

## Ziegler-Natta 촉매에 의한 1-헥사데센의 중합

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## Polymerization of Hexadecene-1 with Ziegler-Natta Catalysts

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**요 약 :** 여러가지 촉매( $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ ,  $\text{MgCl}_2/\text{TiCl}_4$ ,  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$ )와 공촉매 (염화 이에틸알루미늄, 삼에틸알루미늄, 삼이소부틸알루미늄, 삼이소헥실알루미늄, 삼노르말옥틸알루미늄)을 이용한 1-헥사데센의 중합을  $40^\circ\text{C}$ , *n*-헵탄중에서 행하였다. 여러 촉매계에 대한 촉매활성을 조사하였으며 폴리(1-헥사데센)을 디에틸에테르로 추출하여 불용성 및 용해성 부분으로 나눈 다음 열분석, 점도 및 분자량 측정,  $^{13}\text{C}$ -NMR 등으로 분석하였다. 그 결과 유기알루미늄 화합물의 알킬기가 클수록 보다 높은 입체규칙성과 큰 분자량을 가진 중합체가 얻어진다는 것을 알았다.

**Abstract :** The polymerizations of hexadecene-1 were carried out at  $40^\circ\text{C}$  in *n*-heptane by using the different catalysts ( $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ ,  $\text{MgCl}_2/\text{TiCl}_4$ ,  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$ ) with various cocatalysts (diethyl aluminum chloride, triethyl aluminum, triisobutyl aluminum, triisohexyl aluminum, tri-*n*-octyl aluminum). The activities of various catalyst systems for hexadecene-1 polymerization were reported. The poly(hexadecene-1) was fractionated with diethyl ether extraction and the soluble and insoluble parts have been characterized by the thermal analysis, intrinsic viscosity and molecular mass measurements, and  $^{13}\text{C}$ -nuclear magnetic resonance spectroscopy. From the analysis of polymer for various cocatalysts, it was found that the higher alkyl aluminum compound gave the higher stereoregularity and higher molecular mass.

### INTRODUCTION

During recent years the copolymerization of ethylene and higher  $\alpha$ -olefin have been studied intensively due to the commercial significance of the linear or ultra low density polyethylene (LLDPE or ULDPE).<sup>1,2</sup>

It is important to know the efficiency of the catalyst system not only for the copolymerization but also for the homopolymerization of higher  $\alpha$ -olefins. The thermal behaviors and properties of poly( $\alpha$ -olefin) series obtained with the conventional Ziegler-Natta catalysts have been studied by several workers.<sup>3~5</sup>

Recently the polymerization of higher  $\alpha$ -olefins was also conducted by using the highly active magnesium supported  $\text{TiCl}_4$  catalyst<sup>6</sup> and the highly isospecific catalyst.<sup>7</sup> However, there have been less systematic studies on the polymerization of higher  $\alpha$ -olefins with the various catalyst-cocatalyst systems.

In this work we have investigated the effects of the various catalysts and cocatalysts on the activity and stereoregularity for hexadecene-1 polymerization. The poly(hexadecene-1) obtained with the different Ziegler-Natta catalyst systems was also characterized by thermal analysis, intrinsic viscosity and molecular mass measurements, and  $^{13}\text{C}$ -nuclear magnetic resonance spectroscopy.

## EXPERIMENTALS

### Materials

The conventional  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  (from Tosho Akzo Corp.),  $\text{MgCl}_2/\text{TiCl}_4$  and  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$ <sup>8</sup> catalysts were used for the hexadecene-1 polymerization. Diethyl aluminum chloride (DEAC), triethyl aluminum (TEA), triisobutyl aluminum (TIBA), triisohexyl aluminum (TIHA), and tri-*n*-octyl aluminum (TNOA) (from Tosho Akzo Corp.) as cocatalysts were used without further purification.

Hexadecene-1 (from Janssen Chimica.) and *n*-heptane (from Junsei Chemical Co.) were purified by passing it through the columns of molecular sieves 4Å and distillation over sodium metal under nitrogen prior to use. Phenyltriethoxy silane (PTES, from Tokyo Kasei Chem. Co.) of external donor (ED) was used without further treatment.

