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Copolymerization of propylene with a small amount of ethylene using a $MgCl_2/TiCl_4$ and a $TiCl_3$ catalyst system

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SUMMARY

Copolymerization of propylene with a small amount of ethylene and homopolymerization of propylene were performed using a highly active $MgCl_2/TiCl_4$-Et_3Al/ethyl benzoate(EB) and a conventional $TiCl_3$-Et_2AlCl catalyst systems. The obtained polymers were fractionated into n-decane (C_{10}) soluble and insoluble portions. In all homopolymer fractions with the investigated catalyst systems and copolymer fractions with $TiCl_3$ catalyst system, the inversion of the direction of arrangement of the propylene unit was not observed by ^{13}C-NMR analysis. On the other hand, in C_{10} soluble fractions of copolymer using $MgCl_2/TiCl_4$ catalyst system, regardless of the presence of EB, a significant amount of the inversion unit was detected.

INTRODUCTION

In previous papers, the presence of propylene unit inversions in propylene homopolymer(PP) and ethylene-propylene copolymer(EP) produced using homogeneous catalyst based on VCl_4(1-3), $VOCl_3$(4), $TiCl_4$(5) or a mixture of $MgCl_2$ in 2-ethylhexanol/n-decane and $TiCl_4$(4) has been pointed out by ^{13}C-NMR analysis. On the other hand, from ^{13}C-NMR spectra of PP or EP using heterogeneous titanium catalyst based on $TiCl_3$(6,7) or $TiCl_4$ supported on $MgCl_2$ ($MgCl_2/TiCl_4$) (4,8,9), the absence of peaks due to inverted propylene units has been reported.

The purpose of this work is to collect more detailed information on the inversion in polymerization of propylene using $MgCl_2/TiCl_4$ catalyst in conjunction with Et_3Al or Et_3Al/EB by investigating the influences of ethylene as a comonomer and EB which is well known as a very effective stereospecific improver for propylene polymerization(10-23). In addition, the microtacticity, molecular weight and yield of the produced polymer were also discussed, and the results about the inversion were compared with those of the conventional $TiCl_3$ catalyst system.

EXPERIMENTAL

Preparation of catalyst

$MgCl_2/TiCl_4$: Stainless steel balls(2.8 kg, 15 mm in diameter) were put into a pot of internal volume 800 ml. The inside of the pot was purged fully with nitrogen and then 20 g of $MgCl_2$ was added, and the system was milled for 60 h. Ten grams of milled products were suspended in 100 ml of $TiCl_4$ for 2 h at 80°C. Solid product was filtrated, which was washed with n-decane. The said product was found to contain 8 mg-Ti/g-catalyst.

$TiCl_3$(AA) : The commercial product, TAC-131 made by Toho Titanium Co., Japan, was used.

Polymerization

Two hundred ml of n-decane was put into a 500 ml glass flask. After saturating the solvent with propylene or a propylene/ethylene mixture gas,

Et_3Al(2.5 mmol), EB(0 or 1.5 mmol) and $MgCl_2/TiCl_4$ catalyst(1.0 mmol of Ti) were added and polymerization was performed for 2 min at 50 °C under atmospheric pressure. After polymerization, a small amount of ethanol was first added to the system to stop the polymerization and then, a large quantity of methanol was added. The solid polymer product was collected and dried under reduced pressure.

Propylene bulk polymerization with $TiCl_3$(AA)-Et_2AlCl was carried out as follows. Four hundred ml of liquid propylene monomer and/or several amounts of ethylene monomer were put into a 2 l of stainless steel reactor. Et_2AlCl (4 mmol) and $TiCl_3$(2 mmol of Ti) were added, and polymerization was performed for 30 min at 60 °C. After polymerization, a large amount of methanol was added in order to remove the catalyst residues.

Characterization

Fractionation : One gram of polymer was dissolved in n-decane at 150 °C. After cooling the solution for 1 h at 10 °C, the suspension was separated into two parts(soluble and insoluble in n-decane) by the filtration, and the soluble fraction was recovered by the evaporation of n-decane under reduced pressure.

Microstructure : ^{13}C-NMR spectrum was recorded with a JEOL FX-100 spectrometer operating at 25.05 MHz under proton decoupling in Furier Transform (FT) mode.

Molecular weight : Molecular weight of the polymer was determined by GPC (Weter 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 150 °C.

RESULTS AND DISCUSSION

$MgCl_2$ supported $TiCl_4$ catalyst system

Homopolymerization of propylene and copolymerization of propylene with a small amount of ethylene were carried out using a highly active $MgCl_2$ supported $TiCl_4$ catalyst ($MgCl_2/TiCl_4$) prepared by the reaction of $TiCl_4$ with mechanically pulverized $MgCl_2$ in conjunction with Et_3Al (called "without EB") or Et_3Al and ethyl benzoate(EB) (called "with EB") at 50 °C for 2 min and the obtained polymers were fractionated into n-decane(C_{10}) soluble and insoluble portions, followed by the characterization by ^{13}C-NMR and GPC. The results are shown in Table 1.

