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Kinetics of Cyclopolymerization of *N,N'*-Methylenebisacrylamide Initiated by Redox Couples with Mn(III). Part II. Mn(III) with Ethylene Glycol or Mercaptoethanol

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KINETICS OF CYCLOPOLYMERIZATION OF *N,N'*-METHYLENEBISACRYLAMIDE INITIATED BY REDOX COUPLES WITH Mn(III). PART II. Mn(III) WITH ETHYLENE GLYCOL OR MERCAPTOETHANOL

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ABSTRACT

Cyclopolymerization kinetics of the nonconjugated divinyl monomer *N,N'*-methylenebisacrylamide (MBA) initiated by two different redox systems, trisacetatomanganese(III) dihydrate with either ethylene glycol or mercaptoethanol, in aqueous acetic acid at 35-50°C were investigated. Rates of polymerization and manganic ion disappearance were measured, and rate equations were derived from the observed dependence. Rate parameters were correlated with the differences in the reactivities of the radicals produced by the two systems toward the monomer and the metal ion. The rate of polymerization of MBA was compared with that of analogous monovinyl monomers.

INTRODUCTION

The preceding communication [1] deals with the kinetics of cyclopolymerization of *N,N'*-methylenebisacrylamide (MBA) initiated by the $\text{Mn}(\text{OAc})_3$ -glycerol redox system, and here we are reporting a kinetic study of the same cyclopolymerization with two other redox pairs, $\text{Mn}(\text{OAc})_3$ -ethylene glycol (EG) and $\text{Mn}(\text{OAc})_3$ -2-mercaptoethanol (ME), under homogeneous conditions in 30 vol% aqueous acetic acid in the presence of dilute H_2SO_4 . In all these cases the same mechanistic sequence was found to be followed, namely, complexation between Mn(III) and reductant, dissociation of the complex to produce initiating free radicals, propagation by cyclopolymerization [2], and mutual termination of growing polymer radicals, as described in detail in Part I [1].

However, the observed kinetic order with respect to the monomer and the oxidant differed considerably among these three redox pairs, which could be attributed to differences in the reactivity among the initiating radicals toward the monomer and Mn(II). This difference is also reflected in the rate parameters calculated from the observed kinetic data (Table 1).

EXPERIMENTAL

The preparation of trisacetatomanganese(II) dihydrate [3], purification of the monomer, polymerization procedure, and measurements of rates of polymerization and the rate of manganic ion disappearance were all reported in Part I [1]. All experiments were carried out in 30 vol% aqueous acetic acid. The considerable stability of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in glacial acetic acid indicated the absence of the disproportionation of Mn(III) to Mn(II) and Mn(IV). This stability was confirmed by the constancy of the visible spectrum of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ (Fig. 1). The oxidant strength of Mn(III) in solution, determined by cerimetry, was also constant up to 100 min.

RESULTS AND DISCUSSION

Under the polymerization conditions, the steady state was attained within 10 min, as evidenced by the conversion vs time plots. In the following discussion, the symbols and equations of Part I [1] are used.