### Polymerization

The polymerization of hexadecene-1 was carried out at 40°C for 4 hours in *n*-heptane as diluent by using the various catalysts and cocatalysts.

The diluent, monomer, cocatalyst, and catalyst were added with this order into a 1000ml three-necked flask equipped with chemi stirrer, reflux condenser, and thermometer.

After the completion of polymerization, the aci-

dic methanol was added to quench the polymerization. The polyhexadecene-1 (PHD) was washed several times with methanol and dried in vacuum at room temperature.

### Analysis

The weight percentage of the insoluble parts to examine the stereoregularity of PHD was determined by the extraction with boiling diethyl ether for 6 hours and noted as the isotactic index (I. I.).

The intrinsic viscosity was measured in 1,2,4-trichlorobenzene at 135°C using the autoviscometer (Sinkawa Electric Co. AVS-II). The molecular mass and its distributions of PHD were obtained by the gel permeation chromatograph (Waters 150C). The 1,2,4-trichlorobenzene was used as the eluent and the GPC columns (Twin Shodex AT-80 M/S column) as well as the injector was kept at 135°C.

Prior to the measurements of intrinsic viscosity and molecular mass, the approximately 0.1 wt% of antioxidant (2,6-di-*t*-butyl-*p*-cresol) was added to the solution of PHD to inhibit the oxidative degradation.

The melting point of the PHD was determined at the 2nd stage heating by the differential scanning calorimetry (Dupont thermal analyzer 1090 B); i.e. the sample was heated to 120°C for the 1st stage heating and then cooled to -20°C and then heated again to 120°C for the 2nd stage heating at rate of 10°C/min.

The  $^{13}\text{C}$ -NMR analysis of PHD was carried out at 100°C with the Jeol GX-270 NMR spectrometer (at Tokyo Institute of Technology, Japan) operating at 67.8 MHz. The PHD was dissolved in 1,2,4-trichlorobenzene/benzene  $d_6$  (9/1 in vol.) up to 10 wt%. The chemical shift was represented in ppm downfield from the internal hexamethyldisiloxane. The density of PHD was measured by the density gradient column as specified in ASTM D-1505 (Davenport).

## RESULTS AND DISCUSSION

### Catalytic Activity and Stereoregularity

Because the alkylaluminum compounds show

some effects on the catalytic behaviors for Ziegler-Natta catalysts, the changes of activity, I.I., and intrinsic viscosity were examined for the various organoaluminum compounds with the conventional  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  catalyst. The results were shown in Table 1.

As shown in Table 1, the activity of the aluminum compounds with  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  was decreased in the following order ;  $\text{TEA} < \text{DEAC} < \text{TIBA} < \text{TIHA} < \text{TNOA}$

The organoaluminum compounds are reducing agents so that the titanium elements can be present in the different valence states depending on the reducing power of organoaluminum compounds. Soga et. al.<sup>9,10</sup> reported that  $\text{Ti(III)}$  polymerizes  $\alpha$ -olefin including propylene as well as

ethylene, but  $\text{Ti(II)}$  is active only for ethylene polymerization. For the  $\alpha$ -olefin polymerization the alkylaluminum having higher reducing power will show the decrease of activity due to the over-reduction of  $\text{Ti(III)}$  to  $\text{Ti(II)}$ . As the size of alkyl group in the trialkyl aluminum is increased, the reducing power is decreased. With these considerations, the effects of organoaluminum compound on the activity could be explained.

The effects of cocatalyst with the  $\text{MgCl}_2/\text{TiCl}_4$  catalyst on the activity, I.I., and intrinsic viscosity of PHD were shown in Table 2.

The activity of  $\text{MgCl}_2$  supported catalyst was increased and then decreased with the alkyl group size of alkylaluminum.

