RADIATION INDUCED POLYMERISATION OF ACRYLONITRILE

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Polymerisation of acrylonitrile by gamma radiation has been studied at room temperature in the atmosphere of nitrogen or under vacuum. The polymer conversion was estimated gravimetrically. The parameters varied were the pH of the medium, radiation dose and monomer concentration. The effect of sulphate and chloride ions on reaction rate under similar conditions of hydrogen ion concentration was also investigated. It has been seen that the polymer yield is maximum at pH 5.8 and it decreases with the increase or decrease of pH of the medium. The chloride ions decrease the yield to a lesser extent than the sulphate ions. Polymerisation occurs via free radicals formation.

During the last two decades the kinetic studies of acrylonitrile have assumed a position of prime importance in the field of high polymers. Bacon,[1] Morgan,[2] Pinner,[3] Heinaman,[4] Hussain and Haider[5] investigated the kinetics of acrylonitrile polymerisation initiated by $K_2S_2O_8$. The kinetics of radiation induced polymerisation of acrylonitrile in aqueous solution have also been examined by Collinson and Dainton,[6] Okamura and Akihiro Sakamoto.[7]

The present investigation was designed to observe the effect of pH maintained by H_2SO_4 or HCl and NaOH on the rate of acrylonitrile polymerisation initiated by Co-60 gamma radiation and to compare the mechanism with the earlier published work.[5] The two mineral acids were selected with a view to determining the effect of SO_4^- and Cl^- ions under similar hydrogen ion concentration. The effect of salts with reducing properties was also investigated.

Experimental

Materials.—Acrylonitrile supplied by B.D.H. was fractionally distilled to remove inhibitor. The middle fraction boiling at 78.5°C was retained. This gave D_4^{25}=0.8001; n_D^{25} 1.3885, which agree with the values cited by Blout, Mark and Hokenstein.[8] Sulphuric acid (E. Merck), hydrochloric acid (May & Baker) and reducing agents given in Table 2 were used without further purification.

The nitrogen used for deoxygenation purposes was purified according to the method outlined by Vogel[9] while triply distilled water used for irradiation purposes was obtained by redistilling laboratory distilled water over alkaline potassium permanganate and then over acidic potassium dichromate under a stream of oxygen. The glass apparatus used for irradiation was washed with hot chromic acid and thoroughly rinsed with distilled water. It was then heated in the furnace at 500°C for 3 hr before use.

Procedure.—The kinetics and mechanism of Co-60 radiation induced polymerisation of acrylonitrile were studied at 25±0.1°C by the variation of two parameters, the pH of the medium and the monomer concentration. Further, the effect of various reducing agents on the rate of polymerisation was also investigated. The variation in pH was effected with NaOH and HCl or H_2SO_4. The reaction mixture at required pH value was introduced in the specially designed cell and deoxygenated with the purified nitrogen for the optimum time (30 min) determined practically. The reaction cell was then detached from the line and placed in the irradiation chamber for the desired period. After suitable intervals it was removed from the gamma cell and put into ice-cold water to stop the reaction. The percentage polymerisation was determined by filtering out the solid polymer and drying at 110°C to a constant weight.

In some of the experiments the percentage polymerisation was also determined according to the procedure described in earlier work.[5]

In a number of experiments at different pH values, the concentration of the hydrogen ion before and after irradiation was determined using a Beckmann pH meter. The variation in pH was of the order of +0.1.

The radiation source used in this work was gamma cell 220 of A.E.C. Lahore (Canada), Co-60, 12,000 curies. A radiation intensity of 4.23×10^{20} ev/l./min was obtained by means of the ferrous sulphate Fricke dosimeter [10] containing sodium chloride as suggested by Dewhurst [11] with a G-value of 15.6 for ferric iron. Frequent recalibration of the radiation intensity was made. The value was found to change during the period of these investigations from 4.23 to around 4.02×10^{20} ev/l./ min.

Results

The results are given in Tables 1 and 2.

