Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Hexavalent Chromium-Thioacetamide Redox System Initiated Polymerization of Acrylonitrile

R. K. Samal[a]; P. C. Dash[a]; B. Mishra[a]; G. V. Suryanarayana[a]; D. P. Das[a]; M. C. Nayak[a]
[a] Laboratory of Polymers and Fibers Department of Chemistry, S.V.M. College, Cuttack, Orissa, India

To cite this Article Samal, R. K. , Dash, P. C. , Mishra, B. , Suryanarayana, G. V. , Das, D. P. and Nayak, M. C.(1982) 'Hexavalent Chromium-Thioacetamide Redox System Initiated Polymerization of Acrylonitrile', Journal of Macromolecular Science, Part A, 17: 5, 805 — 819

To link to this Article: DOI: 10.1080/00222338208063274

URL: http://dx.doi.org/10.1080/00222338208063274

J. MACROMOL. SCI.–CHEM., A17(5), pp. 805-819 (1982)

Hexavalent Chromium-Thioacetamide Redox System Initiated Polymerization of Acrylonitrile

R. K. SAMAL, P. C. DASH, B. MISHRA, G. V. SURYANARAYANA,
D. P. DAS, and M. C. NAYAK*

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

ABSTRACT

Polymerization of acrylonitrile initiated by the Cr^{6+}/thioacetamide redox system was studied in nitrogen atmosphere in the temperature range 35-45°C. The rate of polymerization and the rate of Cr^{6+} ion disappearance were measured. The effect of certain water-miscible organic solvents, neutral electrolytes, and complexing agents on the rate of polymerization was investigated. Chromic acid alone did not initiate the polymerization under deaerated and undeaerated conditions. Depending on the results obtained, a suitable kinetic scheme was proposed and various rate parameters were evaluated.

INTRODUCTION

Organic sulfur compounds such as thiourea [1-10], thioacetamide [11-13], 2-mercaptoethanol [14], 2-mercaptoethylamine [15], and thioglycollic acid [16] coupled with suitable catalysts have been reported to be useful redox pairs toward vinyl polymerization in

---

*To whom all correspondence should be addressed.

aqueous medium. The generation of complex thio-free radicals by the above redox systems have been observed to initiate vinyl polymerization quite smoothly and effectively. In acid medium, thioacetamide tautomerizes to generate a thiol group which appears to make it an efficient and tempting activator when coupled with a suitable catalyst.

Studies on aqueous vinyl polymerization initiated by metal ions [17-20] in their higher valence states (Co^{3+}, Ce^{4+}, Cr^{6+}, Mn^{3+}, V^{5+}, etc.) have provided valuable information regarding the mechanistic details of individual steps. A literature search reveals that so far thioacetamide has not been employed in the form of a redox couple with Cr^{6+} for a detailed kinetic study of vinyl polymerization. Further, in this laboratory there is an ambitious research program to investigate the graft copolymerization of vinyl monomers onto silk, wool, cellulose, and nylon 6 by the use of the Cr^{6+}/thioacetamide redox system and subsequently subject the grafted samples to physical studies such as x-ray, NMR, and TGA. As a part of this research program, we report the aqueous polymerization of acrylonitrile initiated by the Cr^{6+}/thioacetamide redox system in the temperature range 35-45°C. The polymerization studies were mainly conducted at 40°C. From the experimental observations a suitable reaction scheme is suggested and the various kinetic parameters are evaluated.

EXPERIMENTAL

Acrylonitrile (American Cyanamid, U.S.A.) was purified following the method of Bamford et al. [21]. Chromic acid solutions were prepared by dissolving chromium trioxide (from BDH, AR) in distilled water. Perchloric acid (from E. Merck, GR, 60%) was used to maintain the ionic strength. Other reagents, such as ferrous ammonium sulfate and o-phenanthroline, were commercial products (either BDH (AR) or E. Merck (GR). Thioacetamide (Riedel) was used for the experiments. Water distilled over alkaline permanganate and deionized by passage through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passage through several columns of Fieser's solution, a column of saturated lead acetate solution, and finally a wash bottle containing distilled water. Cr^{6+} was estimated either by titrimetry (for $Cr^{6+} > 5 \times 10^{-4}$ mol/L) or spectrophotometry (for $Cr^{6+} < 5 \times 10^{-5}$ mol/L).

