Polymer Bulletin 8, 261-268 (1982)

Polymer Bulletin

Effect of Hydrogen on the Molecular Weight of Polypropylene with Ziegler-Natta Catalysts

Kazuo Soga and Takeshi Siono

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

Summary

Polymerization of propylene was conducted at 40 °C with the catalytic system of $TiCl_4/MgCl_2/Al(C_2H_5)_3$/ethyl benzoate using hydrogen as a chain transfer agent, and the effect of hydrogen on the molecular weight was examined separately with the soluble and insoluble fractions in boiling n-heptane. It was found that the chain transfer reaction of the atactic and isotactic polymers took place via an atomic hydrogen and a molecular hydrogen, respectively. The result strongly supports the previous mechanism that there exist two types of polymerization centers, one having two vacancies which gives the atactic polymer and the other having one vacancy which gives the isotactic polymer.

Introduction

Numerous publications have claimed a number of additives for Ziegler-Natta catalysts to improve the isotacticity of polypropylene. Among the additives reported so far, ethyl benzoate (EB) seems to be most effective (MONTEDISON S. P. A. 1973, MITSUI PETROCHEMICAL INDUSTRIES 1975). On increasing the molar ratio of $EB/Al(C_2H_5)_3$, a remarkable decrease of the atactic fraction takes place, while the amount of isotactic polymer decreases only a very little (PINO et al. 1980, KASHIWA 1981, KEII et al. 1981), which seems to indicate that polymerization centers having different stereospecificities exist in the catalytic systems. However, the precise role of EB on the improvement of the isotacticity is still unknown. We have recently carried out the polymerizations of propylene and isoprene with the catalytic systems of $TiCl_4/Al(C_2H_5)_3$ and $TiCl_4/MgCl_2/Al(C_2H_5)_3$ using EB and examined the relation between the isotacticity of polypropylene and the cis-1,4-content of polyisoprene produced (SOGA et al. 1982). It was found that a marked increase in the isotacticity was accompanied by a remarkable decrease in the cis-1,4- content with both catalytic systems. From the result we have proposed the following mechanism for the stereospecific polymerizations of propylene and isoprene. There exist two types of polymerization centers in the catalytic systems. The center [C-1] having two

0170-0839/82/0008/0261/$01.60

vacant sites gives the atactic polypropylene and cis-1,4-polyisoprene, while the other center (C-2) having only one vacant site gives the isotactic polypropylene and trans-1,4- or 3,4- polyisoprene. On adding EB one of the vacant sites of C-1 is blocked and consequently C-1 becomes inactive or turns into C-2. If the vacant site of C-2 is blocked, it becomes inactive.

On the other hand, hydrogen is known to be the most efficient industrial regulator of the molecular weight of polypropylene. Many investigations have been carried out on the propylene polymerization using hydrogen as a chain transfer agent (KEII 1972). Most of the results reported so far have shown that the decrease in the molecular weight depends on the square root of the partial pressure of hydrogen. Therefore, it seems to be generally recognized that hydrogen atoms formed on the polymerization centers participate in the transfer reaction. It is considered that such a dissociative adsorption of hydrogen proceeds only on the C-1 center having two vacant sites. If our mechanism shown above is correct, the dependence of the molecular weight on the partial pressure of hydrogen should be different between the atactic and isotactic parts.

From such a viewpoint, in the present paper was conducted propylene polymerization with the catalytic system of $TiCl_4$/$MgCl_2$/$Al(C_2H_5)_3$/EB using hydrogen as a chain transfer agent, and examined the molecular weight of both the atactic and isotactic parts in detail.

Experimental

Materials Research grade propylene and n-heptane were obtained from Takachiho Chemical Co. and were purified according to the same procedures reported earlier (SOGA et al. 1977). Nitrogen (99.9989 %) and hydrogen (99.99999 %) of ultra high purity (from Nihon Sanso Co.) were further purified by passing through the molecular sieve 3A column cooled at -196 °C. Triethylaluminum, $Al(C_2H_5)_3$, 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 seive 3A column at room temperature. The $TiCl_4$/$MgCl_2$/$Al(C_2H_5)_3$/EB catalyst, which had been prepared according to the following procedures, was obtained from the Research Center, Mitsui Petrochemical Industries, Co, Ltd. The mixture of 20 g of $MgCl_2$ and 15 g of $AlCl_3 \cdot EB$ was ground in a ball mill under nitrogen for 24 h at room temperature, followed by washing with $TiCl_4$ at 80 °C for 2 h. The precipitate was separated by filtration under nitrogen and then washed with plenty of n-heptane to remove the unreacted $TiCl_4$ (0.67 matom of Ti/g-cat).

