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Oxygen-Ascorbic Acid-Vanadyl Ion Initiating System. A Kinetic Study of the Polymerization of Methyl Methacrylate and Acrylonitrile in Aqueous Sulfuric Acid

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Oxygen-Ascorbic Acid-Vanadyl Ion Initiating System. A Kinetic Study of the Polymerization of Methyl Methacrylate and Acrylonitrile in Aqueous Sulfuric Acid

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ABSTRACT

The polymerization of methyl methacrylate (MMA) and acrylonitrile (AN) initiated by the oxygen-ascorbic acid (AA)-vanadyl ion (VO^{2+}) system was studied at 40°C in dilute sulfuric acid medium. The rate of polymerization, R_p , was followed gravimetrically and found to be proportional to $[\text{MMA}]^{1.3}$, $[\text{O}_2]^{0.6}$, and $[\text{VO}^{2+}]^0$ at $[\text{VO}^{2+}] = 4-8 \times 10^{-4} \text{ M}$ in the polymerization of MMA. In the polymerization of AN, R_p was dependent on $[\text{AN}]^{1.5}$, $[\text{O}_2]^{0.5}$, and $[\text{VO}^{2+}]^0$ at $[\text{VO}^{2+}] = 4-10 \times 10^{-4} \text{ M}$, while at $[\text{VO}^{2+}] > 10^{-3} \text{ M}$ it was proportional to $[\text{AN}]^{1.7}$,

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$[O_2]^{0.7}$, and $[VO^{2+}]^{-0.6}$. A slight dependence of R_p on $[AA]$ and $[H_2SO_4]$ was observed in both polymerizations. An increase of ionic strength had an accelerating effect on R_p . An initial increase in R_p and then a decrease with temperature was noticed.

A plausible reaction mechanism with initiation by the primary radical R^* produced from the dissociation of the O_2 -AA- VO^{2+} complex and termination by mutual interaction with predominant oxidation of R^* by VO^{2+} was found to be consistent for the observed kinetic results at all $[VO^{2+}]$ for MMA and for AN at low $[VO^{2+}]$. Linear termination was found to be operative at high $[VO^{2+}]$ in the polymerization of AN. The chain length of the polymers was determined viscometrically.

INTRODUCTION

Kinetic investigation on the free radical initiating systems consisting of oxygen as a component is limited owing to the inhibiting effect of oxygen on polymerization through the formation of peroxidic radicals by direct addition for which the relative ease of propagation to termination is much less than for the R^* radicals [1-4]. However, in a few instances the accelerating effect of oxygen on the rate of polymerization was reported to be due to the participation of oxygen in the radical production step [5-10]. Oxidation of ascorbic acid (AA) by oxygen in the presence of Cu^{2+} , Fe^{3+} , and VO^{2+} was studied by Taqui Khan and Martell [11, 12]. The oxidation path was shown to be free radical in nature, going through the dissociation of the oxygen-ascorbic acid-metal ion complex. Choosing an initiating system consisting of oxygen-ascorbic acid and a metal ion, higher rates of polymerization would be expected in the presence of oxygen despite its general tendency to scavenge the primary radicals. In our earlier communications, results on the kinetics of polymerization of MMA initiated by O_2 -AA- Cu^{2+} and O_2 -AA- Fe^{3+} systems were reported wherein the rate of polymerization was observed to be about 5 to 10 times that in the absence of oxygen [13, 14]. The effect of Fe^{3+} and Cu^{2+} on R_p was interesting in that PMMA radicals were susceptible for the oxidative termination by Cu^{2+} while they were resistant to the reaction with Fe^{3+} . In this article, results on the polymerization of MMA and AN initiated by the O_2 -AA- VO^{2+} system are presented.

EXPERIMENTAL

Materials

MMA (Rohm and Haas) and AN (LR, BDH) were purified and distilled under vacuum and stored at 5°C. Fresh solutions of $VOSO_4 \cdot H_2O$

(E. Merck) in 0.1 M H_2SO_4 and ascorbic acid (GR Sarabhai M) in water were used to prevent their aerial oxidation. High purity oxygen (Indian Oxygen Ltd.), sulfuric acid (AR, BDH), and sodium hydrogen sulfate (GR, Sarabhai M) were used as such. Benzene and N,N-dimethylformamide (AR, BDH) were distilled once before use. Water triply distilled over an all-glass quick-fit unit was used for the preparation of reagents and solutions.

Methods

Required amounts of water, sulfuric acid, and vanadyl solution were taken in the reaction tube with inlet and outlet arrangements and thermostated at 40°C . The solution was saturated with oxygen by bubbling oxygen at a rate of 50 cc/min for 25 min. Then the monomer and AA were added and the solution shaken well for thorough mixing. Polymerization (as shown by the appearance of turbidity) started within a few minutes depending on the metal ion concentration. Cooling in freezing mixture was adopted to arrest the reaction. The polymer was filtered and dried at about 70°C to constant weight. R_p , the rate of polymerization, was computed from the weight of the polymer.

Chain lengths (n) of the purified polymers were determined by viscosity measurements for 0.1% solutions using an Ubbelohde suspended level dilution viscometer kept at $25 \pm 0.01^\circ\text{C}$. The Mark-Houwink equations relating $[\eta]$ with chain length (n) or molecular weight (M) employed were

$$n = 2.81 \times 10^3 [\eta]^{1.32} \quad (\text{for PMMA in benzene at } 25^\circ\text{C}) \quad [15]$$

$$[\eta] = 2.43 \times 10^{-4} M^{0.75} \quad (\text{for PAN in dimethylformamide at } 25^\circ\text{C}) \quad [16]$$

Oxygen concentration in the reaction medium was adjusted by using mixtures of N_2 and O_2 in different proportions and was determined by Winkler's method [17]. Oxygen content increased linearly with an increase in oxygen composition in the gas mixture (Fig. 1).