For oxidation experiments a three-necked glass vessel fitted with ground glass joints was used. The reaction was stopped by addition of excess ferrous ammonium sulfate solution; the unreacted ferrous was estimated by cerimetry. For polymerization experiments a Pyrex glass tube (100 mL) fitted with B_{24} ground joint head through which two glass tubes were fused, was used. The reaction mixture containing the reducing agent, the monomer, and the acid was deaerated for 20-30 min. The reaction was carried out for 30 min after which it was stopped by addition of excess Fe^{2+} solution. The precipitated polymer was filtered, washed repeatedly with water, and dried to constant weight at 60° C in a vacuum oven. The rate of polymerization was calculated from the weight of polymer obtained. From the filtrate the change in $[Cr^{6+}]$ was followed by estimating the unreacted $[Fe^{2+}]$ by titration against standard Ce^{4+} solution. From the changes in $[Cr^{6+}]$, the rate of Cr^{6+} disappearance ($-R_M$) was computed.

The molecular weights $\overline{M}_w$ of the purified polymers were determined by viscometry using the appropriate Mark-Houwink relationship. The viscosities of polymer solutions (0.1%) were determined in an Ubbelohde-type suspended level dilution viscometer in DMF at 30° C using the relationship [22]

$$[\eta] = 3.335 \times 10^{-4}\ \overline{M}_w^{\,0.72}$$

RESULTS AND DISCUSSION

Acrylonitrile was polymerized in aqueous solutions at 35-45° C in perchloric acid and in the presence of the redox system Cr^{6+}-thioacetamide. A typical set of time-conversion curves at 40° C at various thioacetamide concentrations (0.005-0.02 M) and at constant $[Cr^{6+}]$ (0.01 M) is shown in Fig. 1. Acrylonitrile was also polymerized under identical conditions in the presence of the amides formamide, acetamide, and succinamide. The results are recorded in Table 1, which shows that under identical conditions the order of reactivity of the amides is thioacetamide > succinamide > acetamide > formamide.

This order of reactivity of the amides can be best understood by considering the existence of resonance and hyperconjugation effects which contribute toward the reactivity of the molecules.

1. Comparison of the structure between formamide and acetamide shows that, in acid medium, the enol form responsible for the generation of free radical is more prevalent in the case of acetamide than of formamide. The greater enol content of acetamide is due to the combined contribution of amidic resonance and the +I effect of the methyl group, whereas in formamide the enol content is only due to amidic resonance.

