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Bis-(cyclopentadienyl)-titanium Dichloride–Alkylaluminum Complexes as Soluble Catalysts for the Polymerization of Ethylene[1,2]

BY DAVID S. BRESLOW AND NORMAN R. NEWBURG

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A soluble catalyst for the polymerization of ethylene has been found in the reaction product of bis-(cyclopentadienyl)-titanium dichloride with alkylaluminum compounds. The catalysts are frequently as active as insoluble Ziegler-type catalysts, proving that a solid surface is not required for Ziegler-type polymerization. The presence of a tetravalent titanium species has been shown to be necessary for high activity. Polyethylene prepared with these catalysts is highly linear and has a narrow molecular weight distribution. The reaction of bis-(cyclopentadienyl)-titanium dichloride with alkylaluminum compounds has been investigated and a crystalline complex has been isolated. The mechanism of the low-pressure polymerization of ethylene is discussed in the light of these findings.

Several years ago Ziegler[3] made the fundamental discovery that ethylene could be polymerized at low temperatures and pressures to a high molecular weight polymer by the use of a catalyst prepared from titanium tetrachloride and an alkylaluminum compound. These catalysts are insoluble in the reaction medium. For a number of reasons we considered it of importance to try to prepare a homogeneous catalyst. Mechanistic studies should be greatly facilitated with a soluble catalyst; catalyst requirements should be lower, inasmuch as all the catalyst would be available instead of only the active surface of a heterogeneous catalyst, and there would be no possibility of catalyst inactivation by polymer coating; a soluble catalyst should be more readily removed from the polymer; and a more uniform molecular weight distribution might be obtained, since there should be only a small change in available catalyst during polymerization. Perhaps most important of all, there was a general feeling at the time our work was initiated that Ziegler catalysts owed their high activity to their heterogeneity; this view is still held in some quarters.[4] That insolubility is not a necessary property has been shown by our finding that ethylene can be polymerized very readily with a soluble complex of bis-(cyclopentadienyl)-titanium dichloride and an alkylaluminum compound.[5]

Reaction between Bis-(cyclopentadienyl)-titanium Dichloride and Alkylaluminum Compounds.—When an orange solution of bis-(cyclopentadienyl)-titanium dichloride in toluene is treated with two moles of diethylaluminum chloride, the solution undergoes an immediate color change to deep red, followed by a gradual change over a period of about 30 minutes at room temperature to a green and finally to a blue solution. With somewhat more than one mole of triethylaluminum a blue solution is formed almost instantaneously. In *n*-heptane the formation of a blue solution with either of these reagents is a much slower process, presumably because of the very low solubility of bis-(cyclopentadienyl)-titanium dichloride in aliphatic hydrocarbons. With ethylaluminum dichloride a green solution is formed slowly.

In Fig. 1 is shown the spectroscopic change that takes place upon mixing bis-(cyclopentadienyl)-titanium dichloride with diethylaluminum chloride in a 1:2 ratio in toluene. Curve I shows the spectrum of uncomplexed bis-(cyclopentadienyl)-titanium dichloride with an absorption maximum at 515 mμ, and curve II is that of the blue complex. The isosbestic point at about 670 mμ indicates that, 2.4 minutes after mixing, the initial "sandwich" compound is absent, and only two other colored species are present. However, inasmuch as the color change on mixing the two ingredients is instantaneous, other reactions may have taken place before the first spectrum was taken; earlier times were not investigated in this work.

Chilling a heptane solution of the blue material formed from bis-(cyclopentadienyl)-titanium dichloride and diethylaluminum chloride yielded a blue, crystalline solid; after several recrystallizations from heptane it melted at 80-90°, apparently with some decomposition. Analyses indicated that the crystalline material was a complex of trivalent titanium with what appeared to be aluminum sesquichloride, $(C_5H_5)_2Ti(III)Cl \cdot 1/2(C_2H_5)_2AlCl \cdot 1/2C_2H_5AlCl_2$. We do not know at present whether this formula is a true representation of the complex or whether the material isolated was not completely pure; the complex is inordinately sensitive to traces of oxygen. There is ample evidence, however, that the complex contains trivalent titanium. Blue crystals could also be obtained from bis-(cyclopentadienyl)-titanium dichloride and triethylaluminum. Although we did not investigate this further, Natta and co-workers[6] have shown that this complex analyzes as $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$; there can be little doubt that this, too, is a trivalent titanium compound.

The formulation of these compounds as complexes of $(C_5H_5)_2Ti(III)Cl$ is based on the following observations: (1) Magnetic susceptibility showed the presence of one unpaired electron. (2) Hy-

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[1] Presented in part at the Symposium on the Mechanisms of Inorganic Reactions in Solution, Northwestern University, July 10, 1958.

[2] A preliminary account of this work appeared in THIS JOURNAL, **79**, 5072 (1957).

