Polymerisation of Dissolved Acrylonitrile in the Presence of Ferric Ions and Hydrogene Peroxide Inhibition by Oxygen

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ÖZET. — Akilonitrilin Fe^{+++} iyonları ve H_2O_2 karşısındaki polimerizasyonuna karıştırmanın ve oksijenin tesiri (küçük pH larda ve 25° C de) incelendi.

Karıştırmanın akrilonitril polimerizasyonuna çok tesir ettiği ve hızını azalttığı müşahede edilerek bunun sebebi araştırıldı.

Reaksiyon, 1 — Karıştırarak 2 — Karıştırmıyarak 3 — Hava muvacehesinde ve 4 — Oksijen ihtiva eden azot gazı muvacehesinde olmak üzere dört muhtelif şekilde cereyan ettirildi, her defasında polimerizasyon hızı tayin edildi.

Karıştırmanın tesirinin oksijen gazının tesiriyle münasebette olduğu, çözelti karıştırıldığı zaman ($Fe^{+++} + H_2O_2$) katalozör sistemi vasıtasiyle meydana gelen radikallerin (veya aktif merkezlerin) daha büyük bir oranda bozulduğu ve bu bozulmanın oksijen gazı tarafından yapıldığı kanaatine varıldı :

Çözelti karıştırılınca oksijen molekülleri ile çözeltideki serbest radikaller daha çok temasa gelmekte ve polimerizasyonu temin edecek olan radikalleri tesirsiz bir hale getirmektedir.

Bu çalışmada kullanılan şartlar sınırı içinde, polimerizasyon hızı, monomerin ve katalizör maddelerin konsantrasyonları arttıkça büyümekte, ayrıca H^+ iyonları konsantrasyonu arttıkça da küçülmektedir.

Introduction.

In this paper the polymerisation of Acrylonitrile in water solution in the presence of ferric ions and hydrogen peroxide (at 25°C and small pH's) was considered and the inhibition - retardation influence of oxygen investigated.

The decomposition of hydrogen peroxide with Fe^{+++} and Fe^{++} ions has been studied experimentally and also theoretically by many authors and different reaction schemes have been given for this decomposition. The review of the reaction between Fe^{++} and H_2O_2 is given by Medalia and Kolthoff (J. Polymer Sc. 4,377, 1949) and in this work reference to older litterature may be found.

Originally Haber and Willstätter[1] proposer the chain reaction scheme which goes over OH and HO_2 radicals:

$$Fe^{+++} + H_2O_2 \rightarrow Fe^{++} + H^+ + HO_2 \quad (1)$$
$$HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH \quad (2)$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (3)$$
$$Fe^{++} + OH \rightarrow Fe^{+++} + OH^- \quad (4)$$

The logical extension of the Haber and Willstätter scheme for $Fe^{++} — H_2O_2$ reaction was given by Haber and Weiss[2] and the main reactions are assumed to be:

$$Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + OH + OH^- \quad (5)$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (6)$$
$$HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH \quad (7)$$
$$Fe^{++} + OH \rightarrow Fe^{+++} + OH^- \quad (8)$$

These two reaction schemes are very similar, the difference being only in their chain initiation reactions. The other steps such as the chain propagation and chain breaking reactions are the same.

The very important role of the free radical OH in chain reactions and polymerisation reactions is commonly accepted. [3, 4, 5, 6] There are however no experiments except that of Parts[7] showing the polymerisation of dissolved monomers in a system containing besides hydrogen peroxide only Fe^{+++} ions.

