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Takashi Tsujino[a]; Atsushi Kaiya[a]; Nobuyuki Kuroda[a]; Mikio Takahashi[a]
[a] Central Technical Research Laboratory Nippon Oil Co. Yako, Kawasaki Kanagawa, Japan

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Polymerization of Ethylene with Al-Ti Oxychloride/Alkylaluminum Catalysts

TAKASHI TSUJINO, ATSUSHI KAIYA, NOBUYUKI KURODA, and MIKIO TAKAHASHI

Central Technical Research Laboratory
Nippon Oil Co.
Yako, Kawasaki
Kanagawa, Japan

SUMMARY

Al-Ti oxychloride was prepared by reacting $AlCl_3$ and $TiCl_4$ with the equimolar amount of water in ethyl ether, followed by thermal treatment of the reaction product. Polymerization of ethylene with the catalyst consisting of Al-Ti oxychloride and $Al(C_2H_5)_3$ or $(C_2H_5)_2AlCl$ was studied. With respect to the catalyst activity, Al/Ti oxychloride having a ratio of 1/1 was found most desirable, and the chlorine content in the oxychloride was of importance and significance. Hydrogen was used for controlling the molecular weight of the polymer. Two peaks of high catalyst activity were observed, one at about 70°C (slurry region) and the other at about 160°C (solution region).

Effects of the conditions of polymerization with Al-Ti oxychloride-$(C_2H_5)_2AlCl$ catalyst on the structure of the polyethylene, which was found to be of high density and high stiffness, are discussed. The amount of double bonds in the polyethylene was very small, but they were mostly of the vinyl group type.

INTRODUCTION

Two types of catalyst for preparing high density polyethylene have been known. One comprises a mixture of a metal alkyl and a transition metal compound, i.e., a Ziegler-type catalyst, and the other consists of a transition metal oxide on a silica-alumina support. Some catalyst components that may be regarded as an intermediate material between transition metal halides and oxides have been reported. For instance, molybdenum oxide/γ-alumina treated with hydrogen halides [1] and titania/alumina catalyst treated with chlorine [2] were used as a component of the catalyst for polymerizing ethylene.

Titanium oxychloride is also considered to be an intermediate material between $TiCl_4$ and TiO_2. Some oxychlorides have been prepared by various methods [3-5]. According to the patent literature, disclosed by Artrite Resins Ltd. [6], aluminum oxychloride is prepared by heating a hydrolysis mixture of $AlCl_3$ with the equimolar amount of water in ethyl ether. In this patent literature it is also claimed that Al-Ti oxychloride copolymer can be prepared from $AlCl_3$, $TiCl_4$, and water in a similar manner though no clear evidence to define the claimed product as a true copolymer is presented.

In the course of our work the product obtained by the thermal treatment of the partial hydrolyzate of $AlCl_3$ and $TiCl_4$ was found to be a complicated material which includes Al-Ti oxychloride, and it initiated the polymerization of ethylene when it was combined with aluminum alkyls. In this paper we describe some aspects of the Al-Ti oxychloride/aluminum alkyls system as a catalyst for polymerization of ethylene. The behavior of polymerization under various conditions and some properties of polyethylenes prepared by this catalyst are reported.

EXPERIMENTAL

Synthetic Procedure of Al-Ti Oxychloride

Aluminum-titanium oxychlorides were prepared according to Artrite Resins' method [6]. The following is a typical procedure of the synthesis.

A 200-ml flask equipped with a dropping funnel, a reflux condenser, and an agitator was used as a reactor. Anhydrous $AlCl_3$ (13.3 g) was dissolved in 50 ml of ethyl ether under an atmosphere of nitrogen, and then 2.2 ml of $TiCl_4$ was added. To the refluxing mixture, 2.16 ml of water was added in 20 min, and refluxing was continued for 5 hr. The ether was distilled off from the reaction mixture, and the residue was kept in the temperature range 80-120°C for about 2 hr in order to remove hydrogen chloride. The pale brown solid obtained was analyzed as described below and it was found to be a crude Al-Ti oxychloride, which was used as a catalyst component without further purification.

Analytical Method of Al, Ti, and Cl

Aluminum and Titanium. Al-Ti oxychloride was hydrolyzed with water. After drying the hydrolyzed mass was fused with potassium pyrosulfate. The fused material was dissolved in aqueous sulfuric acid at pH 2~3. The solution was analyzed for Al and Ti by complexometric titration [7]. A sample, containing 1-10 mg Al and Ti, was kept at pH 3 by addition of aqueous acetic acid and then it was heated with an excess of ethylenediaminetetraacetic acid disodium salt (EDTA) for 30 min up to the boiling point. After cooling of the sample solution, uncomplexed EDTA was titrated by aqueous zinc acetate with xenol orange as an indicator. The amount of Al plus Ti could be calculated from this titration.

For the determination of Al alone, titanium ion was extracted with Cupferron in chloroform solution from the aqueous H_2SO_4 solution of the sample fused with potassium pyrosulfate [8]. Aluminum was determined by titration similar to the determination of Al plus Ti.

