

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Pentavalent Vanadium-Ascorbic Acid Redox System Initiated Polymerization of Acrylonitrile

P. C. Dash^a; D. P. Das^a; B. K. Mohanty^a; R. K. Samal^a; M. C. Nayak^a

^a Laboratory of Polymers & Fibers Department of Chemistry, S.V.M. College, Cuttack, Orissa, India

To cite this Article Dash, P. C. , Das, D. P. , Mohanty, B. K. , Samal, R. K. and Nayak, M. C.(1982) 'Pentavalent Vanadium-Ascorbic Acid Redox System Initiated Polymerization of Acrylonitrile', *Journal of Macromolecular Science, Part A*, 17: 9, 1357 – 1370

To link to this Article: DOI: 10.1080/00222338208074403

URL: <http://dx.doi.org/10.1080/00222338208074403>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Pentavalent Vanadium-Ascorbic Acid Redox System Initiated Polymerization of Acrylonitrile

P. C. DASH, D. P. DAS, B. K. MOHANTY, R. K. SAMAL, and
M. C. NAYAK*

Laboratory of Polymers & Fibers
Department of Chemistry
S.V.M. College
Jagatsinghpur, Cuttack, Orissa, India

ABSTRACT

Kinetics of polymerization of acrylonitrile initiated by the redox system V^{5+} /ascorbic acid were investigated in aqueous sulfuric acid in the temperature range of 35-50°C, and the rates of polymerization, of V^{5+} disappearance, etc. were measured. From the result it was concluded that the polymerization reaction is initiated by an organic free radical arising from the V^{5+} -ascorbic acid complex formation followed by subsequent decomposition and terminated by V^{5+} ions. A suitable kinetic scheme was proposed and the various rate parameters were evaluated.

INTRODUCTION

The kinetic investigations of aqueous vinyl polymerization initiated by higher valent metal ions (Co^{3+} , Ce^{4+} , V^{5+} , Cr^{6+} , Fe^{3+} , Mn^{3+} , etc.) have provided valuable information regarding the mechanistic details

*Author to whom correspondence should be addressed.

of individual steps [1-8]. Littler and Waters [9] reported that V^{5+} in the presence of reducing agents such as hydroxy acids, ketones, and glycols initiated vinyl polymerization quite smoothly and effectively. Quinquevalent vanadium was employed as initiator [10-12] of graft copolymerization in systems of polymer backbone containing groups such as $-CHO$, $=CO$, $-CONH-$ or $-NH_2$ (capable of being oxidized to free radicals on the backbone) and a suitable monomer (which is grafted). A survey of the literature reveals that not much is known on the kinetics of the vinyl polymerization initiated by V^{5+} /reducing agent system. We have reported the polymerization of methyl methacrylate [5] initiated by the V^{5+} /thioacetamide redox system. Mohanty et al. [13] have reported the polymerization of acrylonitrile initiated by the V^{5+} /cyclohexanone redox system. An ambitious research program has been introduced to study chemical initiation graft copolymerization of vinyl monomers on natural and synthetic macromolecules such as wool, silk, collagen, nylon 6, and cellulose with V^{5+} ion. As a part of this program, we wish to report our findings relating to the vinyl polymerization of acrylonitrile (AN) initiated by a V^{5+} -ascorbic acid redox system. From our experimental observations a suitable reaction scheme has been suggested that involves the initial complex formation between the acid in aqueous sulfuric acid medium and the metal ion whose decomposition yields the initiating free radical, with the polymerization being terminated by metal ion. Various kinetic parameters were evaluated.

EXPERIMENTAL

Acrylonitrile (American Cyanamid) was washed with 5% NaOH, dilute H_2SO_4 , and finally with water and dried over calcium chloride. It was further purified by distillation in a nitrogen atmosphere under reduced pressure. Ammonium metavanadate (A.R.), ascorbic acid (A.R., BDH), sodium sulfite (Riedel), and sulfuric acid (18 M, A.R., BDH) were used. Water, distilled twice over alkaline permanganate and de-ionized by passage through a column of Biodeminrolit resin (Permutit Co., U.K.), was used to prepare all solutions. The nitrogen (Indian Oxygen Co., Calcutta) used to deaerate the experimental systems was freed from oxygen by passage through five columns of Fieser's solution, a column of saturated lead acetate solution, and finally through a wash bottle containing distilled water.

