Polymerization of Olefins by Ziegler Catalyst. I. Polymerization of Propylene by AlEt₃–TiCl₄ Catalyst

Shinjiro Kodama, Tsutomu Kagiya, Sueo Machi, Takeo Shimidzu, Sachio Yuasa,

and Kenichi Fukui

Faculty of Engineering, Kyoto University, Kyoto, Japan

INTRODUCTION

Since Ziegler[1] discovered that propylene can be polymerized to high molecular weight polymer at low pressure and temperature by the use of a titanium tetrachloride–triethyl aluminum catalyst, several studies of this type of polymerization have been carried out by Natta,[2] and some characteristics of this catalyst have been revealed.

The present paper is a report of a more detailed study of the polymerization of propylene by means of the AlEt₃–TiCl₄ catalyst. The dependencies of the overall reaction rate and the polymer properties upon various factors such as temperature, pressure, and the amount and composition of catalyst are emphasized.

EXPERIMENTAL

Materials

Propylene was produced by dehydrating isopropyl alcohol (commercial) on activated alumina at 300–350°C., then passing it through several activated alumina columns and a washing bottle containing AlEt₃ solution; the product was then liquefied for storage. Titanium tetrachloride (commercial grade) was purified by repeated distillation to a purity of 99.99%. Triethylaluminum (purity 99.7%) was supplied by Sumitomo Chemical Co., Ltd. The n-heptane used was the product of Shell Development Co., Ltd. (b.p. 98.427°C.) and was dried over metallic sodium.

Apparatus

Polymerization was carried out in a cylindrical stainless steel autoclave of 120 cm.³ capacity equipped with an electromagnetic stirrer which provided adequate agitation. The reaction vessel was immersed in a water bath thermostatted to within ±0.5°C. of the desired reaction temperature. At the beginning of polymerization, a slight evolution of heat was observed, resulting in a temperature rise of 2–3°C. Several minutes later, however, the desired temperature was established. The pressure was measured with a Bourdon tube gage.

Procedure

The two components of catalyst were separately introduced into the autoclave in a nitrogen stream, TiCl₄ first and then AlEt₃, each in a dilute solution in n-heptane. The components reacted with each other at room temperature to form the catalyst. Then the vessel was purged several times with propylene. After the desired temperature was attained, a definite amount of propylene was charged. The reaction was then started by stirring. In all experimental runs, 20 min. elapsed from the introduction of catalyst to the start of polymerization, at which time a slight temperature rise was observed. The pressure drop as the reaction proceeded was recorded for the purpose of estimating the polymerization rate. Also, some experiments were carried out under constant pressure by means of a continuous addition of monomer.

In the range of our reaction conditions, the rate was independent of the frequency of stirring. This indicated that the transfer of propylene from the gas phase to the solvent was not the rate-determining step. The product was treated with aqueous methanolic hydrochloric acid and washed with alcohol several times. The polymers were dried at 70–90°C. and weighed. The intrinsic viscosity was determined in Tetralin solution in an Ostwald viscometer at 135°C. The viscosity measurement was carried out on crude unpurified polymer which had not been extracted by solvents. The formula used to relate the molecular weight $\bar{M}_\eta$ and the intrinsic viscosity is derived from that of Natta:[3]

$$[\eta] = 1.18 \times 10^{-3} \bar{M}_\eta^{0.65}$$

RESULTS AND DISCUSSION

The discussion will concern the following two items: the molecular weight of product and the polymerization rate.

Molecular Weight

Figures 1, 2, 3, and 4 indicate how the molecular weight varies with the reaction conditions.

