Possibility of Mass-Transfer Resistance in Ethylene Polymerization with $MgCl_2$-Supported Catalysts

Introduction. In ethylene polymerization with Ziegler–Natta catalysts, the importance of monomer diffusion through polymer films has been speculated on for some time.[1-5] Addition of a small amount of comonomers into ethylene polymerization often causes a marked increase in the apparent polymerization activity, which is usually explained in terms of mass-transfer resistances.[5] If ethylene polymerization is actually monomer transfer limited, a remarkable decrease in the apparent propagation rate may be observed during the initial very short time of polymerization.

Keii and Terano have recently developed a stopped-flow method[6] for Ziegler–Natta polymerization, which enables us to measure the propagation rate constant, k_p, as well as the concentration of active sites, C^* (mol/mol of Ti).

In the present study, therefore, we have applied the method for ethylene polymerization.

Experimental Section. Preparation of Catalysts. The ethyl benzoate (EB) containing $TiCl_4/MgCl_2$ catalyst was prepared as follows: 30 g of anhydrous $MgCl_2$ and 3.2 cm^3 (22.5 mmol) of EB were coground in a 1-dm^3 stainless steel vibration mill pot with 50 balls (25 mm in diameter) under nitrogen for 20 h at room temperature. The product was contacted with 80 cm^3 of $TiCl_4$ at 80 °C for 2 h, followed by washing with plenty of heptane. The content of Ti in the catalyst as measured by UV spectrometry (Hitachi Ltd., ESP-3T) was 2.1 wt %.

Polymerization. The polymerization apparatus used in this study is similar to the one previously used by Keii and Terano.[6] A catalyst suspension in heptane ([Ti] = 1.25 mmol/dm^2) and a $Al(C_2H_5)_3$– or $Al(i\text{-}C_4H_9)_3$–heptane solution (85 mmol/dm^3) saturated with ethylene (ca. 0.11 mol/dm^3, at 20 °C) were forced to flow out simultaneously at 10 cm^3/s through a glass tube of 3.2-mm inner diameter. When both solutions met at a three-necked joint, polymerization started and continued until quenched by 1.5 dm^3 of methanol contained in a 2-dm^3 flask.

The polymerization of ethylene was performed at 20 °C under an atmospheric pressure (about 103 kPa). The polymerization time was changed in the range from 0.05 to 0.36 s. In order to avoid a significant change in monomer concentration, [M], and temperature of polymerization, the polymerization conditions were adjusted to hold monomer conversions below 10%. To the polymer suspension in methanol was added 20 cm^3 of HCl to remove the catalyst residue. The polymer was than separated by filtration and dried in vacuo at 60 °C.

Measurements. The molecular weight of polymer was measured by gel permeation chromatography (Waters 150C GPC) at 140 °C using o-dichlorobenzene as solvent. From GPC results, the number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calculated by standard procedures based on the molecular weight calibration curve of polyethylene. The melting point and heat of fusion of polymer were recorded on a Shimadzu DSC-50 at a heating rate of 10 °C/min.

The ^{13}C NMR spectrum of polymer was recorded on a JEOL GX-500 spectrometer at 125.65 MHz and 110 °C. The sample solutions, in 5-mm-o.d. glass tubes, were prepared in tetrachloroethane-d_2, which provided the signal for the ^2H NMR internal lock and reference (74.47 ppm downfield from the resonance of tetramethylsilane).

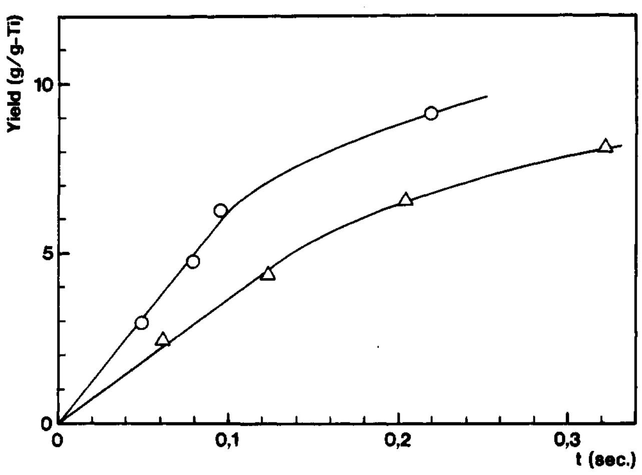

Figure 1. Relationship between the yield of polyethylene and polymerization time: (○) obtained with Cat. A (without external EB); (△) obtained with Cat. B (with external EB).

