β-Hydroxyethylmercuric chloride was prepared according to the method of Cotton and Leto by the reaction of ethylene with aqueous mercuric nitrate; m.p. 152–153° (reported[13] 153–155°).

Determination of Mercuric Ion Concentrations in Hydrochloric Acid.—Out of mercuric chloride solutions in 75% ethanol containing hydrochloric acid, aliquot samples (10 ml.) were withdrawn and added to 10 ml. of cold 10% aqueous sodium hydroxide. Mercuric oxide formed was filtered, washed twice with cold water, dissolved in 10 ml. of 5 *N* nitric acid and titrated with 0.2 *N* potassium thiocyanate. In cases where the concentration of mercuric chloride was lower, lower values for mercuric oxide were obtained because of the solubiliy of mercuric oxide in water.

DETERMINATIONS OF MERCURIC ION CONCENTRATIONS IN 75% ETHANOL CONTAINING VARIOUS AMOUNTS OF HYDROCHLORIC ACID

$HgCl_2$, *M*	HCl, *M*	HgO obtained, %
0.025	0.00	99.0
	.10	98.7
	.15	98.7
	.20	98.3
	.25	96.6
	.50	94.5
.035	.05	99.8
	.15	99.8
.01	.05	94.4
	.10	93.6
	.20	93.5
.05	1.00	88.7

Rate Measurement.—Aliquots (10 ml.) were withdrawn at intervals and added to 10% aqueous sodium hydroxide. The amount of mercuric oxide formed was determined by the method described above.

Conversion of β-Acetoxyethylmercuric Chloride to β-Ethoxy-ethylmercuric Chloride.—In the absence of perchloric acid, β-acetoxyethylmercuric chloride was recovered unchanged from ethanol solution after standing for one week. However, in the presence of perchloric acid, the acetoxy compound was converted to the ethoxy compound. β-Acetoxyethylmercuric chloride (3.2 g.) was dissolved in 95 ml. of ethanol containing 30 ml. of 20% perchloric acid. After 5 days, the solution was neutralized with 0.5 *N* aqueous sodium hydroxide and cooled to −10°. The crystals formed (1.59 g.) melted at 89–90°. Mixed m.p. with authentic sample of β-ethoxyethylmercuric chloride showed no depression.

Acknowledgment.—We wish to express our thanks to Sumitomo Chemical Co. for financial assistance.

YOSHIDA, KYOTO, JAPAN

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[13] F. A. Cotton and J. R. Leto, THIS JOURNAL, **80**, 4824 (1958).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE PLASTICS CO., DIVISION OF UNION CARBIDE CORP.]

Transition Metal Catalysts. I. Ethylene Polymerization with a Soluble Catalyst Formed from an Aluminum Halide, Tetraphenyltin and a Vanadium Halide[1]

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A mixture of an aluminum halide, tin tetraphenyl and a trace of a vanadium halide in cyclohexane forms a clear solution which contains an active catalyst for the low pressure polymerization of ethylene. In this catalyst the optimum weight concentration of the vanadium halide is only 0.1 to 5 parts in 10^3 parts of total components, and polymerization will take place when the concentration is as low as one part in 10^6. Each molecule of the vanadium compound can catalyze the formation of as many as 2000 *polymer* molecules. The polyethylene obtained is linear in molecular structure, high in molecular weight and narrow in molecular weight distribution. The narrow distribution suggests that catalysis is homogeneous and due to a single catalytic species.

Introduction

Organometallic mixed catalysts for ethylene and α-olefin polymerization were first disclosed in a publication by Ziegler, Holzkamp, Breil and Martin[2] describing the polymerization of ethylene at low pressures with a mixture of titanium tetrachloride and an aluminum alkyl. Since then many other catalyst mixtures have been reported which polymerize ethylene at low pressures to a high molecular weight, linear polymer.[3,4] Some of these also polymerize α-olefins to stereoregular polymers. These catalysts ordinarily are formed by combining a reactive organometallic compound with a transition metal compound of groups IV through VI of the periodic table. The catalyst-forming reaction is very complex, and attempts to define the active species generally have led to ambiguous results. At present, there is no general agreement as to whether the reaction is ionic[5] or radical,[6,7] heterogeneous[6] or homogeneous,[8] which transition metal valence is optimum,[9–11] or if the polymer molecule grows from a transition metal center[6,7,10,11] or some other site.[8,12] However, most investigators do agree that a transition metal compound is a necessary part of the active catalyst species.