An increase in the amount of catalyst causes the molecular weight to decrease (Fig. 1), the ratio of AlEt₃ to TiCl₄ being held constant. At lower TiCl₄ concentrations, however, the molecular weight falls off. This might be caused by impurities whose presence might change the nature of the catalyst. As shown in Figure 2, when the ratio of AlEt₃ to TiCl₄ exceeds ca. 1.5, the molecular weight is but little affected by increased amounts of tri-

ethyl aluminum, the amount of TiCl₄ being kept constant. If the ratio is less than ca. 1.5, the molecular weight falls off sharply, and at the ratio of 0.5 only a semisolid polymer can be produced. The reaction temperature is an important factor affecting the molecular weight, as is shown in Figure 3. In the range 2–40°C. it decreases nearly exponentially with temperature, but around 50°C. it increases discontinuously and then decreases again. We suppose that there may be a correlation between this result and the fact that the reaction is most rapid at 40°C., as will be mentioned below. It appears likely that the nature of catalyst changes at
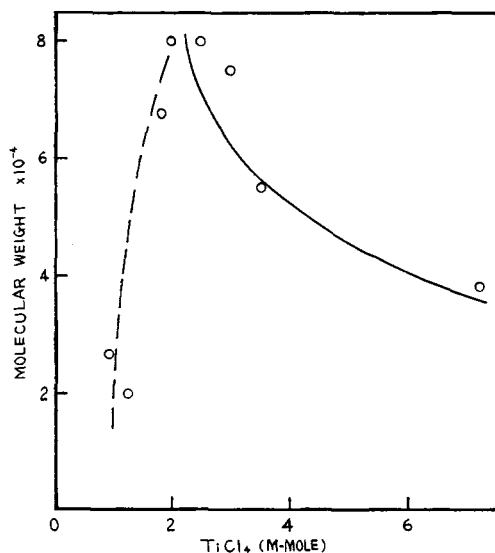

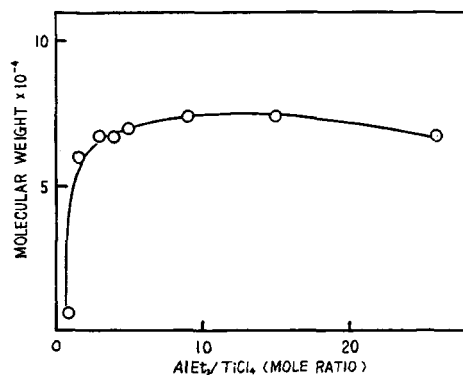Fig. 1. Molecular weight vs. amount of TiCl₄. (AlEt₃/ TiCl₄, 6.7; runs 1–9 in Table I.)

Fig. 2. Molecular weight vs. AlEt₃/TiCl₄ ratio. (TiCl₄, 1.8 millimoles; runs 10–17 in Table I.)
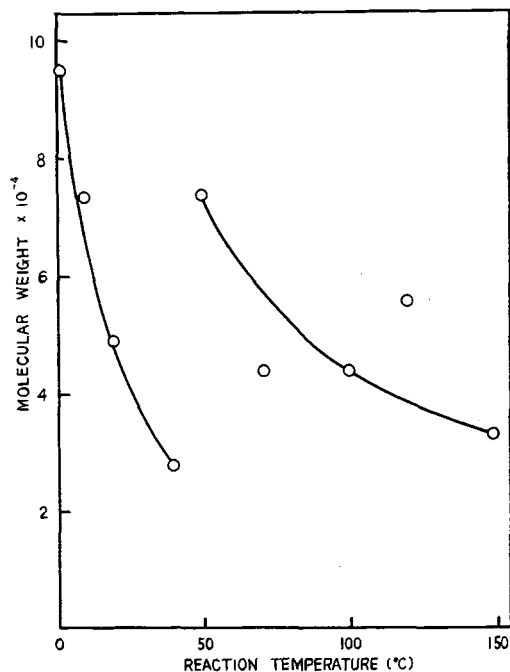

Fig. 3. Molecular weight vs. reaction temperature. (TiCl₄, 1.8 millimoles; AlEt₃, 24 millimoles; runs 18–26 in Table I.)

