

Correlation Between the Oxidation States of Titanium and the Polymerization Activities for Higher α -Olefins and Diene Compounds

Kazuo Soga, Shian-Ing Chen and Rikuo Ohnishi

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Summary

Both the homopolymerization of ethylene, propylene, 1-hexene and 1,3-butadiene and the copolymerization of ethylene with these monomers were conducted over the SiO_2 -supported TiCl_4 catalyst using AlEt_2Cl or AlEt_3 as a reducing reagent. With an increase in the concentration of AlEt_3 , the polymerization activities except for ethylene markedly decreased and the structures of the copolymers drastically changed to polyethylene. From these results, a correlation was established between the oxidation states of titanium and the polymerization activities for these monomers.

Introduction

From a detailed study of the copolymerization of ethylene and propylene over the thermally-reduced $\gamma\text{-Al}_2\text{O}_3$ -supported TiCl_4 catalyst with or without using metal alkyl compounds, we have recently found that the Ti(III) species are active for both monomers, while further reduced titanium species, probably Ti(II), are active only for ethylene (SOGA et al. 1981).

The copolymers of ethylene with higher α -olefins and/or diene compounds 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 species for the polymerization of such monomers are still left to be much studied.

From this point of view, in the present paper were carried out the polymerization of 1-hexene and 1,3-butadiene as well as the copolymerization of ethylene with these monomers over the SiO_2 -supported TiCl_4 catalyst using AlEt_2Cl or AlEt_3 as a reducing reagent, and was established the correlation between the oxidation states of titanium and the polymerization activities for these monomers.

Experimental

Materials Research grade ethylene, propylene, 1-hexene, 1,3-butadiene and n-heptane (from Takachiho Chemical Co.) were

purified according to the usual procedures. SiO_2 (from Fuji Devison Co., $300 \text{ m}^2/\text{g}$) was evacuated at 300°C for 4 h immediately before use. Nitrogen of ultra high purity (from Nihon Sanso Co., 99.9989 %) was purified by passing through the molecular sieve 3A column cooled at -196°C . The other chemicals (research grade) were commercially obtained and used without further purification.

Preparation of the SiO_2 -supported TiCl_4 catalyst To a 300 ml glass reactor equipped with a magnetic stirrer were added 50 ml of n-heptane, 16 g of SiO_2 and 20 ml of TiCl_4 under nitrogen. The mixtures were kept standing with vigorous stirring for 6 h at 98.4°C . To the reactor containing the precipitates was added 150 ml of n-heptane, and the mixtures were again kept standing with vigorous stirring for 2 h at room temperature to remove the unreacted TiCl_4 . Then the precipitates were separated by filtration under nitrogen, adequately washed with n-heptane, followed by evacuation at 90°C for 3 h and then at 300°C for 6 h.

Polymerization and analytical procedures In a 200 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of the catalyst, AlEt_3 (or AlEt_2Cl) and n-heptane under nitrogen. The reactor was cooled by liquid nitrogen, degassed i. vac. and then given amounts of purified monomers were introduced. The polymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The polymer produced was extracted by hot o-dichlorobenzene followed by dring at room temperature. The amount of titanium contained in the catalyst was determined by atomic absorption spectrophotometry ($0.55 \text{ atom Ti/g-cat}$).

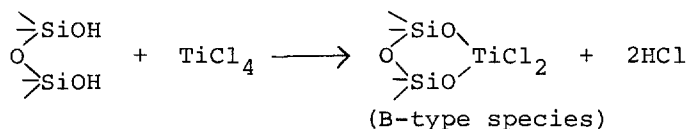
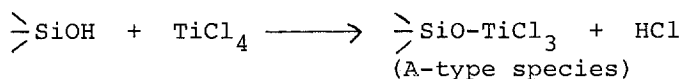
The ^{13}C -NMR spectrum of the copolymer was measured at 120°C using a JEOL JNM PS-100 spectrometer equipped with the PFT-100 Fourier transform system operating at 25.14 MHz. The pulse interval was 11 s and the number of transients accumulated were 1,000 - 2,000. Solutions were made up in o-dichlorobenzene to 3 weight percent. The chemical shift was represented in ppm downfield from internal TMS.

