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Block copolymerization initiated by Mn(III)-poly(ethylene glycol) redox system – general features and kinetics

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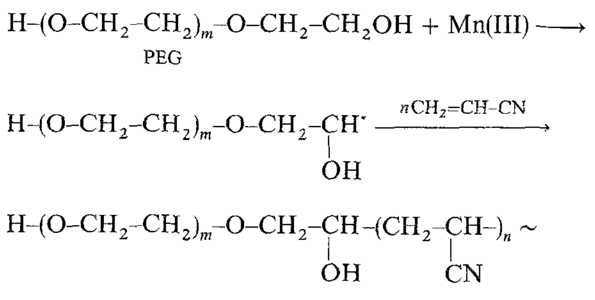
Abstract: The kinetics and mechanism of thermal polymerization of acrylonitrile initiated by Mn(III) pyrophosphate – poly(ethylene glycol) (PEG, molecular weight 6000) redox system in aqueous sulfuric acid medium was studied in the temperature range 30–60 °C. The overall rates of polymerization and the disappearance of Mn^{3+} were determined. The polymerization was initiated by the organic free radical produced from the Mn^{3+}-PEG reaction and the termination was by the metal ions. The rate of polymerization of acrylonitrile was found to be directly proportional to the square of the monomer concentration and first power of PEG concentration, and inversely proportional to the concentration of Mn^{3+}. The rate of manganic ion disappearance was found to be directly proportional to manganic ion concentration and PEG concentration, and independent of the monomer concentration. Based on these observations, a plausible reaction scheme was suggested and suitable kinetic expressions were evaluated.

Key words: Mn(III)-poly(ethylene glycol) – acrylonitrile – block copolymerization – kinetics

Introduction

Several metal ions have been used, either alone or in combination with reducing agents, for the initiation of polymerization of various vinyl monomers [1–5]. Manganese(III) ion (in the form of sulfate or pyrophosphate) reacts with simple organic molecules (reducing agents) to produce a free radical which initiates polymerization. The organic molecules such as ethylene glycol [6], ethyl acetoacetate [7], glycerol [8], diglycolic acid [9], isobutyric acid [10], pinacol [11], malonic acid [12], dimethyl sulfoxide [13], cyclohexanone [14], ascorbic acid [15], mannitol [16], cyano acetic acid [17], oxalic acid [18], etc. have been used in conjunction with Mn(III) ion for polymerization. The manganese(III) ion has also been used for the graft copolymerization of vinyl monomers onto several substrates [19–22].

In an earlier article [23], we reported the results of our studies on the kinetics of block copolymerization initiated by the Ce(IV)-poly(ethylene glycol) [PEG] redox system in an aqueous sulfuric acid medium. As mentioned there, unlike ethylene glycol, in the case of PEG, there is no possibility of cleavage of the main chain as there are no 1,2-glycol units. Hence a possibility of block copolymer synthesis arises by the polymerization of acrylonitrile onto PEG as follows:



$$\underset{\text{PEG}}{\text{H–(O–CH}_2\text{–CH}_2)_m\text{–O–CH}_2\text{–CH}_2\text{OH}} + \text{Mn(III)} \longrightarrow$$

$$\text{H–(O–CH}_2\text{–CH}_2)_m\text{–O–CH}_2\text{–}\underset{\text{OH}}{\text{CH}^{\cdot}} \xrightarrow{n\text{CH}_2\text{=CH–CN}}$$

$$\text{H–(O–CH}_2\text{–CH}_2)_m\text{–O–CH}_2\text{–}\underset{\text{OH}}{\text{CH}}\text{–(CH}_2\text{–}\underset{\text{CN}}{\text{CH}}\text{–)}_n \sim$$

This paper deals with some general features and the kinetics of polymerization of acrylonitrile

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initiated by the redox system, Mn(III)–PEG (molecular weight 6000) in aqueous sulfuric acid medium. From the experimental observations, a suitable reaction scheme and rate expression were suggested.