The reducing power of triethyl aluminum was so

**Table 1.** Results of Hexadecene-1 Polymerization with  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  Catalyst

Cocatalyst	Yield (g)	Activity [g-PHD/(g-Ti.h)]	I.I. (wt%)	Whole PHD				Insoluble Part				Soluble Part	
				$[\eta]^a$	$T_m^b$	$\bar{M}_w(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$	$T_m^b$	$\bar{M}_w(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$	$T_m^b$	$\bar{M}_w(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$
DEAC	11.9	82.1	76.1	1.39	(26.0)/64.2	322	13.5	(26.1)/66.5	—	—	17.4/35.0	—	—
TEA	11.6	80.5	34.7	0.55	26.7/61.9	128	32.5	(26.1)/63.6	398	16.6	25.7/58.1	11.7	4.3
TIBA	12.0	83.0	66.4	1.79	27.1/63.8	496	18.0	26.2/64.0	660	8.6	26.6/54.8	55.5	6.2
TIHA	13.9	96.2	78.8	1.65	25.2/61.9	—	—	26.0/64.4	—	—	26.1/53.9	—	—
TNOA	15.4	106.6	71.1	1.65	25.1/62.0	—	—	(25.8)/63.9	—	—	25.2/(52.7)	—	—

\* Polymerization Condition :  $[\text{Ti}] = 4.85$  mmole/L,  $[\text{Al}]/[\text{Ti}] = 8$ ,  $40^\circ\text{C}$ , 4h, hexadecene-1  $20\text{cm}^3$ ,  $n$ -heptane  $180\text{cm}^3$ .

<sup>a</sup>)  $[\eta]$  : intrinsic viscosity in tetralin at  $135^\circ\text{C}$ .

<sup>b</sup>)  $T_m$  : melting temperature in  $^\circ\text{C}$ , the value in ( ) is corresponding to the negligible peak.

**Table 2.** Results of Hexadecene-1 Polymerization with  $\text{MgCl}_2/\text{TiCl}_4$  Catalyst

Cocatalyst	Yield (g)	Activity [g-PHD/(g-Ti.h)]	I.I. (wt%)	Whole PHD				Insoluble Part				Soluble Part	
				$[\eta]$	$T_m$	$\bar{M}_w(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$	$T_m$	$\bar{M}_w(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$	$T_m$	$\bar{M}_w(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$
DEAC	2.7	305	8.9	0.26	25.6/60.0	—	—	(32.3)/64.9	—	—	25.4/58.1	—	—
TEA	6.0	660	24.1	0.94	24.5/56.8	218	12.5	23.8/60.9	—	—	24.6/53.1	—	—
TIBA	10.3	1140	47.9	1.33	24.1/58.7	408	17.6	(24.3)/63.4	780	12.7	26.7/50.8	127	7.7
TIHA	3.8	430	53.8	1.53	24.6/58.9	—	—	25.4/62.8	—	—	24.5/51.8	—	—
TNOA	4.4	490	54.6	1.68	24.5/58.1	—	—	25.5/60.5	—	—	24.3/51.7	—	—

\* Polymerization Condition :  $[\text{Ti}] = 0.24$  mmole/L,  $[\text{Al}]/[\text{Ti}] = 160$ ,  $40^\circ\text{C}$ , 4h, hexadecene-1  $20\text{cm}^3$ ,  $n$ -heptane  $180\text{cm}^3$ .

\* Notes ; see Tab. 1.

strong that Ti ions on the support was overreduced to Ti(II) while larger alkylaluminum compounds were too weak reducing power to produce enough Ti(III). With these limitations the triisobutyl aluminum was suitable for hexadecene-1 polymerization with  $\text{MgCl}_2$  supported catalyst.

The effects of cocatalyst and ED on the activity, I.I., and intrinsic viscosity of PHD for  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$  catalyst were given at Table 3 and the data for the highly isospecific catalyst of Solvay type  $\text{TiCl}_3\text{-Cp}_2\text{TiMe}_2$ <sup>7</sup> were also included as reference.

