

Solution Copolymerization of Ethylene with α -Olefins by a $MgCl_2$ Supported $TiCl_4$ Catalyst

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SUMMARY

Copolymerization of ethylene with α -olefins, i.e. propylene, butene-1, 4-methyl-pentene-1(4-MP-1), was carried out by a $MgCl_2$ supported $TiCl_4$ catalyst in combination with Et_3Al at a temperature as high as 170 °C at which the polymerization system was homogeneous. This catalytic system showed very a high activity and produced copolymers having a density of 0.91 - 0.94 g/ml. Of these three kinds of comonomers, propylene showed the highest reactivity and caused most frequently the termination of a polymer growing by chain transfer reaction and produced copolymers having the broadest MWD.

INTRODUCTION

Since the discovery of Ziegler-catalyst, a lot of studies on the mechanism and kinetics of olefin polymerization have been carried out. However, most of their studies have been done at the polymerization temperature lower than 120 °C, and there are less studies on polymerization at the high temperatures at which the produced polymer is soluble in the solvent.

In this study, at a temperature as high as 170 °C, copolymerization of ethylene with α -olefins was carried out by a $MgCl_2$ supported $TiCl_4$ catalyst and polymerization behavior was investigated.

EXPERIMENTAL

Materials

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

Preparation of a $MgCl_2$ supported $TiCl_4$ catalyst

One milliliter of $TiCl_4$ and 20 g of $MgCl_2$ were put in a 800 ml stainless steel pot having 2.8 kg of stainless steel balls (15 mm Φ), and the mixture milled for 8 h under nitrogen. The milled solid product was heated with 200 ml of decane at 80 °C for 1 h in a 400 ml flask. Subsequently, the solid products (catalyst) were separated by the filtration and washed with decane repeatedly to remove the unfixed $TiCl_4$. The amount of Ti contained in the solid catalyst was determined by the colorimetric analysis. Twenty one mg of Ti atoms were detected in 1 g of the catalyst.

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 0.005 mmol of Ti and 0.4 mmol of Et₃Al were added. Subsequently, a predetermined amount of hydrogen, and ethylene were introduced. Polymerization was carried out under 25 kg/cm²G of total pressure at 170 °C for 40 min. Ethylene was continuously supplied to keep the total pressure at 25 kg/cm²G. After 40 minutes, 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 150 C), using polystyrene gel columns (10⁷, 10⁶, 10⁵, 10⁴ and 10³ Å pore size) and o-dichlorobenzene as solvent at 135 °C.

The amount of comonomer contained in copolymer was calculated from the number of branching determined by IR spectroscopy (1), and the number of terminal double bond was also determined by IR spectroscopy (2). Intrinsic viscosity was measured in decalin at 135 °C. Density was measured at 23 °C by using a density gradient column employing methanol and sodium acetate solution on the sample of polymer which was cooled down from the molten state at 190 °C to room temperature.

RESULTS AND DISCUSSION

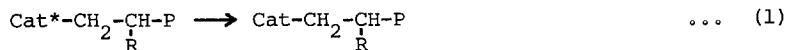
Table 1 shows the results of copolymerization of ethylene with an α -olefin, i.e. propylene, butene-1 or 4-methyl-pentene-1 (4-MP-1), by a MgCl₂ supported TiCl₄ catalyst in combination with Et₃Al at a high temperature of 170 °C at which the polymerization system was homogeneous. $[\eta]$ of polymer was controlled in a range of 1.63 to 1.97 by hydrogen. In every polymerization, this catalyst system showed a high activity, more than 10000 g-polymer/mmol-Ti, in spite of high temperature polymerization (The MgCl₂ supported TiCl₄ catalyst has been known to show high activity at 80 °C (3)).

Next, Fig. 1 shows the relation between the amount of the consumption and the supply of comonomer. The molar ratios of the consumed to the supplied comonomer were higher in the order of propylene > butene-1 > 4-MP-1. Propylene showed the highest reactivity as the comonomers.

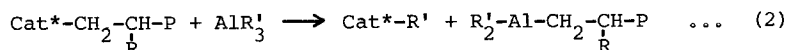
In Fig. 2, the relation between density and comonomer content of the produced copolymer is shown. The efficiency of comonomer on lowering density of polymer was larger in the order of 4-MP-1 > butene-1 > propylene, which can be explained by the differences of bulkiness among comonomers.

Furthermore, the termination reaction in copolymerization was investigated. The following mechanisms are generally considered as the termination and chain transfer reactions.