[3] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

[4] See, for example, G. Natta, P. Pino, G. Mazzanti and R. Lanzo, *Chim. e ind.* (*Milan*), **39**, 1032 (1957).

[5] D. S. Breslow, U. S. Patent 2,827,446 (1958).

[6] G. Natta, P. Pino, G. Mazzanti and U. Giannini, THIS JOURNAL, **79**, 2975 (1957).

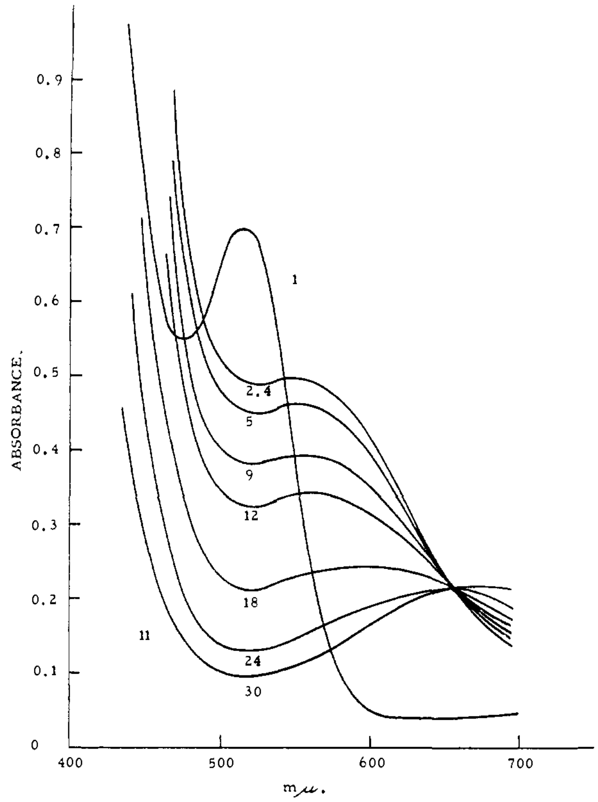


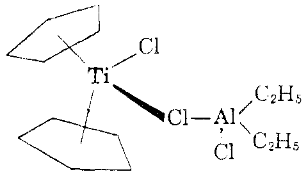
Fig. 1.—Change of spectra with time of 2.9 millimolar $(C_5H_5)_2TiCl_2$ and 5.8 millimolar $(C_2H_5)_2AlCl$ in toluene at 30°, 1-cm. cell. Numbers represent time in minutes after mixing.

drolysis with thoroughly deaerated sulfuric acid gave a green aqueous solution which titrated as Ti(III) with ferric ion[7]; the $(C_5H_5)_2Ti(III)^+$ ion is reported to be green.[8] (3) Treatment of the blue complex with ether gave a green crystalline solid which analyzed as $(C_5H_5)_2TiCl$.

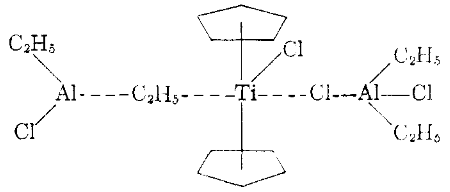
The reduction of the titanium species probably involves three steps: (1) the formation of a complex between the "sandwich" dichloride and the alkylaluminum compound, probably not observed spectroscopically in this work; (2) alkylation of the "sandwich" dichloride; and (3) cleavage of the alkyl–titanium bond. There is little doubt that the initial rapid reaction is the complex formation, as illustrated with diethylaluminum chloride.

$$2(C_5H_5)_2TiCl_2 + [(C_2H_5)_2AlCl]_2 \rightleftarrows 2(C_5H_5)_2TiCl_2\cdot(C_2H_5)_2AlCl$$

A number of possible structures can be written for this complex, a reasonable one being[9]



That the bond is essentially covalent is indicated by the fact that the complex is much more soluble in hydrocarbons than is the uncomplexed "sandwich" compound. Steps 2 and 3 are probably quite complicated. There is a certain amount of evidence, for example, that the alkylation does not involve a simple exchange of alkyl for chlorine in the bridged complex. Thus, it has been found that the rate of alkylation is increased by increasing amounts of diethylaluminum chloride over and above that required to form a 1:1 complex, in spite of spectroscopic evidence that complexing is essentially complete at this level. With triethylaluminum the results are even more surprising. At aluminum to titanium ratios slightly below 1:1, a complex is formed but little or no reduction takes place; the addition of enough triethylaluminum to make the ratio greater than 1:1 leads to immediate reduction.[11] It would seem, therefore, that alkylation involves a reaction between the 1:1 complex and additional alkylaluminum compound, perhaps *via* an SN2 reaction with a transition state such as



Even the reduction appears to be a rather complex reaction. The gas evolved is ethane containing traces of *n*-butane but no ethylene. Although this might be rationalized as a simple homolytic cleavage, in which the ethyl radical abstracts hydrogen from the solvent, there is evidence from other work that this reaction may be higher order in titanium. It is not clear, however, why triethylaluminum effects reduction very rapidly and diethylaluminum chloride only slowly. It would appear that either the stability of the titanium–carbon bond depends on the species with which it is complexed, or perhaps reduction involves dialkylation; inasmuch as triethylaluminum is a stronger alkylating agent than diethylaluminum chloride, reduction would be more rapid.

