boron trifluoride was condensed onto it. After mechanical mixing of the solid mixture it was allowed to warm up to −100° while the excess of boron trifluoride distilled off. In the mixture 0.1 mole of boron trifluoride remained (measured by weight absorbed). The homogeneous, yellow colored, crystalline complex of the mole ratio 1:1:1 was stable up to −50°. About −50° the complex decomposed without melting, while BF_3 was evolved and hydrogen fluoride and *m*-nitro-α,α,α-trifluorotoluene (b.p. 93–95° (35 mm.) were formed in almost quantitative yield.

(B) **Silver Tetrafluoroborate Method.**—One-tenth mole of anhydrous silver tetrafluoroborate was added to an excess of α,α,α-trifluorotoluene with efficient stirring. The stirred mixture was cooled to Dry Ice temperature and 8.15 g. (0.1 mole) of nitryl chloride added. Silver chloride was precipitated and a colored complex layer formed. After removing the silver halide the complex layer was separated. It was found to be identical to the complex formed by the fluoride method and decomposed in a similar way.

Preparation of the $ArHCHO^+BF_4^-$ Complexes with CO + HCl.—Two tenths mole of anhydrous silver tetrafluoroborate was added to an excess of alkylbenzene (toluene, *m*-xylene, mesitylene) with efficient stirring. The stirred mixture then was cooled (−20 to −80°) and a 1:1 ratio mixture of CO:HCl introduced until no more weight increase was observed. The amount of CO:HCl taken off was equimolar with the amount of silver tetrafluoroborate present in the system. Silver chloride was precipitated and a colored complex layer formed. The complex layer was separated after removing the silver halide. The complexes were found to be identical with those prepared from methylbenzenes with formyl fluoride and boron trifluoride and decomposed to the corresponding aldehydes in a similar way.

SARNIA, ONTARIO, CANADA

[CONTRIBUTION FROM RESEARCH LABORATORY, CELANESE CORPORATION OF AMERICA]

Polymerization of Ethylene with Titanium Tetrachloride–Aluminum Triisobutyl

BY ELMER J. BADIN

RECEIVED JUNE 30, 1958

An investigation has been made of the polymerization of ethylene, using titanium tetrachloride–aluminum triisobutyl catalyst, at atmospheric pressure and at 10–70°. Linear polyethylenes in the viscosity molecular weight region 3500 to 940,000 are formed. The molecular weight is decreased by raising the reaction temperature, increasing the ratio $TiCl_4$:$Al(i\text{-}C_4H_9)_3$ and increasing the quantity of catalyst. At a catalyst ratio of 2:1, a quantitative estimate of the apparent activation energy is 10 kcal. per mole.

Within recent years a considerable quantity of literature has appeared on olefin polymerization catalyzed by a mixture of a metal halide of a transition element (*e.g.*, titanium tetrachloride) and a metal alkyl. The unique feature of such a catalyst system is that polymerization to high molecular weight linear polymers may be carried out at atmospheric pressure and at relatively low temperature.

Earlier results contain information regarding polymerizations catalyzed by either of the two catalyst components. For example, polymerization of olefins such as isobutene was carried out[1,2] at low temperatures and atmospheric pressure by using titanium tetrachloride with traces of water or trichloroacetic acid as cocatalyst. Use of metal alkyls alone as polymerization catalyst for olefins at relatively low pressures also has been observed. Friedrich and Marvel[3] found that gaseous ethylene in contact with lithium butyl over a period of days resulted in formation of a solid polymer.

The use of the two component system, titanium tetrachloride–aluminum alkyl, was recorded by Ziegler.[4] Subsequent papers by Natta[5] and coworkers using a similar catalyst have reported results in which the study has been extended to olefins other than ethylene and the concept of regularity of structure has been introduced.

In this paper a brief summary is presented of some results dealing with the polymerization of ethylene, using titanium tetrachloride–aluminum triisobutyl catalyst, at atmospheric pressure and in the temperature range 10–70°.

Experimental

Experiments were carried out in one liter creased flasks equipped with gas inlet tube, thermometer, condenser and stainless steel stirrer. A high speed electric motor adjusted at about 8000 no load r.p.m. was used in all experiments. All glassware was cleaned and oven dried at 110° for at least 3 hours. No solvent other than water was used before drying. Prior to an experiment the flask was heated to 160° during which time a stream of prepurified nitrogen (Matheson Co.) passed through the apparatus. The flask then was allowed to cool to 30°. The solvent (400 ml. sodium-dried, distilled cyclohexane) was then added to the flask and stirred in a nitrogen atmosphere for 10 minutes.