Baxendale, Evans and Park[8] investigated the poly merisation acrylonitrile, methyl methacrylate, methacrylic acid, methyl acrylate and styrene in the presence of ferrous ions and hydrogen peroxide. They have accepted the following reaction mechanism :

$$\mathrm{Fe}^{++} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe}^{+++} + \mathrm{OH}^{-} + \mathrm{OH} \qquad \text{(I)}$$

$$\mathrm{HO} + \mathrm{Fe}^{++} \rightarrow \mathrm{HO}^{-} + \mathrm{Fe}^{+++} \qquad \text{(II)}$$

$$\mathrm{HO} + \mathrm{M} \rightarrow \mathrm{HOM} \qquad \text{(III)}$$

$$\mathrm{HOM} + \mathrm{M} \rightarrow \mathrm{HOMM} \qquad \text{(IV)}$$

$$\mathrm{HO(M)}_n + \mathrm{M} \rightarrow \mathrm{HO(M)}_{n+1} \qquad \text{(IV)}$$

$$\mathrm{HO(M)}_n + \mathrm{(M)}_m\mathrm{OH} \rightarrow \mathrm{HO(M)}_{n+m} \qquad \text{(V)}$$

$$\mathrm{HO(M)}_n + \mathrm{OH} \rightarrow \mathrm{HO(M)}_n\mathrm{OH} \qquad \text{(VI)}$$

M represents one of the monomers cited above which has the general formula ($CH_2 = CH - X$). From the above scheme (which has again been verified in a latter work by the same authors [9] we understand that the free OH radicals formed by reaction (I) attack the double bond of the monomer thus producing a free radical which is then capable of attacking other monomer molecules causing the polymerisation.

Parts[7] has shown that the ferric ions catalysed decomposition of hydrogen peroxide is also capable of bringing the dissolved monomers to polymerisation and the aim of the present work is to study the influence of oxygen upon the polymerisation of acrylonitrile in the presence of $Fe^{+++} - H_2O_2$ redox initiator system.

EXPERIMENTAL

Chemicals :

Acrylonitrile : American Cyanamid Co. (redistilled before use).

$Fe(NO_3)_3 \cdot 9H_2O$; Baker & Adamson, reagent.

HNO_3 : Merck, Darmstad.

H_2O_2 : Merck, pro analysi. The water used in all experiments was double distilled and the second distillation was made from alkaline permanganate solution. The nitrogen gas used in the first five groups of experiments contained 7.9 % oxygen and for the sixth group its oxygen content was decreased by passing the nitrogen through alkaline pyrogallol solution to 1.4 %.

Apparatus :

Most of the experiments have been carried out using a 500 ml flask as in Figure A. All parts of the apparatus were of pyrex glass. The construction of the flask was such that :

a) It was completely gas tight.

b) It allowed stirring of the solution at variable speeds.

c) The gas flow through was such as to allow easy regulation.

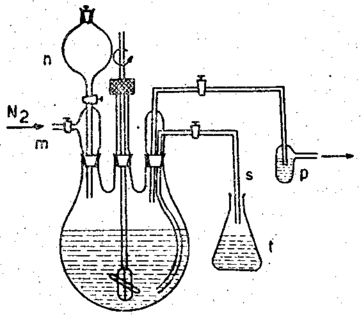

Figure A

Some of the experiments were carried out in ordinary 150 ml Erlenmeyer flasks (pyrex) without stirring and without gas stream.

All the experiments have been carried out in a thermostat, the temperature of which was 25.00 ∓ 0.05°C. pH measurements were made with a glass electrode-Beckman pH meter.

Technique :

Six groups of experiments were carried out each consisting of four different types as follows :

Type a — Experiments in Erlenmeyer flasks the total volume of solution being 50 ml and containing air. A number of flasks were put to the thermostat and first the required amount of $Fe(NO_3)_3$ (containing nitric acid to give the right pH) and then acrylonitrile solutions introduced. After at least 15 minutes the required amount of H_2O_2 solution (which had been in the thermostat) was added to every flask, mixed well closed and the time of H_2O_2 addition noted. As the polymer is insoluble in water the beginning of polymerisation or the induction period was determined, the induction period being the time interval between addition of H_2O_2 and onset of polymerisation indicated by cloudiness. The flasks were removed after intervals of 30, 60,90 and 120 minutes. The reaction was stopped by addition of 4 M nitric acid to each flask.* The polymer substance was filtered and washed several times first with distilled water in a centrifuge, dried at 70°C to constant weight and weighed to the nearest miligram.