Polymerization.—Our initial work on polymerization was carried out using the pressure bottle technique. The usual procedure was to deaerate the solvent, pressure the bottle to 50 lb. per sq. in. with ethylene, and then inject the catalyst. Table I shows some typical results using bis-(cyclopentadienyl)-titanium dichloride and alkyl-

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(7) The trivalent species is readily oxidized by water even at low *p*H; hydrogen is evolved. The reaction with approximately 6 *M* hydrochloric acid is interesting. A blue solution is formed initially; in about a minute this deposits red crystals, presumably $(C_5H_5)_2TiCl_2$, but after this initial rapid reaction the remaining blue color fades very slowly. Perhaps the oxidation is higher order in titanium. This may account for the observation of Natta and co-workers[6] that their complex gave a 90% yield of $(C_5H_5)_2TiCl_2$ when treated with ethereal hydrogen chloride.

(8) G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 4281 (1954).

(9) Natta, Corradini and Bassi[10] have recently reported a preliminary crystallographic determination of the structure of the trivalent complex, $(C_5H_5)_2TiCl\cdot(C_2H_5)_2AlCl$. In this complex the cyclopentadiene rings are tilted and there is a double chlorine bridge between the titanium and the aluminum. It is reasonable to assume that the rings are tilted in the tetravalent species as well, and that the titanium has the same coördination number: a double chlorine bridge would entail increasing the coördination number in the tetravalent species.

(10) G. Natta, P. Corradini and I. W. Bassi, *ibid.*, **80**, 755 (1958).

(11) We are indebted to Dr. W. P. Long for these observations. This work will be published in detail in the near future.

aluminum chlorides. Several things are obvious. Foremost is the fact that in many examples these catalysts were fully as active as a typical Ziegler catalyst prepared from titanium tetrachloride.

TABLE I

EFFECT OF ALUMINUM: TITANIUM RATIO ON POLYMERIZATION OF ETHYLENE WITH A SOLUBLE CATALYST[a]

Solvent	Al compound	Al:Ti ratio	Time, hr.	Pressure drop[b] lb./sq. in.	R.S.V.[c]
Toluene	$(C_2H_5)_2AlCl$	0.5	8	13	10.6
		1	8	25	4.2
		2	0.5	50	1.9
		4	<0.5	50	1.2
		6	2.75	50	1.9
		10	1.5	50	1.6
n-Heptane		2	5	49	4.0
		4	5	36	3.8
		6	5	34	3.4
	$C_2H_5AlCl_2$	2	6	39	2.6

[a] At 30° with a titanium level of 10 millimoles/l. [b] Initial pressure of 50 lb. per sq. in. [c] Reduced specific viscosity, determined as a 0.1% solution in Decalin at 135°.

With diethylaluminum chloride, at aluminum to titanium ratios above 1, both the rate of polymerization and the molecular weight of the polymers were essentially independent of ratio. Polymerization was slower in *n*-heptane than in toluene and molecular weights were higher. Ethylaluminum dichloride was not appreciably different from diethylaluminum chloride. Table II shows the effect of titanium concentration on the polymerization. This variable, too, had little effect on the polymerization, but it bore out our initial prediction that very low levels of catalyst could be used.[12]

TABLE II

EFFECT OF TITANIUM CONCENTRATION ON THE POLYMERIZATION OF ETHYLENE WITH A SOLUBLE CATALYST[a]

Ti, mmoles/l.	Time, hr.	Pressure drop,[b] lb./sq. in.	R.S.V.
20[c]	1.25	50	1.5
10[c]	2	47	2.6
5[c]	0.75	50	1.9
1[c]	3	33	1.3
0.1[d]	0.25	38	3.9

[a] In toluene at 30° with diethylaluminum chloride. [b] Initial pressure 50 lb. per sq. in. [c] Al:Ti ratio of 4. [d] Al:Ti ratio of 50.

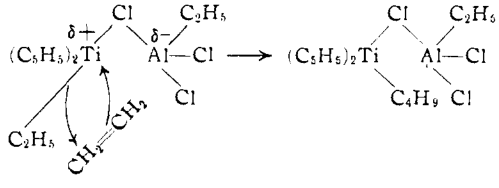
A puzzling factor in this work arose from the occasional variation in the time required for complete polymerization. This was most marked at high ratios of diethylaluminum chloride to bis-(cyclopentadienyl)-titanium dichloride, and especially so when triethylaluminum was used. It was suspected that oxygen might be playing a role in the polymerization, but it was extremely difficult to demonstrate this with the technique being used; as already mentioned, the blue solutions are inordinately sensitive to traces of oxygen. For this reason we turned to flow systems.

