

# Kinetics of polymerization of acrylonitrile initiated by the vanadium(V)-bisulphite redox system in sulphuric and perchloric acid media

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## Abstract

The kinetics of polymerization of acrylonitrile, initiated by the free radicals formed in situ in the vanadium(V)-bisulphite redox system, was studied in aqueous sulphuric acid and perchloric acid media in the temperature range of 28–40 °C. The rate of polymerization was determined at various concentrations of the monomer and initiators. The effect of intermediate injection of catalyst was studied. The temperature dependence of the rate was studied and the activation parameters were computed. The resulting polymer (polyacrylonitrile (PAN)) was characterized by infrared (IR) and <sup>1</sup>H NMR spectral analysis and by its molecular weight determined by the viscometric method. A possible mechanism consistent with the experimental data has been proposed.

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## 1. Introduction

Vanadate in acid solution is found to be a strong oxidant for both organic and inorganic compounds. It was reported that vanadium(V) in the presence of reducing agents initiated vinyl polymerization. Sulphites [1,2], bisulphites [3–5] and metabisulphites [6–9] form efficient redox systems in conjunction with persulphates. Among the large number of oxidants [10–17] used, Cu<sup>2+</sup>, molecular oxygen, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, H<sub>2</sub>O<sub>2</sub>, ClO<sub>3</sub>, KMnO<sub>4</sub>, Fe<sup>3+</sup>, and Ce(IV) form good redox initiators in combination with bisulphite. There is a long induction period, when the V(V)-bisulphite redox system is used in polymerization studies in the presence of oxygen. The increase of V(V) concentration, shaking the reaction mixture, and increasing the temperature lengthen the induction period, decrease the initial rate and the maximum conversion. However, if

polymerization is carried out in inert nitrogen atmosphere, there is no induction period and the percentage conversion increases.

The anomalous kinetic behavior associated with acrylonitrile polymerization in aqueous solution and the importance of polyacrylonitrile (PAN) in the fiber industry [18] has led to the choice of acrylonitrile for this investigation.

## 2. Experimental

### 2.1. Preparation of materials

To remove the inhibitor from acrylonitrile (AN) [19], the latter was treated with alkali, washed with orthophosphoric acid and distilled water, dried over anhydrous CaCl<sub>2</sub>, and finally distilled under reduced pressure in an inert atmosphere of nitrogen. The middle fraction of the second distillate was collected and stored at 5 °C. Ammonium metavanadate, sodium perchlorate, sodium bisulphite, sulphuric acid, perchloric acid and vanadyl sulphate, etc. used were of analytical grade. Water dis-

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tilled twice over alkaline permanganate is used to prepare all solutions. The nitrogen used to deaerate the experimental system is freed from oxygen by passing it through column of Fieser's solution, a column of saturated lead acetate solution, and finally, a wash bottle containing distilled water.

## 2.2. Kinetic measurements

The reaction vessels used for experiments are Pyrex glass vessels fitted with B24 sockets and cone fitted with an inlet and outlet tube for nitrogen. The system consisting of bisulphite,  $\text{H}_2\text{SO}_4$  or  $\text{HClO}_4$ , acrylonitrile,  $\text{NaClO}_4$  (for ionic strength adjustment) and water (to keep the total volume constant) is thermostated at a desired temperature (e.g.,  $28^\circ\text{C}$ ). The system is deaerated by passing oxygen free nitrogen for 20–30 min through the solutions before the addition of the deaerated vanadium(V) solution. Polymerization starts without any induction period as indicated by the appearance of turbidity. At appropriate time intervals, the aliquots of the reaction mixture are withdrawn and, in each case, the reaction is arrested by freezing and blowing air in. The polyacrylonitrile product obtained from each aliquot is filtered using a fritted glass funnel, washed several times with distilled water and dried at  $70^\circ\text{C}$ . The rate of polymerization is calculated from the initial slope of a percentage conversion–time plot.

The filtrate is treated with a mixture containing excess of Fe(II) solution, phosphoric acid and mercuric chloride. The unreacted Fe(II) is titrated with standard vanadium(V) solution using the barium diphenylaminesulphonate redox indicator. The rate of vanadium(V) disappearance ( $-R_V$ ) is found to be independent of acrylonitrile concentration but dependent on the concentration of vanadium(V). The rate of vanadium(V) disappearance shows a first-order dependence on [vanadium(V)].