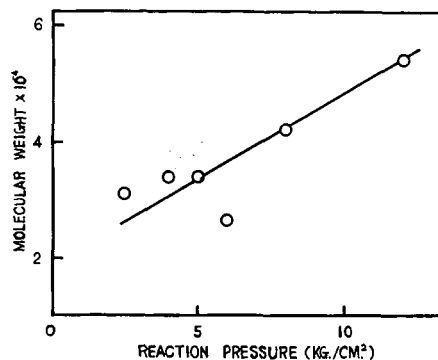

Fig. 4. Molecular weight vs. reaction pressure. (TiCl₄, 3.6 millimoles; AlEt₃, 24 millimoles; solvent, 16 cc.; reaction temperature, 30°C.; reaction time, 90 sec.)

the temperature of 50°C. The influence of re-action pressure on the molecular weight of polymer is also indicated in Figure 4. In each run the pressure was retained constant for 90 sec. of re-action time. The molecular weights of polymers obtained are almost directly proportional to pres-sure.

Rate of Polymerization

1. Treatment of Data

The relation between the reaction pressure, which was held constant, and the weight of polymer pro-duced in 90 sec. and 60 min., respectively, is shown in Figure 5. From this it can be concluded that the rate of polymerization is proportional to the propylene pressure. As the polymerization pro-ceeds at constant pressure, the rate decreases with the duration of the reaction, as is shown in Figure 6. A typical plot of pressure versus time which was
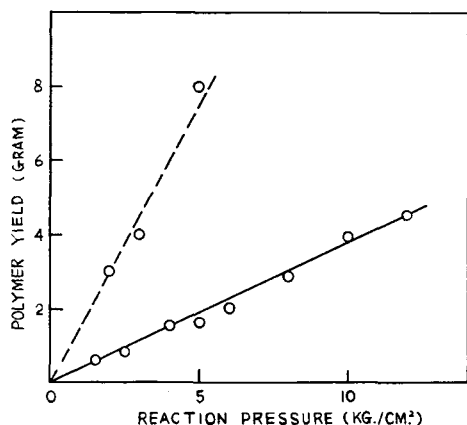
Fig. 7. Pressure vs. time. (Run 7 in Table I.)

obtained from an experiment in the batch reactor is given in Figure 7. A satisfactory kinetic inter-pretation of such curves is difficult because of the fall of rate with time which was observed, even in the constant pressure experiment in Figure 6. In this paper, however, a simple parameter has been chosen as a measure of the rate. This is the pressure drop after 60 min. divided by the mean pressure times the duration of the reaction; this value corresponds to the mean specific rate during the first 60 min. Values of this parameter are tabulated as the "specific rate" in Tables I and II.

2. Dependence of Rate on the Amount of Catalyst

Figure 8 indicates that the specific rate is almost proportional to the amount of TiCl$_4$, the ratio of AlEt$_3$ to TiCl$_4$ being held constant. The fact that the plot does not start at the origin is probably due to impurities in the solvent and the monomer.