Chlorine. Al-Ti oxychloride was dissolved in dilute nitric acid and then chlorine was determined by Volhard's method [9].

Polymerization Procedure

Polymerization was carried out in 100 ml, 300 ml, and 2 liter autoclaves equipped with agitators. The reactor was purged with dry nitrogen in which Al-Ti oxychloride and aluminum alkyl as catalysts and n-heptane or toluene as a solvent were introduced. Ethylene was then introduced into the autoclave from a cylinder to a predetermined polymerization pressure. Polymerization was started at the polymerization temperature by agitating the reaction mixture. During polymerization the pressure in the reactor was maintained by an additional supply of ethylene. If hydrogen was used as a moderator for the molecular weight of the polymer, ethylene and hydrogen were introduced at the predetermined partial pressures, and the total pressure of the reaction mixture was adjusted by an additional supply of ethylene alone.

Ethylene was purged after 2 hr, and the polymer was recovered by pouring the polymerization mixture into isopropanol/hydrochloric acid solution. The polymer was washed several times with isopropanol and dried at 50°C in vacuum for 20 hr.

Determination of Properties of Polymer

The molecular weight of the polymers was calculated by Natta's equation [10], $[\eta] = 1.76 \times 10^{-4} M_V^{0.81}$, from intrinsic viscosity obtained in the xylene solution at 105°C.

Methyl group and double bonds were analyzed by IR spectroscopy. The compensation technique used for the methyl group analysis was essentially similar to that described in ASTM D 2238-64T, Method B. The type of double bonds was examined on a film sample by means of IR bands at 965 cm^{-1} (vinylene), 909 cm^{-1} (vinyl), and 890 cm^{-1} (vinylidene). Molar extinction coefficients reported by Kock and Hol [11] were used for the determinations.

Melt index, density, and stiffness of polyethylene were determined by the methods described in ASTM D 1238-62T, D 1505-63T, and D 747-63, respectively.

RESULTS AND DISCUSSIONS

Composition of Al-Ti Oxychloride

In Table 1 is shown a typical result of elementary analysis for a pale brown solid which was prepared from $AlCl_3$, $TiCl_4$, and water (molar ratio 1/1/2).

Table 1. Typical Examples of Elementary Composition of Al-Ti Oxychloride

	Content (wt %)	Atomic ratio/Ti
Al	11.51	1.02
Ti	20.05	1.00
Cl	33.60	2.26
C[a]	5.50	1.09
H[a]	3.40	8.29

[a] Determined by F&M CHN Analyzer.

The ratio of Al/Ti (= 1) is consistent with that of the reactants, $AlCl_3/TiCl_4$. The chlorine content is appreciably lower than the expected value for the formula corresponding to $AlOCl \cdot TiOCl_2$. Moreover, the C and H analyses show the presence of considerable amounts of organic materials in addition to Al-Ti oxychloride.

Effect of Ti/Al Ratio in Al-Ti Oxychloride on Polymerization

Al-Ti oxychlorides with different molar ratios of Ti/Al were prepared by changing the molar ratios of $TiCl_4/AlCl_3$ in the feed. The catalyst activities of these Al-Ti oxychlorides, combined with $Al(C_2H_5)_3$, were estimated in the polymerization of ethylene in a 100-ml autoclave. The results are shown in Fig. 1.

The Al-Ti oxychloride/$Al(C_2H_5)_3$ system showed the catalyst activity over a wide range of the ratio Ti/Al in oxychoride. The highest activity of the catalyst was observed in the 1/1 ratio of Ti/Al oxychloride.

As shown in Table 2, the results of the polymerization with Ti oxychloride were compared with those obtained with Al-Ti oxychloride. Here, Ti oxychloride was prepared from $TiCl_4$ and water by the same procedure as that of Al-Ti oxychloride preparation. The activity of Ti oxychloride/$Al(C_2H_5)_3$ is lower than that of Al-Ti oxychloride/$Al(C_2H_5)_3$ over a wide range of the $Al(C_2H_5)_3$/Ti ratio. Noticeably, 1/60-Ti/Al oxychloride, combined with $Al(C_2H_5)_3$, showed catalyst activity, in spite of the very small amount of titanium used in the catalyst system. On the other hand, under the same conditions, Ti oxychloride/$Al(C_2H_5)_3$ showed no catalyst activity. These facts indicate that AlOCl in Al-Ti oxychloride is of importance for increasing the activity of catalyst.

Effect of Molecular Weight Moderators

In the preliminary experiment described above, Al-Ti oxychloride/$Al(C_2H_5)_3$ was found to show good catalyst activity for the polymerization of ethylene under study. The effects of some molecular weight moderators were examined in the polymerization with Al-Ti oxychloride combined with $Al(C_2H_5)_3$ and $(C_2H_5)_2AlCl$.