The meso-meso(mm) triad sequences contents of the fractionated polymer by ^{13}C-NMR analysis were 83-85 % at "without EB", 91-93 % at "with EB" for C_{10} insoluble portions, and 41-52 % at "without EB", 45-53 % at "with EB" for C_{10} soluble ones. Thus, the fractionation by C_{10} was made mainly by the difference of the microtacticity of the polymer.

In previous papers(20-23), authors reported about the functions of EB in homopolymerization of propylene using the similar catalyst systems to conclude that EB increased simultaniously yield and molecular weight of isotactic polypropylene(PP), while it decreased yield of atactic PP very rapidly and selectively in $MgCl_2/TiCl_4$ - Et_3Al/EB catalyst system. As is seen in Table 1, those distinctive functions of EB were confirmed both in the homo and copolymerizations in the present experiments, i.e., by the introduction of EB (EB/Ti=15 M/M), yields and molecular weight of C_{10} insoluble portions were increased by 1.3-1.4 times and more than 2 times in respective two catalyst systems, and yields of C_{10} soluble portions were decreased to 1/5 or less compared with those at "without EB".

Moreover, it is to be noted that the microtacticity(mm values) of isotactic portions and the amount of ethylene incorporated into atactic polymer chain were significantly enhanced by EB, thus suggesting that EB

Table 1 Results of polymerization with $MgCl_2/TiCl_4$-Et_3Al/EB catalyst

Run No.	Catalyst system	C_2cont.[a) (mol%)	C_{10} insoluble fraction						C_{10} soluble fraction					
			Yield (g/mmol-Ti)	C_2cont.[b) (mol%)	$\overline{M}w$ ($x10^{-4}$)	$\overline{M}n$ ($x10^{-4}$)	$\overline{M}w/\overline{M}n$	mm[c)	Yield (g/mmol-Ti)	C_2cont.[b) (mol%)	$\overline{M}w$ ($x10^{-4}$)	$\overline{M}n$ ($x10^{-4}$)	$\overline{M}w/\overline{M}n$	mm[c)
1	without EB	0	52	0	13.6	2.71	5.05	85	43	0	4.14	0.88	4.69	41
2	"	4.4	54	1.6	9.14	2.30	3.98	85	47	3.1	3.40	0.80	4.24	44
3	"	7.1	73	2.5	9.00	1.14	7.89	84	79	6.7	2.72	0.66	4.15	49
4	"	11.0	82	4.2	7.14	1.37	5.22	85	78	7.9	3.39	0.73	4.61	47
5	"	13.4	82	6.1	9.12	1.40	6.50	83	100	11.8	3.70	0.76	4.88	52
6	with EB	0	65	0	26.9	5.64	4.77	93	5	0	7.40	0.95	7.78	45
7	"	4.4	77	1.2	25.2	5.09	4.96	91	9	10.1	6.37	0.95	6.70	45
8	"	7.1	94	3.1	28.1	5.78	4.86	93	15	17.4	6.44	0.88	7.33	51
9	"	11.0	86	4.7	25.2	6.16	4.09	91	16	18.9	8.94	1.11	8.84	53

Polymerization conditions : 50 °C for 2 min under atmospheric pressure, 0.5 mmol/l of Ti, 12.5 mmol/l of Et_3Al and 7.5 mmol/l of EB in 200 ml of n-decane.

a) Ethylene content in introduced gas, b) Ethylene content in the fractionated polymer

c) The mm triad sequence content of the fractionated polymer participates directly in the formation of a part of the isotactic active centers in the manner to increase the degree of the isotacticity as well as yield and it selectively poisons the atactic active centers having lower activity toward ethylene monomer.

Next, ^{13}C-NMR analysis was made in order to investigate the propylene unit inversion, particularly about αβ-methylene carbon, in the polymer (the propylene insertion reaction of irregular direction at the propagation stage, i.e., the insertion giving rise to the growing end with a secondary alkyl-Ti bond). When the propylene unit inversion takes place in homopolymerization of propylene, one pair of αβ-methylene carbons should be present in the polymer chain as follows,

while, in copolymerization with ethylene, the presence of αβ-methylene carbons based on ethylene monomer is also considered as indicated below,

Table 2 lists the number of αβ-methylene carbons per 1000 carbons in the fractionated polymers.

