerizations were conducted with various concentrations of $AlEt_3$. In Figs. 1 and 2 are shown the polymer yield as a function of the concentration of $AlEt_3$, and the $^{13}$C-NMR spectra of the copolymers obtained, respectively. With increasing the concentration of $AlEt_3$, the activity for propylene polymerization markedly decreased, whereas that for ethylene polymerization slightly increased.

It should be noted here that the structure of the copolymer drastically changed from a random copolymer to polyethylene with an increase in the concentration of $AlEt_3$. These results strongly suggest that only the $Ti^{3+}$ species is active for propylene polymerization as described previously (SOGA et al. 1980), while further reduced titanium species (probably $Ti^{2+}$) as well as the $Ti^{3+}$ species are active for ethylene polymerization.

The present results may lead to the following conclusion : It is most important for the production of a random copolymer of ethylene and propylene to prevent the catalyst from over-reduction.

A study on the preparation of much highly active catalysts for producing a random copolymer of ethylene and propylene is now in progress from this point of view, and the detailed results will be reported in another paper.

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The assignments of the symbols in Figure 2

(CARMAN et al. 1977)

| | |
|---|---|
| $S_{\alpha\alpha}$ | Methylene sequence length 1 |
| $S_{\alpha\beta}$ | Two in each sequence length 2 |
| $S_{\alpha\gamma}$ | Two in each sequence length 3 |
| $S_{\alpha\delta^+}$ | Two in each sequence length M > 3 |
| $S_{\beta\beta}$ | Methylene sequence length 3 |
| $S_{\beta\gamma}$ | Two in each sequence length 4 |
| $S_{\beta\delta^+}$ | Two in each sequence length M > 4 |
| $S_{\gamma\gamma}$ | Methylene sequence length 5 |
| $S_{\gamma\delta^+}$ | Two in each sequence length M > 5 |
| $S_{\delta^+\delta^+}$ | M - 6 in each sequence length M > 6 |
| $T_{\alpha\beta^+}$ | Two for each ┘└ |
| $T_{\beta\beta}$ | └ └ └ and ┘ ┘ ┘ |

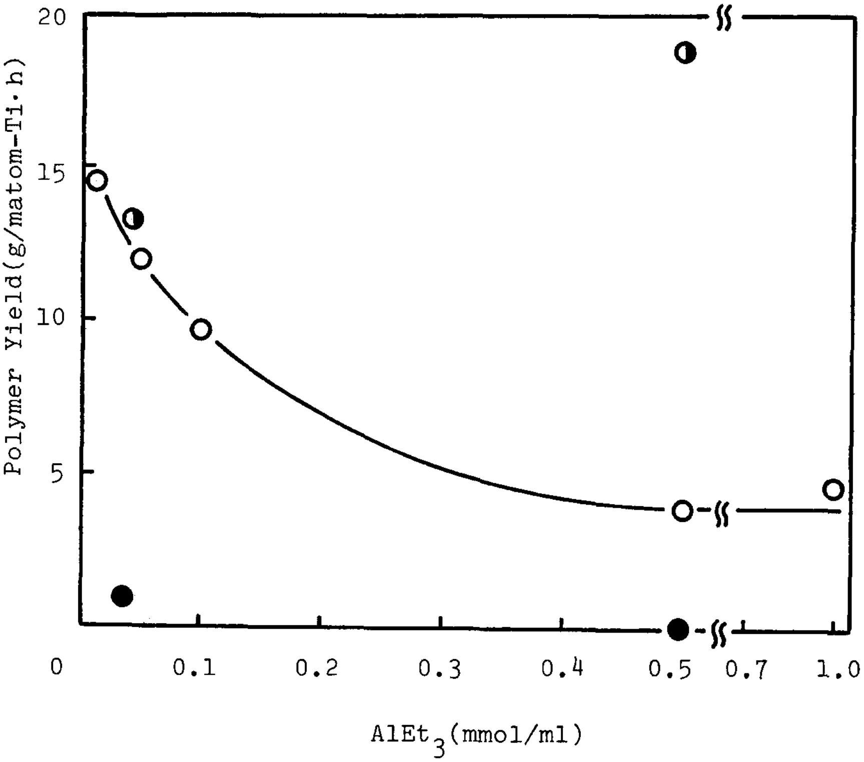

Figure 1. Dependence of polymer yield on the concentration of $AlEt_3$.
Polymerization was conducted at 65 °C over the thermally-reduced (evacuated at 800 °C for 4 h) $\gamma$-$Al_2O_3$-supported $TiCl_4$ catalyst by using 5 ml of n-heptane in a 100 ml stainless steel reactor.