A stock solution of V^{5+} (≈ 0.4 N in ≈ 4 M H_2SO_4) was prepared by suspending ammonium metavanadate (4.7 g) in distilled water (25 cc) and adding, with stirring, 75 cc of 10 N H_2SO_4 . The concentration of V^{5+} in the experimental systems was determined by vanadometry [14]. An aliquot (2 cc) of V^{5+} stock solution was run into a known excess of standard ferrous ammonium sulfate (0.05 N, 20 cc) solution, the excess of Fe^{2+} was titrated with standard V^{5+} (0.01-0.02 N) using Knop's indicator, followed by addition of 5 cc of 80% o-phosphoric acid to violet

end point. The V^{5+} solution (titrant) itself was standardized by titration with standard ferrous solution (0.05 N) using Knop's indicator. The acidity in the V^{5+} stock solution was determined by titrating an aliquot of the former with standard sodium hydroxide using bromocresol green as indicator.

The reactions were carried out in Pyrex tubes (20.3×2.5 cm) fitted with B_{24} sockets and closed by B_{24} cones equipped with gas inlet and outlet tubes. The system (ascorbic acid, 0.1 M; H_2SO_4 , 1 M; acrylonitrile, 0.76 M) in aqueous solution (20 cc total volume) was taken in the reaction tube and thermostated at $40^\circ C$. A wash bottle containing an aqueous solution of acrylonitrile of the same concentration as in the reaction tube was interposed between the nitrogen train and the reaction tube (to avoid loss of monomer during deaeration). Nitrogen freed from O_2 by passage through Fieser's solution was bubbled through the solution for 20-30 min, and the V^{5+} solution was added. Then the system was sealed under nitrogen. It was observed that polymerization took place without any induction period. The reaction was stopped after ≈ 75 min by the addition of a known excess of Fe^{2+} (0.05 M, 20 cc) into the reaction tube. No polymer was formed during the absence of the organic substrate. The polymethacrylonitrile was filtered in a tared sintered glass crucible (I G₃, Jena), washed with distilled water, and dried at $70^\circ C$ to constant weight. The filtrate was analyzed by vanadometry using Knop's indicator, and the rate of V^{5+} disappearance, $-R$, was evaluated from the titre values. The polymer was dried at $65^\circ C$ for 12 h. The rate of polymerization was determined gravimetrically. Experiments were conducted to study the effect of time, $[M]$, $[ascorbic\ acid]$, $[V^{5+}]$, $[H_2SO_4]$, $[HSO_4^-]$, μ , and temperature on both R_p and $t - R_v$. The chain lengths of the polymer were determined viscometrically using the appropriate Mark-Houwink relationship. The viscosities of the polymer solutions (0.1%) were determined in an Ubbelohde-type suspended level dilution viscometer using the equation due to Stockmayer and Cleland [15].

$$[\eta] = 2.43 \times 10^{-4} [M_v]^{0.75}$$

RESULTS AND DISCUSSION

Acrylonitrile (AN) was polymerized in aqueous sulfuric acid solution at $35-50^\circ C$ in the presence of the V^{5+} -ascorbic acid redox system. A typical set of time-conversion curves at $35^\circ C$ and at various ascorbic acid concentrations (0.005-0.06 M) at constant $[V^{5+}]$ concentration (0.02 M) are shown in Fig. 1. Acrylonitrile was also polymerized under identical conditions with V^{5+} in the presence of other carboxylic acids such as tartaric acid, oxalic acid, citric acid, succinic acid, glutaric acid, and adipic acid. There is an induction period involved in each case, and the point of appearance of turbidity

