Polymer Bulletin 12, 105-109 (1984)

Polymer Bulletin

Copolymerization of Ethylene with Propylene by $MgCl_2$-Containing Highly Active Ti Catalysts

Norio Kashiwa, Akira Mizuno and Shuji Minami

Research Center, Mitsui Petrochemical Industries, Ltd., Waki-cho, Kuga-gun,
Yamaguchi-ken, Japan 740

SUMMARY

In the ethylene-propylene copolymerization,two catalyst systems were examined. The one(cat-[a]) was the solid $MgCl_2$-containing Ti treated with ethyl benzoate together with $AlEt_3$, and the other(cat-[c]) was based on a homogeneous mixture of $MgCl_2$ dissolved in 2-ethylhexanol/*n*-decane and $TiCl_4$, which was treated with $AlEt_2Cl$. Both catalyst systems exhibited very high activity in comparison with the conventional catalysts of $TiCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Cl$. These two new systems, however, are different from each other in micro structure of the product copolymer,i.e., the latter(cat-[c]) brings about more random distribution of the monomeric units and also the decreased regiospecificity concerning the arrangement of propylene unit.

INTRODUCTION

It is well known that the $MgCl_2$-containing Ti catalyst combined with alkyl aluminum posesses very high activity in olefin polymerization. In the present study, the characteristics of copolymerizations of ethylene with propylene by the $MgCl_2$-containing Ti catalysts were examined,i.e., both the values of $r_1 \times r_2$ and the regioselectivity for the $MgCl_2$-containing Ti catalyst systems were compared with those for the conventional catalyst systems.

EXPERIMENTAL

Materials; Ethylene and propylene: commercial grade gases produced by Mitsui Petrochemical Industries Ltd.; *n*-decane, $AlEt_3$, $AlEt_2Cl$, $VOCl_3$, $TiCl_4$, ethyl benzoate(EB) and 2-ethylhexanol(EHA): commercially available reagents; $TiCl_3$-AA(TAC-131): a product of Toyo Stauffer Chemical Co. Ltd, Japan.

Preparation of $MgCl_2$-containing catalysts; Solid $MgCl_2$-containing Ti catalyst(Ti component of cat-[a]): Solid $MgCl_2$-containing Ti catalyst($MgCl_2$/$TiCl_4$/EB) was prepared by the same method described in a previous paper(1). ; A homogeneous mixture of $MgCl_2$ dissolved in 2-ethylhexanol/*n*-decane and $TiCl_4$($MgCl_2$/$TiCl_4$/3EHA: Ti component of cat-[c])(2): Anhydrous $MgCl_2$ (0.105 *mol*), EHA(0.315 *mol*) and *n*-decane(200 *ml*) were stirred at 130°C for 2 hrs. The resultant solution was cooled to room temperature, to which $TiCl_4$ was added(Mg/Ti mole ratio = 10) to produce a clear solution. When the solution was reacted with $AlEt_2Cl$ in a nitrogen atmosphere, the system became cloudy by the formation of a small amount of fine insoluble particles.

Copolymerization and copolymer characterization; Copolymerization of ethylene with propylene was carried out in a 500 *ml* glass vessel using 250 *ml* of *n*-decane as solvent. The mixture gas of ethylene and propylene was introduced at 200 *Nl/hr* into the system at the polymerization temperature. Pre-determined amount of alkyl aluminum, EB(if necessary) and Ti or

V catalyst component were added in this order. Copolymerization was performed for 30 *min.* under atmospheric pressure, which was terminated by adding a small amount of isobuthyl alcohol. The polymer solution was introduced to a large amount of mixture of methanol and acetone(vol. ratio 1:1). The obtained precipitate was separated and dried in vaccuo. By the DSC analysis for the obtained copolymer, any peaks assigned to both homopolymer of ethylene and propylene were not detected. The composition of the obtained copolymer was determined by ^{13}C-NMR spectrum measured at 120°C by the same method of Ray et.al.(3). ^{13}C-NMR spectrum was recorded with a JEOL FX-100 spectrometer operating at 25.05 MHz under proton decoupling in Fourier Transform(FT) mode. Instrument conditions were $\pi/4$ pulse of 6μs, 4.23s repitation rate and 1500 Hz sweep width. The copolymer solution was made up in hexachloro-1,3-butadiene to 20 w/v%. The chemical shift was represented in ppm downfield from tetramethyl silane(TMS) as internal standard.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of copolymerizations by the solid $MgCl_2$-containing Ti catalyst system($MgCl_2/TiCl_4$/EB - $AlEt_3$/EB:cat-[a]) and by the conventional $TiCl_3$ catalyst system($TiCl_3$ - $AlEt_2Cl$:cat-[b]), respectively.