RESULTS AND DISCUSSION

From qualitative experiments on the polymerization of MMA and AN initiated by O_2 -AA- VO^{2+} system in aqueous sulfuric acid medium (0.11-0.21 M) at 40°C , the following observations were made. 1) VO^{2+} alone did not initiate polymerization under the experimental conditions. 2) AA, in the presence of oxygen, initiated polymerization only after a long induction period. 3) AA and VO^{2+} initiated polymerization in

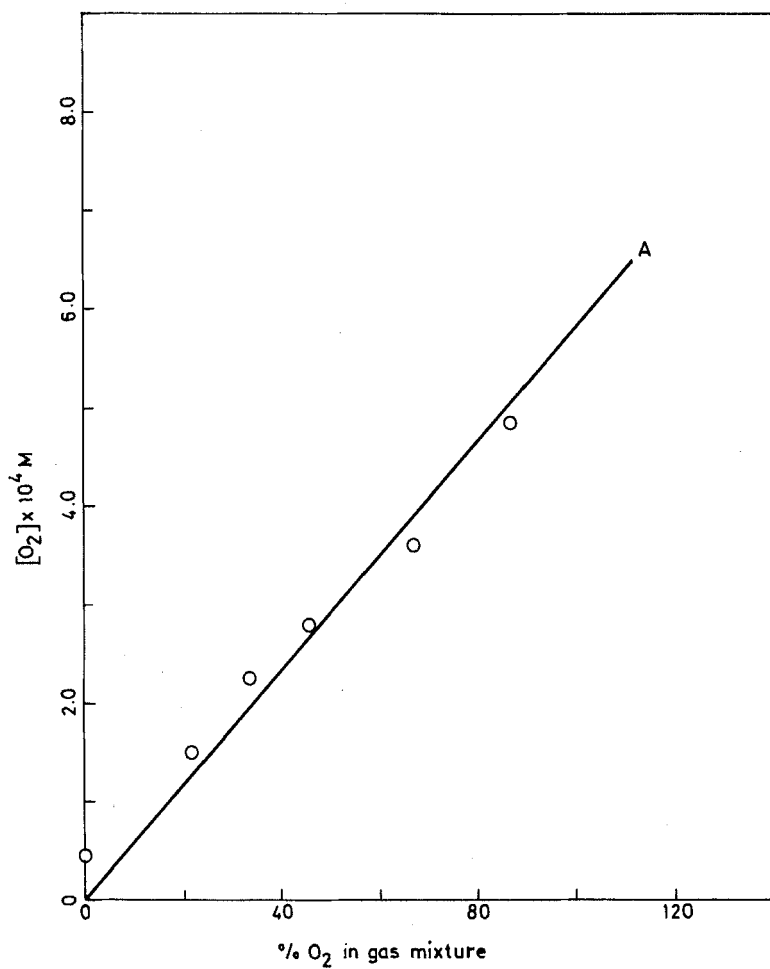


FIG. 1. Relation between $[O_2]$ in the reaction mixture (50 cc) and percent O_2 in the gas mixture.

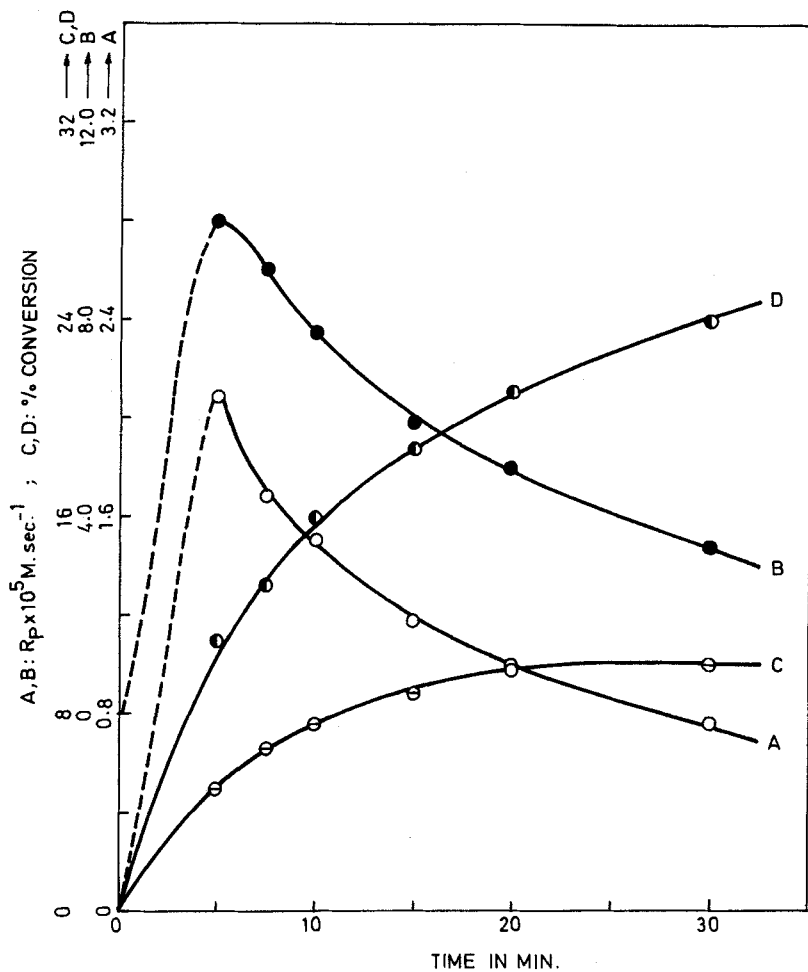


FIG. 2. Steady-state attainment. A, B: R_p vs time. C, D: Percent monomer conversion vs time. $[\text{O}_2] = 8.3 \times 10^{-4} \text{ M}$; $[\text{AA}] = 2.0 \times 10^{-3} \text{ M}$; temperature = 40°C . A, D: $[\text{MMA}] = 5.63 \times 10^{-2} \text{ M}$; $[\text{VO}^{2+}] = 8.0 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.11 \text{ M}$. B, C: $[\text{AN}] = 0.608 \text{ M}$; $[\text{VO}^{2+}] = 1.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.21 \text{ M}$.

the absence of oxygen, but the R_p was very low ($\sim 10^{-6}$ M/s). 4) AA and VO^{2+} gave higher rates in the presence of oxygen ($\sim 10^{-5}$ M/s).

Steady-state rates were obtained within 10 min for MMA below 20% conversion and for AN below 10% conversion (Fig. 2).

Influence of Vanadyl Ion Concentration

Variation of $[VO^{2+}]$ was restricted to a narrow range ($4-20 \times 10^{-4}$ M) because of large induction periods at low $[VO^{2+}]$ and low R_p at high $[VO^{2+}]$. R_p remained almost steady for $[VO^{2+}] = 4-8 \times 10^{-4}$ M and thereafter decreased. R_p was found to depend on $[VO^{2+}]^{-0.5}$ for MMA and $[VO^{2+}]^{-0.6}$ for AN systems in the decreasing region (Fig. 3). This complex effect of metal ion concentration on R_p was similar to that observed in O_2 -AA-Cu $^{2+}$ and O_2 -AA-Fe $^{3+}$ systems in the polymerization of MMA [13, 14]. It may be reasonable to assume that at still lower $[VO^{2+}]$ ($< 4 \times 10^{-4}$ M), a direct dependence of rate with varying $[VO^{2+}]$ would have resulted.

