Kinetics of Cyclopolymerization of *N,N'*-Methylenebisacrylamide Initiated by Redox Couples with Mn(III). Part I. Mn(III) with Glycerol

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KINETICS OF CYCLOPOLYMERIZATION OF *N,N'*-METHYLENEBISACRYLAMIDE INITIATED BY REDOX COUPLES WITH Mn(III). PART I. Mn(III) WITH GLYCEROL

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ABSTRACT

The polymerization kinetics of the divinyl monomer N,N'-methylene-bisacrylamide (MBA) in aqueous acetic acid with the manganic acetate-glycerol (GLY) redox system was investigated. The rate of polymerization, R_p, was proportional to $[\text{monomer}]^{3/2}$ $[\text{Mn(III)}]^{0.5}$ and $[\text{GLY}]^{0.5}$. The rate of manganic ion disappearance, R_m, was directly proportional to $[\text{Mn(III)}]$ and $[\text{GLY}]$ but independent of monomer. Based on these results, a reaction mechanism which involves complex formation between Mn(OH)^{2+} and GLY, cyclopolymerization of the growing radicals, and mutual termination was proposed. The rate of polymerization was compared with those for analogous monovinyl monomers.

INTRODUCTION

N,N'-Methylenebisacrylamide (MBA), a symmetrical nonconjugated divinyl monomer, is normally expected to give rise to crosslinked insoluble polymers, but we previously reported the conditions for homogeneous gel-free polymerization of this divinyl monomer with various redox systems [1-3]. For such cases, Butler and Ingley [4] proposed a novel chain propagation mechanism known as cyclopolymerization. In the polymerization of monovinyl monomers, trivalent manganese has proved itself as a potential initiator, either alone or in the presence of activators [5-8]. The mechanism for the oxidation of a multitude of organic substrates involving trivalent manganese was reported by Waters and Littler [9]. The kinetics of polymerization of methyl methacrylate by the Mn(III)-glycerol redox pair was studied by Nayak et al. [16]. Rout et al. used the same redox system in 30% acetic acid for the polymerization of acrylonitrile [10].

The objective of the present investigation was to study the kinetics of polymerization of the divinyl monomer (MBA), with the Mn(OAc)$_3$-glycerol redox pair in 30 vol% aqueous acetic acid in the presence of added H$_2$SO$_4$ and to elucidate the reaction mechanism.

EXPERIMENTAL

N,N'-Methylenebisacrylamide was recrystallized from acetone at 40°C [1]. Manganese(III) acetate dihydrate was prepared by the standard procedure [11]. The polymerization procedure, the method of estimating monomer disappearance by bromometry [12], and the rate of manganic ion disappearance by cerimetry [13] were all as reported earlier [1-3]. The experiments were carried out under homogeneous condition in 30 vol% aqueous acetic acid containing H$_2$SO$_4$ for the following reasons: (a) this divinyl monomer has very low solubility in water which is very much enhanced in aqueous acetic acid; (b) the homogeneity of the reaction mixture could be maintained even for very high conversions; and (c) the disproportionation which Mn(OAc)$_3$ may undergo in water, 2Mn(III) $\rightleftharpoons$ Mn(II) + Mn(IV), is very much suppressed in acidic solutions [14].

Under our polymerization conditions the steady state was attained within 10 min, as evidenced by plots of conversion vs time.