The general problem of the mechanism of olefin polymerization by organometallic mixed catalysts has been under investigation in this Laboratory for several years, and numerous catalyst combinations have been examined. Studies on the organic derivatives of transition metals, interactions of cata-

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[1] This work was presented before the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13 to 18, 1958. Address inquiries to W. L. Carrick.

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

[3] Soc. Chem. Ind., Reports on the Progress of Applied Chemistry, **42**, 436 (1957).

[4] J. K. Stille, *Chem. Revs.*, **58**, 541 (1958).

[5] G. Natta, *Chim. e ind.* (*Milan*), **37**, 888 (1955).

[6] H. N. Friedlander and K. Oita, *Ind. Eng. Chem.*, **49**, 1885 (1957).

[7] C. D. Nenitzescu and A. H. Ciresicahuch, *Angew. Chem.*, **68**, 438 (1956).

[8] G. Natta, P. Pino, G. Mazzanti, U. Gianini, E. Mantica and M. Peraldo, *J. Polymer Sci.*, **26**, 120 (1957).

[9] D. S. Breslow and N. R. Newburg, THIS JOURNAL, **81**, 81 (1959).

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

[11] W. L. Carrick, *ioid.*, **80**, 6455 (1958).

[12] F. Patat and H. Sinn, *Angew. Chem.*, **70**, 496 (1958).

lyst components, valence determinations, polymerization and copolymerization kinetics, and measurements of polymer structural units will be reported in this series of papers. This initial paper describes the novel catalyst formed from the interaction of an aluminum halide, tetraphenyltin and a small amount of a vanadium halide.

Experimental

Materials.—The ethylene used in most of this work was a C.P. grade obtained from the Matheson Co. Its purity is >99% with the major contaminants being 0.2% butanes, 0.3% butenes, about 300–600 p.p.m. of oxygen and 100 p.p.m. of water. The water content was reduced further by passage through a column of Drierite or Linde molecular sieves. The cyclohexane was a 99% pure grade (Shell) that was further refined by treatment with concentrated sulfuric acid, followed by a water wash, drying over sodium hydroxide and a final distillation. Tin tetraphenyl was obtained from Metal and Thermit Corporation and was recrystallized from a mixture of benzene and cyclohexane before use. Vanadium tetrachloride was supplied by the Union Carbide Metals Co., Division of Union Carbide Corp., and was used without further treatment. Several different samples of aluminum chloride were used, but each was an anhydrous, resublimed, reagent grade. Aluminum bromide was prepared by the direct bromination of aluminum,[13] and the product was triply distilled over aluminum foil to remove vanadium impurities before use. The final product was snow white.

Cyclohexane solutions of aluminum bromide and vanadium tetrachloride were prepared and stored under nitrogen in bottles equipped with serum bottle stoppers. Aliquots were removed with hypodermic syringes.

Polymerization Conditions.—A mixture of 1500 ml. of dry cyclohexane and 1.5 millimoles of tin tetraphenyl was heated to boiling, purged with dry nitrogen to remove volatile impurities, and cooled to 65°. The nitrogen flow was stopped, and ethylene was introduced at 2 l./min. Three millimoles of aluminum chloride (90 ml. of a saturated solution in boiling cyclohexane) and 0.025 millimole of vanadium halide then were added as dilute solutions in cyclohexane by way of hypodermic syringes. Upon addition of the third catalyst component, rapid polymerization commenced, as evidenced by the appearance of a milky precipitate of colloidal polymer particles. As the polymerization progressed, the polymer particles became larger and at the end of the reaction were coarse grains the size of sand. At the end of two hours, the reaction was quenched by the addition of isopropyl alcohol, even though polymerization was still in progress but at a diminished rate. The polymer was removed from the quenched slurry by filtration, washed three times with isopropyl alcohol or acetone, and dried. The yield of fluffy white polymer was 80 g.

