225. *Polymerizations of Ethylene in the Presence of Titanium Tetrachloride and Certain Metal Alkyls.*

By J. C. McGowan and B. M. Ford.

Ethylene has been polymerized at 30° by means of catalysts consisting of titanium tetrachloride with an excess of either butyl-lithium or dibutylzinc. The rates of polymerization varied as the squares of the ethylene pressures: in general, they were proportional to the amount of titanium tetrachloride and independent of the amount or the nature of the metal alkyl, but when small quantities of titanium tetrachloride were used, a large excess of dibutylzinc appeared to retard the polymerization.

The discovery[1] that, in the presence of certain catalysts, ethylene and a number of other olefins can be polymerized at low pressures is of great interest. Catalysts can be prepared from certain metal alkyls and some compounds containing elements of the fourth, fifth, and sixth sub-groups of the Periodic System. Some measurements of the rates of polymerization of olefins at constant pressures in the presence of these catalysts have been reported by Natta and his co-workers[2,3] but, apart from this, the kinetics of the polymerizations have received very little attention. The measurements, reported below, for rates of ethylene polymerizations in the presence of titanium tetrachloride and either butyl-lithium or dibutylzinc are therefore of interest.

Experimental

The apparatus (Fig. 1) consisted of a glass reservoir which, at the start of each experiment, was filled with dry purified ethylene at pressure a little above atmospheric, and to which a mercury manometer was fitted. The reaction was carried out in a flask (1 l. capacity) fitted with a special stirrer, which was capable of speeds up to 2500 r.p.m. and was fitted with Neoprene oil seals so that a vacuum could be maintained with the stirrer running. A stoppered funnel with a system of taps was provided so that a liquid could be introduced into the flask; the flask could be either evacuated or filled with oxygen-free nitrogen; and the ethylene in the reservoir could be connected to the flask. The whole apparatus was kept in an air thermostat at 30°.

The titanium tetrachloride was dissolved in *n*-decane and placed in the reaction flask, which was then evacuated and swept out with the nitrogen several times. Then a solution of the metal alkyl in *n*-decane was sucked in from the funnel where it had previously been stored under nitrogen, and the flask evacuated. The vacuum was next shut off, the flask connected to the ethylene reservoir, the stirrer started, and the pressure (p) read on the manometer after

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[1] Ziegler, Holzkamp, Breil, and Martin, *Angew. Chem.*, 1955, **67**, 541.
[2] Natta, *Chem. and Ind.*, 1957, 296.
[3] Natta, Pasquon, and Giachetti, *Angew. Chem.*, 1957, **69**, 213.

various times (t). The reaction was carried out at constant volume (7·37 l.) and the total amount of *n*-decane, which was carefully dried and fractionated beforehand, was arranged so that the volume of the mixture in the flask at the beginning of the reaction was 100 c.c. It was found that the rate of uptake of ethylene increased with the speed of the stirrer up to a certain speed (about 280 r.p.m. for the fastest reactions) and was independent of the speed above this. In the experiments reported below the stirring speed was 560 r.p.m.

The results of some experiments are shown in Fig. 2 and it will be seen that straight lines are obtained when $1/p$ is plotted against t unless oxygen is present in the ethylene. The rate of polymerization is therefore bimolecular with respect to ethylene, for if p is the partial pressure of ethylene, for a bimolecular reaction, $-\mathrm{d}p/\mathrm{d}t = kp^2$ and so

FIG. 1.

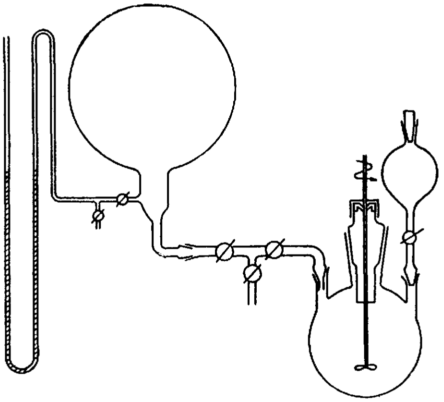
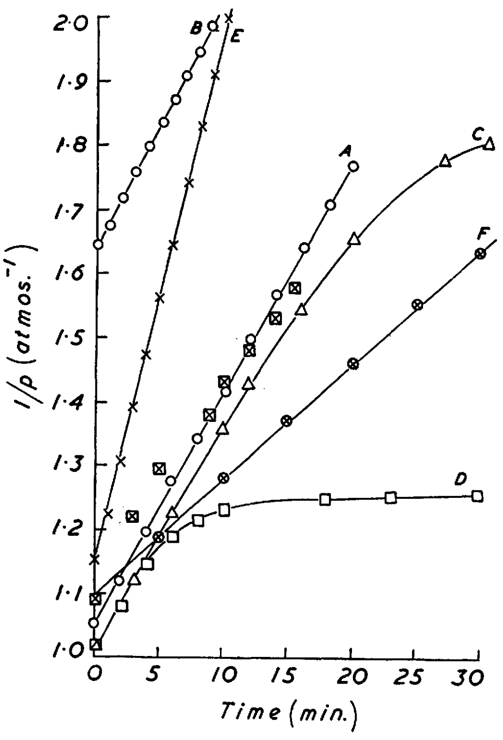