RESULTS AND DISCUSSION

Rate of Monomer Disappearance

The rate of monomer disappearance, R_p, which was taken to be equal to the rate of polymerization, increased linearly with increasing monomer concentration (12.5-75 mmol/L), other factors being kept constant. Plots of R_p vs $[MBA]^{3/2}$ were also linear and passed through the origin, showing that the order with respect to monomer is 1.5 (Fig. 1). The rate of polymerization increased linearly with increasing glycerol (GLY) concentration
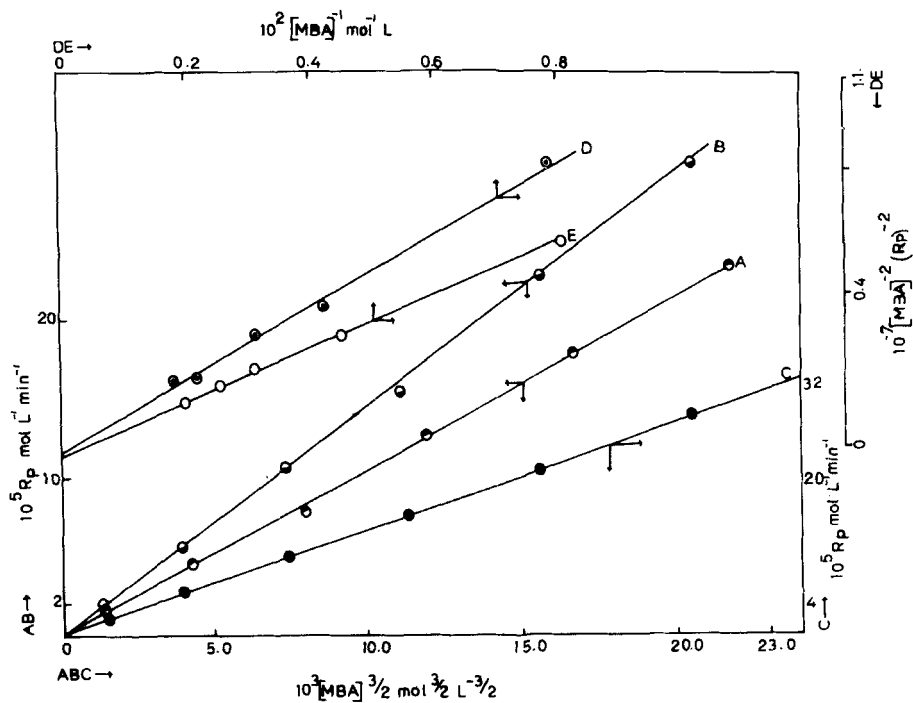
FIG. 1. Dependence of R_p on [Monomer]. A, B, and C are plots of R_p vs $[MBA]^{3/2}$; D and E are plots of $R_p^{-2} \times [MBA]^2$ vs $[MBA]^{-1}$. $[H^+]$ = 0.1 mol/L; temperature = $40°C$; [HOAc] = 30 vol%; μ = 0.5 mol/L; [GLY] = 0.1 mol/L. (A, D): [Mn(III)] = 2.52 mmol/L. (B): [Mn(III)] = 5.1 mmol/L. (C, E): [Mn(III)] = 4.88 mmol/L.
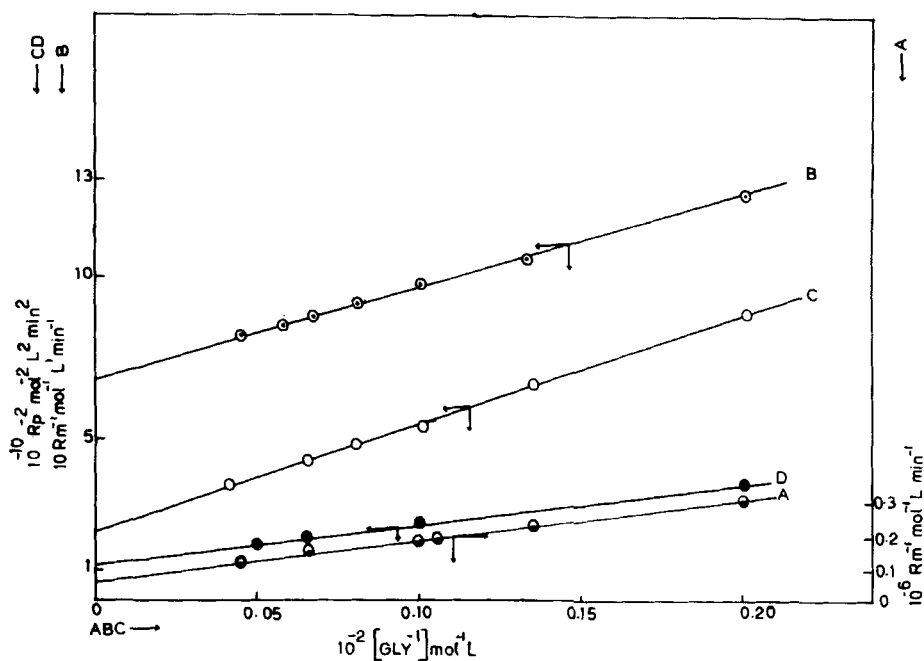
FIG. 2. Dependence of R_p and R_m on [GLY]. A and B are plots of R_m^{-1} vs [GLY]$^{-1}$; C and D are plots of R_p^{-2} vs [GLY]$^{-1}$. [H$^+$] = 0.1 mol/L; temperature = 40°C; [HOAc] = 30 vol%; μ = 0.5 mol/L.

