

Peroxo Salts as Initiators of Vinyl Polymerization IV. Polymerization of Acrylonitrile by the Peroxo- monosulphate–Oxovanadium(IV) System[†]

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ABSTRACT: A detailed kinetic study of the aqueous polymerization of acrylonitrile (AN) initiated by peroxomonosulphate (HSO_5^- , PMS)–oxovanadium(IV) redox system has been made in the temperature range 30°–60°C under deaerated conditions at a constant ionic strength ($\mu = 1.20$). The effects of [monomer], [PMS], [oxovanadium(IV)], $[\text{H}^+]$, μ and temperature on rate of polymerization, R_p were investigated and the R_p was found to be proportional to $[\text{AN}]^{1.5} [\text{HSO}_5^-]^{0.5} [\text{oxovanadium(IV)}]^{0.5}$. The kinetic and thermodynamic parameters were evaluated and are discussed. A suitable reaction scheme involving redox reaction of HSO_5^- and oxovanadium(IV) with mutual termination is proposed. The expression for degree of polymerization, \bar{X}_n was obtained by molecular weight determination of the formed polymers. A comparison was also made with a similar redox system involving peroxodiphosphate.

KEY WORDS Thermal Polymerization / Peroxomonosulphate–Oxovanadium(IV) Redox System / Rate of Polymerization / Monomer / Peroxomonosulphate / Oxovanadium(IV) / Temperature Effect / Degree of Polymerization /

Our previous studies^{1–3} demonstrated clearly that, peroxomonosulphate (HSO_5^- , PMS) can be employed as an efficient water soluble initiator for vinyl polymerization in coupling with suitable reducing agents involving redox reactions. As an extension of this investigation, we now report peroxomonosulphate–oxovanadium(IV) for aqueous, thermal polymerization of acrylonitrile. In the present study, the oxovanadium(IV) ion is represented as VO^{2+} in all discussions.

The kinetics of reduction of PMS by oxovanadium(IV) ion in acidic solution⁴ and the use of trapping agents like HN_3 and Ce(III) proved that the reaction of PMS with oxovanadium(IV) involved a free radical mechanism. Moreover, formation of SO_4^- radical as

the transient intermediate was invoked in one electron reduction of $\text{PMS}^{5,6}$ and in pulse radiolytic studies⁷ of the reduction of PMS by hydrated electrons.

The metal ion, VO^{2+} undergoes oxidation to produce VO_2^+ which can be ineffective as initiating species⁸ but the reaction proceeds with radical intermediates. Furthermore, in redox systems involving metal ion as one of the components (as either reducing or oxidizing agent), linear termination is also a possible reaction and both oxidative and reductive terminations of the polymer radicals by metal ions have already been encountered.^{9–13}

The essential difference between the PMS– VO^{2+} system and our previously reported³ PMS– Co^{2+} system is that the product formed,

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Co(III) in the latter system is capable of initiating polymerization, whereas in the present investigation, VO_2^+ formed is a stable species and not capable of initiating polymerization. However, the formation of SO_4^- as the reactive intermediate has added interest and led to choosing this metal ion, VO^{2+} as reducing agent component of redox initiator with peroxomonosulphate.

EXPERIMENTAL

Materials

Solutions of HSO_5^- were prepared as reported in a previous work.³ Fresh solutions of vanadyl sulphate (0.05 mol dm^{-3}) were prepared for all experiments and standardized by permanganometry in acid medium to pale pink colour.¹⁴ Doubly distilled water was always used for the experiments.

Methods

The purification of the monomer and experimental methods are essentially as described earlier.^{2,3} All the experiments were conducted in aqueous solution at 0.10 mol dm^{-3} $[\text{H}^+]$ under deaerated conditions (with purified N_2) at 40°C with the reactants in the following concentration range

$$\begin{aligned} [\text{AN}] &= 6.08\text{--}9.88 \times 10^{-1} \text{ mol dm}^{-3} \\ [\text{PMS}] &= 0.40\text{--}3.97 \times 10^{-3} \text{ mol dm}^{-3} \\ [\text{VO}^{2+}] &= 1.07\text{--}5.99 \times 10^{-4} \text{ mol dm}^{-3} \\ \mu &= 1.20 \end{aligned}$$

The molecular weights (\bar{M}_w) of the formed polymers were obtained by viscometry by extrapolation methods of Huggins¹⁵ and Kraemer¹⁶ and the Mark-Houwink equation,¹⁷ $[\eta] = 3.35 \times 10^{-4} (\bar{M}_w)^{0.72}$ was used for poly(acrylonitrile) in dimethyl formamide at 30°C .