The activity of  $\text{Mg}(\text{OEt})_2$  supported catalyst with the alkylaluminum of different size alkyl group showed the similar tendency as that of  $\text{MgCl}_2$  supported catalyst systems.

It was also found that the catalyst system with PTES as ED for the hexadecene-1 polymerization gave lower activity and higher I.I. compared to those without PTES. These results are very familiar phenomena for propylene polymerization, indicating that the catalytic centers having different stereospecific sites could exist in this catalyst system.

For the  $\text{MgCl}_2/\text{DNBP}/\text{TiCl}_4\text{-TEA}/\text{PTES}$  catalyst system of propylene polymerization, Soga et.

al.<sup>11</sup> suggested that the PTES coordinated with the potentially isospecific Ti species which were surrounded by the internal donor to give a highly active isospecific Ti species, whereas it reacted with the nonisospecific Ti species to eliminate its activity. It was also reported that the  $\text{Mg}(\text{OEt})_2$  support was converted to  $\text{MgCl}_2$  by the reaction with  $\text{TiCl}_4$  for  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$  catalyst.<sup>8</sup> Therefore these two catalyst systems should have the similar catalytic centers.

The structures of the insoluble and soluble parts of PHD after the ether extraction were examined by <sup>13</sup>C-NMR and shown at Fig. 1.

From these spectra the mmmm pentad distribution of insoluble parts was found to be 92% and the soluble parts have the small amount(35%) of mmmm sequence. Therefore the insoluble part of PHD for the ether extraction was considered to have the isotactic microstructure.

From Tables 1~3, it could be concluded that the isotacticity of PHD increased with the alkyl group size of alkylaluminum compounds irrespective of the type of titanium catalysts. As pointed out previously, the ED gave the higher isotactic structure of PHD.

The DEAC gave the higher values of insoluble

**Table 3.** Results of Hexadecene-1 Polymerization with  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$  Catalyst

Cocatalyst	Yield (g)	Activity [g-PHD/(g-Ti,h)]	I.I (wt%)	Whole PHD				Insoluble Part				Soluble Part			
				$[\eta]$	Tm	$\overline{M}_w(\times 10^4)$	$\overline{M}_w/\overline{M}_n$	Tm	$\overline{M}_w(\times 10^4)$	$\overline{M}_w/\overline{M}_n$	Tm	$\overline{M}_w(\times 10^4)$	$\overline{M}_w/\overline{M}_n$		
TEA	5.6	860	38.4	0.51	(18.6)/63.8	102	22.8	(18.0)/65.0	—	—	25.9/58.1	—	—		
TEA/ED	3.3	520	72.6	1.00	(15.3)/60.9	—	—	—	—	—	—	—	—		
TIBA	11.6	1820	51.2	1.69	25.5/59.5	759	27.6	(25.0)/62.3	1000	11.2	25.6/51.9	83	6.5		
TIBA/ED	8.8	1380	66.2	1.80	25.1/60.8	1012	29.2	24.7/62.6	1430	11.0	24.5/51.2	95	6.2		
TIHA	8.9	1390	67.7	1.99	23.8/59.5	1220	26.2	26.0/62.9	1790	10.2	23.4/48.4	170	7.9		
TIHA/ED	3.8	600	75.5	2.52	24.6/61.3	—	—	24.6/62.6	—	—	22.8/48.2	—	—		
TNOA	6.8	1060	62.6	1.84	20.2/57.3	1180	31.8	(25.2)/62.2	1590	12.3	19.4/43.6	107	6.4		
TNOA/ED	3.4	530	81.9	2.56	23.1/61.8	—	—	26.0/63.8	—	—	21.5/48.0	—	—		
ref. <sup>a)</sup>	—	—	—	1.90	/67.0	719	10.5	—	—	—	—	—	—		

\* Polymerization Condition :  $[\text{Ti}] = 0.22$  mmole/L,  $[\text{Al}]/[\text{Ti}] = 180$ ,  $[\text{ED}] = [\text{PTES}] = 1.0$  mmole/L, 40°C, 4h, hexadecene-1 20cm<sup>3</sup>, *n*-heptane 180cm<sup>3</sup>.