Type b — The flask in Figure A was used in this case the total volume of reaction mixture being 300 ml and containing air. The materials were introduced in the same order as in type a from the funnel n, well mixed, after the addition of H_2O_2 the stirrer was stopped and the induction period determined. 30, 60, 90 and 120 minutes after the appearence of cloudiness, samples of about 50 ml were transferred to small Erlenmeyer flasks (previously weighed and containing 4M HNO) by suitable adjustement of the taps and the aid of nitrogen gas pressure. The flasks were weighed again and the amount of the samples were found from the difference of weights. The polymer were filtered, washed, dried and the percentage of polymerisation determined.

Type c — In this type the technique was the same as in type but the reaction mixture was stirred continuously during the experiment with a constant speed.

Type d — The same technique as in type c with the addition of a controlled flow of nitrogen containing 7.9 % oxygen (actually diluted oxygen).

In all experiments of type d the nitrogen gas was passing with a constant flow rate of two bubles per second. In all cases where agitation was required the speed of the stirrer was kept constant.

(*) It was found experimentally that when concentrated acid is added, polymerisation stops.

Results and Discussion

Figures 1-6 show the experimental results of all groups. In all the figures the letters a, b, c and d correspond to the appropriate types of experiment which are described above.

The results of the first group are shown in Figure 1. According to these curves, in the experiments type a and b, i.e. when the experiments were carried out in small Erlenmeyer flasks and in the big flask with three necks, all containing air on the solutions and no stirring, polymerisation starts after an induction period of ~ 30 minutes, proceeds with a medium velocity and in two hours time 45 % of the monomer originally present is polymerised. (Curve a and b in Fig. 1).

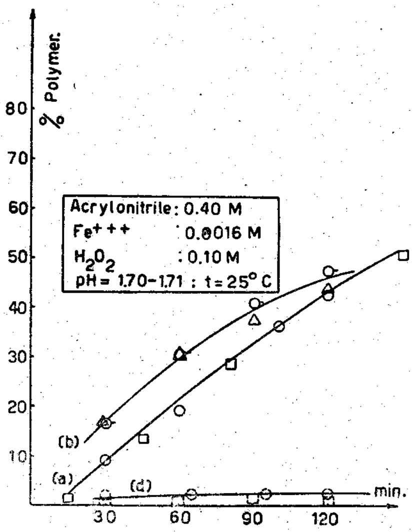

Figure 1

In the experiment type c, i. e. when the reaction mixture was stirred, no polymerisation was observed. (no curve for this type in Fig. 1). In type d, i.e. when the reaction mixture was stirred and nitrogen gas passed through the flask, polymerisation starts in an interval of 12 minutes, proceeds very slowly and after two hours only ~ 3 % of the monomer is polymerised. (curve d in Fig. 1). In this first group of experiments, the influence of stirring and nitrogen gas is very clear.

Under the conditions of this group then if the mixture is stirred polymerisation does not occur but if at the same time we pass nitrogen through the flask (i.e. if the oxygen content of the gas atmosphere is reduced) polymerisation starts after a short time but proceeds very slowly.

In the second group the concentration of ferric ions is increased. From the curves of this group which are shown in Figure 2 we see that in this case even in type c there is polymerisation. (Curve c in Fig. 2). In the other types also the amount of polymer is larger compared with that of the first group and especially in types a and b for instance there is 65 % polymerisation after two hours. (Curve a and b in Fig. 2).

In the third group, the acrylonitrile concentration was doubled, keeping the concentrations of the others the same as in the second group. Figure 3 contains the results of the third group showing that in this case the rate of polymerisation is much greater than in the previous cases. (Compare the curves c and d of Fig. 3 with the corresponding curves of previous figures).

