Polymerization of Acrylonitrile Initiated by the Mn(III)/Ethane Thiol Redox System

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ABSTRACT

Kinetics of vinyl polymerization of acrylonitrile initiated by the redox system Mn(III)/ethane thiol were investigated in aqueous sulfuric acid in the temperature range of 30-45°C. The rate of polymerization, rate of manganic ion disappearance, etc. were measured. The effect of certain water-miscible organic solvents, neutral electrolytes, and organic nitrogen compounds on the rate has been investigated. A mechanism involving the formation of a complex between Mn(III) and the thiol, whose decomposition yields the initiating free radical with the polymerization being terminated by mutual combination of the growing radicals, has been suggested.

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INTRODUCTION

When mercaptans are used as molecular weight modifiers in addition polymerization, they exert an activating influence on metal and nonmetal ions. The use of mercaptans as redox components in free radical polymerization of various vinyl monomers has been much investigated [1-15]. The interaction of these compounds with transition metal ions in their higher valency states [i.e., Ce(IV), V(V), Cr(VI), Co(III), Mn(IV), Mn(III)] to create free radicals seems to be too facile. We have reported the aqueous polymerization of acrylonitrile [16-19] and methyl methacrylate [20] using Cr(VI), V(V) and Mn(III) with thiourea, thioacetamide, and thioglycollic acid as redox couples. The generation of complex thio free radicals by these systems has been found to initiate vinyl polymerization. We now report the aqueous polymerization of acrylonitrile (AN) initiated by the Mn(III)/ ethane thiol redox system.

EXPERIMENTAL

Acrylonitrile from a local firm was purified as reported previously [21]. Manganous sulfide (AR), sodium bisulfate (Riedel), and sulfuric acid (18 M, AR) were used. Ethane-thiol was purified by distillation under reduced pressure, and the middle fraction was collected. All other reagents were of BDH quality.

Water used for the preparation of solutions was purified by distilling thrice over alkaline permanganate and deionized by passage through Biodeminrolit resin (Permutit Co., U.K.). Nitrogen used for the deaeration of the reaction mixture was purified by passage through Fieser's solution, saturated lead acetate solution, and finally through distilled water containing a little monomer.

Mn(III) stock solution (0.07 M) was prepared by electrolytic oxidation of an appropriate $MnSO_4$ solution (0.4-0.6 M) in 4-6 N H_2SO_4 at a platinum anode [22, 23]. Freshly prepared solutions to be used for the experiment were analyzed for Mn(III) content by cerimetry and for total Mn(III) content by EDTA titration.

The reducing agent (ET), monomer, and sodium bisulfate solutions of appropriate concentration were placed in the experimental vessel and deaerated under nitrogen for about 30 min. After deaeration the experimental vessels were stoppered and placed in a thermostat at the desired temperatures for 40 min in order to attain thermal equilibrium. An appropriate amount of Mn(III) stock solution was then added to each reaction vessel by a special technique so that no air was allowed into the vessel. The reactions were carried out for the desired time, after which they were arrested by addition of a known excess of ferrousammonium sulfate solution (0.1 M). As a further precaution for stopping polymerization, the reaction vessels were transferred into an ice bath. The precipitated polymer was

filtered off into a G_3 crucible and dried to constant weight at 60°C in a vacuum oven. The rates of polymerization were obtained by gravimetry. For each reaction vessel the excess of ferrous was estimated by cerimetry using ferroin as indicator. From these estimations the rates of oxidant [Mn(III)] consumption, -d[Mn(III)]/dt, were computed.

The molecular weights of the purified polymers were determined by viscometry using the appropriate Mark-Houwink relationship. The viscosities of the polymer solutions (0.1%) were determined in an Ubbelohde-type suspended level dilution viscometer in dimethylformamide at 30°C using the relationship [24]

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

RESULTS AND DISCUSSION

Acrylonitrile was polymerized in aqueous sulfuric acid at 30-50°C in the presence of the redox system Mn(III)/ethane thiol. Figure 1 shows a typical set of conversion curves at 35°C for various ethanethiol concentrations ($0.5-2 \times 10^{-3}$ M) and at a fixed Mn(III) concentration. Figure 1 also includes a typical set of conversion curves for various temperature (30-50°C) at fixed Mn(III) and ethane thiol concentrations.

