

STUDIES ON $\text{TiCl}_4/\text{Mg}(\text{OEt})_2/\text{EB}$ SUPPORTED CATALYSTS FOR PROPYLENE POLYMERIZATION

XIAO Shijing (肖士镜), LU Honglan (陆宏兰) and ZHANG Minghui (张明辉)

(*Institute of Chemistry, Academia Sinica, Beijing*)

ABSTRACT

The supported catalysts for propylene polymerization were prepared by milling $\text{Mg}(\text{OEt})_2$ with EB (ethylbenzoate) and treating with TiCl_4 solution. When $\text{TiCl}_4/(\text{Mg}(\text{OEt})_2/\text{EB})$ (mol.) ratio was increased, decrease in contents of $-\text{OEt}$ and Ti of the catalysts was observed, while the content of EB increased. It is proved by analyses of IR, X-ray and XPS that during co-milling $\text{Mg}(\text{OEt})_2$ with EB no reactions have taken place. But after treatment with TiCl_4 solution, $\text{Mg}(\text{OEt})_2$ converts into MgCl_2 and EB coordinates on the resulting MgCl_2 carrier, a surface complex forms.

The activity of catalysts, isotacticity and viscosimetric molecular weight of polypropylene increase with the decrease of the content of ethoxyl group. The kinetic curves of propene polymerization obtained with present catalysts system display decay curves. It is found from the triad tacticity calculated from the expanded spectra of methyl carbon region that, ethoxyl group in catalyst has an effect on the configuration of polymer chain.

INTRODUCTION

It has been known in recent years that the $\text{Mg}-\text{Ti}$ supported Ziegler-Natta catalysts are important type of highly efficient catalysts for polymerization of α -olefin.

Various inorganic and organic magnesium compounds such as MgCl_2 , $\text{Mg}(\text{OH})_2$, MgR_2 , $\text{Mg}(\text{OR})_2$, $\text{Mg}(\text{OH})\text{Cl}$ etc. have been used as starting materials to make the support. $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ in combination with triethyl aluminum (TEA) is a highly efficient catalyst system for polymerization of ethylene and is used industrially.

The reaction products of TiCl_4 , alkyl benzoates and magnesium alkoxides have also been described in the patent literature^[1] and discovered to be effective for propene stereospecific polymerization. However, the feature of the catalysts still remain unclear.

In this work, the supported catalysts for propylene polymerization were prepared by milling $\text{Mg}(\text{OEt})_2$ with EB and treating with TiCl_4 solution at various $\text{TiCl}_4/(\text{Mg}(\text{OEt})_2/\text{EB})$ ratios. Their composition and structure were determined. The effect of ethoxyl groups on catalytic behaviour and configuration of the polymer chain were investigated.

EXPERIMENTAL

Preparation of supported catalyst

The supported catalyst was prepared by co-milling $\text{Mg}(\text{OEt})_2$ with ethyl benzoate (EB) at the molar ratio $[\text{Mg}]/[\text{EB}] = 5$ and further treated with the solution of TiCl_4 in *n*-heptane at 92°C for 2 hrs. The co-milling was performed

on a ball-milled vibrator for 30 hrs. After treating $\text{Mg}(\text{OEt})_2/\text{EB}$ with TiCl_4 solution, the solid product was separated by filtration, washed with *n*-heptane and dried under reduced pressure.

Analytical measurements

The Ti content was determined calorimetrically and the $-\text{OEt}$ group and EB contents were determined by gas chromatography method. A weighed sample was dissolved with dilute sulfuric acid and extracted by *n*-heptane, the organic phase was used for determination of EB and the aqueous phase for determination of Ti and $-\text{OEt}$ contents.

Polypropylene obtained was fractionated by extraction with boiling *n*-heptane. The isotactic index of the polymers was expressed as percent of polymer insoluble in boiling *n*-heptane.