DSC measurements (Shimadzu Thermal Analyzer DT-30) were made at a heating rate of $10^\circ\text{C}/\text{min}$.

Results and Discussion

We have previously reported that the polymerization activity of the supported catalysts strongly depends upon the pore size of the carriers, and that the catalytic activity of the active species existing in a small pore is negligibly small (SOGA et al. 1979, SOGA et al. 1980). Therefore, #244 SiO_2 , whose average pore diameter (ca. 20 nm) is much greater than that of $\gamma\text{-Al}_2\text{O}_3$ (ca. 6 nm), was used as a carrier.

The reaction of SiO_2 with TiCl_4 in n-heptane was found to proceed according to the following scheme, and the fractions of A- and B-type species were analytically determined as 66 and 34 %, respectively (SOGA et al. 1980).



The following are established from the ESR analysis of the catalytic system (CHIEN 1971, SOGA et al. 1980).

- (1) The Ti(IV) species in the form of B-type are hardly reduced by alkylaluminum compounds.
- (2) The Ti(IV) species in the form of A-type are quantitatively reduced to Ti(III) by AlEt_2Cl .
- (3) Further reduction (Ti(III) \rightarrow Ti(II)) proceeds by using a sufficient amount of AlEt_3 .

Accordingly, we can easily control the oxidation states of titanium contained in the catalyst.

In Tab. 1 are summarized the activities for the homopolymerization obtained under various conditions. Brief results of propylene polymerization are also shown for reference.

Tab. 1 Polymerization results over the SiO_2 -supported TiCl_4 catalyst^{a)}

Monomer (mol)	Cocatalyst (mmol/l)	Polymer Yield (g/g-cat)	Activity (kg/g-Ti·h)
Ethylene (0.143)	AlEt_2Cl (50)	22.0	3.33
	AlEt_3 (50)	13.2	2.02
	AlEt_3 (100)	7.5	1.14
	AlEt_3 (500)	6.0	0.92
Propylene (0.122)	AlEt_2Cl (50)	8.0	0.30
	AlEt_3 (100)	0.4	0.02
1-Hexene (0.064)	AlEt_2Cl (50)	7.7	0.29
	AlEt_3 (50)	0.8	0.03
	AlEt_3 (100)	0 ^{b)}	0
	AlEt_3 (500)	0 ^{b)}	0
1,3-Butadiene (0.200)	AlEt_2Cl (50)	16.4	0.62
	AlEt_3 (50)	4.3	0.16
	AlEt_3 (100)	1.0 ^{b)}	0.04
	AlEt_3 (500)	0 ^{b)}	0

a) Polymerization was conducted at 65 °C for 15 min in case of ethylene and for 1 h in case of other monomers by using 50 mg of the catalyst and 5 ml of n-heptane

b) Considerable amounts of oligomers were produced

With increasing the concentration of AlEt_3 , the activities for the polymerization of propylene, 1-hexene and 1,3-butadiene markedly decreased, whereas that for ethylene polymerization didn't change so much as reported previously (SOGA et al. 1981).

The ^{13}C -NMR spectra of the copolymers of ethylene with 1-hexene obtained under typical conditions are shown in Fig. 1, which indicates that the structure of the copolymer drastically changes from a random copolymer to polyethylene with an increase in the concentration of AlEt_3 .

On the other hand, in Fig. 2 are shown the ^{13}C -NMR spectra of the copolymers of ethylene with 1,3-butadiene obtained under typical conditions. Fig. 2 clearly shows that the polymer obtained with the use of AlEt_2Cl contains a considerable amount of 1,3-butadiene. However, it seems to be difficult to judge only from the ^{13}C -NMR spectrum whether the polymer is actually a copolymer or the mixture of polyethylene and polybutadiene.