## 2.3. Molecular weights ( $M_v$ )

Molecular weights ( $M_v$ ) of the purified samples of polyacrylonitrile are determined by viscosity measurements using an Ubbelohde suspended level dilution viscometer. The intrinsic viscosities ( $\eta$ ) for the polymer solutions are determined, and the ( $M_v$ ) values are calculated using the Mark–Houwink equation as given by Stockmayer and Cleland [20]:

$$[\eta] = (3.335 \times 10^{-4})$$

$$M_v^{0.72} \text{ for polyacrylonitrile in DMF at } 30^\circ\text{C}.$$

## 3. Results and discussion

From a qualitative stand point, it is noted that vanadium(V) or sodium bisulphite alone does not initiate polymerization under the experimental conditions. There is an induction period under undeaerated condition and no induction period is noticed in deaerated conditions. Thus, it is evident that the polymerization is initiated by free radicals generated in situ by the reaction

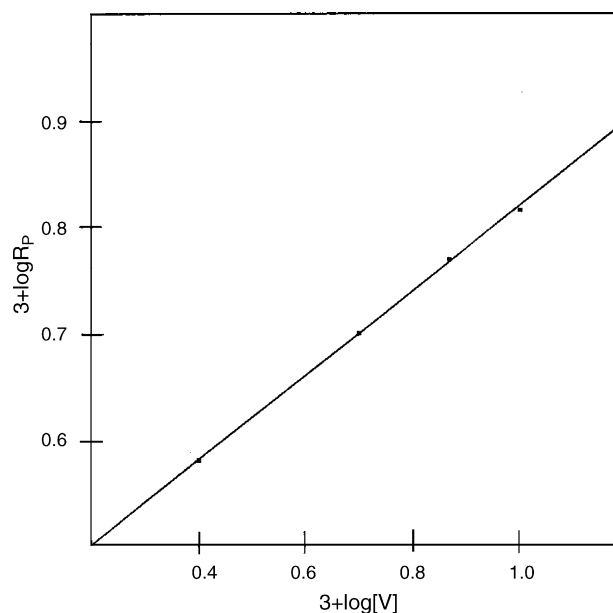


Fig. 1. Plot of  $\log R_p$  vs.  $\log [V^{5+}]$ :  $[V^{5+}] = 0.0025, 0.005, 0.0075$  and  $0.01 \text{ mol dm}^{-3}$ ,  $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$ ,  $[\text{AN}] = 0.3034 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol dm}^{-3}$ ,  $I = 3.0 \text{ mol dm}^{-3}$  and at  $28^\circ\text{C}$ .

between vanadium(V) and bisulphite. The steady state is reached within 30 min.

### 3.1. Effect of vanadium(V) concentration on the rate

An increase in the rate of polymerization occurs with an increase in vanadium(V) concentration in the range ( $2.5 \times 10^{-3}$  to  $10.0 \times 10^{-3} \text{ mol dm}^{-3}$ ). This is attributed to an increased concentration of the active species. The reaction shows a fractional (one-half) order dependence on vanadium(V) concentration as shown by the slope of the  $\log R_p$  versus  $\log [V(V)]$  plot (Fig. 1). The rate of polymerization in  $\text{H}_2\text{SO}_4$  is slightly greater than that in perchloric acid medium. This is due to the greater rate of oxidation in perchloric acid medium in comparison with the rate of polymerization.

### 3.2. Effect of bisulphite ion concentration

The initial rate as well as the maximum conversion increase linearly with the increase in bisulphite concentration in the range ( $5 \times 10^{-4}$  to  $20 \times 10^{-4} \text{ mol dm}^{-3}$ ). At higher bisulphite concentrations, the rate decreases due to over concentration of free radicals generated [18]. A plot of  $\log R_p$  versus  $\log [\text{HSO}_3^-]$  shows a fractional (one-half) order dependence on bisulphite ion concentration. The molecular weight of the polymer formed also decreases with increase in the concentration of bisulphite ion (Fig. 2).