Fig. 5. Polymer yield vs. reaction pressure; (——) poly-mer yield during initial 90 sec.; (–), polymer yield during in-itial 60 min. (TiCl$_4$, 3.6 millimoles; AlEt$_3$, 24 millimoles; solvent, 16 cc.; temperature, 30°C.)
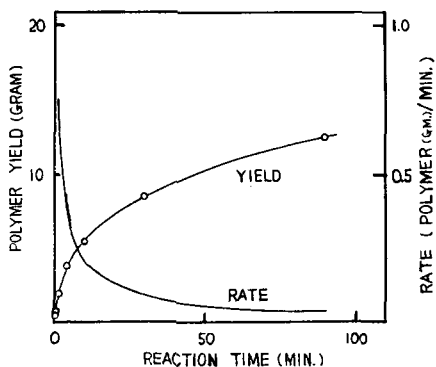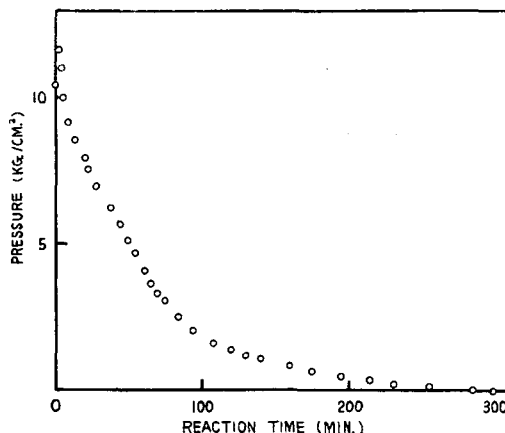
Fig. 6. Polymer yield and reaction rate vs. reaction time. (TiCl$_4$, 3.4 millimoles; AlEt$_3$, 24 millimoles; temperature, 30°C; pressure, 6 kg./cm.^{2}; solvent, 16 cc.)
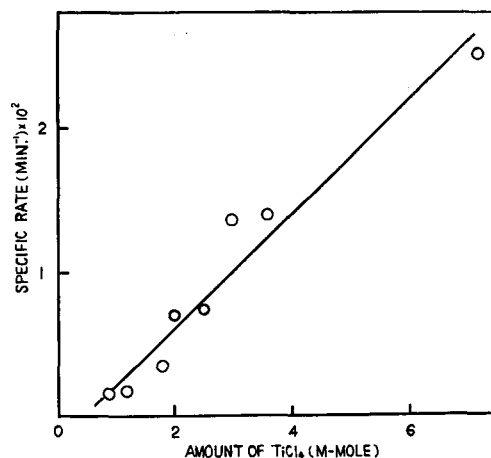
Fig. 8. Specific rate vs. amount of TiCl$_4$. (AlEt$_3$/TiCl$_4$, 6.7; runs 1–9 in Table I.)

TABLE I
Results of Experiments
(Reaction time, 60 min.; solvent, n-heptane, 16 ml.)

Run	$TiCl_4$, millimoles	$AlEt_3$, millimoles	Molar ratio, $AlEt_3/TiCl_4$	Reaction temp., °C.	Initial reaction pressure, kg./cm.²	Yield, g.	Conversion, %	Specific rate, min.$^{-1} \times 10^2$	$\bar{M}\eta \times 10^{-4}$
1	0.3	2.0	6.7	50	10.0	0	0	0	—
2	0.9	6.0	6.7	50	10.0	4.0	35	0.14	2.7
3	1.2	7.9	6.7	50	10.0	5.6	62	0.16	1.9
4	1.8	12.1	6.7	50	10.0	10.3	96	0.37	6.8
5	2.0	13.4	6.7	50	10.0	10.8	100	0.70	8.0
6	2.2	14.7	6.7	50	10.0	10.5	100	0.75	8.0
7	3.0	20.0	6.7	50	10.4	13.9	100	1.35	7.4
8	3.6	24.0	6.7	50	11.0	13.5	100	1.40	5.5
9	7.2	48.0	6.7	50	10.5	13.5	100	2.50	3.8
10	1.8	1.7	0.94	50	10.5	5.7	44	0.35	0.3
11	1.8	2.7	1.5	50	12.0	9.5	79	0.46	6.0
12	1.8	5.4	3.0	50	10.0	11.5	99	0.62	6.7
13	1.8	7.2	4.0	50	10.7	10.0	100	1.23	6.7
14	1.8	9.0	5.0	50	11.5	14.5	95	0.60	7.0
15	1.8	16.7	9.0	50	12.0	9.1	68	0.33	7.4
16	1.8	28.0	15.0	50	10.7	6.7	65	0.23	7.4
17	1.8	46.5	26.0	50	10.8	7.6	65	0.30	6.7
18	1.8	12.1	6.7	2	3.7	9.7	93	0.45	9.5
19	1.8	12.1	6.7	10	4.5	10.2	100	0.95	7.4
20	1.8	12.1	6.7	20	7.8	11.7	92	1.15	4.9
21	1.8	12.1	6.7	40	9.0	10.8	100	1.67	2.8
22	1.8	12.1	6.7	50	9.5	10.8	100	0.63	7.4
23	1.8	12.1	6.7	71	14.4	12.6	94	0.63	4.4
24	1.8	12.1	6.7	100	14.0	2.9	35	0.18	4.4
25	1.8	12.1	6.7	120	25.0	2.4	24	0.10	6.1
26	1.8	12.1	6.7	149	37.0	0.6	5	0.02	3.3

TABLE II
Dependence of Rate on the Treatment of the Catalyst
($TiCl_4$, 1.8 millimoles; $AlEt_3$, 12.1 millimoles; solvent, n-heptane, 16 cc.; reaction time, 120 min.)

