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Effect of Ethyl Benzoate on the Copolymerization of Ethylene with Higher α-Olefins over $TiCl_4/MgCl_2$ Catalytic Systems

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Summary

Copolymerization of ethylene with propylene (or 1-butene) was conducted with the catalyst system of $TiCl_4/MgCl_2/Al(C_2H_5)_3$/ethyl benzoate. With increasing the concentration of ethyl benzoate, the content of propylene (or 1-butene) in copolymer significantly decreased. From the result combined with the previous ones, we have proposed the mechanism that the monomer reactivity ratio strongly depends on the number of vacant sites around the active Ti(III) center.

Introduction

From the detailed studies of homopolymerizations of various α-olefins as well as copolymerizations between them over γ-Al_2O_3- or SiO_2-supported $TiCl_4$ catalyst, we have recently reached a conclusion that the Ti(III) species are active for all monomers, while further reduced species, probably Ti(II), are active only for ethylene (SOGA et al. 1981, 1982). We also examined the effect of additives such as ethyl benzoate on the microstructures of polypropylene and polyisoprene using the catalyst systems of $TiCl_4/Al(C_2H_5)_3$ and $TiCl_4/MgCl_2/Al(C_2H_5)_3$. It was found that a marked increase in the isotacticity of polypropylene is accompanied by a remarkable decrease in the cis 1,4-content of polyisoprene. The conclusions reached were that there exist two types of active Ti(III) species, one having two Cl vacancies and the other having only one Cl vacancy and that additives such as ethyl benzoate selectively block one of the former vacancies (SOGA et al. 1982).

On the other hand, in the copolymerizations of ethylene with various α-olefins over Ti catalysts it is generally recognized that the copolymer compositions strongly depend upon the catalyst systems, polymerization conditions, etc. It may be considered, therefore, that the copolymer compositions can be controlled by changing the fractions of these two active Ti(III) species.

From such viewpoints, in the present paper was carried out the copolymerization of ethylene with propylene (or 1-butene) with the catalyst system of $TiCl_4/MgCl_2/Al(C_2H_5)_3$ combined with various amounts of ethyl benzoate and was examined the copolymer compositions in detail.

Experimental

Materials Research grade ethylene, propylene, 1-butene and n-heptane were obtained from Takachiho Chemical Co. and were purified according to the same procedures reported earlier (SOGA et al. 1977). Nitrogen of ultra high purity (99.9989 %) was obtained from Nihon Sanso Co. and purified by passing through the molecular sieve 3A column cooled at -196 °C. Triethylaluminium $Al(C_2H_5)_3$, was commercially obtained and used without further purification. Commercial extra pure grade ethyl benzoate (EB) from Tokyo Kasei Co. Ltd. was purified by passing through the molecular sieve 3A column at room temperature. The $TiCl_4/MgCl_2$ catalys (Cat-I) was prepared by grinding a mixture of $TiCl_4$ and $MgCl_2$ in nitrogen atmosphere (1.8 mmol of Ti/g-cat). The $TiCl_4/MgCl_2$/EB catalyst (Cat-II) was obtained from the Research Center, Mitsui Petrochemical Industries, Co. Ltd. (0.67 mmol of Ti/g-cat).

Polymerization and analytical procedures Copolymerization of ethylene with propylene (or 1-butene) was carried out in a conventional gas circulation system with a dead space of about 5.0 l including the glass reactor (50 ml) equipped with a magnetic stirrer. Into the reactor which had been filled with nitrogen were added n-heptane, one of the catalysts, EB and $Al(C_2H_5)_3$ and then was introduced the mixture of ethylene and propylene (or 1-butene). The copolymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitate was dried i. vac. at room temperature. The composition of the copolymer was determined by ^{13}C NMR spectrum (RAY et al. 1977). ^{13}C NMR spectra were recorded on a JEOL JUM PS-100 spectrometer operating at 25.14 MHz under proton decoupling in the Fourier Transform (FT) mode. Instrument conditions were $\pi/4$ pulse of 9.0 μs, 8.0 s repitation rate and 5000 Hz sweep width. Solutions of copolymers were made up in trichlorobenzene to 15 w/v %. The chemical shift was presented in p.p.m. downfield from tetramethylsilane (TMS) as internal standard. Propylene polymerization was conducted in a usual semi-batch system. The isotacticity of polypropylene was determined by the method of LUONGO (1960) with IR.