The rates of polymerization as well as the maximum conversion gradually increase with an increase in  $[\text{H}^+]$  in the range ( $0.1\text{--}0.4 \text{ mol dm}^{-3}$ ). At higher  $[\text{H}^+]$ , there is a decrease in the rate of polymerization that may be due to a higher rate of oxidation in comparison with the rate of polymerization.

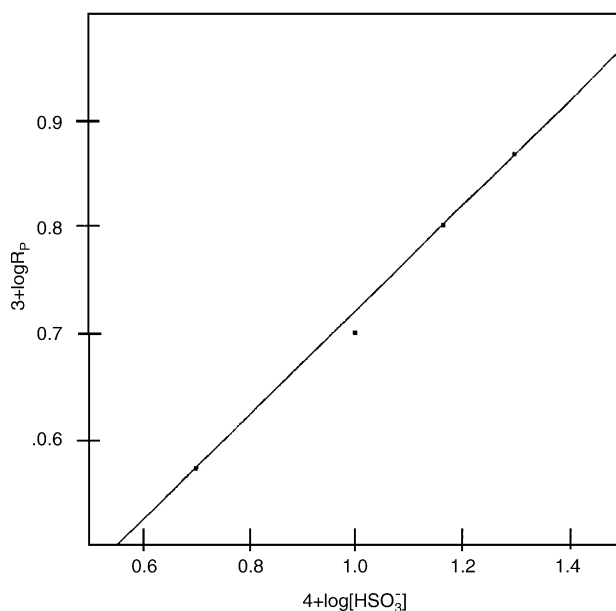


Fig. 2. Plot of  $\log R_p$  vs.  $\log [\text{HSO}_3^-]$ :  $[\text{HSO}_3^-] = 0.0005, 0.001, 0.0015$  and  $0.002 \text{ mol dm}^{-3}$ ,  $[\text{V}^{5+}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{AN}] = 0.3034 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol dm}^{-3}$ ,  $I = 3.0 \text{ mol dm}^{-3}$  and at  $10^\circ\text{C}$ .

### 3.3. Effect of monomer concentration

The rates of polymerization and maximum conversion increase with increase in monomer concentration in the range ( $0.4517$ – $0.6068 \text{ mol dm}^{-3}$ ). From the plot of  $\log R_p$  versus  $\log [M]$ , the order of reaction with respect to the monomer concentration is found to be 1.4 in sulphuric acid medium and 1.1 in perchloric acid medium (Figs. 3 and 4).

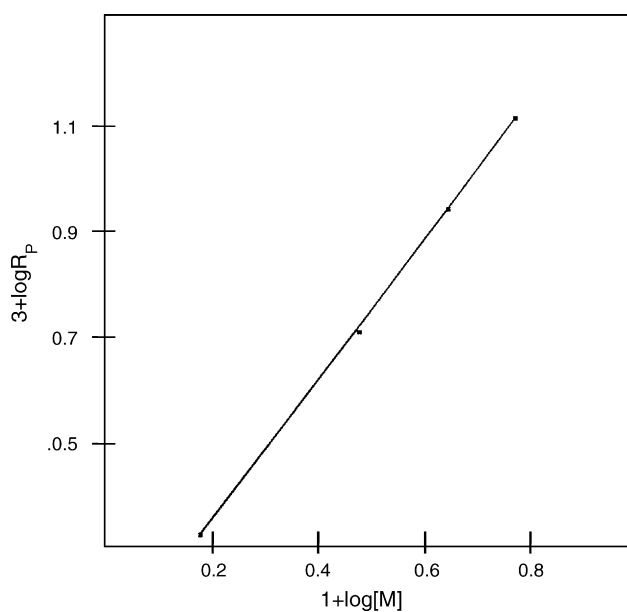


Fig. 3. Plot of  $\log R_p$  vs.  $\log [M]$ :  $[M] = 0.1517, 0.3034, 0.4551$  and  $0.6068 \text{ mol dm}^{-3}$ ,  $[\text{V}^{5+}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol dm}^{-3}$ ,  $I = 3.0 \text{ mol dm}^{-2}$  and at  $28^\circ\text{C}$ .