Viscosimetric method was employed to measure the molecular weight of polymer at $135 \pm 0.2^\circ\text{C}$ in decahydronaphthalene. $\overline{M}_\eta$ values were calculated according to following equation: $[\eta] = 1.1 \cdot 10^{-4} \cdot \overline{M}_\eta^{0.8}$.

The IR spectra were recorded as a plaste which was made by mixing solid catalysts with paraffin oil between two pieces of CsI crystalline flat on SP-2000 spectrophotometer.

X-ray powder diffraction (XD) patterns were recorded on RIGAKU 3013 X-ray diffractor using $\text{CuK}\alpha$ radiation. The samples were sealed in sample's frame by two pieces of scotch tape. XPS measurements were done on the same instrument and procedures reported earlier^[2], the contamination carbon C_{1s} was taken as an internal standard at 285.0 eV.

^{13}C NMR spectra of the polymer were recorded at 140°C in *o*-dichlorobenzene- d_4 solution with a JEOL JNMFX-100 spectrometer operating in the Fourier transform mode at 25MHz.

Polymerization

The polymerization of propylene was carried out at 60°C under a constant pressure of 580 mmHg in a glass reactor equipped with a mechanical stirrer in 100 ml of *n*-heptane solvent for 2 hrs and terminated with 100 ml of ethanol.

RESULTS AND DISCUSSION

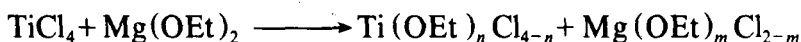
1. Effect of $\text{TiCl}_4/(\text{Mg}(\text{OEt})_2/\text{EB})$ ratios on the composition of catalyst

The chemical analytic results of catalysts prepared with $\text{TiCl}_4/(\text{Mg}(\text{OEt})_2/\text{EB})$ at various ratio are shown in Table 1.

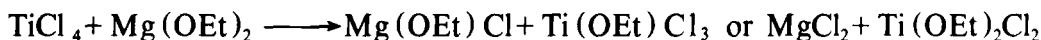
Table 1 The composition of catalysts

Run No.	$\text{TiCl}_4/(\text{Mg}(\text{OEt})_2/\text{EB})$ (MOL. / MOL.)	Ti		EB		$-\text{OEt}$		$-\text{OEt}/\text{Ti}$ mol. / mol.
		wt. %	mol.	wt. %	mol.	wt. %	mol.	
1	1	10.27	0.210	5.91	0.039	17.71	0.394	1.88
2	2	7.93	0.166	7.05	0.047	7.35	0.163	0.98
3	4	6.58	0.137	7.86	0.052	5.87	0.130	0.95
4	8	5.98	0.130	7.95	0.053	4.24	0.094	0.75
5	5 (first 1, second 4)	4.47	0.093	9.92	0.066	2.61	0.058	0.62

When $[\text{Ti}] / [\text{Mg}]$ ratio was increased, a decrease in contents of $-\text{OEt}$ group and Ti of catalysts was observed. OEt/Ti molar ratio also decreased, while the EB content increased. The interaction between TiCl_4 and $\text{Mg}(\text{OEt})_2$ during the preparation of catalysts can be described simply as follows:



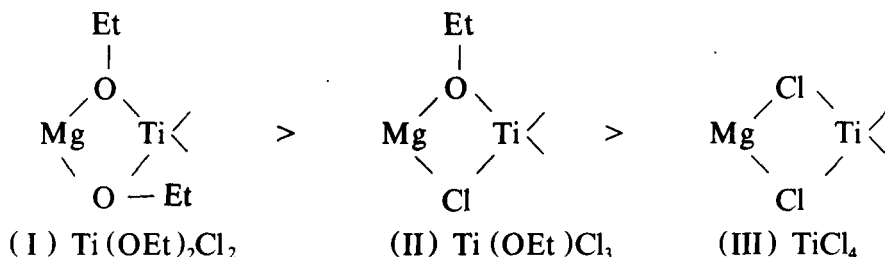
Where $n=0-2$; $m=0-2$. The n and m values depend mainly on the ratio of $[\text{Ti}] / [\text{Mg}]$ in the case of other condition being certain. An ethoxyl titanium chloride is presumably formed directly in the course of the transformation of $\text{Mg}(\text{OEt})_2$ to MgCl_2 ($m=0$):



A portion of the resulting ethoxyl Ti chloride dissolves in solvent and was washed off; the other portion as an active species fixed on the resulting magnesium chloride.