Here it was quite apparent that oxygen affected the polymerization rate with these catalysts. For example, a solution was prepared of five millimoles of bis-(cyclopentadienyl)-titanium dichloride and ten millimoles of diethylaluminum chloride in one liter of toluene. After the solution had turned blue, ethylene containing 0.003% oxygen was passed in at atmospheric pressure and 15° solution temperature. A slow polymerization took place and 17.8 g. of polymer was formed in 80 minutes; the rate was not increased by the addition of diethylaluminum chloride. If, however, ethylene containing 0.025% oxygen was introduced, the solution turned a greenish-brown; the addition of diethylaluminum chloride to maintain this color resulted in the formation of 300 g. of polymer in four hours. Actually, almost any desired rate of polymerization can be realized by a judicious balance of oxygen and alkylaluminum compound. On the assumption that the oxygen was acting to convert trivalent titanium to tetravalent, a polymerization was carried out by adding diethylaluminum chloride to a solution of the tetravalent compound, bis-(cyclopentadienyl)-titanium dichloride, in toluene while passing in ethylene containing 0.003% oxygen. Polymerization took place smoothly and 125 g. of polymer was formed in 90 minutes.

These results leave little doubt that some tetravalent titanium must be present for these catalysts to show their high activity.[13] It remains to be proved, however, whether a tetravalent titanium species is a sole requirement, or whether perhaps a combination of tetravalent and trivalent titanium is necessary for high activity; this question is under active investigation.

These results shed considerable light on the puzzling behavior observed in our early work. Undoubtedly, oxygen reacts with the trivalent titanium species to oxidize it to a tetravalent form. This reacts with the alkylaluminum compound to form an active catalyst, which probably is reduced; *i.e.*, an oxidation–reduction system is set up. If the alkyl compound is too highly active, it either reacts with the oxygen preferentially or reduces the Ti(IV) too rapidly and a good catalyst does not result; this serves to explain the variable results with triethylaluminum, which reacts with oxygen very rapidly.

It is our belief that the active catalyst is a species such as $(C_5H_5)_2TiEtCl \cdot EtAlCl_2$ or a reaction product of this with ethylene, and that the polymer grows by insertion of a monomer molecule between the alkyl group and the titanium. The first step in the polymerization would probably involve a π-type complex between the titanium and the olefin; if our structure is correct, the aluminum



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[12] The very high ratio of aluminum to titanium at the very low level probably was required as a scavenger.

[13] Natta and co-workers[6,14] have indicated recently that soluble complexes containing trivalent titanium will polymerize ethylene slowly at 95° and 40 atmospheres pressure.

[14] G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo. *Chim. e ind.* (*Milan*), **39**, 19 (1957); *J. Polymer Sci.*, **26**, 120 (1957).

is already tetracoördinated and a complex of the olefin with it is unlikely. The function of the aluminum would therefore be first to alkylate the titanium and then to put a formal or potential positive charge on the titanium and increase its complexing ability. The second step involves transfer of the ethyl group (or a long chain alkyl in a growing polymer) to the ethylene and formation of a new titanium–carbon bond. If it is assumed that the alkyl group is transferred as an anion,[15] the positive charge on the titanium would hinder the breaking of the titanium–carbon bond. However, complexing with the olefin would decrease the charge on the metal and would facilitate anionic migration. Actually, if the migration of the alkyl group and the formation of the new titanium–carbon bond is considered to be a concerted reaction, it is probably meaningless to postulate where the electrons come from.

The rearrangement could take place as shown, or it could involve an alkyl group on the aluminum. Natta and co-workers[14] have presented evidence that growth is on aluminum, based on the following observations. Phenyl groups are found on the polymer when polymerization is carried out with $(C_5H_5)_2TiCl_2$ or $(C_5H_5)_2Ti(C_6H_5)_2$ and triphenylaluminum, but not with $(C_5H_5)_2Ti(C_6H_5)_2$ and triethylaluminum. The objection to this argument is the fact that the groups on titanium and aluminum can exchange quite readily. It is quite reasonable to conclude that a metal–alkyl bond will break in preference to a metal–phenyl bond if there is a choice between the two. We prefer a mechanism in which growth is on titanium because polymerization systems involving only titanium are known[4,16] and because sodium, lithium and magnesium alkyls can be substituted for aluminum alkyls[5]; growth on sodium appears especially unlikely. However, additional evidence on this point is required.