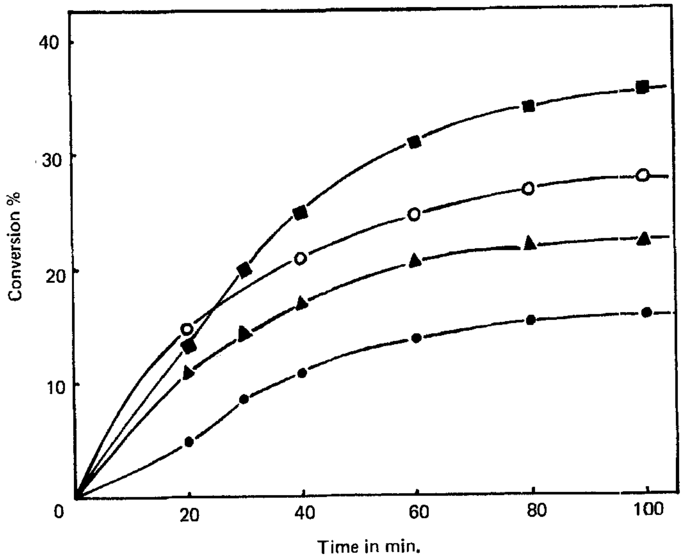


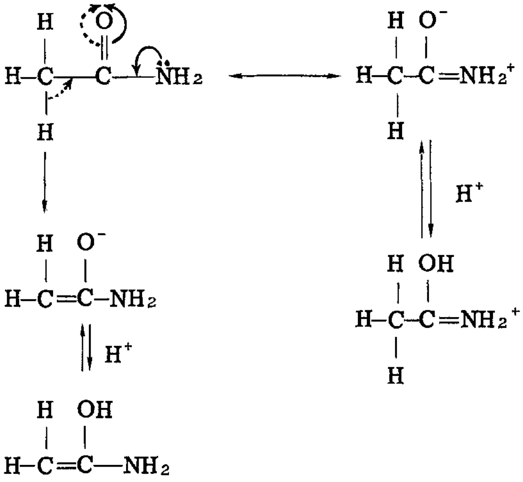
FIG. 1. Variation of % conversion with time: effect of substrate concentration. [Cr^{6+}] = 0.01 M, [H^+] = 1.17 M, [AN] = 0.7539 M, μ = 1.3 M, temperature = 40°C. (●) [TA] = 0.005 M, (▲) [TA] = 0.01 M, (■) [TA] = 0.015 M, (○) [TA] = 0.02 M.

TABLE 1. Polymerization of Acrylonitrile by Various Cr^{6+}-Amide Redox Systems at 40°C[a]

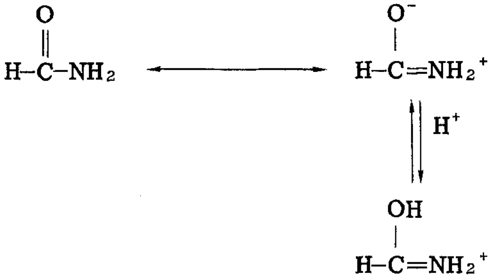
Amide and thioamide	Concentration (mol/L)	Initial rate ($10^4 \times R_p$ mL^{-1} s^{-1})
Thioacetamide	1.5×10^{-2} M	34.5582
Succinamide	1.5×10^{-2} M	7.8996
Acetamide	1.5×10^{-2} M	5.008
Formamide	1.5×10^{-2} M	3.0619

[a] Recipe: [Cr^{6+}] = 0.01 M, [H^+] = 1.17 M, [AN] = 0.754 M, μ = 1.3 M.

Acetamide:



Formamide:



2. The difference in reactivity between acetamide and succinamide is attributed to the greater acidity of the methylene hydrogen adjacent to the amido groups and partly due to the biamido function.

3. Comparison of the R_p value of thioacetamide with that of acetamide indicates that the rate of generation of the free radical is much faster in the case of thioacetamide due to the available d-orbital of the sulfur atom. In acid medium the formation of thiols is easier than that of enols, though in both substrates the resonance and +I effect contribute toward reactivity.

In the initiating system containing thioacetamide, the redox component contains the thiol form of the substrate (existing in tautomeric equilibrium with thioacetamide in the aqueous solution) is the reductant. The generation of initiating free radical in this system takes

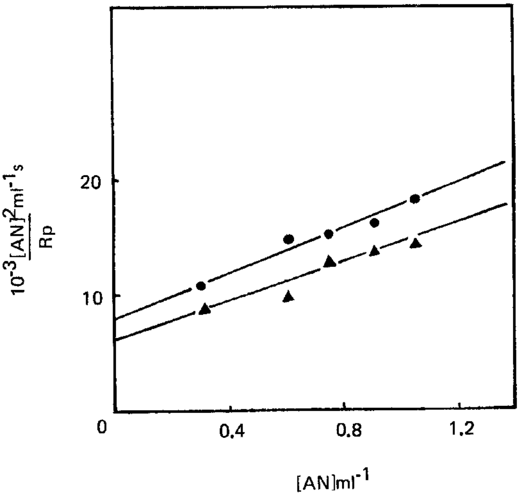


FIG. 2. Variation of R_p with monomer at different temperatures. $[Cr^{6+}] = 1 \times 10^{-2}$ M, $[H^+] = 1.17$ M, $\mu = 1.3$ M, [TA] = 1.5×10^{-2} M. (●) 35°C, (▲) 40°C.

place by the abstraction of the reactive hydrogen atom attached to the sulfur atom of the thiol group through oxidation by the Cr^{6+} ion.

The initiation of polymerization takes place by the interaction of the initiating free radical with the vinyl monomer, leading to the formation of more stable simple macroradical $R{-}CH_2{-}\overset{\bullet}{C}H$ with CN attached below the $\overset{\bullet}{C}H$.