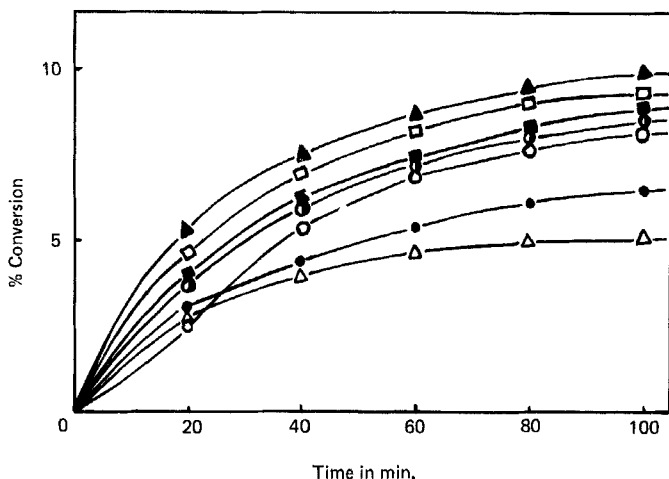


FIG. 1. Variation of % conversion with time: effect of activator concentration. $[V^{5+}] = 0.02$ M, $[H^+] = 0.525$ M, $[AN] = 0.7539$ M, $\mu = 1.4$ M, temperature = 35°C . Conversion % vs time for $[AA]$ of (●) 0.005 M, (▲) 0.01 M, (■) 0.016 M, (○) 0.04 M, (△) 0.06 M. Variation of % conversion with time: effect of water-miscible organic solvents. $[V^{5+}] = 0.02$ M, $[H^+] = 0.525$ M, $[AN] = 0.7539$ M, $\mu = 1.4$ M, $[AA] = 0.01$ M, temperature = 35°C . Conversion % vs time: (▲) Control, (●) $[\text{CH}_3\text{COOH}] = 10\%$ (v/v), (□) $[\text{CH}_3\text{COCH}_3] = 10\%$ (v/v).

in the reaction mixture is taken as the starting point of polymerization. The results are recorded in Table 1, which shows that under identical conditions, the reactivity of the carboxylic acids are: citric acid > tartaric acid > ascorbic acid > oxalic acid > succinic acid > glutaric acid > adipic acid.

RATE OF POLYMERIZATION: (R_p)

A regular increase in rate (R_p) was noticed with an increase in monomer concentration ($[M]$) (0.3016-1.0555 M), R_p versus $[M]^2$ plots being linear with zero intercept (Fig. 2) and therefore the order with respect to $[M]$ was 2.

The rate was inversely proportional to $[V^{5+}]$ (0.005-0.06 M), $1/R_p$ versus $[V^{5+}]$ plots being linear with the intercept on the ordinate (Fig. 3).

The rate increased linearly with an increase in ascorbic acid concentration ($[AA]$) (0.005-0.06 M). Linear plots of $\log R_p$ versus \log

TABLE 1. Polymerization of Acrylonitrile (AN) Initiated by Various V^{5+} -Carboxylic Acid Redox Systems at $35 \pm 10^\circ C^a$

Acid	$R_p \times 10^4$
Citric acid	68.3424
Tartaric acid	28.0973
Ascorbic acid	10.6536
Oxalic acid	6.9737
Succinic acid	3.8302
Glutaric acid	2.8744
Adipic acid	2.0017

^aRecipe: $[V^{5+}] = 0.02 \underline{M}$, $[H^+] = 0.525 \underline{M}$, $\mu = 1.4 \underline{M}$, $(AN) = 0.754 \underline{M}$, $(Acid) = 1 \times 10^{-2} \underline{M}$.

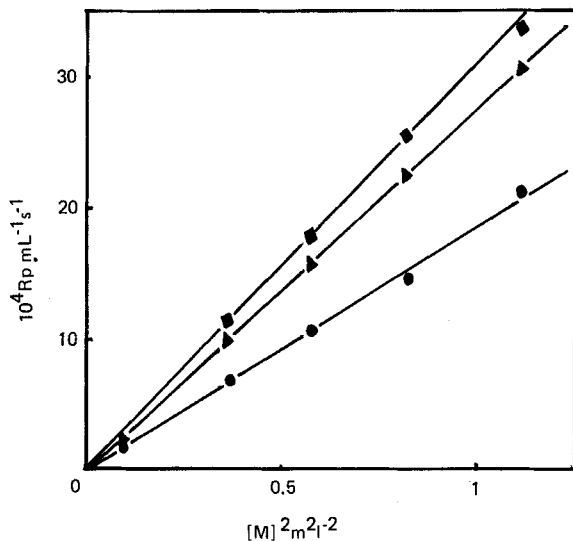


FIG. 2. Variation of R_p with monomer at different temperatures. $[V^{5+}] = 0.02 \underline{M}$, $[H^+] = 0.525 \underline{M}$, $[AA] = 0.01 \underline{M}$, $\mu = 1.4 \underline{M}$. R_p vs $[M]^2$: (•) $30^\circ C$, (\blacktriangle) $35^\circ C$, (\blacksquare) $40^\circ C$.