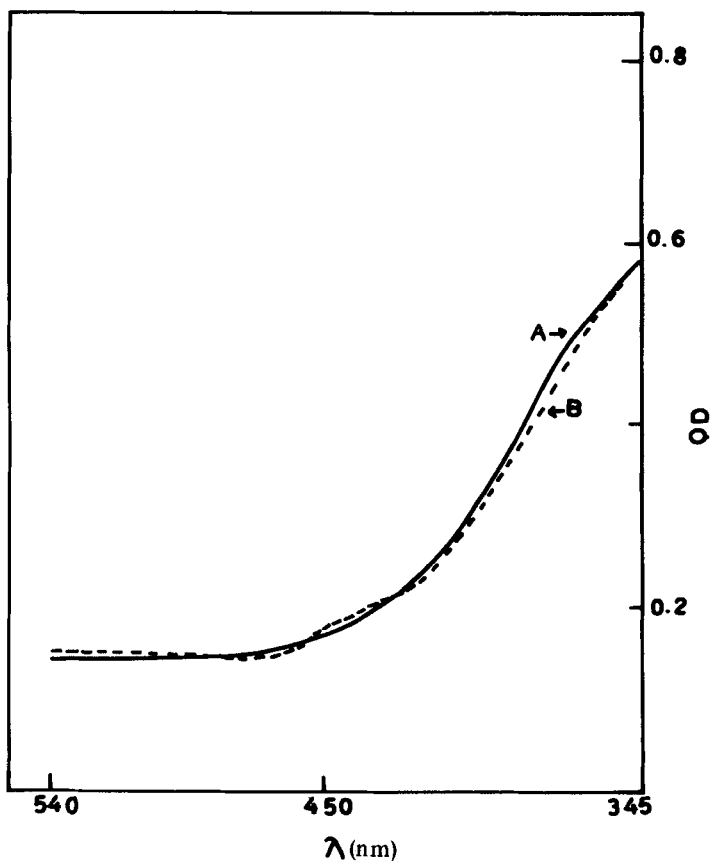
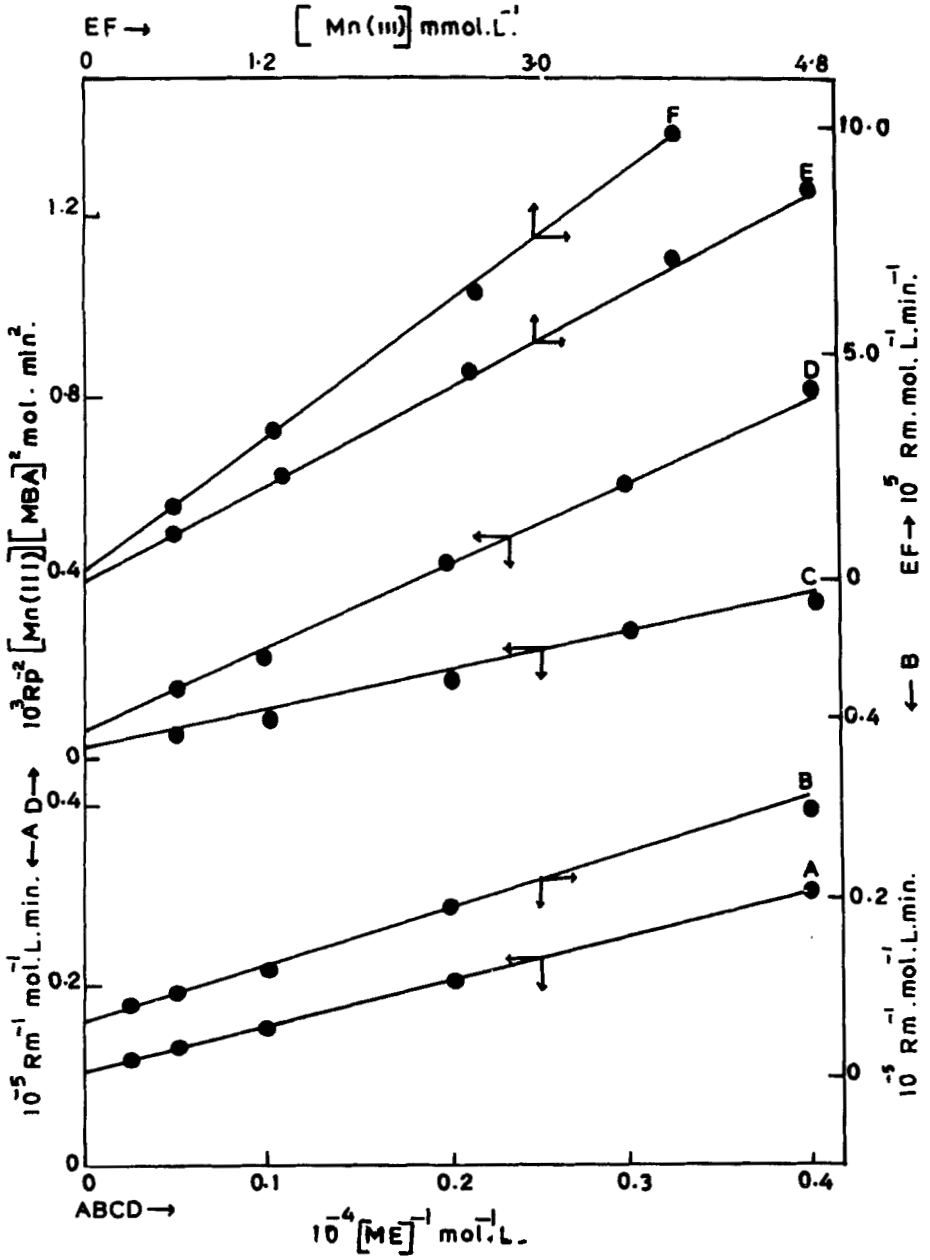


FIG. 1. Visible spectra of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2$ in glacial acetic acid: (A) 5 min, (B) 100 min after dissolution. $[\text{Mn}(\text{III})] = 0.613 \text{ mmol/L}$.