The unpaired electron participates in resonance with the –CN group. The steric factor favors this reaction. The propagation follows the successive addition of macroradicals with other vinyl monomeric units continuously until dead polymers are formed by termination.

Chromic acid alone was not effective as an initiator of vinyl polymerization. However, the redox system Cr^{6+}-reducing agent was found to initiate polymerization of AN.

Rate of Polymerization (R_p)

The rate of polymerization, R_p, increased with an increase in the monomer concentration (0.3016-1.055 M). Plots of log R_p versus log [AN] were linear with a slope varying from 1.2 to 1.5 (Fig. 3), and a decrease in rate with an increase in $[Cr^{6+}]$ indicated the termination to be of the linear type. The terminating species might be either Cr^{6+}

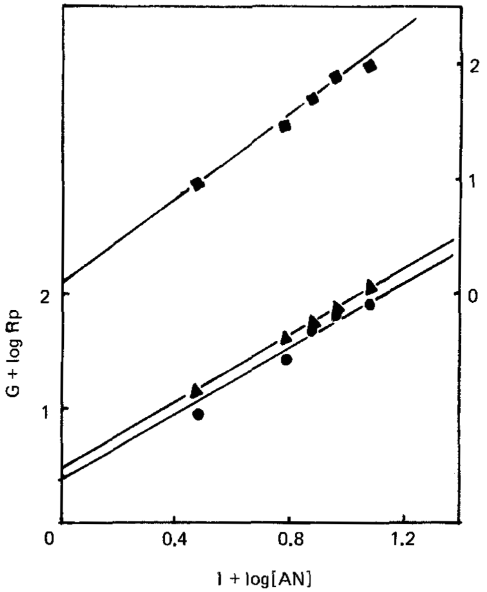


FIG. 3. Variation of R_p with monomer at different temperatures. $[Cr^{6+}] = 1 \times 10^{-2}$ M, $[H^+] = 1.17$ M, $\mu = 1.3$ M, [TA] $= 1.5 \times 10^{-2}$ M: (●) 35°C, (▲) 40°C. Variation of R_p with [M] at different $[Cr^{6+}]$. $[Cr^{6+}] = 1 \times 10^{-2}$ M, $[H^+] = 1.17$ M, $\mu = 1.3$ M, [TA] $= 1.5 \times 10^{-2}$ M: (■) 45°C.

or Cr^{4+}, but the latter, on the basis of interaction of two unstable species of low concentration (Cr^{4+} + M) seemed unlikely. Plots of $[AN]^2/R_p$ versus [AN] were found to be linear (Fig. 2).

The rate of polymerization increased with [TA] (where TA represents thioacetamide). But at concentration beyond 0.015 M, there is a decreasing trend. This is probably caused either due to chain transfer or by the accompanying changes in polarity of the system. Similar observations have been reported by Morgan [23], Josefowitz and Mark [24], Kolthoft and Harris [25], and Whitby et al. [26] for other systems. The dependence of R_p on the first power of [TA] (Fig. 4) may be understood in terms of linear termination by Cr^{6+}. A similar observation has also been advanced by Palit and Konar [27] for permanganate-oxalic acid and by Katai et al. [28] for the Ce^{4+}-initiated polymerization. Additional evidence for linear termination is that R_p varies inversely with $[Cr^{6+}]$, the plots of $1/R_p$ versus $[Cr^{6+}]$ being linear (Fig. 5).