There have been several publications recently concerned with the valence of the transition metal in Ziegler catalysts. McGowan and Ford[17] considered that catalysts prepared from titanium tetrachloride and alkyllithium or dialkylzinc compounds owe their activity to a trivalent titanium species. Ludlum, Anderson and Ashby,[18] using titanium tetrachloride and a variety of alkylating agents, have presented evidence that a divalent titanium compound is the active ingredient. Carrick and co-workers[19] found that divalent vanadium is the active ingredient in a catalyst prepared from a vanadium halide, aluminum chloride and tetraphenyltin. In our work there is little doubt that a tetravalent titanium compound is required for activity. It is our belief that there is not one but a family of Ziegler-type catalysts, depending on the valence of the transition metal, which differ in degree but not fundamentally in mechanism. The major difference appears to be related to the stability of the metal–carbon bond; a decrease in valence results in a more stable bond, higher molecular weight polymers, and longer-lived catalytic species. Because of the obvious similarity of the polymerization of ethylene and propylene and in view of the work described here, it appears reasonable to conclude that a solid surface is not required for the polymerization of 1-olefins in general; the solid surface is required only for stereospecificity in the polymerization of the higher 1-olefins.

Properties of a typical polymer prepared with a bis-(cyclopentadienyl)-titanium dichloride–diethylaluminum chloride catalyst are shown in Table III. The properties of a representative polymer prepared with a heterogeneous Ziegler-type catalyst are given for comparison.

TABLE III

PROPERTIES OF HIGH-DENSITY POLYETHYLENES

	Soluble catalyst	Ziegler type
Reduced specific viscosity	2.3	2.3
Melting point, °C.	137	132
Degree of crystallinity, %	85	79
$\bar{M}_w/\bar{M}_n$	3.6	7.0
Methyl groups, %	0.05	0.86
Vinyl groups, %	.036	.044
Vinylidene groups, %	.006	.007
trans-Vinylene groups, %	.004	.024

It is quite apparent that the polymer prepared with the soluble catalyst differs from that prepared with the Ziegler-type catalyst in two major respects. It is a much more linear polymer, as shown by its very low methyl group content, its high melting point, and its high degree of crystallinity. In fact, we believe this polymer is essentially unbranched, the only methyl group present being that at the end of the chain. A second major difference is the considerably narrower molecular weight distribution obtained with this soluble catalyst.

Acknowledgments.—We are indebted to the Physical Chemistry Division of the Hercules Research Center for the paramagnetic measurements and for the data listed in Table III, and to the Analytical Division for their numerous analyses.

Experimental

Materials.—Bis-(cyclopentadienyl)-titanium dichloride was prepared according to the procedure of Wilkinson and Birmingham[8]; it was recrystallized several times from toluene, m.p. 285–287° (reported[8] m.p. 289 ± 2°). Ethylaluminum dichloride, diethylaluminum chloride and triethylaluminum were prepared according to the procedure of Grosse and Mavity[20]; they were made up as approximately 1 *M* solutions in toluene or *n*-heptane. *n*-Heptane (Phillips Petroleum Co.) was distilled from phosphorus pentoxide and stored in a closed container over sodium. Toluene (Mallinckrodt analytical grade) was dried by passage through silica gel and stored in a closed container under nitrogen. The ethylene was either C.P. (Matheson Co.) or was obtained from the Gulf Oil Corp., and was used as received.

Analytical Procedures.—The analysis for total titanium was carried out by oxidizing the compounds with a mixture of nitric and perchloric acids; titanium then was determined colorimetrically with hydrogen peroxide in the usual manner. Trivalent titanium was determined by adding the

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(15) G. Natta, *Angew. Chem.*, **68**, 393 (1956).

(16) Belgian Patent 553,477 (1957).

(17) J. C. McGowan and B. M. Ford, *J. Chem. Soc.*, 1149 (1958).

(18) D. B. Ludlum, A. W. Anderson and C. E. Ashby, THIS JOURNAL, **80**, 1380 (1958).

(19) W. L. Carrick, W. T. Reichle, R. W. Kluiber, E. F. Bonner and J. J. Smith, Abstracts 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958, p. 19-R.

(20) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

sample to 6 *M* sulfuric acid and titrating with ferric ion. Aluminum was determined by the well known colorimetric procedure with 8-hydroxyquinoline.

Polymer Properties.—The properties of the polymers listed in Table III were determined as follows. Reduced specific viscosity (R.S.V.) was determined in Ubbelohde viscometers using 0.1% solutions of polymer in decalin at 135°. The details of the method have been described.[21] The crystalline melting point was determined by the disappearance of birefringence after the sample had been melted to remove strains, cooled until crystallization set in, and remelted; heating rate was 3° per minute. The degree of crystallinity was based on the amorphous polyethylene band at 7.73 μ; samples were melted and then cooled to about 100° at a rate of 0.67° per hour to develop maximum crystallinity. The molecular weight distribution was determined by a modified Desreux fractionation as described by Francis, Cooke and Elliott.[21] The methyl group content and the various types of unsaturation were determined by the infrared absorption at the following wave lengths: methyl, 7.25 μ; vinyl, 11.0 μ; vinylidene, 11.25 μ; *trans*-vinylene, 10.35 μ.