Catalyst addition was made by pipetting in a solution of the aluminum triisobutyl (Hercules Powder Co.) (1.00 molar solution in cyclohexane) followed by addition of titanium tetrachloride (Matheson, Coleman and Bell Co.) (1.82 molar solution in cyclohexane). The aluminum triisobutyl analyzed for 14.0% aluminum and contained a small quantity (*ca.* 7% based on aluminum analysis) of aluminum diisobutyl hydride. Addition of titanium tetrachloride to aluminum triisobutyl led to formation of a finely divided black to brownish black precipitate and was accompanied by some heat evolution.

Immediately after addition of the two catalyst materials, the nitrogen was turned off and ethylene was introduced through a calibrated flowmeter. Pyrex capillary-type flowmeters (manometer fluid Silicone) were used. Addition of ethylene to the catalyst slurry led to heat evolution. In certain experiments without cooling baths this could account for a temperature rise of from 30 to 60° within a few minutes. Throughout an experiment temperatures were maintained to within ± 1° by means of ice-water or water-baths. Tank ethylene (Matheson, C.P. grade) was used without further purification.

At the end of each experiment 200 ml. of methanol containing 3% concentrated hydrochloric acid was added directly to the reaction flask. This was followed by filtration of the polymer, water washing and washing with dry methanol. In some cases washing of the polymer was carried out by vigorous stirring using a Waring Blendor. The polymer then was dried at a temperature below 100°.

Melting points were obtained using a Fisher–Johns ap-

(1) A. G. Evans, D. Holden, P. Plesch, M. Polanyi, H. A. Skinner and M. A. Weinberger, *Nature*, **157**, 102 (1946).

(2) M. Polanyi, *ibid.*, **157**, 520 (1946).

(3) M. E. P. Friedrich and C. S. Marvel, THIS JOURNAL, **52**, 376 (1930).

(4) K. Ziegler, Belgian Patent 533,362 (1953); K. Ziegler, Holzkamp and Briel, *Angew. Chem.*, **67**, 541 (1955).

(5) G. Natta, paper presented at meeting of Gesellschaft Deutscher Chemiker, Bad Nauheim, Germany, April, 1956.

TABLE I

ETHYLENE POLYMERIZATION

(Solvent, 400 ml. cyclohexane; ethylene rate, 1900 ml. per min.)

Temp. (°C.)	Reaction time (min.)	Catalyst			Polymer		
		$TiCl_4$ (mmole)	$Al(i\text{-}C_4H_9)_3$ (mmole)	$TiCl_4$: $Al(i\text{-}C_4H_9)_3$ ratio	Wt. (g.)	M.p. range (°C.)	Viscosity mol. wt.
Temperature:							
10	10	5	2.5	2	2.8	113–122	78,000
	20	5	2.5	2	5.2	120–127	77,000
30	10	5	2.5	2	10.3	125–130	47,000
	20	5	2.5	2	18.7	120–124	66,000
70	10	5	2.5	2	11.5	123–126	45,000
	20	5	2.5	2	21.0	124–126	55,000
Catalyst ratio:							
30	30	1	20	0.05	2.7	132–136	.....
	30	2	20	.10	4.8	132–136	.....
	30	3	20	.15	15.0	132–138	940,000
	30	4	20	.20	29.8	134–137	830,000
	30	6	20	.30	30.5	132–137	.....
	30	8	20	.40	34.9	137–142	620,000
	30	4	8	.50	26.0	134–137	528,000
	30	4	10	.40	28.5	132–137	600,000
	30	4	20	.20	29.8	134–137	830,000
Large quantities of catalyst:							
30	20	5	2.5	2	18.7	120–124	66,000
	20	10	5	2	35.9	121–127	71,000
	20	40	20	2	44.2 (1.7)[a]	118–123 (34–39)	13,000 (410)
	20	100	50	2	43.4 (3.8)	110–116 (45–64)	4,800 (470)
	20	200	100	2	34.6 (11.9)	100–113 (45–50)	3,500

[a] Figures in parentheses refer to a white, waxy, cyclohexane soluble polymer separate from the main portion.

paratus. The polymers in general had melting ranges in the region of 130°. They agreed well with the limiting value of 137°.[6]

Molecular weights were estimated from viscosities using a formula based on viscosity data for linear polyethylenes.[7] This formula supplies a viscosity average molecular weight which is closer in value to a weight average molecular weight than to a number average molecular weight. In place of intrinsic viscosity the quantity $\ln \eta_r/c$, measured in tetralin at 130°, was used. At concentrations of $c = 0.1$ to $c = 0.4$ g. per dl. the quantity $\ln \eta_r/c$ was essentially constant.