Experimental

PEG (L.R., s.d. chem., India) was purified as described in our earlier article [23]. The monomer, acrylonitrile (L.R., s.d. chem., India) was purified by the standard procedure [24]. Water twice distilled using alkaline permanganate in a pyrex all-glass set-up was used for the preparation of all reagents and solutions.

Commercial manganous sulfate (A.R., s.d. chem., India), ceric ammonium sulfate (A.R., s.d. chem., India) and sodium pyrophosphate (Loba-Chemie, India) were used as such.

All the other reagents such as ferrous ammonium sulfate, potassium permanganate, sodium bisulfate, sodium hydroxide, o-phosphoric acid, potassium dichromate, oxalic acid, and indicators such as diphenylamine, phenolphthalein and ferroin were A.R. grade samples.

The solvent N,N′-dimethylformamide (DMF) (E. Merck), distilled under vacuum using a BUCHI 461 Rotavapor was used.

Nitrogen (Indian Oxygen Co., India) used to deaerate the experimental system was freed from oxygen by passing through Fieser's solution, and then saturated lead acetate solution, and finally through distilled water.

Standardization of the reagents

Ceric ammonium sulfate solution used for the determination of the concentration of Mn^{3+} ion and ferrous ammonium sulfate solution used for arresting the polymerization reaction were standardized as described in our previous article [23].

Preparation and Characterization of the Initiator

The manganic pyrophosphate initiator was prepared as follows:

5 ml of a solution of Mn^{2+} ions, prepared by dissolving $MnSO_4 \cdot H_2O$ (3.2460 g) in double distilled water (100 ml) was added to a solution of sodium pyrophosphate (2.6760 g) in double distilled water (50 ml). The pH of the resulting solution was adjusted to 6 by adding a few drops of concentrated sulfuric acid. The Mn^{2+} ions were then oxidized to Mn^{3+} ions by titrating potentiometrically against Mn^{7+} ions (obtained by dissolving 0.7580 g of $KMnO_4$ in 100 ml of double distilled water). The resulting solution had an intense red-violet color. The visible spectrum of the solution agreed with that reported for Mn(III) and had no trace of the Mn(VII) (Fig. 1). The initiator solutions thus prepared were used immediately and fresh solutions were prepared as and when required.

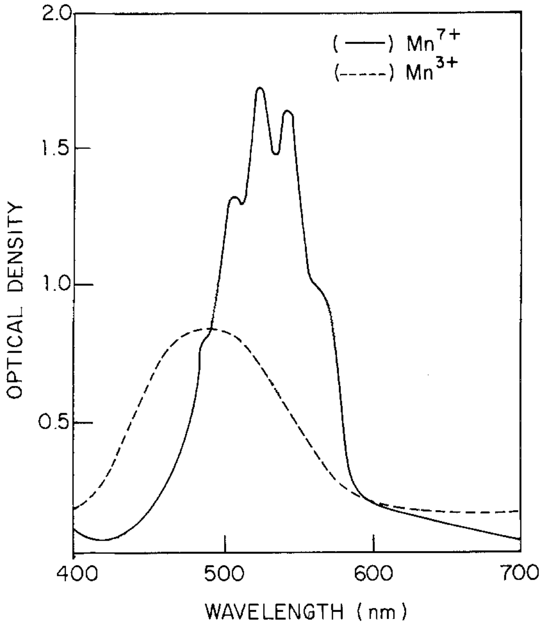

Fig. 1. UV-visible spectra of (——) Mn^{7+}, (– – – –) Mn^{3+}

Polymerization procedure

The polymerizations were carried out in pyrex glass tubes of 6-inch length fitted with a $B_{24/29}$ socket carrying a $B_{24/29}$ cone with inlet and outlet tubes. The reaction tube was covered entirely with a black cloth during the course of the reaction to ensure that the kinetic studies were made in the absence of light.

