Polymerization of Olefines by Ziegler Catalyst. II. Polymerization of Ethylene by $AlEt_3$-$TiCl_4$ Catalyst[*]

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Since polymerization of ethylene at low pressure and temperature in the presence of the catalyst obtained from the interaction of titanium tetrachloride with aluminum trialkyl has been discovered by Ziegler1), several studies on this type of polymerization have been reported.

The present paper concerns a study on ethylene polymerization with $AlEt_3$-$TiCl_4$ catalyst as an extension of the investigation previously reported2) for propylene polymerization with the same catalyst. The reaction conditions are correlated with the polymerization rate as well as with the properties of polymers.

Experimental

Ethylene was produced by dehydrating ethanol over activated alumina at 350°C and then liquefied under pressure and distilled. The purity of the gas is more than 99.9%. Other materials and the apparatus were exactly the same as those described

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[*] Presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

1) K. Ziegler, Belg. Pat. 533362 (1954).

2) S. Kodama, T. Kagiya, S. Machi, T. Shimidzu, S. Yuasa and K. Fukui, *J. Appl. Polymer Sci.*, 3, 20 (1960).

in the previous paper²⁾. Introduction of catalyst into the reaction vessel was made in a nitrogen stream by pipetting a definite amount of titanium tetrachloride solution (0.15 M. solution in *n*-heptane) followed by adding triethyl aluminum solution (0.9 or 3.0 M solution in *n*-heptane) at room temperature (15~20°C). Immediately after the addition of the catalyst, the inner nitrogen was purged under reduced pressure. After the temperature was raised to the desired one, the pressure was then raised to a definite one by introducing compressed ethylene gas. The polymerization then started. It always took 20 min. from the addition of the catalyst to the introduction of ethylene gas. The pressure decreased during the reaction, and was recorded to estimate the reaction rate. In addition, some experiments were carried out under constant pressure.

The number average molecular weight, $\overline{M}_n$, was estimated by the intrinsic viscosity measurement in tetralin at 130°C, using Tung's formula³⁾,

$$[\eta]=5.10\times10^{-4}\overline{M}_n^{0.725}$$

Results and Discussion

The experimental results obtained are shown in the following several figures. The discussions will be made in regard to two items; namely, the molecular weight and the polymerization rate.

Molecular Weight.—The dependence of the molecular weight on the various factors is shown in Figs. 1, 2 and 3, which make it clear that the important factors affecting the molecular weight are the ratio of triethylaluminum to titanum tetrachloride. The increase in the reaction temperature and the amount of catalyst makes the molecular weight decreased to some extent, as shown in Fig. 1, where the ratio of triethylaluminum to titanium tetrachloride is kept constant. As shown in Fig. 2, the molecular weight also increases sharply with the ratio of triethylaluminum to titanium tetrachloride in the range from 0 to 3, but it is only slightly affected with more addition of trithylaluminum, where the amount of titanium tetrachloride is kept constant. The molecular weight decreases nearly exponentially with temperature rise. As shown in Fig. 3, the plot of the logarithm of molecular weight versus the reciprocal of absolute temperature gives a straight line. The dependences of the molecular weight on the temperature and the ratio of two components of catalyst are almost the same as the case of polypropylene produced by the same catalyst²⁾.

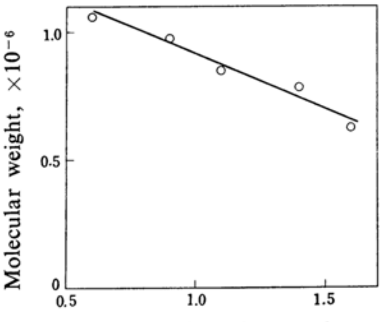

Fig. 1. Molecular weight vs. amount of $TiCl_4$. ($AlEt_3/TiCl_4$, 6.7; Solvent, 16 ml.; Temperature, 50°C; Initial pressure, 43 kg./cm²; Reaction time, 120 min.)

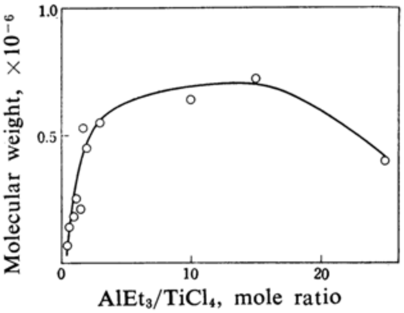

Fig. 2. Molecular weight vs. $AlEt_3/TiCl_4$ ratio. ($TiCl_4$, 1.2 mmol.; Solvent, 16 ml.; Temperature, 50°C; Initial pressure, 43 kg./cm²; Reaction time, 120 min.)