(25-200 mmol/L). At higher concentrations of glycerol (>250 mmol/L), deviation from normal behavior was observed, which may be attributed to the increase in the viscosity of the medium, as reported by Nayak et al. [16] and Samal et al. [17]. Plots of R_p^{-2} vs [GLY]$^{-1}$ were linear with definite intercepts on the rate axis (Fig. 2), as were also observed for the polymerization of MBA with the Mn(III)-ethylene glycol system. The rate of polymerization increased with increasing manganic ion concentration over a wide range (2-20 mmol/L) with a half-order dependence on [Mn(III)] (Fig. 3).

Further, the plot of R_p^{-2} × [MBA]^2 vs [MBA]$^{-1}$ was a straight line with an intercept on the Y-axis (Fig. 1), as was the plot of R_p^{-2} × [MBA]^3 vs [Mn(III)]$^{-1}$ (Fig. 4).
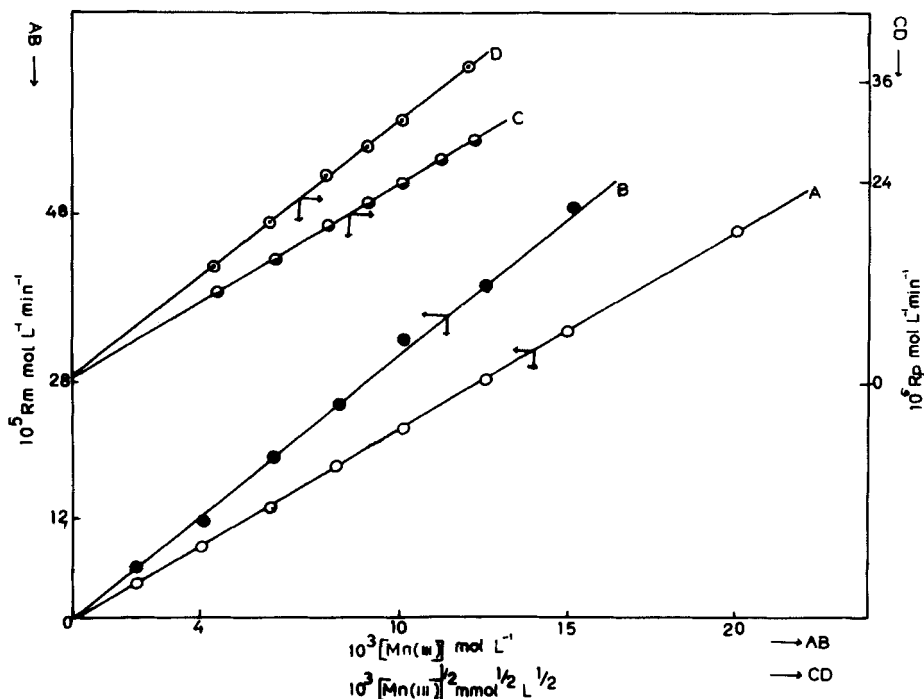
FIG. 3. Dependence of R_p and R_m on [Mn(III)]. A and B are plots of R_m vs [Mn(III)]; C and D are plots of R_p vs [Mn(III)]$^{1/2}$. [H$^+$] = 0.1 mol/L; temperature = 40°C; [HOAc] = 30 vol%; μ = 0.5 mol/L; [GLY] = 0.1 mol/L. (A, C): [MBA] = 48.0 mol/L. (B, D): [MBA] = 58.0 mmol/L.