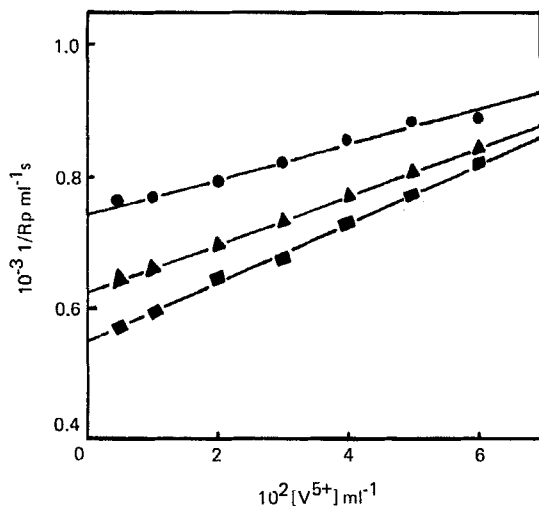


FIG. 3. Variation of R_p with $[V^{5+}]$ at different temperatures $[H^+] = 1.3 \text{ M}$, $[AA] = 0.01 \text{ M}$, $[AN] = 0.7539 \text{ M}$, $\mu = 1.9 \text{ M}$. $1/R_p$ vs $[V^{5+}]$: (\bullet) 35°C , (\blacktriangle) 40°C , (\blacksquare) 50°C .

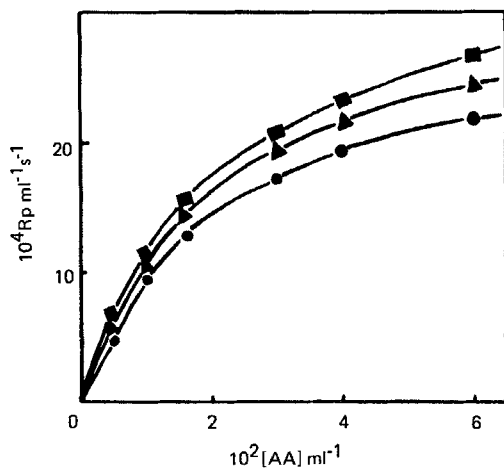


FIG. 4. Variation of R_p with $[AA]$ at different temperatures. $[V^{6+}] = 0.02 \text{ M}$, $[H^+] = 0.525 \text{ M}$, $\mu = 1.4 \text{ M}$, $[AN] = 0.7539 \text{ M}$. R_p vs $[AA]$: (\bullet) 35°C , (\blacktriangle) 40°C , (\blacksquare) 45°C .

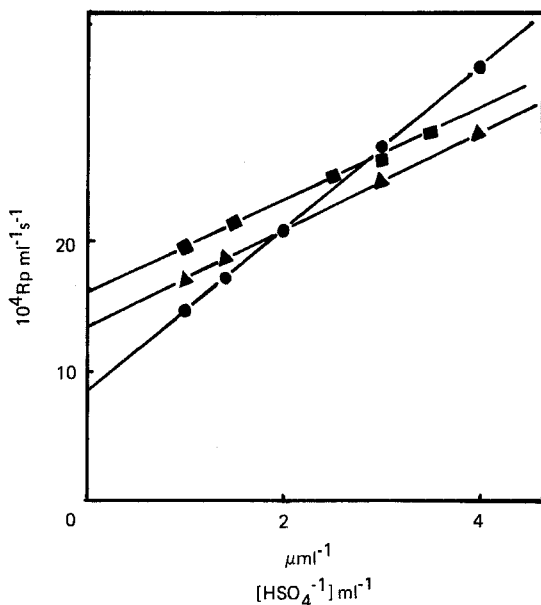
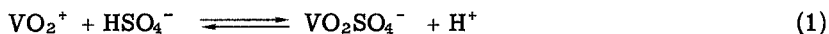


FIG. 5. Variation of R_p with $[\text{HSO}_4^-]$ and μ . $[\text{V}^{5+}] = 0.02 \text{ M}$, $[\text{H}^+] = 0.525 \text{ M}$, $[\text{AN}] = 0.7539 \text{ M}$, temperature = 40°C . R_p vs $[\text{HSO}_4^-]$: (■) 40°C , (●) $[\text{NaClO}_4]$, (▲) $[\text{ZnSO}_4]$.