Numerous polymerizations were carried out by this same general procedure using total catalyst concentrations ranging from 0.5 to 25 millimoles per liter. Polymer yield per unit of catalyst increased with decreasing catalyst concentration, increasing reaction time and increasing purity of reagents. The highest yield obtained was 300 g. of polymer per gram of catalyst mixture.

Infrared Measurements.—Determinations of the various structural units were carried out on pressed polymer films (10–20 mils) using a Perkin–Elmer model 21 infrared spectrophotometer. Methyl groups were determined using the 7.25 μ band, phenyl groups at 14.35 μ, vinyl groups at 11.0 μ, pendent methylene at 11.25μ, and internal unsaturation at 10.35 μ. The absorption coefficient for the phenyl group measurement was the essentially constant (±3%) value obtained from reference solutions of a number of *n*-alkylbenzenes in cyclohexane.

For the measurement of some of these groups, poly-ethylene films of appropriate structure and comparable thickness were placed in the reference beam of the infrared instrument to compensate for absorptions which were immediately adjacent to the analytical wave length. For example, the highest molecular weight ($M_n > 120{,}000$) linear polyethylene prepared with the catalyst described in this paper was used in the reference beam for methyl determinations. This sample showed less absorption at 7.25 μ than a polymethylene prepared from diazomethane. Linear polyethylenes prepared and isolated so that no phenyl groups were present were used in the reference beam for measuring phenyl content.

Polymer Fractionation.—Sixty grams of polyethylene, 0.6 g. of di-*t*-butyl-*p*-cresol antioxidant and 1500 ml. of distilled ethylbenzene was maintained at 115°. After the resin dissolved, about 1575 ml. of *n*-amyl alcohol was added, with agitation, to reach a cloud point. This quantity of non-solvent usually was not sufficient to precipitate the first, highest molecular weight, fraction of polymer. A nitrogen blanket was kept over the solution, and about 25-ml. increments of *n*-amyl alcohol were added, successively with stirring. When roughly 5 g. of polymer had precipitated, the bath temperature was raised to 120° to redissolve the resin, and reprecipitation then was allowed to proceed slowly, overnight, by cooling to 115°. After each fraction was precipitated, the soluble polymer was siphoned off into a second flask and another increment of precipitant added. The fraction in the first flask was dissolved in 1 l. of ethylbenzene and siphoned off into a large beaker containing 2500 ml. of methanol at room temperature. The precipitated resin was removed by filtration, dried, weighed, and its intrinsic viscosity in tetralin at 130° was obtained using Ubbelohde viscometers.

Successive fractions were collected by repetition of the same technique. If, toward the end of a fractionation, more than 300 ml. of *n*-amyl alcohol was required to precipitate a fraction, the bath temperature was dropped about 5° instead. The initial temperature of 115° was chosen because this is about 20° above the crystallization temperature of completely linear polyethylene in this solvent system, thus permitting fractionation according to molecular weight rather than crystallinity.

Results

Reaction Conditions.—A mixture of an aluminum halide ($AlCl_3$ or $AlBr_3$), tin tetraphenyl and a minor amount of a vanadium halide (VCl_4, $VOCl_3$, etc.) in an inert hydrocarbon, such as cyclohexane, forms a highly active catalyst for the low pressure polymerization of ethylene. The ratios of the three components can be varied at least 20-fold with retention of good catalytic activity; however, the composition used in this work consisted of a mixture of the aluminum, tin and vanadium compounds in the mole ratios of approximately 1–3:1:0.02. In contrast to the usual organometallic mixed catalysts which are heterogeneous, this mixture is soluble in cyclohexane. When the total concentration of the three components was less than 20 millimoles per liter, the solution did not show a Tyndall Beam effect and was filtered through a 1 μ bacterial filter without loss of catalytic activity. Aluminum chloride and aluminum bromide are interchangeable, and other organometallic compounds can be substituted for tin tetraphenyl[14]; however, the vanadium compound is essential, and its function cannot be replaced by compounds of other transition metals without destroying or radically changing the catalytic behavior.

