Polymerization of Propylene with Tin Tetraalkyl-Titanium Tetrachloride Catalyst

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(Received November 19, 1960)

Many studies[1] on the catalyst for preparing polypropylene have been performed, since Natta obtained the polypropylene having high molecular weight and high stereoregularity. On the polymerization of propylene using tin tetraalkyl as a catalyst component, only a Du Pont patent[2] has been known. However, the description is so brief that the details are not explained. From our preliminary experiments of the polymerization of propylene using tin tetraalkyl in combination with titanium tetrachloride, titanium trichloride, dichlorodialkyl titanate, or tetraalkyl titanate, it was found that the effective catalyst was only the complex comprising titanium tetrachloride as a component. Moreover, when the catalyst was used as soon as the two components were mixed, the polymer produced thereby contained a greater part of low polymer. Accordingly, the polymerization in this study was performed considering the adequate times for the production of the complex.

Experimental and Results

Reaction between Tin Tetraalkyl and Titanium Tetrachloride.—The reaction between tin tetraalkyl and titanium tetrachloride does not proceed very fast, and so prolonged reaction times are required for the completion of the complex. The reaction rate depends, of course, upon the reaction temperature, the length of alkyl chain in the tin tetraalkyl, and the ratio of the catalyst components. Besides, the presence of a solvent will affect the reaction rate. However, the catalyst preparation in this study was performed without solvent, because the presence of the solvent makes the end-point of reaction obscure.

When the catalyst is prepared in a solvent without vigorous stirring, the product precipitates at the bottom of the vessel as an adhesive mass which can not be easily dispersed into the solvent. Generally, if the ratio of the two components deviates greatly from unity, both components still remain in liquid form after the reaction is over. Therefore, in this case, the end-point of reaction is not clear. On the other hand, when the ratio is about 1.0, the whole becomes solid exhibiting a comparatively apparent end-point. Therefore, the experiments for observing the times required for the production of the complex were carried out without any solvent at about equimolar composition of tin tetraalkyl and titanium tetrachloride. In Fig. 1, the effects of the alkyl radical in the tin tetraalkyl molecule and the reaction temperature upon the rate of the production of the complex are represented.

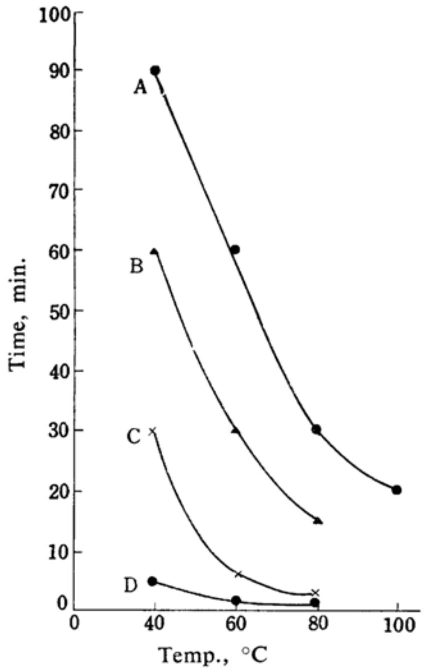

Fig. 1. Time required for the complex production.

A; *n*-Butyl C; Isopropyl
B; *n*-Propyl D; Ethyl

The vertical axis in Fig. 1 represents the times required for the solidifying of the two components which were mixed at a given temperature. The preparation of catalyst complex in the following experiments was performed referring to this condition; also analogously in the case where the ratio of the two component deviates passably from unity.

Polymerization Procedure. — In a cooled polymerization tube containing the complex which had been prepared by mixing the two components, a definite amount of monomer was introduced. The complex was shattered in a high speed shaker. In the case of polymerization in solution, the shattering of the complex was taken before the monomer

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[1] For example, G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957).

[2] E. I. Du Pont de Nemours & Co., Brit. Pat. 777538 (June 26, 1957).

was introduced. The tube was immersed in a constant temperature bath. After the reaction proceeded for definite reaction times, the tube was cooled by dry ice-methanol, and vented. Then, the contents of the tube were treated with methanol acidified by hydrochloric acid to decompose the catalyst, washed with methanol several times, and dried under reduced pressure.