Run	Treatment of catalyst Temp., °C.	Treatment of catalyst Duration, min.	Reaction temp., °C.	Reaction pressure, kg./cm.²	Yield, g.	Conversion, %	Specific rate, min.$^{-1} \times 10^2$
1	30	10	30	10.5	9.0	72	0.73
2	30	60	30	8.2	10.0	82	0.88
2	30	240	30	8.0	10.5	80	0.77
4	40	30	40	10.2	9.0	81	0.67
5	40	90	40	8.2	8.5	76	0.50
6	40	240	40	8.8	8.5	67	0.43
7	60	10	60	13.5	15.0	97	0.95
8	60	30	60	11.5	9.5	84	0.68
9	60	90	60	12.5	6.0	56	0.28
10	60	240	60	12.7	2.2	29	0.13

3. Dependence of Rate on Catalyst Composition

With a constant amount of $TiCl_4$, the rate varies with the amount of $AlEt_3$ as shown in Figure 9. The rate rises to a maximum at an $AlEt_3/TiCl_4$ ratio of ca. 4 and then decreases with increasing $AlEt_3$.

Natta et al.[2] reported that the ratio giving maximum rate was 2 when the two components of catalyst were submitted to reaction at 60°C., is the temperature at which the polymerizations in the present study were carried out.
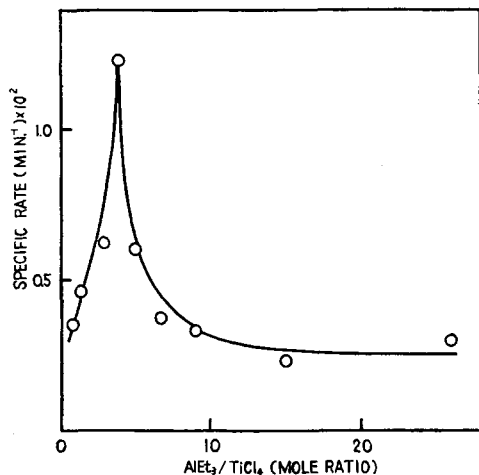
Fig. 9. Specific rate vs. AlEt₃/TiCl₄ ratio. (TiCl₄, 1.8 millimoles; runs 10–17 in Table I.)

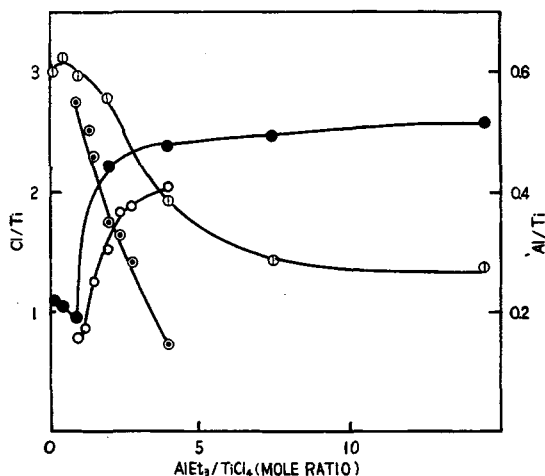
Fig. 10. Composition of precipitate from AlEt₃ and TiCl₄ vs. mole ratio. Data of (⊙) Natta et al.[2] and (Ⓘ) Hirata et al. for Cl/Ti; data of (O) Natta et al.[2] and (●) Hirata et al. for Al/Ti. In Natta's experiments, two components are combined at 60°C., while in Hirata's case, at room temperature.)