Table I describes a representative series of polymerizations carried out at 65° with an ethylene flow of 2 l./min. for two hours at atmospheric pressure. Although titanium tetrachloride is a common co-catalyst in organometallic systems and polymer melt index is increased by an increase in its relative concentration,[15] the first five experiments in the table show that the addition of this halide to the AlX_3–VX_n–$Sn(C_6H_5)_4$ system causes no significant

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(13) L. F. Audrieth, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 30.

(14) W. L. Carrick, Italian Patent 573,809.

(15) E. J. Badin, THIS JOURNAL, **80**, 6545 (1958).

change in either the yield or melt index of the resin. Under these conditions, the titanium valence is essentially unchanged, and the titanium tetrachloride is obviously inert in the system. Experiment 8 shows that aluminum bromide is also a good cocatalyst, and experiment 7 again shows that titanium tetrachloride is not an adequate substitute for the vanadium halide. The small amount of polymer obtained in experiment 6 without the external addition of a vanadium halide is due to the fact that this particular reagent grade sample of aluminum chloride contained a few parts per million of vanadium compounds. This latter effect is more pronounced if certain commercial grades of aluminum bromide, which contain 0.01–0.1% vanadium halides, are used without purification. However, rigorous purification of these materials by double distillation gives an aluminum bromide that is inactive as a cocatalyst with tin tetraphenyl, either alone or in combination with titanium tetrachloride under the conditions described here (expt. 7). External addition of a small amount of a vanadium halide regenerates the catalytic activity (expt. 8).

TABLE I

Expt.	Millimoles per 1500 ml. $AlCl_3$	$TiCl_4$	$Sn(C_6H_5)_4$	VCl_4	Polymer yield,[a] g.
1	3	0.0	1.5	0.025	65–85
2	3	1.2	1.5	.025	58
3	3	3.6	1.5	.025	71
4	3	6.0	1.5	.025	81
5	3	12.0	1.5	.025	71
6	3	..	1.5	...	6
	$AlBr_3$				
7	3	1–12	1.5	...	<0.5
8	3	..	1.5	0.025	53

[a] All samples had a melt index (ASTM D-1238-52T) of <0.05. These values correspond to number average molecular weights of about 100,000.

In normal use, the vanadium concentration is only 0.02 mole per mole of aluminum halide, and even this is more than is really required for good catalytic activity. Vanadium concentrations as low as one part in 10^6 parts of combined aluminum halide and tetraphenyltin are sufficient to initiate the polymerization of ethylene; however, catalysts containing such low vanadium concentrations are more susceptible to poisons. In one case 100 g. of polyethylene was produced in a 3-hour polymerization at 65° and atmospheric pressure using 15 millimoles of highly purified aluminum bromide, 5 millimoles of tin tetraphenyl and 0.1 *milligram* of vanadium tetrachloride. From these data one can calculate that 10^6 g. of polymer was formed for each gram of vanadium halide, and nearly 2000 complete polymer molecules (assuming $M_n = 100{,}000$) were formed for each molecule of vanadium halide in the system. The very efficient utilization of the vanadium component is consistent with the soluble nature of this catalyst, since in a soluble system the active component is highly dispersed and would be expected to give much higher efficiency than is observed with heterogeneous catalysts. Compared to other low pressure catalysts, either homogeneous[8,16,17] or heterogeneous,[10] the rate of ethylene polymerization is vastly greater per unit of transition metal and is equivalent based on total catalyst components.

Effect of Impurities.—Ethers, alcohols, ketones, water and other polar molecules inhibit polymerization with this catalyst. If the ethylene feed contained less than about 100 p.p.m. of oxygen, the polymer formed as strings or large balls rather than as discrete particles. The presence of more than 500 p.p.m. of oxygen in the ethylene decreased the molecular weight and ultimate yield but caused the polymer particles to be smaller. Studies on the specific chemical action of oxygen are still in progress and will be reported later.