Rate of Manganic Ion Disappearance

The rate of manganic ion disappearance (-d[Mn(III)]/dt) was first order in [Mn(III)] and independent of monomer concentration. The plots of the reciprocal of the rate $(-d[Mn(III)]/dt)^{-1}$ vs $[ET]^{-1}$ (where ET represents ethane thiol) were linear with the intercept on the rate axis (Fig. 2), showing Lineweaver-Burk kinetics [25] for complex formation. $-R_{Mn}$ values were found to increase with an increase in activator concentration. This enhancement in the rate is due to an increase in the rate of oxidation of the activator.

Rate of Polymerization (R_p)

R_p increased regularly on increasing the monomer concentration (0.3016-0.9048 M). Plots of R_p vs $[M]^{3/2}$ were linear and passed through the origin (Fig. 3), indicating a 3/2 order with respect to [AN]. R_p also increased on increasing activator concentration [ET] in the range $0.5-1.5 \times 10^{-3}$ M. Further, plots of $(1/R_p^2)$ vs $[ET]^{-1}$ were linear with the intercept on the rate axis (Fig. 4).

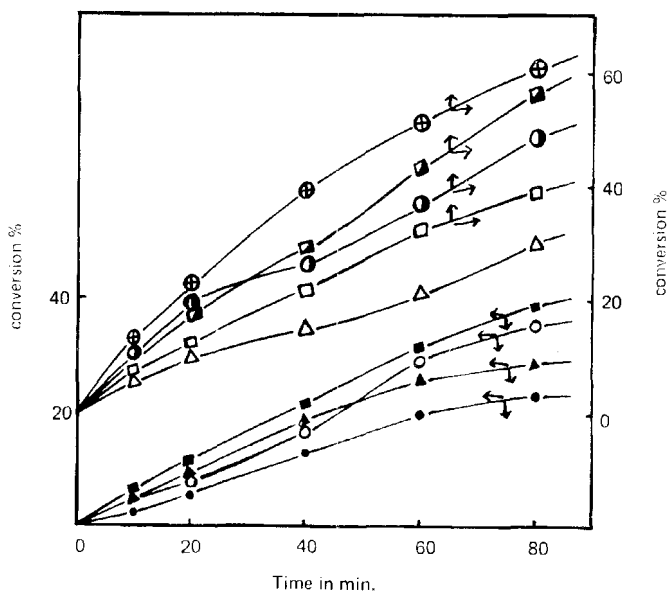FIG. 1. Plots of conversion % vs time at different activator con-
centrations. $|Mn^{3+}| = 7 \times 10^{-3}$ $\underline{M}$, $|H^+| = 0.55$ $\underline{M}$, $[AN] = 0.754$ $\underline{M}$,
$\mu = 1.5$ $\underline{M}$, temperature = 35°C. $[ET]$: (●) 0.5×10^{-3} $\underline{M}$, (▲)
1×10^{-3} $\underline{M}$, (■) 1.5×10^{-3} $\underline{M}$, (○) 2×10^{-3} $\underline{M}$. Plots of conversion
% vs time at different temperatures. $|Mn^{3+}| = 7 \times 10^{-3}$ $\underline{M}$, $|H^+| =$
0.55 $\underline{M}$, $[ET] = 1.5 \times 10^{-3}$ $\underline{M}$, $|AN| = 0.754$ $\underline{M}$, $\mu = 1.5$ M. Tempera-
tures: (△) 30°C, (⊡) 35°C, (◑) 40°C, (◢) 45°C, (⊕) 50°C.

