Polymer Bulletin 13, 511-517 (1985)

Polymer Bulletin

Copolymerization

Solution Copolymerization of Ethylene with α-Olefin by Vanadium Catalyst

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SUMMARY

Copolymerization of ethylene with an α-olefin, i.e. propylene, butene-1 and 4-methyl-pentene-1(4-MP-1), was carried out by vanadium catalyst prepared by treating $VOCl_3$ with $(n\text{-}C_8H_{17})_3Al$ in decane in combination with Et_3Al and $CHCl_3$. The copolymerization system was homogeneous at a temperature as high as 170 °C. It has been revealed that the monomer insertion reaction of irregular direction, i.e. the insertion giving rise to the growing end of secondary alkyl / catalyst bond, occurs occasionally at the propagation of the α-olefin comonomer. The irregular insertion takes place most frequently with 4-MP-1. The chain transfer with hydrogen takes place more preferentially at the irregular propagation end in comparison with the regular one.

INTRODUCTION

Our previous paper(1) reported the copolymerization of ethylene with α-olefin carried out at a temperature as high as 170 °C by $MgCl_2$ supported $TiCl_4$ catalyst. In this paper, by vanadium catalyst prepared by treating $VOCl_3$ with $(n\text{-}C_8H_{17})_3Al$ in decane, copolymerization of ethylene with α-olefin at the same temperature was carried out to investigate the termination and chain transfer reactions.

EXPERIMENTAL

Materials

$TiCl_4$(Osaka Titanium Co., Japan), $VOCl_3$, $CHCl_3$(Wako Jyun-yaku Co., Japan), Et_3Al(Nippon Alkyl-Aluminum Co., Japan) and $(n\text{-}C_8H_{17})_3Al$(Toyo Stauffer Chemical, Japan) were used without further purification. Decane, cyclohexane and 4-methyl-pentene-1(4-MP-1) were used after nitrogen bubbling for 2 h. $MgCl_2$(Wako Jyun-yaku Co., Japan) was used without further treatment. Ethylene(Seitetsu Kagaku Co., Japan), propylene(Mitsui Toatsu Chem. Co., Japan) and butene-1(Mitsubishi Kasei Co., Japan) had a purity of over 99.9, 99.9 and 98.7 %, respectively.

Preparation of catalyst

Vanadium catalyst ; Ten millimoles of $(n\text{-}C_8H_{17})_3Al$ and 100 *ml* of decane were put in a 400 *ml* flask equipped with a stirrer under nitrogen, which was cooled down to 0 °C. Then, 5 *mmol* of $VOCl_3$ was added dropwise and the mixture was heated at 80 °C for 1 h. The resulting product was soluble in decane.

$MgCl_2$ supported $TiCl_4$ catalyst ; This catalyst was prepared according to our previous paper(1).

Polymerization

One liter of a mixture of cyclohexane and comonomers, i.e. propylene, butene-1 and 4-MP-1, was added to a 2 *l* stainless steel reactor equipped with a stirrer under nitrogen, which was heated to 165 °C, and then a predetermined amount of vanadium(or titanium) catalyst, alkyl-aluminum and $CHCl_3$(only in the polymerization with vanadium catalyst) were added. Subsequently, a predetermined amount of hydrogen and ethylene were introduced. Polymerization was carried out under 25 *kg/cm²G* of the total pressure at 170 °C for 40 min. Ethylene was continuously supplied to keep the total pressure at 25 *kg/cm²G*. After 40 min., a small amount of ethanol was added to the reactor to stop polymerization, and then the whole product was poured into a large amount of methanol. The produced polymer was filtrated and vacuum-dried at 80 °C for 12 h.

Characterization of polymer

Molecular weight distribution(MWD) of the produced polymer was examined by GPC(Waters Associates, Model ALC/GPC 150C), using polystyrene gel columns (10^7, 10^6, 10^5, 10^4 and 10^3 Å pore size) and o-dichlorobenzene as solvent at 135 °C. The amount of comonomer contained in copolymer and the number of terminal double bond were determined by IR spectroscopy(2,3). Intrinsic viscosity was measured in decalin at 135 °C.

RESULTS AND DISCUSSION

In Table 1, the activity(in *g*-polymer/*mmol*-V) of the vanadium catalyst prepared by treating $VOCl_3$ with $(n\text{-}C_8H_{17})_3Al$ in decane in combination with Et_3Al and $CHCl_3$(hereinafter called Vc catalyst system) in the ethylene homopolymerization at a high temperature of 170 °C at which the polymerization system was homogeneous was compared with that of $VOCl_3$ in combination with Et_3Al and $CHCl_3$. The Vc catalyst system showed a high activity, 11100 *g*-polymer/*mmol*-V, which was over 5 times as high as that with the catalyst system directly prepared in situ from Et_3Al and $VOCl_3$ in the polymerization system.