RESULTS AND DISCUSSION

The polymerization was found to start without any significant induction period. The radical nature of the reaction was evident by the

inhibition of polymerization in presence of atmospheric oxygen. The polymerization proceeded approximately for twenty minutes and then attained steady state (Figure 1).

Effect of [monomer] on R_p

The polymerization reactions were carried out with varying concentrations of acrylonitrile ($[\text{AN}] = 6.08\text{--}9.88 \times 10^{-1} \text{ mol dm}^{-3}$) at constant $[\text{PMS}]$ and $[\text{VO}^{2+}]$ ($0.97\text{--}4.94 \times 10^{-3} \text{ mol dm}^{-3}$ and $4.92 \times 10^{-4} \text{ mol dm}^{-3}$ respectively) at 40°C with 0.10 mol dm^{-3} $[\text{H}^+]$ and constant ionic strength (1.20 mol dm^{-3}) to observe the effects of variation of monomer concentration on R_p . R_p was found to vary linearly with increase in [monomer] and the plot of R_p versus $[\text{AN}]^{1.5}$ (Figure 2) with lines passing through the origin indicated the 1.5 order dependence of R_p on [monomer]. Similarly, plots of $\log R_p$ versus $\log [\text{AN}]$ were also found to be linear with a slope equal to 1.5. The higher monomer order normally represents the monomer involvement in the primary radical producing reactions.

Effect of [PMS] on R_p

The variation of $[\text{PMS}]$ in the range $0.40\text{--}3.97 \times 10^{-3} \text{ mol dm}^{-3}$ at fixed [monomer] and $[\text{VO}^{2+}]$ (0.99 mol dm^{-3} and $4.92 \times 10^{-4} \text{ mol dm}^{-3}$ respectively) with an ionic strength of 1.20 in presence of H^+ (0.10 mol dm^{-3}) was carried out to investigate the effect of $[\text{PMS}]$ on R_p . R_p was found to increase linearly upto $1.06 \times 10^{-3} \text{ mol dm}^{-3}$ at various $[\text{VO}^{2+}]$ ($1.07\text{--}4.92 \times 10^{-4} \text{ mol dm}^{-3}$). R_p was found to be proportional to $[\text{PMS}]^{0.5}$, which was revealed by a linear plot of R_p versus $[\text{PMS}]^{0.5}$ (Figure 3) passing through the origin.

Effect of $[\text{VO}^{2+}]$ on R_p

The concentration of VO^{2+} was varied in the range $1.07\text{--}5.99 \times 10^{-4} \text{ mol dm}^{-3}$ at constant [monomer], $[\text{H}^+]$ and ionic strength (0.99 mol dm^{-3} , 0.10 mol dm^{-3} and 1.20 mol dm^{-3} respectively) with varying $[\text{PMS}]$ ($1.18\text{--}4.92 \times 10^{-3} \text{ mol dm}^{-3}$). R_p was found to in-