Rate of Manganic Ion Disappearance

The rate of manganic ion disappearance, R_m, was first order with respect to [Mn(III)] but independent of monomer concentration. Plots of R_m vs [Mn(III)] were straight lines passing through the origin (Fig. 3). The Line-weaver-Burk plots of R_m^{-1} vs [GLY]$^{-1}$ were also linear with intercepts on the Y-axis (Fig. 2) showing Michaelis-Menton type kinetics for complex formation [16]. Such complex formation between aquated Mn(III) and glycerol [15] and between ethylene glycol and aquated Mn(III) [17] was reported earlier.
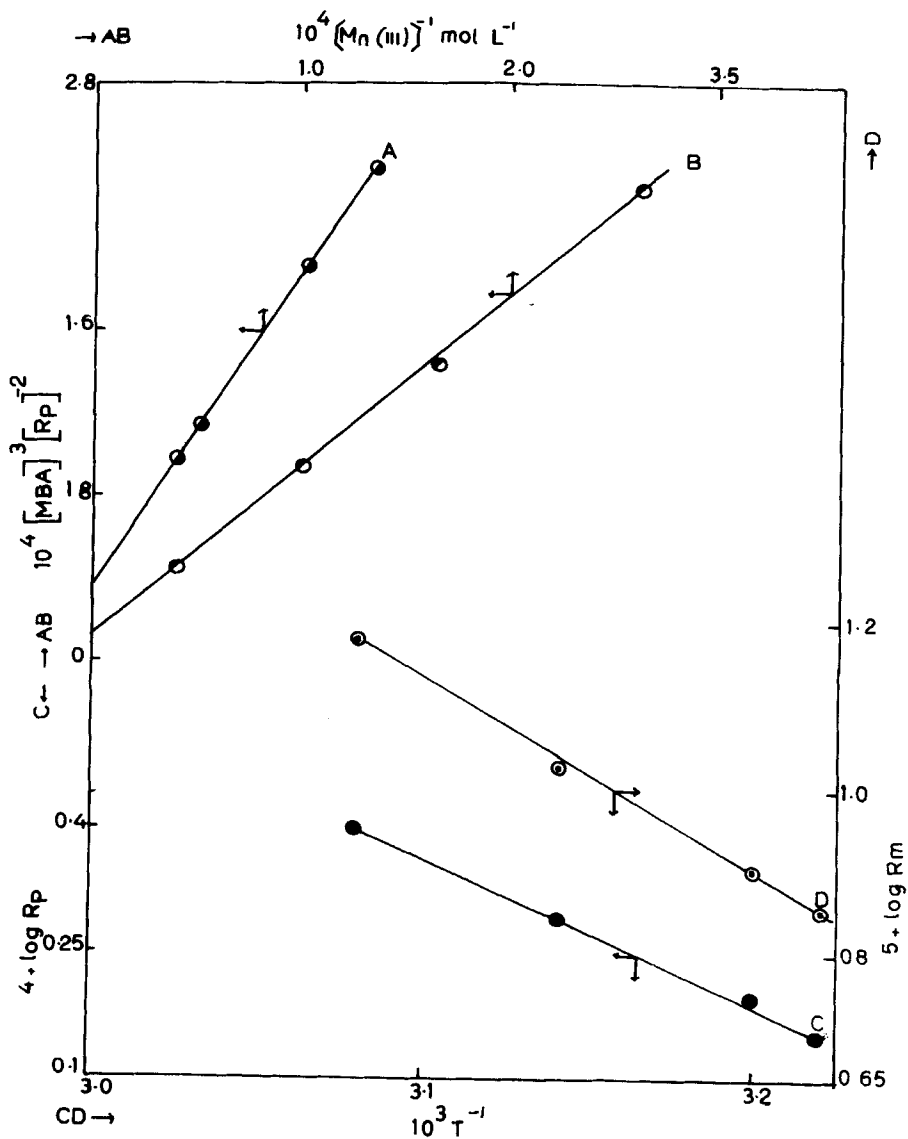
FIG. 4. C and D are Arrhenius plots of $\log R_p$ and $\log R_m$ vs T^{-1}. A and B are plots of $[MBA]^3 \times R_p^{-2}$ vs $[Mn(III)]$. $[H^+] = 0.1$ mol/L; temperature $= 40°C$; $[HOAc] = 30$ vol%; $\mu = 0.5$ mol/L. (A): $[MBA] = 48.0$ mmol/L. (B): $[MBA] = 58.0$ mmol/L. (C, D): $[MBA] = 52.0$ mmol/L, $[Mn(III)] = 4.0$ mmol/L.