In this connection, the composition of solid precipitate produced by the interaction of TiCl₄ and AlEt₃ was previously investigated as a function of AlEt₃/TiCl₄ molar ratio by Natta et al.[2] and Hirata et al.[4] These results are shown in Figure 10. Natta's and Hirata's experiments differ as to such reaction conditions as temperature and concentration of catalyst components. Figure 10 shows that the composition of the solid catalyst depends on the interaction conditions as well as on the ratio of components used. In our case, as was mentioned in the experimental section, the two catalyst components were brought together under almost the

same conditions as those of Hirata et al. By combining the results of Natta, Hirata, and the present study, it was found that the polymerization rate is most favored by the solid catalyst in which the ratio of Cl/Ti is ca. 1.8.

4. Temperature Dependence of Rate

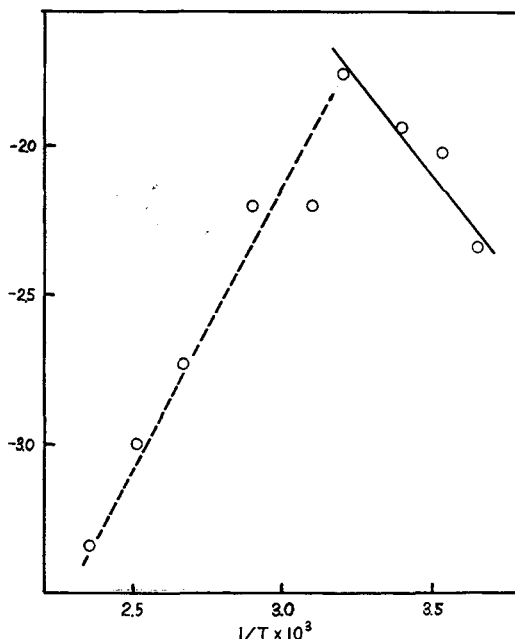The logarithm of the rate is plotted against the reciprocal of the absolute temperature in Figure 11.

Fig. 11. Specific rate (log, ordinate) vs. reaction temperature. (TiCl₄, 1.8 millimoles; AlEt₃, 12.1 millimoles; runs 18–26 in Table I.)

The rate first increases with temperature and then falls off beyond 50°C. The straight line in the range from 2–40°C. gives an apparent activation energy of 5.7 kcal./mole.

5. Deactivation of Catalyst at Higher Temperatures

It was pointed out by Natta et al.[2] that the activity of the catalyst decreased with time at 60°C. Attention was paid to this problem also in our experiments. The catalyst was maintained at a definite temperature for a definite time interval, and then it was used as the polymerization catalyst. The results of this treatment are shown in Table II and in Figure 12. The activity decreases remarkably at 60°C., as was observed by Natta. However, at 30°C. it does not undergo any considerable change for as long as 4 hr. Thus, the "time-dependent" deactivation of catalyst, which may be
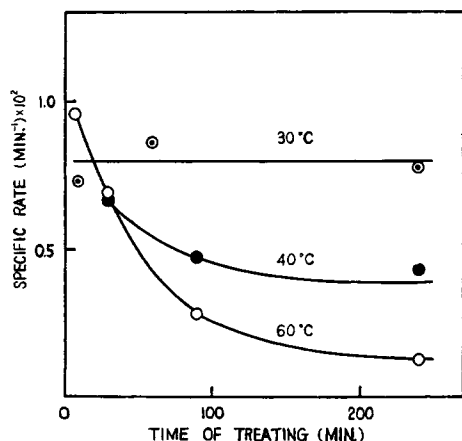
Fig. 12. The relation of the duration of treatment of catalyst and the polymerization rate at various temperatures. (Polymerization was carried out at the temperature at which the catalyst was treated.)

due to a change in the nature of the catalyst, can take place only above 40°C. Nevertheless, even at 30°C. the rate of polymerization decreases with the reaction time, as has been seen in Figure 6. It is impossible, therefore, to attribute this decrease of rate to the deactivation of catalyst. The nature of this type of rate decrease will be discussed later.