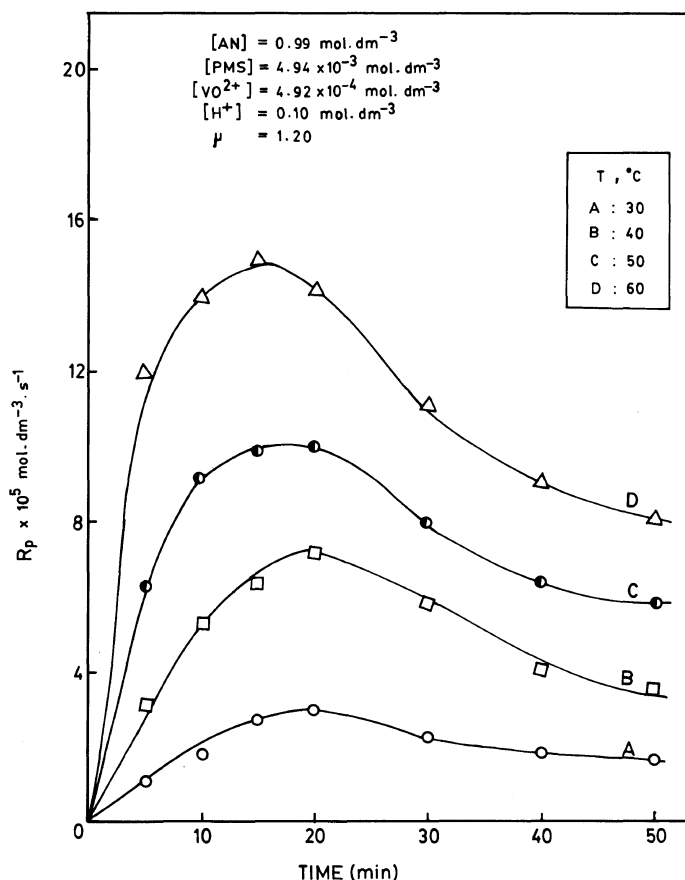


Figure 1. Effect of time on rate of polymerization, R_p .

crease with increase in $[VO^{2+}]$ with 0.5 order dependence. A plot of R_p versus $[VO^{2+}]^{0.5}$ was also linear with zero intercept (Figure 4) showing the half-order dependence of R_p on $[VO^{2+}]$.

Effect of Ionic Strength (μ) and $[H^+]$ on R_p

Ionic strength (μ) was varied in the range 0.80–1.50 keeping all other reactants constant at 40°C ($[AN]=0.99 \text{ mol dm}^{-3}$ $[PMS]=4.94 \times 10^{-3} \text{ mol dm}^{-3}$, $[VO^{2+}]=4.92 \times 10^{-4} \text{ mol dm}^{-3}$ and $[H^+]=0.10 \text{ mol dm}^{-3}$). R_p showed a slow increase upto $\mu=1.20$ as was normally observed for the reaction between oppositely charged ions.¹⁸ Similarly, $[H^+]$ was varied from 0.06–0.50 mol dm^{-3} at

constant ionic strength (1.20) and at constant concentrations of AN, PMS, VO^{2+} . R_p was found to increase a little and then decrease upto 0.50 mol dm^{-3} $[H^+]$.

Effect of Temperature on R_p

The temperature variation of the reaction exerted a significant positive influence on R_p which increased with temperature. From the plot of $\log R_p$ versus T^{-1} (Figure 5), the overall activation energy, E_a was evaluated to be 56.10 kJ mol^{-1} .

Degree of Polymerization, \bar{X}_n

The variation of [monomer], [PMS] and $[VO^{2+}]$ showed a marked influence on the