FIG. 2.



$$k(t_B - t_A) = 1/p_B - 1/p_A$$

In experiments with butyl-lithium, 0·02 mole of this and 0·005 mole of titanium tetrachloride were taken in each case. When dibutylzinc was used, the amounts of the metal alkyl and titanium tetrachloride were varied. It was found that, in general, the slopes of these lines were independent of the amount of dibutylzinc (provided an excess was used) and were proportional to the amount of titanium tetrachloride, so that

$$k^1(t_B - t_A) \times \text{moles of } TiCl_4 = 1/p_B - 1/p_A$$

Values of k^1 are given below (in atm.$^{-1}$ mole^{-1} min.$^{-1}$) and refer to reactions in 100 c.c. of *n*-decane.

It is of interest that this relation holds for the experiments with titanium tetrachloride and butyl-lithium. It seems therefore that the rate of polymerization is proportional to the product of the square of the ethylene concentration and to the amount of titanium tetrachloride taken and is independent of the nature and quantity of metal alkyl, provided this is in excess. When the molar ratio of $TiCl_4 : ZnBu_2$ exceeded 1, the polymerization was usually very rapid at first but soon slowed almost to a stop; the effect was rather like that found with oxygen in the ethylene. In fact, the effect of oxygen is probably merely to use up the excess of metal alkyl.

After the polymerization had proceeded for a time, the flask containing the polymer was opened and a stream of air was passed through its contents for 15 min. The solid was then filtered off and air was sucked through it for 10 min. After this, the solid was well washed successively with hydrochloric acid, water, methanol, and ether and dried at 60° under vacuum. One g. was dissolved in boiling toluene, and the hot solution filtered through steel gauze. The solution was stored for 24 hr. and the polymer which had separated was filtered off on sintered glass and dried under high vacuum in a vessel with a jacket containing boiling toluene. The molecular weight of the polymer from experiment B141/88, from which curve *E* was drawn, is given and discussed in a paper by Smith.[4] Some other values for the intrinsic viscosities (η) of the polymers made with titanium tetrachloride and dibutylzinc are given below. Provided an excess of dibutylzinc was used, the molecular weights of the products did not seem to vary much or to depend on any of the more obvious possible factors.

The curve *A* in Fig. 2 is for an experiment ($k^1 = 7{\cdot}8$) with butyl-lithium and titanium tetrachloride. Curve *B* is for a similar experiment ($k^1 = 7{\cdot}5$) started at a reduced pressure of ethylene, and the results confirmed the bimolecular law. It was found, in fact, that the rate of polymerization varies as the square of the ethylene pressure over the range 0·2—1 atm. Experiments carried out with small amounts of oxygen in the ethylene show that the reaction proceeds at much the same rate as without oxygen for a time and thereafter stops quite suddenly. The curve *C* was obtained with 0·36% by volume of oxygen in the ethylene, and curve *D* with 1·38%.

When the same amount of titanium tetrachloride (0·005 mole) was again taken but with 0·04 mole of dibutylzinc, the points fell close to curve *A* and k^1 was 6·6. A similar rate ($k^1 = 7{\cdot}0$ and $\eta = 1{\cdot}35$) was found with 0·005 mole of titanium tetrachloride and a quarter of the amount of dibutylzinc (0·01 mole). Curve *E* shows the effect on the rate ($k^1 = 8{\cdot}8$ and $\eta = 2{\cdot}55$) of double the concentration of titanium tetrachloride, and curve *F* the effect on the rate ($k^1 = 8{\cdot}0$ and $\eta = 1{\cdot}69$) at half the concentration; in both experiments 0·01 mole of dibutylzinc was taken.

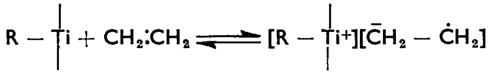
The above relation between pressure, time, and amount of titanium tetrachloride did not hold for experiments with small amounts of titanium tetrachloride (0·0025 mole) and relatively large amounts of dibutylzinc (0·2—0·4 mole). In these experiments, the excess of dibutylzinc appeared to be inhibiting the reaction and

$$0{\cdot}075(t_B - t_A) \times \text{moles of } TiCl_4/\text{moles of } ZnBu_2 = 1/p_B - 1/p_A$$

It is of interest that for $ZnBu_2 = 0{\cdot}01$ mole, this expression equals the one above with $k^1 = 7{\cdot}5$.