References

1. Ziegler, K., assigned to Montecatini S.p.A., Belgian Pat. 538,782 (1955).
2. Natta, G., P. Pino, G. Mazzanti, and P. Longi, *Gazz. chim. ital.*, **87**, 528 (1957).
3. Natta, G., I. Pasquon, and E. Giachetti, *Chim. e ind.*, (*Milan*), **40,** 100 (1958).
4. Hirata, M., and K. Shirayama, Paper presented at the 11th Annual Meeting, Chemical Society as Japan, Tokyo, 1958.

Synopsis

The polymerization of propylene with AlEt₃–TiCl₄ catalyst was studied in detail. The molecular weight of polymers decreases with the temperature in the range 2–40°C., and increases proportionally to the pressure, but it does not depend on the AlEt₃/TiCl₄ ratio. The rate is proportional to the amount of catalyst as well as to the propylene pressure. The optimum mole ratio of AlEt₃ to TiCl₄ is 4. In regard to the temperature, the rate is maximum at 40°C. The apparent activation energy is about 5.7 kcal./mole for the range 2–40°C. The activity of the catalyst decreases with the length of time it is kept at 40–60°C. after its for-

mation, but at 30°C. the activity is retained almost completely for 4 hr. The polymerization rate is observed to decrease as the reaction proceeds, even at constant pressure. It is unreasonable to attribute this fact solely to the deactivation of catalyst observed at above 40°C., because such a decrease in rate occurs even at 30°C.

Résumé

Une étude fondamentale de la polymérisation du propylène avec AlEt₃–TiCl₄ comme catalyseur a été effectuée. Le poids moléculaire du polymère décroît avec la température dans l'intervalle de 2–40°C et augmente proportionnellement à la pression, mais il ne dépend pas du rapport AlEt₃/TiCl₄. La vitesse est proportionnelle à la quantité de catalyseur aussi bien qu'à la pression en propylène. Le rapport molaire optimum AlEt₃/TiCl₄ est égale à 4. Par rapport à la température la vitesse maximum est située à 40°C. L'énergie d'activation apparente est environ 5,7 Kcal/mole pour l'intervalle de 2–40°C. L'activité du catalyseur décroît avec le temps pendant lequel il a été porté à 40–60° depuis sa formation; à 30°C, l'activité du catalyseur reste toutefois inchangée pendant 4 heures. On observe que la vitesse de polymérisation décroît, même à pression constante, à mesure que la réaction progresse. Il n'est pas logique d'attribuer ce fait uniquement à la désactivation du catalyseur, car une telle diminution de la vitesse se manifeste même à 30°C.

Zusammenfassung

Eine grundlegende Untersuchung über die Polymerisation von Propylen mit einem Al(C₂H₅)₃–TiCl₄-Katalysator wurde durchgeführt. Das Molekulargewicht der Polymeren nimmt im Bereich von 2–40°C mit steigender Temperatur ab und proportional dem Druck zu, hängt aber nicht vom Verhältnis Al(C₂H₅)₃/TiCl₄ ab. Die Geschwindigkeit ist sowohl der Menge des Katalysators, als auch dem Propylendruck proportional. Das optimale Molverhältnis von Al(C₂H₅)₃ zu TiCl₄ ist 4. Was die Abhängigkeit von der Temperatur betrifft, so wird die Maximalgeschwindigkeit bei 40°C erreicht. Die scheinbare Aktivierungsenergie liegt im Bereich von 2–40°C bei etwa 5,7 kcal/Mol. Die Aktivität des Katalysators nimmt mit der Länge der Zeit, während welcher er nach seiner Bildung bei 40–60°C gehalten wurde, ab; bei 30°C kann aber der Katalysator 4 Stunden lang ohne Änderung seiner Aktivität aufbewahrt werden. Die Versuche zeigen, dass die Polymerisationsgeschwindigkeit mit Fortschreiten der Reaktion sogar bei konstant gehaltenem Druck abnimmt. Es erscheint nicht gerechtfertigt, diese Tatsache bloss der Deaktivierung des Katalysators zuzuschreiben, da eine solche Geschwindigkeitsabnahme sogar bei 30°C stattfindet.