*Polymerization of Olefines by Ziegler Catalyst. III. Polymerization of Ethylene by $AlEt_3$-$TiCl_3$ Catalyst**

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As an extension of the investigation previously reported for ethylene[1] and propylene[2] polymerization with $AlEt_3$-$TiCl_4$ catalyst, a study on the polymerization of ethylene by means of $AlEt_3$-$TiCl_3$ catalyst is described in the present paper. No report of the study on the ethylene polymerization with $AlEt_3$-$TiCl_3$ catalyst is found, while the polymerization of propylene with the same catalyst has been studied by Natta et al.[3]

Experimental

The apparatus and the procedure adopted was utterly the same as those described in the previous paper[1,2]. Titanium trichloride was due to the Sumitomo Chemical Co., Ltd. Introduction of the catalyst components into the autoclave was made by pipetting an amount of a dispersion of titanium trichloride in *n*-heptane (78 g. titanium trichloride

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1) K. Fukui, T. Kagiya, S. Machi, T. Shimidzu and S. Yuasa, This Bulletin, 35, 303 (1962).

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

3) G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, 69, 213 (1957).

in 1000 ml. *n*-heptane) followed by addition of triethylaluminum solution (0.9 mol. solution in *n*-heptane), and then a suitable amount of *n*-heptane), was added to make the total volume of solvent 16 ml. The number average molecular weight, $\bar{M}_n$, is estimated by the intrinsic viscosity at 130°C in tetralin solution, using Tung's formula[4],

$$[\eta] = 5.10 \times 10^{-4} \times \bar{M}_n^{0.725}$$

Result and Discussion

Molecular Weight.—Figures 1, 2 and 3 indicate that important factors affecting the molecular weight of polyethylene are the reaction temperature and the amount of catalyst. Figure 1 shows that the melecular weight decreases with the increase in the amount of titanium trichloride where the ratio of triethylaluminum to titanium trichloride is kept constant. The dependence of the molecular weight on the amount of catalyst is almost the same as in the case of ethylene polymerization using $AlEt_3$-$TiCl_4$ catalyst. It may be a characteristic feature of the Ziegler type catalysts that the molecular weight decreases with the amount of the catalyst. As shown in Fig. 2, the molecular weight is but little affected by the quantity of triethylaluminium with a constant amount of titanium trichloride. But, in the range of 6~25 of $AlEt_3/TiCl_3$ ratio a tendency is observed that the molecular weight decreases slightly with the increase in the amount of triethylaluminum. The plot of the logarithm of the molecular weight versus the reciprocal of reaction temperature in an absolute scale is shown in Fig. 3. A decrease in the molecular weight with the increase in temperature has also been observed in the present case, as in the preceding two papers[1,2].

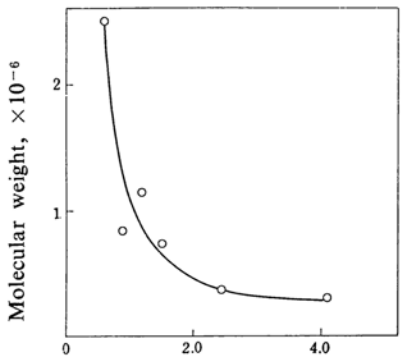

Fig. 1. Molecular weight vs. amount of $TiCl_3$. ($AlEt_3/TiCl_3$, 6.7; Temperature, 50°C; Initial pressure, 42 kg./cm²: Reaction time, 120 min.)

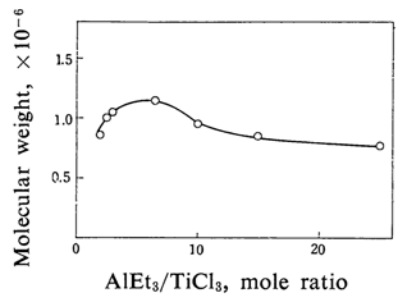

Fig. 2. Molecular weight vs. $AlEt_3/TiCl_3$ ratio. ($TiCl_3$, 1.2 mmol.; Temperature, 50°C; Initial pressure, 42 kg./cm²; Reaction time 120 min.)

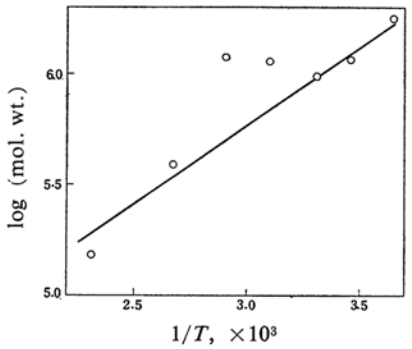

Fig. 3. Molecular weight vs. reaction temperature.
($TiCl_3$, 1.2 mmol.; $AlEt_3$, 8.0 mmol.; Temperature, 50°C; Initial pressure, 42 kg./cm²; Reaction time, 120 min.)