In the aqueous polymerization of AN initiated by the potassium peroxydiphosphate- VO^{2+} system, a 0.5 order in $[VO^{2+}]$ at low $[VO^{2+}]$ and 0.1 to zero order at high $[VO^{2+}]$ was reported [18]. This result was attributed to a change in the mode of termination from mutual to linear type at high $[VO^{2+}]$. A decrease in R_p with $[VO^{2+}]$ was reported in the polymerization of acrylamide [19]. Similar results were obtained for the effects of Ce $^{4+}$ [20] and Fe $^{3+}$ concentrations on vinyl polymerization [21].

Influence of Monomer Concentration

R_p was found to depend on $[MMA]^{1.3}$ and the order did not change with varying $[VO^{2+}]$ (Fig. 4). In the polymerization of MMA initiated by the O_2 -AA-Fe $^{3+}$ system, the order with respect to $[MMA]$ remained steady at 1.5 under all $[Fe^{3+}]$ [14]. $[AN]$ was varied in the range 0.303 to 1.06 M and the order was found to be variable: 1.5 at $[VO^{2+}] = 1.0 \times 10^{-3}$ and 1.7 at $[VO^{2+}] = 1.6 \times 10^{-3}$ M (Fig. 5). This is similar to the result obtained in O_2 -AA-Cu $^{2+}$ initiated polymerization of MMA where the monomer order increased with an increase in $[Cu^{2+}]$. This was explained on the basis of change in mode of termination mechanism [13]. In the Ce $^{4+}$ -glycerol initiated vinyl polymerization, the order with respect to $[M]$ changed from 1.5 to 2.0 at high $[Ce^{4+}]$ [22].

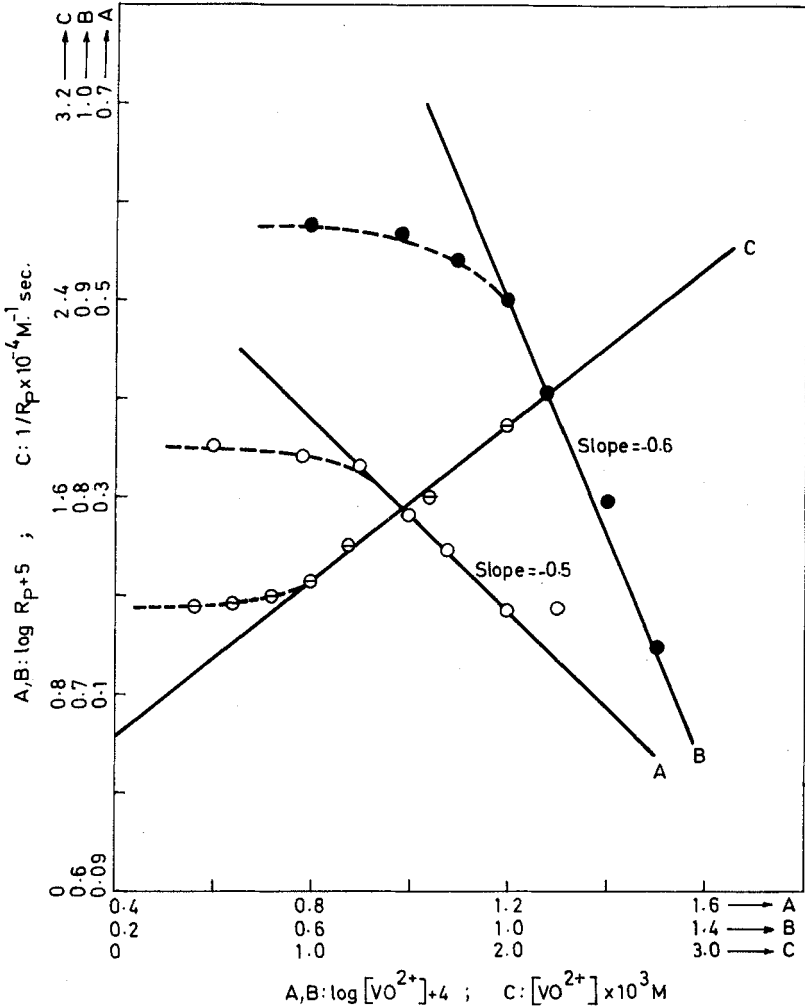


FIG. 3. Dependence of R_p on $[VO^{2+}]$. A, B: $\log R_p$ vs $\log [VO^{2+}]$. C: $1/R_p$ vs $[VO^{2+}]$. $[AA] = 2.0 \times 10^{-3} M$; $[O_2] = 8.3 \times 10^{-4} M$; $[H_2SO_4] = 0.21 M$; temperature = $40^\circ C$. A: $[MMA] = 5.63 \times 10^{-2} M$. B, C: $[AN] = 0.608 M$.