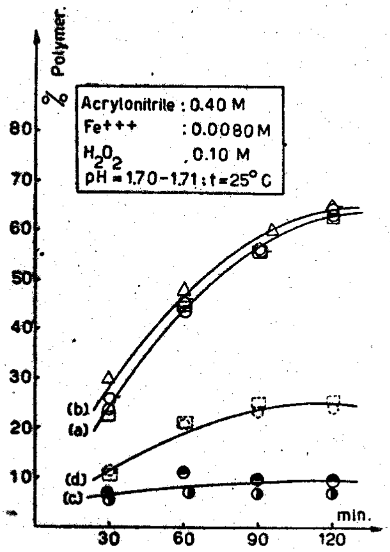

Figure 2

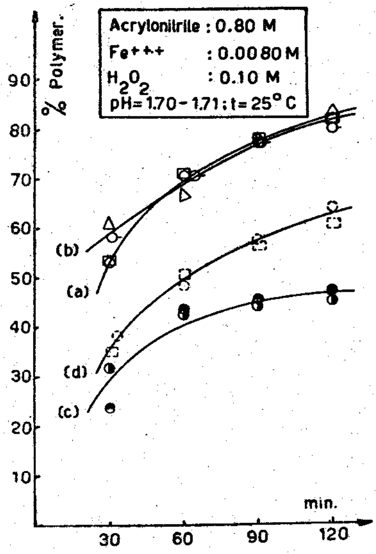

Figure 3

Table 1 and Figure 4 show the results of the fourth group where the concentrations were the same as in the second group (Fig. 2) except the H_2O_2 concentration which is now reduced to 0.020 M. No polymerisation was observed in type c (as in figure 1) and generally the rates for the other types were also small compared with the second and third groups.

TABLE 1

Arcylonitrile : 0.40 M; Fe$(NO_3)_3$: 0.0080 M; H_2O_2 : 0.02 M; pH: 1.70

Experiment type	Expt. No	Induction period min.	Time of reaction min.	% Polymerisation
a	1	20	30.5	12.8
			60	28.9
			90	42.8
			120	52.4
	2	21	30	14.5
			61.5	28.4
			91	42.8
			120	51.2
b	1	21	30	19.7
			65	38.7
			90	45.7
			120	52.1
	2	19	30	18.7
			62.5	34.0
			94	44.1
			120	49.7
c	1	Observed for 7 hours no polmerisation		
	2	Observed for 5 hours no polmerisation		
d	1	30	30	0.1
			60	0.2
			96	0.1
			120	0.1
	2	40	30	0.1
			60	0.2
			90	0.1
			120	0.2

The conditions of the 5 th group were the same as in the second group except the pH which is now diminished to 1.32. As we see from Figure 5, the rate of polymerisation is always smaller than in Fig. 2 and the difference is especially large in the experiments of type c and d of both groups.