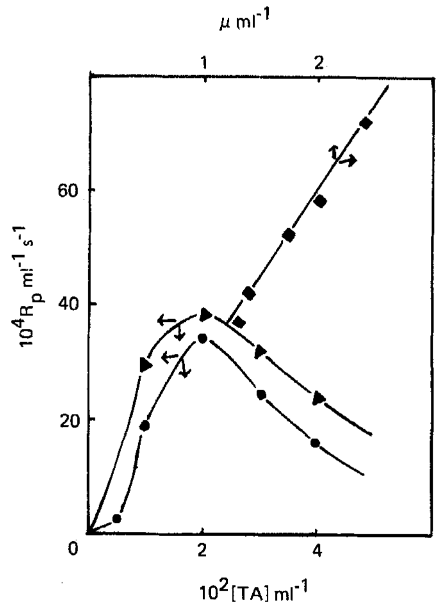


FIG. 4. Variation of R_p with substrate at different temperatures. $[Cr^{6+}] = 1 \times 10^{-2}$ M, $[H^+] = 1.17$ M, $\mu = 1.3$ M, [AN] = 0.7539 M: (●) 35°C, (▲) 40°C. Variation of R_p with ionic strength (μ). $[Cr^{6+}] = 1 \times 10^{-2}$ M, $[H^+] = 1.17$ M, [TA] = 1.5×10^{-2} M, [AN] = 0.7539 M: (■) 40°C.

R_p increased with an increase in $[HClO_4]$. R_p values were highest in an $HClO_4$ medium and decreased in the order $HClO_4 > HNO_3 > H_2SO_4$. The acid anions complex with monochromate ion, reducing the latter's oxidizing power.

An increase in the ionic strength of the medium at constant $[H^+]$ increased the R_p, in keeping with the observations with other metal ions [29]. A linear plot was obtained from R_p versus μ (Fig. 4). The increase in R_p may be attributed either due to the salt effect in the propagation step or to an increase in the rate of oxidation with μ.

Effect of Organic Solvents

The addition of 5% (v/v) methanol, acetone, acetic acid, DMF, and dioxane tends to depress the initial rate as well as the limiting

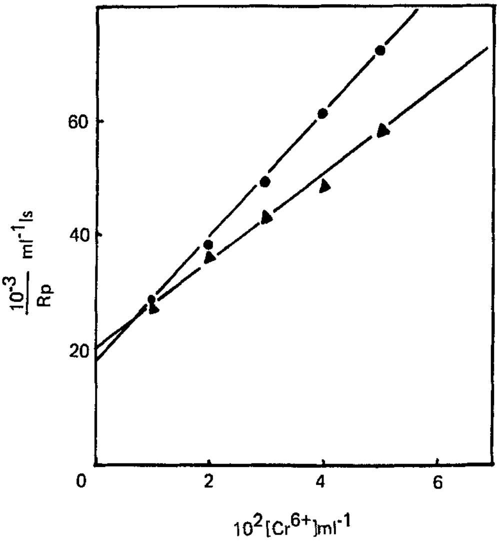


FIG. 5. Variation of R_p with oxidant at different temperatures. $[H^+] = 1.17$ M, $\mu = 1.3$ M, [TA] $= 1.5 \times 10^{-2}$ M, [AN] $= 0.7539$ M. (●) 40°C, (▲) 45°C.

conversion (Fig. 6). Similar observations have been made by other workers [30, 31]. This behavior is due to the following reasons: 1) the decrease of the area of shielding of a strong hydration layer in aqueous medium results in the termination of the growing chain. 2) The increase of the regulated rate of production of primary radicals, which renders the termination rate relatively fast compared to the growing rate; this is in accordance with the view of Kern et al. [32]. 3) The interchain hydrogen bonding, interlocking the polymer chain, is not rigid and therefore the tendency of mutual termination of polymer chain increases.

Rate of Cr^{6+} Disappearance ($-R_M$)

The rate of Cr^{6+} disappearance, $-R_M$, was found to be dependent on the first power of $[Cr^{6+}]$. The pseudo-first-order rate constant, k_{obs}, remained almost constant for a wide range of $[Cr^{6+}]$. $-R_M$ was found to be independent of [AN], showing that Cr^{6+} was not directly involved in initiation.