All solutions except the initiator were taken in the reaction tube, deaerated and kept in a thermostatic reservoir at a temperature of 30 ± 0.1 °C. Then the initiator solution deaerated and thermostated separately was added to the reaction system as quickly as possible, while noting the time.

The polymerization reactions were heterogeneous, with the polymer precipitating out continuously. After the reaction time, the polymerization was arrested by adding a known excess of standard ferrous ammonium sulfate solution such that all the unreacted manganic ions were instantaneously reduced to manganous ions. The precipitated polymer was filtered using a sintered glass crucible, washed well with water to remove any unreacted PEG, Mn^{3+}, acrylonitrile as well as Mn^{2+}, and any other oxidation products of PEG, dried under vacuum at 60–70 °C, and weighed. From the weight of the polymer, the rate of polymerization (initial rate) was calculated using the relation,

$$Rp = \frac{1000\ \mathrm{W}}{VtM}, \tag{1}$$

where W = weight of the polymer formed (in gms); V = total volume of the reaction mixture (in ml); t = reaction time (in seconds), and M = molecular weight of the monomer used.

The filtrate having excess ferrous ions was back-titrated with standard ceric ammonium sulfate solution to determine the rate of manganic ion disappearance. Duplicate runs were carried out for the determination of the rate of monomer disappearance and the rate of manganic ion disappearance.

Characterization

UV-visible spectra were carried out using Shimadzu UV-160 A UV-visible recording spectrophotometer at ambient temperature. FT-IR spectra were recorded using NICOLET 20 DXB Fourier-transform infrared spectrophotometer. Intrinsic viscosities of the polymers were determined using a Ubbelohde suspended-level dilution viscometer (Specification D 445-46 T) with DMF as the solvent at 30 °C.

Results and discussions

General features

No polymer was formed on adding Mn^{3+} solution to acrylonitrile monomer in the range of concentrations used for the kinetic studies in the dark, indicating no homopolymerization of acrylonitrile. Photochemical initiation of polymerization by Mn^{3+} in the presence of the reducing agent was not observed. No induction period was observed in deaerated system, whereas in aerated system an induction period (ca. 5 min.) was usually observed, indicating the free radical initiation of polymerization. The oxidation of water by Mn^{3+} in our experimental conditions was found to be negligible. The rate of polymerization under normal conditions was found to be greater than those under stirred conditions. This might be due to the greater probability of encounters between the chain radicals and the terminating agent under stirred condition.

The FT-IR spectrum of the polymer showed peaks corresponding to both PEG and poly(acrylonitrile).

$O\text{–}H_{str.}$: 3450 cm^{-1}; $C\text{–}H_{str.}$: 2950 cm^{-1}; $C\text{–}H_{def.}$: 1400 cm^{-1}; $C\text{–}O_{str.}$: 1125 cm^{-1}; $C{\equiv}N_{str.}$: 2260 cm^{-1}.

Kinetics

Rate of monomer disappearance (*Rp*): The concentration of the monomer, M was varied from 0.2355 to 1.4130 M. Rp had a square dependence on the [M]. The log *Rp* vs log [M] plot gave a slope of 2 (Fig. 2A) and the plot of *Rp* against $[M]^2$ was linear with zero intercept (Fig. 2B), indicating that the order with respect to monomer is 2. A similar dependence was also observed in our earlier work [23]. This observation is of great significance since it completely rules out the possibility of mutual termination which requires the dependence of rate on $[M]^{3/2}$. The concentration of Mn^{3+} was varied from 2.5×10^{-4} to 15.0×10^{-4} M. The rate decreased linearly with increase in the concentration of Mn^{3+} (Fig. 3A). This observation excludes the participation of Mn(III) ion directly in the initiation process. The rate increased linearly with the concentration of PEG ($5.0 \times 10^{-3} - 17.5 \times 10^{-3}$ M); *Rp* vs [PEG] plot was linear with zero intercept (Fig. 4A) and a plot of log *Rp* vs log [PEG] was linear with a slope of 1 (Fig. 4B), indicating that the order with respect to [PEG] is unity. The rate was unaffected by changes in $[H^+]$ (0.2–2.0 M) at constant ionic strength.