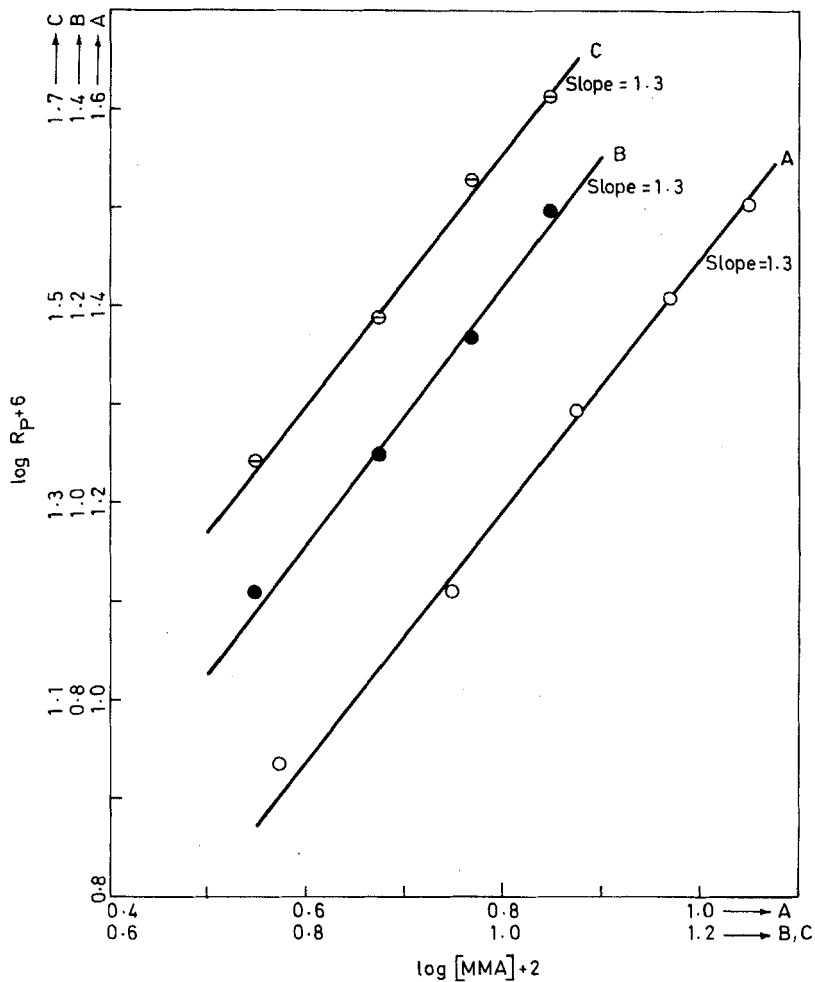


FIG. 4. Plots of $\log R_p$ vs $\log [MMA]$. $[AA] = 2.0 \times 10^{-3} \text{ M}$; $[O_2] = 8.3 \times 10^{-4} \text{ M}$; temperature = 40°C . A: $[VO^{2+}] = 8.0 \times 10^{-4} \text{ M}$, $[H_2SO_4] = 0.11 \text{ M}$. B: $[VO^{2+}] = 1.4 \times 10^{-3} \text{ M}$, $[H_2SO_4] = 0.11 \text{ M}$. C: $[VO^{2+}] = 8.0 \times 10^{-4} \text{ M}$, $[H_2SO_4] = 0.21 \text{ M}$.

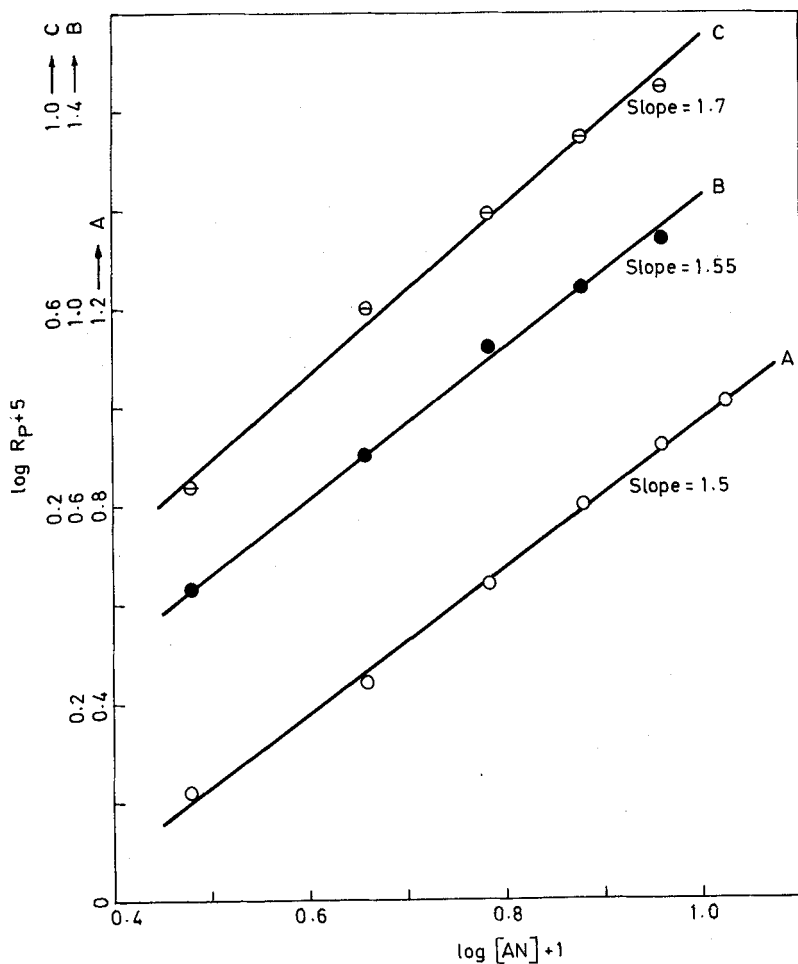


FIG. 5. Plots of $\log R_p$ vs $\log [AN]$. $[AA] = 2.0 \times 10^{-3} \text{ M}$; $[O_2] = 8.3 \times 10^{-4} \text{ M}$; temperature = 40°C . A: $[VO^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $[H_2SO_4] = 0.11 \text{ M}$. B: $[VO^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $[H_2SO_4] = 0.21 \text{ M}$. C: $[VO^{2+}] = 1.6 \times 10^{-3} \text{ M}$, $[H_2SO_4] = 0.21 \text{ M}$.

TABLE 1. R_p in Oxygen and in the Absence of Oxygen ($[AA] = 2.0 \times 10^{-3} M$, $[H_2SO_4] = 0.21 M$)

| Monomer | [Monomer] \underline{M} | $[VO^{2+}] \times 10^4$ \underline{M} | In oxygen, $R_p \times 10^5$ M/s | In absence of O_2 , $R_p \times 10^6$ M/s |
|---------|------------------------------|--|--|--|
| MMA | 0.056 | 8 | 2.23 | 5.00 |
| AN | 0.608 | 10 | 7.57 | 8.50 |

Influence of Oxygen Concentration

R_p in the presence and in the absence of oxygen is given in Table 1. Polymerization in the absence of oxygen may be due to radicals from the AA and VO^{2+} reaction [12]. A constant R_p was obtained at $[O_2] > 6.5 \times 10^{-4} M$ for these monomers (Table 2). The order in $[O_2]$ was observed to be 0.6 for MMA. The 0.5 order in $[O_2]$ changed to 0.7 at high $[VO^{2+}]$ for AN (FIG. 6).

Influence of Ascorbic Acid Concentration

R_p was found to increase marginally with an increase in $[AA]$ unlike the Cu^{2+} and Fe^{3+} systems where R_p did not depend on $[AA]$ after a particular concentration (Table 3). The increase in R_p in the present investigation may be attributed to the influence of $[AA]$ on the complex concentration. It is of interest to note that the $[AA]$ used in this system was comparable to the $[O_2]$ and $[VO^{2+}]$ employed.