Effect of Organic Solvents

Acetic acid, chloroform, acetone, and dimethylformamide of 10%
(v/v) in the reaction mixture depress the initial rate as well as the
maximum conversion (Fig. 4). Such depression in the rate might be
due to (1) an increase in the rate of production of primary radicals
in all cases except DMF, which under the existing experimental
conditions renders the termination rate relatively fast as compared
to the rate of growth of polymer chains, as pointed out by Kern et al.
[26] and Palit et al. [27]; (2) the solubility of polyacrylonitrile in
dimethylformamide; and (3) the interchain hydrogen bonding inter-
locking in the polymer chain is not rigid, so that the rate of mutual
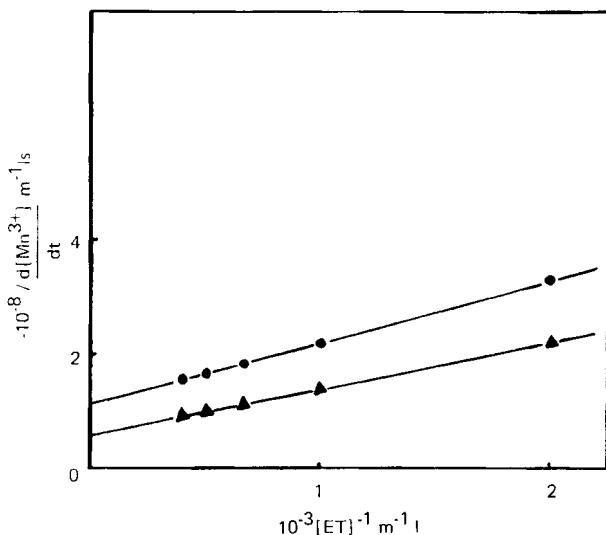combination increases.

FIG. 2. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs $[ET]^{-1}$ at different tempera-
tures. $[Mn^{3+}] = 7 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.85$ $\underline{M}$, $[AN] = 0.754$ $\underline{M}$, $\mu = $
2.2 $\underline{M}$. Temperatures: (●) 30°C, (▲) 35°C.

Effect of Amines

0.02 $\underline{M}$ heterocyclic and aromatic amines in the reaction mixture
have a pronounced effect on the initial rate of polymerization and
maximum conversion (Fig. 5). In the case of α-picoline and piperidine,
a retardation in the rate is noticed which is probably due to the N-
oxides produced by the oxidation of the additives by Mn(III). N-
Oxides are known to be ideal retarders of vinyl polymerization [28].
With aniline the reaction was completely inhibited, and a reddish
coloration was produced which persisted. This behavior of aniline
is due to its facile oxidation to quinolines [29] which are strong
inhibitors. Similar phenomena has been noticed by Saha et al. [30]
in the polymerization of acrylonitrile by Ce(IV) in the presence of
N,N-dimethyl aniline.

Effect of Salts

Addition of 0.02 $\underline{M}$ solutions of Na_2SO_4, KCl, and $ZnSO_4$ to the
reaction mixture retard the initial rate of polymerization as well as
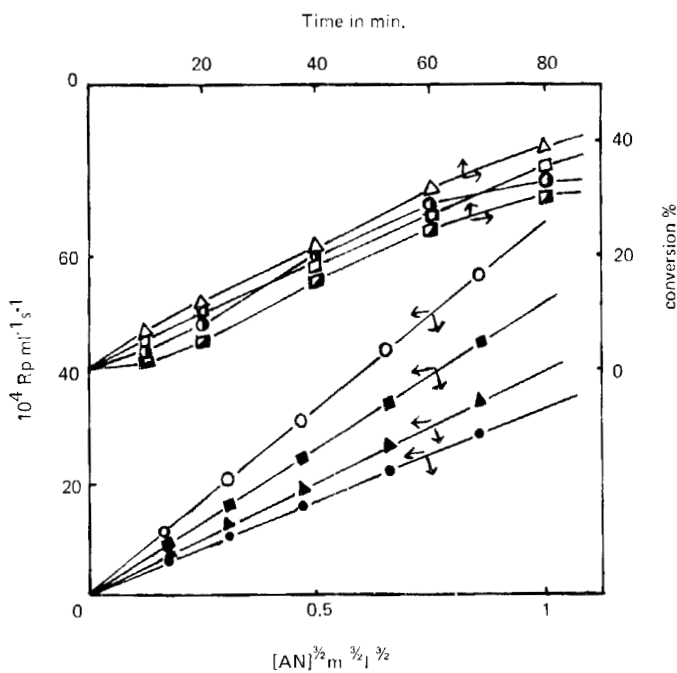the maximum conversion (Fig. 3) possibly due to the resultant increase