Rate of Mn^{3+} ion disappearance, $-R_M$

Monomer concentration (0.2355–1.4130 M) had no effect on the rate of disappearance of Mn^{3+} ion, indicating the absence of monomer oxidation by Mn^{3+} ion under the conditions employed. Increase of $[Mn^{3+}]$ (2.5×10^{-4} to 15.0×10^{-4} M) increased the rate, and the first-order dependence of rate on $[Mn^{3+}]$ was concluded from the linear plot of $-R_M$ vs $[Mn^{3+}]$ (Fig. 3B). An increase in [PEG] (5.0×10^{-3} to 17.5×10^{-3} M) increased the rate; plot of $-R_M$ vs

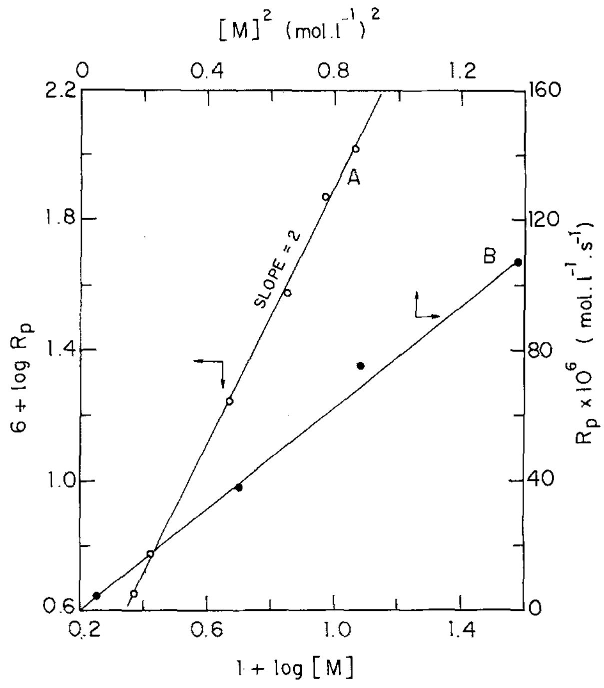

Fig. 2A) Plot of log*Rp* against log [M], B) Dependence of *Rp* on [M], [Mn(III)] = 0.001 M; [PEG] = 0.01 M; $[H^+]$ = 2.0 M; Temp. = 30 °C; Time = 30 min.

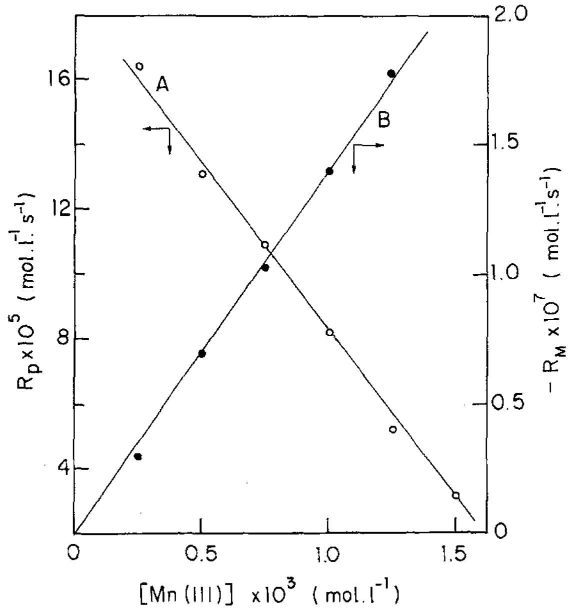

Fig. 3. Effect of [Mn(III)] on, A) *Rp* and B) $-R_M$ [PEG] = 0.01 M; [M] = 0.9423 M; $[H^+]$ = 2.0 M; Temp. = 30 °C; Time = 30 min.