So it implies that the supported catalysts prepared when $[\text{Ti}] / [\text{Mg}] < 2$ contain higher $[\text{OEt}] / [\text{Ti}] (> 1)$ (see run 1 and 2 in Table 1) and the Ti component as active species is predominantly ethoxyl titanium chloride but the catalysts prepared in case of $[\text{Ti}] / [\text{Mg}] > 2$ (Table 1 run 3-5) have lower $[\text{OEt}] / [\text{Ti}]$ ratio (less than 1), and consist of ethoxyl Ti chloride and TiCl_4 and both as active species, furthermore the amount of TiCl_4 increases with $-\text{OEt}/\text{Ti}$ decreases.

The Ti content in the present catalysts increases with the increase of the content of ethoxyl group. This indicated that the ethoxyl titanium chloride firmly fixed on the surface of the MgCl_2 through ethoxyl group bridge due to its stronger Lewis base than chlorine bridge. The bond between $\text{Mg}-\text{Ti}$ may be shown as the following scheme.



$\text{Mg}-\text{Ti}$ bond strength decreases in the order of $\text{I} > \text{II} > \text{III}$.

The effect of steric hindrance of $-\text{OEt}$ group may cause the decrease in the content of EB which fixed on MgCl_2 .

2. Formation of catalyst and its structure

(1) Comilling product of $\text{Mg}(\text{OEt})_2$ with EB

The interactions between $\text{Mg}(\text{OEt})_2$ and EB by comilling were investigated for getting some basic information about the support.

Fig. 1 shows IR spectra of (1) $\text{Mg}(\text{OR})_2$ and (2) comilling product of $\text{Mg}(\text{OEt})_2/\text{EB}$. The $\text{C}-\text{O}$ bond at 1131 cm^{-1} , 1077 cm^{-1} and two intense bands at 574 cm^{-1} , 500 cm^{-1} observed and $\nu_{\text{C}=\text{O}}$ at 1730 cm^{-1} of (2) are similar to those

of (1) and free EB respectively (the IR spectra of free EB not showed in this Fig.). This indicated that there is no interaction between $\text{Mg}(\text{OEt})_2$ and EB in the course of comilling. To confirm the conclusion, the comilling product of $\text{Mg}(\text{OEt})_2 / \text{EB}$ was measured by other methods such as X-ray diffraction and

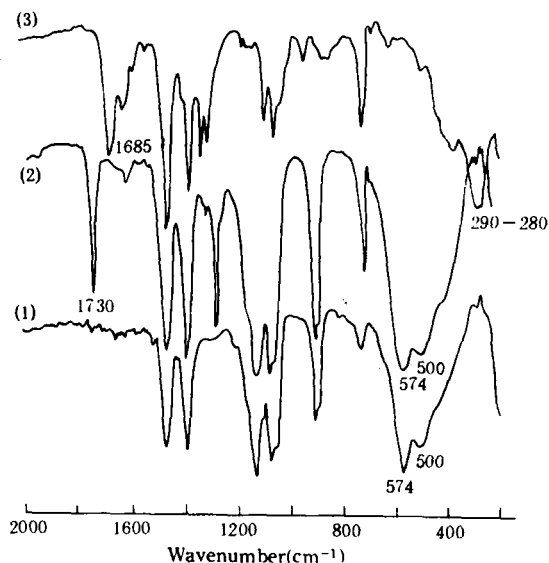


Fig. 1 The IR spectra of (1) $\text{Mg}(\text{OEt})_2$ (2) $\text{Mg}(\text{OEt})_2 / \text{EB}$ and (3) $\text{TiCl}_4 / (\text{Mg}(\text{OEt})_2 / \text{EB})$