Table 1 Ethylene-propylene copolymerization by the catalyst system of $MgCl_2/TiCl_4$/EB - $AlEt_3$/EB(cat-[a])

Run No.	Ethylene/propylene in feed(in liquid phase) (*mol%*)	Ethylene contents in copolymers (*mol%*)	Copolymer yields in Kg per *mmol* of Ti
1	6.9/93.1	21.5	1.28
2	11.7/88.3	30.0	1.55
3	16.4/83.6	42.5	1.52
4	22.8/77.2	52.5	1.62
5	30.7/69.3	67.3	1.59

Copolymerization conditions:[Al]=1.8 *mmol/l*, [Ti]=0.03 *mmol/l*, [EB]=0.6 *mmol/l*, temp.=70°C, time=30 *min.*

Table 2 Ethylene-propylene copolymerization by the catalyst system of $TiCl_3$ - $AlEt_2Cl$(cat-[b])

Run No.	Ethylene/propylene in feed(in liquid phase) (*mol%*)	Ethylene contents in copolymers (*mol%*)	Copolymer yields in Kg per *mmol* of Ti
1	6.1/93.9	23.5	0.0078
2	11.4/88.6	35.2	0.012
3	17.4/82.6	54.4	0.076
4	23.5/76.5	70.7	0.083
5	30.3/69.7	77.2	0.011

Copolymerization conditions:[Al]=10 *mmol/l*, [Ti]=1.0 *mmol/l*, temp.=70°C, time=30 *min.*

In comparison with the conventional $TiCl_3$ catalyst system(cat-[b]), the solid $MgCl_2$-containing Ti catalyst system(cat-[a]) showed about a twenty times higher activity in the ethylene-propylene copolymerization, which gave copolymers having slightly lower ethylene units contents at the same ethylene/propylene feed ratio.

The values of the reactivity ratios (r_1 and r_2) for both catalyst systems were calculated by Fineman-Ross method using the results of Tables 1 and 2, which are given in Table 3, where the values are being compared with those calculated in the same way for $MgCl_2/TiCl_4$/3EHA - $AlEt_2Cl$(cat-[c]) and those for $VOCl_3$ - $AlEt_2Cl$(cat-[d]) cited from a literature(4).

Table 3 Reactivity ratios for various catalyst systems

Catalyst system	r_1	r_2	$r_1 \times r_2$
cat-[a]:$MgCl_2/TiCl_4$/EB - $AlEt_3$/EB	5.5	0.36	2.0
cat-[b]:$TiCl_3$ - $AlEt_2Cl$	11.6	0.35	4.1
cat-[c]:$MgCl_2/TiCl_4$/3EHA - $AlEt_2Cl$[a)]	6.0	0.02	0.13
cat-[d]:$VOCl_3$ - $AlEt_2Cl$	12.1[b)]	0.018[b)]	0.22[b)]

a) r_1 and r_2 were calculated in the same way as for cat-[a] and [b]. Copolymerization conditions:[Al]=2.4 *mmol/l*, [Ti]=0.04 *mmol/l*, temp.=90°C, time=30 *min.*, ethylene/propylene feed ratio(in solution) was varied from 4/96 to 58/42(*mol/mol*).

b) From reference (4).

It is of interest to note in Table 3 that the values of $r_1 \times r_2$ for the solid Ti based catalyst systems(cat-[a] and [b]) are higher than 1.0, whereas those for the catalyst systems derived from the homogeneous Ti and V catalyst components(cat-[c] and [d]) are lower than 1.0. Thus, the distribution of the ethylene and propylene monomeric units is more random with cat-[c] and [d] in comparison with the cases of cat-[a] and [b].

In Table 4, characteristics of four catalyst systems of cat-[a] to cat-[d], i.e., catalyst activity(copolymer yield in Kg per mol of Ti or V) and the micro structure of copolymer, are illustrated at a copolymer composition of about 70 *mol%* ethylene unit. It is noteworthy that cat-[c] derived from the homogeneous $MgCl_2$-containing Ti catalyst($MgCl_2/TiCl_4$/3EHA) also exhibits very high activities. These results indicate $TiCl_4$ is not necessarily fixed on the solid state $MgCl_2$ before the introduction to the polymerization system.