$[\text{AA}]$ with unit slopes as well as R_p versus $[\text{AA}]$ plots with zero intercepts (Fig. 4) indicated that the order with respect to $[\text{AA}]$ was unity. The dependence of R_p on $[\text{M}]^2$, $1/[\text{V}^{5+}]$, and $[\text{AA}]$ will be discussed later. The increase of rate with an increase of $[\text{HSO}_4^-]$ (1-3.5 M) (Fig. 5) may be understood in terms of the equilibrium



This also indicates that the bisulfate complexes of V^{5+} were more effective initiators or less effective terminators. R_p increased with μ when ZnSO_4 and sodium perchlorate were used to adjust the ionic strength, and this increasing rate may be understood in terms of the salts catalyzing the propagation step since Bamford [16] reported that salts like LiCl and LiNO_3 formed complexes with the polar monomer acrylonitrile, which would catalyze the propagation step.

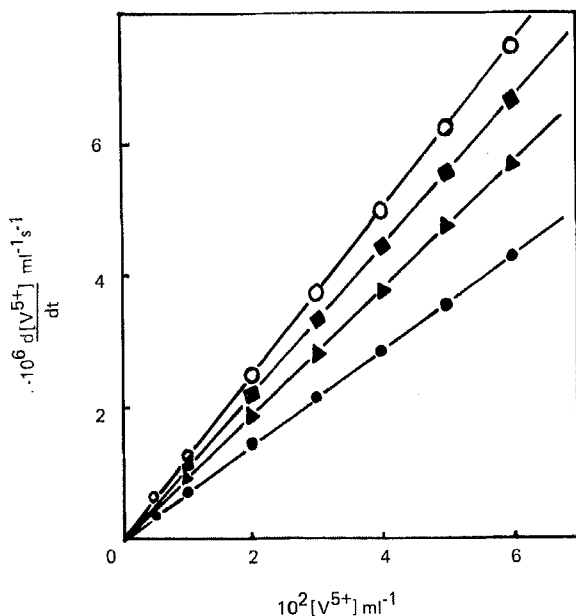


FIG. 6. Plots of $-d[V^{5+}]/dt$ vs $[V^{5+}]$ at different temperatures. $[H^+] = 0.9 \text{ M}$, $[AA] = 0.01 \text{ M}$, $[AN] = 0.7539 \text{ M}$, $\mu = 1.8 \text{ M}$. (\bullet) 35°C , (\blacktriangle) 40°C , (\blacksquare) 45°C , (\circ) 50°C .

RATE OF V^{5+} DISAPPEARANCE ($-R_v$)

The monomer concentration had no effect on the rate. An increase in $[V^{5+}]$ (0.005 - 0.06 M) increased the rate, and a first-order dependence of the rate on $[V^{5+}]$ was concluded from the linear plots of $-R_v$ versus $[V^{5+}]$ (Fig. 6).

An increase in $[AA]$ (0.5×10^{-2} to $6 \times 10^{-2} \text{ M}$) increased the rate. At high $[AA]$, plots of $-R_v$ versus $[AA]$ were curved (Fig. 7). At $[AA] \approx 3 \times 10^{-2} \text{ M}$, there is a change in the nature of the plot at all $[V^{5+}]$.

