티탄이 기본인 Ziegler-Natta 촉매에 의한 선형저밀도폴리에틸렌의 제조

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Linear Low Density Polyethylene Preparation by Titanium-Based Ziegler-Natta Catalysts

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요 약. 선형저밀도폴리에틸렌(LLDPE)의 제조를 위해 여러가지 티탄알콕시드-알킬알루미늄 화합물을 촉매로 하여 에틸렌과 1-부텐을 슬러리 상태로 공중합하였다. 이때 촉매성분의 종류 및 농도, 숙성시간, 중합시간과 중합온도 등이 촉매활성과 공중합체 조성에 미치는 영향을 연구하였다. 그리고 공중합체의 성질과 1-부텐 함량과의 관계를 조사하였다. 그 결과 티탄사노르말부톡시드-염화디에틸알루미늄의 촉매를 사용하였을 때 가장 큰 촉매활성, 보다 많은 1-부텐 함량 및 가장 작은 가용성 부분의 LLDPE를 얻을 수 있었다. 얻은 공중합체의 밀도, 유리전이온도, 녹는점 및 녹음열 등은 1-부텐의 함량이 증가함에 따라 감소하였다.

ABSTRACT. For the preparation of linear low density polyethylene (LLDPE), the copolymerization of ethylene and 1-butene was carried out with various catalysts of titanium alkoxide-alkylaluminum compound in slurry phase. The effects of catalyst components, aging time, concentration of catalyst components, polymerization time and temperature on the catalytic activity and copolymer composition were examined. The properties of copolymer obtained were also considered with the correlation to the 1-butene contents. It has been found that the titanium tetra-*n*-butoxide-diethylaluminum chloride catalyst system was the most suitable for the production of LLDPE with higher catalytic activity, more 1-butene content and less soluble parts. The density, glass transition temperature, melting point and heat of fusion of copolymer were decreased with increasing 1-butene contents.

INTRODUCTION

Polyethylene is the first and still the most important one in production of polyolefin resins, and prepared by using many kinds of catalyst systems. Imperial Chemical Industries(ICI) of England produced first the low density polyethylene(LDPE) under high pressure with the trace of oxygen. On the other hand, the high density polyethylene(HDPE) with low branches was prepared by Ziegler-Natta catalysts at low pressure[1]. These two polyethylene are used for

different purposes[2].

Recently copolymers of ethylene and α-olefin (1-butene, 1-hexene or 1-octene) were prepared and named the linear low density polyethylene (LLDPE)[3]. Because LLDPE has better physical properties of melting point, rigidity, low impact temperature, tensile strength and elongation compared to LDPE, commercial interest has naturally gravitated[4].

The manufacturing processes for LLDPE are classified into the three ways; gas phase developed by Union Carbide, liquid phase improved by Dow and Dupont of Canada, and slurry phase investigated by Solvay, Montedison, Mitsui and Hoechst[5]. But it is considered that the tricks in the manufacture of LLDPE seems to involve the choice of catalyst for higher catalytic activity, higher 1-butene content and less production of soluble copolymers.

In this paper, we would like to report the preparation of LLDPE by copolymerization of ethylene and 1-butene in slurry phase using various titanium alkoxide-alkylaluminum compound catalyst systems and the effects of catalyst component or other reaction conditions on catalytic activity, 1-butene content, amounts of soluble parts and properties of copolymer produced.

EXPERIMENTAL

Materials. The monomers of ethylene and 1-butene supplied by the Dae-han Petrochemical Co., Korea were used without any purification. The alkylaluminum compounds of diethylaluminum chloride (DEAC), triethylaluminum (T-EA) and ethylaluminum sesquichloride (EASC) obtained from the Dae-han Petrochemical Co., Korea, and the titanium compounds of titanium tetrachloride (TTC), titanium tetra-n-butoxide (TTB), titanium tetra-n-propoxide (TTP) and titanium tetra-i-propoxide (TTIP) of Alfa Chemical Co., U.S.A. were diluted with distilled n-hexane and used as catalyst components.