Rate of Polymerization.—The pressure drop was observed at every moment with regard to each run of an experiment. As shown in Fig. 4, the plot of $\log(P_0/P)$ versus reaction time

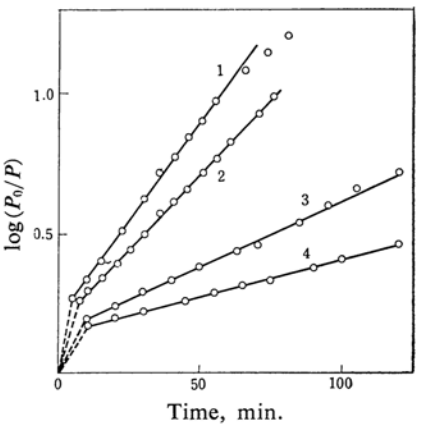

Fig. 4. $\log(P_0/P)$ vs. reaction time.

	$TiCl_3$ mmol.	$AlEt_3$ mmol.	Temperature °C
(1)	1.2	12.0	50
(2)	1.2	8.0	50
(3)	1.2	3.6	50
(4)	1.2	8.0	50

P_0, 42 kg./cm²

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

gives almost a straight line. This means that the rate is approximately proportional to the pressure except an initial short interval of reaction time.

In regard to all runs of an experiment, the specific rate is calculated and is related to the various factors as follows.

Dependence of Rate on the Amount of Catalyst. —Figure 5 indicates that the relation between the specific rate and the amount of catalyst is almost linear, where the ratio of triethylaluminum to titanium trichloride is kept constant.

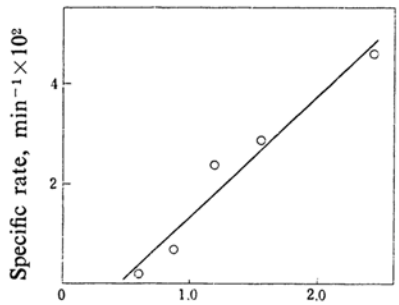

Fig. 5. Specific rate vs. amount of $TiCl_3$. ($AlEt_3/TiCl_3$, 6.7; Temperature, 50°C; Initial pressure, 42 kg./cm²)

Dependence of Rate on Catalyst Composition. —With a constant amount of titanium trichloride, the rate grows with the increasing amount of triethylaluminum used, as shown in Fig. 6. The curve is very simple in comparison with that of the polymerization by means of $AlEt_3$-$TiCl_4$ catalyst. Natta et al.[3] already reported that the ratio of triethylaluminum to titanium trichloride did not affect the rate in the polymerization of propylene.

Temperature Dependence of Rate.—The logarithm of the rate is plotted against the reciprocal of absolute temperatue in Fig. 7. The straight line, obtained at 0~100°C, gives an apparent activation energy of 1.6 kcal./mol.

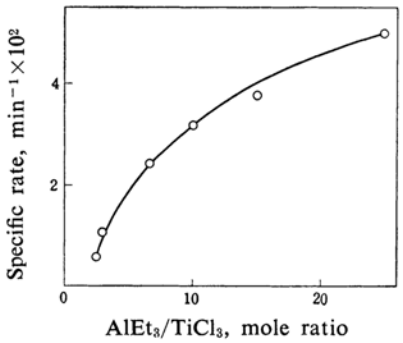

Fig. 6. Specific rate vs. $AlEt_3/TiCl_3$ ratio. ($TiCl_3$, 1.2 mmol.; Temperature, 50°C; Initial pressure, 42 kg./cm²)

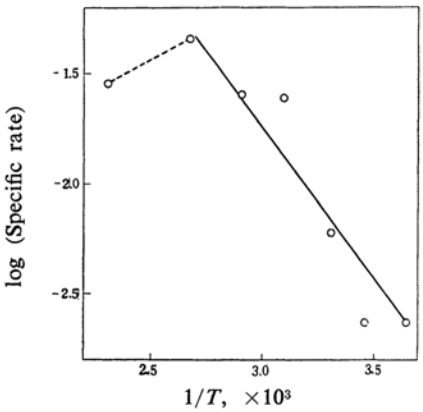

Fig. 7. Specific rate vs. reaction temperature. ($TiCl_3$, 1.2 mmol.; $AlEt_3$, 8.0 mmol.; Initial pressure, 42 kg./cm²)

If the heat of solution of ethylene in the solvent, *n*-heptane, is added to the above value, 7.8 kcal./mol. is obtained as the activation energy of polymerization. Optimum temperature is 100°C and at higher temperatures a fouling up of the catalyst arises as has been observed in $AlEt_3$-$TiCl_4$ catalyst[2].

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