Table 4 Distributions of $+CH_2+_n$ sequences in Ethylene-propylene copolymers with various catalyst systems

Catalyst system	Poly. temp. (°C)	Copolymer yields in Kg per mol of Ti or V	Ethylene contents in copolymers (*mol%*)	Distribution of $+CH_2+_n$					
				n=1	n=2	n=3	n=4	n=5	n>6
cat-[a][a)]	70	1.59	67.3	43	0	24	0	12	21
cat-[b][b)]	70	0.011	77.2	36	0	26	0	3	36
cat-[c][c)]	90	0.88	68.2	30	4	27	3	10	27
cat-[d][d)]	30	0.13	69.9	21	11	19	6	8	35

a) Run No.5 in Table 1.

b) Run No.5 in Table 2.

c) Ethylene/propylene in feed(in solution)=18.4/81.6(*mol/mol*); other copolymerization conditions are given in Table 3.

d) Copolymerization conditions: [Al]=2.0 *mmol/l*, [V]=0.2 *mmol/l*, time=30 *min.*, ethylene/propylene in feed(in solution)=12.7/87.3(*mol/mol*).

Distribution of $+CH_2+_n$ sequences in Table 4 were calculated using Eqs. (I) to (VII) (3).

$$+CH_2+_1 \quad (n=1) \quad I_{\alpha\alpha}/S \qquad (I)$$

$$+CH_2+_2 \quad (n=2) \quad 0.5I_{\alpha\beta}/S \qquad (II)$$

$$+CH_2+_3 \quad (n=3) \quad I_{\beta\beta}/S= 0.5I_{\alpha\gamma}/S \qquad (III)$$

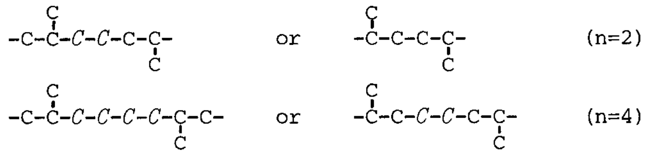
$$+CH_2+_4 \quad (n=4) \quad 0.5I_{\beta\gamma}/S= 0.5(I_{\alpha\delta^+} - I_{\beta\delta^+})/S \qquad (IV)$$

$$+CH_2+_5 \quad (n=5) \quad I_{\gamma\gamma}/S= 0.5(I_{\beta\delta^+} - I_{\gamma\delta^+})/S \qquad (V)$$

$$+CH_2+_{>6} \quad (n>6) \quad 0.5I_{\gamma\delta^+}/S \qquad (VI)$$

$$S=I_{\alpha\alpha}+0.5(I_{\alpha\beta} + I_{\alpha\delta} + I_{\alpha\gamma^+}) \qquad (VII)$$

where I_{ij} is the peak area of secondery carbon atoms, and two Greek subscripts(i,j) indicating the position of secondery carbon atoms are the same as the definitions reported by C.J.Carman et.al.(5). $+CH_2+_2$ and $+CH_2+_4$ (Eqs.(II) and (IV); n=2, 4) represent that the propylene units take head-to-head or tail-to-tail arrangement(propylene inversions), i.e.,



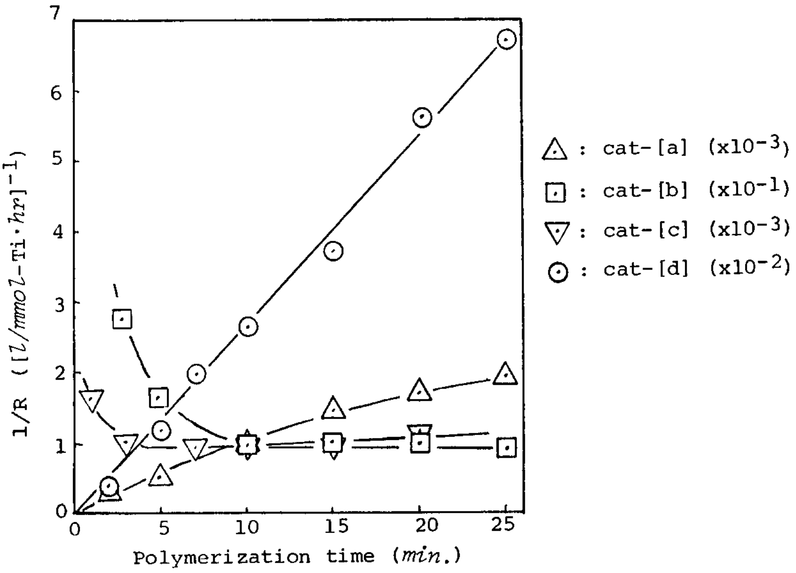
$-\mathrm{C}-\overset{\mathrm{C}}{\mathrm{C}}-C-C-\mathrm{C}-\underset{\mathrm{C}}{\mathrm{C}}-$ or $-\overset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-\mathrm{C}-\underset{\mathrm{C}}{\mathrm{C}}-$ (n=2)