Measurement of Viscosity.—The viscosity of the polymer solution was measured using tetralin, as a solvent, which had been purified by distillation after being dried over sodium, using an improved Ubbelohde viscometer of dilution type, at 135± 0.05°C. The viscometer was filled with nitrogen during the measurement.

The molecular weight of the polymer was calculated using Ciampa's equation[3] shown below.

$$[\eta]=0.25\times10^{-4}M$$

Dependence of Conversion and Insoluble Part of Polymer in Boiling *n*-Hexane on the Composition of Catalyst. — The influence of the ratio of catalyst components upon the conversion and the insoluble part of polymer in boiling *n*-hexane was investigated by the polymerization using a catalyst complex of tin tetraethyl-titanium tetrachloride. In each experiment, 5 g. of monomer was polymerized with a catalyst containing 9.26×10^{-2} mol. of titanium tetrachloride and a definite amount of tin tetraethyl (which is represented in Table I), in 5 cc. of *n*-hexane at 30°C for 25 hr. The Results are shown in Table I.

TABLE I. EFFECT OF THE RATIO OF COMPONENTS IN THE COMPLEX UPON THE CONVERSION AND THE INSOLUBLE PART IN BOILING *n*-HEXANE

No.	$SnR_4/TiCl_4$	Convertion %	Insoluble part in *n*-hexane, %
1	0.54	4.01	8.61
2	0.82	2.72	11.52
3	1.09	0.71	12.21
4	1.36	2.11	15.14
5	1.64	15.75	18.32
6	1.91	8.73	17.26

$TiCl_4$; 9.26×10^{-2} mol., Monomer ; 5 g. *n*-Hexane ; 5 cc., Temp. ; 30°C.

It is seen that a minimum for the rate of polymerization exists where the ratio of tin tetraethyl to titanium tetrachloride is about unity. This respect is discussed afterward.

Effects of Alkyl Radical in SnR_4 and the Temperature of Complex Preparation upon the Conversion and the Molecular Weight of Polymer.—In each experiment, 15 g. of monomer was polymerized with the catalyst which was prepared by mixing the two components, i. e., 2.024×10^{-2} mol. of tin tetraalkyl and 1.852×10^{-2} mol. of titanium tetrachloride, in a sealed tube at 40°C for 15 hr. Each polymer was then extracted by boiling *n*-hexane. This procedure was made to find the percentage of so-called isotactic polymer which had been defined by Natta as an isoluble part in boiling *n*-heptane. In this sence, the extraction has to be made, if possible, by *n*-heptane. However, the greater part of the polymer which would be extracted by boiling *n*-heptane is also extracted by boiling *n*-hexane, as is shown in Table III. Accordingly, the solvent, *n*-hexane was used. These results are shown in Table II.

The effect of the temperature of catalyst preparation upon the conversion is represented in Fig. 2.

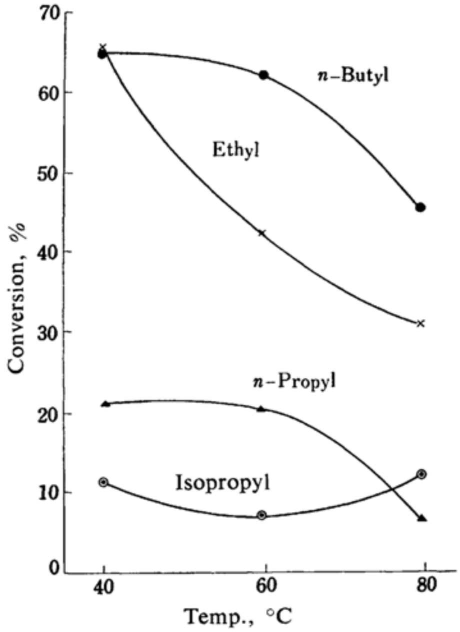

Fig. 2. Effect of the temperature of the catalyst preparation upon the conversion.