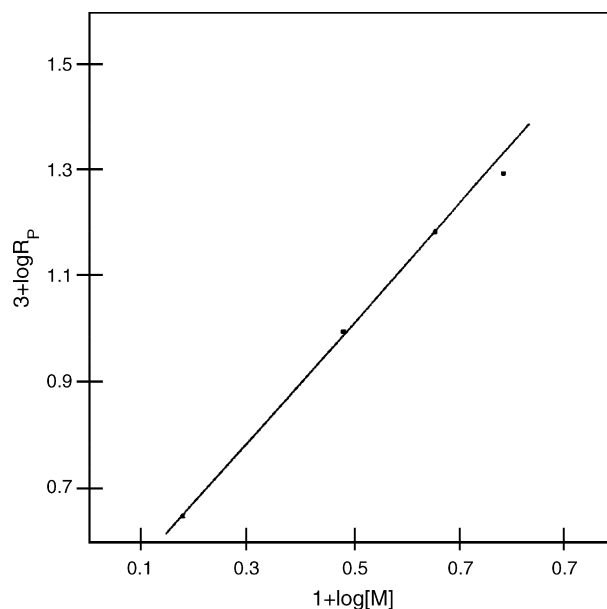


Fig. 4. Plot of  $\log R_p$  vs.  $\log [M]$ :  $[M] = 0.157, 0.3034, 0.4551$  and  $0.6068 \text{ mol dm}^{-3}$ ,  $[\text{V}^{5+}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$ ,  $I = 3.0 \text{ mol dm}^{-3}$  and at  $28^\circ\text{C}$ .

### 3.4. Effect of ionic strength

The ionic strength of the medium was varied by adding sodium perchlorate. The rate of polymerization increased with increase in the ionic strength. This may be understood in terms of the salt catalyzing the propagation step via formation of a complex with the acrylonitrile as reported by Bamford et al. [21].

### 3.5. Effect of water miscible organic solvents

Water miscible organic solvents such as methanol, ethanol and DMF are found to depress the rate of polymerization and reduce the maximum conversion. This could be explained by the fact that these solvents decrease the area of the shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain [22].

### 3.6. Effect of temperature

The rate of polymerization increases with increase in temperature, in both sulphuric acid and perchloric acid media in the  $28$ – $40^\circ\text{C}$  range. The molecular weight ( $M_v$ ) of the polymer decreases with increase in temperature (Figs. 5 and 6). Activation parameters calculated are presented in Table 1.

### 3.7. Polymer characterization

#### 3.7.1. Molecular weight

The viscosity-average molecular weight of the polymer product in a typical standard run was found to be  $3.5 \times 10^4$ .

Table 1  
Activation parameters for the polymerization of acrylonitrile in acid solutions<sup>a</sup>

Acid	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^b$ (kJ mol <sup>-1</sup> )	$\Delta S^b$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^b$ (kJ mol <sup>-1</sup> )
Sulphuric acid medium	40.54	38.30	-125.4	76.05
Perchloric acid medium	32.75	30.03	-200.5	90.65

<sup>a</sup> Values were obtained from plots shown in Figs. 5 and 6.

<sup>b</sup> Rate constants used for determining activation parameters were reproducible within  $\pm 3$ –4%.

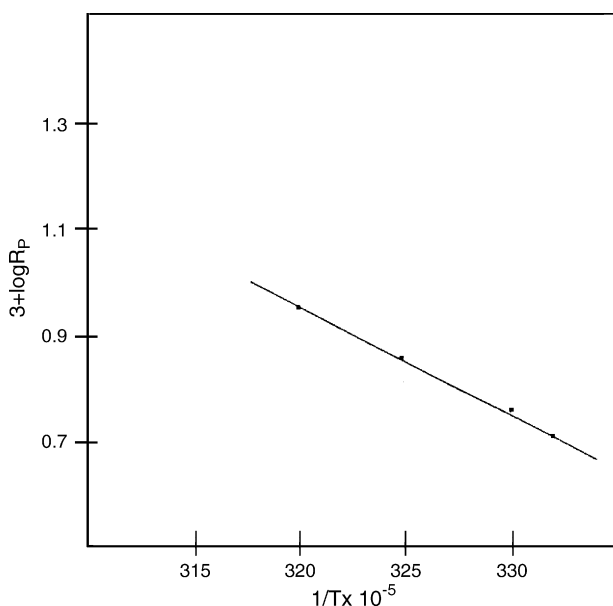


Fig. 5. Arrhenius plot of  $\log R_p$  vs.  $1/T$ :  $[V^{5+}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$ ,  $[M] = 0.3034 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol dm}^{-3}$ ,  $I = 3.0 \text{ mol dm}^{-3}$  and at 28, 30, 35 and 40 °C.