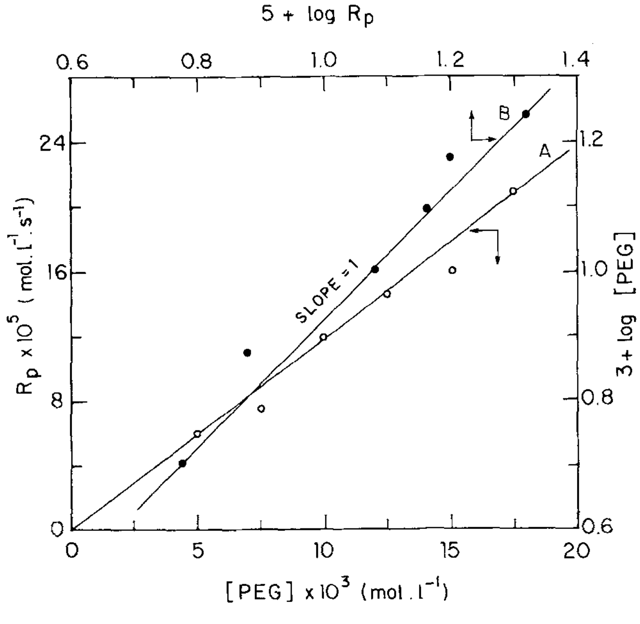

Fig. 4A) Dependence of *Rp* on [PEG], B) Plot of log*Rp* against log[PEG], [Mn(III)] = 0.001 M; [M] = 0.9423 M; $[H^+]$ = 2.0 M; Temp. = 30 °C; Time = 30 min.

[PEG] was linear passing through origin, indicating the absence of complex formation between PEG and manganic ion (Fig. 5). The rate was found to increase with increasing acid concentration at constant ionic strength. The ionic strength was adjusted with sodium bisulfate.

Intrinsic viscosity measurements

The intrinsic viscosities [η] of the polymers determined in DMF at 30 °C with Ubbelohde viscometer, increased with increase in the polymerization time. These results are reported in Table 1.

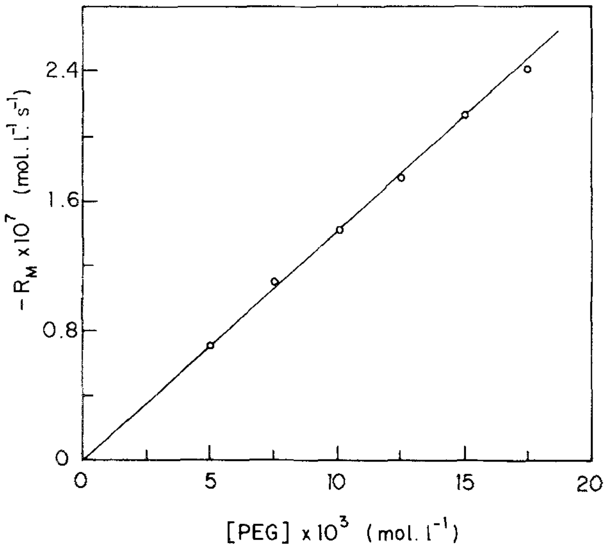

Fig. 5. Plot of $-R_M$ against [PEG], [Mn(III)] = 0.001 M; [M] = 0.9423 M; [H$^+$] = 2.0 M; Temp. = 30 °C; Time = 30 min.