Diethyl aluminum chloride/Al-Ti oxychloride system also showed a good catalyst activity, which is comparable to that of Al-Ti oxychloride/$Al(C_2H_5)_3$ system. In the moderators as shown in Table 3, the addition of some zinc compounds, i.e., $Zn(C_2H_5)_2$, $ZnCl_2$, and zinc acetyl acetonate (acac), decreased not only the molecular weight but also the yield of polymer. Apparently these zinc compounds caused both chain transfer and termination although they have been known to be useful moderators of

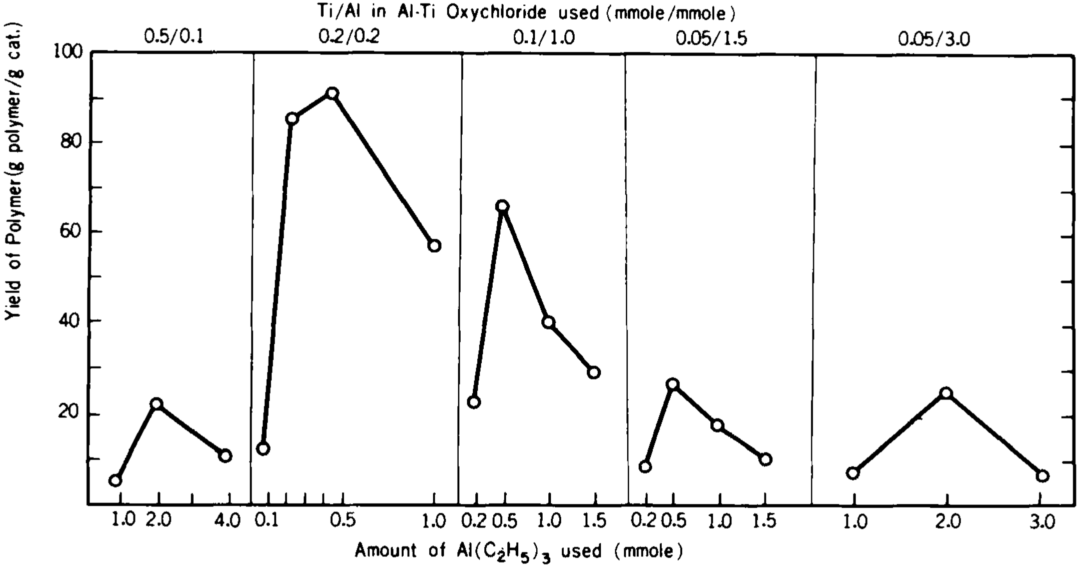


Fig. 1. Polymerization of ethylene with $Al(C_2H_5)_3$/Al-Ti oxychlorides, having different ratio. Polymerization conditions: Pressure of ethylene 30 $kg/cm^2 \cdot g$; 50 ml of n-heptane as a solvent. Polymerization was carried out in a 100-ml autoclave at 30°C for 2 hr.

molecular weight in polymerization with Ziegler catalyst [13-15]. On the other hand, in the case of hydrogen used as a moderator, the yield of polymer was not affected, but its molecular weight was decreased. Thus, hydrogen is an efficient chain transfer agent in polymerization with this catalyst. In the hydrogen-moderator experiments, Al-Ti oxychloride/ $(C_2H_5)_2AlCl$ catalyst gave a slightly lower molecular weight polymer than that given with Al-Ti oxychloride/$Al(C_2H_5)_3$.

Effect of Chlorine Content in Al-Ti Oxychloride

Al-Ti oxychloride is, admittedly, of rather complicated composition. It is therefore expected that the activities of the catalyst may be changed by the preparative recipes and conditions. The procedure for preparing the oxychloride can be considered in three stages. The first one is the reaction of $AlCl_3$ and $TiCl_4$ with water in ethyl ether. In this stage the

Table 2. Comparison of Catalyst Activity for Al-Ti Oxychloride to Ti Oxychloride[a]

Catalysts				
Al-Ti Oxychlorides			Yield of	
Al component (mmole)	Ti component (mmole)	$Al(C_2H_5)_3$ (mmole)	polymer (g)	Polymer (g)/ Ti oxychloride (g)
–	0.2	0.4	0.36	13
0.2	0.2	0.4	8.03	297
–	0.2	1.0	1.55	57
1.0	0.2	1.0	10.66	395
–	0.1	1.0	1.0	74
0.5	0.05	0.5	6.7	993
–	0.1	2.0	4.5	334
1.5	0.05	1.0	4.5	668
–	0.05	2.0	0	0
3.0	0.05	2.0	11.34	1680

[a] Polymerization conditions: pressure of ethylene, 30 kg/cm^{2}g (constant); solvent 50 ml of toluene. Polymerization was carried out in a 100-ml autoclave at 30°C for 2 hr.

