MACROPOLYMERIZATION OF ETHYLENE. I.

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I. Introduction.

The polymerization of ethylene in the gaseous phase has been studied by many investigators[1–16], at elevated pressures as well as at the atomospheric pressure. They have reported that at the reaction temperature higher than 350°C a considerable amount of liquid products is formed besides the gaseous hydrocarbons, such as propylene and butylene. Further it has also been found that in this reaction a small amount of oxygen acts as a catalyser[5,9,13], the reaction is of the 2nd order[7,12,15,16] (a different result has also been reported)[13], and when the oxygen content, the pressure of the temperature exceed certain limits the reaction becomes explosive, resulting a decomposition of ethylene into carbon and hydrogen.

Now, in the latest patents[17,18] it is described that, when the ethylene is polymerized at extremely high pressures, such as 1500–3000 atm., the tough and high melting paraffin called polyethylene is obtained as the product.

In the present paper some experimental results regarding the macropolymerization of ethylene will be reported.

II. Apparatus and experimental procedure.

Ethylene was prepared by the dehydration of ethylalcohol using almina as catalyst and it was refined. Its average composition was as follows:

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2) E. N. Hague & R. V. Wheeler, *J. Chem. Soc.*, **131**, 378 (1929).
3) R. N. Pease, *J. Am. Chem. Soc.*, **52**, 1158 (1930).
4) E. Berl and W. Frost, *Z. angw. chem.*, **44**, 193 (1931).
5) A. E. Dunstan, E. N. Hague and R. V. Wheeler, *J. Soc. Chem. Ind.*, **50**, 313T (1931).
6) H. I. Waterman and A. J. Tulleners, *J. Inst. Pet. Tech.*, **17**, 506 (1931).
7) R. N. Pease, *J. Am. Chem. Soc.*, **53**, 613 (1931).
8) S. Lehner, *J. Am. Chem. Soc.*, **53**, 3737 (1931).
9) S. Lehner, *J. Am. Chem. Soc.*, **53**, 3752 (1931).
10) A. E. Dunstan, E. N. Hague and R. V. Wheeler, *J. Soc. Chem. Ind.*, **51**, 131T (1932).
11) G. Egloff and R. E. Schaad, *J. Inst. Pet. Tech.*, **19**, 800 (1933).
12) M. V. Krauze, M. S. Nemtzov and E. A. Soskina, *C.R.* (*U.R.S.S.*) **2**, 301 (1934), *C. A.* 5320^{9} (1934).
13) H. H. Storch, *J. Am. Chem. Soc.*, **56**, 374, (1934).
14) M. V. Krauze, M. S. Nemtzov and E. A. Soskina, *J. Gen. Chem.* (*U.R.S.S.*) **5**, 343 (1935), *C.A.* 6204^{9} (1935).
15) H. H. Storch, *J. Am. Chem. Soc.*, **57**, 2598 (1935).
16) F. P. Jahn, *J. Am. Chem. Soc.*, **61**, 798 (1939).
17) E. W. Fawcett, R. O. Gibson and M. W. Perrin, *U.S. Pat.*, 2,153,553 (1939).
18) M. W. Perrin, J. G. Peton and E. G. Wicliams, *U.S. Pat.*, 2,188,465 (1940).

C_2H_4 : 98.87, O_2 : 0.16, CO : 0.53, N_2 : 0.44.

The autoclave of 12 m/m internal diameter and of 40 cc. capacity was heated externally. Ethylene was compressed in it at room or lower temperature, and then the temperature of the autoclave was gradually raised. The reaction velocity is determined by the decrease of the pressure at a fixed temperature. The products were drawn out, at room temperature, after the reaction and then weighed. They were white and powder-like. The melting points of them were determined by the conventional method. The molecular weights were calculated from the viscosity of their solution in tetraline at 75°C according to the formula:

$$\lim_{c \to 0} \frac{\eta_{sp}}{c_{gm}} = 0.93 \times 10^{-4} M.$$

III. Experimental results.

1) *The behaviour of the reaction and its velocity.*

Fig. 1 represents an example of the pressure change during the polymerization. Similar curves were obtained in all experiments. Plotting $\frac{1}{p} - \frac{1}{p_0}$ against the reaction time t (in minuite), straight lines are obtained, as shown in the same figure, where p and p_0 represent the pressures at the beginning of the reaction and the time t respectively. This indicates that the reaction is to be of the second order. The velocity constant k is calculated using the equation $\frac{1}{p} - \frac{1}{p_0} = kt.$