Reaction of Bis-(cyclopentadienyl)-titanium Dichloride with Alkylaluminum Compounds.—A solution of 72 mg. (0.29 mmole) of bis-(cyclopentadienyl)-titanium dichloride in 100 ml. of dry toluene was placed in an 8-ounce pressure bottle. The bottle was capped with a crown cap in which two small holes had been punched and equipped with a self-sealing neoprene liner. The bottle was then evacuated with an oil-pump through a hypodermic needle until the toluene began to boil, pressurized with nitrogen, and the evacuation and pressurizing repeated several times to remove all oxygen. After the titanium compound had dissolved, 0.6 ml. (0.58 mmole) of a 0.97 *M* solution of diethylaluminum chloride in toluene was added with a hypodermic syringe. An absorption cell of 1-cm. light path was fitted with a short length of glass tubing. The cell was dried, fitted with a self-sealing rubber stopper, and filled with nitrogen by evacuating and pressurizing. A portion of the solution was added to this cell with a hypodermic syringe, and then removed and discarded to clean the system. The cell was then filled with a fresh portion of solution and the course of the color change as a function of time was recorded with a Cary model 14M spectrophotometer. Results are shown in Fig. 1. The spectrum of bis-(cyclopentadienyl)-titanium dichloride at the same concentration is given in curve I.

To a solution of 125 mg. (0.5 millimole) of bis-(cyclopentadienyl)-titanium dichloride in 100 ml. of toluene was added 0.45 ml. of a 1 *M* solution of triethylaluminum in *n*-heptane. The initial orange solution turned reddish-brown immediately, and no further color change was observed over a period of several hours. Repetition of the same experiment with 1 ml. of triethylaluminum gave a clear blue solution instantly.

Isolation of Blue Complex.—The apparatus consisted of two 50-ml. flasks sealed together and separated by a coarse fritted disk. To the neck of one flask was sealed a short piece of glass tubing for filling the apparatus, and to the other neck was sealed a short length of 12-mm. tubing inside of which was a break-tip. In the flask were placed 1.25 g. (5 millimoles) of bis-(cyclopentadienyl)-titanium dichloride and 10 ml. of *n*-heptane. The apparatus was evacuated through a hypodermic needle and 14 ml. (12 millimoles) of 0.85 *M* diethylaluminum chloride in *n*-heptane was added. The sidearm was then sealed off. The initially colorless solution turned blue in several days at room temperature. The solution was then filtered into the second flask, chilled to −20°, and the supernatant liquid was decanted from the blue crystals. The filtrate was distilled back onto the crystals by chilling the flask containing the crystals in Dry Ice and warming the filtrate to about 30°. Three recrystallizations were carried out in this fashion. After the last recrystallization, part of the solvent was distilled back and the flask containing the recrystallized solution was sealed off. It is conceivable, but rather unlikely, that some diethylaluminum chloride distilled back with the solvent and interfered with the final analysis. The sidearm was closed off with a self-sealing rubber stopule, evacuated to remove air, and the break-tip was snapped off with a heavy hypodermic needle while attached to an evacuated gas sampling bulb. Mass spectroscopic analysis showed the presence of ethane, a small amount of butane and traces of hydrogen; ethyl chloride and ethylene were absent. For analysis, a sample was removed with a hypodermic syringe and added to thoroughly deaerated 6 *M* sulfuric acid; a clear green solution was formed. The following results were obtained: total Ti, 0.215 millimole/g.; Ti(III), 0.204; Al, 0.23; Cl, 0.57. Normalizing for titanium, there is obtained: Ti (III), 0.95; Al, 1.05; Cl, 2.63.

Another portion of the solution was analyzed for carbon and hydrogen by placing a sample in a weighed Vycor tube, removing solvent *in vacuo*, finally at room temperature and 0.07 mm. for 3 hours, and sealing the tube under nitrogen. The tube was then cracked open and rapidly placed in a combustion tube.

Anal. Calcd. for $C_{13}H_{17.5}TiAlCl_{2.5}$: C, 46.28; H, 5.23. Found: C, 46.36; H, 5.26.

Magnetic susceptibility measurements on a solution of the blue complex with a Gouy balance showed the presence of one unpaired electron.