Table 3. Effects of Moderators on Molecular Weight of Polymer Prepared with Al-Ti Oxychloride Catalyst[a]

Catalyst system	Moderator (mmole)	Temp. (°C)	Yield of polymer (g polymer/g catalyst)	MW, $M_V \times 10^{-4}$
$Al(C_2H_5)_3$–Al-Ti oxychloride (2:1)	None	30	91.3	160
	$ZnEt_2$ 0.1	"	84	74
	$ZnEt_2$ 0.3	"	22	53
	$ZnCl_2$ 0.3	"	66	70
	$Zn(acac)_2$ 0.3	"	25	70
	None	70	188	130
	$ZnEt_2$ 0.6	"	25	20

	Zn(acac)$_2$ 1.6	"	25	60
	Hydrogen[d]	"	187	18.3
$(C_2H_5)_2AlCl$–Al-Ti oxychloride (2:1)[c]	None	70	206	46
	ZnEt$_2$ 0.6	"	110	16
	ZnCl$_2$ 0.6	"	121	26
	Hydrogen[d]	"	178	15

[a] Polymerization was carried out in 150 ml of n-heptane at an ethylene pressure of 30 kg/cm^{2}g for 2 hr.

[b] $Al(C_2H_5)_3$ 1.2 mmole, Al-Ti oxychloride (Al/Ti = 1) 0.6 mmole as Ti.

[c] $(C_2H_5)_2AlCl$ 1.2 mmole, Al-Ti oxychloride (Al/Ti = 1) 0.6 mmole as Ti.

[d] Ethylene and hydrogen were fed initially at a partial pressure of 20 kg/cm^2, respectively. During polymerization the pressure of the reaction mixture was kept at 40 kg/cm^{2}g by an additional supply of ethylene.

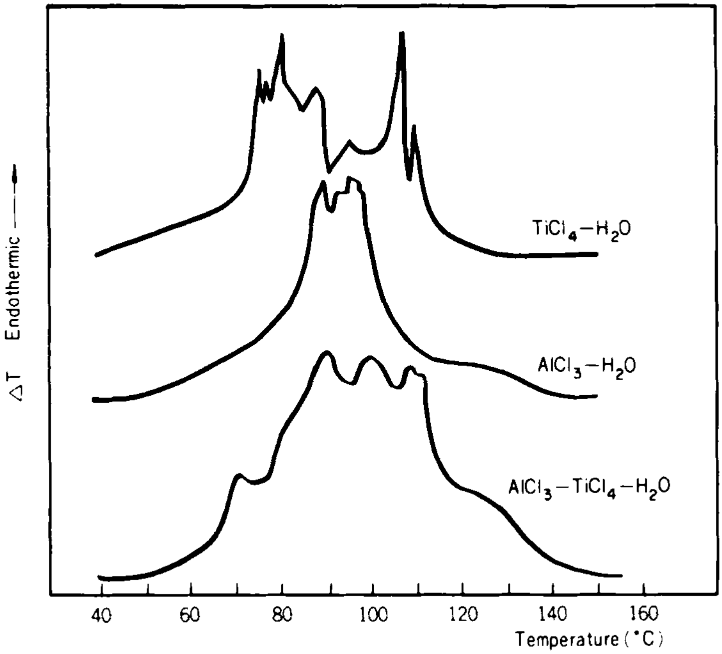


Fig. 2. Thermograms on preparation of Al oxychloride, Ti oxychloride, and Al-Ti oxychloride.

amount of water and the reaction temperature may be the factors affecting the nature of the oxychloride. The second one is the removal of ethyl ether from the reaction product obtained in the first stage. This stage was found to have a minor influence on the catalyst activity and the chlorine content of the Al-Ti oxychloride. The third one is the thermal treatment or the pyrolysis of the residual material. The preferable pyrolysis temperature was determined by the differential thermal analysis of the second stage product. Figure 2 shows the thermograms of three semisolids, i.e., the second stage products, which were prepared from $TiCl_4-H_2O$, $AlCl_3-H_2O$, and $AlCl_3-TiCl_4-H_2O$, respectively.

For the $TiCl_4-H_2O$ system, endothermal peaks appeared at 80° and 110°C. For the $AlCl_3-H_2O$ system, a broad peak was observed at about 90°. For the $AlCl_3-TiCl_4-H_2O$ system, some broader peaks were observed at the temperature range 80-110°, and no peaks appeared above 120°; therefore, 120° was selected as the preferable pyrolysis temperature.