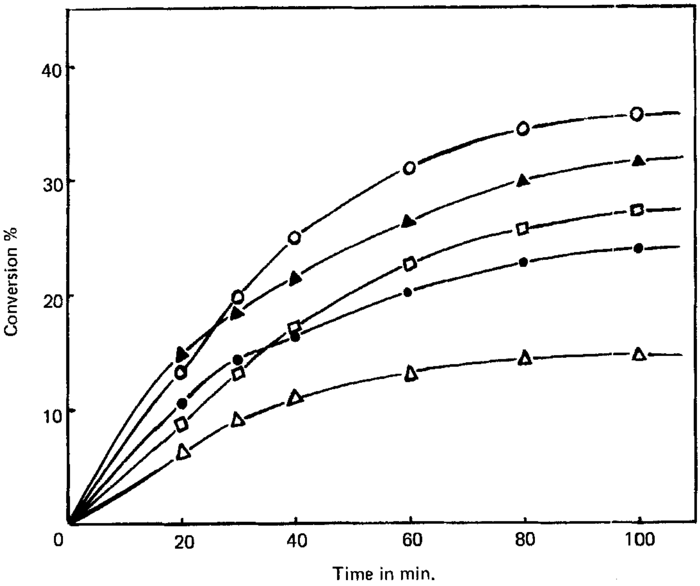


FIG. 6. Variation of % conversion with time: effect of 5% water miscible organic solvents. $[Cr^{6+}] = 1 \times 10^{-2}$ M, $[H^+] = 1.17$ M, $\mu = 1.3$ M, [TA] = 1.5×10^{-2} M, [AN] = 0.7539 M, temperature = 40°C. (○) Control, (△) [CH_3OH] = 5% (v/v), (□) [acetone] = 5% (v/v), (●) [acetic acid] = 5% (v/v), (▲) [dioxane] = 5% (v/v).

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 two 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 activity of chromium ion due to ion-pair coupling with the added electrolytes.

Effect of Complexing Agents

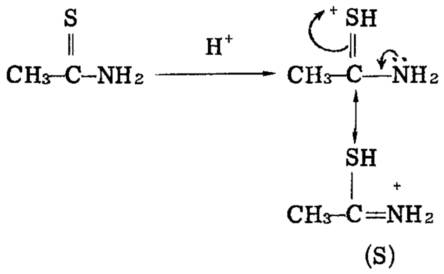
On addition of 0.02 M complexing agents like NaF, succinic acid, pyridine, and piperidine, the initial rate as well as the maximum conversion were depressed considerably. With aniline as the complexing agent, the reaction was completely inhibited. The most probable explanations for this type of behavior are that the pH of the medium changes due to the consumption of the H^+ ion by the amines and that activity of Cr^{6+} ion is greatly reduced due to complex formation with amines behaving as ligands.

Reaction Mechanism and Rate Law

Heterogeneity is a characteristic feature of aqueous polymerization of acrylonitrile initiated by Cr^{6+} ion in the presence of thioacetamide as the activator. The reaction mixture, though homogeneous before initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to the insolubility of polyacrylonitrile (PAN) in the aqueous phase.

From the proportionalities obtained between the measurable parameters and variables, a suitable reaction scheme is proposed. Of the various possible schemes examined, that involving initiation by Cr^{6+} or $R^{\bullet}$ and termination by Cr^{6+} satisfied the experimental results, the active oxidizing agent being the acid chromate ion $HCrO_4^-$. The initiating free radical is produced by the oxidation of thioacetamide by Cr^{6+} ion:

1.



2. Reaction of acid chromate ion with the reducing agent (S):

$$HCrO_4^- + S + H^+ \xrightarrow{k_1} Cr^{4+} + \text{products}$$

3. Reaction of tetravalent chromium with S:

$$S + Cr^{4+} \xrightarrow{k_2} R^{\bullet} + Cr^{3+} + H^+$$

4. Reaction of primary radical $R^{\bullet}$ with Cr^{4+}

$$R^{\bullet} + Cr^{4+} \xrightarrow{k_3} Cr^{5+} + \text{product}$$

5. Reduction of Cr^{5+} to Cr^{3+} by reacting with S:

$$S + Cr^{5+} \xrightarrow{\qquad} \text{products} + Cr^{3+}$$

6. Initiation of polymerization by the reaction of a primary radical with the monomer M:

$$R^{\bullet} + M \xrightarrow{k_i} M^{\bullet}$$

7. Initiation of polymerization by reaction of Cr^{4+} with the monomer:

$$Cr^{4+} + M \xrightarrow{k_i} M^{\bullet} + Cr^{3+} + H^+$$

8. Propagation:

$$M^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$\vdots$$

$$\dot{M}_{n-1} + M \xrightarrow{k_p} M_n^{\bullet}$$

9. Termination of polymerization:

$$M_n^{\bullet} + Cr^{6+} \xrightarrow{k_{t_2}} M_n + Cr^{5+} + H^+$$

Under condition of Step 6 for the initiation and making the usual steady-state assumptions for free radicals and unstable intermediates, we have