Rate of Manganic Ion Disappearance

In the absence of monomer, the rate of oxidation $R_m = -d[\text{Mn}(\text{III})]/dt$ of either of the reductants (Red), EG or ME, by Mn(III) was proportional to $[\text{Mn}(\text{III})]$, as indicated by the plots of R_m vs $[\text{Mn}(\text{III})]$. The variation of R_m with the reductant concentration, $[\text{Red}]$, indicated complex formation



which could be graphically treated by the method of Lineweaver and Burk [4]. The plots of R_m^{-1} vs $[\text{Red}]^{-1}$ at constant $[\text{Mn(III)}]$ were linear with an intercept on the rate axis for both ME (Fig. 2A) and EG.

The 1:1 complex formation between Mn(III) and EG or ME was also evidenced by Job's method of continuous variation with an optical density maximum for the 1:1 molar mixture of Mn(III) and reductants (Fig. 3).

In the presence of the monomer, the rate of manganic ion disappearance followed the same order. The plots of R_m vs $[\text{Mn(III)}]$ were linear (Fig. 2E and F). With EG, R_m in the presence of monomer was not very much different from that in the absence of monomer (Fig. 4A and B); but with ME, the rate in the presence of monomer (Fig. 2B) was lower than that in its absence (Fig. 2A). This may be taken as positive evidence that the primary radicals $R\cdot$ are effectively scavenged by the monomer in the MBA-Mn(III)-ME system, that is, $k_i[\text{MBA}] \gg k_0[\text{Mn(III)}]$; but in the MBA-Mn(III)-EG system, the free radical initiation of the monomer is negligible, that is, $k_0[\text{Mn(III)}] > k_i[\text{MBA}]$. This is substantiated by the values of the rate parameters k_d , K , and k_0/k_i calculated from the slope and intercept of the plots of R_m^{-1} vs $[\text{Red}]^{-1}$, and R_p^{-2} vs $[\text{Red}]^{-1}$ (Fig. 4C). These values, along with those for the MBA-Mn(III)-glycerol systems, are given in Table 1.

The manganic ion disappearance in the presence and absence of monomer was independent of added $[\text{Mn(II)}]$, $[\text{H}^+]$, and ionic strength. The rate law for the disappearance of Mn(III) was found to follow Eq. (11) part of [1]. The measured rate R_m is related to total Mn(III), regardless of the species. Since $k_0[\text{Mn(III)}] > k_i[\text{MBA}]$ in the MBA-Mn(III)-EG system, R_m obeys Eq. (13) of Part I [1]. For the MBA-Mn(III)-ME system, since $k_i[\text{MBA}] > k_0[\text{Mn(III)}]$, the rate equation reduces to

$$R_m = \frac{k_d K [\text{Mn(III)}]_T [\text{ME}]}{1 + K [\text{ME}]} \quad (1)$$

FIG. 2. Kinetic plots for mercaptoethanol. A and B: Plots of R_m^{-1} vs $[\text{ME}]^{-1}$. (A) $[\text{MBA}] = 0$, $[\text{Mn(III)}] = 5.0$ mmol/L, temperature = 30°C; (B) $[\text{MBA}] = 10.9$ mmol/L, $[\text{Mn(III)}] = 2.64$ mmol/L, temperature = 40°C. C and D: Plots of $R_p^{-2} [\text{Mn(III)}] [\text{MBA}]^2$ vs $[\text{ME}]^{-1}$. $[\text{Mn(III)}] = 2.5$ mmol/L. (C) $[\text{MBA}] = 10.9$ mmol/L, temperature = 40°C; (D) $[\text{MBA}] = 26.4$ mmol/L, temperature = 30°C. E and F: Plots of R_m vs $[\text{Mn(III)}] \cdot [\text{MBA}] = 10.2$ mmol/L, temperature 40°C. (E) $[\text{ME}] = 1.0$ mmol/L; (F) $[\text{ME}] = 0.5$ mmol/L.