Several lots of 1/1-Ti/Al oxychlorides were prepared under various

Table 4. Catalytic Activity and Composition of 1/1-Al/Ti Oxychlorides Prepared in Various Conditions[a]

Lot No.	Hydrolysis condition: Amount of water (mole/mole Ti)	Hydrolysis condition: Temp. (°C)	Duration of thermal treatment (hr)	Elementary ratio: Ti	Elementary ratio: Al	Elementary ratio: Cl	Activity of catalyst (g polymer/g catalyst)
1	2	50	1	1.00	1.00	3.71	179
2	"	"	2	1.00	0.93	2.79	166
3	"	"	3	1.00	1.02	2.41	219
4	"	80	5	1.00	1.03	2.54	200
5	"	"	2	1.00	1.02	2.26	266
6	3	80	3	1.00	0.99	1.95	18
7	"	50	3	1.00	0.99	2.07	85
8	4	80	3	1.00	1.01	1.97	10
9	2	80	20 (40°C in vacuum)	1.00	1.14	4.36	177

[a] Catalytic activity was determined by polymerization of ethylene under the following conditions: $(C_2H_5)_2AlCl$, 1.2 mmole; Al-Ti oxychloride, 0.6 mmole (as Ti); 150 ml of n-heptane as solvent; partial pressure of ethylene, 20 kg/cm^{2}g; partial pressure of hydrogen, 20 kg/cm^{2}g. Polymerization was carried out in a 300-ml autoclave at 70°C for 2 hr.

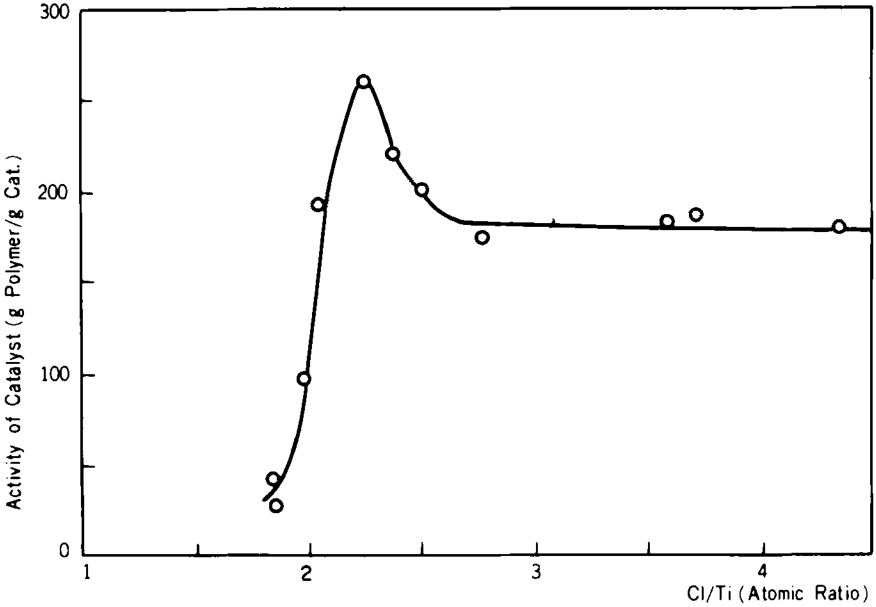


Fig. 3. Correlation between chlorine content in oxychloride and catalyst activity for polymerization. Polymerization was carried out in a 300-ml autoclave.

conditions where the above-mentioned factors were changed. As shown in Table 4, the chlorine content was decreased as the amount of water and the time of pyrolysis were increased.

Polymerization of ethylene with these oxychlorides of varying chlorine content, combined with $(C_2H_5)_2AlCl$, was carried out in a 300-ml autoclave where hydrogen was used for the control of molecular weight of the polymers. Figure 3 shows the plots of the activity of the catalysts versus the ratio of Cl/Ti in Al-Ti oxychlorides.

The highest activity was observed at Cl/Ti = 2.3. This ratio is a little lower than that corresponding to the formula $AlOCl \cdot TiOCl_2$. When the Cl/Ti ratio was higher than that of $AlOCl \cdot TiOCl_2$, the increase in Cl/Ti ratio in Al-Ti oxychloride did not influence the activity of the catalyst. On the other hand, when the Cl/Ti ratio was decreased below the optimum value, the activity of the catalyst was decreased very sharply.