$-\mathrm{C}-\overset{\mathrm{C}}{\mathrm{C}}-C-C-C-C-\underset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-$ or $-\overset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-C-C-\mathrm{C}-\underset{\mathrm{C}}{\mathrm{C}}-$ (n=4)

where C represents propylene carbons and *C* represents ethylene carbons. Doi(6) reported that any irregular inverse arrangement of the monomeric unit could not be detected in polypropylene prepared by $MgCl_2$-supported Ti catalyst systems. The data for cat-[a] in Table 4 agrees to Doi's report. On the other hand, cat-[c] composed of the homogeneous $MgCl_2$-containing Ti and $AlEt_2Cl$ as well as the homogeneous V based catalyst(cat-[d])(7) gave copolymer having the inverse arrangement of propylene units. The randomness and the regioselectivity for the copolymer obtained with cat-[c] suggest that the active centers for cat-[c] are rather similar to those for the homogeneous V based catalyst system(cat-[d]) than those for the heterogeneous Ti based catalyst systems(cat-[a] and cat-[b]), although the homogeneous $MgCl_2$-containing Ti catalyst resulted in the formation of a small amount of fine insoluble particles by the reaction with cocatalyst, $AlEt_2Cl$.

Next, Fig.1 shows a parameter of 1/R($[l/mmol\text{-}Ti\cdot hr]^{-1}$) as a function of polymerization time, where R is the copolymerization rate.

Fig.1 Relation between 1/R and polymerization time.



The kinetics for cat-[d] in Fig.1, which shows a linear relationship, agrees to the fact that V based homogeneous catalyst system shows a second-order deactivation of active species by the coupling(8). On the other hand, cat-[c] does not show a second-order deactivation and the kinetics is similar to the heterogeneous cat-[b] in which solid $TiCl_3$ is used.

Table 5 Summarized results

Catalyst system	Reactivity ratio $r_1 \times r_2$	Second-order decay in activity	Propylene inversions in the copolymer	The physical state of Ti or V catalyst component
cat-[a]:$MgCl_2/TiCl_4/EB$ $-AlEt_3/EB$	2.0	no	no	solid
cat-[b]:$TiCl_3-AlEt_2Cl$	4.1	no	no	solid
cat-[c]:$MgCl_2/TiCl_4/3EHA$ $-AlEt_2Cl$	0.13	no	yes	solution
cat-[d]:$VOCl_3-AlEt_2Cl$	0.22[a)]	yes	yes	solution

a) From reference(4).

Table 5 summarizes the results of the present study which lead to the following conclusions.

1) $MgCl_2$-containing Ti catalyst in conjunction with alkyl aluminum shows a very high activity in ethylene-propylene copolymerization, whether Ti catalyst component is in the solid state or the homogeneous state.
2) The micro structure of the copolymer with the solid $MgCl_2$-containing Ti based catalyst system is similar to that with the conventional solid $TiCl_3$ catalyst system.
3) The homogeneous $MgCl_2$-containing Ti based catalyst system resembles the homogeneous V based catalyst system in the values of $r_1 \times r_2$ and the inverse arrangement of propylene unit, whereas the kinetics character of the homogeneous $MgCl_2$-containing Ti based catalyst system is rather similar to that of the conventional $TiCl_3$ catalyst system.

REFERENCES

(1) N.Kashiwa and J.Yoshitake, Makromol.Chem., Rapid Commun. 3,211(1982)
(2) Mitsui Petrochemical Industries, Japan Pat.(Open), 55-78004(1980)
(3) G.J.Ray, P.E.Johnson and J.R.Knox, Macromolecules 10,773(1977)
(4) C.Cozewith and G.Ver strate, ibid 4,482(1971)
(5) C.J.Carman, R.A.Harrington and C.E.Wilkes, ibid 10,536(1977)
(6) Y.Doi, Makromol.Chem., Rapid Commun. 3,635(1982)
(7) J.Van Schooten and S.Mostert, Polymer 4,135(1963)
(8) W.E.Smith and R.G.Zelmer, J.Polymer Sci., Part A 1,2587(1963)

Accepted July 27, 1984