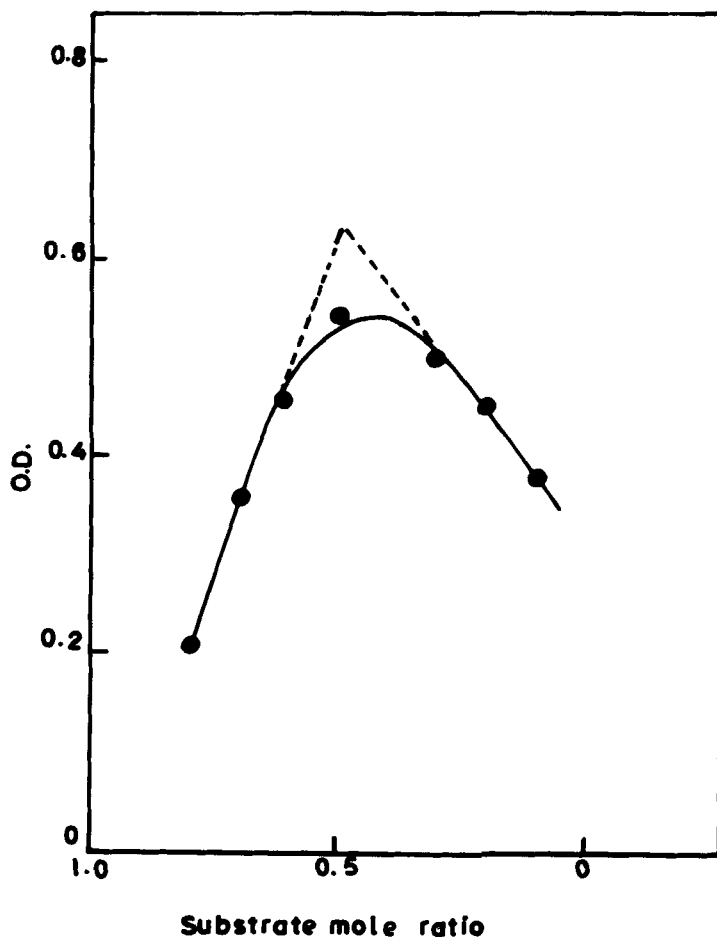


FIG. 3. Job's method of continuous variation for the complex formation between Mn(III) and EG or ME. Maximum optical density at 420 nm for $[\text{Mn(III)}] = [\text{Red}] = 1.25 \text{ mmol/L}$.

Equation (13) of Part I and Eq. (1) above differ only in the stoichiometric factor of 2.

Rate of Polymerization

The rate of polymerization $R_p = -d[\text{MBA}]/dt$ was proportional to the first power of $[\text{MBA}]$ (Fig. 5A and B) and to the half power of $[\text{Mn(III)}]$ (Fig. 4D)