FIG. 3. Plots of R_p vs $[AN]^{3/2}$ at different temperatures.
$[Mn^{3+}] = 7 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.85$ $\underline{M}$, $[ET] = 1.5 \times 10^{-3}$ $\underline{M}$. $\mu = 2.2$
$\underline{M}$. Temperatures: (•) 30°C, (▲) 35°C, (■) 40°C, (○) 45°C. Plots
of conversion % vs time in the presence of added electrolytes. $[Mn^{3+}]$
$= 7 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.85$ $\underline{M}$, $[ET] = 1.5 \times 10^{-3}$ $\underline{M}$, $\mu = 2.2$ $\underline{M}$, temperature = 35°C. (△) Control. (▪) $[CuSO_4] = 0.02$ $\underline{M}$. (◻) $[Na_2SO_4]$
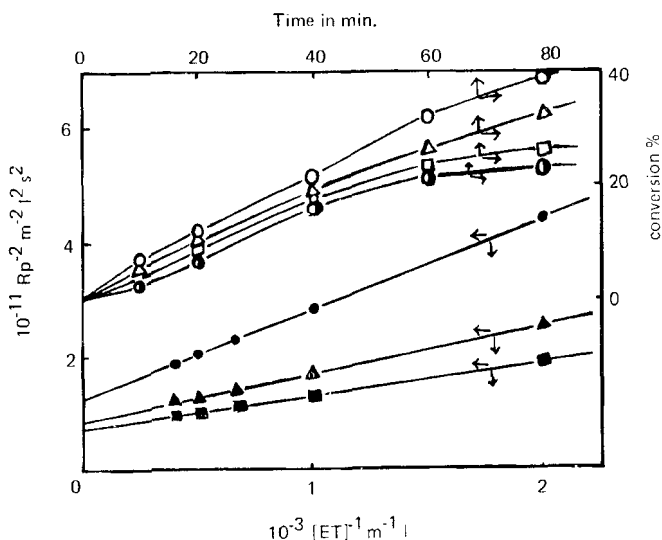$= 0.02$ $\underline{M}$. (◐) $[ZnSO_4] = 0.02$ $\underline{M}$.

FIG. 4. Plots of $1/R_p^2$ vs $[ET]^{-1}$ at different temperatures. $[Mn^{3+}] = 7 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.85$ $\underline{M}$, $\mu = 2.2$ $\underline{M}$, $[AN] = 0.754$ $\underline{M}$, Temperatures: ($\bullet$) 30°C, ($\blacktriangle$) 35°C, ($\blacksquare$) 40°C. Plots of conversion % vs time in the presence of organic solvents. $[Mn^{3+}] = 7 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.85$ $\underline{M}$, $[ET] = 1.5 \times 10^{-3}$ $\underline{M}$, $\mu = 2.2$ $\underline{M}$, temperature = 35°C. ($\circ$) Control. ($\triangle$) $[C_2H_5OH] = 10\%$ (v/v). ($\square$) $[Acetone] = 10\%$ (v/v). ($\bullet$) $[DMF] = 10\%$ (v/v).

in ionic strength of the medium. Similar explanation has been furnished by Misra et al. [7] in KMnO₄/thiourea-initiated polymerization of acrylonitrile. Further, the rate depression in the presence of CuSO₄ might be due to competition between mutual termination and linear termination, and the rate of linear termination predominates over the rate of mutual termination. Identical explanations have been put forward by Bamford et al. [31] in AIBN-initiated polymerization of acrylonitrile in the presence of FeCl₃ and by Bengough et al. [32] in the AIBN-initiated polymerization of methyl methacrylate in the presence of CuCl₂.