The diluents of n-hexane and others were dried in column packed with molecular sieve 5A for 5 to 7 days[6]. And commercial methanol was simple-distilled. The solvent of n-hexane for catalyst components was refluxed over sodium metal for 10 to 15 hours with benzophenone and then distilled while having dark blue color due to the metal ketyl formation[7]. All of the catalyst components were handled with syringe under a nitrogen atmosphere for their instability to oxygen and moisture.

Copolymerization. The high-pressure reactor (Parr Instrument Co., U.S.A.) equipped with temperature regulator and circulating water bath (Julabo F-40, West Germany) was used as reaction vessel for the copolymerization of ethylene and 1-butene. The autoclave was assembled while the glass liner of reactor was hot, and the moisture and air were throughly excluded by evacuation and purging with dry nitrogen several times. After 150ml of n-hexane and appropriate amounts of catalyst components were added, the polymerization reaction was carried out by charging comonomer mixture (5.8 ±0.7mole% of 1-butene and 94.2±0.7mole% of ethylene) with 4kg/cm^2 of total pressure.

After 1 hour of polymerization, the reactor was degased and the small amounts of methanol was added as a terminating agent. The copolymer was precipitated with methanol and dried at room temperature under vacuum to measure the weight. In order to evaluate catalytic activity, the weight of copolymer produced per gram of titanium alkoxide was calculated and expressed by g-polymer/g-Ti. After 20 hours of extraction with n-hexane, the remained copolymer was dried and weighed to estimate the percentage of insoluble parts.

Measurements. The composition of como-

nomer was identified with gas chromatography (Shimadzu GC-3BT, Japan). The 1-butene content in copolymer was determined using IR spectrophotometer (Perkin–Elmer 283B, U.S. A.) by Bryant method[8] and ^{13}C-NMR of Queen's University, Canada[9]. It showed about 10% difference between these two extremes. The glass transition temperatures, melting point and heat of fusion of copolymer were recorded on a differential scanning calorimeter (Perkin–Elmer DSC-2, U.S.A.) equipped with thermal analysis data system(TADS). The density of copolymer was measured at 23±0.5°C with 1% aqueous glycerin and ethanol.[10]

RESULTS AND DISCUSSION

Catalyst Components. It is well known that the catalytic activity of Ziegler–Natta catalyst depends not only on the property of anionic group of transition metal but also on the kind of organoaluminum compound.[11]

To compare catalytic behaviours of various titanium alkoxides in the presence of cocatalyst TEA, the catalytic activity, 1-butene content and amounts of insoluble copolymer has been decided and shown in *Table* 1. The TTC–TEA system was used for reference which has been extensively studied.[12,13] As might be seen in *Table* 1, the activities of three alkoxides were similar but the copolymer prepared by TTP or TTIP component had too much soluble fractions to study for an industrial application.

The influence of the organic group of organoaluminum cocatalyst used with TTB was shown at *Table* 2 and it was known that DEAC gave the greater catalytic activity. For carrying out the study of ethylene and 1-butene copolymerization, the TTB–DEAC system was selected from the many different possible catalyst systems. This system was proved to be suitable for our

Table 1. The effects of various titanium compounds for the copolymerization of ethylene and 1-butene (with TEA cocatalyst)

titanium compounds	[Ti] ×10⁴ (mole/l)	[Al]/[Ti]	activity[a]	1-butene (mole %)	$\dfrac{CH_3{}^b}{1000-C}$	insoluble[c] (wt %)
TTP	3.33	40.8	137.9	2.2	11.2	76.1
TTIP	3.33	40.8	187.2	3.2	16.0	78.3
TTB	3.44	39.5	130.9	0.5	2.3	98.8
TTC	3.33	40.8	446.8	2.1	10.4	97.1

[TEA] =1.36×10⁻²mole/1, diluent ; 150ml n-hexane, aging time ; 60min., temperature ; 70°C, pressure ; 4kg/cm², polymerization time ; 1hr, [C₂H₄]/[C₄H₈] =94.2/5.8. [a] g-polymer/g-Ti. [b] number of CH₃ group per 1000 carbons. [c] wt % of remained polymer after extration with n-hexane.