Table 1. Variation of Rp with [SO$_4^{2-}$] Ions[a] and of [η] with time[b]

a) Variation of [SO$_4^{2-}$]		b) Variation of time	
[SO$_4^{2-}$] (mol l^{-1})	$Rp \times 10^5$ (mol l^{-1} s^{-1})	Reaction time (min)	[η] (dl g^{-1})
0.02	11.53	30	4.09
0.04	10.86	45	4.24
0.06	9.92	60	4.68
0.08	9.13	75	4.93
0.10	8.04	90	5.27

[a] [Mn(III)] = 0.001 M; [PEG] = 0.01 M; [M] = 0.9423 M; [H$^+$] = 2.0 M; Temp. = 30 °C; Time = 30 min.
[b] Solvent = DMF; Temp. = 30 °C

Effect of added sulfate ions

The effect of addition of sulfate ions on the rate of polymerization was studied keeping the other parameters a constant at 30 °C. The results are reported in Table 1. The rate decreased steadily with increasing sulfate ion concentration from 11.53×10^{-5} mol l^{-1} s^{-1} (at 0.02 M) to 8.04×10^{-5} mol l^{-1} s^{-1} (at 0.10 M). This might be due to the formation of inactive complexes involving sulfate and Mn(III) ions.

Effect of temperature

The reaction temperature was varied from 35–60 °C and its effect on the rate of polymerization and the rate of Mn^{3+} ion disappearance was investigated. Both the rates increased with increase in temperature (Table 2). The overall activation energy (Ea) of the polymerization reaction as calculated from the Arrhenius plot (Fig. 6) was found to be 47.87 kJ/mol, which is of the same order as those found in other aqueous systems [25, 26].

Kinetic scheme

Based on the above observations, a plausible mechanism may be formulated:

i) Production of organic free radical:

$$\mathrm{Mn}^{3+} + \mathrm{R} \xrightarrow{\mathrm{Kr}} \mathrm{R}^{\bullet} + \mathrm{Mn}^{2+} + \mathrm{H}^{+} ,$$

where R is the reducing agent (PEG) and R$^\bullet$ is the organic free radical produced from it.

ii) Reaction of R$^\bullet$ with Mn^{3+} to give the oxidation products:

$$\mathrm{Mn}^{3+} + \mathrm{R}^{\bullet} \xrightarrow[\text{fast}]{\mathrm{Ko}} \begin{matrix}\text{Oxidation}\\ \text{products}\end{matrix} + \mathrm{Mn}^{2+} + \mathrm{H}^{+} .$$

Table 2. Effect of temperature on Rp and $-R_M$[a])

Sl No	Temperature (°C)	$Rp \times 10^5$ (mol l^{-1} s^{-1})	$-R_M \times 10^7$ (mol l^{-1} s^{-1})
1	35	15.62	1.495
2	40	22.26	2.048
3	45	27.21	2.823
4	50	35.32	3.653
5	55	45.19	4.538
6	60	60.26	5.368

[a] [Mn(III)] = 0.001 M; [PEG] = 0.01 M; [M] = 0.9423 M; [H$^+$] = 2.0 M; Time = 30 min.

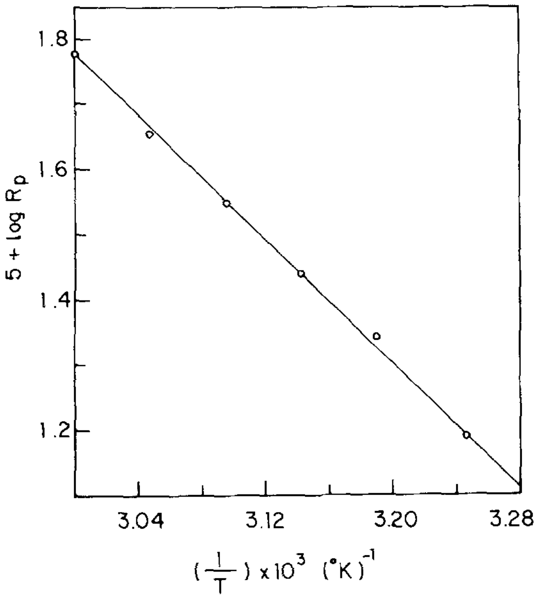

Fig. 6. Arrhenius plot [Mn(III)] = 0.001 M; [PEG] = 0.01 M; [M] = 0.9423 M; [H$^+$] = 2.0 M; Time = 30 min.