Polymerization and analytical procedures The polymerization of propylene was carried out at 40 °C for 30 min by using a semi-batch system. In a 300 ml glass reactor equipped with a magnetic stirrer were placed 100 ml of purified n-heptane, 30 mg of the catalyst and 1.0 mmol of EB under nitrogen. After the nitrogen in the reactor was completely pumped out, given amounts of hydrogen, nitrogen and propylene were introduced into the reactor so that the total pressure [$P_{H_2} + P_{N_2} + P_{C_3H_6}$ (35 cmHg) + $P_{n\text{-hep.}}$ (9.5 cmHg)] became an atmospheric pressure. Polymerization was then started by adding 3.0 mmol of $Al(C_2H_5)_3$. The polymerization was terminated by adding plenty of dilute hydrochloric acid solution in methanol. The polymer produced was extracted by boiling n-heptane for 15 h under nitrogen. The molecular weight distribution of the polymer was measured at 150 °C by GPC (Shodex LC HT-3) using o-dichlorobenzene as solvent.

Results and Discussion

The polymerization of propylene was conducted at 40 °C for 30 min with the catalytic system of $TiCl_4/MgCl_2/Al(C_2H_5)_3$/EB under pressures of propylene (35 cmHg) and hydrogen (0 - 25 cmHg). The polymer produced was extracted by boiling n-heptane for 15 h under nitrogen. The polymer soluble in boiling n-heptane was precipitated by adding plenty of methanol. Then the polymers, soluble [usually called "atactic"] and insoluble [usually called "isotactic"], were dried i. vac. at room temperature overnight. In Tab. 1 are summarized the polymerization results together with the molecular weights determined by GPC. The fraction insoluble in boiling n-heptane gradually decreased with an increase in the pressure of hydrogen. However, the isotactic index of the whole polymers measured by the method of Luongo (1960) with IR from 995 and 974 cm^{-1} bands remained almost unchanged. These results strongly suggest that the decrease in the insoluble fraction with increasing the pressure of hydrogen is attributed to the decrease in the molecular weight. To obtain a better insight into this point, the IR spectra were taken on the soluble polymers. The results shown in Tab. 1 clearly indicate that the soluble fraction contains a considerable amount of isotactic polypropylene.

Growth of a particular chain at the metal-carbon bond center can be terminated by hydrogen, $Al(C_2H_5)_3$, propylene and so on. However, the present polymerizations were carried out under the same conditions except for the partial pressure of hydrogen, so the rate of the chain transfer reactions, r_{tr}, may be represented by eq. (1).

$$r_{tr} = k_H P_{H_2}^n C^* + \alpha(=\sum_i k_i [X_i] C^*) \qquad (1)$$

where k_H, P_{H_2} and C^* are the rate constant of the chain transfer reaction by hydrogen, the partial pressure of hydrogen and the concentration of the growing chains, and n and α are constants.

The number-average degree of polymerizaiton of the total polymer produced, $\overline{P_n}$, after a time t is generally given by eq. (2).

$$\overline{P}_n = \frac{\int_0^t r_p dt}{C^* + \int_0^t r_t dt + \int_0^t r_{tr} dt} \qquad (2)$$

where r_p and r_t represent the rates of polymerization and termination, respectively. It is well established that the propagation rate with the present catalytic system is extremely high and that $\overline{P}_n$ is independent of the polymerization time (SUZUKI 1982). This fact strongly implies that $\int_0^t r_{tr} dt$ is far greater than $C^* + \int_0^t r_t dt$. Thus eq. (2) can be simplified as

$$\overline{P}_n = \frac{\int_0^t r_p dt}{\int_0^t r_{tr} dt} = \frac{r_p}{r_{tr}} = \frac{k_p [M] C^*}{k_H P_{H_2}^n C^* + \sum_i k_i [X_i] C^*} = \frac{k_p [M]}{k_H P_{H_2}^n + \sum_i k_i [X_i]} \qquad (3)$$

Tab. 1 shows that the rate of polymerizaiton gradually decreases with an increase in the partial pressure of hydrogen. This may be attributed to the decrease in C^* caused by the time lag of the recovery of the polymerizaiton center from the metal-hydride bond formed by the chain transfer by hydrogen (eq. (4)).

$$\text{Cat-H} \xrightarrow[\text{slow}]{C_3H_6} \text{Cat-R} \ (R=C_3H_7) \qquad (4)$$

Eq. (3) is, however, free from C^*, and hence we have the following relation between $\overline{P}_n^0$ and $\overline{P}_n^H$.