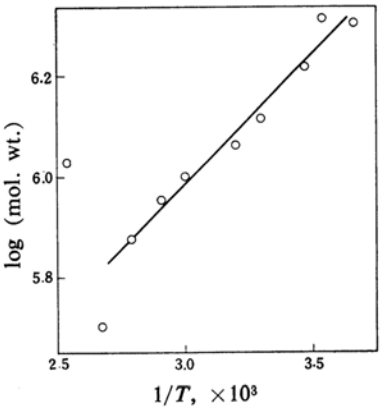

Fig. 3. Molecular weight vs. reaction temperature. ($TiCl_4$, 1.2 mmol.; $AlEt_3$, 8.0 mmol.; Solvent, 16 ml.; Initial pressure, 43 kg./cm².; Reaction time, 120 min.)

Recently, Badin⁴⁾ reported that the molecular weight of polyethylene produced by $TiCl_4$-$Al\cdot(i\text{-}C_4H_9)_3$ catalyst, was decreased with raising reaction temperature, with increased ratio of $TiCl_4$ to $Al(i\text{-}C_4H_9)_3$, and with increasing amount of catalyst. These are coincident with our present results.

Rate of Polymerization. — Several pressure-reaction time curves are shown in Fig. 4. This

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3) L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

4) E. J. Badin, *J. Am. Chem. Soc.*, **80**, 6545 (1958).

experiment is carried out in a batch type reaction vessel. These curves, of course, represent the diminishing ethylene pressure which causes the fall of polymerization rate. But, as was previously observed in the polymerization of propylene with the same catalyst, the polymerization rate falls even at a constant ethylene pressure. An experiment is carried out at a constant ethylene pressure, and the result is shown in Fig. 5.

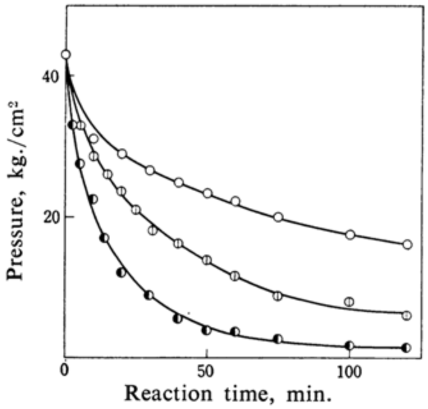

Fig. 4. Pressure vs. reaction time.
○ $TiCl_4$, 1.2 mmol.; $AlEt_3$, 0.96 mmol.;
⦶ $TiCl_4$, 1.1 mmol.; $AlEt_3$, 7.4 mmol.;
◑ $TiCl_4$, 1.6 mmol.; $AlEt_3$, 10.7 mmol.;
Solvent, 16 ml; Temperature, 50°C.

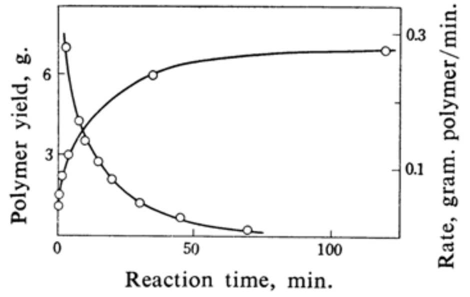

Fig. 5. Polymer yield vs. reaction time. ($TiCl_4$, 0.68 mmol.; $AlEt_3$, 4.65 mmol.; Solvent, 16 ml.; Temperature, 30°C; Pressure, 11 kg./cm².)

In order to decide the dependence of the rate on ethylene pressure, the initial rate is analyzed. Figure 6 shows that the initial rate is almost proportional to the ethylene pressure over the range of 0∼30 kg./cm² (Ludlum et al.[5] reported that the rate of ethylene polymerization with $TiCl_4$-$LiAlR_4$ catalyst was also proportional to ethylene pressure). Thus the "specific" rate should be defined by the rate divided by ethylene pressure. The estimation

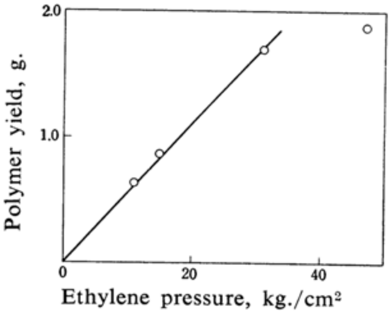

Fig. 6. Polymer yield during initial 90 sec. vs. reaction pressure.
($TiCl_4$, 0.6 mmol.; $AlEt_3$, 3.6 mmol.; Solvent, 16 ml.; Temperature, 30°C; Reaction time, 90 sec.)

of the rate of polymerization from the curves of Fig. 4 is made in the same manner as described in the previous paper. Namely, the pressure drop during the first 30 min. divided by the mean pressure times the duration of reaction (30 min.) is used as a measure of the rate. This value is indicated in Figs. 7, 8 and 9 as the "mean specific rate".