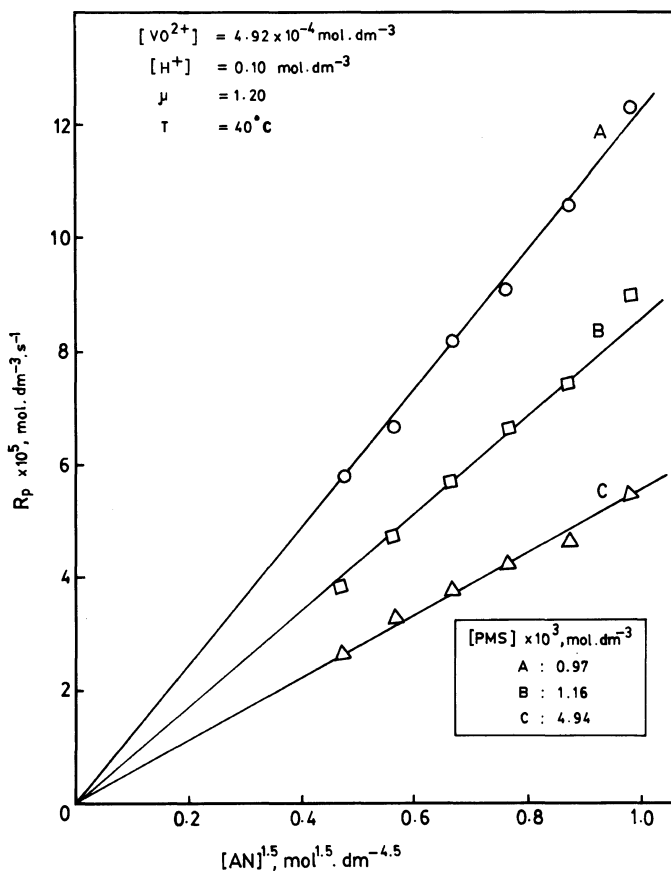


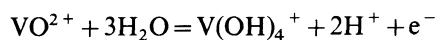
Figure 2. Effect of [monomer] on R_p at constant [PMS] and $[\text{VO}^{2+}]$.

degree of polymerization, \bar{X}_n . Increase of [monomer], [PMS] and $[\text{VO}^{2+}]$ showed a marked influence on the degree of polymerization, \bar{X}_n . With increase in monomer, \bar{X}_n increased, whereas the increase in [PMS] and $[\text{VO}^{2+}]$ had a negative influence on \bar{X}_n . The individual plot of $\log \bar{X}_n$ versus $\log[\text{monomer}]$, and $\log[\text{PMS}]$ and $\log[\text{VO}^{2+}]$ revealed the above effect (Figure 6).

REACTION SCHEME AND MECHANISM

R_p was found to depend upon $[\text{monomer}]^{1.5}$ $[\text{PMS}]^{0.5}$ and $[\text{VO}^{2+}]^{0.5}$. In acidic solution, the existence of oxovanadium(IV) as VO^{2+} was confirmed by an electronic spectral and paramagnetic resonance data.^{19,20} The data

obtained at high acidities also indicated the presence of VO^{2+} ions (but did not rule out $\text{V}(\text{OH})_2^{2+}$). At higher pH, the measurements were difficult to interpret because of the presence of hydrolysis products of both the oxidation states V(IV) and V(V). Indeed, the complexities which arise at pH 2.5 due to the formation of isopolyvanadates and vanadylvanadates, have been recently investigated.²¹ The standard potential²² for the system $\text{V}^{5+}/\text{V}^{4+}$ was 0.97 V in H_2SO_4 . The E^0 value for the reaction,



is reported²³ as -1.00 V. Since in the present polymerization study, the pH of the reaction medium is 1.25–1.30, the active species of