Influence of $[H_2SO_4]$, μ , and Temperature

An increase in $[H_2SO_4]$ from 0.05 to 0.5 M resulted only in a small increase in R_p (Table 4). In the oxidation of AA by O_2 catalyzed by VO^{2+} , a direct dependence of the rate on $[H_2SO_4]$ was reported [12]. Hence the observed minor effect of $[H_2SO_4]$ on R_p may result from the enhanced oxidation of primary radicals by VO^{2+} or termination of growing radicals by VO^{2+} or both.

Ionic strength had an accelerating effect on R_p (Table 5). Bamford, Jenkins, and Johnston [23] showed that the acrylonitrile radical can

TABLE 2. Influence of $[O_2]$ on R_p and Chain Length ($[AA] = 2.0 \times 10^{-3} M$, $[H_2SO_4] = 0.11 M$, temperature = $40^\circ C$)

| $[O_2] \times 10^4$ \underline{M} | $[MMA] = 5.63 \times 10^{-2} \underline{M}$, $[VO^{2+}] = 8.0 \times 10^{-4} \underline{M}$ | | $[AN] = 0.608 \underline{M}$, $[VO^{2+}] = 1.0 \times 10^{-3} \underline{M}$ | |
|--|---|------|--|------|
| | $R_p \times 10^5$ M/s | n | $R_p \times 10^5$ M/s | n |
| 5.20 | 1.29 | 948 | 4.42 | 1830 |
| 6.55 | 1.37 | 1090 | 4.78 | 1760 |
| 7.28 | 1.27 | 959 | 4.59 | 1690 |
| 8.25 | 1.33 | 990 | 4.84 | - |
| 8.31 | 1.35 | - | 5.38 | 1780 |
| 8.40 | 1.33 | 992 | 4.70 | 1680 |
| 8.37 | 1.31 | 985 | 5.07 | 1620 |

form complexes with added salts such as LiCl and LiNO₃, and that the increase in R_p was due to the catalytic effect of salts on the propagation step.

R_p was observed to increase up to $35^\circ C$, remained almost constant at 35 to $45^\circ C$, and then decreased in the polymerization of MMA while a decrease in R_p was noticed above $35^\circ C$ in the polymerization of AN (Table 6). The above thermal behavior may be explained on the basis of the relative magnitudes of two factors: 1) the decrease in the stability constant of the complex (O_2 -AA- VO^{2+} complex [12]) with increasing temperature and 2) the increase in $(k_p/k_t^{1/2})k_1$ value (which depends on the nature of the monomer) with increasing temperature.

Chain Length

Chain length (n) increased with $[M]$ (Fig. 7) and decreased with $[O_2]$ (Fig. 8), $[AA]$ (Table 3), and $[H_2SO_4]$ (Table 4) for both MMA and AN systems. n values increased with $[VO^{2+}]$ in the MMA system, while a reverse trend was observed in the AN system (Fig. 9). Chain lengths increased with polymerization temperature for MMA while in the AN system they decreased (Table 6). Chain lengths remained almost independent of $[O_2]$ in the region where R_p was also independent of $[O_2]$ (Table 2).

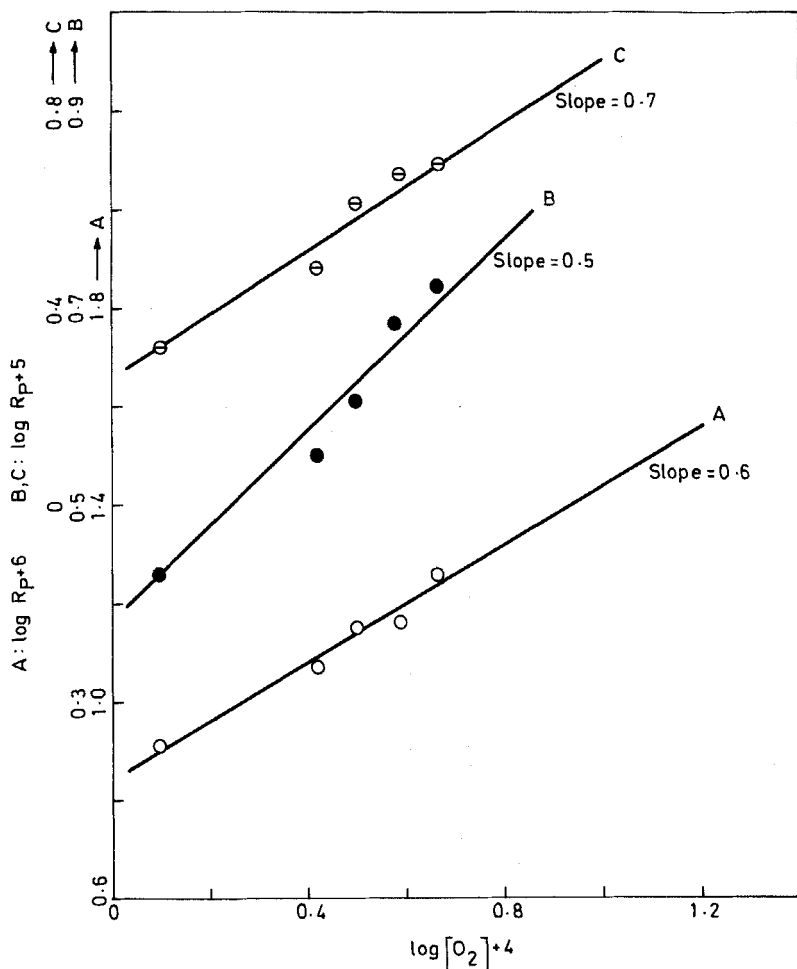


FIG. 6. Plots of $\log R_p$ vs $\log [O_2]$. A: MMA. B, C: AN. $[AA] = 2.0 \times 10^{-3} \text{ M}$; $[H_2SO_4] = 0.21 \text{ M}$; temperature = 40°C . A: $[MMA] = 5.63 \times 10^{-2} \text{ M}$, $[VO^{2+}] = 8.0 \times 10^{-4} \text{ M}$. B: $[AN] = 0.608 \text{ M}$, $[VO^{2+}] = 1.0 \times 10^{-3} \text{ M}$. C: $[AN] = 0.608 \text{ M}$, $[VO^{2+}] = 1.6 \times 10^{-3} \text{ M}$.