Table 2 shows the results of copolymerization of ethylene with *α*-olefin i.e. propylene, butene-1 or 4-methyl-pentene-1(4-MP-1), at 170 °C by the Vc catalyst system. As a reference, the results with a highly active of $MgCl_2$ supported $TiCl_4$ catalyst in combination with Et_3Al are also shown. In the copolymerization, the activity of the Vc catalyst system was much lowered to less than 2000 *g*-polymer/*mmol*-V, which was under 1/5 times as low as the ethylene homopolymerization. On the other hand, the $MgCl_2$ supported $TiCl_4$ catalyst showed a high activity, more than 10000 *g*-polymer/*mmol*-Ti, in both polymerizations.

Our previous paper(1) reported that the termination at comonomer unit by chain transfer reaction with monomer or β-elimination takes place more easily when propylene unit is present at the growing polymer chain in the copolymerization of ethylene with *α*-olefin by $MgCl_2$ supported $TiCl_4$ catalyst. The following scheme(the next page) is generally considered as the termination and chain transfer reactions. The terminal bonds of the produced polymer are classified into two types, the terminal saturated bond by eqs.(1), (2) and (3) and the terminal unsaturated bond by eqs.(4) and (5). In the copolymerization of ethylene with *α*-olefin, if the *α*-olefin comonomer inserts to active sites only in the direction so as to produce the primary alkyl / catalyst bond, two kinds of the terminal unsaturated bond can be formed

Table 1 Activity of vanadium catalyst in ethylene homopolymerization

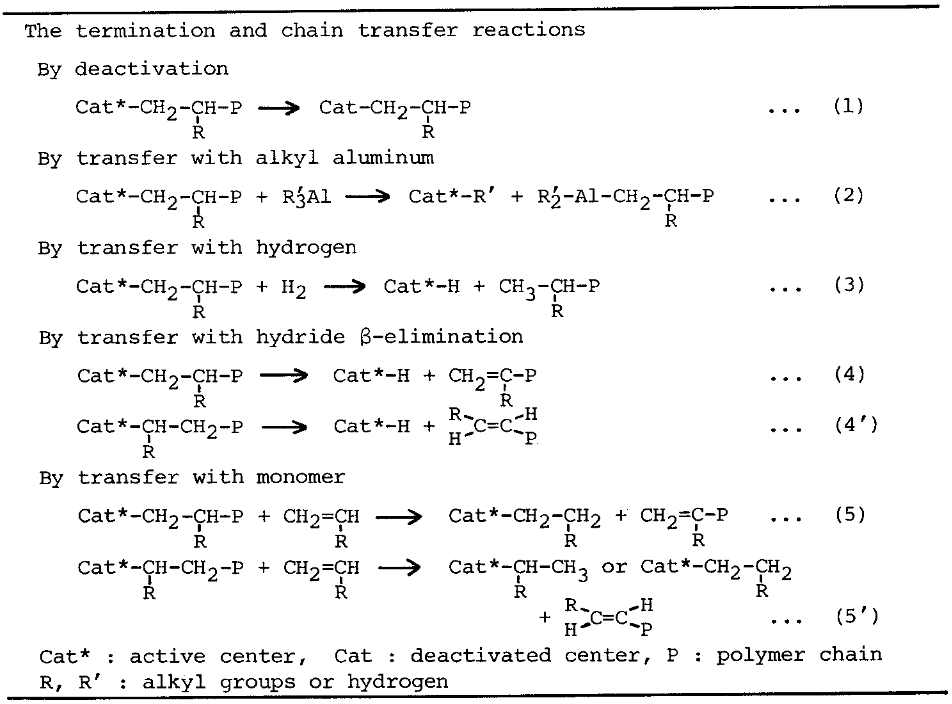
Catalyst systems	Activities(*g*-polymer/*mmol*-V)
$VOCl_3\text{-}Et_3Al/CHCl_3$	2100
$VOCl_3/(n\text{-}C_8H_{17})_3Al\text{-}Et_3Al/CHCl_3$	11100