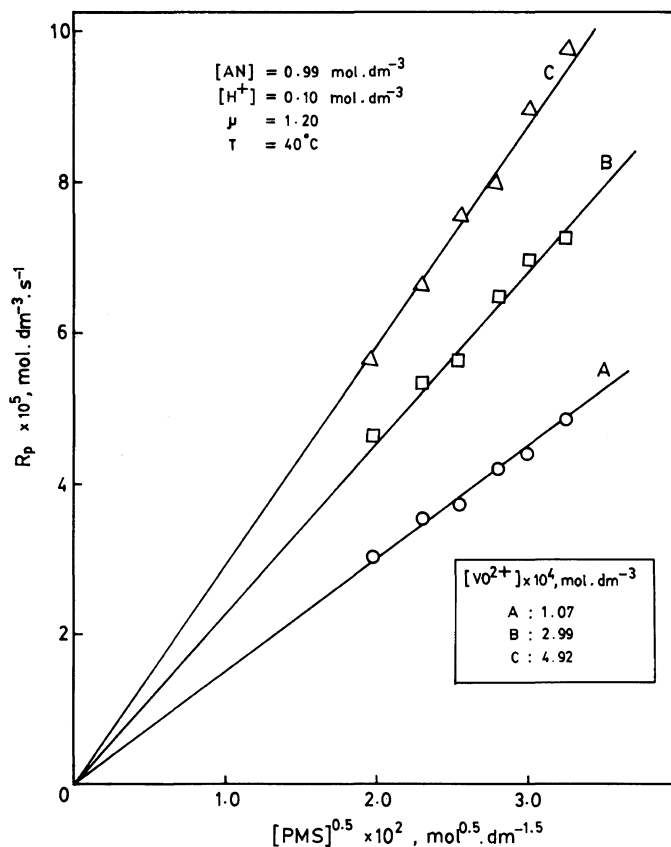


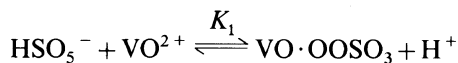
Figure 3. Effect of [PMS] on R_p at constant [monomer] and $[\text{VO}^{2+}]$.

oxovanadium(IV) is V(IV). The V(IV) undergoes oxidation by peroxomonosulphate to give the final product V(V) *via* free radical intermediates.

There is no reference in the literature with V(V) as a single initiator for polymerization. Littler and Waters²⁴ indicated that V(V) does not initiate vinyl polymerization in the absence of reducing agents in acidic solution. In the oxidation of vanadyl ion by peroxodisulphate in aqueous acid solution reported by Anderson *et al.*,²⁵ interactions of anions with VO^{2+} were observed and the authors related this interaction to the fact that anions acted as ligands in complexes of VO^{2+} . The extinction coefficient at 770 nm for VO^{2+} was observed to be constant at pH 1.0–3.5, emphasising the presence

of the only species VO^{2+} in this pH range. Since the present investigation was carried out in the pH range 1.25–1.30, it is reasonable to assume that only the VO^{2+} ion is present as the rate of polymerization was observed in the hydrolysis.

A mild inverse hydrogen ion dependence on the rate of polymerization was observed in the present investigation as reported earlier.⁴ This may be due to a rapid pre-equilibrium step with the formation of a precursor complex, VOSO_5 .



This precursor complex undergoes reaction with monomer to produce a monomer radical.

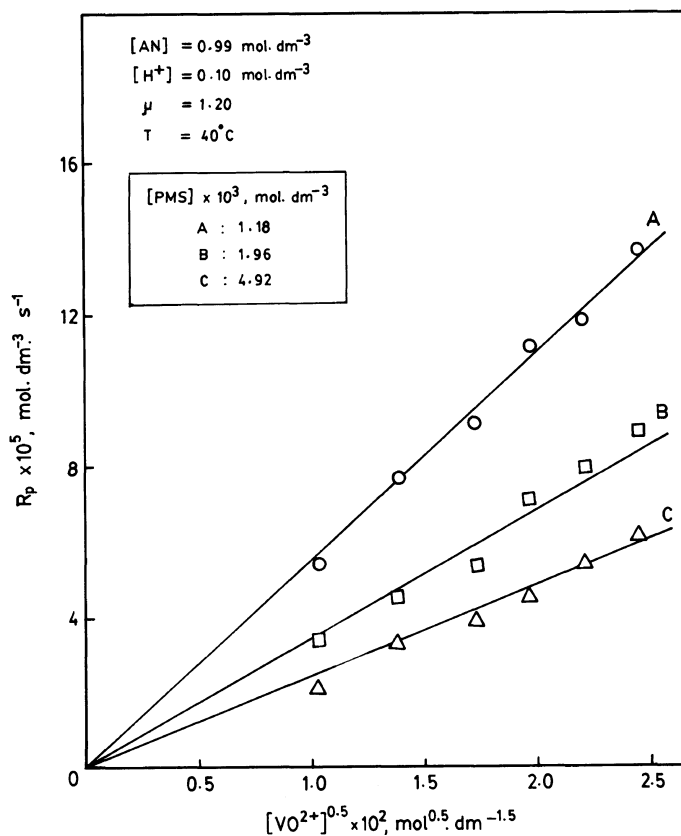
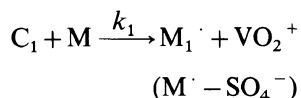
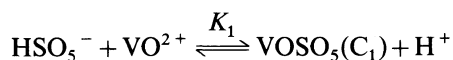


Figure 4. Effect of $[\text{VO}^{2+}]$ on R_p at constant [monomer] and [PMS].

