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

S. Ratnasabapathy[a]; N. Marisami[a]; S. P. Manickam[a]; K. Venkatarao[b]; N. R. Subbaratnam[c]
[a] Arulmigu Palani Andavar College of Arts and Culture, Palani, India [b] Department of Polymer Science, University of Madras, Madras, India [c] Department of Physical Chemistry, Madurai Kamarj University, Madurai, India

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

S. RATNASABAPATHY, N. MARISAMI, and S. P. MANICKAM

Arulmigu Palani Andavar College of Arts and Culture
Palani 624602, India

K. VENKATARAO

Department of Polymer Science
University of Madras
Madras 600025, India

N. R. SUBBARATNAM*

Department of Physical Chemistry
Madurai Kamarj University
Madurai 625021, India

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ABSTRACT

Redox-initiated free-radical cyclopolymerization of the nonconjugated divinyl monomer *N,N'*-methylenebisacrylamide was studied at 25-40°C, involving trisacetatomanganese(III) dihydrate as oxidant with four different reductants, methyl ethyl ketone (2-butanone), cyanoacetic acid, malic acid, and thiomalic acid. While the general mechanistic sequence is the same, the modes of termination are different in these cases. Because the reactivities of the different free radicals from the four redox

*To whom correspondence should be addressed.

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pairs are different, the kinetic order with respect to the monomer, oxidant, and reductant differ considerably in magnitude. The kinetic and thermodynamic parameters were calculated.

INTRODUCTION

As part of our research program to study the reactivity of different free radicals from redox systems toward the same nonconjugated divinyl monomer *N,N'*-methylenebisacrylamide (MBA) [1-3], we have reported the cyclopolymerization of MBA with the Mn(III)-glycerol redox system in Part I [4] and with the Mn(III)-ethylene glycol and Mn(III)-mercaptoethanol systems in Part II [5]. It was found that, in these cases, the free radicals produced, besides initiating the polymerization, could also be oxidized by the Mn(III), which leads to change in the course of the polymerization. By changing the reductants from alcohols or thioalcohols [4] to ketones, acids, or thioacids, it was hoped to learn more about the relative roles of initiating radicals with different structures in determining the mechanistic sequence. With this in view, we have taken up in this Part III the study of cyclopolymerization of MBA initiated by four different redox systems involving methyl ethyl ketone (2-butanone) (MEK), cyanoacetic acid (CAA), malic acid (MA), or thiomalic acid (TMA) as reductants with $Mn(OAc)_3 \cdot 2H_2O$ as oxidant. In the vinyl polymerization of monomers derived from acrylic acid with the $Mn(OAc)_3$-CAA or MEK redox systems in aqueous sulfuric acid, studied by Jayakrishnan et al. [6], exclusively mutual termination was proposed. Elayaperumal et al. reported aqueous polymerization of the above monomers initiated by Mn(III)-isobutyric acid or diglycolic acid redox systems, where they found the termination to involve metal ion and metal ion-reductant complexes [7, 8].

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EXPERIMENTAL METHODS

Cyanoacetic acid (Koch-Light) was purified by recrystallization from ether. All other experimental procedures were as reported in our previous communications [4, 5].

RESULTS AND DISCUSSION

Rate of Manganic Ion Disappearance (R_m)

The dependence of R_m on the concentrations of Mn(III), [Mn(III)], and reductant, [Red], but not on [MBA], corresponds to that observed previously

[4, 5]. The rate expressions for R_m, Eqs. (13) and (14) of Part I [4], explain the observed trends here also. From the intercept and slope of the Lineweaver-Burk plots of R_m^{-1} vs $[\text{Red}]^{-1}$ (Fig. 1), the equilibrium constants K of the complexes between Mn(III) and the reductants, and unimolecular decomposition constants, k_d, of the complexes to produce free radicals, were calculated (Table 1).

The k_d values calculated for the MBA-Mn(III)-TMA system during polymerization experiments agreed with the values determined in the absence of monomer (Table 1). This trend is to be expected if the free radicals are mostly consumed by Mn(III) oxidation rather than by the initiation step. The high calculated values of $k_0\,[\text{Mn(III)}]/k_i[\text{MBA}]$ (Table 1) lead to the same conclusion. In the MBA-Mn(III)-MEK system, the k_d values are found to be low during polymerization compared to those during oxidation, which means that almost all the free radicals R′ are likely to initiate polymerization with little or no oxidation by Mn(III). In this case, $k_i[\text{MBA}] >> [\text{Mn(III)}]$. In the MBA-Mn(III)-MA system, the k_d values during polymerization are lower than in the absence of monomer, but the difference is small. This may be because, here, $k_0\,[\text{Mn(III)}] \approx k_i[\text{MBA}]$ (Table 1).