Polymerization conditions ; 170 °C for 40 min under 25 *kg/cm²G* of total pressure, 2.1 *mmol* of hydrogen, 0.01 *mmol* of V, 0.4 *mmol* Et_3Al and 0.2 *mmol* of $CHCl_3$ in 1 *l* of cyclohexane

Table 2 Copolymerization of ethylene with *α*-olefin

Run No.	Supplied comonomers (*mol*)	H_2 (*mmol*)	Polymer yields (*g*)	Activities (*g*-polymer/*mmol*-V or Ti)	[η] (*dl*/*g*)	Comonomer contents (*mol*%)	$\overline{Mw}/\overline{Mn}$	$\overline{Mn}$ (10^{-3})	Note
1	-	2.1	110.5	11100	1.64	-	2.25	33.0	V-CAT.
2	Propylene 0.38	2.1	139.5	1400	1.30	3.1	2.27	24.0	V-CAT.
3	Propylene 0.63	2.1	146.2	1500	1.16	4.2	2.29	19.9	V-CAT.
4	Butene-1 0.32	2.1	174.2	1700	1.37	2.1	2.33	25.7	V-CAT.
5	Butene-1 0.53	2.1	108.0	1100	1.23	3.1	2.52	18.5	V-CAT.
6	Butene-1 1.05	2.1	33.8	340	0.81	7.4	3.00	9.8	V-CAT.
7	4-MP-1 0.79	2.1	57.5	580	1.21	2.1	3.00	15.8	V-CAT.
8	4-MP-1 1.57	2.1	28.3	280	0.99	4.3	3.25	10.9	V-CAT.
9	4-MP-1 2.36	2.1	21.0	210	0.86	5.3	5.83	5.3	V-CAT.
10	4-MP-1 0.79	0	38.7	390	3.75	1.5	4.81	51.3	V-CAT.
11	4-MP-1 1.57	0	21.1	210	3.87	3.1	7.36	37.0	V-CAT.
12	4-MP-1 2.36	0	16.4	160	3.88	4.8	8.87	35.2	V-CAT.
13	-	14	84.4	16900	1.97	-	4.30	22.8	Ti-CAT.
14	Propylene 0.50	0	74.0	14800	2.33	2.5	6.61	18.8	Ti-CAT.
15	Propylene 0.50	5	75.7	15100	2.14	2.2	6.23	17.7	Ti-CAT.
16	Propylene 0.50	11	77.0	15400	1.71	2.3	5.34	15.1	Ti-CAT.
17	Propylene 0.88	0	72.6	14500	1.93	4.6	6.73	14.2	Ti-CAT.
18	Propylene 0.88	5	74.8	15000	1.70	4.3	5.81	13.8	Ti-CAT.
19	4-MP-1 1.57	14	78.0	15600	1.79	2.5	4.35	19.7	Ti-CAT.

Polymerization conditions ; 170 °C for 40 min under 25 *kg*/*cm*^{2}*G* of total pressure, (Run 1) 0.01 *mmol* of V, 0.4 *mmol* of Et_3Al and 0.2 *mmol* of $CHCl_3$, (Run 2 to 12) 0.1 *mmol* of V, 2.0 *mmol* of Et_3Al and 1.0 *mmol* of $CHCl_3$, (Run 13 to 19) 0.005 *mmol* of Ti and 0.4 *mmol* of Et_3Al in 1 *l* of a mixture of cyclohexane and comonomer.



The termination and chain transfer reactions

By deactivation

$$\mathrm{Cat^*\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P \longrightarrow Cat\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P} \quad \cdots \quad (1)$$

By transfer with alkyl aluminum

$$\mathrm{Cat^*\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P + R'_3Al \longrightarrow Cat^*\text{-}R' + R'_2\text{-}Al\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P} \quad \cdots \quad (2)$$

By transfer with hydrogen

$$\mathrm{Cat^*\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P + H_2 \longrightarrow Cat^*\text{-}H + CH_3\text{-}\underset{R}{C}H\text{-}P} \quad \cdots \quad (3)$$

By transfer with hydride β-elimination

$$\mathrm{Cat^*\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P \longrightarrow Cat^*\text{-}H + CH_2{=}\underset{R}{C}\text{-}P} \quad \cdots \quad (4)$$

$$\mathrm{Cat^*\text{-}\underset{R}{C}H\text{-}CH_2\text{-}P \longrightarrow Cat^*\text{-}H + \begin{matrix}R & & H\\ & C{=}C & \\ H & & P\end{matrix}} \quad \cdots \quad (4')$$