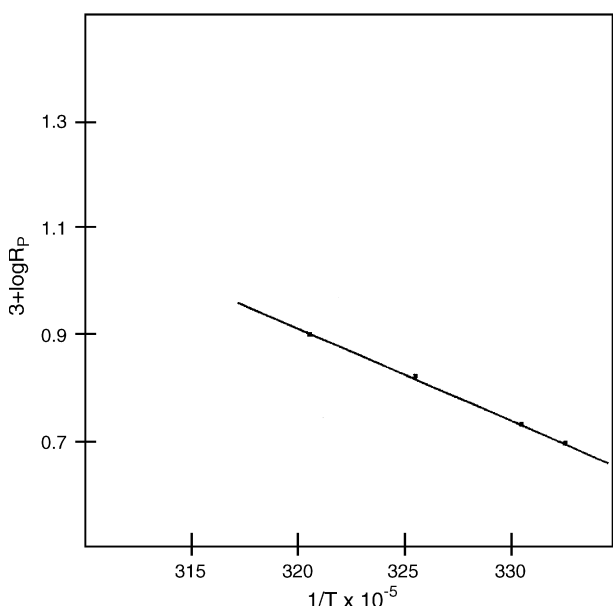


Fig. 6. Arrhenius plot of  $\log R_p$  vs.  $1/T$ :  $[V^{5+}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$ ,  $[M] = 0.3034 \text{ mol dm}^{-3}$ ,  $[\text{HCHO}_4] = 0.2 \text{ mol dm}^{-3}$ ,  $I = 3.0 \text{ mol dm}^{-3}$  and at 28, 30, 35, 40 °C.

### 3.7.2. Spectral analysis

Infrared (IR) spectrum of the polymer produced under different conditions was recorded in KBr pellet on a Shimadzu FTIR spectrophotometer in the range of 400–4000  $\text{cm}^{-1}$  (spectrum not shown here). The spectrum was analyzed for the presence of expected end group and functional group. A sharp absorption band at 2250  $\text{cm}^{-1}$  was observed for the C $\equiv$ N stretching vibration mode of the cyano group attached to the polymer chain. A sharp and medium bands at 1050 and 1200  $\text{cm}^{-1}$  and a weak signal at 650  $\text{cm}^{-1}$  confirmed the sulphite ion free radical used as an initiator of polymerization. The remaining IR peaks may be assigned for the various C–H or C–C vibration modes in the polymeric chain. The broad absorption peak observed around 3500  $\text{cm}^{-1}$  is attributable to the H-bonded O–H stretching vibration frequency of the moisture in the KBr pellet.

The <sup>1</sup>H NMR spectrum of the polymer product was recorded on a Bruker DRX-500 NMR spectrometer in DMSO-*d*<sub>6</sub> solvent (Fig. 7). The spectrum shows the presence of CH<sub>2</sub> protons in the range  $\delta$ : 2.04–2.15 ppm and CH protons at  $\delta$ : 3.12–3.16 ppm. The intensities are in the ratio 2:1. The observed signals have relatively lower  $\delta$  values than that of the protons of CH<sub>2</sub> and CH of the monomer. Thus, the decrease in  $\delta$  value confirms the formation of the polymer product.

The inset in Fig. 7 shows the expanded region from  $\delta$ : 1.0–4.7 ppm. The sharp singlet at 2.49 ppm corresponds to residual solvent (DMSO) signal and the strong singlet at 3.37 ppm corresponds to protons of moisture in the solvent.

### 3.8. Effect of intermediate injection of catalyst

Introduction of a fresh amount of catalyst ( $V^{5+}$ ) at any stage of the polymerization process leads to an overall increase in the rate and conversion of polymerization (Fig. 8). Since bisulphite remains in excess over vanadium(V) concentration, a small amount of fresh catalyst injected at any intermediate stage will naturally generate new primary radicals to carry on the reaction with increased rate. Similar observations were also reported by Palit and Konar [23], Mishra and Rebello [24] and Bajpai and Bajpai [25].