By deactivation



By transfer with aluminum alkyl



By transfer with hydrogen

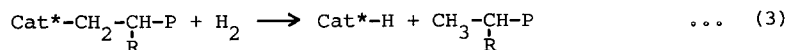


Table 1 Copolymerization of ethylene with α -olefin

Run No.	Supplied comonomers ($mmol$)	H_2 ($mmol$)	Polymer yields (g)	Activities (g -polymer/ $mmol$ -Ti)	$[\eta]$ (dl/g)	Densities (g/ml)	Comonomer contents ($mol\%$)	\bar{M}_w/\bar{M}_n	\bar{M}_n (10^{-3})
1	-	14	84.4	16900	1.97	0.960	0	4.30	22.8
2	Propylene 0.50	11	77.0	15400	1.71	0.940	2.3	5.34	15.1
3	Propylene 0.88	5	74.8	15000	1.70	0.928	4.3	5.81	13.8
4	Propylene 1.13	3	54.9	11000	1.65	0.919	6.8	6.53	11.7
5	Butene-1 0.63	14	80.5	16100	1.63	0.935	2.4	4.25	17.7
6	Butene-1 0.95	8	63.9	12800	1.90	0.926	3.5	5.10	18.3
7	Butene-1 1.26	8	57.1	11400	1.80	0.919	5.6	5.42	16.0
8	4-MP-1 1.57	14	78.0	15600	1.79	0.929	2.5	4.35	19.7
9	4-MP-1 2.36	11	70.0	14000	1.76	0.921	3.9	4.91	17.1
10	4-MP-1 3.14	8	60.8	12200	1.92	0.915	4.8	5.63	16.8

Polymerization conditions ; 170 °C for 40 min under 25 kg/cm^2 G of total pressure, 0.005 $mmol$ of Ti and 0.4 $mmol$ of Et_3Al in 1 l of a mixture of cyclohexane and comonomer

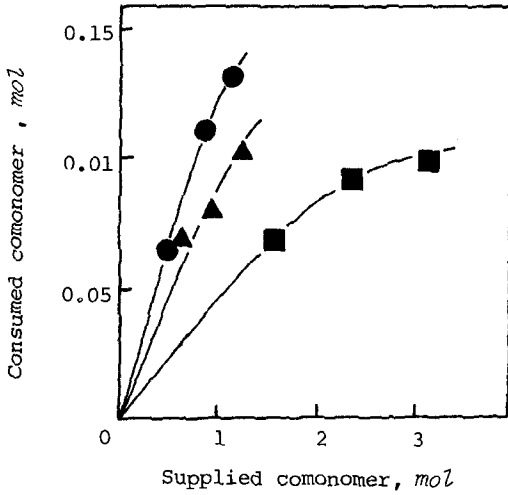


Fig. 1 Relation between the amount of the consumed* and the supplied comonomer

* Calculated from comonomer content and polymer yield.

- Propylene copolymers
- ▲ Butene-1 copolymers
- 4-MP-1 copolymers

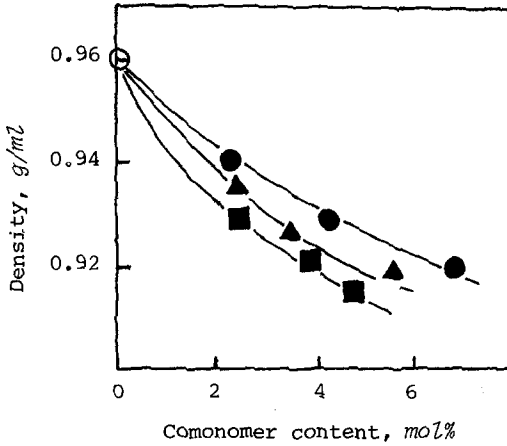
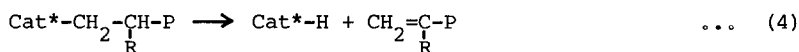


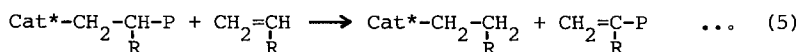
Fig. 2 Relation between density and comonomer content

- Propylene copolymers
- ▲ Butene-1 copolymers
- 4-MP-1 copolymers
- Ethylene homopolymer

By transfer with hydride β -elimination



By transfer with monomer



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

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 copolymerization of ethylene with α -olefin, two kinds of the terminal unsaturated bond can be formed 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.

Table 2 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 \bar{M}_n by GPC. In Run 1, homopolymerization of ethylene, 0.64 unit of only vinyl double bond per unit polymer chain was detected, indicating approximately a half of the growing polymer chains was terminated according to eqs. (4) and (5). On the other hand, in the copolymerizations of Run 2 to 10, the total terminal double bonds were also found with the level of 0.5 to 0.6 unit per unit polymer chain, and the contents of the vinyl and vinylidene bonds strongly depended on the kind of comonomer.