Reaction Mechanism and Rate Law

The polymerization of acrylonitrile in aqueous media initiated by Mn(III) in the presence of ET shows the characteristic features of
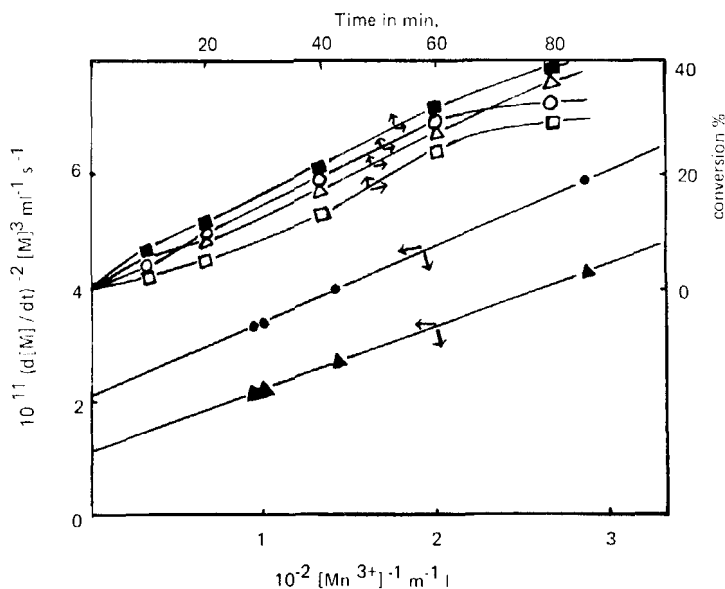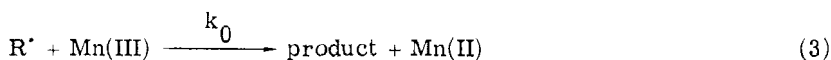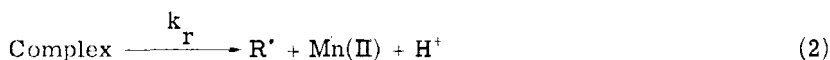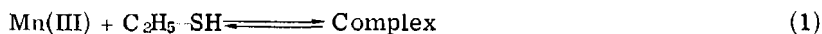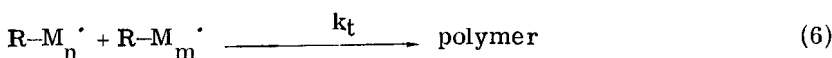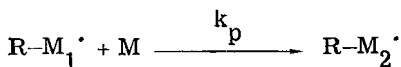
FIG. 5. Plots of $(-d[M]/dt)^{-2}[M]^3$ vs $[Mn^{3+}]^{-1}$ at different
temperatures. $[ET] = 1.5 \times 10^{-3}$ $\underline{M}$, $[AN] = 0.754$ $\underline{M}$, $\mu = 3.2977$
$\underline{M}$. Temperatures: ($\bullet$) 30°C, ($\blacktriangle$) 35°C. Plots of conversion % vs
time in the presence of amines. $[Mn^{3+}] = 7 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.85$ $\underline{M}$,
$[ET] = 1.5 \times 10^{-3}$ $\underline{M}$, $\mu = 2.2$ $\underline{M}$, temperature = 35°C. ($\blacksquare$) Control.
($\circ$) [Pyridine] = 0.02 $\underline{M}$. ($\triangle$) [Piperidine] = 0.02 $\underline{M}$. ($\square$) [α-
Picoline] = 0.02 $\underline{M}$.

heterogeneous polymerization. The reaction mixture becomes hetero-
geneous as soon as the polymerization starts, due to the insolubility
of the polymer in the aqueous phase.