Discussion

The polymerization of olefins in the presence of Ziegler's and related catalysts has been reviewed by Eirich and Mark,[5] who make a number of suggestions concerning the mechanism, one of which is that, in the presence of a strong reducing agent, metal alkyl compounds may be formed with monomer. It is well known that olefins can react with " Lewis acids " and it has also been suggested by Nash [6] that certain olefins can react with " Lewis bases " (*i.e.*, they can acquire electrons from reducing agents). The polymerizations described above were carried out in the presence of excess of the metal alkyl which is a very strong reducing agent. The formation of a complex by the transfer of an electron from a tervalent alkyl titanium derivative to ethylene might be one stage in the polymerization:



$$R - \overset{|}{\underset{|}{Ti}} + CH_2{:}CH_2 \rightleftharpoons [R - \overset{|}{\underset{|}{Ti}}{}^+][\bar{C}H_2 - \dot{C}H_2] \quad (I)$$

The complex might resemble the structures suggested by Nash, in which the negative charge and free valency are equally shared by the two carbon atoms of the ethylene, or it

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[4] Smith, *J. Polymer Sci.*, 1956, **21**, 563.
[5] Eirich and Mark, *J. Colloid Sci.*, 1956, **11**, 748.
[6] Nash, *Nature*, 1957, **179**, 868.

might have at least some covalent character and approach the structure of the metal alkyl compound suggested by Eirich and Mark. The titanium in the complex is quadrivalent, and if another electron were to be given up by the complex to an ethylene molecule one of the groups attached to the titanium atom would have to be split off, since compounds of quinquevalent titanium are not known. The carbon–titanium bond is a weak one and is the likely bond to split. The following reaction suggests a possible mechanism for the polymerization:

$$[\mathrm{R}-\overset{|}{\underset{|}{\mathrm{Ti}}}{}^{+}][\bar{\mathrm{C}}\mathrm{H}_2-\dot{\mathrm{C}}\mathrm{H}_2]+\mathrm{CH}_2{:}\mathrm{CH}_2 \rightleftharpoons \mathrm{R}^{+}[\overset{|}{\underset{|}{\mathrm{Ti}}}{}^{+}][\bar{\mathrm{C}}\mathrm{H}_2-\dot{\mathrm{C}}\mathrm{H}_2]_2 \longrightarrow [\mathrm{R{\cdot}CH_2{\cdot}CH_2}-\overset{|}{\underset{|}{\mathrm{Ti}}}{}^{+}][\bar{\mathrm{C}}\mathrm{H}_2-\dot{\mathrm{C}}\mathrm{H}_2] \qquad \text{(II)}$$

The overall rate of the polymerization consisting of reactions (I) and (II) can be proportional to the amount of titanium available and to the square of the ethylene pressure provided the equilibria are quickly established and the conversion of titanium tetrachloride into the alkyl(*i.e.*, butyl)titanium derivative is complete when there is an excess of metal alkyl.

In most cases the polymerizations seemed to be independent of the concentration of dibutylzinc used but with small quantities of titanium and large amounts of dibutylzinc, the rate seems to be inversely proportional to it. It may be that the tervalent alkyltitanium compound can combine reversibly with metal alkyl to form a bivalent dialkyltitanium derivative devoid of catalytic activity:

$$\mathrm{R}-\overset{|}{\underset{|}{\mathrm{Ti}}}+\mathrm{R}^{-} \rightleftharpoons \mathrm{R}-\overset{|}{\underset{|}{\mathrm{Ti}}}{}^{-}-\mathrm{R} \qquad \text{(III)}$$

Some reaction kinetics which differ from those reported above have been mentioned by Natta,[2,3] who, however, emphasizes that his catalysts differ from ordinary Ziegler catalysts. Whereas a large number of the latter are suitable for polymerization of ethylene, only a limited number are suitable for the polymerizations of higher α-olefins, and even fewer give high yields of crystalline isotactic polymers. The useful stereospecific catalysts are completely heterogeneous and must be coarsely crystalline. It is also essential that the compound of titanium (or vanadium) should be in its lower valency state before it is mixed with the metal alkyl. The polymerizations described in the experimental section were carried out under conditions far removed from those laid down by Natta. The titanium was added in the quadrivalent state, the solid precipitated was amorphous, and the reaction may have been partly homogeneous. With a stereospecific catalyst, Natta states that the rate of polymerization is proportional to the surface area of the catalyst and to the concentration of monomer: it is independent of the concentration of metal alkyl provided this is above a certain value. In order to explain these results reported by Natta, it is only necessary to assume that the titanium on the surface of the stereospecific catalysts is so very reactive towards ethylene that, after the induction period which Natta observed, reaction (I) is complete. Reaction (III) will not then occur. The rate of polymerization will be controlled by reaction (II) and will be proportional to the product of the ethylene pressure and quantity of available titanium.

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