TABLE 3. Influence of [AA] on R_p and Chain Length ($[O_2] = 8.3 \times 10^{-4} M$, $[H_2SO_4] = 0.21 M$, temperature = 40°C)

| $[AA] \times 10^3$ M | $[MMA] = 5.63 \times 10^{-2} M$, $[VO^{2+}] = 8.0 \times 10^{-4} M$ | | $[AN] = 0.608 M$, $[VO^{2+}] = 1.0 \times 10^{-3} M$ | | $[AN] = 0.608 M$, $[VO^{2+}] = 1.6 \times 10^{-3} M$ | |
|-------------------------|---|------|--|------|--|------|
| | $R_p \times 10^5$ M/s | n | $R_p \times 10^5$ M/s | n | $R_p \times 10^5$ M/s | n |
| 1.0 | 1.82 | 1120 | 6.50 | 2290 | 5.30 | 2110 |
| 1.2 | 1.82 | 1080 | 6.95 | 2150 | 5.48 | 2060 |
| 1.6 | 1.94 | - | 7.49 | 2010 | 5.91 | 1920 |
| 2.0 | 2.00 | 1010 | 7.73 | 2280 | 6.18 | 1950 |
| 3.0 | 2.15 | 890 | 8.23 | 1960 | 6.83 | 1870 |
| 4.0 | 2.25 | 816 | 8.21 | 1870 | 6.86 | 1690 |
| 6.0 | 2.50 | 685 | 8.64 | 1720 | 6.92 | 1420 |
| 8.0 | 2.43 | 692 | 8.98 | 1810 | 7.43 | - |

TABLE 4. Influence of $[H_2SO_4]$ on R_p and Chain Length ($[AA] = 2.0 \times 10^{-3} M$, $[O_2] = 8.3 \times 10^{-4} M$, temperature = $40^\circ C$, $\mu = 0.5 M$)

| $[H_2SO_4]$ <u>M</u> | $[MMA] = 5.63 \times 10^{-2} M,$ $[VO^{2+}] = 8.0 \times 10^{-4} M$ | | $[AN] = 0.608 M,$ $[VO^{2+}] = 1.0 \times 10^{-3} M$ | |
|-------------------------|--|-----|---|------|
| | $R_p \times 10^5 M/s$ | n | $R_p \times 10^4 M/s$ | n |
| 0.05 | 2.37 | 695 | 0.916 | 2270 |
| 0.10 | 2.51 | 637 | 0.965 | 2230 |
| 0.15 | 2.69 | 608 | 1.030 | - |
| 0.20 | 2.63 | 514 | 1.080 | 2110 |
| 0.30 | 2.88 | 437 | 1.110 | 2130 |
| 0.40 | 3.17 | 347 | 1.190 | 1890 |
| 0.50 | 3.46 | 282 | 1.210 | 1630 |

TABLE 5. Influence of μ on R_p ($[AA] = 2.0 \times 10^{-3} M$, $[O_2] = 8.3 \times 10^{-4} M$, temperature = $40^\circ C$, $[H_2SO_4] = 0.21 M$)

| μ <u>M</u> | $[MMA] = 5.63 \times 10^{-2} M,$ $[VO^{2+}] = 8.0 \times 10^{-4} M$ | | $[AN] = 0.608 M,$ $[VO^{2+}] = 1.0 \times 10^{-3} M$ | |
|-------------------|--|--|---|--|
| | $R_p \times 10^5 M/s$ | | $R_p \times 10^5 M/s$ | |
| 0.1 | 1.52 | | 1.77 | |
| 0.2 | 1.85 | | 3.34 | |
| 0.3 | 2.09 | | 5.36 | |
| 0.4 | 2.41 | | 6.80 | |
| 0.5 | 2.64 | | 8.76 | |
| 0.6 | 2.78 | | 9.82 | |

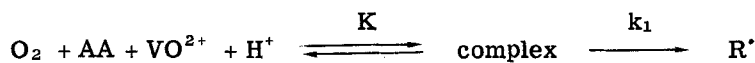
TABLE 6. Influence of Temperature on R_p and Chain Length ($[AA] = 2.0 \times 10^{-3} \text{ M}$, $[H_2SO_4] = 0.21 \text{ M}$, $[O_2] = 8.3 \times 10^{-4} \text{ M}$, temperature = 40°C)

| Temperature ($^\circ\text{C}$) | $\frac{[MMA] = 5.63 \times 10^{-2} \text{ M},}{[VO^{2+}] = 8.0 \times 10^{-4} \text{ M}}$ | | $\frac{[AN] = 0.608 \text{ M},}{[VO^{2+}] = 1.0 \times 10^{-3} \text{ M}}$ | |
|-------------------------------------|---|-----|--|------|
| | $R_p \times 10^5 \text{ M/s}$ | n | $R_p \times 10^5 \text{ M/s}$ | n |
| 25 | 1.67 | 414 | 7.12 | 1740 |
| 30 | 1.83 | 488 | 7.54 | 1780 |
| 35 | 2.02 | 542 | 8.02 | 1790 |
| 40 | 2.06 | 630 | 7.64 | 1710 |
| 45 | 2.07 | 645 | 6.97 | 1630 |
| 50 | 1.85 | 722 | 5.60 | 1410 |
| 55 | 1.55 | 800 | 5.02 | 1380 |

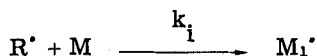
Kinetic Scheme and Rate Law

The kinetic results can be explained by the following reaction scheme which is similar to that assumed for O_2 -AA- Cu^{2+} and O_2 -AA- Fe^{3+} systems with the difference that the complex is a protonated species [12].