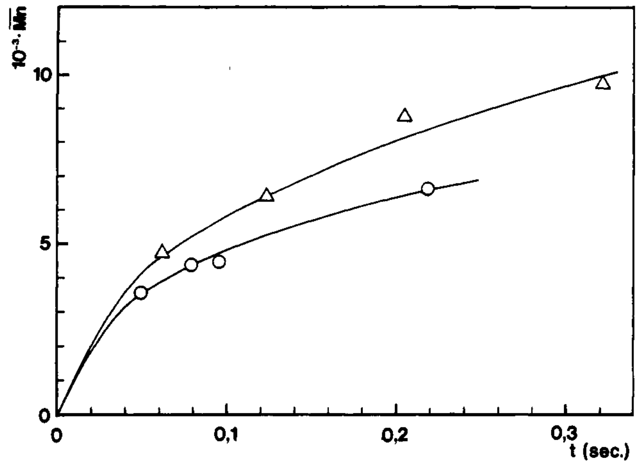

Figure 2. Relationship between the number-average molecular weight and polymerization time: (○) obtained with Cat. A (without external EB); (△) obtained with Cat. B (with external EB).

Results and Discussion. Polymerization of ethylene was performed at 20 °C by using a stopped-flow method with the following catalyst systems, which differ in isospecificity; $TiCl_4/EB/MgCl_2–Al(C_2H_5)_3$ (Cat. A) and $TiCl_4/EB/MgCl_2–Al(C_2H_5)_3/EB$ (Cat. B; [Ti]/[external EB] = 1). Polymerization of propylene at 40 °C under an atmospheric pressure gave the polymers with isotactic indexes (weight fraction of the boiling heptane-insoluble part) of 55% for Cat. A and 93% for Cat. B. It has already been confirmed that both the yield (Y) and number-average molecular weight ($\bar{M}_n$) of the polymers are proportional to a polymerization time (t) up to approximately 1 s in the case of propylene polymerization with these catalyst systems.[7]

In Figures 1 and 2 are plotted the Y and $\bar{M}_n$ of polyethylene against t, indicating that both Y and $\bar{M}_n$ are not proportional to t. On the other hand, the concentrations of the active sites, C^* (mol/mol of Ti), calculated from eq 1 are plotted in Figure 3 as a function of t, which

$$C^* = Y/\bar{M}_n \tag{1}$$

indicates that C^* values do not change so much during the experimental time, whereas the apparent propagation rate constants, k_p' ($=k_p$[M]), estimated from eq 2 decrease markedly with an increase in t as shown in Figure 3.

$$k_p' = k_p[\mathrm{M}] = \bar{M}_n/28t \tag{2}$$

The tendency is very different from that observed in propylene polymerization, where the k_p' values remained unchanged. It may be plausible to suppose that the

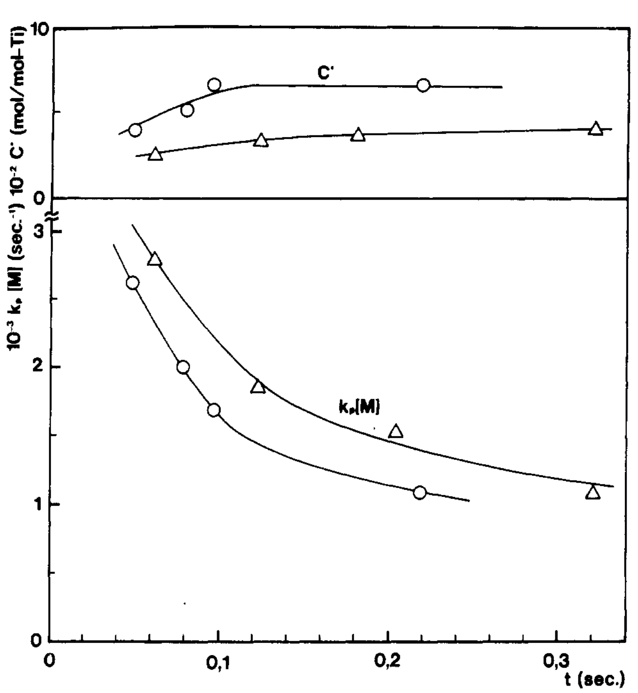

Figure 3. Plots of k_p[M] and C^* against t: (○) obtained with Cat. A (without external EB); (△) obtained with Cat. B (with external EB).