iii) Initiation of polymerization:

$$R^{\bullet} + M \xrightarrow{Ki} RM^{\bullet} .$$

iv) Propagation:

$$RM^{\bullet} + M \xrightarrow{Kp} RM_2^{\bullet}$$

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$$RM_{n-1}^{\bullet} + M \xrightarrow{Kp} RM_n^{\bullet} .$$

v) Termination by Mn^{3+} ions:

$$RM_n^{\bullet} + Mn^{3+} \xrightarrow{Kt} \text{polymer} + Mn^{2+} + H^+ .$$

Now, applying the stationary-state principle for radicals and assuming the principle of non-variation of rate constants with the size of the polymer radical, the following expressions were derived.

$$Rp = \frac{KpKr[M]^2[R]}{K_t\{[M] + Ko/Ki[Mn^{3+}]\}} \tag{2}$$

$$-R_M = 2Kr[Mn^{3+}][R] . \tag{3}$$

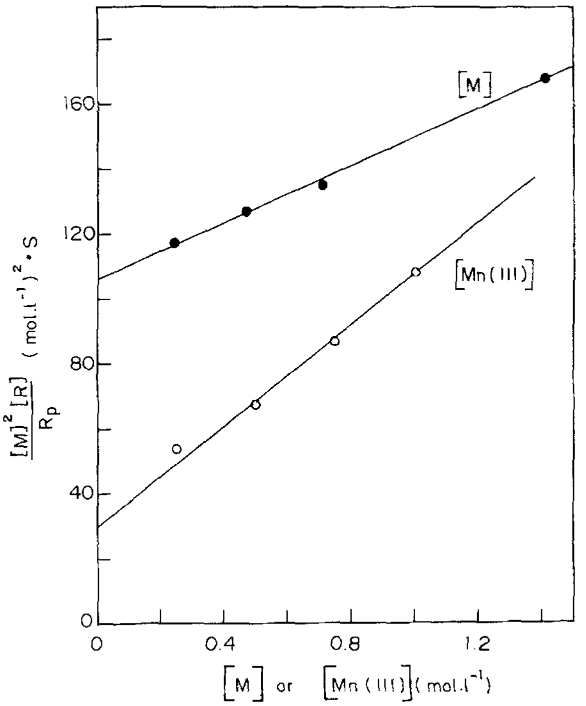

Fig. 7. Plot of [M]^2 [R]/Rp against [M] and [Mn(III)], Experimental conditions same as in Figs. 2 and 3

Rearranging Eq. (2),

$$\frac{[M]^2[R]}{Rp} = \frac{K_t[M]}{K_pK_r} + \frac{K_tK_o[Mn^{3+}]}{K_iK_pK_r} . \tag{4}$$

A plot of LHS of Eq. (4) against [Mn^{3+}] for [Mn^{3+}] variation gave a straight line (Fig. 7) and the ratio slope/intercept gave the value of (Ko/Ki) (= 2512). Similarly, a plot of LHS of Eq. (4) against [M] for [M] variation also gave a straight line (Fig. 7). The (Ko/Ki) values calculated from the slope/intercept ratio (= 2434) agreed with the one calculated previously, within experimental error. The Kr value, calculated using Eq. (3) for monomer variation was found to be 6.225×10^{-3} l·mol^{-1}s^{-1}. With known (Ko/Ki) and Kr values, being substituted in the slope or intercept, (Kp/Kt) (= 3.67) was evaluated.

With the values for these constants in hand, it is instructive to return to Eq. (2) in order to appreciate their significance. Thus, the value of (Ko/Ki) being considerably high ensures that the term (Ko/Ki) [Mn^{3+}] is always greater than [M] in Eq. (2), assuring the dependences as observed.

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