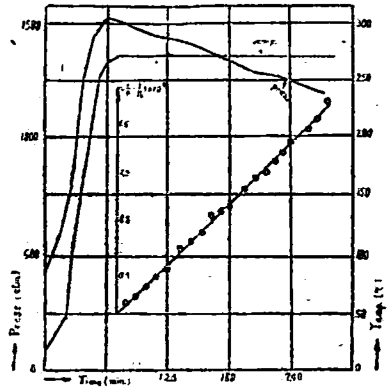

Fig. 1. Change of temperature and pressure during the reaction.

Table I. Influence of the reaction temperatures.

Run No.	Highest pressure (atm.)	Reaction temp. (°C)	Velocity constant $k \times 10^5$ (atm.$^{-1}$ min.$^{-1}$)	Melting point of the products (°C)	Moleculur Weight of the products
B-20	1480	260	0.53	97-102	10,200
B-15	1475	270	0.95	91-104	20,400
B-16	1490	„	0.87	95-102	11,300
B-21	1535	„	0.86	103-106	11,200
B-25*	1585	„	0.88	104.5-106.5	—
B-17	1375	280	2.24	89- 92	8,300
B-18	1460	„	2.22	95-100	8,200
B-19	1430	285	2.92	85- 91	6,400

* Autoclave was filled with the lathe wastes of its material.

2) *The reproducibility and homogeneity of the reaction.*

Table I shows the influence of the temperature on the reaction. The 4th column of it gives the constants of the reaction velocity evaluated as above.

The fact that various experiments at the same temperature and the same pressure give similar velocity constants, as seen in this table, seems to indicate that the reaction is sufficiently reproducible. The molecular weight of the product in the experiment B–15 is larger than that of the other in the similar experiments. This may be attributed to extraordinarily gradual heating in this experiment. This view can also be justified by the other experiments.

In order to know the effect of wall on the reaction, in the experiment B–25 the autoclave was filled with 24.5 gr. of the lathe waste of the same material as the reaction vessel, so that the surface area in the autoclave was increased 3.5 times as large. In this experiment any appreciable influence could not be found in the reaction velocity as compared with those in the autoclave without the lathe waste (B–15, B–16, B–21). We can conclude from this experiment the homogeneity of the reaction quite definitely. The same conclusion was obtained by M. V. Krauze and others[12] in the experiments at the temperatures of 315°C–380°C.

3) *The influence of the temperature.*

As is seen in Table I, the reaction is accelerated as the temperature is raised. The relation between $\frac{1}{p}-\frac{1}{p_0}$ and t is also represented by a straight line at different temperatures as Fig. 2 shows. This verifies that the reaction is of the 2nd order likewise at various temperatures under the present conditions of experiment. In Fig. 3 the logarithms of the velocity constants, $\log k$, are plotted against the reciprocals of the absolute temperature, $\frac{1}{T}$. From this curve the activation

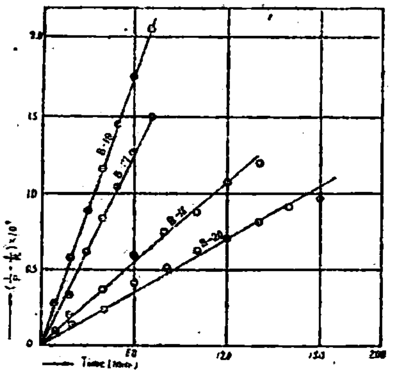

Fig. 2.
Influence of the reaction temperature.

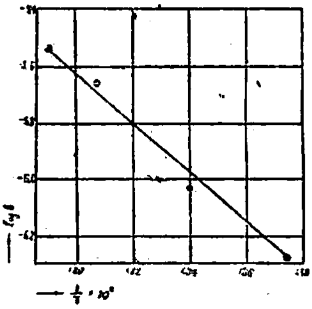

Fig. 3.
Relation between log k and $\frac{1}{T}$.

energy is evaluated as 40,000 cals.