Results and discussion

Copolymerization of ethylene with propylene was first conducted over Cat-II by changing the concentration of EB. In Table 1 are shown the copolymerization results together with the isotacticity of polypropylene produced under the same conditions. In Table 2 are summarized the areas of the resonance peaks in the ^{13}C NMR spectra of the copolymers together with the ^{13}C chemical shift assignments.

The chemical shift assignments for ^{13}C resonances and a nomenclature system are the same as those reported by CARMAN et al. (1977). Tertiary and secondary carbon atoms are denoted as T and S with two Greek subscripts indicating the position relative to the nearest tertiary carbon atoms in both directions along the copolymer chain. All primary carbon atoms are represented by P since these separate subspecies are indistinguishable due to low stereoregularity. The intensities of three peaks at 34.9 p.p.m. ($S_{\alpha\beta}$), 33.6 p.p.m. ($T_{\gamma\gamma}$) and 27.9 p.p.m. ($S_{\beta\gamma}$), which are assigned to the carbons in the sequences with inverted propylene units, were negligible in all the spectra.

Table 1 Ethylene-propylene copolymerization over the catalyst system of $TiCl_4/MgCl_2/Al(C_2H_5)_3/C_6H_5COOC_2H_5$ a)

Run no.	EB [mmol]	Time b) [min]	Propylene in copolymer c) [mol%]	I.I. d) of PP [%]
1	0	14	44	72
2	0.05	90	38	91
3	0.10	330	29	95

a) Copolymerization conditions: temp. = 40 °C, Cat-II = 15 mg $Al(C_2H_5)_3$ = 0.3 mmol, n-heptane = 10 ml, total pressure = 400 Torr, propylene in feed (in liquid phase) = 76 mol%.
b) The time required to reach 10 % conversion.
c) Determined by ^{13}C NMR (For more details see Table 3).
d) Isotacticity of polypropylene determined by IR (LUONGO, 1960).

Table 2 ^{13}C NMR area data for ethylene-propylene copolymer samples 1 through 3

Carbon type	^{13}C Chemical shift (p.p.m.)	Monomer sequence	Peak areas [%] Run no. 1	2	3
$S_{\alpha\alpha}$	45.8-47.7	PP	10.4	9.6	7.1
$S_{\alpha\gamma}$	38.0-38.8	2PEP	6.7	6.4	4.8
$S_{\alpha\delta}$	37.6	$PPE_n (n \geq 1)$	6.7	6.8	7.1
$S_{\gamma\gamma}$	30.8	PEEP	0.6	0.8	0.6
$S_{\gamma\delta}$	30.4	$PEEE_n (n \geq 1)$	4.9	4.4	4.2
$S_{\delta\delta}$	30.0	$EEE_n (n \geq 1)$	21.4	29.9	41.6
$S_{\beta\delta}$	27.5	$PEE_n (n \geq 1)$	6.7	6.8	7.1
$S_{\beta\beta}$	24.6-24.9	PEP	3.4	3.2	2.4
$T_{\delta\delta}$	33.3	EPE	5.5	3.6	3.6
$T_{\beta\delta}$	31.0	PPE	8.0	7.2	5.4
$T_{\beta\beta}$	28.6-29.0	PPP	6.1	5.2	4.2
P	20.0-21.8	-	19.6	16.1	11.9

The absence of propylene inversion in the present copolymers is considered due to a high regiospecificity of the catalytic system as reported earlier (DOI, 1982). Thus, the present copolymerization can be analyzed as a binary copolymerization of ethylene (E) and propylene (P). The dyad and triad sequence distributions were determined by using the following relations.