By transfer with monomer

$$\mathrm{Cat^*\text{-}CH_2\text{-}\underset{R}{C}H\text{-}P + CH_2{=}\underset{R}{C}H \longrightarrow Cat^*\text{-}CH_2\text{-}\underset{R}{C}H_2 + CH_2{=}\underset{R}{C}\text{-}P} \quad \cdots \quad (5)$$

$$\mathrm{Cat^*\text{-}\underset{R}{C}H\text{-}CH_2\text{-}P + CH_2{=}\underset{R}{C}H \longrightarrow Cat^*\text{-}\underset{R}{C}H\text{-}CH_3 \text{ or } Cat^*\text{-}CH_2\text{-}\underset{R}{C}H_2 + \begin{matrix}R & & H\\ & C{=}C & \\ H & & P\end{matrix}} \quad \cdots \quad (5')$$

Cat* : active center, Cat : deactivated center, P : polymer chain
R, R′ : alkyl groups or hydrogen

depending on the end unit of the growing polymer chain. Namely, vinyl bond and vinylidene bond are to be formed when ethylene and *α*-olefin are placed at the end unit, respectively. If the *α*-olefin comonomer is inserted so as to produced the growing chain end of a secondary alkyl / catalyst bond (secondary insertion), trans-vinylene bond is to be formed through eqs.(4′) and (5′) in addition to vinyl bond and vinylidene bond. Table 3 shows the average number of terminal double bonds contained in unit polymer chain, which has been calculated from the number of the terminal double bond by IR and the number average molecular weight($\overline{Mn}$) by GPC. Vinyl and vinylidene bonds were detected in the copolymer by both of the Vc catalyst system and the $MgCl_2$ supported $TiCl_4$ catalyst system. However, trans-vinylene bonds could be detected appreciably only in case of the Vc catalyst system. These results indicate that by the Vc catalyst, the secondary insertion of monomers to active sites also takes place in addition to the primary insertion in the copolymerization. In Fig. 1, the relation between the total number of vinylidene and trans-vinylene bonds and the number of comonomer per unit chain of the polymer by the Vc catalyst system is shown. In the 4-MP-1 copolymer compared with the propylene and butene-1 copolymer, a remarkable increase of the total number of vinylidene and trans-vinylene bonds is seen with an increase of the content of comonomer. These facts mean that the termination by chain transfer reaction through (4),(4′), (5) and (5′) takes place more easily when 4-MP-1 unit is present at the growing polymer chain in contrast to the $MgCl_2$ supported $TiCl_4$ catalyst system.

Next, the effect of hydrogen on chain transfer reaction according to (4),(4′), (5) and (5′) was examined. In Fig. 2 and 3, the variation of the number of vinylidene bond and that of trans-vinylene bond were plotted against the number of 4-MP-1 unit per unit chain of the polymer by the Vc catalyst system, respectively. In addition, in Fig. 4, the relation between the number of vinylidene bond and that of propylene unit per unit chain of

Table 3 The average number of terminal double bond per unit polymer chain *

Run No.	Comonomer contents (*mol%*)	$R\text{-}CH=CH_2$	$\begin{smallmatrix}R\\R\end{smallmatrix}\!>\!C=CH_2$	$\begin{smallmatrix}R\\H\end{smallmatrix}\!>\!C=C\!<\!\begin{smallmatrix}H\\R\end{smallmatrix}$	Addition of H_2	Note
1	-	0.14	nd	nd	Yes	V-CAT.
2	Propylene 3.1	0.08	0.06	nd	Yes	V-CAT.
3	Propylene 4.2	0.07	0.04	0.03	Yes	V-CAT.
4	Butene-1 2.1	0.07	nd	0.05	Yes	V-CAT.
5	Butene-1 3.1	0.05	0.03	0.07	Yes	V-CAT.
6	Butene-1 7.4	0.06	nd	0.06	Yes	V-CAT.
7	4-MP-1 2.1	0.10	0.07	0.04	Yes	V-CAT.
8	4-MP-1 4.3	0.10	0.09	0.05	Yes	V-CAT.
9	4-MP-1 5.3	0.04	0.05	0.03	Yes	V-CAT.
10	4-MP-1 1.5	0.37	0.18	0.22	No	V-CAT.
11	4-MP-1 3.1	0.34	0.19	0.29	No	V-CAT.
12	4-MP-1 4.8	0.40	0.23	0.38	No	V-CAT.
13	-	0.64	nd	nd	Yes	Ti-CAT.
14	Propylene 2.5	0.39	0.20	nd	No	Ti-CAT.
15	Propylene 2.2	0.43	0.21	nd	Yes	Ti-CAT.
16	Propylene 2.3	0.42	0.18	nd	Yes	Ti-CAT.
17	Propylene 4.6	0.34	0.31	nd	No	Ti-CAT.
18	Propylene 4.3	0.40	0.27	nd	Yes	Ti-CAT.
19	4-MP-1 2.5	0.55	nd	nd	Yes	Ti-CAT.