As shown, in all homopolymers, both for C_{10} soluble and insoluble portions, the inversion unit was not found at all regardless of "with EB" or "without EB" catalyst systems. On the other hand, in the copolymers, αβ-methylene carbons were detected significantly, for all C_{10} soluble portions and for C_{10} insoluble ones prepared by "without EB" having a large amount of ethylene units. In previous papers concerning the inversion, Doi(8) has reported the same results for the homopolymer, however, he(9)

Table 2 Number of αβ-methylene carbons per 1000-carbons in polymer chain

Run No.	Catalyst system	C_{10} insol.fraction C_2cont.$^{a)}$ (mol%)	C_{10} insol.fraction αβ-CH_2 (1/1000-C)	C_{10} sol.fraction C_2cont.$^{a)}$ (mol%)	C_{10} sol.fraction αβ-CH_2 (1/1000-C)
1	without EB	0	nd	0	nd
2	"	1.6	nd	3.1	2.1
3	"	2.5	nd	6.7	3.2
4	"	4.2	0.8	7.9	4.2
5	"	6.1	1.9	11.8	4.5
6	with EB	0	nd	0	nd
7	"	1.2	nd	10.1	4.6
8	"	3.1	nd	17.4	5.5
9	"	4.7	nd	18.9	6.2

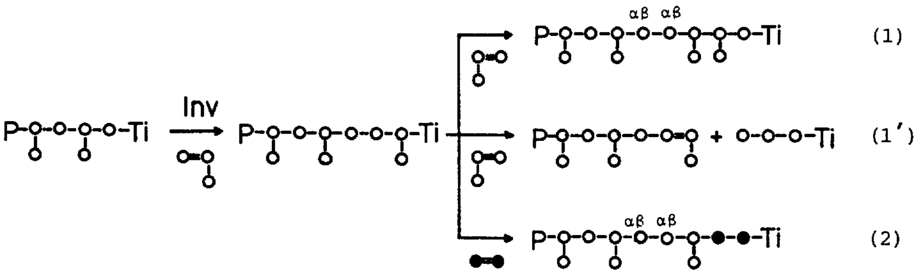
a) Ethylene content of the fractionated polymer
nd : not detected

and the authors(4) have not detected the propylene unit inversion also in the ethylene copolymers with the heterogeneous $MgCl_2/TiCl_4$/EB catalyst systems. These results suggest the differences in the nature of the active centers among the $MgCl_2/TiCl_4$ catalysts prepared by the different methods.

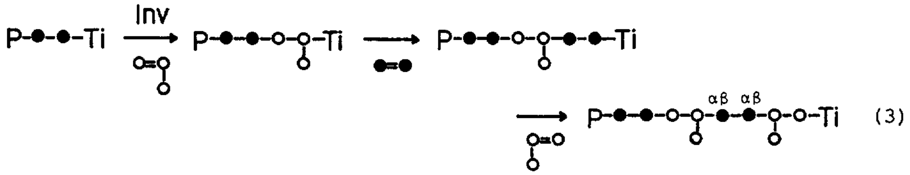
Figure 1 shows that the frequency of inversion was increased from zero with the increase of the ethylene content in the polymer, which was always higher in C_{10} soluble portions than insoluble ones. From the obtained results, one can see that the formation of αβ-methylene carbon takes place occasionally at the non or less isotactic active centers, more often at the former, particularly when ethylene unit would be present at (or near) a growing chain end, but it dose not take place at the highly isotactic active center, perhaps due to its highly sterically hindered structure to regulate strictly the orientation of incoming propylene monomer, and moreover, that the atactic active center in "with EB" and "without EB" catalyst systems has similar regiospecificity.

The reaction scheme to generate αβ-methylene carbon in a polymer chain can be drawn as follows.

(A) Propylene unit inversion at the propylene sequences end



(B) Propylene unit inversion at the ethylene unit end



Inversion in case (A) is considered not to take place due to a fact that αβ-methylene carbon which is formed by scheme(1) is not found in the homopolymer. If it should happen, a growing chain end would be always chain -transfered by propylene monomer as shown in scheme (1′) (no αβ-methylene carbon is formed in a dead polymer). In this case, when ethylene insertion after propylene unit inversion would proceed without chain transfer, αβ -methylene carbon could be formed(scheme(2)).

In case (B), αβ-methylene carbons are formed by ethylene unit, when primary propylene insertion takes place at the ethylene unit after the propylene unit inversion(scheme(3)).

As a consequence, the schemes (2) and (3) would be the possible candidates for the explanation for the observed αβ-methylene carbons in the copolymers.