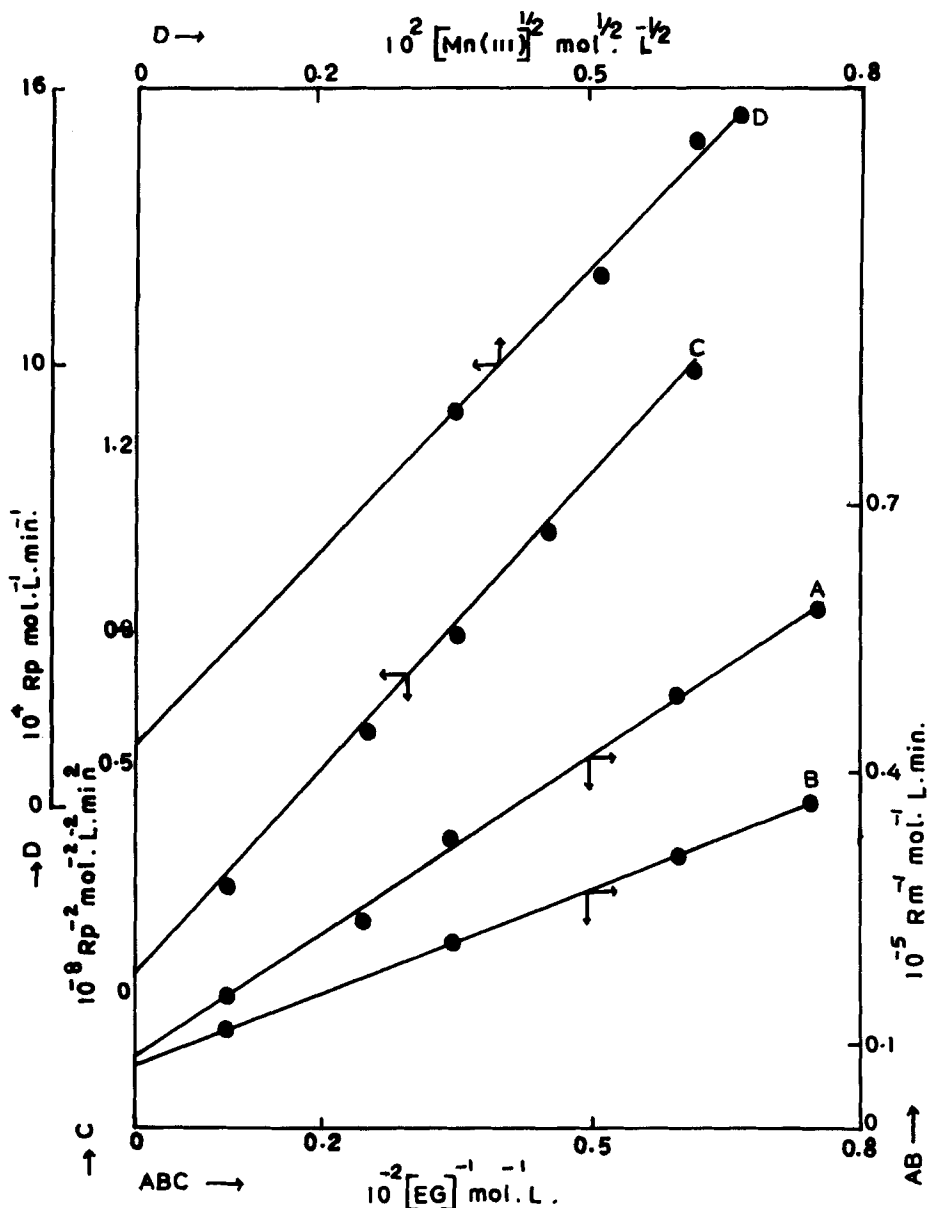


FIG. 4. Kinetic plots for ethylene glycol and mercaptoethanol. A and B: Plots of R_m^{-1} vs $[EG]^{-1}$; temperature = 40°C . (A) $[\text{MBA}] = 34.1 \text{ mmol/L}$, $[\text{Mn(III)}] = 2.29 \text{ mmol/L}$; (B) $[\text{MBA}] = 48.8 \text{ mmol/L}$, $[\text{Mn(III)}] = 4.88 \text{ mmol/L}$. (C) Plot of R_p^{-2} vs $[EG]^{-1}$; $[\text{MBA}] = 48.8 \text{ mmol/L}$, $[\text{Mn(III)}] = 4.58 \text{ mmol/L}$, temperature = 40°C . (D) Plot of $[\text{Mn(III)}]^{1/2}$ vs R_p ; $[\text{ME}] = 1.0 \text{ mmol/L}$, $[\text{MBA}] = 10.2 \text{ mmol/L}$, temperature = 30°C .

TABLE I. Mean Value of Rate Parameters^a

Systems	Temperature, K	E_a , kJ/mol	K , mol/L	$10^4 k_d$, s ⁻¹	k_0 [Mn(III)] k_t [MBA]	$k_p/k_t^{1/2}$ mol ^{1/2} L ^{1/2} min ^{-1/2}
MBA-Mn(III)-GLY ^b	308		7.4	5.2	0.985	2.4
	313		10.8	13.4	1.025	3.2
	—	31.0	—	—	—	—
MBA-Mn(III)-EG	308		6.2 (5.8)	3.2 (3.8)	31.0	2.8
	313		11.05 (9.8)	4.5 (4.8)	42.0	3.58
	—	30.0 (23.0)	—	—	—	—
MBA-Mn(III)-ME	303		186.3 (119.5)	5.7 (14.0)	0.028	3.88
	313		288.0 (245.4)	9.5 (17.0)	0.058	4.22
	—	15.3 (17.0)	—	—	—	—

^aValues in parentheses were obtained in the absence of monomer.^bPart I [1].