○ : copolymerization of ethylene (1 ℓ) with propylene (6 ℓ)
● : homopolymerization of propylene (7 ℓ)
◑ : homopolymerization of ethylene (5 ℓ)

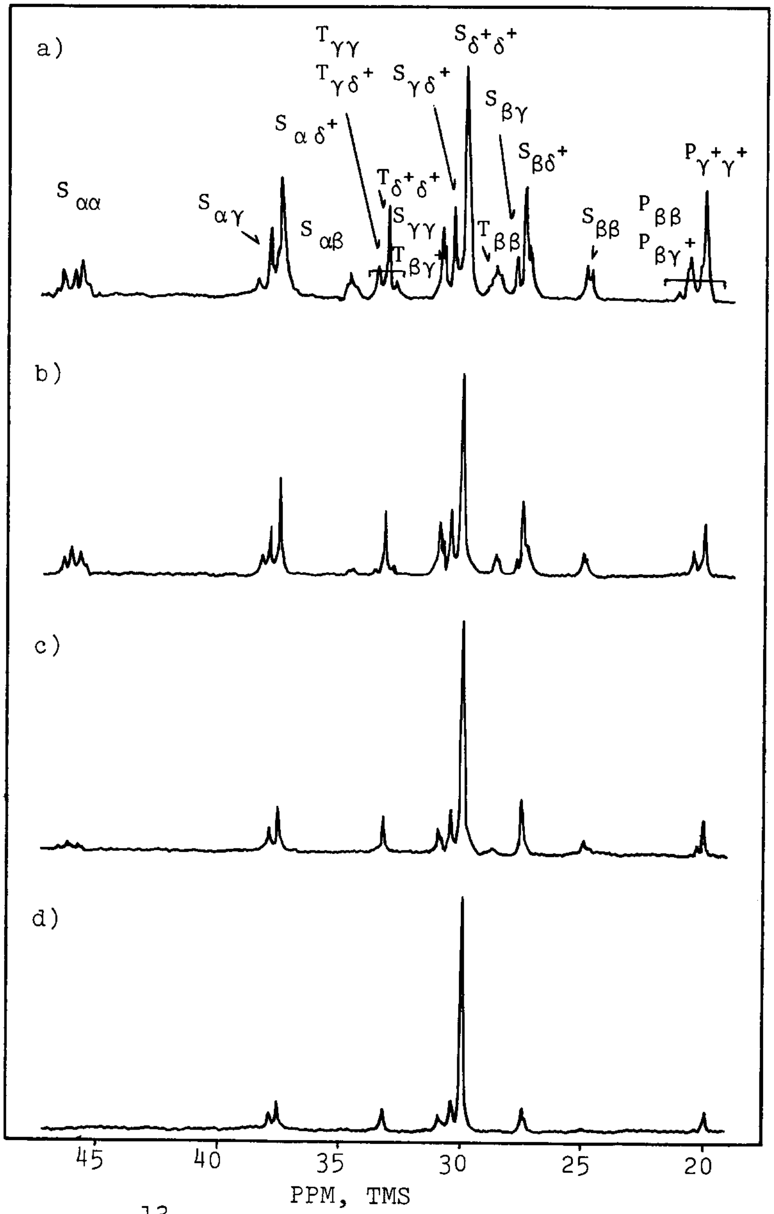

Figure 2. $^{13}$C-NMR spectra of ethylene-propylene copolymers measured at 120 °C in 1,2,4-trichlorobenzene. Copolymerization of ethylene with propylene was conducted at 65 °C over the thermally-reduced (evacuated at 800 °C for 4 h) $\gamma$-Al$_2$O$_3$-supported TiCl$_4$ catalyst by using 5 ml of n-heptane, 1 ℓ of ethylene and 6 ℓ of propylene.
a) without AlEt$_3$.
b), c) and d) with 0.01, 0.1 and 0.5 mmol-AlEt$_3$/mℓ-n-heptane, respectively.

| | |
|---|---|
| $T_{\beta\gamma^+}$ | _ └ └, _ ┘ ┘, └ └ _, └ └ ┘, └ ┘ ┘, ┘ ┘ _ |
| $T_{\gamma\gamma}$ | └ ┘ _ └ and ┘ _ └ ┘ |
| $T_{\gamma\delta^+}$ | _ _ └ ┘, _ ┘ _ └, └ _ └ ┘, └ ┘ _ _, └ ┘ _ ┘,<br>┘ _ └ _ |
| $T_{\delta^+\delta^+}$ | _ _ └ _, _ ┘ _ _, _ ┘ _ ┘, └ _ └ _ |
| $P_{\alpha\beta^+}$ | Attached to $T_{\alpha\beta^+}$ (┘└) |
| $P_{\beta\beta}$ | Attached to $T_{\beta\beta}$ (└ └ └ and ┘ ┘ ┘) |
| $P_{\beta\gamma^+}$ | Attached to $T_{\beta\gamma^+}$ (_ ┘ ┘, └ └ _, etc.) |
| $P_{\gamma^+\gamma^+}$ | Attached to $T_{\gamma\gamma}$, $T_{\delta\delta^+}$, and $T_{\delta^+\delta^+}$ |

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