nd ; ≤ 0.02

* Calculated from the number of the terminal double bond by IR and $\overline{Mn}$ by GPC

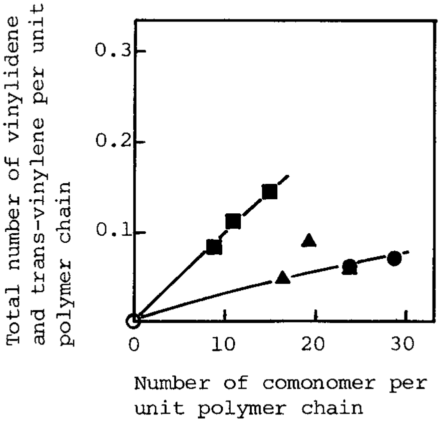


Fig. 1 Relation between the total number of vinylidene and trans-vinylene bond and the number of comonomer per unit chain of the polymer by Vc catalyst.

- ● Propylene copolymers
- ▲ Butene-1 copolymers
- ■ 4-MP-1 copolymers
- ○ Ethylene homopolymer

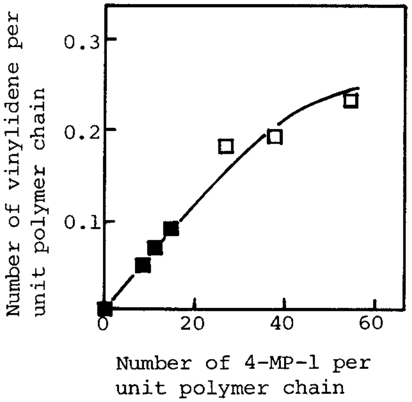


Fig. 2 Relation between the number of vinylidene bond and 4-MP-1 per unit chain of the polymer by Vc catalyst.

- ■ System with hydrogen
- □ System without hydrogen

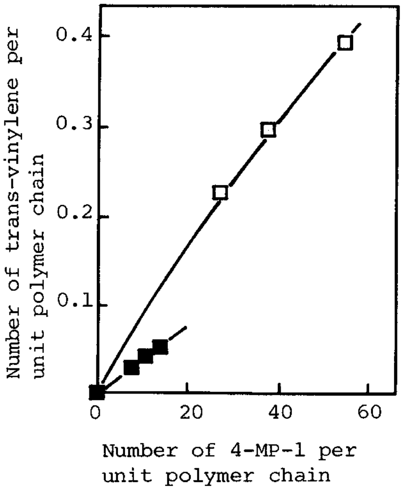


Fig. 3 Relation between the number of trans-vinylene bond and 4-MP-1 per unit chain of the polymer by Vc catalyst.

- ■ System with hydrogen
- □ System without hydrogen

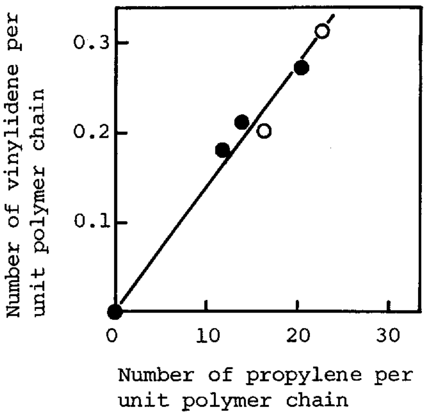


Fig. 4 Relation between the number of vinylidene bond and propylene per unit chain of the polymer by $MgCl_2$ supported $TiCl_4$ catalyst.
● System with hydrogen
○ System without hydrogen

the polymer by the $MgCl_2$ supported $TiCl_4$ catalyst system was also shown. In every polymer, an increase of the comonomer content caused an increase of the number of vinylidene bonds, which was hardly influenced by the amount of added hydrogen. On the other hand, the number of trans-vinylene bonds was reduced by the addition of hydrogen. These results suggest that the termination by chain transfer reaction with hydrogen preferentially takes place at the end of the growing polymer by the secondary insertion of 4-MP-1.

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Accepted June 10, 1985

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