EFFECT OF WATER-MISCIBLE ORGANIC SOLVENTS

Addition of 10% (v/v) water-miscible organic solvents such as acetic acid and acetone to the reaction mixture depresses the initial rate as well as the maximum conversion (Fig. 1). This is probably caused by the decrease in the area of shielding of a strong hydration

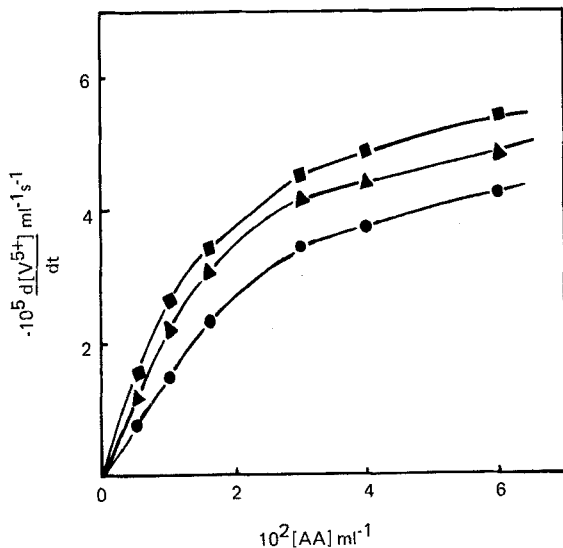


FIG. 7. Plots of $-R_v$ vs $[AA]$ $[V^{5+}] = 0.02 \text{ M}$, $[H^+] = 0.525 \text{ M}$, $\mu = 1.4 \text{ M}$, $[AN] = 0.7539 \text{ M}$. (\bullet) 35°C , (\blacktriangle) 40°C , (\blacksquare) 45°C .

layer in the aqueous medium, resulting in the termination of the radical and of the growing chain, or the increase in the regulated rate of production of primary radicals caused by the solvents which, under the existing experimental conditions, renders the termination rate relatively fast compared to the rate of growth of the polymer chains, as pointed out by Kern et al. [17]. Palit et al. [18] have made a similar observation for the homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking the polymer chain is not rigid, which causes a premature termination of the polymer chains. Similar observations have been noted by Samal et al. [19] in the aqueous polymerization of acrylamide.

EFFECT OF ADDED ELECTROLYTES

The addition of certain neutral electrolytes such as CuSO_4 , Na_2SO_4 , KCl , and ZnSO_4 to the reaction mixture reduces both the initial rate of polymerization and the maximum conversion. This might be due to the following reasons: (1) the ionic dissociation of the added electrolyte which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chain; and (2) the great reduction of the activity of the vanadium ion due to ion-pair coupling with the added electrolytes.

EFFECT OF COMPLEXING AGENTS

On addition of 0.02 M complexing agents such as NaF, succinic acid, pyridine, and piperidine, the initial rate as well as the maximum conversion were depressed considerably and with aniline as the complexing agent the reaction was completely inhibited. The most probable explanations for this type of behavior are that the pH of the medium changes due to the consumption of the H^+ ion by the amines and that the activity of the V^{5+} ion is greatly reduced due to complex formation with the amines behaving as ligands.

EFFECT OF CATALYST CONCENTRATION

The initial rate as well as the maximum conversion increased with increasing concentration of the catalyst over the range 0.005-0.03 M . A set of time-conversion plots at a definite temperature are shown in Fig. 8. At higher concentrations of the catalyst (above 0.03 M), a