(i) Production of primary radicals by the interaction of O_2 , AA, VO^{2+} , and H^+ preceded by the formation of a complex:



(ii) Initiation:



(iii) Propagation:



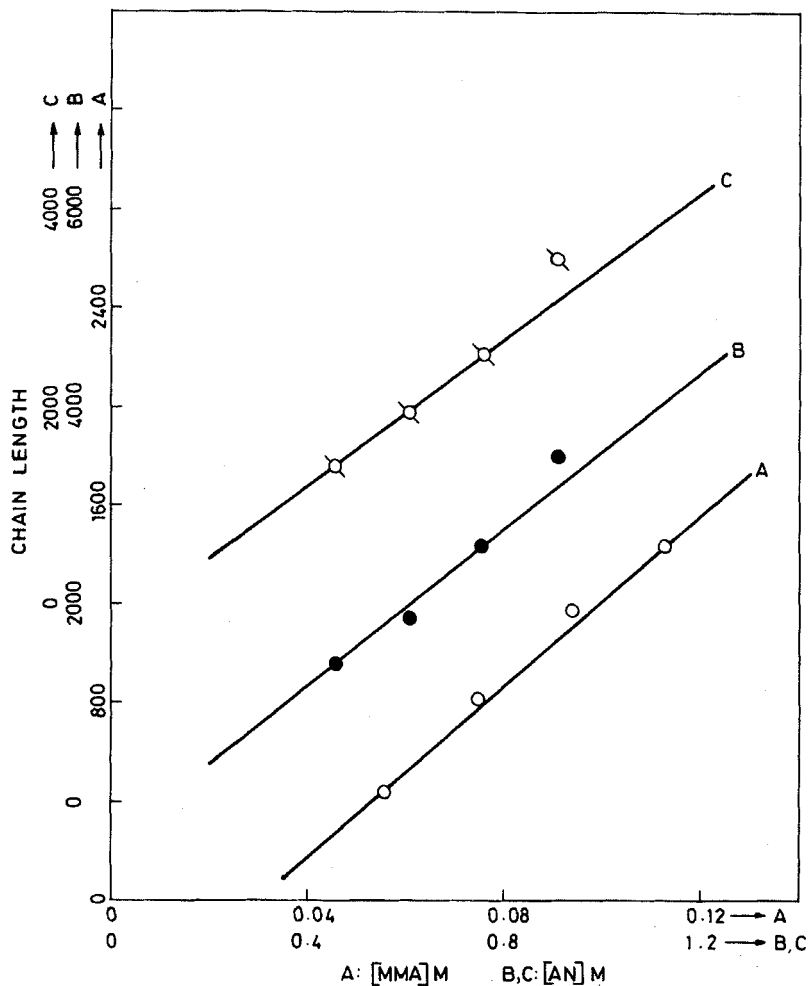


FIG. 7. Plots of chain length vs [monomer]. A: MMA. B, C: AN. $[AA] = 2.0 \times 10^{-3} \text{ M}$; $[O_2] = 8.3 \times 10^{-4} \text{ M}$; temperature = 40°C . $[H_2SO_4] = 0.21 \text{ M}$. A: $[VO^{2+}] = 8.0 \times 10^{-4} \text{ M}$. B: $[VO^{2+}] = 1.0 \times 10^{-3} \text{ M}$. C: $[VO^{2+}] = 1.6 \times 10^{-3} \text{ M}$.

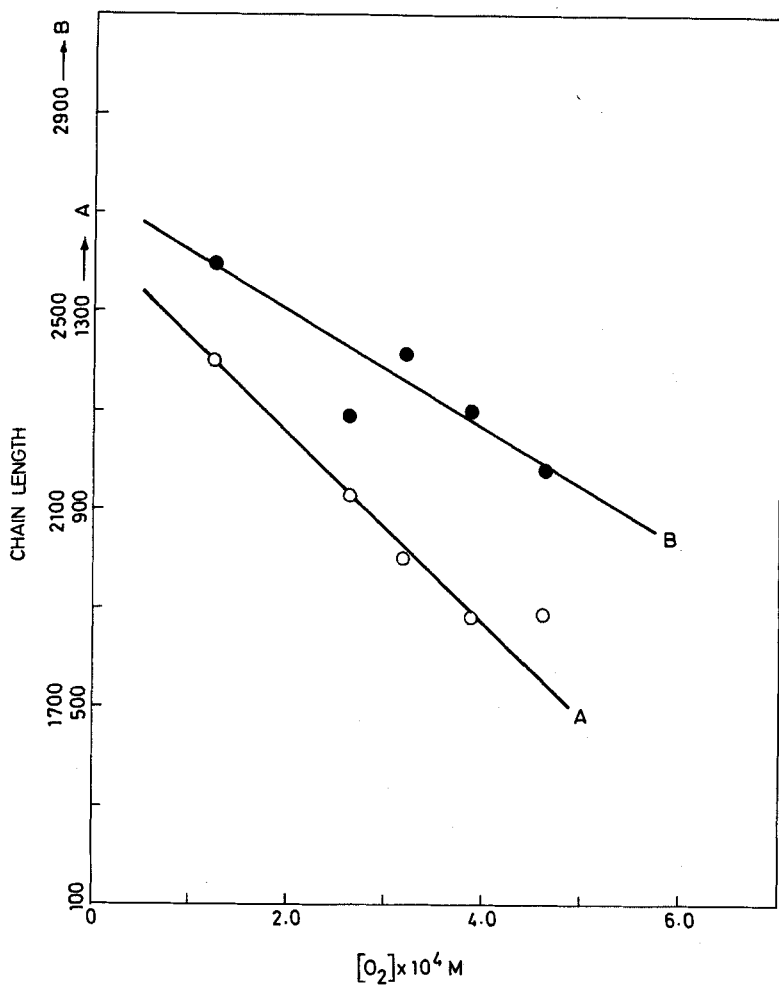


FIG. 8. Plots of chain length vs $[O_2]$. A: MMA. B: AN. $[AA] = 2.0 \times 10^{-3} M$; $[H_2SO_4] = 0.21 M$; temperature = $40^\circ C$. A: $[MMA] = 5.63 \times 10^{-2} M$, $[VO^{2+}] = 8.0 \times 10^{-4} M$. B: $[AN] = 0.608 M$, $[VO^{2+}] = 1.0 \times 10^{-3} M$.