$$R_p = \frac{k_p k_1 k_i [AN]^2 [TA][H^+]}{k_{t_2}\{k_3[Cr^{6+}] + k_i[AN]\}} \qquad (1)$$

which rearranges to

$$\frac{[AN]^2}{R_p} = \frac{k_{t_2} k_3 [Cr^{6+}]}{k_p k_1 k_i [TA][H^+]} + \frac{k_{t_2}[AN]}{k_p k_1 [TA][H^+]} \qquad (2)$$

TABLE 2. Values of the Rate Parameters in the Polymerization of Acrylonitrile [AN] Initiated by the Redox System Cr^{6+}-Thioacetamide

Temperature (°C)	$10^3 \times k_i$[a] (m^{-1} s^{-1})	k_{t_2}/k_p[b]	k_3/k_i[c]
35	17.9	1.0063	0.8785
40	28.6	1.962	1.0046

[a] From oxidation.

[b] From plots of $[AN]^2/R_p$ versus [AN].

[c] From $[AN]^2/R_p$ versus [AN] and $1/R_p$ versus $[Cr^{6+}]$.

Then

$$-R_M = 2k_1[Cr^{6+}][TA][H^+]$$

and the chain length n is given by

$$n = k_p[AN]/k_{t_2}[Cr^{6+}] \tag{3}$$

The fact that Cr^{6+} alone is unable to initiate the polymerization of AN by the system Cr^{6+} + TA in acid medium and the reduction of Cr^{6+}, suggested that the possible radical production steps might be Cr^{6+} + TA, or Cr^{5+} + TA, or Cr^{4+} + TA. On the basis of the reasonable assumption that Cr^{6+} is a two-electron oxidant, Step 2 of the kinetic scheme is predominant. The reaction Cr^{6+} + TA (Step 3 in the kinetic scheme) rather than Cr^{5+} + TA (Step 5 in the scheme) appears as a plausible radical production step. Another possibility for the radical production might be the reaction between Cr^{4+} and the production in Step 2 of the kinetic scheme. Mosher and Driscoll [33] have predicted that the polymerization of AN in the Cr^{6+} oxidation of phenyl-tert-butyl alcohol would be due to the production of radicals from the reaction between Cr^{4+} and the product. But under the present experimental conditions with large [TA], it is likely that the reaction Cr^{4+} + TA takes precedence, and hence the reaction Cr^{4+} + product might be discounted. Another possible radical production reaction is Cr^{4+} + M (Step 7 in the kinetic scheme). If Step 7 in preference to Step 6 were to take place, Eqs. (1)-(3) would be identical except for the replacement of k_i by k_i' in Eqs. (1) and (3). In the presence of an organic substrate, the reaction between Cr^{4+} and TA would take place in preference to that between Cr^{4+} and monomer, and hence Step 7 could be neglected. The species responsible for the radical production might be Cr^{4+} and not Cr^{5+}. The work of Rocek et al. [34] also showed that Cr^{4+} and not Cr^{5+} oxidized cyclobutanol.

Evaluation of Rate Constants

The values of k_i in the presence of the monomer and in its absence were obtained from plots of k_{obs} versus [TA] (where k_{obs} is the pseudo-first-order rate constant). The composite rate constants k_{t_2}/k_p and k_3/k_i were obtained from slopes and intercepts of the plots of $[AN]^2/R_p$ versus [AN] (Table 2).

ACKNOWLEDGMENTS

Thanks are due to Y. Muduli, S.V.M. College, Jagatsinghpur, Cuttack, Orissa, India, for constant inspiration and assistance in carrying out this work.