Acetylene also reacted with the catalyst in a very complex manner. In the absence of ethylene, it reacted with the mixed catalyst giving a red color. When ethylene then was added, no polymerization occurred. Addition of about 1200 p.p.m. of acetylene to a normal ethylene polymerization stopped the reaction. When the acetylene flow was discontinued and the reaction vessel purged with ethylene, polymerization resumed in 10–15 minutes. This cycle of acetylene inhibition, outgassing, and resumption of polymerization was repeated more than once; however, each time the reaction was inhibited the ultimate yield of polymer was reduced significantly. Therefore, acetylene must have two functions: (1) reversible inhibition of polymerization and (2) irreversible poisoning of the catalyst which likely involves reaction with the active hydrogens. The polymer produced in these experiments did not show any significant increase in unsaturation indicating that the acetylene did not copolymerize.

Polymer Structure.—The molecular structure and composition of the polyethylene normally obtained with this catalyst very closely approaches that of the idealized polymethylene, $(CH_2)_n$. The crystalline melting points of 135–136° are only slightly lower than the 136–137° values obtained for polymethylenes prepared from diazomethane. Infrared measurements show that there is less than one methyl group for every 2,000 carbon atoms and less than one unsaturated group for every 10,000 carbon atoms. Polyethylenes prepared by use of the triisobutylaluminum-titanium tetrachloride catalyst (Al/Ti ratio = 0.7) of Ziegler[2] contained from 5 to 10 methyl groups per 2,000 carbon atoms and about 8 unsaturated groups per 10,000 carbons. Those prepared by the Phillips Petroleum Co. using chromium oxide–silica–alumina catalyst were found to contain about 2 methyl groups per 2,000 carbons and about 14 unsaturated groups per 10,000 carbons.

Number average molecular weight (M_n) values for this polymer are in the range 65,000–120,000 and have been determined reliably by osmotic pressure techniques since there is essentially no low molecular weight polymer present to diffuse through the membranes of the osmometer. For example, less than 0.3% by weight of the polymer is sufficiently low in molecular weight to be extracted by boiling cyclohexane in a Bailey–Walker extractor during 24 hours. The polyethylenes obtained by use of the triisobutylaluminum–

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[16] J. C. W. Chien, THIS JOURNAL, **81**, 86 (1959).

[17] D. S. Breslow and N. R. Newburg, *ibid.*, **79**, 5072 (1957).

titanium tetrachloride and the chromium oxide-silica–alumina catalysts contain from 1 to 6% cyclohexane extractables in this test and give erroneous osmotic pressure values due to diffusion of low polymer through the membranes. Molecular weights determined by freezing point depression show that these latter polyethylenes have M_n values in the 5,000 to 15,000 range.

From the infrared and M_n values, calculations have been made for the terminal groups per molecule and the branches per 1,000 carbon atoms in a series of polyethylenes obtained with the AlX_3–VX_n–$Sn(C_6H_5)_4$ catalyst (Table II). Polymers having M_n values lower than about 65,000 have been obtained by quenching the catalyst after the first 1 to 5 minutes of polymerization or by using a total catalyst concentration of 100 millimoles per liter. Regardless of molecular weight, these polymers consistently contain no more than one vinyl group for every ten molecules. At M_n values greater than about 40,000, there are between 2.0 and 2.5 methyl groups per molecule but only one phenyl group for every three to five molecules. Branches per 1,000 carbons are calculated from the excess terminal groups over the two per molecule assumed for a completely linear chain. Branches due to $RRC{=}CH_2$ groups are negligible since there is much less than one of these groups (or $RCH{=}CHR$, *trans*) for every 10,000 carbons.

TABLE II

END GROUP ANALYSES

	Terminal groups/molecule				Branches per 1000 carbons
M_n	H_3C–	$RCH{=}CH_2$	Phenyl	Total	
18,000[a]	1.4	0.1	1.7	3.2	1.0
40,000	2.1	.1	0.3	2.5	0.2
61,000	2.4	.1	.4	2.9	.2
87,000	2.3	.1	.2	2.6	.1
99,000	~2.3	~ .1	~ .2	~2.6	< .1

[a] 100 millimoles of total catalyst components per liter of diluent was used in this polymerization.

