Polymer Bulletin 7, 547–552 (1982)

Polymer Bulletin

Copolymerization of Ethylene and Propylene Over the SiO_2-Supported $MgCl_2/TiCl_3$ Catalyst

Kazuo Soga, Rikuo Ohnishi and Tsuneji Sano

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Summary

The SiO_2-supported $MgCl_2/TiCl_3$ catalyst was prepared by treating the mixture of $TiCl_3 \cdot 3C_5H_5N$, $MgCl_2 \cdot (THF)_n$ and SiO_2 with $AlEt_2Cl$ in n-heptane solvent. The catalyst combined with $AlEt_3$ showed a very high activity for the copolymerization of ethylene and propylene and gave a moderately random copolymer. A plausible model for the copolymerization was proposed from the kinetic study of the copolymerization.

Introduction

A large number of patents and publications claim the synthesis of random and block copolymers from ethylene and propylene (BOOR 1979). The copolymer composition strongly depends on the catalytic systems. Soluble catalysts such as $VOCl_3$ and VCl_4 combined with $AlEt_2Cl$ give a random or moderately alternating copolymer. On the other hand, heterogeneous catalysts which seem to contain multiple active species usually give block copolymers.

Carring out the copolymerization of ethylene and propylene over the thermally-reduced γ-Al_2O_3-supported $TiCl_4$ catalyst with or without using metal alkyl compounds, we have recently found that the structure of the copolymer drastically depends on the valency states of the transition metal. The conclusion reached is that the Ti^{3+} species are active for both monomers, while further reduced titanium species (probably Ti^{2+}) are active only for ethylene (SOGA et al. 1981). Therefore, it seems to be most important for the production of a random copolymer by using titanium-based catalysts to prevent the titanium species from over-reduction. More recently, we have found that the Ti^{3+} species containing in the SiO_2-supported $MgCl_2/TiCl_3$ catalyst, which has been proved to be very effective for propylene polymerization (SOGA et al. 1981), are hardly reduced even in the presence of $AlEt_3$.

From such points of view, in the present paper was carried out the copolymerization of ethylene and propylene over the SiO_2-supported $MgCl_2/TiCl_3$ catalyst combined with $AlEt_3$.

0170-0839/82/0007/0547/$ 01.20

Experimental

Materials Research grade ethylene, propylene and n-heptane (from Takachiho Chemical Co.) were purified according to the same procedures reported earlier (SOGA et al. 1977). Pyridine (C_5H_5N) and tetrahydrofurane (THF) (from Takachiho Chemical Co.) were purified according to the usual procedures. 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. SiO_2 (from Fuji Devison Co., 300 m^2/g) was evacuated at 300 °C for 4 h immediately before use. The other chemicals (research grade) were commercially obtained and used without further purificataion.

Preparation of the SiO_2-supported $MgCl_2/TiCl_3$ catalyst
The complexes of $TiCl_3 \cdot 3C_5H_5N$ and $MgCl_2 \cdot (THF)_n$ were prepared from the reactions of $TiCl_3$ with pyridine and $MgCl_2$ with THF at room temperature (SOGA et al. 1979). To 5 ml of n-heptane containing 4 mmol of $AlEt_2Cl$ were added the measured amounts of SiO_2, $TiCl_3 \cdot 3C_5H_5N$ and $MgCl_2 \cdot (THF)_n$ under nitrogen. The mixture was kept standing with vigorous stirring for 20 h at room temperature. The precipitate was separated by filtration under nitrogen and washed with n-heptane, followed by evacuating at room temperature to give the catalyst.

Copolymerization and analytical procedures The copolymerization of ethylene and propylene was carried out in a conventional gas circulation system with a dead space of about 5.0 l including the glass reactor (300 ml) equipped with a magnetic stirrer. Into the reactor which had been substituted with nitrogen, were added the measured amounts of n-heptane, the catalyst and $AlEt_3$ and then was introdued the mixture of ethylene and propylene. The copolymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitate was dried i. vac. at room temperature.