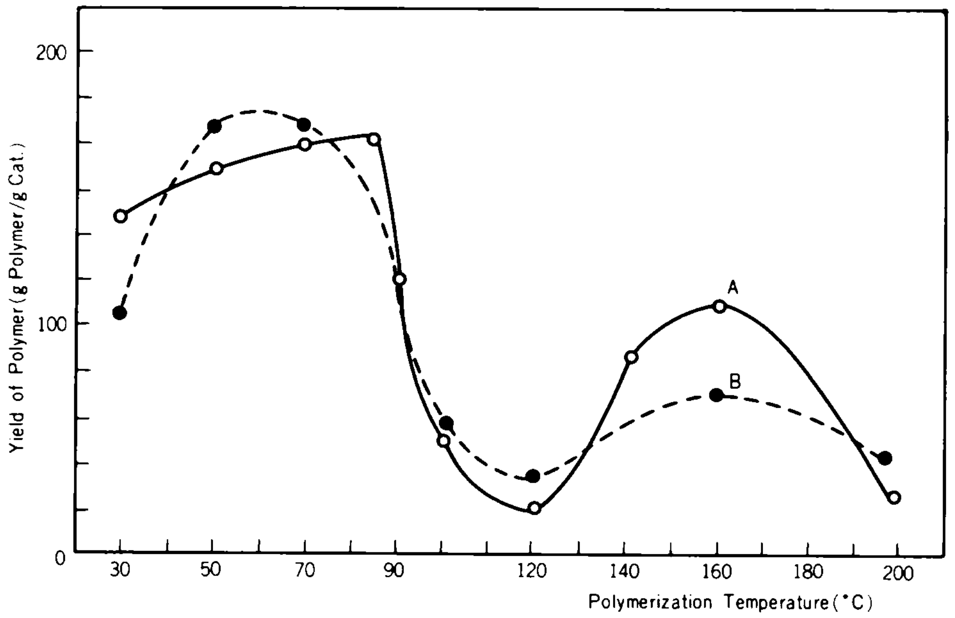


Fig. 4. Effect of temperature on the yield of polymer. Catalyst: $(C_2H_5)_2AlCl$ 1.2 mmole, Al-Ti oxychloride 0.6 mmole as Ti. Polymerization for 2 hr. A; Partial pressure of ethylene 20 kg/cm^2, and partial pressure of hydrogen 20 kg/cm^2. B: Pressure of ethylene 30 kg/cm^2.g.

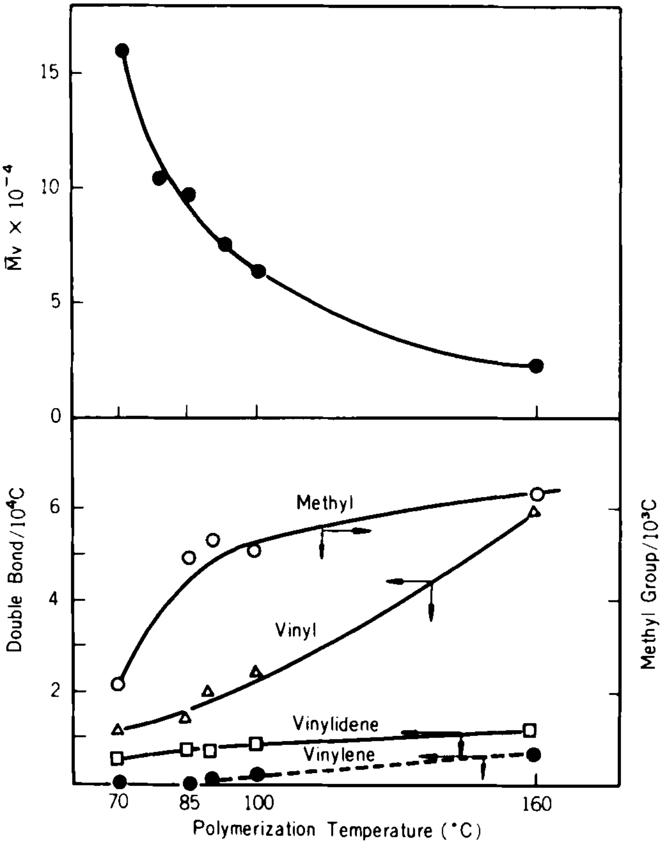


Fig. 5. Effect of polymerization temperature on molecular weight and structure of polyethylene. Polymerization was carried out in a 300-ml autoclave for 2 hr under partial pressure of ethylene 20 kg/cm^2 and of hydrogen 20 kg/cm^2. Other conditions were same as those shown in Fig. 4.

Effect of Temperature on Yield of Polymer

Figure 4 shows the relation between temperature and yield in the polymerization with Al-Ti oxychloride/$(C_2H_5)_2AlCl$. The yield of polymer was high at about 70°C, dropped abruptly at about 120°C, and then increased again at about 160°C. This pattern may well be explained by the change of the dispersion state of the reaction mixture which has already been reported by Juveland and co-workers [12]. At temperatures below 85°C, the polymer formed in fine powders, which will suspend in n-heptane used as solvent. At about 120°C, the polymer swells in the solvent and occludes the catalyst. However, at temperatures above 140°C the polymer melts and becomes soluble in the solvent.

Thus, the yield-temperature relationship is understandable when the dispersion-state of the reaction mixture is considered; i.e., the formation of well dispersed slurry and the dissolution of the polymer in the polymerization give higher yield of polymer, while the formation of swollen gel prevents the progress of polymerization.

Correlation between Polymer Properties and Polymerization Conditions

Figure 5 shows the effect of the polymerization temperature on the molecular weight and the structure of the polymer (i.e., amounts of methyl groups and double bonds). The molecular weight of the polymer decreased with an increase in the polymerization temperature.