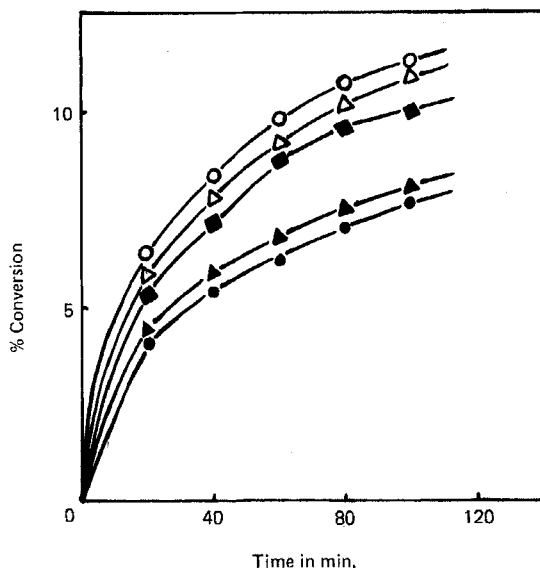


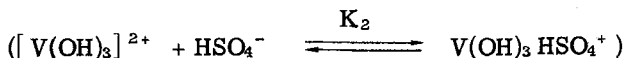
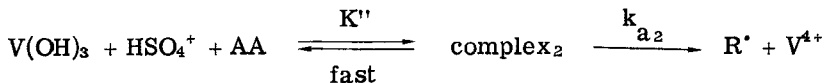
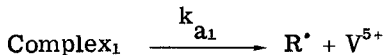
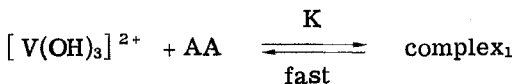
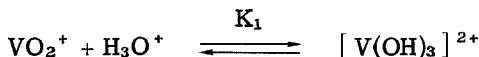
FIG. 8. Variation of % conversion with time: effect of $[V^{5+}]$. $[AA] = 0.01 M$, $[H^+] = 0.9 M$, $[AN] = 0.7539 M$, $\mu = 1.8 M$. Conversion % vs time for $[V^{5+}]$ of (●) 0.005 M , (▲) 0.01 M , (■) 0.02 M , (○) 0.03 M , (△) 0.04 M .

decrease in the rate was noticed. This might be due to the fact that at higher concentrations of the catalyst, the oxidation rate becomes relatively fast compared to the polymerization rate, as pointed out by Samal et al. [19].

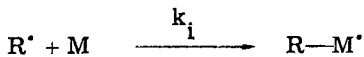
REACTION MECHANISM AND RATE LAW

The following reaction scheme appears to explain our experimental results.

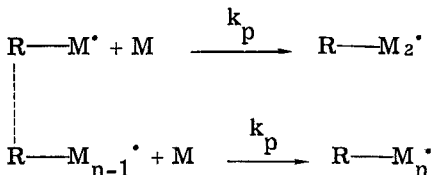
1. Production of the primary radical by the interaction of V^{5+} + ascorbic acid, preceded by the formation of the complex between V^{5+} and ascorbic acid:

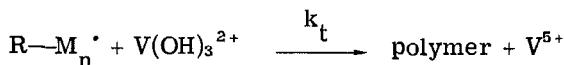


2. Initiation by primary radical:

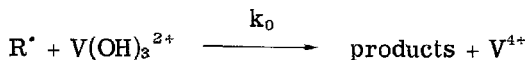


3. Propagation:



4. Linear termination by V^{5+} :

Linear termination of vinyl polymerization by metal ions is now well recognized [20].

5. Reactions of the primary radical with V^{5+} :

On the basis of the above scheme, the following expressions may be derived for R_p , $-R_v$, and the chain length n :

$$R_p = \frac{k_p}{k_t} \times \frac{k[AA][M]^2}{\left\{ [M] + \frac{k_0}{k_i} [V^{5+}] \right\}} \quad (1)$$

$$-R_v = 2k[AA][V(OH)_3^{2+}] \quad (2)$$

where

$$k' = (K_1 K' k_{a1} + K_1 K_2 K' k_{a2} [HSO_4^-])$$

and for the chain length:

$$n = \frac{k_p}{k_t} \times \frac{[M]}{[V(OH)_3^{2+}]} \quad (3)$$

The other modes of termination—mutual termination and primary radical termination—were discounted on the basis that the expressions for R_p , $-R_v$, and n involved proportionalities which were not experimentally realized. In the case of mutual termination, the expressions involved proportionalities such as $[M]$, $[V^{5+}]^{1/2}$, and $[AA]^{1/2}$ for R_p ; $[V^{5+}]^2$ for $-R_v$; $[AA]^{1/2}$ for n ; and in the case of primary radical termination, the expressions involved terms like $1/[M]$ for $-R_v$; $[M]^2$ and $1/[AA]$ for n ; and R_p involved no $[V^{5+}]$ - and $[AA]$ -terms.