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Mechanism and Rate Law

Complexation of oxidant with reductant, the decomposition of the complex to the initiating free radicals, which either react with MBA or with Mn(III), alternate intramolecular cyclization, and intermolecular propagation are the mechanistic sequence, as observed in the previous systems [4, 5]. But the termination steps differ considerably and alter the rates of the cyclopolymerization in these systems.

Linear termination by Mn(III)

$$\text{M}_n^{\bullet} + \text{Mn(III)} \xrightarrow{k_{t_1}} \text{polymer.} \tag{1}$$

Linear termination by Mn(III)-S complex

$$\text{M}_n^{\bullet} + \underset{\text{Complex}}{\text{Mn(III)S}} \xrightarrow{k_{t_2}} \text{polymer,} \tag{2}$$

where S stands for reductant. Under steady-state conditions, the rate of monomer disappearance is as given in Eq. (3).

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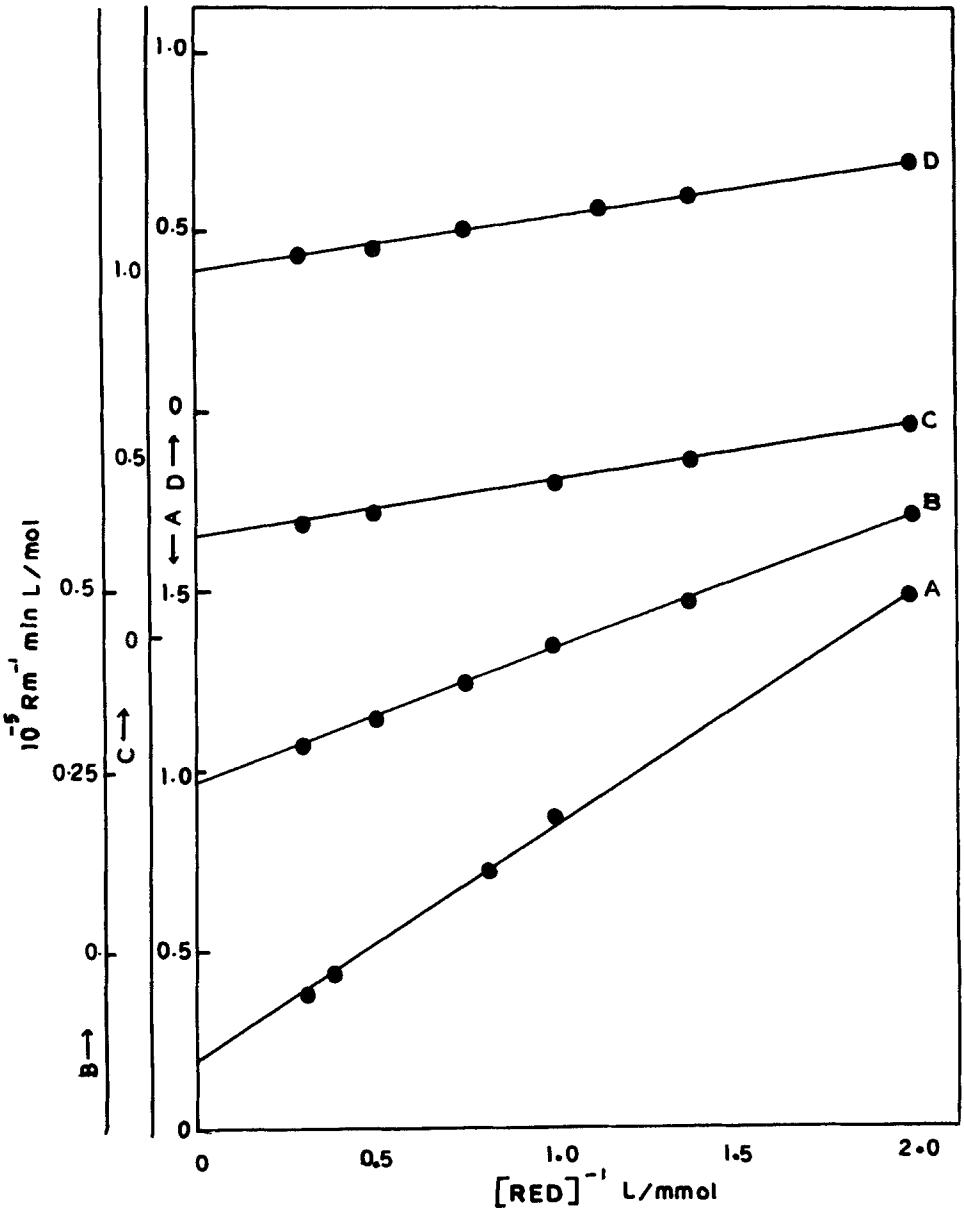