The polymerization with the catalyst prepared at lower temperature resulted in higher conversion, which gave lower molecular weight and further lower percentage of polymer insoluble in boiling *n*-hexane (except for the case of tin tetraethyl).

Extraction of the Polymer with Various Solvents. — To find the percentage of atactic and isotactic parts which are contained in the polymer prepared with the tin tetraethyl-titanium tetrachloride catalyst, 55.774 g. of the polymer was successively extracted by such series of solvents as acetone, diethyl ether, *n*-hexane, and *n*-heptane. The sample employed in this extraction was prepared by polymerizing 75 g. of monomer with the catalyst which had been prepared at 20°C by the reaction between 1.012 mol. of tin tetraethyl and 0.926 mol. of titanium tetrachloride. In this polymerization reaction (at 40°C, for about 15 hr.), 57.428 g. of the polymer was obtained (conversion ; 76.6%). The viscosity of each fraction was measured by means of the aforementioned method. These results are shown in Table III.

It[4] has already been known that an organo

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[3] G. Ciampa, *Chim. e ind.* (*Milan*), **38**. 298 (1956).

[4] N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers" Interscience Publishers, Inc., New York (1959), p. 129.

TABLE II. POLYMERIZATIONS AT VARIOUS TEMPERATURES USING VARIOUS TIN TETRAALKYLS

R in SnR_4	Cat. preparation temp., °C	Conversion %	Insoluble part (%) in boiling hexane	$[\eta]\times 10$	$M\times 10^{-3}$
Ethyl	40	65.7	18	2.4	9.7
〃	60	42.5	12	1.5	6.2
〃	80	31.6	14	1.9	5.1
n-Butyl	40	65.4	4	0.8	3.2
〃	60	62.4	3	1.0	4.1
〃	80	45.7	5	1.4	5.6
Isopropyl	40	11.5	—	0.4	1.4
〃	60	7.4	—	0.4	1.7
〃	80	12.1	—	0.3	1.1
n-Propyl	40	21.1	2.6	0.8	3.2
〃	60	20.4	4.2	1.1	4.0
〃	80	6.4	4.0	1.3	5.1

The viscosity was measured for the original polymer.
Monomer; 15 g., Temp.; 40°C, Time; 15 hr.
SnR_4; 2.024×10^{-2} mol., $TiCl_4$; 1.852×10^{-2} mol.
The polymers prepared with $Sn(i\text{-}C_3H_7)_4\text{-}TiCl_4$ were grease-like, and so, the extractions were not carried out.

TABLE III. EXTRACTION WITH VARIOUS SOLVENTS

Solvent	Polymer, g.	Fraction, %	$[\eta]$	$M\times 10^{-3}$	M. p., °C
Acetone	2.584	4.6	—	—	
Ether	22.370	40.1	0.11	4.4	
n-Hexane	20.363	40.4	0.13	5.2	
n-Heptane	2.036	3.7	0.26	10.4	120
(Residue)	6.255	11.2	1.02	40.8	155~160

metallic compound containing the metal with smaller ionic radius, results in a higher yield of isotactic polymer. Accordingly, it is natural that the polymerization using a compound of tin as a catalyst component results in a lower yield of isotactic polymer.

Rate of Polymerization.—In order to find the rate of polymerization, the following experiment was performed. Each polymerization was carried out in a sealed tube with tin tetraethyl-titanium tetrachloride catalyst consisting of 2.024×10^{-2} mol. of the former and 1.852×10^{-2} mol. of the latter. The catalyst was shattered finely by a high speed shaker in 15 cc. of *n*-hexane before the monomer (10 g.) was introduced. The polymers were treated by means of the aforementioned method. The relation between the conversion and the reaction time is represented in Fig. 3.

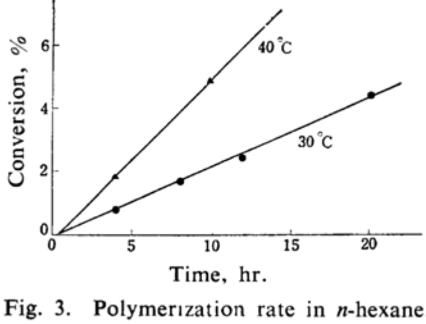

Fig. 3. Polymerization rate in *n*-hexane.