\* Notes ; see Tab. 1.

<sup>a)</sup> Solvay type  $\text{TiCl}_3\text{-Cp}_2\text{TiMe}_2$  catalyst<sup>7</sup>.

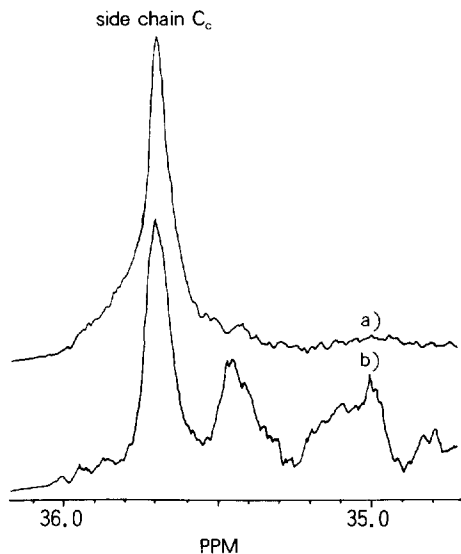


Fig. 1. Expanded  $^{13}\text{C}$  NMR spectra in the side chain methylene carbon( $\text{C}_\alpha$ ) region of poly(hexadecene-1) obtained with  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4\text{-TIBA}$  catalyst : a) ether extracted insoluble part, b) ether extracted soluble part.

parts and intrinsic viscosity for the conventional  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  catalyst but lower values for the Mg-supported catalyst.

#### Melting Behaviors

To study the melting behaviors of PHD, melting temperature ( $T_m$ ) of polymer obtained with the various catalyst systems was measured and shown at Table 1~3.

The most of unextracted PHD obtained with the various catalyst systems gave two endothermic peaks at  $20\sim 27^\circ\text{C}$  and  $57\sim 64^\circ\text{C}$ . For examples, the DSC thermograms of PHD were shown at Fig. 2 for  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3\text{-TIBA}$  catalyst and Fig. 3 for  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4\text{-TIHA}$  catalyst.

At Fig. 2 the unextracted PHD showed the two endothermic peaks at  $27.1^\circ\text{C}$  and  $63.8^\circ\text{C}$ . After the ether extraction, the insoluble parts of PHD gave the main endothermic peak at  $63.7^\circ\text{C}$  while the soluble parts showed the main peak at  $26.6^\circ\text{C}$ . For the unextracted PHD obtained with the highly isospecific catalyst of Solvay type  $\text{TiCl}_3\text{-Cp}_2\text{Ti}$

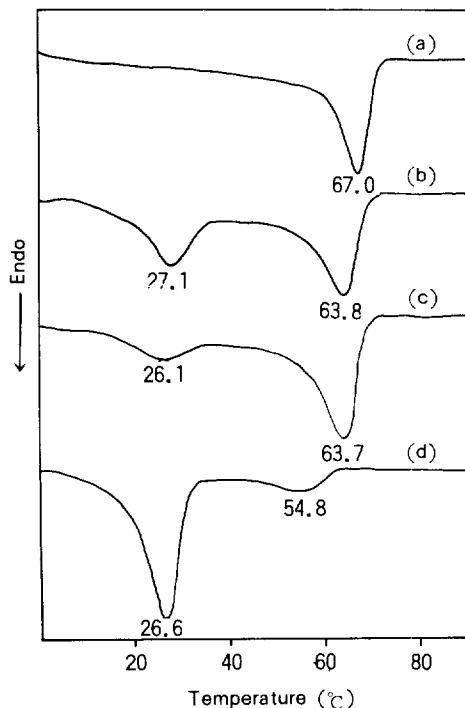


Fig. 2. DSC thermogram of poly(hexadecene-1) obtained with : (a), Solvay type  $\text{TiCl}_3\text{-Cp}_2\text{Ti}(\text{CH}_3)_2$  catalyst : unextracted ; (b),  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3\text{-TIBA}$  catalyst : unextracted (I.I.=66.4%) ; (c),  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3\text{-TIBA}$  catalyst : ether extracted insoluble part ; (d),  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3\text{-TIBA}$  catalyst : ether extracted soluble part.