The reaction product of the largest molecular weight was obtained at a temperature of 270°C.

4) *The influence of the pressure.*

Dunstan and his co-workers[19] found that the increase of the pressure has the effect to lower the temperature of the polymerization. The same fact is described in the patents.[17,18]

Table 2. Influence of the pressure.

Run No.	Highest pressure (atm.)	Reaction temp. (°C)	Melting point of the products (°C)	Molecular weight of the product
B-23	1845	270	103-108	16,300
B-26	1665	"	94-99	8,800
B-21	1535	"	103-106	11,200
B-24	1265	"	91-97	11,800

Table 3. Velocity constonts of the reaction of Table 2.

Run No.	Press. range (atm.)	React. time (min.)	Velocity const. $k\times10^6$	Press. range (atm.)	React. time (min.)	Velocity const. $k\times10^6$	Press. range (atm.)	React. time (min.)	Velocity const. $k\times10^6$
B-23	1845 →1500	0→80	1.46						
B-26	1660 →1260	0→130	1.46	1260 →1000	130 →300	0.92			
B-21				1530 →1200	0→120	0.86			
B-24				1265 →1100	0→120	0.87	1100 →1000	120 →130	0.56

As we have seen in 3) of this paper, the reaction velocity can be represented by the equation of the 2nd order reaction, in the pressure range of 1500–1200 atm. In order to examine the applicability of the equation to wider range of pressure the experiments shown in Table 2 were carried out. The relations between $\frac{1}{p}-\frac{1}{p_0}$ and t of these experiments were plotted in Fig. 4.

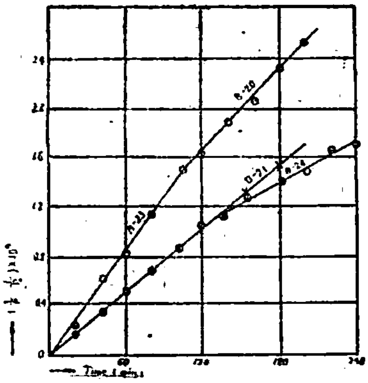

Fig. 4. Influence of the pressure.

It can be found that the relation between $\frac{1}{p}-\frac{1}{p_0}$ and t can not, in any of those experi-

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[19] A. F. Dunstan, E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 26, 309 (1934).

ments, be represented by a single straight line, but by a broken one consisting of two or three straight lines. This shows that reaction constant becomes suddenly smaller in the course of polymerization, although the second order equation holds in each instant during the reaction. Thus, in an extreme case, the three stages of the different second order reaction are observed in an experiment as shown in Table 3. Although the reaction constants of different experiments are found to coincide pretty well each other, they have not always the same value in the same pressure range. The lapse of time from the beginning of the reaction seems to play some roles for sudden change of the velocity, so that this reaction can not be simply interpreted as a simple second order chemical reaction.

It may be found from Table 2 that the molecular weight of product is increased with increasing pressure.

5) *The influence of oxygen.*

As mentioned in the beginning of the present paper, many investigators found that oxygen has a catalytic action even in its small amount. Especially S. Lenher[7] assumed that the first step of polymerization is the reaction between ethylene and oxygen. In the patent description[17,18] it is also found that, as the oxygen content is increased, the reaction temperature becomes lower. The present experiments in which the oxygen content in ethylene was gradually increased gave an unexpected result, as shown in Table 4, that the reaction velocity was decreased with increasing oxygen content. The molecular weights of products seem to become larger as oxygen content is increased.

Table 4. Influence of oxygen.

Run No.	Oxygen content (%)	Highest pressure (atm.)	Reaction temp. (°C)	Velocity constant $k\times10^6$ (atm.$^{-1}$ min.$^{-1}$)	Melting point of the products (°C)	Molecular weight of the products
B-27	0.30	1530	250	0.53	105-113	22,400
B-28	0.35	1530	250	0.48	100-109	20,400
B-29	0.45	1525	250	0.22	98-109	21,400
B-30	0.65	1565	250	0.27	95-103	—

Discussion.