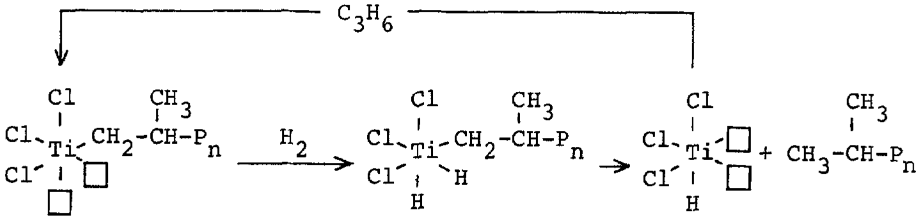
$$\frac{\overline{P}_n^0}{\overline{P}_n^H} = \frac{\overline{Mn}^0}{\overline{Mn}^H} = \frac{\sum_i k_i [X_i] + k_H P_{H_2}^n}{\sum_i k_i [X_i]} = \frac{\alpha + k_H P_{H_2}^n}{\alpha} = 1 + \frac{k_H}{\alpha} P_{H_2}^n \qquad (5)$$

where $\overline{P}_n^0$ and $\overline{P}_n^H$ are the number-average degree of polymerization without and with hydrogen, and $\overline{Mn}^0$ and $\overline{Mn}^H$ the number-average molecular weight without and with hydrogen, respectively.

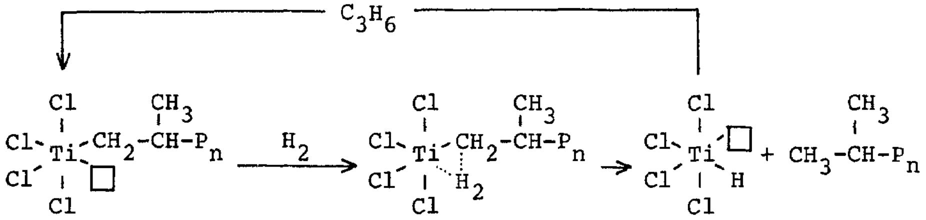
In Fig. 1 are plotted the values of $(\overline{Mn}^0/\overline{Mn}^H - 1)$ against the partial pressure of hydrogen using the data shown in Tab. 1, which gives n=0.8 and 0.7 for the fractions insoluble and soluble in boiling n-heptane. Since the present polymerizations were conducted at a very low pressure of propylene, the poly mers produced had considerably low molecular weight. The discrepancy between the observed values and the expected ones (n=1 for isotactic and n=0.5 for atactic) may be owing to the fact that the soluble fraction contains a considerable amount of isotactic polypropylene with low degree of polymerization as mentioned above.

From this point of view, we have analyzed the data reported by Keii et al. (1972, 1976) using the catalytic systems of $TiCl_3$-$Al(C_2H_5)_3$ and $TiCl_3$-$Al(C_2H_5)_2Cl$. The analytical results are shown in Fig. 2, which gives n=0.9 for the polymers with $Al(C_2H_5)_2Cl$ having the isotactic index (I.I.) of as high as 94 % and $\overline{M}n$ from $71x10^3$ (at P_{H_2}=0) to $14x10^3$ (at P_{H_2}=16.8cmHg), and n=0.5 for the polymers with $Al(C_2H_5)_3$ having the I.I. of 64 % and $\overline{Mn}$ from $61x10^3$ (at P_{H_2}=0) to $11x10^3$ (at P_{H_2}=29cmHg).

These results strongly suggest that our mechanism previously reported (SOGA et al. 1982) is plausible and that the chain transfer reaction by hydrogen proceeds according to the following model.



[C-1 center]



[C-2 center]

Acknowledgements

The authors express their gratitude to the Research Center, Mitsui Petrochemical Industries, Co. Ltd., for supplying the $TiCl_4/MgCl_2/EB$ catalyst.

Table 1. Polymerization results with the $TiCl_4/MgCl_2/Al(C_2H_5)_3/EB$ catalytic system.[a]

Run No.	Partial Press. of Hydrogen [cmHg]	Yield [g]	Activity [kgPP/g-Ti·h]	Number-Average Molecular Weight[b] $\overline{Mn}$ ($\times 10^{-3}$)		Q-value[b] ($\overline{Mw}/\overline{Mn}$)		Ratio of $\overline{Mn}^0/\overline{Mn}$		I.I.[c] [%]	I.I.[d] [%]	I.I.[e] [%]
				Insol.	Sol.	Insol.	Sol.	Insol.	Sol.			
1	0	1.45	3.02	26.2	4.1	6.1	5.9	1.0	1.0	90.2	94.2	61.0
2	1.00	1.22	2.55	20.8	3.6	6.1	4.7	1.3	1.1	85.9	94.2	-
3	4.05	1.40	2.93	15.5	3.0	4.4	3.6	1.7	1.4	86.8	95.2	70.0
4	9.15	1.00	2.09	10.3	2.4	4.6	2.5	2.5	1.7	86.1	92.2	-
5	14.70	0.75	1.57	8.0	2.2	4.7	2.5	3.3	1.8	84.2	94.4	72.5
6	25.05	0.68	1.42	6.2	1.8	4.3	2.8	4.3	2.3	83.0	96.1	-