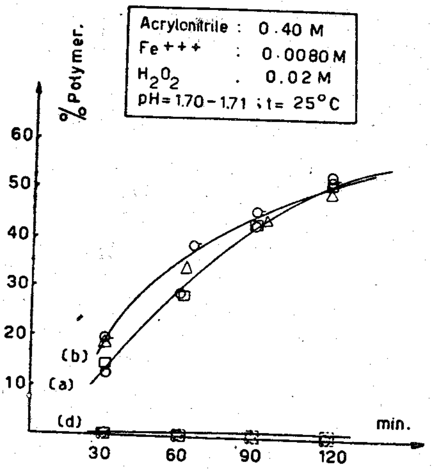

Figure 4

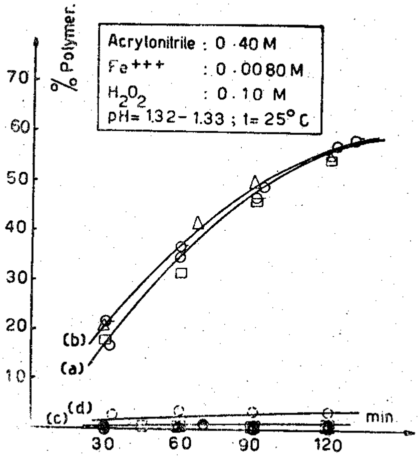

Figure 5

The fact that the rate of polymerisation is decreased when the H ions concentration is increased, is not in contradiction with our previous knowledge. We know that concentrated nitric acid (as well as HCl or H_2SO_4) is able to stop polymerisation. The reaction of hydrogen peroxide decomposition by ferric ions is also affected by concentrated sulphuric acid which practically stops the reaction. This follows from assuming that

$$Fe^{+++} + HO_2^-$$

is one of the important reactions in initiating the decomposition of H_2O_2, and that the equilibrium

$$H_2O_2 \rightleftarrows H^+ + HO_2^-$$

is displaced to the left with increasing acid. The decrease of the rate of polymerisation with the increase of H^+ ions seems to be reasonable because when the decomposition of H_2O_2 is supressed by H^+ ions, the amount of OH radicals which cause polymerisation will also decrease.

The 6 th group consists only of experiments type c and d. The concentration were the same as in group 4 (Fig. 4) the only difference being in the composition of the gas used.

Experiments of type c were carried out using the flask in Figure A with the side necks closed with glass stoppers. The flask was completely filled with the solution (hydrogen peroxide being added last) so that there could be no air (oxygen) in contact with the liquid. Polymerisation occured, showing a medium induction period and a normal rate. (Table 2 and Figure 6). In group 4 on the other hand no polymerisation was observed. (Compare the figures 4 and 6, and the tables 1 and 2).

TABLE 2

Concentrations are as in group 4 (Fig. 4 or Table 1)

Experiment type	Expt. No	Induction period min	Time of reaction min	% Polymerisation
c	1	18	63	23.0
			120	44.2
	2	20	63	22.5
			120	44.7
d	1	15	30	1.1
			60	1.1
			90	1.0
			120	1.0
	2	13	30	1.8
			62	1.8
			90	1.8
			120	1.7

Although in these latter experiments the contact of the liquid with air was practically prevented, there is still an induction period and the rate of polymerisation is not very large. The reason for this is obviously the oxygen content of the solution itself, because the water and thus the solutions used were not deaerated and the oxygen which is dissolved in the reaction mixture reacts as a retarder and inhibitor.

In the experiments type d the nitrogen gas was purified and contained 1.4 % oxygen. (In all the previous groups it contained 7.9 % oxygen). Table 2 and Figure 6 show clearly that when the oxygen content of the gas atmosphere is reduced, the induction period decreases and the rate of polymerisation increases. (Compare the tables 1 and 2, and also the figures 4 and 6).

In table 3 the results of another similar work done by Parts[7] and those of the present work are given for comparison and to show the reproducibility of the experiments. In this work Parts has proved H_2O_2 by ferric ions is a chain reaction. Working with the concentrations of our second group (Fig. 2), the author[7] found that the velocity of decomposition of H_2O_2 (in the absence of monomer) by ferric ions, is slowed down ~ 60 fold when monomer is present. The ratio of disappearing monomer to that of hydrogen peroxide (expressed as molar ratio) is ~ 70. These experimental results and others can be explained (as the author proposed) only by the existence of a chain reaction during the decomposition of H_2O_2.

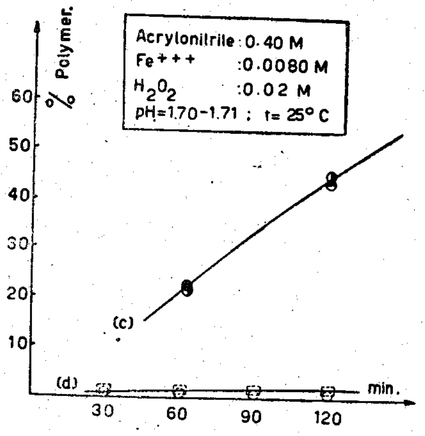

Figure 6

In the present work we see that under the conditions used the rate of polymerisation of acrylonitrile increases with the increase in the concentrations of 1) monomer 2) ferric ions 3) hydrogen peroxide and decreases with the concentration of H^+ ions.