XPS. Fig. 2 is powder X-ray diffraction patterns of (1) $\text{Mg}(\text{OEt})_2$ and (2) $\text{Mg}(\text{OEt})_2 / \text{EB}$. The peaks of (1) and (2) are considerably similar to each other except that the peaks in (2) is slightly broadened. The bind energy (E_b) of MgCl_2 , $\text{Mg}(\text{OEt})_2$, $\text{Mg}(\text{OEt})_2 / \text{EB}$ and the catalyst are shown in Table 2

Table 2 XPS analysis of samples

Samples	E_b values (eV)			
	Mg_{2s}	$\text{Ti}_{2p3/2}$	$\text{Cl}_{2p3/2}$	O_{2p}
MgCl_2	90.5		199.3	
$\text{Mg}(\text{OEt})_2$	89.6			532.1
$\text{Mg}(\text{OEt})_2 / \text{EB}$	89.7			532.3
$\text{TiCl}_4 / \text{Mg}(\text{OEt})_2 / \text{EB}$	90.9	458.5	199.0	

The E_b values of Mg and O_{2p} of $\text{Mg}(\text{OEt})_2 / \text{EB}$ are similar to those of $\text{Mg}(\text{OEt})_2$. It can be seen that the results obtained by XD and XPS are consistent with that obtained by IR spectra. So, we can conclude that the EB in comilling product of $\text{Mg}(\text{OEt})_2 / \text{EB}$ exists in free state of being absorbed physically on $\text{Mg}(\text{OEt})_2$.

(2) The interaction between $\text{Mg}(\text{OEt})_2 / \text{EB}$ and TiCl_4

After treating $\text{Mg}(\text{OEt})_2 / \text{EB}$ with TiCl_4 solution, great change has taken place. In the IR spectra of resulting catalyst, the C-O band of OEt group shift to lower wave number due to the formation of ethoxyl titanium chloride. Fig. 1 - (3) is the IR spectrum of the catalyst obtained by the reaction at $[\text{Ti}] / [\text{Mg}] = 8$ in which the peaks at 1131 cm^{-1} and at 1077 cm^{-1} shift to

1093 cm^{-1} and 1062 cm^{-1} respectively.

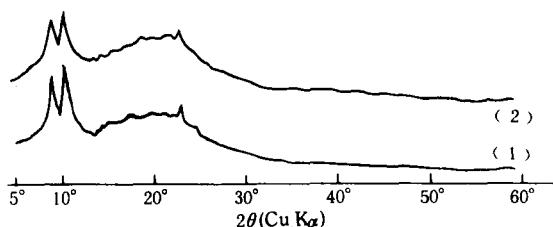


Fig.2 Powder X-ray diffraction patterns of (1) $\text{Mg}(\text{OEt})_2$ and (2) $\text{Mg}(\text{OEt})_2/\text{EB}$

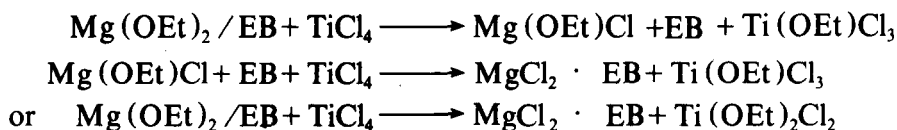
The IR data on C–O bonds in the samples obtained by treating the $\text{Mg}(\text{OEt})_2/\text{EB}$ with TiCl_4 solution at various $[\text{Ti}]/[\text{Mg}]$ ratio are given in Table 3.