The amounts of titanium and magnesium contained in the catalyst were determined by atomic absorption spectrophotometry (Shimadzu AA-6105) [Ti:0.25 matom/g-cat., Mg:0.40 matom/g-cat.]. The ESR spectrum was taken in a pyrex glass tube of 3 mm diameter at room temperature on a JEOL JES-PX-IX ESR spectrometer with $100 \cdot 10^3$ cycles per s field modulation. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) and Mn^{2+} doped on MgO were used to determine the concentration of Ti^{3+} and the g-value, respectively. The composition of the copolymer was determined by ^{13}C-NMR spectra (RANDALL 1978, CARMAN et al. 1977). ^{13}C-NMR spectra were measured at 120 °C using a JEOL JNM PS-100 spectrometer equipped with the PFT-100 Fourier transform system operating at 25.14 MHz. Solutions were made up in trichlorobenzene to 15 w/v %. The chemical shift was represented in ppm downfield from internal tetramethylsilane (TMS). The molecular weight distribution of the copolymer was measured at 150 °C by GPC (Shodex LC HT3) using o-dichlorobenzene as solvent. The calibration curve of the molecular weight was obtained on the basis of the universal calibration with 10 standard samples of monodisperse polystyrene with molecular weights from 2,100 to 2,610,000.

Results and Discussion

The ESR spectrum of the catalytic system (8 mg of the catalyst and 0.025 mmol of $AlEt_3$ in 0.5 ml of n-heptane), which had been kept at 65 °C for 10 min, displayed a strong, broad signal at g=1.95 and a weak sharp one at g=1.97. When the catalytic system was dried up and evacuated at 50 °C for 3 h, the latter signal disappeared completely, while the former one remained unchanged. From the result together with those reported by KEII et al. (1970) and by the present authors (1980), these signals can be assigned as $Ti^{3+}Cl_3$ and $Ti^{3+}EtCl_2$ supported on SiO_2. Then the time dependence of the intensities of these signals was examined at 65 °C. The intensities of both signals remained unchanged even after 4 h, and the spin concentrations were estimated to be 5.2 x 10^{19} spin/g-cat. (35 % based on the total supported titanium). These results strongly suggest that $TiCl_3$ is highly dispersed on SiO_2 and that the Ti^{3+} species in the present catalyst are very stable even in the presence of $AlEt_3$.

Then the copolymerization of ethylene and propylene was carried out at 40 °C for 2 h at various molar ratios of ethylene/propylene by using the catalyst combined with $AlEt_3$. The results obtained are summarized in Tab. 1. The number average molecular weight of the copolymer obtained at propylene/ethylene = 1 was about 29,000 with a Q value of 6.8. The copolymers obtained were found to be random or moderately alternating from the IR and ^{13}C-NMR spectra of them. It should be noted that the content of propylene in the copolymer obtained over the present catalyst is much higher as compared with those produced over the conventional Ziegler-Natta catalysts. The conventional Ziegler-Natta catalysts seem to contain an appreciable amount of the Ti^{2+} species in addition to the Ti^{3+} species, while the present catalyst hardly contains the Ti^{2+} species which are active only for the ethylene polymerization (SOGA et al. 1981). The marked difference in the copolymer composition may result from such a difference in the catalytic composition.

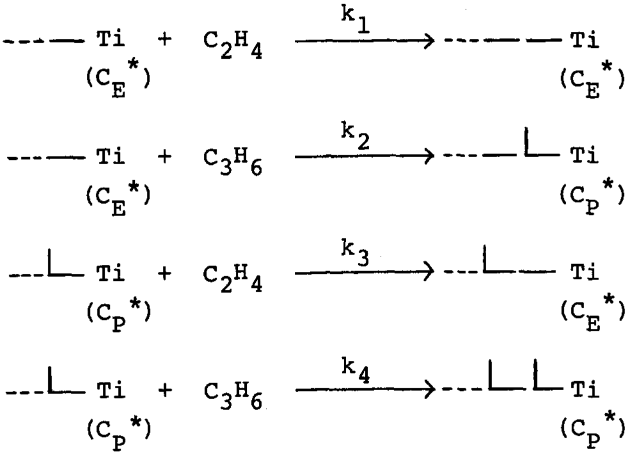
Table 1 Results of ethylene-propylene copolymerization[a)]

Propylene (mol %)	Activity (mol/g-Ti·h) Total	Ethylene	Propylene	Propylene in Copolymer[b)] (mol %)
0	49.4	49.4	0	0
25	32.6	27.7	4.9	15
37	25.3	18.8	6.5	26
48	21.7	13.9	7.8	36
57	19.0	11.8	7.2	38
73	11.4	5.5	5.9	52
91	4.8	1.6	3.2	67
100	1.8	0	1.8	100

a) Copolymerization was conducted at 40 °C for 1 h at an initial total pressure of 40 cmHg over the $TiCl_3 \cdot 3Py\text{-}MgCl_2 \cdot (THF)_x\text{-}SiO_2$ catalyst (treated with 4 mmol of $AlEt_2Cl$ in 5 ml of n-heptane) by using 0.5 mmol of $AlEt_3$ in 10 ml of n-heptane.
b) Measured by ^{13}C-NMR.