Table 2. The effects of various alkylaluminum compounds for the copolymerization of ethylene and 1-butene (with TTB catalyst)

alkylaluminum compounds	[Al] ×10³ (mole/1)	[Al]/[Ti]	activity[a]	1-butene (mole %)	$\dfrac{CH_3{}^b}{1000-C}$	insoluble[c] (wt %)
DEAC	5.52	15.7	97.7	2.8	14.1	95.4
TEA	5.65	16.0	42.6	3.1	15.5	97.7
EASC	5.48	15.7	20.6	1.7	8.4	—

[TTB] =3.52×10⁻⁴ mole/1, diluent ; 150ml n-hexane, aging time ; 60 min., temperature ; 70°C, pressure ; 4kg/cm², polymerization time ; 1hr, [C₂H₄]/[C₄H₈] =94.2/5.8. [a] g-polymer/g-Ti. [b] number of CH₃ group per 1000 carbons. [c] wt % of remained polymer after extration with n-hexane.

study because it gave higher catalytic activity, 1-butene content and lower soluble fractions of copolymers.

Aging Time Effect. The aging time, the contact period of both catalyst components, affects the catalytic activity markedly. It has been reported that polymerization rate decreased gradually with the increase of catalyst aging time for the preparation of poly(ethylene-propylene) with $Al(C_5H_{13})_3-VCl_4$[14] and poly(ethylene-1-butene) by $Cp_2TiCl_2-(i-Bu)AlCl_2$[15].

For this TTB-DEAC catalyat system, the effects of aging time on the catalytic activity and 1-butene content of the copolymer were investigated and plotted in *Fig.*1. As seen at this figure, the catalytic activity and 1-butene content were nearly independent of aging time up to 60 minutes but decrease for longer aging time. It was believed that this tendency was due to the decrease of active sites on catalyst in the

absence of monomer[7]. Therefore the aging time of 60 minutes was good for the catalytic activity and 1-butent.

Influences of Reaction Time and Temperature. The yields of copolymer were determined at the different reaction time for the TTB-DEAC system(*Fig.*2). As expected, the yield and 1-butene content increased with reaction time but the slope of curve, *i.e.* the polymerization rate decreased gradually. The decrease of polymerization rate appeared due to not the diminish of monomer concentration but the decrease of active sites of catalyst[16] because the comonomer mixture was feeded continuously with $4kg/cm^2$ of total pressure. And the increase of 1-butene content of copolymer was considered to be owing to the gradual increase of 1-butene amounts in reactor because the 1-butene has lower reactivity than ethylene.

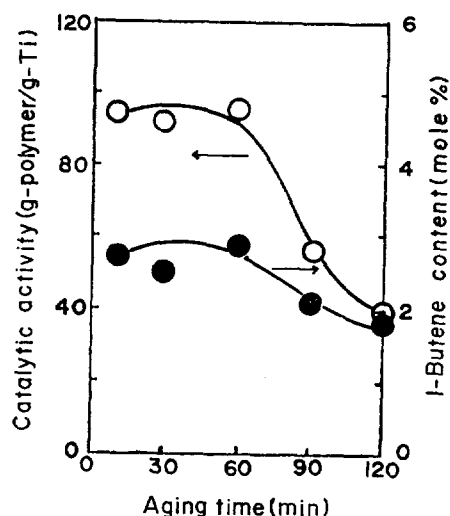For the preparation of copolymer, the polymerization temperature effects on the catalytic