Methyl and vinyl groups were increased remarkably with temperature. As hydrogen was used for controlling the molecular weight in these polymerization reactions, the amount of methyl group was comparatively large. However, in Fig. 5 it was observed that the temperature dependency of the increase in methyl group was different from that of the increase in vinyl group. Figure 7 shows the plots of methyl groups and double bonds versus the inverse molecular weight, respectively, the data being taken from Fig. 5. The number-average molecular weight of the polyethylenes formed was approximately 1/10 of $\bar{M}_v$; for the molecular weight dispersity, $\bar{M}_w/\bar{M}_n$, which was determined for a few samples of these polymers on gel permeation chromatography, it was about 10 [16]. Therefore, the methyl groups and double bonds content were mostly contributed by the end groups. Most of the methyl groups are supposed to be formed by the chain transfer of growing chains to hydrogen, and the vinyl groups are formed by the chain transfer to ethylene, as shown in the following scheme.

$$[\mathrm{Cat}]\overset{*}{\mathrm{C}}\mathrm{H_2{-}CH_2}\sim\!\sim\!\sim\mathrm{P} + \mathrm{H_2} \longrightarrow [\mathrm{Cat}]\overset{*}{\mathrm{H}} + \mathrm{CH_3{-}CH_2}\sim\!\sim\!\sim\mathrm{P}$$

$$[\mathrm{Cat}]\overset{*}{\mathrm{C}}\mathrm{H_2{-}CH_2}\sim\!\sim\!\sim\mathrm{P} + \mathrm{CH_2{=}CH_2} \longrightarrow [\mathrm{Cat}]\overset{*}{\mathrm{C}}\mathrm{_2H_5} + \mathrm{CH_2{=}CH}\sim\!\sim\!\sim\mathrm{P}$$

The increase in vinyl groups was approximately linear to the inverse molecular weight, though the increase in methyl groups was not linear. Although the values of vinyl content are too small for the mechanism of chain transfer to be discussed quantitatively, the results in Figs. 5 and 7 suggest that the

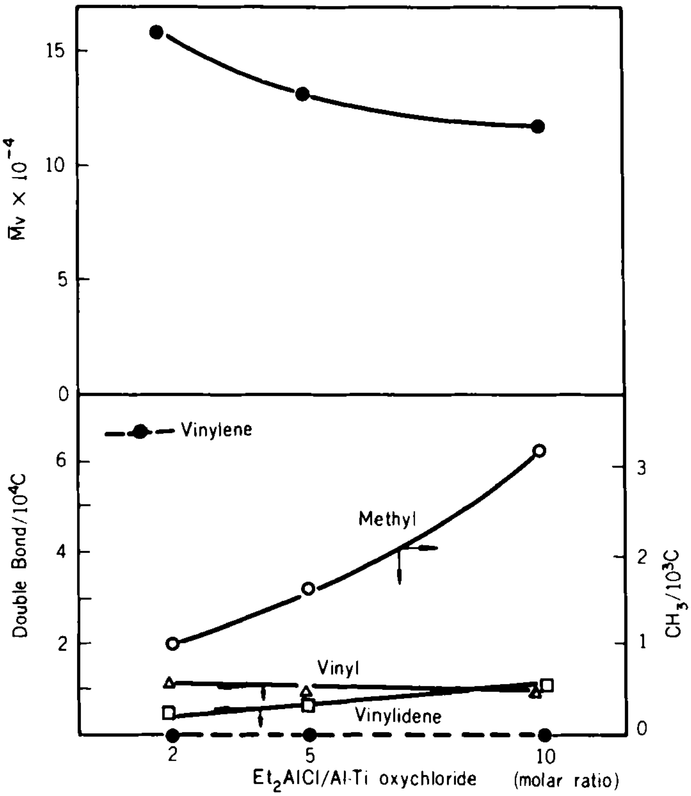
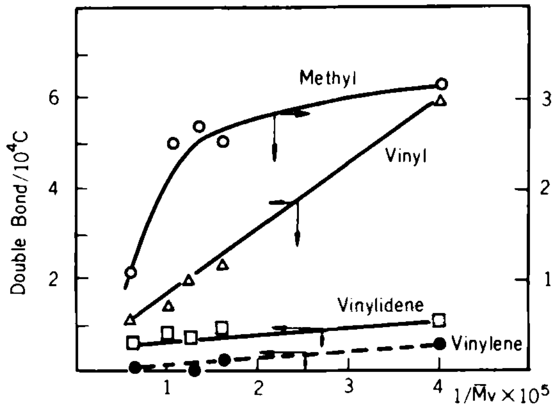


Fig. 6. Effect of molar ratio of $(C_2H_5)_2AlCl$/Al-Ti oxychloride on molecular weight and structure of polyethylene. Polymerization conditions: Catalyst; Al-Ti oxychloride 0.6 mmole. Partial pressure of ethylene 20 kg/cm^2, partial pressure of hydrogen 20 kg/cm^2. Solvent: n-heptane 150 ml. Polymerization was carried out at 70°C for 2 hr.