$\text{TiMe}_2$  catalyst,<sup>7</sup> the only one endothermic peak appeared at  $67^\circ\text{C}$ .

The above observations could be explained that the peak at higher temperature is due to the crystalline domain of isotactic PHD involving both of the main chain and side chains whereas the lower transition temperature is from the crystallization of the side chains of atactic PHD. These similar melting behaviors were also reported for poly (tridecene-1)<sup>3</sup> and poly (octadecene-1).<sup>5</sup>

As shown at Fig. 3 the  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4\text{-TIHA}$  catalyst showed the similar thermograms but gave the clearer extraction and the negligible minor peak for extracted samples compared to the  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3\text{-TIBA}$  catalyst.

The clearer extraction might be resulted from the higher molecular mass of PHD obtained with the  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$ -TIHA catalyst because the extraction was occurred due to the difference of molecular mass as well as the tacticity.<sup>12</sup>

The density(g/cc) of PHD obtained with the  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$ -TIBA catalyst system was also measured as the following ; unextracted PHD=0.909, insoluble PHD=0.914, soluble PHD=0.870. As expected the density of ether insoluble parts of PHD was the highest due to the higher isotacticity. With PTES as ED, the densities of each parts of PHD were 0.889, 0.897 and 0.873 respectively. Although it could not be explained until now, it was interesting to note that the above density values are higher compared to 0.895 for PHD polymerized with the very high isospecific

Solvay type  $\text{TiCl}_3\text{-Cp}_2\text{TiMe}_2$  catalyst.

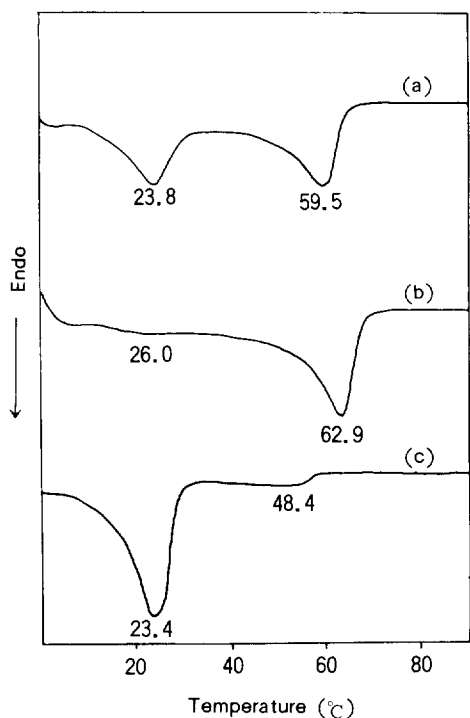
#### Molecular Mass and its Distribution

It was well known that the organoaluminum compounds occur the chain transfer reaction for Ziegler-Natta polymerization. As shown at Table 1~3, the intrinsic viscosity and molecular mass of PHD were also increased with the alkyl group size of alkylaluminum compounds. This results showed that the chain transfer reaction of alkylaluminum compounds was profound for the smaller alkyl group of alkylaluminum compounds having the higher reducing activity. The ED gave higher intrinsic viscosity and molecular mass.

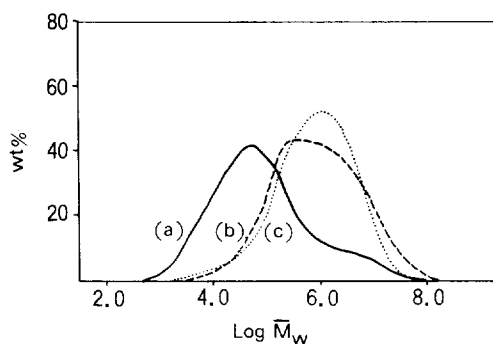
The molecular mass of insoluble part was larger than that of whole PHD, which was higher compared to that of soluble part. On the other hand, the polydispersity index,  $\bar{M}_w/\bar{M}_n$  was decreased ; whole PHD>insoluble part>soluble part.