Polymer densities were obtained on pelletized samples of the polymer. They were measured in a pycnometer at 25° using 1-butanol as the liquid.

Results and Discussion

Some results obtained for the polymerization of ethylene are shown in Table I. Examination of the first set of these data shows that the rate of polymer formation with excess of ethylene is essentially linear during short reaction periods (approximately 30 minutes). This is further illustrated in Fig. 1 for polymerization at 10 and 30°. Although the rate is essentially linear in the first 30 or 40 minutes of reaction, the rate levels off after this period of time.

The second set of data in Table I shows a series of experiments in which the catalyst ratio is varied. Increase in the titanium tetrachloride concentration while maintaining the aluminum alkyl concentration constant leads to an increase in the rate of polymerization. Increase in the aluminum alkyl concentration while the titanium tetrachloride is held constant leads to no such pronounced effect. The conclusion is reached that, of the two catalyst components, titanium tetrachloride has the most pronounced effect on the reaction. It may be added that catalyst quantity limits and catalyst ratio ($TiCl_4:AlR_3$) limits existed within which polymerization rates were highest.

In the third set of data in Table I the effect on the reaction of the use of unusually large quantities of catalyst is shown. Here it may be seen that increase of catalyst quantity leads to formation of increasing amounts of a white, waxy cyclohexane soluble polymer of markedly lower molecular weight than the main portion of the polymer (which is essentially insoluble in all solvents at low temperatures).

It is also evident from Table I that the viscosity molecular weight is decreased by (a) raising the reaction temperature, (b) increasing the ratio $TiCl_4$: $Al(i\text{-}C_4H_9)_3$ and (c) increasing the quantity of catalyst.

A calculation of the apparent activation energy of the polymerization reaction has been made using a catalyst ratio of 2:1 ($TiCl_4:Al(i\text{-}C_4H_9)_3$). From Fig. 1 at 10° the slope of the line is 9.2 mmoles per minute. At 30° the slope is 31.1 mmoles per minute. Taking the ratio of these two values as equivalent to the ratio of the two rate constants, use of the Arrhenius equation leads to a value for the activation energy of 10.4 kcal. per mole. A check on this value is supplied by a series of independent experiments also at a catalyst ratio of 2:1. In this series, metered rates of ethylene were introduced

---

(6) See *e.g.* H. Mark, *J. Appl. Phys.*, **12**, 41 (1941).

(7) Tung, *J. Polymer Sci.*, XXIV, 333 (1957).

TABLE II

PHYSICAL PROPERTIES OF POLYETHYLENE

(Reaction conditions: temperature, 30°; solvent, 400 ml. cyclohexane; reaction time, 30 minutes; ethylene rate, 1900 ml./min.)

Catalyst			Polymer				Groups per 100 C atoms of polymer[a]		
$TiCl_4$ (mmole)	$Al(i\text{-}C_4H_9)_3$ (mmole)	$TiCl_4$: $Al(i\text{-}C_4H_9)_3$ ratio	Wt., g.	M.p. range (°C.)	Density at 25°	Viscosity mol. wt.	Vinyl (11.1 *M*)	Vinylidene (11.3 *M*)	Methyl (7.25 *M*)
2.5	10	0.25	40.7	127–133	0.96	.....	0.011	0.002	0.00
2.5	5	0.50	36.5	128–139	.96	.....	.009	.004	.00
2.5	2.5	1.0	28.6	123–129	.96	170,000	.012	.014	.13
2.5	2.5	1.0	30.1	127–132	.97	.....	.014	.014	.20
2.5	1.9	1.3	13.3	112–119	.97	92,000	.027	.041	.58
2.5	1.25	2.0	2.0	116–123		67,000	.040	.026	.47

[a] Infrared data obtained using a Perkin–Elmer instrument with 10-mil and 40-mil polyethylene discs.

into the reaction bulb. For a given catalyst concentration the rate of ethylene was increased until the point was reached at which all the ethylene introduced was not consumed to form polymer. Such a series of results is shown in Fig. 2. At 10° the point of deviation from this curve is 6.5 mmoles per minute and at 30° the point of deviation is 21 mmoles per minute. Here one arrives at a value of the apparent activation energy equivalent to 9.9 kcal. per mole. The two values obtained are in good agreement. It may be added that other experiments led to results in which the apparent activation energy decreased as the catalyst ratio ($TiCl_4$:$Al(i\text{-}C_4H_9)_3$) was changed from 1:1 where the maximum value of 13 kcal. per mole resulted. One explanation of this is that variation in the catalyst ratio may lead to changes in the catalyst nature; in addition the heat of adsorption of the monomer, if surface is involved, can cause variations in the apparent activation energy.