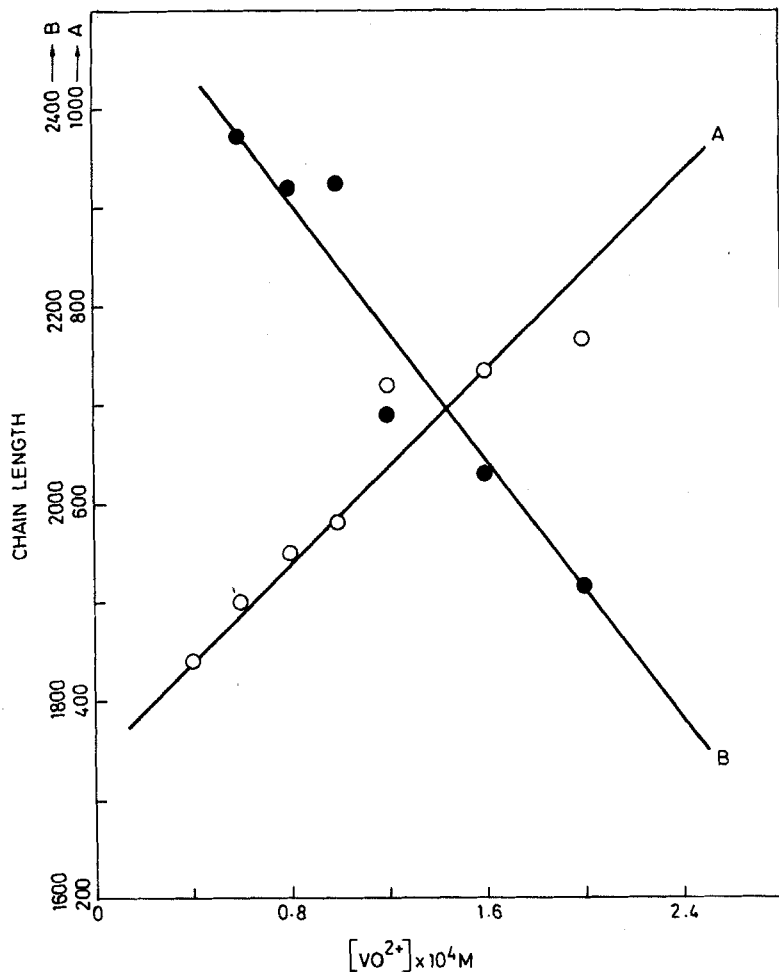
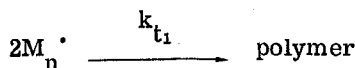


FIG. 9. Plots of chain length vs $[VO^{2+}]$. A: MMA. B: AN. $[AA] = 2.0 \times 10^{-3} M$; $[O_2] = 8.3 \times 10^{-4} M$; $[H_2SO_4] = 0.21 M$; temperature = $40^\circ C$. A: $[MMA] = 5.63 \times 10^{-2} M$. B: $[AN] = 0.608 M$.

(iv) Termination:

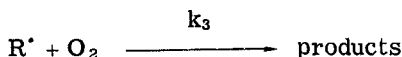
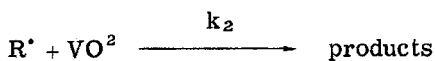
(a) By mutual interaction:



(b) By metal ions (linear termination):



(v) Primary radical deactivation:



The expression for the rate of monomer disappearance ($-d[M]/dt = R_p$) and n of the polymer were derived from the scheme presented above assuming stationary state concentrations for free radicals and nondependence of rate constants (k_p and k_t) on chain length.

Assuming initiation by $R \cdot$ and termination by the mutual interaction of the growing radicals, the expression for R_p may be derived as

$$R_p = \frac{k_p}{k_{t1}^{1/2}} [M] \left[\frac{Kk_1k_i[O_2][AA][VO^{2+}][H^+][M]}{(k_i[M] + k_2[VO^{2+}] + k_3[O_2])} \right]^{1/2} \quad (1)$$

Under conditions $k_2[VO^{2+}] \gg k_i[M] + k_3[O_2]$, Eq. (1) reduces to

$$R_p = \frac{k_p}{k_{t1}^{1/2}} [M]^{3/2} \left[\frac{Kk_1k_i[AA][O_2][H^+]}{k_2} \right]^{1/2} \quad (2)$$

Equation (2) satisfies the majority of the experimental observations at low $[VO^{2+}]$ ($4-8 \times 10^{-4} M$) for MMA and AN. Similar kinetics were reported in the polymerization of MMA and AN initiated by Mn^{3+} malonic acid system to explain the independence of R_p on $[Mn^{3+}]$ [24].

It may be reasonable to assume the preponderance of metal ion oxidation of R^* over the reaction between R^* and monomer.

The expression for n can be written as

$$n = \frac{k_p}{k_{t1}^{1/2}} [M]^{1/2} \left[\frac{k_2}{Kk_1k_i[AA][O_2][H^+]} \right]^{1/2} \quad (3)$$

Experimentally observed direct dependence of n on $[M]$ and inverse dependence on $[AA]$, $[O_2]$, and $[H_2SO_4]$ at these $[VO^{2+}]$ confirms the above equation.

At $[VO^{2+}] > 10^{-3} M$, the constancy of the order with respect to $[MMA]$ may be due to the fact that PMMA radicals resist oxidation by VO^{2+} similar to the MMA and Fe^{3+} system [14]. Increase in chain length with $[VO^{2+}]$ also supports the belief that VO^{2+} does not react with PMMA radicals. The decrease in R_p with $[VO^{2+}]$ in this region while the order in $[MMA]$ remaining the same, i.e., 1.3, parallels the observation made in the polymerization of MMA initiated by the O_2 -AA- Fe^{3+} system at high $[Fe^{3+}]$. In both cases the results could not be explained. However, the variation of the order with respect to $[AN]$ from 1.5 to 1.7 at high $[VO^{2+}]$ indicates that PAN radicals are likely to interact with VO^{2+} , just as in the polymerization of AN initiated by the potassium peroxydiphosphate and VO^{2+} system. Linear termination of polymer chains by oxidative and reductive mechanisms [28] has been well established. However, the specific mechanism of termination, whether oxidative or reductive, is not certain in the present investigation. In view of the oxidation potential required for the process $VO^{2+} \rightarrow VO_2^+$ (-1.00 V in 1 M acid), Cavell and Meeks [19] have ruled out the possibility of reduction of polyacrylamide radicals by VO^{2+} . Similar to terminations with Cu^{2+} and Fe^{3+} , it was assumed that VO^{2+} also terminates the PAN radicals by oxidation.

The rate expression for monomer disappearance, assuming linear termination, may be written as

$$R_p = \frac{k_p}{k_{t2}} \frac{K k_1 k_i [AA] [O_2] [H^+] [M]^2}{(k_1 [M] + k_2 [VO^{2+}] + k_3 [O_2])} \quad (4)$$

In Eq. (4) the orders with respect to $[O_2]$, $[VO^{2+}]$, and $[M]$ can have any values from 0 to 1, 0 to -1, and 1 to 2, respectively, depending on the magnitudes of k_1 , k_2 , and k_3 terms, thus justifying the fractional orders with respect to $[O_2]$, $[VO^{2+}]$, and $[AN]$ observed at high $[VO^{2+}]$ in the polymerization of AN. A plot of $1/R_p$ vs $[VO^{2+}]$

(Fig. 3) also gave a straight line with an intercept on the Y-axis, thus verifying Eq. (4).

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