The GPC chromatograms of PHD were shown at Fig. 4 for  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  and Fig. 5 for  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$  catalyst with the various alkylaluminum compounds.

The molecular mass distribution curves were bimodal and shifted to the higher molecular mass with increasing the alkyl group size of alkylaluminum compounds. For same alkylaluminum compound, the GPC chromatogram of PHD with  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$  catalyst have similar pattern as that of



**Fig. 3.** DSC thermogram of poly(hexadecene-1) obtained with :  $\text{Mg}(\text{OEt})_2/\text{DCE}/\text{DIBP}/\text{TiCl}_4$ -TIHA catalyst : (a), unextracted (II=67.7%) ; (b), ether extracted insoluble part ; (c), ether extracted soluble part.



**Fig. 4.** GPC chromatograms of poly(hexadecene-1) obtained with : (a),  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ -TEA catalyst (—) ; (b),  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ -TIBA catalyst (---) ; (c),  $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ -DEAC catalyst (·····).

Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub> catalyst. These results were consisted with the explanation of intrinsic viscosity changes.

To examine the bimodal distribution, the PHD

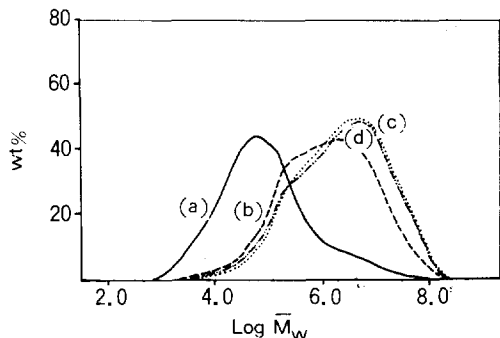


Fig. 5. GPC chromatograms of poly(hexadecene-1) obtained with : (a), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TEA catalyst (—); (b), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TIBA catalyst (---); (c), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TIHA catalyst (·····); (d), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TNOA catalyst (- · - ·).

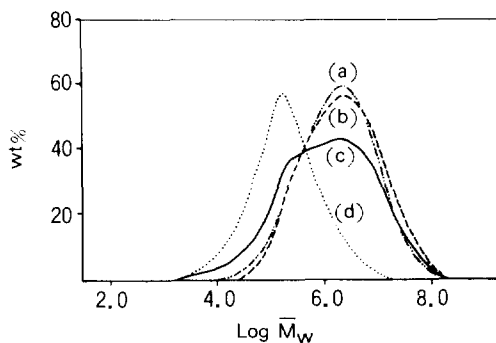


Fig. 6. GPC chromatograms of poly(hexadecene-1) obtained with : (a), solvay type TiCl<sub>3</sub>-Cp<sub>2</sub>Ti(CH<sub>3</sub>)<sub>2</sub> catalyst : unextracted(- · - ·); (b), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TIBA catalyst : unextracted (—); (c), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TIBA catalyst : insoluble part (---); (d), Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TIBA catalyst : soluble part (·····).

obtained with the Mg(OEt)<sub>2</sub>/DCE/DIBP/TiCl<sub>4</sub>-TIBA catalyst was fractionated and the GPC chromatograms for the unextracted PHD, insoluble and soluble parts were shown at Fig. 6.

From Fig. 6 the unextracted PHD was found to be composed of two different parts, that is, the insoluble part of higher molecular mass and the soluble part of lower molecular mass. Especially the distribution curve of insoluble part was nearly same with that for the highly isospecific Solvay type TiCl<sub>3</sub>-Cp<sub>2</sub>TiMe<sub>2</sub> catalyst, indicating the insoluble part was isospecific. With these results, it could be considered that the Mg-supported catalyst has at least two active species for the hexadecene-1 polymerization.

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