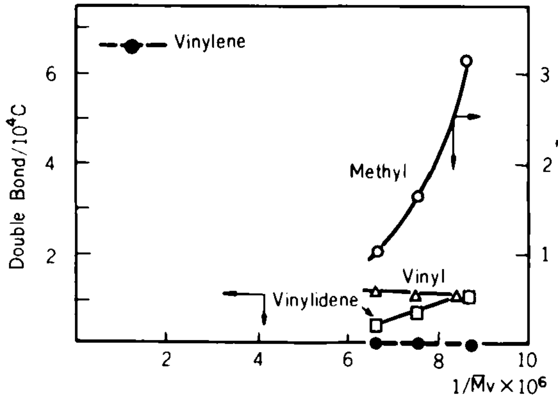
extent of the contribution of chain transfer to ethylene increase remarkably with temperature.

Vinylene groups increased appreciably with an increase in temperature, which may be explained in terms of the isomerization of vinyl groups with the catalyst.

The effect of the ratio of $(C_2H_5)_2AlCl$/Al-Ti oxychloride on the structure of the polymer was investigated. As shown in Fig. 6, the increase in the ratio brings about a slight decrease of molecular weight and a remarkable increase in methyl groups. The vinyl and vinylene contents were not



from the Data in Fig. 5



from the Data in Fig. 6

Fig. 7. Correlation between structure and inverse of molecular weight.

affected by the ratio, and the vinylidene group content increased with the ratio. The plots of methyl groups and the double bonds contents versus the inverse molecular weight, as shown in Fig. 7, suggest that the increase in methyl groups is not in parallel with the number of end group. This implies that the methyl groups are partly due to branching of the polymer. The increase in vinylidene is parallel to the increase in methyl groups. Branching seems to proceed by the same mechanism as that of vinylidene formation, as shown below.

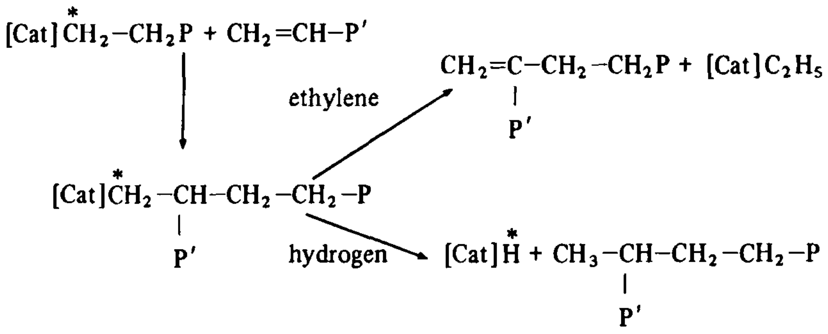
Branching is formed by the reaction of a propagated polymer with

Table 5. Properties of Polyethylene Prepared with Al-Ti Oxychloride/$(C_2H_5)_2AlCl$

No. of Sample	1	2	3	4
Polymerization condition[a]				
Temperature (°C)	160	160	170	170
Pressure of ethylene (kg/cm^2g)	50	40	45	40
Pressure of hydrogen (kg/cm^2)	5	15	10	15
Yield of polymer (g polymer/g catalyst)	400	268	291	239
Properties				
Molecular weight ($M_V \times 10^{-4}$)	7.8	6.3	5.2	4.4
Melt index (g/10 min)	0.22	0.55	1.40	3.25
Density (g/ml)	0.969	0.970	0.972	0.973
Stiffness (kg/cm^2)	9,400	9,400	10,200	10,200
Structure				
Methyl/10^3 carbon atom	1.59	3.68	2.72	3.22
Vinylene/10^3 carbon atom	0.05	0.03	0.05	0.06
Vinyl/10^3 carbon atom	1.14	1.31	1.71	1.75
Vinylidene/10^3 carbon atom	0.06	0.13	0.18	0.18

[a] Catalyst Al-Ti oxychloride, 1.2 mmole as Ti; $(C_2H_5)_2AlCl$, 2.4 mmole. Solvent; n-heptane, 1 liter. Polymerization was carried out in a 2-liter autoclave for 2 hr.

a polymer having a vinyl group. If the chain transfer to ethylene or hydrogen occurs consecutively after the above reaction, vinylidene or a branching-methyl group is formed as shown below.



As described above, an increase in the ratio of $(C_2H_5)_2AlCl$/Al-Ti oxychloride is thought to induce more and more branching reactions.

Some Properties of Polyethylene Prepared with Al-Ti Oxychloride-$(C_2H_5)_2AlCl$ Catalyst

The following conditions are favorable for preparing high density polyethylene having a molecular weight range for practical use.

As a catalyst, $(C_2H_5)_2AlCl$–1/1-Al/Ti oxychloride, in which Cl/Ti is about 2.5, is highly active, and polymerization with hydrogen at the temperatures of solution region, i.e., about 160°C, gives polymers with moderate molecular weights.

Four illustrative samples of polyethylene were prepared at 160-170°C by changing the partial pressures of hydrogen and ethylene. Table 5 shows the properties of these polymers. These polymers were found to be of high density and high stiffness, and have melt indexes 4.0-0.2. Double bonds are mostly of the vinyl group. These characteristics may be considered to be of commercial significance.

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