Table 2 The average number of terminal double bond per unit polymer chain*

Run No.	comonomer contents (mol%)	R-CH=CH ₂	$\begin{matrix} \text{R} \\ \text{R}' \end{matrix} \text{C}=\text{CH}_2$	total of terminal double bond
1	-	0.64	nd	0.64
2	Propylene 2.3	0.42	0.18	0.60
3	Propylene 4.3	0.40	0.27	0.67
4	Propylene 6.8	0.31	0.36	0.67
5	Butene-1 2.4	0.51	0.05	0.56
6	Butene-1 3.5	0.54	0.08	0.62
7	Butene-1 5.6	0.49	0.09	0.58
8	4-MP-1 2.5	0.55	nd	0.55
9	4-MP-1 3.9	0.52	nd	0.52
10	4-MP-1 4.8	0.50	nd	0.50

nd ; negligibly detected

* Calculated from the number of the terminal double bond by IR and \bar{M}_n by GPC

In Fig. 3, the relation between the number of vinylidene bonds and the number of comonomer per unit polymer chain is shown. In propylene and butene-1 copolymer, particularly, in propylene copolymer, a remarkable increase of the number of vinylidene bonds is seen with an increase of the

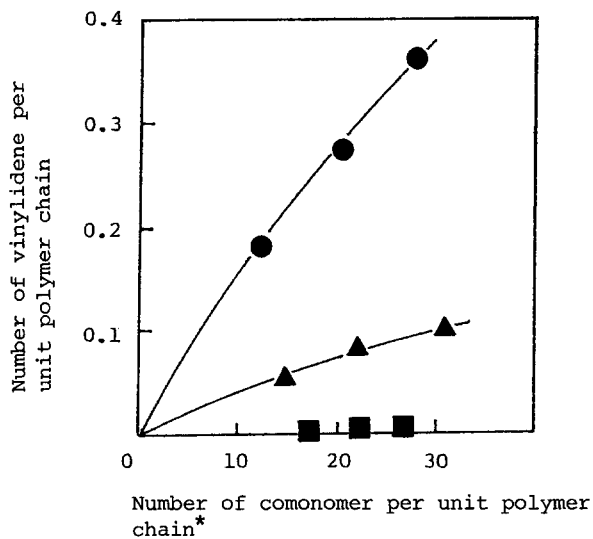


Fig. 3 Relation between the number of vinylidene bond and comonomer per unit polymer chain

* Calculated from comonomer content and \bar{M}_n

- Propylene copolymers
- ▲ Butene-1 copolymers
- 4-MP-1 copolymers

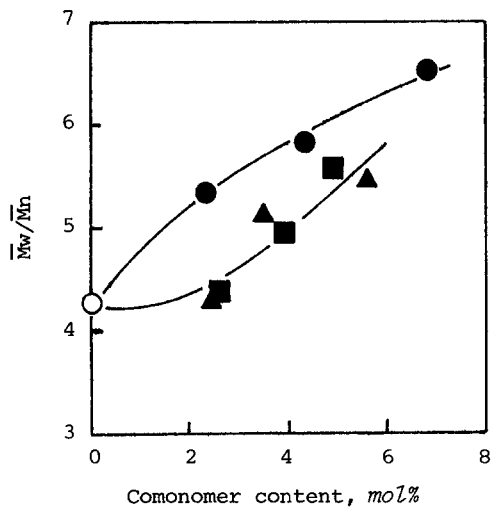


Fig. 4 Relation between \bar{M}_w/\bar{M}_n and comonomer content

- Propylene copolymers
- ▲ Butene-1 copolymers
- 4-MP-1 copolymers
- Ethylene homopolymer

content of comonomer, whereas, in 4-MP-1 copolymer, vinylidene bond is negligibly small. These facts mean that the termination reaction by chain transfer through eqs. (4) and (5) takes place more easily when propylene unit is present at the growing polymer chain. On the contrary, such phenomenon takes place very hardly in the case of 4-MP-1.

Molecular weight distribution (MWD) of the produced polymer was also examined. Fig. 4 shows the relation between the $\overline{M_w}/\overline{M_n}$ value and comonomer contents of polymer. The $\overline{M_w}/\overline{M_n}$ value increased with an increase of the comonomer contents, and the propylene copolymer showed the highest $\overline{M_w}/\overline{M_n}$ value among three kinds of copolymers. As the factors responsible for the MWD in Ziegler type polymerization, the monomer diffusion control in polymerization system and the diversity of active centers in nature (wide variety in propagation rate constant and chain transfer constant among active centers) are considered (4). As shown Table 1, the molecular weight in each run was almost the same. If the monomer diffusion control is responsible for the MWD, the higher polymer yields should correspond to the higher $\overline{M_w}/\overline{M_n}$ value, because the viscosity of the systems becomes more viscous. However, Table 1 shows the opposite results. Therefore, we consider that an increase of the $\overline{M_w}/\overline{M_n}$ value with an increase of comonomer content should be caused by the diversity of active centers in nature.

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