Dependence of Rate on the Amount of Catalyst.—Figure 7 indicates that the mean specific rate is almost proportional to the amount of titanium tetrachloride, where the ratio of triethylaluminum to titanium is kept constant. This result is the same as that obtained in the polymerization of propylene. That this curve does not pass through the origin might be due to the impurities.

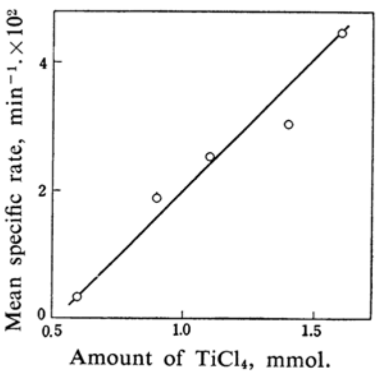

Fig. 7. Mean specific rate vs. amount of $TiCl_4$. ($AlEt_3$/$TiCl_4$, 6.7; Solvent, 16 ml.; Temperature, 50°C; Initial pressure, 43 kg./cm².)

Dependence of Rate on Catalyst Composition.—With a definite amount of titanium tetrachloride, the rate varies with the amount of triethylaluminum added as shown in Fig. 8. The rate increases rapidly with the increase in the amount of triethylaluminum and then maintains an almost constant value over the range of which the ratio of triethylaluminum

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[5] D. B. Ludlum, A. W. Anderson and C. E. Ashby, ibid., **80**, 1380 (1958).

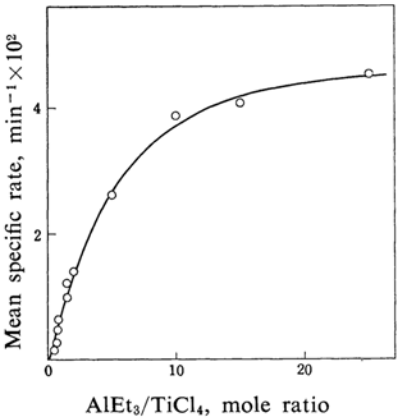

Fig. 8. Mean specific rate vs. AlEt$_3$/TiCl$_4$ ratio. (TiCl$_4$, 1.2 mmol.; Solvent, 16 ml.; Temperature, 50°C; Initial pressure, 43 kg./cm^2)

to titanium tetrachloride is from 10 to 25.

Temperature Dependence of Rate.—The plot of the logarithm of the rate against the reciprocal of absolute temperature is shown in Fig. 9. The rate first increases with temperature rise and then falls off at higher temperatures. The temperature to give the maximum rate is 85°C. The straight line in the range from 0 to 85°C gives an "apparent" activation energy of 1.0 kcal./mol. To estimate the value of activation energy corresponding to the pure polymerization step in the liquid phase, the heat of solution of ethylene in *n*-heptane is calculated from known data⁽⁶⁾, which amounts to −1.7 kcal./mol. Consequently, 2.7 kcal./mol. for the activation energy of polymerization in the liquid phase is obtained.

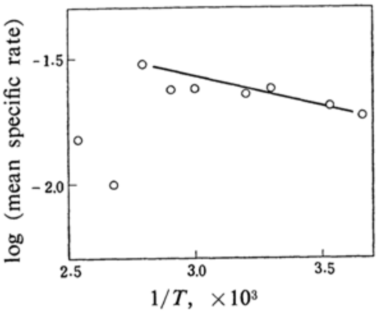

Fig. 9. Mean specific rate vs. reaction temperature.
(TiCl$_4$, 1.2 mmol.; AlEt$_3$, 8.0 mmol.; Solvent, 16 ml.; Initial pressure, 43 kg./cm^2)

The decrease of the rate at higher temperatures may be due to the deterioration of the catalyst as has been observed in the propylene polymerization by AlEt$_3$-TiCl$_4$ catalyst⁽²⁾.

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[6] "International Critical Table," Vol. 3, 269 (1928).