Bis-(cyclopentadienyl)-titanium(III) Chloride.—To a suspension of 2.5 g. (10 millimoles) of bis-(cyclopentadienyl)-titanium dichloride in 10 ml. of toluene was added under nitrogen 20 ml. of a 1 *M* solution of diethylaluminum chloride in *n*-heptane. The reaction mixture was shaken overnight and then centrifuged to remove a small amount of dark precipitate. The clear, blue solution was transferred to another vessel and 50 ml. of dry, deaerated ether was added; a green, crystalline precipitate formed. The mixture was chilled in a Dry Ice-bath and the supernatant liquid was removed. The green crystals were washed twice with 5-ml. portions of ether and twice with 5-ml. portions of toluene. Analysis showed titanium and chlorine to be present in a 1:1 ratio; aluminum was absent.

General Procedure for Polymerization of Ethylene in Pressure Bottles.—About 50 ml. of solvent was added to an 8-ounce pressure bottle from an automatic buret in an atmosphere of nitrogen and, after capping with a self-sealing neoprene liner, the bottle was evacuated with a vacuum pump and pressurized with nitrogen twice. The bottle was again evacuated and pressured with ethylene (to about 50 lb. per sq. in.) until 2 g. of ethylene had been added by weight. The bottle was then placed in a rotating bath at 30°, rotated for 15 minutes, and a preformed catalyst was injected with a hypodermic syringe. The catalyst was prepared by treating bis-(cyclopentadienyl)-titanium dichloride suspended in toluene or in *n*-heptane with a solution of diethylaluminum chloride under nitrogen, and shaking the container for several hours until a clear blue solution was formed. After the catalyst had been injected, the bottles were rotated in the constant temperature bath, and pressure readings were taken at intervals with a Bourdon gauge connected to a hypodermic needle. The polymerization was stopped by the addition of 5 ml. of ethanol, the polymer was filtered, refluxed for 15 minutes with a 10% solution of hydrochloric acid in methanol, filtered, washed well with methanol and dried *in vacuo* at 80°. Results are shown in Tables I and II. Matheson ethylene was used in these experiments.

Polymerization of Ethylene in a Flow System.—These polymerizations were carried out in a one-liter resin kettle equipped with a stainless steel paddle stirrer, a thermometer, a gas inlet tube, an outlet tube leading to a gas washing bottle containing mineral oil, and a small inlet tube closed off with a self-sealing rubber stopple through which a hypodermic needle could be inserted. In the flask were placed 625 mg. (2.5 millimoles) of bis-(cyclopentadienyl)-titanium dichloride and 500 ml. of dry toluene. The flask was evacuated and filled with nitrogen several times, and 5.2 ml. (5 millimoles) of 0.96 *M* diethylaluminum chloride in toluene was added. The mixture was stirred for one hour at room temperature, cooled to 15° with water, and Gulf ethylene containing 0.003% oxygen was passed in. After 80 minutes the polymer was filtered and purified as described above; 8.9 g. of polymer was isolated with an R.S.V. of 1.3.

Effect of Oxygen on Polymerization of Ethylene with Blue Catalyst.—The same materials were used as described in the above experiment, except that Gulf ethylene containing 0.025 mole % oxygen was passed into the solution. In a short time the solution turned a greenish-brown. A 0.97 *M* solution of diethylaluminum chloride in *n*-heptane was

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[21] P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, *J. Polymer Sci.*, **31**, 453 (1958).

added very slowly to keep the ethylene absorption at an arbitrarily chosen figure of 650 ml. per minute, running water maintaining the reaction at about 20°. Polymerization was continued in this fashion for 4 hours, at which time the rate began to fall off because of stirring difficulties; a total of 8 ml. of diethylaluminum chloride was added. The usual isolation yielded 150 g. of polymer, R.S.V. 3.0.

Polymerization of Ethylene with Bis-(cyclopentadienyl)-titanium Dichloride.—In the reaction flask were placed 500 ml. of dry toluene and 625 mg. (2.5 millimoles) of bis-(cyclopentadienyl)-titanium dichloride. The solution was deaerated as described above, Gulf ethylene containing 0.003 mole % oxygen was passed in, and a 0.96 *M* solution of diethylaluminum chloride in *n*-heptane was added drop by drop. The temperature was maintained at 13° by running water. Polymerization started after 30 minutes, at which time 3.2 ml. (3.0 millimoles) of diethylaluminum chloride had been added; the solution was a greenish-brown. Addition of the aluminum compound was continued and ethylene was absorbed smoothly at 500–650 ml. per minute at 18–19°. The polymerization was continued for 90 minutes, at which time the reaction was stopped with ethanol, and the polymer isolated; 62.5 g. of polymer was obtained, R. S. V. 1 5.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

Kinetics of Ethylene Polymerization Catalyzed by Bis-(cyclopentadienyl)-titanium Dichloride–Dimethylaluminum Chloride[1]