Effect of Temperature

The rates R_p and R_m increased linearly with increasing temperature. The overall activation energies for the polymerization and the reduction of Mn(III) were calculated to be 31.0 and 39.8 kJ/mol, respectively (Fig. 4).

Effect of Acid Concentration and Ionic Strength

The rate of polymerization as well as the rate of manganic ion disappearance were unaffected by changes in [H⁺] (0.025-2.0 mol/L) and ionic strength (0.1-1 mol/L). However, at high [H⁺] (>2.5 mol/L) and with a threefold increase of the ionic strength, the R_p values were found to decrease (Table 1).

TABLE 1. Effect of Acid Concentration and Ionic Strength on Rates[a]

[H⁺], mol/L	μ, mol/L	$10^5 R_p$, mol·L^{-1}·min^{-1}	$10^5 R_m$, mol·L^{-1}·min^{-1}
0.0125	0.5	3.78	6.03
0.10	0.5	3.85	6.10
1.00	0.5	3.85	6.13
2.00	0.5	3.85	6.13
2.50	0.5	3.00	5.10
4.00	0.5	1.95	4.28
0.10	0.1	3.52	6.08
0.10	0.25	3.85	6.10
0.10	0.50	3.83	6.15
0.10	1.00	3.85	6.10
0.10	2.00	3.01	5.20
0.10	3.0	2.58	4.25

[a][MBA] = 2.25 mmol/L, [Mn(III)] = 2.65 mmol/L, [GLY] = 0.1 mol/L, 40°C.

TABLE 2. Effect of Acetic Acid Concentration and Comparison of Rates with Monovinyl Monomers[a]

Monomer	Monomer concentration, mmol/L	[HOAc], vol%	$10^5 R_p$, $\mathrm{mol \cdot L^{-1} \cdot min^{-1}}$	$10^5 R_m$, $\mathrm{mol \cdot L^{-1} \cdot min^{-1}}$
AA	24.5	30	1.70	5.99
MAA	24.5	30	0.56	6.23
MBA	24.5	30	4.21	6.13
MBA	22.8	10	3.23	5.43
MBA	22.8	20	3.49	5.92
MBA	22.8	30	3.86	6.13
MBA	22.8	40	3.19	6.23
MBA	22.8	50	2.57	6.29
MBA	22.8	60	2.22	6.54

[a][Mn(III)] = 2.65 mmol/L, [GLY] = 0.1 mol/L, [H$^+$] = 0.1 mol/L, 40°C, μ = 0.5 mol/L. AA = acrylamide, MAA = methacrylamide.

Effect of Acetic Acid Concentration

The rate of polymerization increased with increasing acetic acid concentration (10-30 vol%), but above 30 vol% the rate decreased. This may be attributed to the increase in the viscosity of the medium (Table 2).
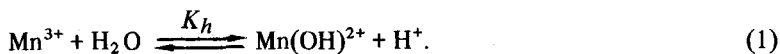
Comparison with Analogous Monovinyl Monomers

The rates of polymerization of acrylamide (AA) and methacrylamide (MAA), measured under the same experimental conditions, were found to decrease in the order MBA > AA > MAA (Table 2), i.e., cyclopolymerization of MBA is fastest [1-3, 20, 21].