*Fig.*1. Effects of aging time on the catalytic activity and 1-butene content of copolymer for the copolymerization of ethylene and 1-butene with TTB-DEAC catalyst; $[C_2H_4]/[C_4H_8]=94.2/5.8$, $[TTB]=3.52\times10^{-4}mole/1$, $[DEAC]/[TTB]=15.7$, diluent; 150m*l* *n*-hexane, temperature; 70°C, pressure; $4kg/cm^2$, polymerization time; 1hr.
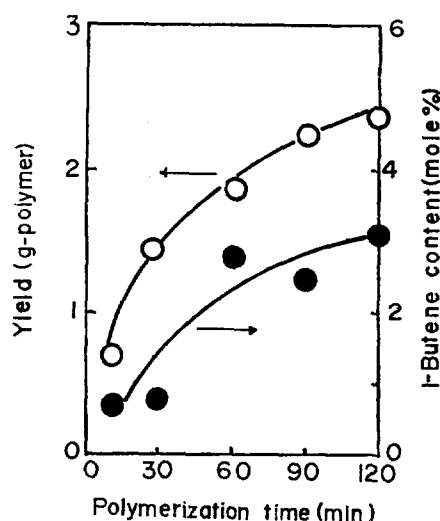
*Fig.*2. Effects of polymerization time on the yield and 1-butene content of copolymer for the copolymerization of ethylene and 1-butene with TTB-DEAC catalyst; $[C_2H_4]/[C_4H_8]=94.2/5.8$, $[TTB]=3.52\times10^{-4}mole/1$, $[DEAC]/[TTB]=15.7$, diluent; 150m*l* *n*-hexane, temperature; 70°C, pressure; $4kg/cm^2$, aging time; 60min.
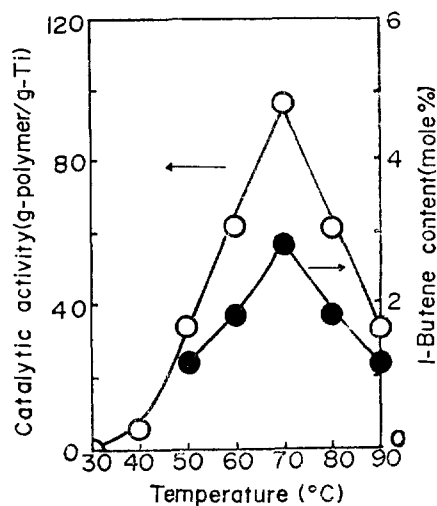
Fig. 3. Effects of polymerization temperature on the catalytic activity and 1-butene content of copolymer for the copolymerization of ethylene and 1-butene with TTB-DEAC catalyst; $[C_2H_4]/[C_4H_8]$ =94.2/5.8, [TTB] =3.52×10^{-4}mole/1, [DEAC]/ [TTB] =15.7, diluent; 150m*l* *n*-hexane, aging time; 60min, pressure; 4kg/cm^2, polymerization time, 1hr.
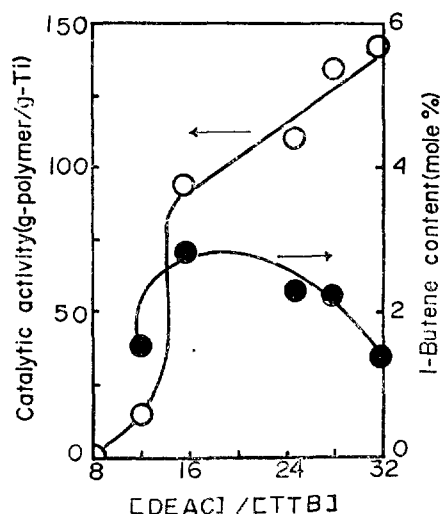

Fig. 4. Effects of [DEAC]/[TTB] ratio on the catalytic activity and 1-butene content of copolymer for the copolymerization of ethylene and 1-butene with TTB-DEAC catalyst; $[C_2H_4]/[C_4H_8]$ =94.2/5.8, [TTB] =3.52×10^{-4}mole/1, diluent; 150m*l* *n*-hexane, temperature; 70°C, aging time; 60min, pressure; 4kg/cm^2, polymerization time; 1 hr.

activity and 1-butene content were studied and given in *Fig.* 3. With increasing temperature the catalytic activity increased but had a maximum at 70°C. The 1-butene content changed with similar pattern as the catalytic activity. These trends were in agreement with the results for the homopolymerizations and copolymerizations of ethylene and propylene.[17, 18]