### 3.9. Mechanism and rate law

The polymerization of acrylonitrile in aqueous medium initiated by vanadium(V) in the presence of bisulphite in sulphuric acid and perchloric acid media shows characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before initiation of polymerization, becomes

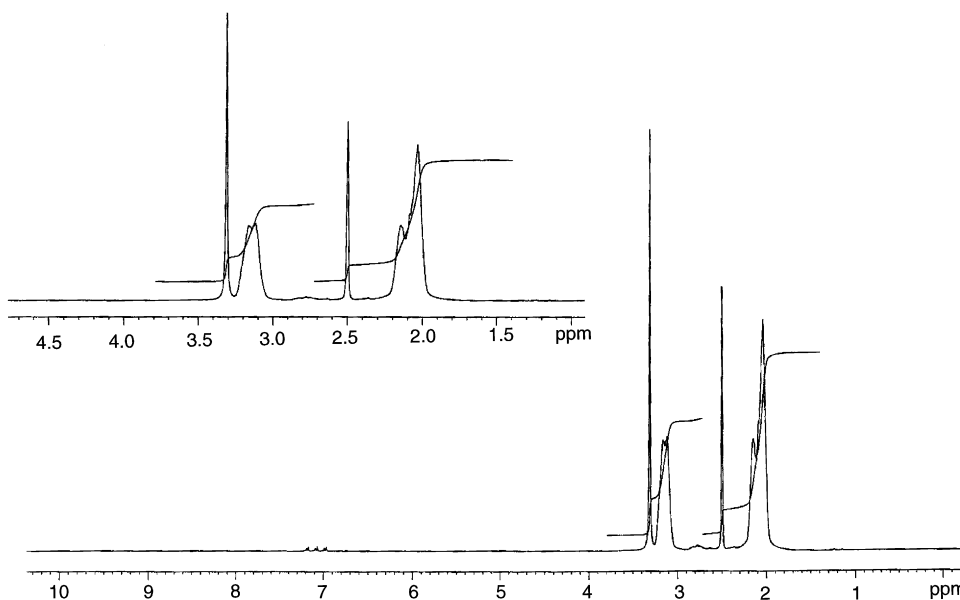


Fig. 7. The  $^1\text{H}$  NMR spectrum of polyacrylonitrile.

heterogeneous as soon as polymerization starts, due to the insolubility of the polymer in the aqueous phase.

From the proportionalities obtained between the measurable parameters and the variables, the following reaction scheme is suggested, involving initiation by the free radicals produced by the interaction of vanadium(V) with bisulphite and the termination by mutual interaction of the growing radicals:

a. Primary radical production



In the presence of the acrylonitrile monomer, the free radical ( $\text{R}^\bullet$ ) starts the chain reaction as shown below:

b. Initiation



c. Propagation

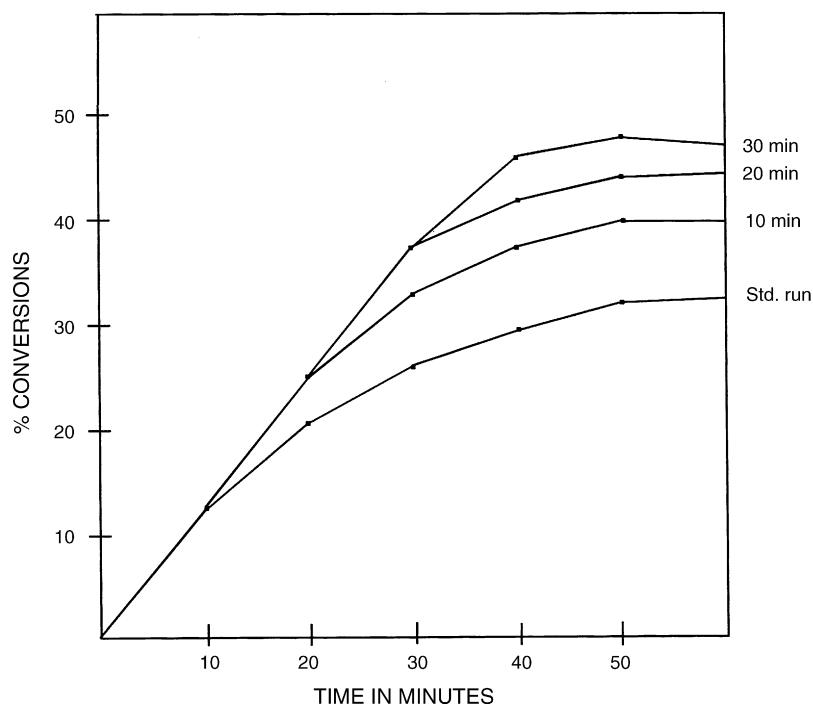
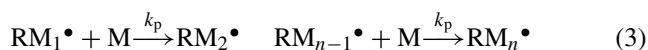
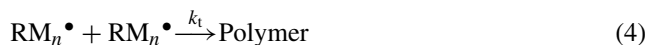