From the kinetic results a reaction scheme has been proposed
involving initiation by organic free radicals produced by the inter-
action of Mn(III) with ET and termination by mutual combination.

$$Mn(III) + C_2H_5-SH \rightleftharpoons Complex \qquad (1)$$

$$Complex \xrightarrow{k_r} R^\bullet + Mn(II) + H^+ \qquad (2)$$

$$R^\bullet + Mn(III) \xrightarrow{k_0} product + Mn(II) \qquad (3)$$

$$R^{\cdot} + M \xrightarrow{\quad k_i \quad} R\text{-}M_1^{\cdot} \tag{4}$$

$$R\text{-}M_1^{\cdot} + M \xrightarrow{\quad k_p \quad} R\text{-}M_2^{\cdot}$$

$$R\text{-}M_{n-1}^{\cdot} + M \xrightarrow{\qquad\qquad} R\text{-}M_n \tag{5}$$

$$R\text{-}M_n^{\cdot} + R\text{-}M_m^{\cdot} \xrightarrow{\quad k_t \quad} \text{polymer} \tag{6}$$

Applying the steady-state principle (i.e., the rates of formation and destruction of propagating radicals are equal) to the primary radical and to the growing polymer chains, and taking radical reactivity as independent of radical size, we obtain

$$-d[\,Mn(III)\,]/dt = k_r K[\,Mn(III)\,]_{eq}[\,ET\,] + \frac{k_0 k_r K[\,Mn(III)\,]_{eq}^2[\,ET\,]}{(k_0[\,Mn(III)\,]_{eq} + k_i[\,M\,])} \tag{7}$$

The second term in Eq. (7) is due to Reaction (3).
  If $k_0[\,Mn(III)\,] \gg k_i[\,M\,]$, we have

$$-d[\,Mn(III)\,]/dt = 2k_r K[\,Mn(III)\,]_{eq}[\,ET\,] \tag{8}$$

Since the measured rates $-d[\,Mn(III)\,]/dt$ apply to total $[\,Mn(III)\,]$ regardless of the species, and since

$$[\,Mn(III)\,]_T = [\,Mn(III)\,]_{eq}(1 + K[\,ET\,])$$

we obtain

$$-d[\,Mn(III)\,]/dt = 2k_r K[\,Mn(III)\,]_T[\,ET\,]/(1 + K[\,ET\,]) \tag{9}$$

Rearranging Eq. (9), we obtain

$$\left(\frac{-d[\,Mn(III)\,]}{dt}\right)^{-1} = \frac{1}{2k_r K[\,Mn(III)\,]_T[\,ET\,]} + \frac{1}{2k_r[\,Mn(III)\,]_T} \tag{10}$$

R_p is given by

$$-d[\,M\,]/dt = k_p[\,M\,][\,R\text{-}M_n^{\cdot}\,]$$

$$\frac{-d[\,M\,]}{dt} = \frac{k_p k_i^{1/2}(k_r K[\,Mn(III)\,]_{eq}[\,ET\,])^{1/2}[\,M\,]^{3/2}}{k_t^{1/2}(k_0[\,Mn(III)\,] + k_i[\,M\,])^{1/2}} \tag{11}$$

TABLE 1. Values of Rate Parameters in the Polymerization of Acrylonitrile Initiated by the Mn(III)/Ethane Thiol Redox System

Temperature (°C)	$k_r \times 10^{-2}$ (s^{-1})	K m^{-1} L	$k_p/k_t^{1/2}$ ($m^{-1/2}$ $L^{1/2}$ $s^{1/2}$)	$k_0/k_i \times 10$
30	0.649	1.0	1.173	1.205
35	2.38	0.375	1.3567	1.222

If $k_0[Mn(III)] \gg k_i[M]$, we obtain

$$\frac{-d[M]}{dt} = \frac{k_p k_i^{1/2} (k_r K[ET])^{1/2} [M]^{3/2}}{k_0^{1/2} k_t^{1/2}} \qquad (12)$$

Equation (11) can be arranged to

$$\left(\frac{-d[M]}{dt}\right)^{-2} = \frac{k_t k_0}{k_p^2 k_i k_r K[ET][M]^3} + \frac{k_t}{k_p^2 k_r K[Mn(III)]_T[ET][M]^2}$$

$$+ \frac{k_t}{k_p^2 k_r [Mn(III)]_T[M]^2} \qquad (13)$$

The plots of $(-d[M]/dt)^{-2}$ vs $[ET]^{-1}$ are linear with an intercept on the ordinate (Fig. 4). From the intercepts of these plots we can calculate the ratio $k_p/k_t^{1/2}$. Equation (13) also requires that plots of $(-d[M]/dt)^{-2}[M]^3$ vs $[Mn(III)]^{-1}$ (Fig. 5) be linear with the intercept $k_t k_0/k_p^2 k_i k_r K[ET]$. By using the values of $k_p/k_t^{1/2}$, the ratio k_0/k_i can be calculated (Table 1) from the intercepts.