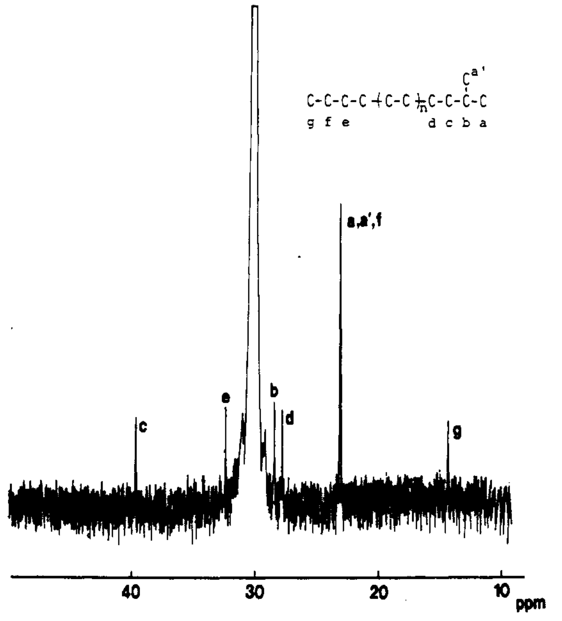

Figure 4. ^{13}C NMR spectrum of polyethylene obtained with Cat. A at 20 °C for 0.1 s.

Table I
Some Thermodynamic Parameters of Polyethylene and Polypropylene

polymer	catal syst[a]	MP, °C	ΔH_f,[b] cal g^{-1}	crystallinity, %
polyethylene	Cat. A	133.7	54.0	83.7
	Cat. B	131.1	53.6	83.1
polypropylene	Cat. A	161.2	25.8	51.8
	Cat. B	162.5	28.0	56.3

[a] See the Experimental Section. [b] Heat of fusion.

propagation rate constants, k_p, do not change so much in such a very short time. Therefore, the decrease in k_p' may most probably be due to the continuous decrease in the ethylene concentration [M] around the active sites.

To get better information on this point, polymerization of ethylene was performed by using $Al(i\text{-}C_4H_9)_3$ in place of $Al(C_2H_5)_3$ and the structures of polymer ends were analyzed by ^{13}C NMR. Figure 4 shows a typical ^{13}C NMR spectrum of the polymer obtained with the assignments according to the method reported by Lindeman and Adams,[8] indicating that the intensities of initiated ($-CH_2-CH(CH_3)CH_3$) and terminated (CH_3CH_2-) groups are almost identical. In addition, the absorption peak around 110–140 ppm attributed to the $CH_2{=}CH-$ end group, arising from the transfer reaction by monomer, could not be observed. These results clearly indicate that living polymerization of ethylene takes place during such a short polymerization time. The distribution of the molecular weights was, however, very broad ($\bar{M}_w/\bar{M}_n = 8$), which is general in olefin polymerization using heterogeneous catalysts even for a living one. For example, the catalyst system composed of Solvay-type $TiCl_3$ and $Cp_2Ti(CH_3)_2$, which is known to catalyze isotactic living polymerization of propylene,[8] also gives polypropylene with $\bar{M}_w/\bar{M}_n = 5$. The heats of fusion of as-made polyethylene and polypropylene were then measured by DSC, and their crystallinities were estimated by using eq 3 where ΔH_f is the

$$\text{crystallinity (in \%)} = (\Delta H_f/\Delta H_f^*) \times 100 \qquad (3)$$

heat of fusion of the sample, as determined from the DSC curve, and ΔH_f^* is that of the folded-chain polyolefin crystal (64.5 cal/g for polyethylene[10] and 49.8 cal/g for polypropylene[11]; Table I). The crystallinity of as-made polyethylene was evaluated to be as high as ca. 83%.

On the other hand, the results shown in Figure 3 suggest that the external EB causes a significant increase in k_p' with a marked decrease in C^*.

Although further tests on the data are necessary to reach the final conclusion, the present results may strongly suggest that the monomer diffusion through highly crystalline polyethylene films plays an important role on the apparent rate of ethylene polymerization.

To get more information on this point, copolymerizations of ethylene with α-olefins are now being carried out by using the stopped-flow method. The detailed results will be reported in another paper.

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Kazuo Soga,* Masaaki Ohgizawa, and Takeshi Shiono

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

Dong-ho Lee

Department of Polymer Science, Engineering College
Kyungpook National University, Taegu 635, Korea

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