Fig. 8. Effects of intermediate injection of catalyst on the rate of polymerization.

## d. Termination



Taking into account the above reaction scheme and applying the steady state assumption to both  $[R \bullet]$  and  $[RM_n \bullet]$  separately, the following expression is derivable for the rate of polymerization:

$$\begin{aligned} \frac{d[R \bullet]}{dt} &= k_r[V^{5+}][HSO_3^-] - k_i[R \bullet][M] - k_o[R \bullet][V^{5+}] = 0 \\ &= k_r[V^{5+}][HSO_3^-] - [R \bullet]\{k_i[M] + k_o[V^{5+}]\} = 0 \end{aligned} \quad (6)$$

$$[R \bullet] = \frac{k_r[V^{5+}][HSO_3^-]}{\{k_i[M] + k_o[V^{5+}]\}} \quad (7)$$

Since propagation is the stage that involves the major consumption of the monomer, the rate of monomer loss can be expressed in terms of propagation only:

$$R_p = -\frac{d[M]}{dt} = k_p [RM_1 \bullet][M] \quad (8)$$

Based on the usual assumption that the radical reactivity is independent of the radical chain length, the rate of polymerization ( $R_p$ ) is given by:

$$R_p = k_p [RM_n \bullet][M] \quad (9)$$

In the overall polymerization process, the rate of initiation and the rate of termination become equal, resulting in a steady concentration of free radicals.

$$k_i[R \bullet][M] = k_t [RM_n \bullet]^2 \quad (10)$$

or

$$[RM_n \bullet] = \left(\frac{k_i}{k_t}\right)^{1/2} [M]^{1/2} [R \bullet]^{1/2} \quad (11)$$

Substituting for  $[R \bullet]$  from Eq. (7), we get:

$$[RM_n \bullet] = \left(\frac{k_i}{k_t}\right)^{1/2} [M]^{1/2} \left(\frac{k_r[V^{5+}][HSO_3^-]}{k_i[M] + k_o[V^{5+}]}\right)^{1/2} \quad (12)$$

The rate of polymerization,  $R_p$ , is given by:

$$R_p = k_p [RM_n \bullet][M] \quad (13)$$

Then, substituting for  $[RM_n \bullet]$  from Eq. (12), we get:

$$R_p = k_p \left(\frac{k_i k_r}{k_t}\right)^{1/2} \frac{[M]^{3/2} [V^{5+}]^{1/2} [HSO_3^-]^{1/2}}{[k_i[M] + k_o[V^{5+}]]^{1/2}} \quad (14)$$

Accordingly, the dependencies of  $R_p$  on  $[M]^{3/2}$ ,  $[V^{5+}]^{1/2}$  and  $[HSO_3^-]^{1/2}$  are supported by the above scheme.

#### 4. Conclusions

The polymerization of acrylonitrile by the V(V)-bisulphite redox system in two acid media, sulphuric and perchloric acid, proceeds by the same mechanism. The rate of V(V) disappearance is slower in  $H_2SO_4$  than in  $HClO_4$ . The rate of polymerization is lower in sulphuric acid than in perchloric acid. This is due to the greater rate of oxidation in perchloric acid medium as compared to the rate of polymerization.

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