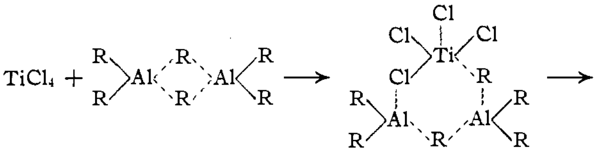
The over-all activation energy for this particular catalyst for the polymerization of ethylene has not previously been reported. Eirich and Mark[8] on the basis of theoretical considerations have predicted an over-all activation energy of between 8 and 12 kcal. per mole. The value obtained here falls within this region. Natta,[5] for propylene polymerization, has reported a value of 11 kcal. per mole. Later, using titanium trichloride–aluminum triethyl, a value of 12 to 14 kcal. per mole for the over-all process was obtained.[9]

In the present investigation it has been found that the polymer structure is to some extent dependent on the catalyst ratio, $TiCl_4$:$Al(i\text{-}C_4H_9)_3$. Infrared results regarding this are shown in Table II. Increase in the relative concentration of titanium tetrachloride leads to a polymer containing more methyl groups. To account for this the postulate has been made that small polymers (dimers, trimers, etc.) were formed and reincorporated into the main polymer chain.

As to the initiating species and the mechanism of the reaction the reduction of titanium tetrachloride by the metal alkyl is postulated as the first step in the reaction. This may be written as

$$TiCl_4 + AlR_3 \longrightarrow RTiCl_3 + AlR_2Cl \qquad (1)$$

Since the aluminum alkyl is known to exist in dimer form, the reaction may be more clearly written as



$$RTiCl_3 + AlR_2Cl + AlR_3 \qquad (2)$$

This is followed by the dissociation reaction

$$RTiCl_3 \longrightarrow R + TiCl_3 \qquad (3)$$

The radical R may then initiate the reaction. The titanium trichloride molecules, containing unpaired electrons, could function in aligning and activating the olefin molecules prior to polymerization. It would be expected that the internal diradical state of the reactive double-bond electrons would be induced. Reactions similar to (1), (2) and (3) could account for the results of Levy[10] in the reduction of

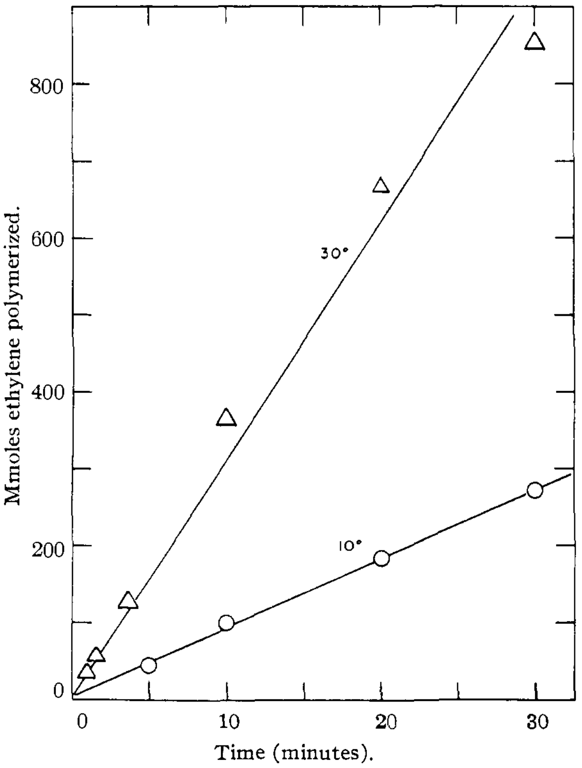


Fig. 1.—Ethylene polymerization; catalyst, 5 mmoles $TiCl_4$, 2.5 mmoles Al ($i\text{-}C_4H_9)_3$; ethylene rate, 1900 ml. per min.

---

[8] F. Eirich and H. Mark, "Kunstoffe-Plastics," Vol. III, No. 2, 1956, p. 136.

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

[10] L. Levy, *Ann. chim. phys.*, [6] **25**, 477 (1892).