TABLE 1.—DEPENDENCE OF THE % POLYMERISATION ON pH.

Acrylonitrile=1.0 mole/l.; dose rate=4.23×10^{20} ev/l. / min.

pH of the reaction mixture	Polymer yield % deoxygenated with N_2 and pH maintained with		Polymer yield % degassed upto 10^{-5} mm and pH maintained with	
	H_2SO_4 NaOH	HCl NaOH	H_2SO_4 NaOH	HCl NaOH
1.0	33.0	35.9	33.5	37.08
2.0	34.434	37.453	34.67	38.43
3.0	35.8	38.0	36.5	39.67
4.0	37.4	40.02	37.88	40.5
5.0	40.09	41.65	40.61	42.01
5.8	42.0	42.0	42.5	42.5
6.0	41.5	41.5	42.3	42.3
7.0	39.6	39.6	40.0	40.0
8.0	38.25	38.25	39.0	39.0

TABLE 2.—EFFECT OF REDUCING SALTS ON POLYMER YIELD.

Acrylonitrile=1.0 mole/l; pH=5.0; reducing agent added=10^{-3}M; dose rate=4.02×10^{20} ev/l./min; time of irradiation=15 min.

Reducing agents added	Polymer yield (%)
$Na_2S_2O_3.5H_2O$	22.4
$Na_2S_2O_4$	0
$N_2H_4.H_2SO_4$	23.02
$N_2H_4.2HCl$	39.72
$NH_2OH.HCl$	39.43
$FeSO_4.7H_2O$	23.634
$CuSO_4.5H_2O$	22.217
$AgNO_3$	35.38
$K_2S_2O_8$	36.9
$SnCl_2.2H_2O$	40.2
None	42.00

Discussion

Radiolysis of water is represented as follows:

$$H_2O \xrightarrow{\sim\!\sim} aH + bH_2 + cOH + dH_2O_2 \qquad (a)$$

The hydrogen atom and hydroxyl radicals possess an unpaired electron and hence initiate the polymerisation by adding to the monomer, forming an organic radical.

The following reaction scheme is proposed:

$$\text{(i)}\quad H_2O \;+\; \xrightarrow{\sim\!\sim} 2R\ (H+OH)$$

$$\text{(ii)}\quad R + M \xrightarrow{ki} RM^{\bullet}$$

$$\text{(iii)}\quad RM^{\bullet}_{x-1} + M \xrightarrow{kp} RM^{\bullet}_{x}$$

$$\text{(iv)}\quad RM^{\bullet}_{x} + R \xrightarrow{kt} RM_xR$$

$$\text{(v)}\quad RM^{\bullet}_{x} + RM^{\bullet}_{y} \xrightarrow{kt} RM_xM_yR\ (\text{or } RM_x + RM_m)$$

$$\text{(vi)}\quad 2R \longrightarrow H_2O\ (\text{or } H_2 \text{ or } H_2O_2)$$

where R=H or OH, $RM^{\bullet}_x$ is a growing polymer chain and RM_xR or RM_xM_yR is a dead polymer chain. Chain transfer with water is unlikely in view of the high dissociation energy of water.

Mathematically it can be deduced that the rate of consumption of the monomer is given by the equation:-

$$-\frac{dM}{dt} = k_p \left(\frac{\phi\, I_{abs}}{k_t}\right)^{\frac{1}{2}} M \qquad (1)$$

where M, ϕ, k_p and k_t represent monomer concentration, primary quantum efficiency of chain initiation, rate of propagation and rate of termination respectively. When $-dM/dt$ is plotted against the first power of the monomer concentration, straight line is to be expected. Figure 1 shows this fact in accordance with the equation (1).