REACTION MECHANISM AND RATE LAW

The following mechanism (Eqs. 1-7), involving complex formation between Mn(III) and glycerol, followed by intramolecular cyclization, intermolecular

propagation, and mutual termination between growing polymer radicals, is proposed. Our previous work [1-3] established beyond doubt that this divinyl nonconjugated monomer (MBA) normally undergoes cyclopolymerization. Arguments leading to this conclusion were presented, drawing largely from the work of Gibbs and Barton [18], Butler and Angelo [19], and Ziegler and Host [20].
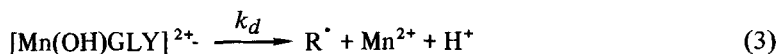
1. Hydrolysis of the Mn^{3+} species

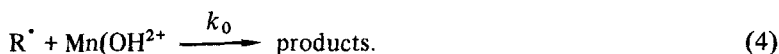$$Mn^{3+} + H_2O \xrightleftharpoons{K_h} Mn(OH)^{2+} + H^+. \tag{1}$$

2. Complex formation

$$Mn(OH)^{2+} + GLY \xrightleftharpoons{K} [Mn(OH)GLY]^{2+}. \tag{2}$$

3. Production of primary free radicals

$$[Mn(OH)GLY]^{2+} \xrightarrow{k_d} R^{\cdot} + Mn^{2+} + H^+ \tag{3}$$

where $R^{\cdot}$ represents $^{\cdot}CH(OH)\text{-}CH(OH)\text{-}CH_2OH$.

4. Primary radical oxidation

$$R^{\cdot} + Mn(OH^{2+} \xrightarrow{k_0} \text{products}. \tag{4}$$

5. Initiation by $R^{\cdot}$

$$R^{\cdot} + M \xrightarrow{k_1} M_1^{\cdot}. \tag{5}$$

6. Propagation

$$M_1^{\cdot} \xrightarrow{k_c} M_2^{\cdot}. \tag{6}$$

$$M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot}.$$

7. Termination

$$M_n^{\cdot} + M_n^{\cdot} \xrightarrow{k_t} \text{polymer}. \tag{7}$$
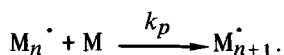
Rate of Polymerization

Under the assumption of steady-state conditions and radical reactivity independent of radical size, the following rate expressions were derived (where [Red] denotes the concentration of glycerol, also shown elsewhere as [GLY]):

$$R_p = \frac{k_p k_i^{1/2} (k_d K [\text{Mn(III)}]_{eq} [\text{Red}])^{1/2} \text{MBA}^{3/2}}{k_t^{1/2} (k_0 [\text{Mn(III)}]_{eq} + k_i [\text{MBA}])^{1/2}} . \tag{8}$$

Since the total Mn concentration is given by

$$[\text{Mn(III)}]_T = [\text{Mn(III)}]_{eq} (1 + K [\text{Red}]), \tag{8a}$$

Eq. (8) becomes

$$R_p = \frac{k_p k_i^{1/2} (k_d K [\text{Mn(III)}]_T [\text{Red}] [\text{MBA}]^3)^{1/2}}{(k_t k_0 [\text{Mn(III)}]_T + k_t k_i [\text{MBA}] (1 + K [\text{Red}])^{1/2}}, \tag{9}$$

or

$$R_p^{-2} = \frac{k_t k_0}{k_p^2 k_i k_d K [\text{Red}] [\text{MBA}]^3} + \frac{k_t}{k_p^2 k_d K [\text{Mn(III)}]_T [\text{Red}] [\text{MBA}]^2}$$

$$+ \frac{k_t}{k_p^2 k_d [\text{Mn(III)}]_T [\text{MBA}]^2} . \tag{10}$$

Rate of Manganic Ion Disappearance

$$R_m = K k_d [\text{Mn(III)}]_{eq} [\text{Red}] + \frac{k_0 [\text{Mn(III)}]_{eq} K k_d [\text{Mn(III)}]_{eq} [\text{Red}]}{k_i [\text{MBA}] + k_0 [\text{Mn(III)}]_{eq}} \tag{11}$$