$$PP = I\ (S_{\alpha\alpha}) \qquad (1)$$

$$EP = I\ (S_{\alpha\gamma}) + I\ (S_{\alpha\delta}) \tag{2}$$

$$EE = 1/2\ [\ I\ (S_{\beta\delta}) + I\ (S_{\delta\delta})] + 1/4\ I\ (S_{\gamma\delta}) \tag{3}$$

$$PPP = I\ (T_{\beta\beta}) \tag{4}$$

$$PPE = I\ (T_{\beta\delta}) \tag{5}$$

$$EPE = I\ (T_{\delta\delta}) \tag{6}$$

$$PEP = I\ (S_{\beta\beta}) = 1/2\ I\ (S_{\alpha\gamma}) \tag{7}$$

$$PEE = I\ (S_{\alpha\delta}) = I\ (S_{\beta\delta}) \tag{8}$$

$$EEE = 1/2\ I\ (S_{\delta\delta}) + 1/4\ I\ (S_{\gamma\delta}) \tag{9}$$

The monomer compositions in the copolymers were calculated from both the dyad and triad sequence distributions using Eqs. (10) and (11).

$$P = PP + 1/2\ PE = PPP + PPE + EPE \tag{10}$$

$$E = EE + 1/2\ PE = EEE + EEP + PEP \tag{11}$$

The observed sequence distributions of connecting monomer units may be interpreted in terms of a first-order Markovian process of a binary copolymerization involving the following four propagation steps.

$$\text{---}\ E\text{-}Ti + C_2H_4 \xrightarrow{k_{11}} \text{---}\ EE\text{-}Ti \tag{12}$$

$$\text{---}\ E\text{-}Ti + C_3H_6 \xrightarrow{k_{12}} \text{---}\ EP\text{-}Ti \tag{13}$$

$$\text{---}\ P\text{-}Ti + C_2H_4 \xrightarrow{k_{21}} \text{---}\ PE\text{-}Ti \tag{14}$$

$$\text{---}\ P\text{-}Ti + C_3H_6 \xrightarrow{k_{22}} \text{---}\ PP\text{-}Ti \tag{15}$$

Here k_{ij} is the rate constant of step ij, and the subscripts 1 and 2 refer to ethylene and propylene. Assuming a statistical stationary condition in the copolymerization, we can calculate the monomer reactivity ratios r_1 and r_2 using Eqs. (16) and (17).

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{2(EE)}{(PE)X} \tag{16}$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{2(PP)X}{(PE)} \tag{17}$$

where X is the ratio of ethylene concentration to propylene concentration in the feed.

In Table 3 are summarized the results obtained. The triad sequence distributions were then calculated using the values of r_1 and r_2 in Table 3. Both the calculated and observed triad sequence distributions are shown in Table 4.

The results in Table 4 appear to indicate a significant disagreement between the observed and calculated triad fractions of the copolymer prepared in the absence of EB (Run no. 1).

Table 3 Copolymer compositions, sequence distributions and reactivity ratios in each sample

Run no.	1	2	3
P	0.44	0.38	0.29
E	0.56	0.62	0.71
PP	0.26	0.23	0.16
PE	0.34	0.31	0.27
EE	0.39	0.46	0.57
PPP	0.15	0.12	0.09
PPE	0.19	0.17	0.12
EPE	0.13	0.09	0.08
PEP	0.08	0.08	0.05
EEP	0.16	0.16	0.16
EEE	0.29	0.38	0.59
r_1	7.35	9.21	13.4
r_2	0.72	0.46	0.38
r_1r_2	5.29	4.24	5.09

Table 4 Comparison of observed and calculated triad sequence distributions in each sample

Run no.	1		2		3	
	obs.	calc.	obs.	calc.	obs.	calc.
PPP	0.15	0.25	0.12	0.13	0.09	0.09
PPE	0.19	0.21	0.17	0.19	0.12	0.15
EPE	0.13	0.05	0.09	0.06	0.08	0.06
PEP	0.08	0.05	0.08	0.04	0.05	0.03
EEP	0.16	0.21	0.16	0.23	0.16	0.22
EEE	0.29	0.24	0.38	0.34	0.49	0.47