TABLE 2. Rate Parameters for the System V^{5+} -Ascorbic Acid-Acrylonitrile in Aqueous Sulfuric Acid

Temper- ature (°C)	From $\log a/(a - x)$ vs time	$10^4 k/Lm^{-1}s^{-1}$ from $-R_v$ vs $[V^{5+}]$	From $-R_v$ vs [AA]	k_p/k_t from $1/R_p$ vs $[V^{5+}]$	k_0/k_i from $1/R_p$ vs $[V^{5+}]$
40	2.7	3.05	3.26	7.35	-
45	-	3.3	4.01	7.14	-

EVALUATION OF RATE PARAMETERS

The second-order rate constant k' (in the presence of monomer) was obtained from the plots $-R_v$ versus $[V^{5+}]$, $-R_v$ versus [AA] (from the initial slopes), and from the slopes of plots of $\log a/(a - x)$ versus time (where a is the initial concentration of the reactant and x is the decrease in concentration in time t). The values are reported in Table 2. k_p/k_t and k_0/k_i were evaluated from plots of $1/R_p$ versus $[V^{5+}]$. The reciprocal of the rate expression for R_p (Eq. 1) can be rearranged to give

$$\frac{1}{R_p} = \frac{k_t}{k_p k [AA] [M]} + \frac{k_t (k_0/k_i) [V^{5+}]}{k_p k [AA] [M]^2}$$

Plots of $1/R_p$ versus $[V^{5+}]$ according to Eq. (4) were linear, and (k_0/k_i) from $(\text{slope/intercept}) \times [M]$ and k_p/k_t from the reciprocal of $(\text{intercept}) \times k [AA] [M]$ and k' (obtained by the three methods indicated above) were obtained.

ACKNOWLEDGMENT

Thanks are due to Prof G. V. Suryanarayan, Head of Chemistry Department, S.V.M. College, Jagatsinghpur, Orissa, India, for providing necessary laboratory facilities to carry out this work and for his constructive criticisms.

REFERENCES

- [1] E. A. S. Cavell and A. C. Meeks, Polymer, **8**, 79 (1967).
- [2] V. S. Ananthanarayan and M. Santappa, J. Appl. Polym. Sci., **9**, 2437 (1965).
- [3] S. Saccubai and M. Santappa, J. Polym. Sci., Part A-1, **7**, 643 (1969).
- [4] N. G. Devi and V. Mahadevan, Makromol. Chem., **152**, 177 (1972).
- [5] M. C. Nayak, G. V. Suryanarayan, D. P. Das, and R. K. Samal, J. Macromol. Sci.-Chem., **A15(3)**, 467 (1981).
- [6] M. C. Nayak, P. L. Nayak, and R. K. Samal, Eur. Polym. J., **14**, 287 (1978).
- [7] M. C. Nayak, P. L. Nayak, A. K. Dhal, and R. K. Samal, J. Polym. Sci., **18**, 2001 (1980).
- [8] G. Panda, P. C. Dash, D. P. Das, N. K. Dash, R. K. Samal, and M. C. Nayak, J. Macromol. Sci.-Chem., **A15(3)**, 479 (1981).
- [9] J. S. Littler and W. A. Waters, J. Chem. Soc., p. 1299 (1958).
- [10] Z. A. Rogovin and R. M. Livshits, Vysokomol. Soedin., **4**, 784 (1963); **60**, 4260 (1964).
- [11] R. M. Livshits, R. Mampov, and R. G. Zhibankov, Vysokomol. Soedin. Tsellyulose Proz. Sb. Statchi, p. 65 (1963); Chem. Abstr., **60**, 134299 (1964).
- [12] H. Singh, R. T. Thamby, and V. B. Chipalkatti, J. Polym. Sci., **A(3)**, 1247 (1965).
- [13] T. R. Mohanty, P. L. Nayak, and B. C. Singh, Makromol. Chem., **175**, 2345 (1974).
- [14] R. Shankar and S. N. Joshi, Indian J. Chem., **1**, 289 (1963).
- [15] W. H. Stockmayer and R. C. Cleland, J. Polym. Sci., **17**, 473 (1955).
- [16] C. H. Bamford, A. D. Jenkins, and R. Johnston, Ibid., **29**, 355 (1958).
- [17] R. Schulz, G. Reuner, A. Henglein, and W. Kern, Makromol. Chem., **12**, 20 (1954).
- [18] R. S. Konar and S. R. Palit, J. Indian Chem. Soc., **38**, 481 (1961).
- [19] R. K. Samal, P. L. Nayak, and T. R. Mohanty, Macromolecules, **10**, 489 (1977).
- [20] S. V. Subramaniam, PhD Thesis, Madras University, 1967.

Accepted by editor May 4, 1981

Received for publication June 2, 1981