Table 3 The IR spectra of samples (cm^{-1})

	$\text{Mg}(\text{OEt})_2$	$\text{Mg}(\text{OEt})\text{Cl}$	$\text{Mg}(\text{OEt})_2/\text{EB}$	$\text{Ti}/(\text{Mg}/\text{EB})$ (mol. ratio)			
				1	2	4	8
$\nu_{\text{C-O}}^{\text{as}}$	1134	1122	1131	1110	1100	1096	1093
$\nu_{\text{C-O}}^{\text{s}}$	1077	1067	1077	1070	1068	1065	1062
C=O			1730				1685

The wavenumber of C–O bands decreases with the increase of $[\text{Ti}]/[\text{Mg}]$ ratio, which is similar to the results of reference^[3], in which the decrease in n value of $\text{Ti}(\text{OEt})_n\text{Cl}_{4-n}/\beta\text{-MgCl}_2$ ($n=1,2,3$) cause a decrease in $\nu_{\text{C-O}}^{\text{as}}$ and $\nu_{\text{C-O}}^{\text{s}}$. Furthermore, the strong band at 574 cm^{-1} for Mg–O bond was removed and accompanied by the appearance of the band at 650 cm^{-1} for Ti–O bond and at around 380 cm^{-1} for Ti–Cl bond (Fig. 1–(3)). These results demonstrated the inference as mentioned above that the Ti component is in the form of ethoxyl titanium chloride in catalysts prepared by treating $\text{Mg}(\text{OEt})_2/\text{EB}$ with TiCl_4 solution. The C=O band appeared at 1685 cm^{-1} can be assigned to characteristic absorption band of MgCl_2/EB surface complexes as already suggested in the $\text{MgCl}_2/\text{EB}/\text{TiCl}_4$ catalyst system^[4].

In the far IR region, there is a rather strong broad band around 280 cm^{-1} . It indicates the presence of Mg–Cl bond. These observation shows that the $\text{Mg}(\text{OEt})_2$ has been transformed into MgCl_2 which is presumably a $\delta\text{-MgCl}_2$ modification^[5]. This conclusion has also been further confirmed by data of the XPS in Table 2. The EB value of Mg_{2s} (90.9 eV) $\text{Cl}_{2p3/2}$ (199.0 eV) of $\text{TiCl}_4/(\text{Mg}(\text{OEt})_2/\text{EB})$ is quite rather close to that of MgCl_2 (Mg_{2s} 90.5 eV, $\text{Cl}_{2p3/2}$ 199.3 eV) but different from that of $\text{Mg}(\text{OEt})_2/\text{EB}$ (Mg_{2s} 89.7 eV). Therefore, the interaction between TiCl_4 and $\text{Mg}(\text{OEt})_2/\text{EB}$ may be denoted as follows:



3. Effect of –OEt group on propylene polymerization

(1) Effect on activity, stereospecificity and molecular weight

It was observed that catalytic activity and also isotacticity index show a rapid decrease with the increase in content of $-OEt$ group (Fig.3). The effect on activity may be attributed to that the active species ethoxyl titanium chloride is not easily to be reduced by co-catalysts $AlEt_3$.

Ligands around Ti are believed to exert considerable influence on catalytic activity and stereospecificity. The larger $-OEt$ group may cause an unfavourable effect in the chain propagation for propylene polymerization. On the other hand, propylene could be less likely to get into a sterically crowded environment than to a more open one that suitable for the generation of atactic polymer.

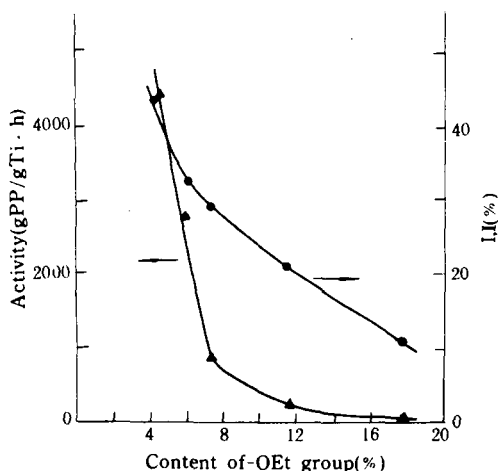


Fig.3 Effect of $-OEt$ group on activity of propylene polymerization and isotactic index of polypropylene