a) Polymerization was conducted at 40 °C for 30 min at a propylene pressure of 35 cmHg by using ca. 30 mg of the catalyst, 100 ml of n-heptane, 3.0 mmol of $Al(C_2H_5)_3$ and 1.0 mmol of EB.
b) Determined by GPC ($Q=\overline{Mw}/\overline{Mn}$).
c) Isotactic index of the whole polymer determined by extraction (weight fraction of the polymer insoluble in boiling n-heptane).
d) Isotactic index of the whole polymer determined by the method of Luongo (1960) with IR.
e) Isotactic index of the polymer soluble in boiling n-heptane determined with IR.

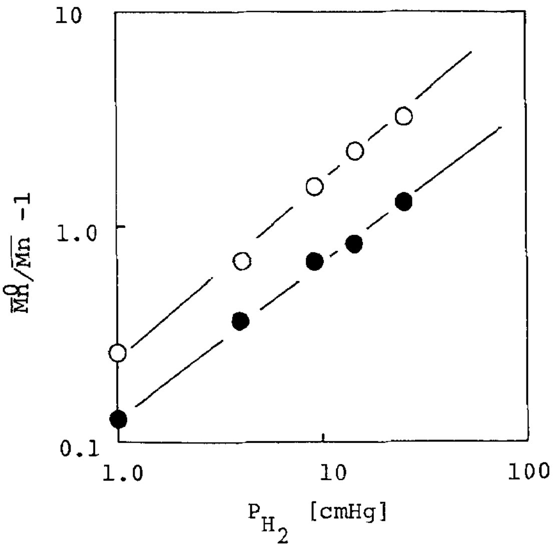


Figure 1. Plots of $(\overline{Mn}^0/\overline{Mn} - 1)$ against the hydrogen pressure (Conditions as in Tab. 1).

● : Polymer soluble in boiling n-heptane.

○ : Polymer insoluble in boiling n-heptane

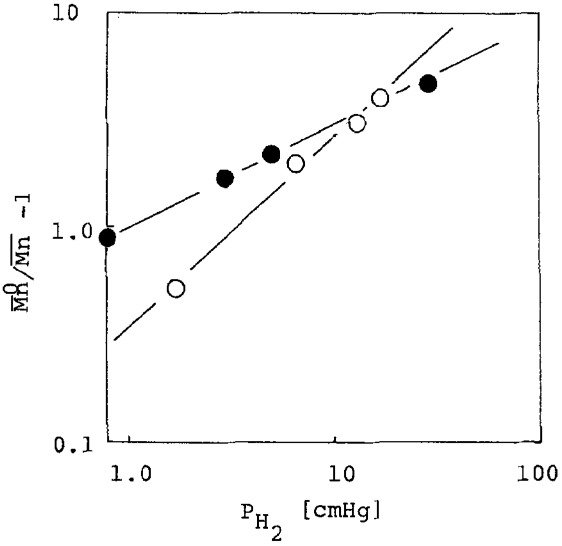


Figure 2. Plots of $(\overline{Mn}^0/\overline{Mn} - 1)$ against the hydrogen pressure.

● : Whole polymer obtained with $TiCl_3/Al(C_2H_5)_3$ [After Keii et al. (1976)].

○ : Whole polymer obtained with $TiCl_3/Al(C_2H_5)_2Cl$ [After Keii et al. (1972)]

References
MONTEDISON S. P. A. : Japan Pat. (Open), 48-16986 (1973)
MITSUI PETROCHEMICAL INDUSTRIES : Japan Pat. (Open), 50-126590 (1975)
PINO, P., R. MULHAPT : Angew. Chem. Int. Ed. Engl. 19, 857 (1980)
KASHIWA, N. : "MMI International Symposium on Transition Metal Catalyzed Polymerization (Midland)", p. 13 (1981)
KEII, T. : ibid., p. 6 (1981)
SOGA, K., T. SANO, K. YAMAMOTO, T. SHIONO : Chem. Lett. (Japan), 1982, 425
KEII. T. : "Kinetics of Ziegler-Natta Polymerization", Kodansha Ltd., Tokyo, 1972
LUONGO, J. P. : J. Appl. Polym. Sci., 3, 302 (1960)
SUZUKI. E. : Dr. Eng. Thesis, Tokyo Inst. Technology, 1982

Received and accepted August 3o, 1982