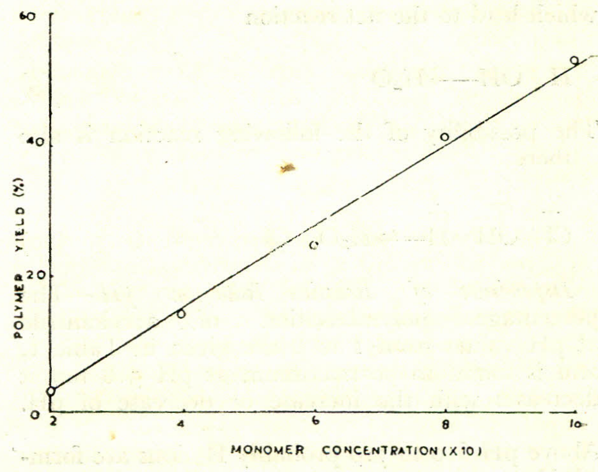

Fig. 1.—Effect of monomer concentration on polymer yield.

The sulphuric acid in dilute solutions is unaffected by gamma rays, but at higher concentration hydrogen atoms and hydroxyl radicals obtained by radiolysis of water react with sulphuric acid as follows:

$$H_2SO_4 \longrightarrow \overset{+}{H} + \overset{-}{HSO_4} \qquad (2)$$

The first step may be

$$H + \overset{-}{HSO_4} \xrightarrow{\text{Fast}} \overset{-}{H_2SO_4} \qquad (3)$$

forming a sulphuric acid radical.

The hydroxyl radical attack on sulphuric acid leads to hydrogen sulphate radicals

$$OH + \overset{-}{HSO_4} \xrightarrow{\text{Fast}} HSO_4 + \overset{-}{OH} \qquad (4)$$

The radicals formed in reactions (3) and (4) above recombine and reform sulphuric acid.

$$\overset{-}{H_2SO_4} + HSO_4 + \overset{-}{OH} \xrightarrow{\text{Fast}} 2\overset{-}{HSO_4} + H_2O \qquad (5)$$

In case of hydrochloric acid the following reaction scheme is possible:

$$OH + \overset{-}{Cl} \xrightarrow{\text{Fast}} \overset{-}{OH} + Cl \qquad (6)$$

$$Cl + Cl \xrightarrow{\text{Fast}} Cl_2 \qquad (7)$$

$$H + Cl_2 \xrightarrow{\text{Slow}} H + \overset{-}{Cl} + Cl \qquad (8)$$

which lead to the net reaction

$$H + OH \longrightarrow H_2O \qquad (9)$$

The possibility of the following reaction is also there

$$\overset{-}{Cl} + OH + \overset{+}{H} \longrightarrow H_2O + Cl \qquad (10)$$

Dependence of Reaction Rate on pH.—The percentage polymerisation of acrylonitrile at pH values from 1 to 8 are given in Table 1, and is found to be maximum at pH 5.8 but it decreases with the increase or decrease of pH. Above pH 6.0 to 7.0 probably $\overset{+}{H_2}$ ions are formed:[12]

$$\overset{+}{H} + H \rightleftharpoons \overset{+}{H_2}$$

consequently the hydrogen atoms formation in reaction (a) decreases and the rate falls. According to Hart, Gordon and Hutchison[13] at pH above 7.0 the OH radical dissociates in accordance with the equation:

$$OH \rightleftharpoons \overset{+}{H} + \overset{-}{O}$$

thus decreasing the rate dependent free radicals which result in the decrease of rate.

In strongly acidic medium in case of sulphuric acid the reactions (2 to 5) are taking place while in the case of HCl, the reactions (6 to 10) are proceeding. In either case there is a consumption of the hydrogen atom and the hydroxyl radicals which result in the decrease of percentage polymerisation with the fall of pH. Practically, the percentage polymerisation at different pH values is higher in case of HCl as compared with H_2SO_4. This is due to the fact that reaction (8) is the slow reaction in case of HCl.

For comparison purposes percentage polymerisation in aerated, deaerated and nitrogen purged solutions, at different pH values maintained with H_2SO_4 or HCl and NaOH are graphically shown in Fig. 2, while the effect of radiation dose is depicted in Fig. 3.