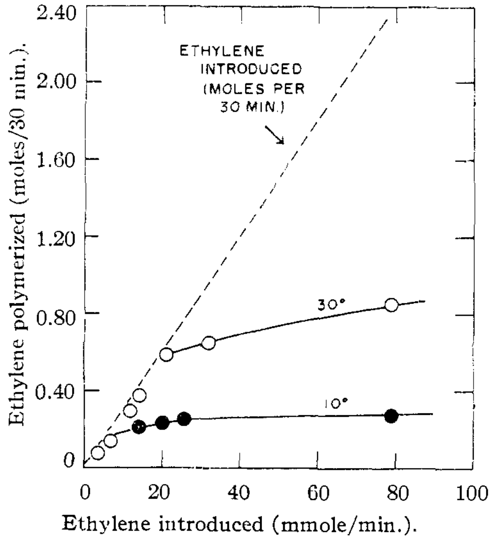


Fig. 2.—Polymer formation dependence on rate of ethylene introduction; catalyst, 5 mmoles $TiCl_4$, 2.5 mmoles $Al(i\text{-}C_4H_9)_3$.

titanium tetrachloride by mercury diethyl. It is also possible that formation of a species such as TiR_2Cl_2 might occur. Evidence for formation of Ti^{II} with excess of metal alkyl is supplied by Ludlum, Anderson and Ashby.[11] Their results show that maximum catalytic activity occurs when the average valence state of titanium is reduced to two. Friedlander[12] and Nenitzescu[13] have postulated reduction as in equation 1 followed by dissociation leading to initiation of the reaction. A summary of some of the mechanisms postulated is given by Curphey.[14]

Several remarks may be made regarding the dependence of the reaction on the olefin concentration and on the catalyst concentration. From Fig. 2 it may be seen that at low ethylene rates, before levelling off of the curve takes place, the rate of polymer formation is dependent on the rate (or concentration) of ethylene. For example, changing the ethylene rate from 8.3 to 16.6 mmoles per minute doubles the rate of polymer formation. Using the same procedure, the effect of doubling the catalyst concentration pointed to the fact that the catalyst concentration figures in the reaction to a power of less than one. However, this result was altered when catalyst components were allowed to react for 30 minutes prior to admission of ethylene. Under these circumstances the rate of polymer formation was found to be more nearly dependent on the first power of the titanium tetrachloride concentration. This points to the probability that an unusual type of termination step is involved in the reaction.

Additional evidence that titanium tetrachloride may be considered as the initiator is shown by separate data obtained using titanium tetrachloride–lithium phenyl catalyst. Here the reactions involving catalyst formation are probably

$$TiCl_4 + LiPh \longrightarrow PhTiCl_3 + LiCl \qquad (4)$$

and

$$PhTiCl_3 \longrightarrow Ph + TiCl_3 \qquad (5)$$

If the material $PhTiCl_3$ is formed and reaction initiated by the phenyl group, the phenyl group might be expected to appear in the polymer formed. A series of experiments was carried out at slightly elevated pressure (250 pounds per square inch), at room temperature and using the solvent cyclohexane. The lithium phenyl concentration was held constant at 20 mmoles and the titanium tetrachloride concentration varied from a molar ratio, $TiCl_4$: LiPh, of 0.25 to 1.00. Infrared data on the polyethylenes formed in this series showed about a fourfold increase in phenyl content (from 0.011 to 0.04 phenyl groups per 100 carbon atoms) as the titanium tetrachloride concentration was increased by a factor of four. Although incorporation in the polymer molecule of groups from the metal alkyl previously has been reported,[5,15] results obtained supply initial information relating such observations to the concentration of the transition element compound rather than to the organometallic compound. It is thus concluded that the scheme proposed[16] for olefin polymerization postulating continuous interposition of the olefin at an Al–C bond is not justified.

Brief mention may be made of inhibition of the reaction. Preliminary experiments showed that the catalyst slurry was affected by addition of practically any reagent. Several of these (*e.g.*, ethanol, di-*t*-butyl peroxide, selenium oxychloride and chlorodifluoroacetic acid) destroyed the catalyst slurry leaving a clear solution. Other materials (*e.g.*, triethylamine) added in small quantities affected the catalyst slurry in such a way that it could still be used as a catalyst for ethylene polymerization. The polymerization with larger concentrations, however, was strongly inhibited.

SUMMIT, NEW JERSEY

---

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

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

[13] C. D. Nenitzescu, G. Huch and A. Huch, *Angew. Chem.*, **68**, 438 (1956).

[14] E. G. Curphey, *British Plastics*, **30**, 486 (1957).

[15] See *e.g.* G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *J. Poly. Sci.*, **26**, 120 (1957).

[16] See *e.g.* R. A. V. Raff and J. B. Allison, "Polyethylene," Interscience Publishing Co., New York, N. Y., 1956, p. 79.