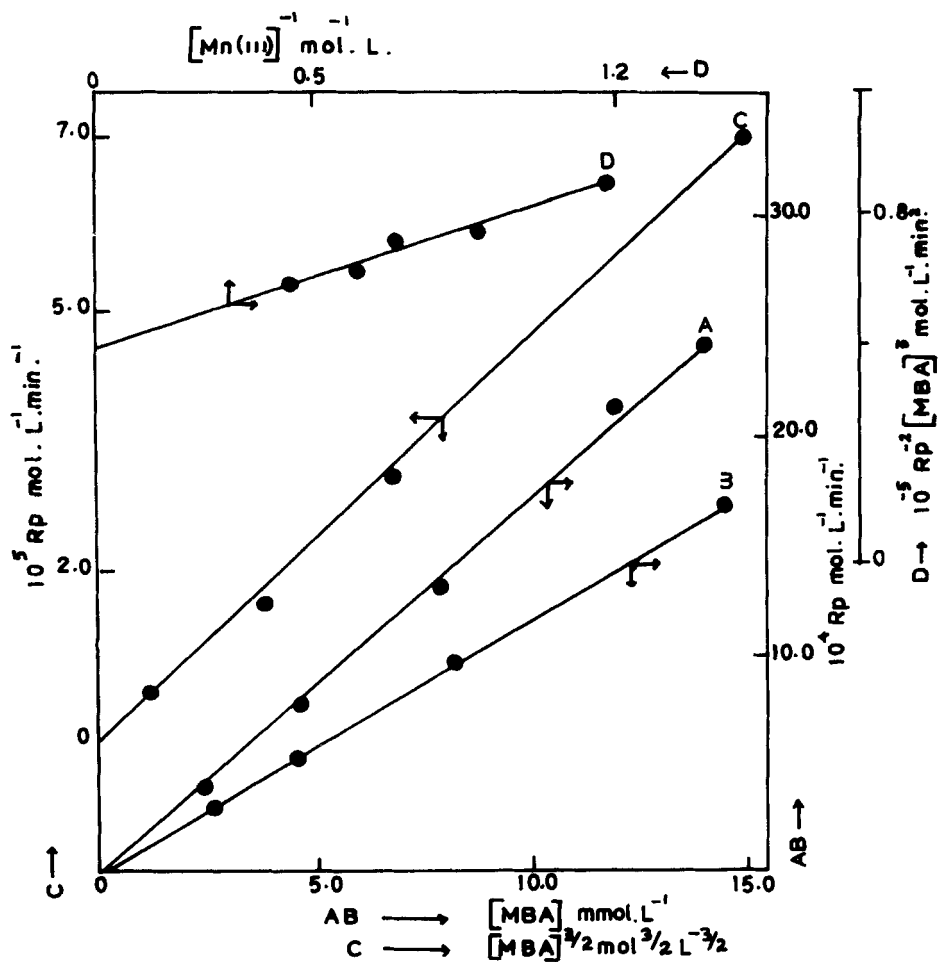


FIG. 5. Polymerization rate plots. A and B: Plots of R_p vs $[MBA]$; (A) $[ME] = 1.0$ mmol/L, $[Mn(III)] = 2.5$ mmol/L, temperature = 30°C ; (B) $[ME] = 0.5$ mmol/L, $[Mn(III)] = 2.64$ mmol/L, temperature = 40°C . (C) Plot of R_p vs $[MBA]^{1.5}$; $[EG] = 0.1$ mol/L, $[Mn(III)] = 4.85$ mmol/L. (D) Plots of $R_p^{-2} [MBA]^3$ vs $[Mn(III)]^{-1}$; $[EG] = 0.1$ mol/L, $[MBA] = 48.8$ mmol/L, temperature = 40°C .

in the MBA-Mn(III)-ME system. With EG, R_p was proportional to $[\text{MBA}]^{1.5}$ (Fig. 5C) and increased with increasing $[\text{Mn(III)}]$ up to a certain limit (0.5 to 2.0 mmol/L) and then remained constant. With either of the reductants, R_p increased with increasing $[\text{Red}]$, and plots of R_p^{-2} vs $[\text{Red}]^{-1}$ (Fig. 4C) were straight lines from which $k_p/k_t^{0.5}$ was calculated (Table 1). Further, according to Eq. (3) below, plots of $R_p^{-2} [\text{MBA}]^3$ vs $[\text{Mn(III)}]^{-1}$ are also linear (Fig. 5D) with an intercept equal to $k_t k_0/k_i k_d K [\text{EG}] k_p^2$. The ratio k_0/k_i was calculated from the values of $k_p k_d/k_t$ and K , (Table 1).