The influence of oxygen on polymerisation reactions has been studied by many investigators[12-17] and it has been found that oxygen acts in some cases as inhibitor[12] and in others as promotor.[13,17] Baxendale, Evans and Park[8] olso observed the inhibiting role of oxygen and they proposed that the radicals formed in reaction (III) and (IV) react with the oxygen which is present in the solution and so the growing polymer chain is stopped or slowed down (see introduction). The oxygen gas is absorbed by the reaction mixture and if the radicals are present in very small concentrations, polymerisation does not occur in the presence of the oxygen, while in the absence of oxy-

TABLE 3(*)

Experiments of type a Conditions as in :		% polymerisation				Induction period min.
		30 min.	60 min.	90 min.	120 min.	
Figure 1	Şenvar	9	21	33	43	30
	Parts	8	21	34	45	30
Figure 2	Şenvar	23	44	56	64	9—10
	Parts	25	48	59	65	4—6
Figure 3	Şenvar	53	71	78	83	4—5
	Parts	53	72	79	—	4—5
Figure 4	Şenvar	13	28	42	52	20
	Parts	18	33	45	54	22—26
Figure 5	Şenvar	17	33	46	55	18—20
	Parts	18	35	48	58	19—21

gen, polymerisation starts immediately showing no induction period. The influence of stirring is thus due to the oxygen which is present in the solution and in the gas atmosphere. When the solution is stirred oxygen molecules go into the solution, come into contact with the free radicals and in this way the active centers are destroyed. This fact can be accepted as the reason for the induction period and also for the inhibition or retardation of polimerisation.

We see generally from all the figures that there is always a difference between the curves a and b, i.e. the first curves are always below the seconds. That means under the same conditions the rate of polymerisation is bigger when the volume of the reaction mixture is bigger. This fact can be explained in two different ways:

1. The polymerisation is exothermic and therefore during the reaction the temperature of the solution rises. (It is ob-

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(*) I am indebted to Dr. A. G. Parts for permission to make use of some results of his unpublished work.

served experimentally that in the range of the concentrations used in this work, the temperature rises by 1-2°C during the polymerisation). As the heat conduction from a smaller volume of the solution to the thermostat is bigger, the temperature of the reacting solution in smaller flasks (as in type a) is not as high as in the bigger flask which explains qualitatively the fact that the curves b are above a.

Figure 7 shows the plot of $\log\left(-\frac{dc}{dt}\right)$ and log c values for the curves a and b of Fig. 3 where the rates of polymerisation were big. (c represents the monomer concentration at time t). Since these graphs are linear, from

$$-\frac{dc}{dt} = kc^n \quad \text{and} \quad \log\left(-\frac{dc}{dt}\right) = \log k + n \log c$$

the order of the reaction n and the velocity constant k are determined. The order of the reaction is 2 for both types of experiments. The velocity constants are : 9.7×10^{-4} lit. mol^{-1} sec^{-1} and 1.2×10^{-3} lit. mol^{-1} sec^{-1} for type a and b respectively.

2. The second explanation for the difference of curves a and b is that: the solutions in Erlenmeyer flasks have a bigger specific surface (surface per ml of total solution). Oxygen, which clearly inhibits the reaction, diffuses into solutions of series b less than of a.