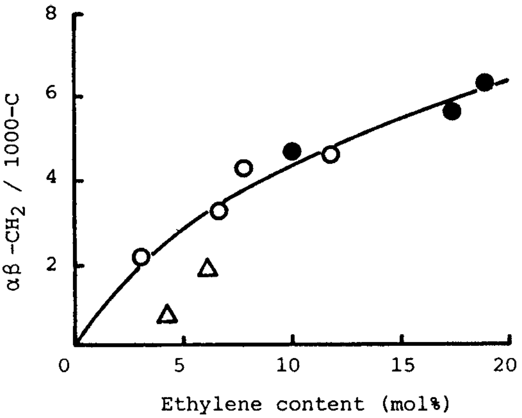


Fig. 1 Relation between the number of αβ-methylene carbons per 1000-carbons and ethylene content in copolymer

○ C_{10} sol. without EB

● C_{10} sol. with EB

△ C_{10} insol. without EB

$TiCl_3$ catalyst system

Copolymerization of propylene with a small amount of ethylene and homopolymerization of propylene were performed using a conventional $TiCl_3$-Et_2AlCl catalyst system at 60°C for 30 min, in which the presence of the propylene unit inversion was investigated for the polymers fractionated by the same method as that with $MgCl_2/TiCl_4$ catalyst system. The results are shown in Table 3. As is seen, all fractions of homopolymer and copolymer were found to contain no propylene unit inversion at all, being in accordance with the results of Ray(6) and Kakugo(7).

One can point out that there is an interesting difference in the nature, particularly, of the atactic active centers between $TiCl_3$ and the $MgCl_2/TiCl_4$ catalyst systems.

Table 3 Number of αβ-methylene carbons per 1000-carbons in polymer chain

Run No.	C_{10} insol.fraction		C_{10} sol.fraction	
	C_2cont.[a) (mol%)	αβ-CH_2 (1/1000-C)	C_2cont.[a) (mol%)	αβ-CH_2 (1/1000-C)
10	0	nd	0	nd
11	3.2	nd	16.8	nd
12	4.5	nd	21.6	nd
13	8.0	nd	24.6	nd

a) Ethylene content of the fractionated polymer
nd : not detected

References

1. F.A.Bovey, M.C.Sacchi and A.Zambelli, Macromolecules, 7, 752 (1974)
2. Y.Doi, ibid, 12, 248 (1979)
3. T.Asakura, I.Ando, A.Nishioka, Y.Doi and T.Keii, Makromol. Chem., 178, 791 (1977)
4. N.Kashiwa, A.Mizuno and S.Minami, Polym. Bull., 12, 105 (1984)

5. Y.Doi, Makromol. Chem., 180, 2447 (1979)
6. G.J.Ray, P.E.Johnson and J.R.Knox, Macromolecules, 10, 773 (1977)
7. M.Kakugo, Y.Naito, K.Mizunuma and T.Miyatake, ibid, 15, 1150 (1982)
8. Y.Doi, Makromol. Chem., Rapid Commun. 3, 635 (1982)
9. Y.Doi, R.Ohnishi and K.Soga, ibid, 4, 169 (1983)
10. P.Pino and R.Mulhaupt, Angew. Chem., Ind. Ed. Engl., 19, 857 (1980)
11. Ye.Ye.Vermel, V.A.Zakharov, Z.K.Butatova, G.P.Shkurina, L.G.Yechevskay, E.M.Moroz and S.V.Sudakova, Vysokomol.Soyed., A22, 22 (1980)
12. K.Soga and M.Terano, Polym. Bull., 4, 39 (1981)
13. B.Keszler and A.Simon, Polymer, 23, 916 (1982)
14. P.Pino and B.Rotzinger, Makromol. Chem. Suppl., 7, 41 (1984)
15. Y.V.Kissin and A.J.Sivak, J. Polym. Sci., Polym. Chem. Ed., 22, 3747 (1984)
16. V.Busico, P.Corradini, L.De Martino, A.Proto, V.Savino and E.Albizzati, Makromol. Chem., 186, 1279 (1985)
17. V.Busico, P.Corradini, L.De Martino, A.Proto and E.Albizzati, ibid, 187, 1115 (1986)
18. P.Pino, B.Rotzinger and E.Von Acherbach, Makromol. Chem. Suppl., 13, 105 (1985)
19. K.Soga, T.Sano, K.Yamamoto and T.Shiono, Chem. Lett., 425 (1982)
20. N.Kashiwa, "Transition Metal Catalyzed Polymerizations, Alkenes and Dienes" (Ed. R.P.Quirk) Harwood Academic Publishers, New York, Vol 4, p379 (1983)
21. N.Kashiwa and J.Yoshitake, Makromol. Chem., Rapid. Commun., 4, 41 (1983)
22. N.Kashiwa and J.Yoshitake, Polym. Bull., 12, 99 (1984)
23. N.Kashiwa, M.Kawasaki and J.Yoshitake, "Catalytic Polymerization of Olefins" (Eds. T.Keii and K.Soga) Kodansha and Elsevier, Tokyo, p43

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