FIG. 1. Plots of R_m^{-1} vs $[\text{Red}]^{-1}$. Concentrations in mmol/L. (A) $[\text{Red}]^{-1} = [\text{CAA}]^{-1}$, [MBA] = 9.57, [Mn(III)] = 1.49, temperature = 36°C. (B) $[\text{Red}]^{-1} = [\text{MEK}]^{-1}$, [MBA] = 19.3, [Mn(III)] = 2.49, temperature = 30°C. (C) $[\text{Red}]^{-1} = [\text{MA}]^{-1}$, [MBA] = 4.74, [Mn(III)] = 0.54, temperature = 26°C. (D) $[\text{Red}]^{-1} = [\text{TMA}]^{-1}$, [MBA] = 18.9, [Mn(III)] = 0.54, temperature = 36°C.

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TABLE 1. Mean Value of Rate Parameters and Kinetic Orders

System	Kinetic order for rate of polymerization			Activation energy		Temperature	Parameters				
	[MBA]	[Mn(III)]	[Red]	R_p, kJ/mol	R_m, kJ/mol	K	K, L/mol	$k_d \times 10^4$,[a] s^{-1}	$\frac{k_0[\text{Mn(III)}]}{k_i[\text{MBA}]}$	$\frac{k_p}{k_{t_1}}$	$\frac{k_p}{k_{t_2}}$
MBA-Mn(III)-MEK	1.0	0	1	45.0	52.0	303	29.0	3.04	–	1.805	1.92
						313	39.8	3.4	–	1.17	1.94
								(7.5)			
MBA-Mn(III)-MA	1.25	-1	0.8	38.3	23.9	299	124	5.04	1.02	1.62	1.07
						304	137	7.56	0.9	1.41	0.88
								(8.2)			
MBA-Mn(III)-CAA	1.3	-1	0.7	76.6	58.7	303	158	2.66	0.92	4.10	2.50
						309	257	3.29	1.06	4.40	3.01
								(4.45)			
MBA-Mn(III)-TMA	1.8	-1	0.7	45.4	14.4	305	210	3.9	11.5	–	2.8
						309	228	4.31	14.3	–	3.32
								(3.65)			

[a]Values of k_d in parentheses were obtained in the absence of monomer.

$$R_p = \frac{Kk_pk_ik_d[\mathrm{Mn(III)}]\,[\mathrm{S}]\,[\mathrm{MBA}]^2}{\left\{k_{t_1}[\mathrm{Mn(III)}] + k_{t_2}K[\mathrm{Mn(III)}]\,[\mathrm{S}]\right\}\left\{k_1[\mathrm{MBA}] + k_0[\mathrm{Mn(III)}]\right\}}, \tag{3}$$

which can be rearranged to

$$R_p^{-1} = \frac{k_{t_1}}{k_pKk_d[\mathrm{S}]\,[\mathrm{MBA}]} + \frac{k_{t_2}}{k_pk_d[\mathrm{MBA}]} + \frac{k_{t_1}(k_0/k_i)[\mathrm{Mn(III)}]}{Kk_pkd[\mathrm{S}]\,[\mathrm{MBA}]^2} + \frac{k_{t_2}(k_0/k_t)[\mathrm{Mn(III)}]}{k_pk_d[\mathrm{MBA}]^2}, \tag{4}$$

$$[\mathrm{MBA}]^2R_p^{-1} = \frac{k_{t_1}[\mathrm{MBA}]}{k_pKk_d[\mathrm{S}]} + \frac{k_{t_2}[\mathrm{MBA}]}{k_pk_d} + \frac{k_{t_1}(k_0/k_t)[\mathrm{Mn(III)}]}{Kk_pk_d[\mathrm{S}]} + \frac{k_{t_2}(k_0/k_i)[\mathrm{Mn(III)}]}{k_pk_d}. \tag{5}$$

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Rate of Polymerization (R_p)

The general Eq. (3), derived above, is found to account for the observed order of R_p with respect to [MBA], [Mn(III)], and [Red] in the different systems studied. It is seen that R_p will follow an order of 1 to 2 (Fig. 2) depending on the relative rates of monomer initiation k_i[MBA] and the rate of primary radical oxidation by Mn(III), k_0 [Mn(III)]. R_p should depend on the first power of [MBA] (Fig. 2B) and be independent of [Mn(III)], if $k_i[\mathrm{MBA}] >> k_0[\mathrm{Mn(III)}]$, as exemplified by the MBA-Mn(III)-MEK system. Incorporating this condition, $k_0[\mathrm{Mn(III)}]/k_i[\mathrm{MBA}]$ would become negligible in Eq. (4). Hence,

$$[\mathrm{MBA}]^2R_p^{-1} = \frac{k_{t_1}[\mathrm{MBA}]}{Kk_pk_d[\mathrm{MEK}]} + \frac{k_{t_2}[\mathrm{MBA}]}{k_pk_d}. \tag{6}$$

From the slopes and intercepts of the plots of $[\mathrm{MBA}]^2R_p^{-1}$ vs [MBA] (Fig. 3D) and by substituting the values of K and K_d, the values of k_p/k_{t_1} and k_p/k_{t_2} can be obtained (Table 1).