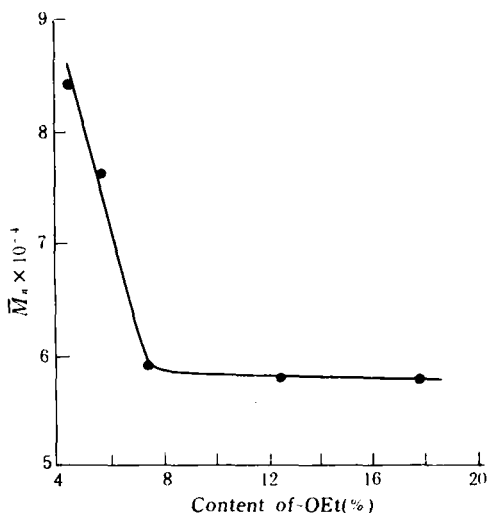


Fig. 4 Effect of $-OEt$ group on molecular weight of polypropylene

The molecular weight of the polymer decrease with increasing amount of $-OEt$ group (Fig.4). It may be interpreted as follows:

As we know the MW of polymer mainly depends on the chain transfer during polymerization. Because of the stronger electron-donating capability of $-OEt$ group, the electron density of active Ti species increases to some extent and this is conducive to elimination of $\beta-H$ of polymer chain and causes to decrease in ratio between the rate constant of propagation and the rate constant of chain transfer and results in a decline of polymer MW .

(2) Effect on rate of polymerization

We have examined the effect of $-OEt$ group content in catalysts on propylene polymerization. In Fig. 5 it shows the kinetic curves of propylene polymerization with present catalysts in various $[Ti]/[Mg]$ ratio, the other series of kinetic curves obtained using the catalysts $Ti(OEt)_nCl_{4-n}/MgCl_2$ ($n=0, 1$ and 4) are illustrated for comparison.

All kinetic curves show decaying type curves. However, in the case of $n=0$ (Fig.6(c)) the rate of polymerization rises very rapidly to a maximum value and then decrease rapidly with time. In the other cases, there is a definite settling period during which the rate increase with time rather moderately. These suggest that the present catalyst seems to be slightly stable as compared with usual catalysts

system $\text{TiCl}_4/\text{MgCl}_2-\text{AlEt}_3$.

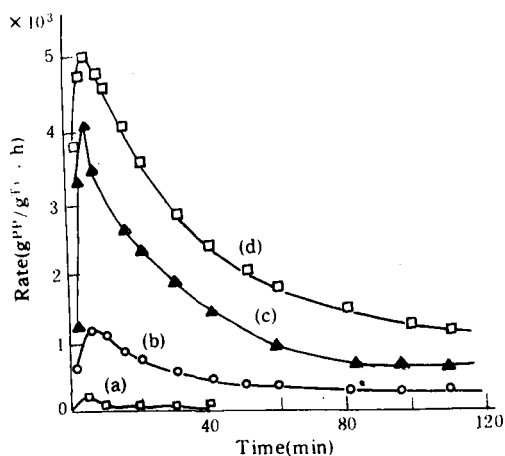


Fig. 5 Kinetic curves of propylene polymerization with catalysts $\text{TiCl}_4/\text{Mg}(\text{OEt})_2/\text{EB}-\text{AlEt}_3$ at various Ti/Mg molar ratio: (a) 1, (b) 2, (c) 4 and (d) 8. ($\text{Al}/\text{Ti}=40$)

(3) Effect on microstructure of polymer

The microstructure of polypropylene prepared with present catalyst was determined by means of $125\text{MHz}^{13}\text{C}$ NMR spectroscopy. The triad tacticities of boiling n -heptane soluble and insoluble fractions were calculated from proton-decoupled ^{13}C NMR expanded spectra of the methyl carbon region and listed in Table 4.