To obtain a better insight into this point, DSC measurements were made on the polymer together with polyethylene and polybutadiene obtained with the use of AlEt_2Cl . From the results shown in Fig. 3, it may be said that the polymer is actually a copolymer of ethylene and 1,3-butadiene. In Tab. 2 are summarized the copolymerization activities together with the contents of comonomers.

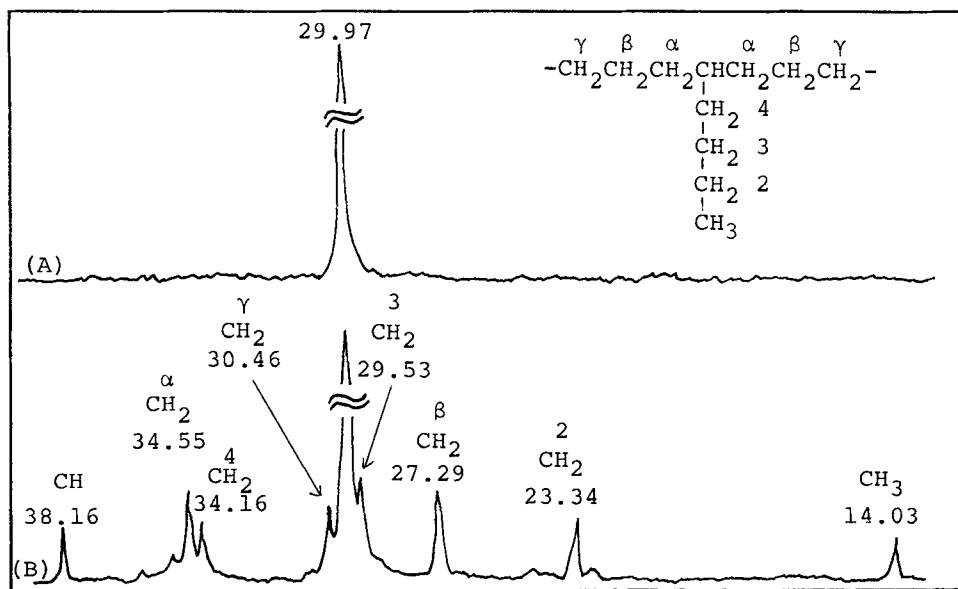


Fig. 1 ^{13}C -NMR spectra of the ethylene-1-hexene copolymers measured at 120 °C in *o*-dichlorobenzene. Chemical shifts are in ppm from TMS (RANDALL 1973).