1) According to our experimental results, the polymerization of ethylene at pressures of 1000-1800 atm. and temperatures of 260°C-285°C seems to be a homogeneous reaction of the 2nd order, the activation energy of which is 40,000 cals. However, as the velocity constant decreases in case of very high pressure stepwise in the course of the reaction, it cannot be concluded simply that the

reaction is a real bimolecular one.

The reason why three stages appear in the reaction velocity may be, on one hand, the deviation of the ethylene from the ideal gas, though the reaction proceeds really homogeneous and bimolecular, as the deviation must be eminent under such a condition of the pressure as applied in our experiment. On the other hand, it may be attributed to some complicated chemical circumstances, such as disappearance of some catalytic substances present in a small quantity. In our present situation it is not possible to decide which assumption is more plausible.

At any rate it may be convenient, at least for the practical purpose, to represent our experimental results by the second order equation.

Pease[7] found that the polymerization of ethylene at a pressure of 10 atm. and temperatures of 350–355°C is a second order reaction, whose activation energy is 35,000 cals, and its steric factor is $\frac{1}{2000}$, while F. P. Jahn[16] calculated the velocity constant of the reaction from the theory of the absolute reaction rate, obtaining the same value as Pease's results, and he explained successfully the smallness of its steric factor. Calculating the reaction constant under our experimental conditions by Jahn's formula, we find that the theoretical values are in complete agreement with our experimental results as shown in Table 5.

Table 5. Calculatedand experimental values of the reaction constant.

Run No.	Velocity constant $k \times 10^6$ (atm.$^{-1}$ min.$^{-1}$)		Reaction temp. (°C)
	cal. value by Jahn's formulae	experimental value	
B-20	1.04	0.53	260
B-16	1.90	0.87	270
B-18	3.40	2.22	280
B-19	4.50	2.92	285

Jahn's formula was derived on the assumption that two etylene molecules polymerize to butylene. The products of our experiments are of the molecular weight 8,000–20,000, or the polymers of 300–7000 ethylene molecules. The results of the calculation according to Jahn's formula should, therefore, be multipled by 150–350. Thus the agreement between the theory and the experimental results given in Table 5 is to be interpleted as it reveals contradiction of the theory to the experiments.

2) If this reaction proceeds actually by a bimolecular mechanism, it may be explained as follows. Assume that, as the first process, the collision of two

ethylene molecules forms an activated ethylene, which grows, by the collision with ethylene molecules step by step into a higher polymer sustaining activated state, until it is deactivated by the collision with an ethylene molecule resulting a normal polymer. Then the velocity of chain intiation is given by k_1c^2, where k_1 is the velocity constant of the chain initiation and c is the concentration of ethylene. The deactivation velocity of activated molecule is given by k_3ca, where k_3 is the reaction constant of the deactivation, and a is the concentration of the activated molecules.

At the steady state will be

$$k_1c^2 = k_3ca \tag{1}$$

The final reaction velocity $-\frac{dc}{dt}$ is given by the velocity, with which the activated molecule reacts with the normal ethylene:

$$-\frac{dc}{dt} = k_2ca \tag{2}$$

where k_2 is the velocity constant of the chain growth of the activated molecule.

From (1) and (2) we obtain

$$-\frac{dc}{dt} = \frac{k_1k_2}{k_3}c^2$$

This shows that the polymerization is the reaction of the second order.

Further, the average polymerization-degree can be calculated, in this case, as the quotient of the final reaction velocity divided by the velocity of the chain initiation as follows:

$$\frac{k_1k_2}{k_3}c^2 \div k_1c^2 = \frac{k_2}{k_3}$$

3) As regard the effect of the oxygen content our results, showing a decrease of the reaction velocity in its presence, contradict with the results of the former investigators. This seems to require detailed studies.

V. Summary.

1) The macropolymerization of ethylene is studied under the conditions of the temperature range 250–285°C and the pressure range 1800–1000 atm.

2) It is found that, within a certain pressure range this reaction proceeds apparently according to the equation of the 2nd order reaction.

3) The oxygen content in ethylene is found to decrease the reaction velocity.

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