The rates at 30 and 40°C were calculated from Fig. 3 as 0.22%-conversion/hr. and 0.5%-conversion/hr., respectively. The values indicate that the polymerization of propylene with tin tetraalkyl-titanium tetrachloride catalyst proceeds very slowly in the solution system.

Infrared Spectra. — In order to compare the microstructure of the polymer prepared by the tin tetraethyl-titanium tetrachloride catalyst with that

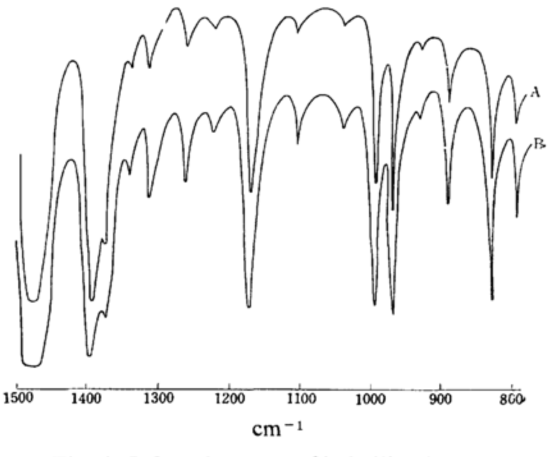

Fig. 4. Infrared spectra of in boiling heptane insoluble polymers.

A; Polymer prepared with SnR_4-$TiCl_4$
B; Moplen

of ' Moplen ', the polymer prepared by aluminium-trialkyl-titanium trichloride catalyst, the infrared spectrum of the insoluble part in boiling *n*-heptane was observed. B is a spectrum of *n*-heptane insoluble part of Moplen. From the comparison of A with B, it is obvious that these polymers are strikingly similar in their microstructures.

Discussion

Generally, the Ziegler catalyst consists of Lewis acid and Lewis base. Therefore, a cationic or an anionic reaction will predominantly occur according to the catalyst composition in which Lewis acid or base is contained in excess, respectively.

The double bond of propylene, of course, is easily attacked by a cationic catalyst, owing to the effect of the methyl group. Moreover, it is also well known that, in the case of cationic polymerization, the growth of the chain easily terminates by a chain transfer. Thus, the rate of cationic polymerization is steady, but the polymer produced has usually a low molecular weight and further low stereoregularity. On the other hand, in the case of anionic polymerization, a polymer having a high molecular weight and further high stereoregularity is usually obtained, while the rate of reaction becomes smaller than that of cationic reaction.

From the facts mentioned above, it may be said that the decrease of conversion (from No. 1 to No. 3) with an increase in the amount of tin tetraethyl will mean that the cationic character is replaced gradually by the anionic character. It is also considered that, in Nos. 3—6, the effective anionic catalyst increases with the increase of the amount of tin tetraethyl.

Next we discuss the effects of temperature of catalyst preparation upon the convertion, the insoluble part in boiling *n*-hexane and stereospecificity. As is apparent from Fig. 1, the reducing power is the strongest in the case of tin tetraethyl, so that the effective anionic catalyst will be produced even at a lower temperature, in such a case. The fact that both the conversion and the stereospecificity decrease with an increase in the temperature will mean a decreasing of the active center which is in suitable valence state.

In the case of the propyl or butyl radical, the reducing power is so much weaker than that of the ethyl radical, that a temperature which is suitable for preparing the effective complex containing the latter, is unsuitable for producing the effective one containing the former. At such a lower temperature, the somewhat cationic character will still remain in the complex. When the temperature becomes higher, the cationic character will decrease, and so the conversion decreases while the stereospecificity increases, as is seen in Table II.

In regard to the effects of the length of the alkyl radical upon the conversion and the stereospecificity, no distinct relations between them were obtained.

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