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REFERENCES

[1] A. Bonvincine and C. Caldo, Chem. Ind. (Milan), 45, 444 (1963).

[2] T. Sujimura, N. Yasumoto, and Y. Miroura, 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, 1069 (1966).

[5] B. M. Mandal, U. S. Nandi, and S. R. Palit, Ibid., A-1, 7, 1407 (1969).

[6] A. R. Mukherjee, R. P. Mitra, A. M. Biswas, and S. Maitai, Ibid., A5, 135 (1967).

[7] J. S. Shukla and D. C. Misra, Makromol. Chem., 173, 91 (1973).

[8] G. S. Mishra and C. V. Gupta, Ibid., 168, 105 (1973).

[9] R. K. Samal, M. C. Nayak, and P. L. Nayak, J. Macromol. Sci.–Chem., A12(6), 827-836 (1978).

[10] R. K. Samal, M. C. Nayak, A. K. Dhal, and P. L. Nayak, J. Polym. Sci., Polym. Chem. Ed., 18, 2001 (1980).

[11] M. M. Husain, A. Gupta, and S. N. Misra, Makromol. Chem., 176, 2861 (1975).

[12] M. M. Husain, A. Gupta, and S. N. Misra, Ibid., 179, 295 (1978).

[13] M. M. Husain, A. Gupta, and S. N. Misra, Ibid., 177, 2916 (1976).

[14] M. M. Husain and S. N. Misra, Ibid., 179, 41 (1978).

[15] S. R. Palit and S. Maiti, J. Polym. Sci., A9, 253 (1971).

[16] R. K. Samal and P. L. Nayak, J. Polym. Sci., Polym. Chem. Ed., 15, 2603 (1977).

[17] R. K. Samal, M. C. Nayak, and P. L. Nayak, J. Macromol. Sci.–Chem., A12, 827 (1978).

[18] R. K. Samal, M. C. Nayak, A. K. Dhal, and D. P. Das, Ibid., In Press.

[19] R. K. Samal, M. C. Nayak, G. V. Suryanarayan, and D. P. Das, Eur. Polym. J., In Press.

[20] R. K. Samal, M. C. Nayak, and D. P. Das, J. Appl. Polym. Sci., 26, 41 (1981).

[21] R. K. Samal, T. R. Mohanty, and P. L. Nayak, Makromol. Chem., 176, 2937 (1975).

[22] R. G. Selin and J. J. Lingane, Anal. Chim. Acta, 21, 536 (1959).

[23] C. F. Wells and G. Davies, Nature, 205, 692 (1965).

[24] T. Shibukawa, M. Sume, A. Vehida, and K. Swahori, J. Polym. Sci., A-1, 6, 147 (1968).

[25] H. Lineweaver and D. Burk, J. Am. Chem. Soc., 56, 658 (1934).

[26] R. Schulz, G. Renner, A. Henglein, and W. Kern, Makromol. Chem., 12, 20 (1954).

[27] R. S. Konar and S. R. Palit, J. Indian Chem. Soc., 38, 481 (1961).

[28] Y. Mivra, S. Masuda, and M. Kinoshita, Makromol. Chem., 160, 243-249 (1972).

[29] P. A. S. Smith, The Chemistry of Open Chain Organic Nitrogen Compounds, Benjamin, New York, 1965, p. 108.

[30] S. K. Saha and A. K. Chaudhuri, J. Polym. Sci., Polym. Chem. Ed., 10, 797-808 (1972).

[31] C. H. Bamford, A. D. Jenkins, and R. Johnston, Proc. R. Soc. London, A, 239, 214 (1957).

[32] W. I. Bengough and W. H. Fairservice, Ibid., p. 1206 (1965).