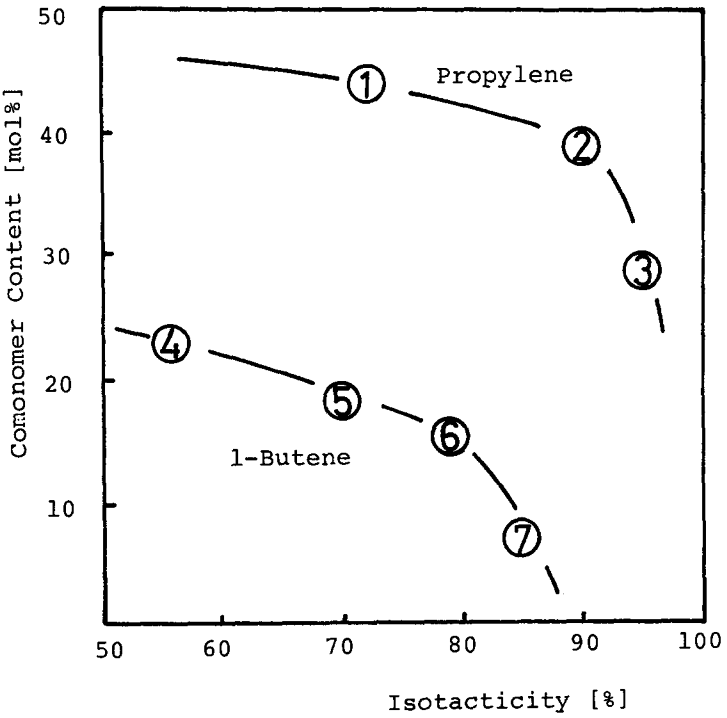
The disagreement may be interpreted in terms of the previous model (SOGA et al. 1982) that two types of active Ti(III) species are present in the original catalyst, one having two Cl vacancies and the other having only one Cl vacancy. These species seem to show different monomer reactivity ratios. Upon adding EB to the catalyst, the former species may be selectively blocked by EB to become inactive. Consequently, only the latter species may be left alive. The good agreement between the observed and calculated triad fractions of the copolymer prepared under a high concentration of EB (Run no. 3) supports this inference.

Table 5 Ethylene-1-butene copolymerization over the catalyst system of $TiCl_4/MgCl_2/Al(C_2H_5)_3/C_6H_5COOC_2H_5$[a)]

Run no.	EB [mmol]	Time[b)] [min]	1-Butene in copolymer[c)] [mol%]	I.I.[d)] of PP [%]
4	0	3.5	22.7	56
5	0.04	3.0	18.8	70
6	0.11	7.0	16.1	79
7	0.15	13.0	7.4	85

a) Copolymerization conditions: temp. = 40 °C, Cat-I = 80 mg, $Al(C_2H_5)_3$ = 0.2 mmol, n-heptane = 10 ml, total pressure = 530 Torr, 1-butene in feed in gas phase = 20 mol%.
b) The time required to reach 10 % conversion.
c) Determined by ^{13}C NMR.
d) Isotacticity of polypropylene (LUONGO, 1960).

Figure 1 Relations between the comonomer contents in the copolymers and the isotacticity of polypropylene. Figures in open circles denote Runs no.



The copolymerization of ethylene with 1-butene was then carried out over Cat-I by changing the concentration of EB and the copolymers obtained were analyzed by ^{13}C NMR. In Table 5 are shown the results together with the isotacticity of polypropylene obtained under the same conditions.

In Figure 1 are plotted the relations between the copolymer composition and the isotacticity of polypropylene. It can be seen from Figure 1 that the comonomer contents in the copolymers significantly decrease with increasing the isotacticity of polypropylene.

Thus, the non-stereospecific (atactic) Ti(III) sites having two Cl vacancies seem more favorable to prepare copolymers of ethylene with higher α-olefins. This idea is in good accordance with the fact that the soluble $Ti(OBu)_4/MgCl_2/Al(C_2H_5)_2Cl$ catalyst, which seems to have multiple vacant sites, affords desirable copolymers of ethylene with higher α-olefins (MITSUI PETROCHEMICAL INDUSTRIES 1980).

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