Effects of Catalyst Components Concentration. For the propylene polymerization using VCl$_4$-DEAC catalyst at constant concentration of VCl$_4$, the polymer yield increased but the weight-average molecular weight decreased with increasing the DEAC concentration.[19] According to the study of Natta et. al. on the copolymerization of ethylene and propylene by VCl$_4$-trihexylaluminum(THA) catalyst with constant concentration of VCl$_4$, the conversion had a maximum at the [THA]/[VCl$_4$] ratio of 2.5[14]

Therefore the catalytic activity and 1-butene

content of copolymer were examined for different concentration of DEAC at constant concentration of TTB and given at *Fig.* 4. As shown in *Fig.* 4,copolymer was not produced below the [DEAC] /[TTB] ratio of 8 and for higher ratio the catalytic activity increased with the concentration of DEAC, but 1-butene content of copolymer had a maximum near [DEAC]/[TTB] ratio of 16.

In addition, the effects of TTB concentration at constant [DEAC]/[TTB] on catalytic activity and 1-butene content were measured and shown at *Fig.* 5. As appeared in *Fig.* 5, the minimum TTB concentration of 2×10^{-4}mole/1 was necessary for the production of copolymer and above this value the catalytic activity increased with TTB concentration. These tendencies were consistent with the results reported by others.[14, 19] It could be considered that this relationship between the concentration of TTB and catalytic
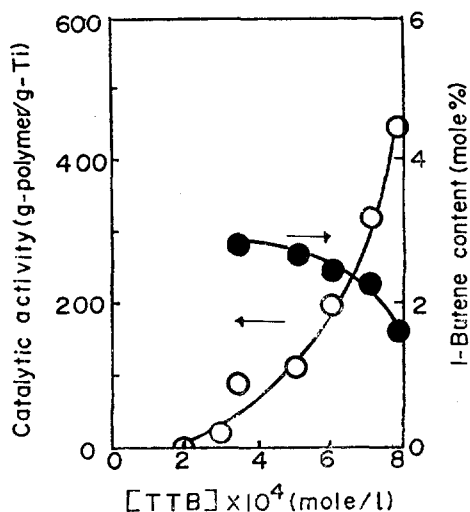
Fig. 5. Effects of [TTB] on the catalytic activity and 1-butene content of copolymer for the copolymerization of ethylene and 1-butene with TTB-DEAC catalyst; $[C_2H_4]/[C_4H_8]=94.2/5.8$, [DEAC]/[TTB]=15.7, diluent; 150ml-n-hexane, temperature; 70°C, agign time; 60min, pressure; 4kg/cm², polymerization time; 1hr.

activity was due to the increase of active site with TTB concentration at a certain conditions. It was also found that the 1-butene content of copolymer decreases with the TTB concentration.

Effect of Diluents. In the polymerization of propylene with VCl_4-DEAC, Zambelli[19] found that the diluent of n-heptane gave more polymer yield but lower tacticity compared to that of toluene. For ethylene polymerization using $Cp_2 Ti(C_2H_5)Cl$-DEAC catalyst the polymer was formed more with dichloromethane than in the case of n-hexane.[20]

Therefore the catalytic activities of TTB-DEAC system were measured with various diluents and shown at *Table* 3. It was found that the n-hexane gave the highest catalytic activity and n-pentane produced the fine polymer particle but almost no polymer was obtained for toluene or dichloroalkane.

Density Changes of Copolymers. It is well

Table 3. Diluent effects for the copolymerization of ethylene and 1-butene with TTB-DEAC catalyst

Diluents	activity[a]	1-butene (mole/1)	$\frac{CH_3^{b}}{1000\text{-}C}$	insoluble[c] (wt %)
n-Hexane	115.8	2.0	10.1	98.1
Cyclohexane	68.4	2.2	10.8	94.4
n-Pentane	60.6	2.4	11.8	91.3
n-Heptane	31.7	2.4	12.0	91.5
Toluene	0.3	—	—	—
Dichloromethane	none	—	—	—
Dichloroethane	none	—	—	—