Table 4 Triad stereosequence of polypropylene fractions

Catalysts	Samples	mm (%)	mr (%)	rr (%)
$\text{TiCl}_4/\text{MgCl}_2$ (A)	Insoluble	94.7	4.4	0.9
	Soluble	39.2	29.6	31.2
$\text{Ti}(\text{OEt})\text{Cl}/\text{MgCl}_2$ (B)	Insoluble	92.9	2.9	4.2
	Soluble	52.4	26.8	20.8
$\text{TiCl}_4/\text{Mg}(\text{OEt})_2/\text{EB}=1$ (C)	Soluble	54.0	2.3	23.7
$\text{TiCl}_4/\text{Mg}(\text{OEt})_2/\text{EB}=8$ (D)	Soluble	49.6	28.2	22.2

The triad sequences are described in terms of combination of m (meso isotactic diad) and r (racemic syndiotactic diad). Comparison of the content of triad of insoluble fraction of two polymers prepared by using catalyst A and catalyst B respectively, shows that the content of mm and mr in the former is higher than those in the latter, on the contrary, the rr content is lower. This is presumably contributed to the change of the chemical and spatial environment of the active species causing the change of the mechanism of propylene insertion due to the existence of OEt group. In soluble fraction mm value increase relatively, while the mr and rr values decrease relatively. This means that there are considerable isotactic polymer of lower molecular weight in the soluble fraction and it increases with

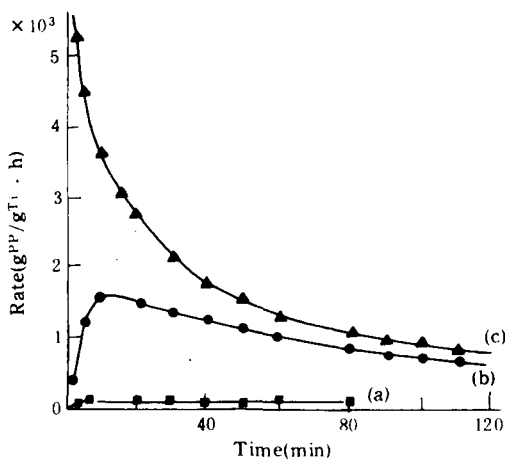


Fig. 6 Kinetic curves of propylene polymerization with catalysts $\alpha\text{-MgCl}_2/\text{Ti}(\text{OEt})_n\text{Cl}_{4-n}-\text{AlEt}_3$. (a) $n=4$; (b) $n=1$ and (c) $n=0$. ($\text{Al}/\text{Ti}=40$)

the increase in OEt group content in catalyst. These results have given further evidence for the isotactic indexes of polymer decrease with the increase in the OEt group content.

Keywords :

Supported catalyst; Polypropylene; $\text{Mg}(\text{OC}_2\text{H}_5)_2$

REFERENCES

- [1] USP 4, 613, 581. Toa Nenryo K.K.
Jpn. Kokai, Tokyo, Koho JP 59,184,206. Idemitsu Kosan Co. Ltd.
- [2] 肖士镜; 蔡世绵; 刘焕勤; 张书清; 周珣蓉. 催化学报 (*Journal of Catalysis*) **1980**, 1(4), 291.
- [3] 赵明阳; 谢仪. 石油化工 (*Petrochemical Technology*) **1987**, (3), 206
- [4] Xiao, Shijing; Cai, Shimian; Chen, Zampo and Liu, Huanqin. "Catalytic Polymerization of Olefins", T. Keii; K. Soga eds., **1986** p.413.
- [5] Zhang, Minghui; Xiao, Shijing. "Proceeding of Third China -Japan -U. S. A. Symposium on Catalysts", Xiamen, China. **1987** p.79.