Molecular Weight Distribution.—The fractionation results listed in Fig. 1 and Table III show that the AlX_3–VX_n–$Sn(C_6H_5)_4$ polymer contains very much less low, and intermediate, molecular weight polymer than a typical low pressure polymer prepared by the aluminum triisobutyl and titanium tetrachloride catalyst. This latter polymer also contains a larger fraction of extremely high molecular weight polymer with intrinsic viscosities of 2.8 and greater. Using the method of Tung,[18] it has been calculated that the weight average to number average molecular weight ratio for the AlX_3–VX_n–$Sn(C_6H_5)_4$ polymer is about 1.5. The polyethylene produced by the AlR_3–$TiCl_4$ catalyst has a very broad distribution with M_w/M_n of the order of 15–30[18–21]; however, another soluble catalyst also has been reported to give a narrow distribution product.[9]

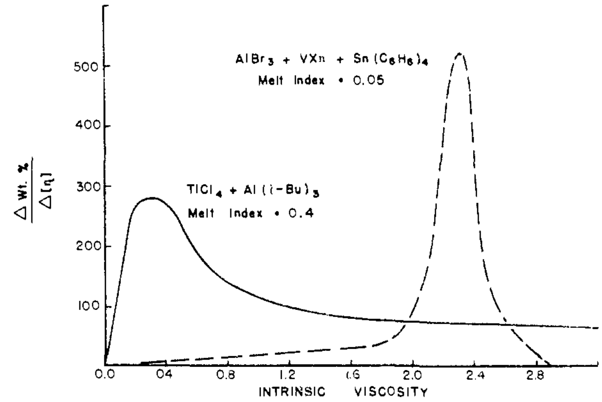

Fig. 1.—Differential molecular weight distributions of high density polyethylenes.

TABLE III

POLYMER FRACTIONATION

Fraction	Weight % of total	Intrinsic viscosity[a]	No. av.[b] mol. wt.
1	10.2	2.58	120,000
2	12.5	2.41	110,000
3	10.3	2.28	102,000
4	11.7	2.24	100,000
5	7.5	2.20	98,000
6	14.1	2.13	95,000
7	6.0	1.97	84,000
8	15.3	1.59	63,000
9	4.5	1.27	46,000
10	4.4	1.20	41,000
11	2.1	0.88	28,000
12–15	1.3	0.38	9,000
Whole resin	100	2.16	95,000

[a] In tetralin at 130°. [b] Estimated from the data of Tung, ref. 18.

Discussion

Because of the complexity of the disproportionation reactions between the aluminum, vanadium and tin compounds, the data presented here only establish that the catalyst is a soluble organometallic compound or complex containing vanadium[11,22] and do not further indicate its structure. Solubility of the active catalyst makes every molecule of the vanadium species potentially available for the formation of an active site. The production of high molecular weight polymer with this catalyst at a rate equivalent to that obtained with the better heterogeneous catalysts confirms the view that a surface is not necessary[6] and that the required monomer activation can be provided on a molecular scale.[8,9,17] This catalyst does not homopolymerize propylene or other α-olefins so the question of stereospecificity does not arise. It has been proposed, without supporting evidence, that the critical monomer activation process is accomplished by preliminary coördination of the monomer to the d-orbitals of a transition metal compound.[10,11] The observed reversible inhibition of ethylene polymerization by the presence of acetylene is consistent with this theory since it may be assumed that acetylene displaces ethylene from the active catalyst site and remains bound to it, without copolymerizing. Since each mole-

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

(19) R. S. Aries and A. P. Sachs, *ibid.*, **21**, 551 (1956).

(20) H. Smith, *ibid.*, **21**, 563 (1956).

(21) H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).

(22) W. L. Carrick, W. T. Reichle, R. W. Kluiber, R. F. Bonner and J. J. Smith, Paper No. 47, Polymer Division, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

cule of the vanadium compound can catalyze the formation of hundreds of polymer molecules, termination of a growing molecule must take place by some chain transfer or oxidation–reduction process in which the active site is regenerated with retention of its function. The molecular termination process is very likely a combination of two reactions since not all the polymer molecules have the same end groups. The mechanism by which the active vanadium center is regenerated is still under investigation and will be discussed further at a later date.