[TTB] $=3.44\times10^{-4}$mole/1,   [DEAC]/[TTB] $=23.5$, diluent; 150ml, aging time; 60min., temperature; 70°C, pressure; 4kg/cm², polymerization time; 1hr, $[C_2H_4]/[C_4H_8]=94.2/5.8$.   [a] g-polymer/g-Ti. [b] number of CH_3 group per 1000 carbons. [c] wt % of remained copolymer after extration with n-hexane

known that the short branches of polymer show some effects on crystallinity, *i. e.* melting point, and the melt flow and viscosity are changed with the presence of the long branch.[21]

Since the degree of crystallinity is changed linearly with the density[22] the changes of density were measured against the 1-butene contents of poly(ethylene-1-butene) and shown at *Fig.* 6. As can be seen at figure, the densities of copolymer decreased with the increasing the 1-butene content. This result was similar to that for the copolymerization of ethylene and 1-hexene[23] and considered to show the lack of
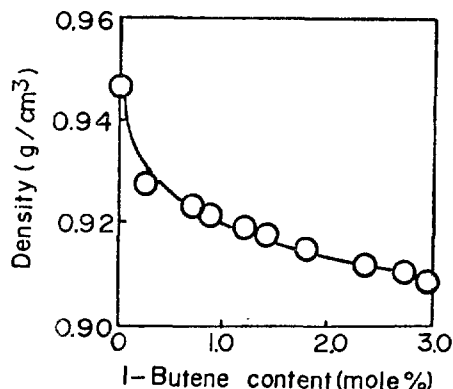

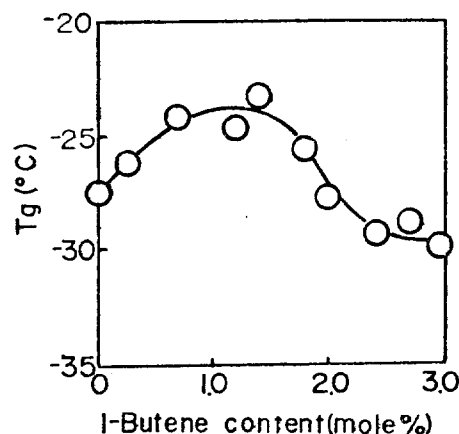*Fig.* 6. Changes of density with 1-butene content of poly(ethylene-1-butene).

Fig. 7. Changes of the glass transition temperature with 1-butene content of poly (ethylene-1-butene).

Fig. 8. Changes of the melting point and heat of fusion with 1-butene content of poly (ethylene-1-butene).

molecular orientation due to the ethyl branch of 1-butene.

Thermal Properties of Copolymers. It is well known that the thermal properties of copolymers are dependent on the composition of copolymer.[24] Therefore the glass transition temperature, the melting point and the heat of fusion of copolymer were examined by DSC.

The changes of glass transition temperature (Tg) with the 1-butene contents of copolymer were shown at Fig. 7. The Tg of copolymer increased with the 1-butene content at first stage but decreased with larger content of 1-butene. The reason of these changes was not clear now but it could be considered that the energy barrier between different conformations might increase due to the presence of large ethyl group in place of tiny hydrogen atom for small amounts(up to 1.0 mole %) of 1-butene, and the internal plasticization[25] appeared to decrease the Tg for higher 1-butene content.

The melting point(Tm) of copolymer decreased with decreasing density[26] and the density of copolymer decreased with increasing 1-butene content. Therefore the Tm and heat of fusion of copolymer were measured against 1-butene content and showed in Fig. 8. As could be ex-
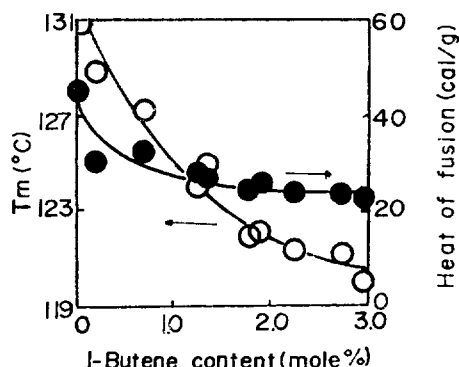
pected, the melting point and heat of fusion of copolymer decreased with the increasing 1-butene content. This phenomenon could be also explained by the decrease of crystallinity due to the increase of ethyl group of 1-butene.[27]

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