The present copolymerization was carried out at a very low pressure (total pressure = 40 cmHg) in order to measure the copolymerization rate with a reasonable degree of accuracy, so that the activity of the catalyst seems to be not so high. In this connection the copolymerization was conducted in a 100 ml stainless steel reactor by using 0.13 mol of ethylene and 0.54 mol of propylene at 65 °C, and was obtained a moderately alternating copolymer with the specific activity of 176 kg/g-Ti•h. Thus it is also to be noted that the present catalyst shows a very high activity for the copolymerization.

In the following are analyzed the results using a kinetic method. The growing polymer chain terminates in either ethylene or propylene monomer, and subsequently each growing end may add the same or the opposit monomer unit. On the other hand, in the polymerization of propylene over titanium-based catalysts, it is well established that propylene monomer adds into the active Ti-carbon bond by primary insertion (DOI 1979). There are therefore four reactions to be considered; these are given as



(1)

(2)

(3)

(4)

where — and ∟ represent the ethylene and propylene (in the orientation $-CH(CH_3)CH_2-$) units.

Since the present copolymerization was conducted under the constant total pressure (P), the partial pressures of propylene (P_P) and ethylene (P_E) are expressed as

$$P_P = fP \qquad (5)$$

$$P_E = (1-f)P \qquad (6)$$

where f is the molar fraction of propylene [$f=P_P/(P_E+P_P)=P_P/P$]. The solubility of propylene into n-heptane at 40 °C was confirmed to be 3.7 times as large as that of ethylene. Therefore, the ratio, x, of the concentration of propylene, C_P, to that of ethylene, C_E, is given by

$$x = \frac{C_E}{C_P} = \frac{1-f}{3.7f} \qquad (7)$$

Then the rates of polymerizations of propylene (r_P) and ethylene (r_E) can be expressed as

$$r_P = k_2C_p[C_E^*] + k_4C_p[C_p^*] \qquad (8)$$

$$r_E = k_1C_E[C_E^*] + k_3C_E[C_p^*] \qquad (9)$$

$$\frac{r_E}{r_p} = \frac{k_1\left(\frac{[C_E^*]}{[C_p^*]}\right) + k_3}{k_2\left(\frac{[C_E^*]}{[C_p^*]}\right) + k_4}\,x \qquad (10)$$

where k_1, k_2, k_3 and k_4 are the rate constants of eqs. (1), (2), (3) and (4), and $[C_E^*]$ and $[C_p^*]$ represent the concentrations of the active species whose growing chains terminate in ethylene and propylene monomer, respectively. Under steady-state conditions, both $d[C_E^*]/dt$ and $d[C_p^*]/dt$ should be zero, which leads to

$$k_2C_p[C_E^*] = k_3C_E[C_p^*] \qquad (11)$$

Eq. (10) reduces to eq. (12) by using eq. (11).

$$\frac{r_E}{r_p} = \frac{k_1}{k_2}\cdot x\cdot\frac{x + \frac{k_2}{k_1}}{x + \frac{k_4}{k_3}} = r_1\cdot x\cdot\frac{x + \frac{1}{r_1}}{x + r_2} \qquad (12)$$

where r_1 and r_2 denote the monomer reactivity ratios, k_1/k_2 and k_4/k_3, respectively.

Fig. 1 shows the relation between r_E/r_p and x by using the data in Tab. 1, which leads to eq. (13).

$$\frac{r_E}{r_p} = 7x \qquad (13)$$

Eq. (13) requires that r_2 should coincide with $1/r_1$ in eq. (12).

$$r_1 = 7 \quad \text{and} \quad r_2 = \frac{1}{7} \qquad (14)$$

On the other hand, the rate of ethylene homopolymerization is about 27 (49.4/1.8) times as large as that of propylene homopolymerization under the same pressure of 40 cmHg.