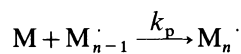
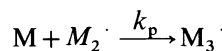
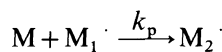
Since the deliberately added H^+ reverted the equilibrium to the left hand side resulting in the decrease of the complex concentration, the rate of polymerization decreased with $[\text{H}^+]$.

Based on the above findings, following reaction scheme is proposed, involving the complex formation between PMS and VO^{2+} followed by initiation of the formed complex with monomer.

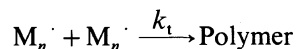
Initiation



Propagation



Termination



The possibility of the formation of hydroxyl radical ($\dot{\text{O}}\text{H}$) can be ruled out on the basis that, the formed complex reacts with monomer to give $\text{M} \cdot$ with sulphate group ($\text{M} - \text{SO}_4^-$) and VO_2^+ .

Applying the steady state approximation for

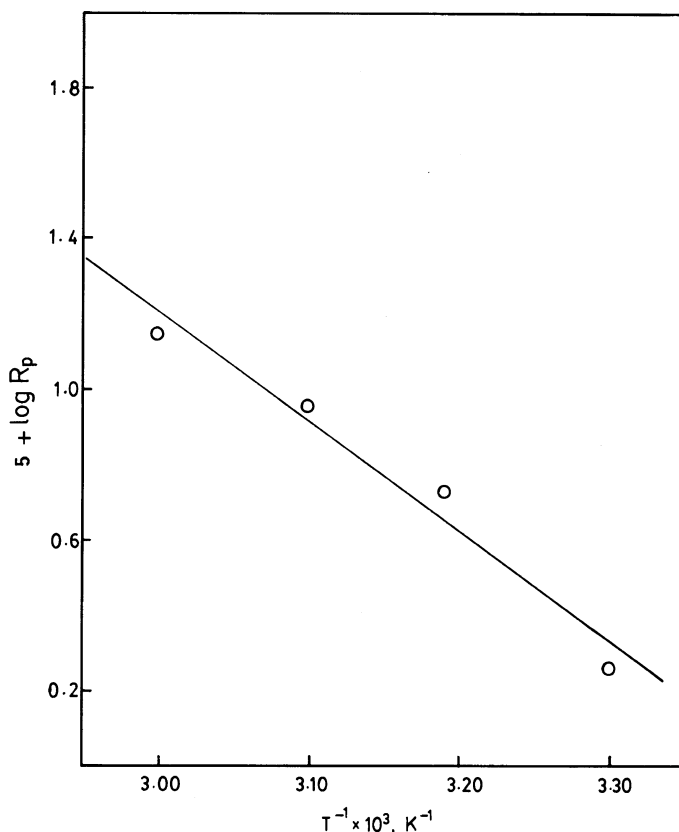


Figure 5. Effect of temperature on R_p .

both the primary and chain free radicals, and assuming only the mutual termination as the effective one, the observed expressions for R_p and the degree of polymerization are given below.

$$R_p = k_p \left[\frac{k_i \cdot K_1}{2k_t} \right]^{0.5} \times \frac{[M]^{1.5} [\text{HSO}_5^-]^{0.5} [\text{VO}^{2+}]^{0.5}}{[\text{H}^+]^{0.5}}$$

Since the concentration of H^+ is very low compared to the concentrations of other reactants, its effect can be neglected in the absence of any H^+ added deliberately and by substituting the constant k_i for $(k_i \cdot K_1/2)$,

$$R_p = k_p \cdot \left(\frac{k_i}{k_t} \right)^{0.5} [M]^{1.5} [\text{HSO}_5^-]^{0.5} [\text{VO}^{2+}]^{0.5}$$

$$\bar{X}_n = k_p \left\{ \frac{[M]}{k_t \cdot k_i [\text{HSO}_5^-] [\text{VO}^{2+}]} \right\}^{0.5}$$

This expression for the degree of polymerization reveals the dependence of \bar{X}_n on [monomer], [PMS] and $[\text{VO}^{2+}]$ (Figure 6).