A kinetic treatment of vinyl polymerizations, assuming any of the conventional termination reactions, ordinarily leads to a predicted weight average to number average molecular weight ratio of between one and two,[23] when the reaction is carried out under equilibrium conditions. In this case the M_w/M_n ratio of about 1.5 is probably not sufficiently exact to argue for a specific mechanism on kinetic grounds; however, the low value of the M_w/M_n ratio is good evidence that this catalyst system has only a *single active species*. The M_w/M_n ratios of 15–30 observed for polymers produced with the AlR_3–$TiCl_4$ catalyst suggest that this system has several different active sites, each producing its own characteristic polymer. For this reason, the heterogeneous catalyst is much more difficult to investigate from a mechanistic point of view.

Acknowledgment.—The authors are indebted to Miss P. Payton and Mr. E. G. Hendricks for the osmotic and cryoscopic molecular weight determinations, and to Mr. W. E. Wright for assistance with some of the polymerizations.

BOUND BROOK, N. J.

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(23) Paul J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE PLASTICS CO., A DIVISION OF UNION CARBIDE CORP.]

Transition Metal Catalysts. II. Formation and Catalytic Activity of Organovanadium Compounds Formed by Interaction of Diphenylmercury and Vanadium Halides[1]

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The organovanadium compounds $C_6H_5VOCl_2$ and $C_6H_5VCl_3$ are formed by the interaction of diphenylmercury and vanadium oxytrichloride or vanadium tetrachloride in cyclohexane solution. These compounds are unstable and spontaneously decompose giving a quantitative yield of biphenyl and the lower valence vanadium halide according to the equation: $C_6H_5VX_n \rightarrow {}^1/_2C_6H_5C_6H_5 + VX_n$. This reaction is a concerted process and does not involve the intermediate formation of phenyl radicals. Ethylene polymerization tests with these compounds at room temperature and atmospheric pressure were negative. However, other tests using mixtures believed to contain di- or trivalent organovanadium compounds produced a low yield of high molecular weight polyethylene. These results are interpreted as support of the theory that the active catalyst species in low-pressure, organometallic, olefin polymerization catalysts contains an organic derivative of a transition metal in a low valence state.

Introduction

Catalysts for the polymerization of ethylene and other olefins to high molecular weight polymers are formed by the interaction of certain reactive organometallic compounds and transition metal halides.[2,3] Reactions between these species presumably lead to the intermediate formation of alkyl or aryl transition metal compounds; therefore a definition of the role of such intermediates would significantly advance our understanding of these polymerization catalysts. Investigation of the structure and properties of the alkyls of the catalytically active Groups IV–VI transition metals is difficult due to the inherent instability of these compounds.[4] The only authentic examples of the catalytic behavior of such compounds, in which there is a carbon to transition metal single bond are phenyl titanium triisopropoxide[5] and methyl titanium trichloride.[6] Phenyl titanium triisopropoxide has been reported to polymerize styrene, presumably by a free radical mechanism, but its catalytic behavior toward ethylene or other α-olefins was not mentioned. Methyl titanium trichloride is reported to form a catalyst for the low pressure polymerization of ethylene,[7] but its activity is appreciable only after partial thermal decomposition.

An additional feature of organometallic catalysts which has not been rigorously investigated is the influence of valence on the stability and reactivity of the various transition metal species. Theoretical treatments have shown that a metal center should become less electronegative with a decrease in valence,[8,9] and the stability of its organometallic compounds should also increase with decreasing electronegativity of the metal center.[10] Therefore, the most stable organotransition metal compounds should be those in the lowest valence states. The more polar character of the C–M bond in the low valence species may also be important in

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(1) This work was presented in part before the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13 to 18, 1958, Polymer Division.

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

(3) Soc. Chem. Ind., Reports on the Progress of Applied Chemistry, **42**, 436 (1957).

(4) F. A. Cotton, *Chem. Revs.*, **55**, 551 (1955).

(5) D. F. Herman and W. K. Nelson, THIS JOURNAL, **75**, 3877, 3882 (1953).

(6) Belgian Patent 553,477.

(7) (a) Belgian Patent 553,478; (b) C. Beermann and H. Bestian, *Angew. Chem.*, **71**, 618 (1959).

(8) M. Haissinsky, *J. Phys. Radium*, **7**, 7 (1946).

(9) T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).

(10) H. H. Jaffe and G. O. Doak, *ibid.*, **21**, 196 (1953).