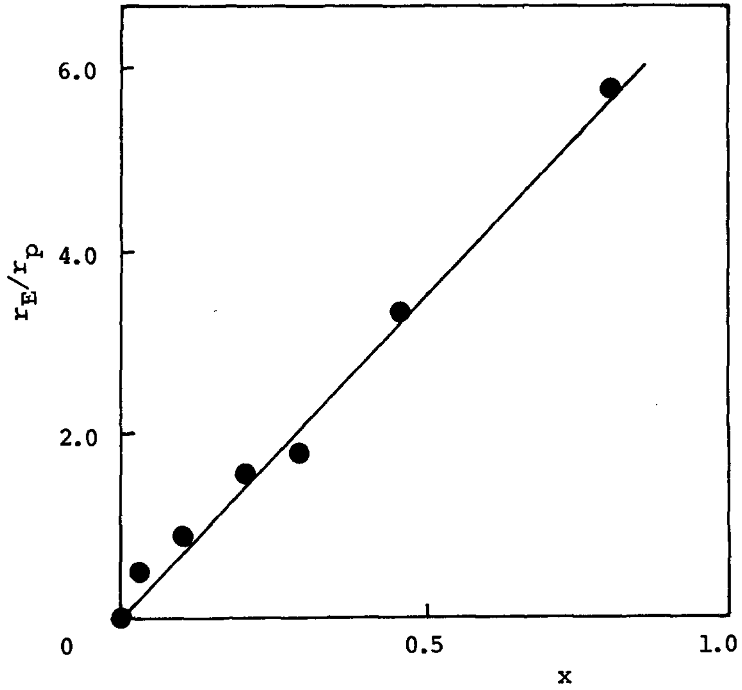
$$\frac{r_E(\text{homo})}{r_p(\text{homo})} = \frac{k_1}{k_4}\cdot\frac{C_E}{C_p} = \frac{k_1}{k_4}\cdot\frac{C_E}{3.7C_E} = \frac{k_1}{3.7k_4} \fallingdotseq 27 \qquad (15)$$

From eqs. (14) and (15), we can obtain

$$k_1 : k_2 : k_3 : k_4 \fallingdotseq 100 : 14 : 7 : 1 \qquad (16)$$

Eq. (16) shows that the rate of monomer addition to the growing polymer chain terminated in ethylene is about 14 times as large as that to the growing polymer chain terminated in propylene ($k_1/k_3=k_2/k_4=14$). This may be attributed to the fact that the insertion of either ethylene or propylene monomer into the Ti-carbon bond of Ti-CH_2-$CH(CH_3)$--- is disturbed by the steric hindrance of the methyl group attached to the β-carbon.

Fig. 1 Relation between r_E/r_p and x[a)].



a) Calculated by using eq. (7) and the data in Tab. 1.

In conclusion, the SiO_2-supported $MgCl_2/TiCl_3$ catalyst combined with $AlEt_3$ showed a very high activity for the copolymerization of ethylene and propylene and gave a moderately random copolymer, and a plausible model for the copolymerization was proposed from the kinetic study of the copolymerization.

References

BOOR, J. Jr. : "Ziegler-Natta Catalysts and Polymerization", Academic Press Inc., New York, 1979
SOGA, K., T. SANO and R. OHNISHI : Polym. Bull., 4, 157 (1981)
SOGA, K. and M. TERANO : Polym. Bull., 4, 39 (1981)
SOGA, K., K. IZUMI, S. IKEDA and T. KEII : Makromol. Chem., 178, 337 (1977)
SOGA, K., M. TERANO and S. IKEDA : Polym. Bull., 1, 849 (1979)
RANDALL, J. C. : Macromolecules, 11, 33 (1978)
CARMAN, C. J., R. A. HARRINGTON and C. E. WILKES : Macromolecules, 10, 536 (1977)
OKURA, I., Y. SENDODA and T. KEII : Kogyo kagaku Zasshi (Japanese), 73, 276 (1970)
SOGA, K., K. IZUMI, M. TERANO and S. IKEDA : Makromol. Chem., 181, 657 (1980)
SOGA, K., K. IZUMI, T. SANO and M. TERANO : Shokubai, 23, 124 (1981)
DOI, Y. : Makromol. Chem., 180, 2447 (1979)

Received June 19, accepted June 21, 1982