If $k_0 [\text{Mn(III)}]_{eq} >> k_i [\text{MBA}]$,

$$R_m = 2 k_d K [\text{Mn(III)}]_{eq} [\text{Red}] . \tag{12}$$

Since the measured rate, R_m, applies to the total [Mn(III)], regardless of the species and in view of Eq. (8a),

$$R_m = \frac{2k_dK\,[\text{Mn(III)}]_T\,[\text{Red}]}{1 + K\,[\text{Red}]}, \tag{13}$$

$$R_m^{-1} = \frac{1}{2Kk_d\,[\text{Mn(III)}]_T\,[\text{Red}]} + \frac{1}{2k_d\,[\text{Mn(III)}]_T}. \tag{14}$$

Calculation of Rate Parameters

The plot of R_m^{-1} vs $[\text{Red}]^{-1}$ with an intercept (Fig. 2) is in agreement with Eq. (14). From the ratio slope/intercept, the unimolecular decomposition constant of the complex, k_d, and its formation constant, K, were evaluated as 10.8 L/mol and 13.4×10^{-3} s^{-1}, respectively, at 40°C.

As required by Eq. (10), the plot of $R_p^{-2}\,[\text{MBA}]^3$ vs $[\text{Mn(III)}]^{-1}$ is linear (Fig. 4) with an intercept equal to $(k_t k_0)/(k_p^2 k_i k_d K\,[\text{Red}])$. By using the value $k_p/k_t^{1/2}$, the ratio k_0/k_i was calculated.
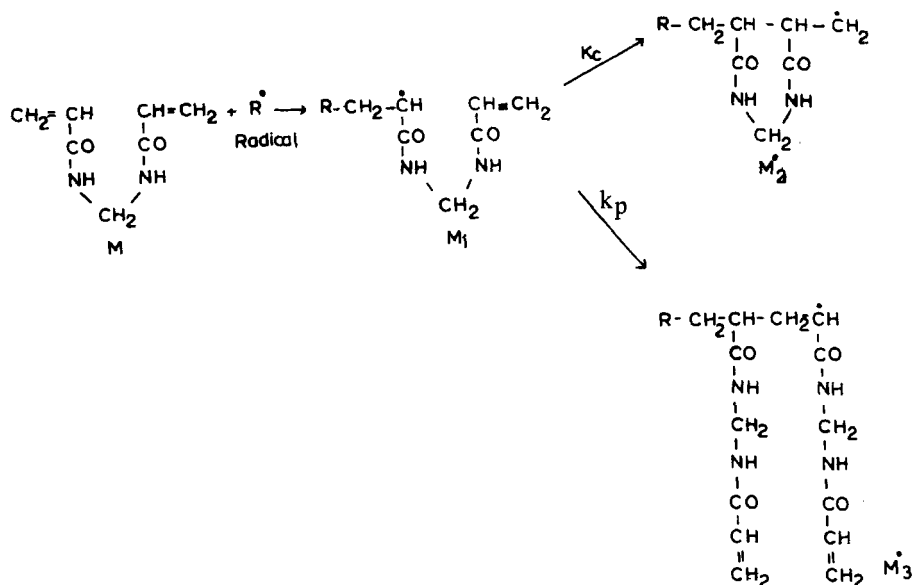
SCHEME 1.

Cyclopolymerization

$M_1{}^\bullet$ could react through either of the double bonds of this symmetrical monomer. $M_1{}^\bullet$ is the radical produced through the reaction of an $R^\bullet$ radical with the monomer which cyclizes intramolecularly to yield a new radical $M_2{}^\bullet$. If this cyclization is much slower than the addition of another monomer molecule, $M_3{}^\bullet$ may be formed with pendant groups with double bonds (Scheme 1).

Intramolecular cyclization depends on the monomer structure and the stability of the ring formed during cyclization [18]. Formation of a seven-membered ring during cyclization is suggested here in preference to an eight-membered one purely on analogy to Matsumoto et al.'s conclusions on acrylic anhydride cyclopolymerization. Steric and electrostatic factors are the major considerations here [22]. The carbonyl groups reduce the strain in the ring [19]. Hence this monomer, MBA, can undergo radical cyclization with greater ease. The linear monovinyl-type propagation is sterically hindered due to the long pendant groups with double bonds in the $M_3{}^\bullet$ radical.

That the overall rate of polymerization decreases in the order MBA > AA > MAA provides added evidence for cyclopolymerization.

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