Thermodynamic Parameters

The energy of activation (E_a) obtained from the plot of $\log R_p$ versus T^{-1} and the thermodynamic parameters, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger computed using standard equations are,

$$\Delta G^\ddagger = 88.49 \text{ kJ mol}^{-1}$$

$$\Delta H^\ddagger = 53.49 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = -111.87 \text{ J K}^{-1} \text{ mol}^{-1}$$

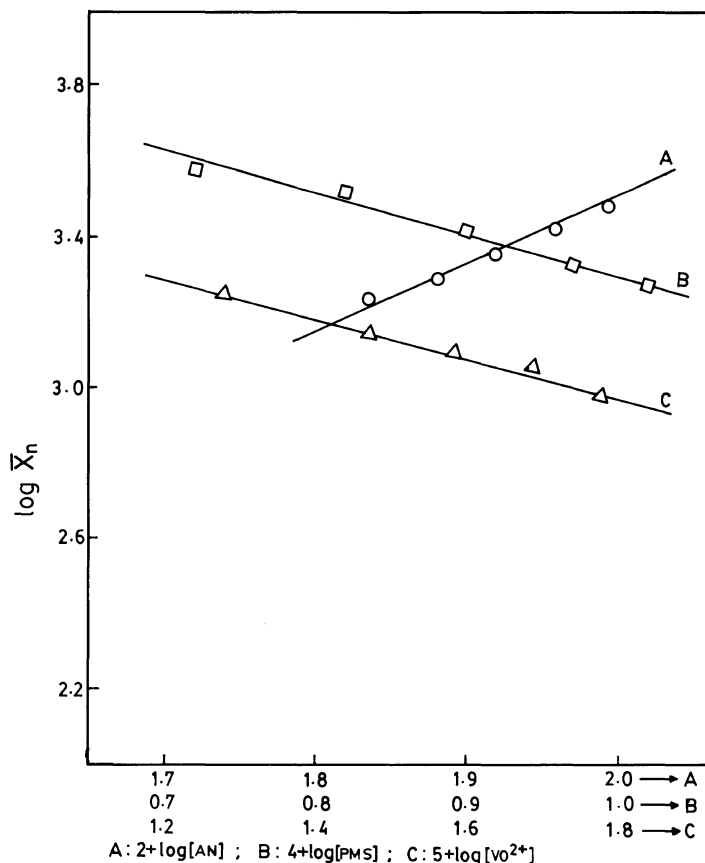


Figure 6. Effect of [monomer], [PMS] and $[\text{VO}^{2+}]$ on degree of polymerization, \bar{X}_n .

Comparison with Peroxodiphosphate, $\text{P}_2\text{O}_8^{4-}$

The kinetics of polymerization of acrylonitrile initiated by peroxodiphosphate ($\text{P}_2\text{O}_8^{4-}$)-vanadyl ion in aqueous medium have been reported²⁶ and the primary radical producing steps proposed in the reaction scheme consist of the formation of a complex between VO^{2+} and $\text{P}_2\text{O}_8^{4-}$ followed by the decomposition of the complex to produce HPO_4^- as the initiating species. The formation of hydroxyl radical was also suggested and two types of termination depending upon the concentration of vanadyl ion are proposed. Mutual termination was found to occur at low concentrations of VO^{2+} ($2.5\text{--}5.0 \times 10^3 \text{ mol dm}^{-3}$), whereas linear termination to be predominant in the concentration range $1.0\text{--}2.5 \times 10^{-2} \text{ mol dm}^{-3}$.

R_p depended on $[\text{monomer}]^{1.0}$, $[\text{P}_2\text{O}_8^{4-}]^{0.5}$ and $[\text{VO}^{2+}]^{0.5}$ at lower concentrations of VO^{2+} and $[\text{monomer}]^{1.0}$ and $[\text{P}_2\text{O}_8^{4-}]^{1.0}$ and $[\text{VO}^{2+}]^0$ at higher concentrations. The energy of activation was 28.5 kJ mol^{-1} , which was almost one half the value estimated in this system. The E_a was higher in $\text{HSO}_5^- - \text{VO}^{2+}$ redox system, which might be due to involvement of the monomer in coupling with complex to produce primary radicals.

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