REFERENCES

[1] A. Bonvincine and C. Caldo, Chim. Ind. (Milan), 45, 444 (1963).
[2] T. Sugimura, N. Yasumoto, and Y. Minoura, J. Polym. Sci., A-3, 2935 (1965).
[3] Y. Minoura and T. Sugimura, Ibid., A-1, 4, 2721 (1966).
[4] G. Delzenne, W. Dewinter, S. Toppet, and G. Smets, Ibid., A-2, 4, 1069 (1966).
[5] A. R. Mukherjee, R. P. Mitra, A. M. Biswas, and S. Maitai, Ibid., A-1, 5, 135 (1967).
[6] B. M. Mandal, U. S. Nandi, and S. R. Palit, Ibid., A-1, 1407 (1969).
[7] J. S. Sukla and D. C. Mishra, Makromol. Chem., 173, 91 (1973).
[8] G. S. Mishra and C. V. Gupta, Ibid., 168, 105 (1973).
[9] R. K. Samal and P. L. Nayak, J. Polym. Sci., Polym. Chem. Ed., 15, 2975 (1977).
[10] M. C. Nayak, P. L. Nayak, and R. K. Samal, J. Macromol. Sci.–Chem., A12(6), 827 (1978).
[11] M. C. Nayak, A. K. Dhal, P. L. Nayak, and R. K. Samal, J. Polym. Sci., Polym. Chem. Ed., 18, 2001 (1980).
[12] D. P. Das, G. V. Suryanarayana, M. C. Nayak, and R. K. Samal, J. Macromol. Sci.–Chem., A15(3), 467 (1981).
[13] D. P. Das, G. V. Suryanarayana, G. Panda, N. K. Dash, M. C. Nayak, and R. K. Samal, J. Polym. Sci., Polym. Chem. Ed., communicated.
[14] A. Gupta, M. M. Hussain, and S. N. Mishra, Makromol. Chem., 177, 2919 (1976).
[15] S. N. Mishra and M. M. Hussain, Ibid., 179, 41 (1978).
[16] D. P. Das, M. C. Nayak, G. Panda, G. V. Suryanarayana, and R. K. Samal, J. Appl. Polym. Sci., 26, 41-48 (1981).

[17] E. A. S. Cavell and A. C. Meeks, Polymer, 8, 79 (1967).
[18] V. S. Ananthanarayan and M. Santappa, J. Appl. Polym. Sci., 9, 2437 (1965).
[19] S. Saccubai and M. Santappa, J. Polym. Sci., A-1, 7, 643 (1969).
[20] N. G. Devi and V. Mahadevan, Makromol. Chem., 152, 177 (1972).
[21] C. H. Bamford and A. D. Jenkins, Proc. R. Soc. (London), A216, 515 (1953).
[22] T. Shibukawa, M. Sume, A. Vehida, and K. Swahori, J. Polym. Sci., A-1, 6, 147 (1968).
[23] L. B. Morgan, Trans. Faraday Soc., 42, 169 (1946).
[24] D. Josefowitz and H. Mark, Polym. Bull., 1, 140 (1945).
[25] I. M. Kolthoft and W. E. Harris, J. Polym. Sci., 2, 41 (1947).
[26] G. S. Whitby, M. D. Gross, J. R. Miller, and A. J. Costanza, Ibid., 16, 549 (1955).
[27] A. A. Katai, V. K. Kulsretha, and R. H. Marchessault, in Fourth Cellulose Conference (R. H. Marchessault, ed.), Wiley-Interscience, New York, 1963, p. 403.
[28] W. A. Waters, Oxidation in Organic Chemistry, Part A (K. B. Wiberg, ed.), Academic, New York, p. 69.
[29] V. S. Ananthanarayan and M. Santappa, J. Appl. Polym. Sci., 9, 2437 (1965).
[30] S. R. Palit, G. S. Mishra, and C. V. Gupta, Makromol. Chem., 156, 195 (1972).
[31] S. R. Palit and R. S. Konar, J. Polym. Sci., 58, 85 (1962).
[32] R. Schulz, G. Renner, H. Henglein, and W. Kern, Makromol. Chem., 12, 20 (1954).
[33] W. A. Mosher and E. L. Driscoll, J. Am. Chem. Soc., 90, 4189 (1968).
[34] J. Rocek and A. E. Radkowsky, Ibid., 95, 7123 (1973).

Accepted by editor March 3, 1981
Received for publication March 24, 1981