Effect of Reducing Agents on Polymer Yield.—In case of reducing agents the reducing ions not already in their highest oxidation state will probably be oxidised by OH radicals. For example, in case of iron and tin

$$M^{n+} + OH \longrightarrow M^{n+1} + \overset{-}{OH} \qquad (11)$$

where M^{n+} represents Fe^{2+} or Sn^{2+}.

M^{n+1} formed in reaction (11) reacts with organic polymer radical and terminates the chain reaction as follows:[14]

$$\text{-}CH_2\text{-}CH(CN)^{\bullet} + \overset{n+1}{M} \longrightarrow \text{-}CH{=}CH(CN) + \overset{n+}{M} + \overset{+}{H} \qquad (12)$$

hence reactions (11) and (12) are responsible for the marked decrease in the percentage of polymerisation.

In case of copper as suggested by Kolthoff and Coetzee,[15] Cu^{+} ions are not stable in water containing acrylonitrile and a stable complex is formed whereas $Na_2S_2O_3$, $Na_2S_2O_4$ in aqueous

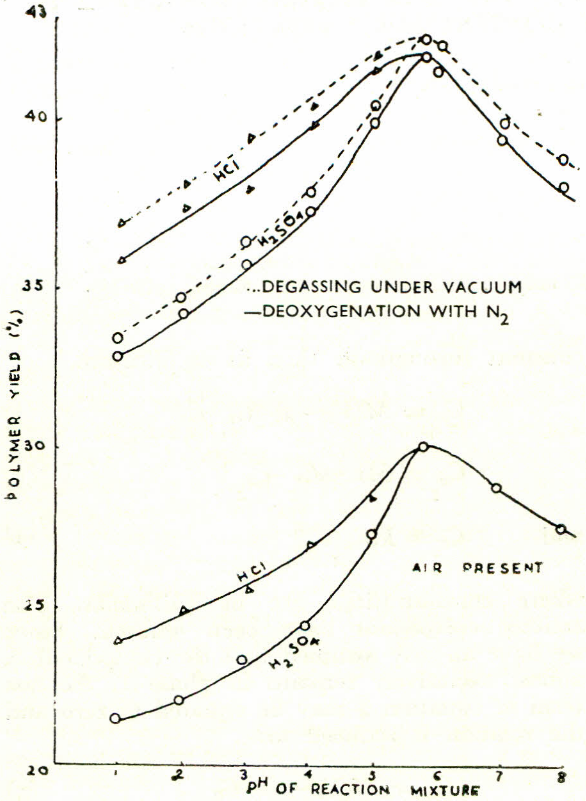

Fig. 2.—Effect of pH variation on polymer yield.

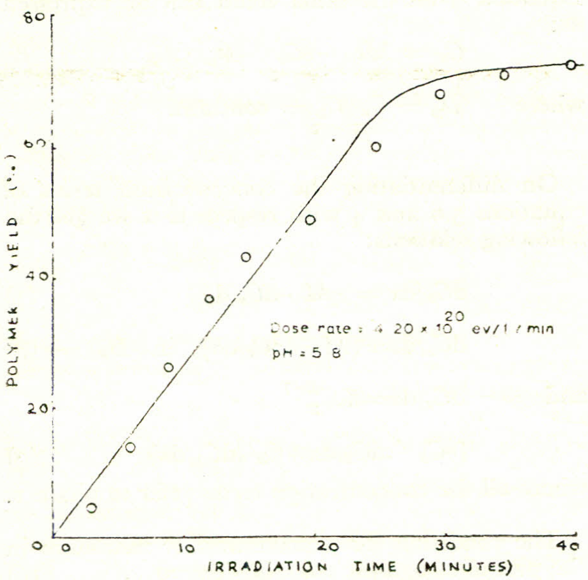

Fig. 3.—Effect of radiation dose on polymer yield.

solution in the presence of acrylonitrile decompose to S, H_2S, SO_3,SO_4 etc. during irradiation, which somehow or the other hinder the reaction. In order to know the detailed mechanism of the reaction more work is needed in this field.

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