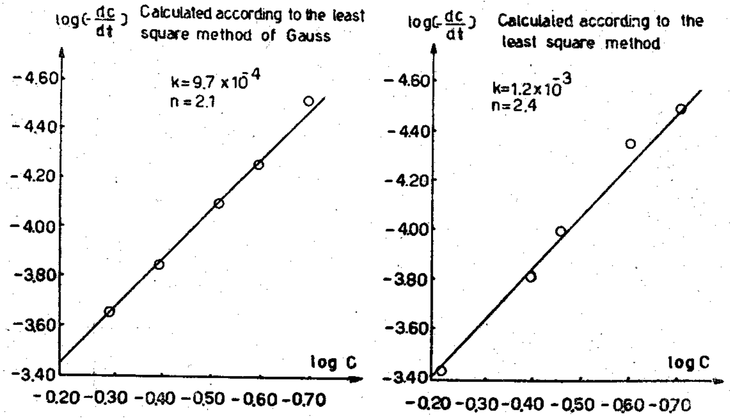

Figure 7

In the case of types c and d we readily see that from consideration of oxygen diffusion aspect the diffusion of oxygen into solution in type c is 2.5 times greater than in type d. When no stirring takes place, the entry of oxygen into the solution is by way of the stationary layer of solution adjacent to the dividing surface, this layer becoming saturated with oxygen and the oxygen eventually reaching the inside of the solution from this layer. While in stirring the layer adjacent to the gas surface is continuously renewed, and the saturated layer is brought by convection into the inside where it distributes itself into liquid. So the amount of oxygen absorbed by the solution is greater in the liquid which is stirred and the rate of polymerisation is les in the solution which is stirred under a gas phase containing more oxygen. Therefore type c experiments give less polymer than type d and these less than type a or b.

Another point of view can be also discussed to explain the influence of stirring, i.e. the possibility of the annihilation of free radicals by their reaction with one another for instance, in the liquid-gas surface or in the liquid-solid surface. But these effects are not detectable as long as oxygen influence predominates

One fact for which a satisfactory explanation could not be found was as follows :

In Figure 2, 27 units of monomer are polymerised in 30 minutes (assuming 100 units for 0.40 M acrylonitrile and 200 units for 0.80 M) (curve a and b). In Figure 3, however, 120 units are polymerised. That is 4.5 times the amount. Why then the increase in the concentration of acrylonitrile twice increases the velocity of polymerisation not twice but more than 4 times in the initial stages of the reaction. In type c the situation is also the same, i.e. after 60 minutes in Figure 2, 8 units and in Figure 3, $2 \times 40 = 80$ units are polymerisde. That is $\sim$ 10 times as much Perhaps the polymer formed in initial stages has some influence on further polymerisation and this influence is probably a function of the concentration of monomer present.

The mechanism of the effect of oxygen and stirring on the polymerisation of acrylonitrile in the presence of Fe^{+++} ions and H_2O_2 is still an interesting problem to be investigated. Such an investigation can be realised by studying all the reaction mechanism once more in carefully deaerated solutions and atmospheres (or in vacuum) using completely purified gases.

SUMMARY

The influence of stirring and oxygen upon the polymerisation of acrylonitrile in the presence of ferric ions and hydrogen peroxide (at small pH's and 25°C) was investigated.

Under the experimental conditions the effect of stirring was observed and the reason studdied.

The reaction is carried out in four different ways, i.e. 1. Stirring, 2. Without stirring, 3. In air atmosphere, 4. In nitrogen atmosphere containing oxygen.

It is observed that the effect of stirring is related to the oxygen which destroys the active centers produced by the Fe^{+++} H_2O_2 catalyst system and necessary for the polymerisation. When
catalyst system and necessary for the polymerisation. When
the reaction mixture is stirred, the free radicals and oxygen molecules come in contact with one another more abondantly and so the radicals causing the polymerisation are easily destroyed. Under the conditions used in this work, the rate of polymerisation increases when the concentration of the monomer or of the catalysts increases, and it decreases with increase in the hydrogen ions concentration.

Acknowledgement.

I wish to thank and express my gratitude to Dr. A. G. Parts who suggested the field of study and helped continuously during the work.

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(Manuscript received 4 June 1952)