BY JAMES C. W. CHIEN

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The kinetics of ethylene polymerization catalyzed by bis-(cyclopentadienyl)-titanium dichloride–dimethylaluminum chloride has been studied. Initiation was followed by using C^{14}-labeled $(CH_3)_2AlCl$. Instantaneous concentration of propagating metal alkyl complex, [C], was obtained by quenching aliquots of polymerizing mixtures with I_2^{131}. The propagation step was first order in monomer and [C], with an activation energy of 12.2 kcal. mole^{-1}; k_p at 30° was 13.6 ± 1.4 liter mole^{-1} sec.$^{-1}$ Termination was second order with respect to [C] with an activation energy of 16.4 kcal. mole^{-1}; k_t at 30°, and an Al to Ti ratio of 2.5 was 9.07 ± 0.58 liter mole^{-1} sec.$^{-1}$, which decreased with increase of the ratio. Each polymer molecule was found to contain 1.07 ± 0.27 $C^{14}H_3$ groups, thus eliminating a number of transfer processes. These kinetic data were used to calculate number-average molecular weight, $\overline{M}_n$, which agreed well with the ones obtained by fractionation of polymers.

Introduction

The discovery of polymerization of ethylene at low pressure by Ziegler[2] using catalysts which cannot be considered to operate by any of the known polymerization mechanisms has stimulated much investigation. The most studied catalyst systems, usually consisting of a transition metal halide and a metal organic compound, are heterogeneous. Determinations of kinetic parameters in these systems are necessarily difficult. Recently, Breslow and Newburg[3] and Natta and co-workers[4] described a soluble catalyst system consisting of bis-(cyclopentadienyl)-titanium dichloride–alkylaluminum compounds. This catalyst is soluble in toluene, and remains in solution during and after reduction of titanium.

Preliminary studies with such a soluble catalyst in this Laboratory have shown that (1) the life times of growing polymer chains are of the order of tens of minutes, making possible a measurement of their concentrations as a function of time, and (2) alkyl groups of the metal complex catalysts are incorporated in the polymer, enabling a determination of initiation events using C^{14}-labeled metal alkyls. Thus, it is possible to obtain the individual rate constants of the polymerization under nonsteady state conditions. The objective of this investigation was the study of the kinetics of ethylene polymerization by the catalyst $(C_5H_5)_2TiCl_2$–$(CH_3)_2AlCl$, in order to aid in interpreting the mode of operation of such a catalyst.

Experimental

Materials.—Bis-(cyclopentadienyl)-titanium dichloride was prepared according to the procedure of Wilkinson and Birmingham.[5] Dimethylaluminum chloride labeled with C^{14} was prepared from $C^{14}H_3Cl$ (Tracerlab, Houston, Texas) in a vacuum system according to the method of Grosse and Mavity.[6] Mallinckrodt analytical reagent grade toluene was purified by shaking with concentrated sulfuric acid. This was followed by separation, neutralization, washing, drying over anhydrous magnesium sulfate and filtration. The treated toluene was passed through a 20-in. silica gel column directly into the reaction vessel under an atmosphere of nitrogen. Phillips Petroleum research grade ethylene was used without further purification. It was 99.96% pure, with ethane the major impurity.

Polymerization was carried out in a one-liter reaction vessel equipped with magnetic stirrer, immersed in a constant temperature bath (±0.2°). The monomer pressure was kept constant to ±0.5 cm. at 100 cm. by means of a Hoke low-pressure regulator no. 804. At higher pressures, 175 and 255 cm., constant pressure of ±2 cm. was maintained by a Matheson regulator no. 501. The pressure of the system was measured by calibrated Stratham transducers and recorded. Three calibrated Fisher–Porter triflat flowmeters in parallel arrangement determined the instantaneous rate of monomer consumption. The maximum rates of polymerization were usually 0.02 to 0.05 g. liter^{-1} sec.$^{-1}$. A copper–constantan thermocouple was inserted to measure the internal temperature of the polymerizing mixture. A temperature rise of less than 2° was observed at the peak of a fast polymerization.

Aliquots of fine polymer slurry were taken from the polymerization mixture during a run. This was done with a syringe connected through a Hoke valve (stainless steel throughout with Teflon packings) to a 13-gage 12-in. long hypodermic needle. The sampling technique was found to have a reproducibility of better than 2.0%; 15 to 20 such samples were usually taken at predetermined intervals.

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(1) Presented in part at the Gorden Research Conference on Polymers, New London, N. H., June 30, 1958.

(2) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew Chem.*, **67**, 541 (1955).

(3) D. S. Breslow and N. R. Newburg, THIS JOURNAL, **79**, 5072 (1957).

(4) G. Natta, P. Pino, G. Mazzanti, V. Giannini, E. Mantica and M. Peraldo, *Chim. e ind.* (*Milan*), **39**, 19 (1957); *C.A.*, **51**, 7049 (1957); G. Natta, P. Pino, G. Mazzanti and V. Giannini, THIS JOURNAL, **79**, 2975 (1957).

(5) G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954).

(6) A. V. Grosse and J. N. Mavity, *J. Org. Chem.*, **5**, 106 (1940).