(A): Obtained by using 200 mmol- AlEt_3 /1-n-heptane

(B): Obtained by using 50 mmol- AlEt_2Cl /1-n-heptane

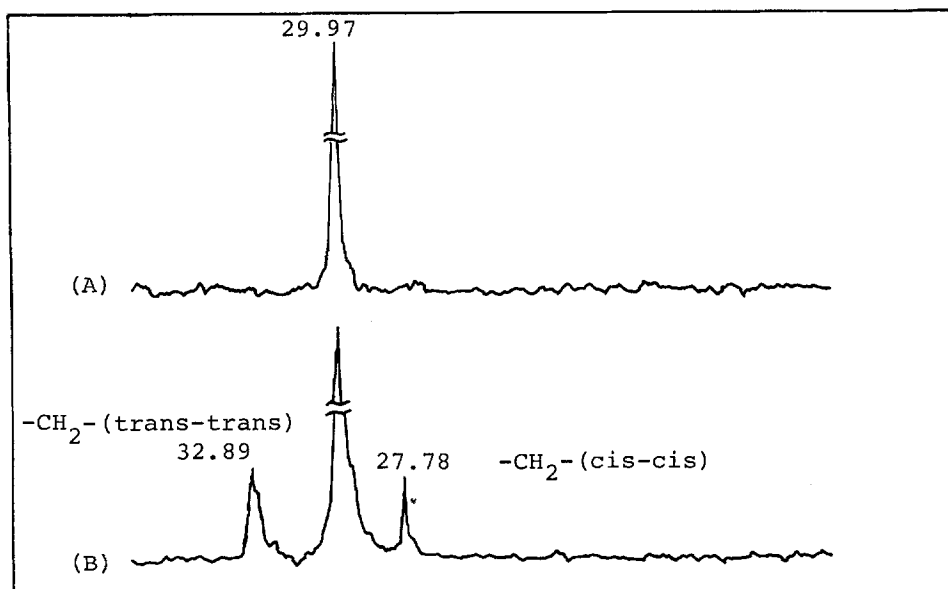


Fig. 2 ^{13}C -NMR spectra of the ethylene-1,3-butadiene copolymers measured at 120 °C in *o*-dichlorobenzene. Chemical shifts are in ppm from TMS (TANAKA et al. 1977).

(A): Obtained by using 200 mmol- AlEt_3 /1-n-heptane

(B): Obtained by using 50 mmol- AlEt_2Cl /1-n-heptane

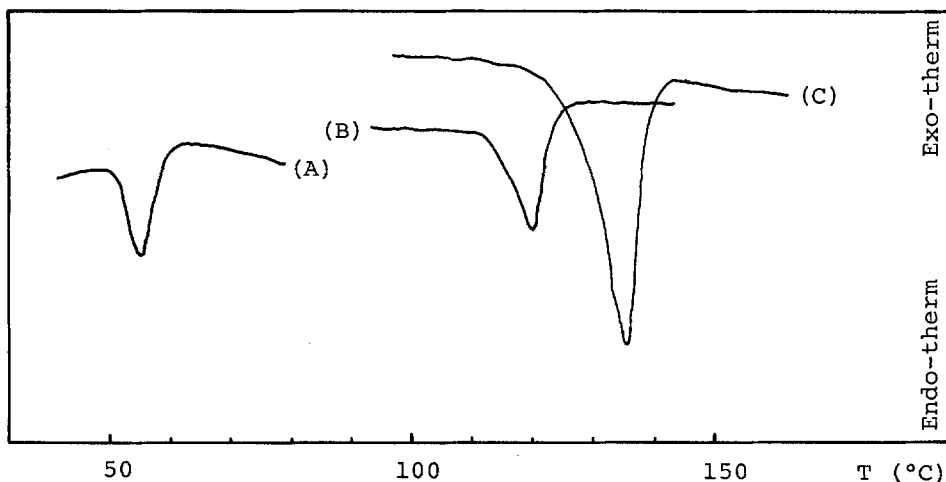


Fig. 3 DSC curves of the copolymer, polyethylene and polybutadiene obtained by using AlEt_2Cl ($\Delta T=10^\circ\text{C}/\text{min}$ in N_2).

(A): Polybutadiene, (B): Copolymer, (C): Polyethylene

Tab. 2 Copolymerization results over the SiO₂-supported TiCl₄ catalyst^{a)}

Comonomer (mol)	Cocatalyst (mmol/l)	Activity (kg/g-Ti·h)	Content of Comonomer (%)
1-Hexene (0.064)	AlEt ₂ Cl (50)	1.44	18.0
	AlEt ₃ (200)	0.55	0
1,3-Butadiene (0.143)	AlEt ₂ Cl (50)	0.81	7.2
	AlEt ₃ (200)	0.05	0

a) Copolymerization was conducted at 65 °C for 1 h by using 0.143 mol of ethylene, 50 mg of the catalyst and 10 ml of n-heptane

The present results combined with the previous ones strongly suggest that the Ti(III) species are active for the polymerization of various α -olefins and diene compounds, while further reduced titanium species (probably Ti(II)) are active only for ethylene polymerization.

Therefore, it seems to be most important for the production of the copolymers of ethylene with various α -olefins and/or diene compounds to prevent the catalyst from over-reduction. However, the reason why only ethylene is exceptional is still obscure at present.

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Received October 4, accepted October 5, 1982