The equation for R_p is given by Eq. (8) of Part I [1]. For the MBA-Mn(III)-EG system, $k_0 [\text{Mn(III)}] > k_i [\text{MBA}]$, and this reduces to

$$R_p^2 = k_p^2 k_i k_d K [\text{MBA}]^3 [\text{EG}] / k_t k_0, \quad (2)$$

and for lower concentrations of Mn(III), Eq. (8) of Part I can be rearranged to

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

For the MBA-Mn(III)-ME system, since $k_i [\text{MBA}] > k_0 [\text{Mn(III)}]$, Eq. (8) of Part I becomes

$$R_p^2 = \frac{k_p^2 k_d K [\text{Mn(III)}]_T [\text{ME}] [\text{MBA}]^2}{k_t (1 + K [\text{ME}])}. \quad (4)$$

This equation can be rearranged to

$$R_p^{-2} [\text{MBA}]^2 [\text{Mn(III)}]_T = \frac{k_t}{k_p^2 k_d K [\text{ME}]} + \frac{k_t}{k_p^2 k_d}. \quad (5)$$

Figures 2C and D represent plots of this relation.

Effect of Temperature

R_p as well as R_m increased with increasing temperature up to 45°C and remained constant thereafter. The normal increase in R_p with increasing temperature observed in most of the systems is the result of 1) the increase in the steady-state concentration of the initiating radicals and 2) the increase in the rate of propagation. However, the constancy of rate at higher temperatures may be indicative of a third factor, viz., the formation constant of the com-

TABLE 2. Effect of Acetic Acid Concentration and Comparison with Monovinyl Monomers^a

Monomer	Monomer concentration, mmol/L	HOAc, vol%	$10^5 R_p$ mol L ⁻¹ min ⁻¹	
			For ME	For EG
AA	24.5	30	1.57	0.58
MAA	24.5	30	0.98	0.21
MBA	24.5	30	30.5	1.73
MBA	12.2	10	12.0	0.50
MBA	12.2	20	14.8	0.59
MBA	12.2	30	17.2	0.62
MBA	12.2	40	17.0	0.61
MBA	12.2	50	13.5	0.52
MBA	12.2	60	11.5	0.44

^a[H⁺] = 0.1 mol/L, [Mn(III)] = 2.5 mmol/L, μ = 0.5 mol/L, 40°C.

plex may actually decrease with temperature above a certain limit to offset the first two factors. Removal of initiating species at higher temperature by side reactions may also cause similar abnormal temperature effects.

The activation energy for the polymerization reaction was obtained from Arrhenius plots (Table 1).

Evidence of Cyclopolymerization

The cyclopolymerization mechanism for the MBA-Mn(III)-glycerol system has been described in detail in Part I [1]. That a similar mechanism operates in the present systems was also evidenced by the following: 1) The polymerization rates of the analogous monovinyl monomers acrylamide (AA) and methacrylamide (MAA) were measured under identical conditions (Table 2). The rate R_p for MAA is far lower than that for AA, which is the consequence of steric hindrance due to the α -methyl group in MAA during propagation. One would therefore expect a further lowering of R_p for MBA, compared to AA or MAA, because the long pendent group of MBA would cause even greater steric hindrance to normal vinyl propagation. However, the observed R_p for MBA is

much greater than for MAA (Table 2), which suggests that cyclopolymerization, and not linear propagation, is involved in the MBA system. 2) The polymers obtained in the present systems were precipitated by adding a large excess of ethanol. The polymer had no residual unsaturation, as proved by bromometry.

The rate of polymerization of MBA was independent of $[H^+]$, ionic strength, and added Mn(II). The effect of $[HOAc]$ was the same as that reported for the MBA-Mn(III)-GLY system [1] (cf. Table 2).

REFERENCES

- [1] S. Rathnasabapathy, N. Marisami, S. P. Manickam, K. Venkatarao, and N. R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25**, 83 (1988).
- [2] A. Gopalan, P. Venuvanalingam, S. P. Manickam, and N. R. Subbaratnam, *Ibid.*, **A23**, 117 (1986).
- [3] P. J. Andrusis Jr, M. J. S. Dewar, R. Dietza, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).
- [4] H. Lineweaver and D. Burk, *Ibid.*, **56**, 658 (1934).

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