Likewise, for the systems MBA-Mn(III)-CAA and MBA-Mn(III)-MA, Eq. (8) explains the fractional order for R_p with respect to [MBA] (Fig. 2A, 2C)

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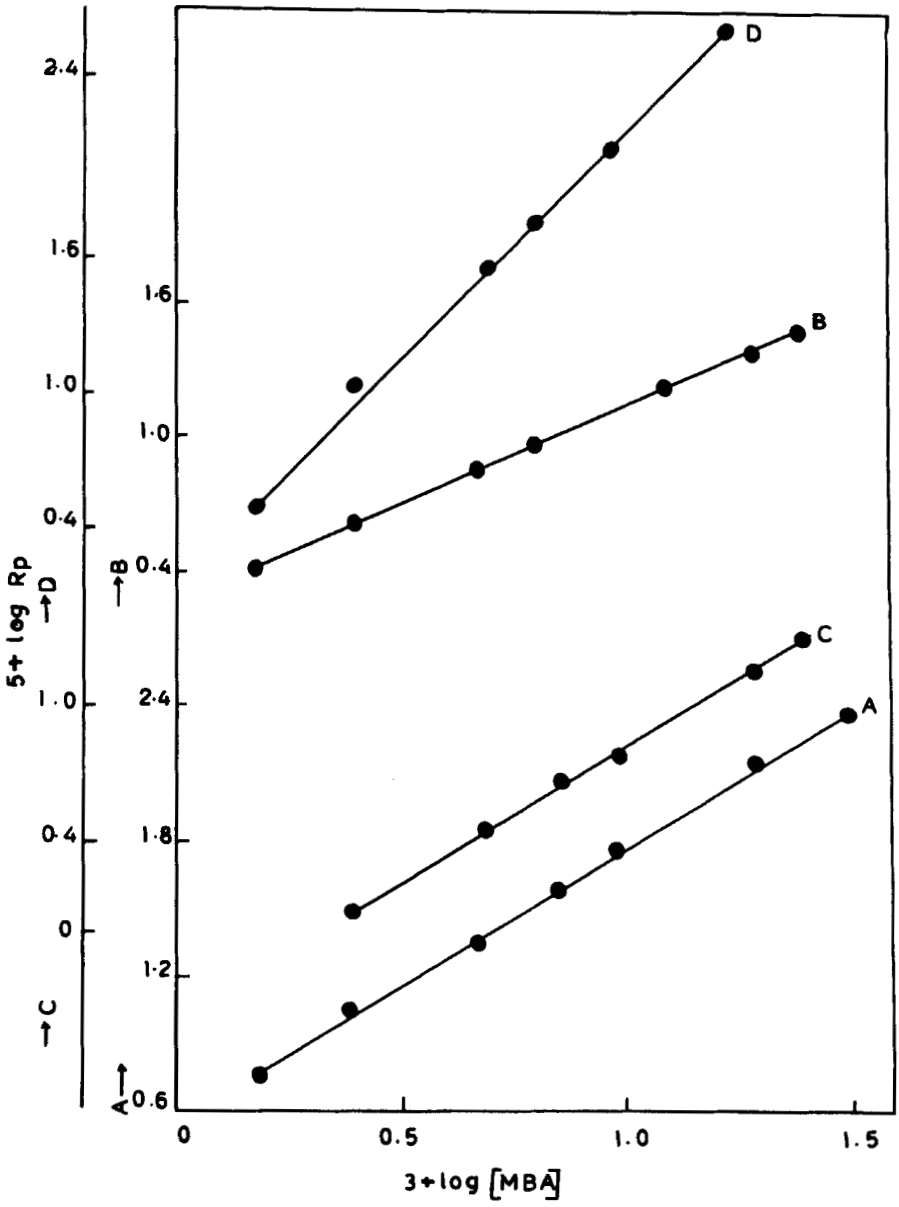

FIG. 2. Plots of log R_p vs log [MBA]. Concentrations in mmol/L. (A) [MA] = 10.0, [Mn(III)] = 0.508, temperature = 31°C. (B) [MEK] = 5.0, [Mn(III)] = 2.99, temperature 40°C. (C) [CAA] = 12.5, [Mn(III)] = 1.49, temperature = 36°C. (D) [TMA] = 10.0, [Mn(III)] = 0.535, temperature = 36°C.

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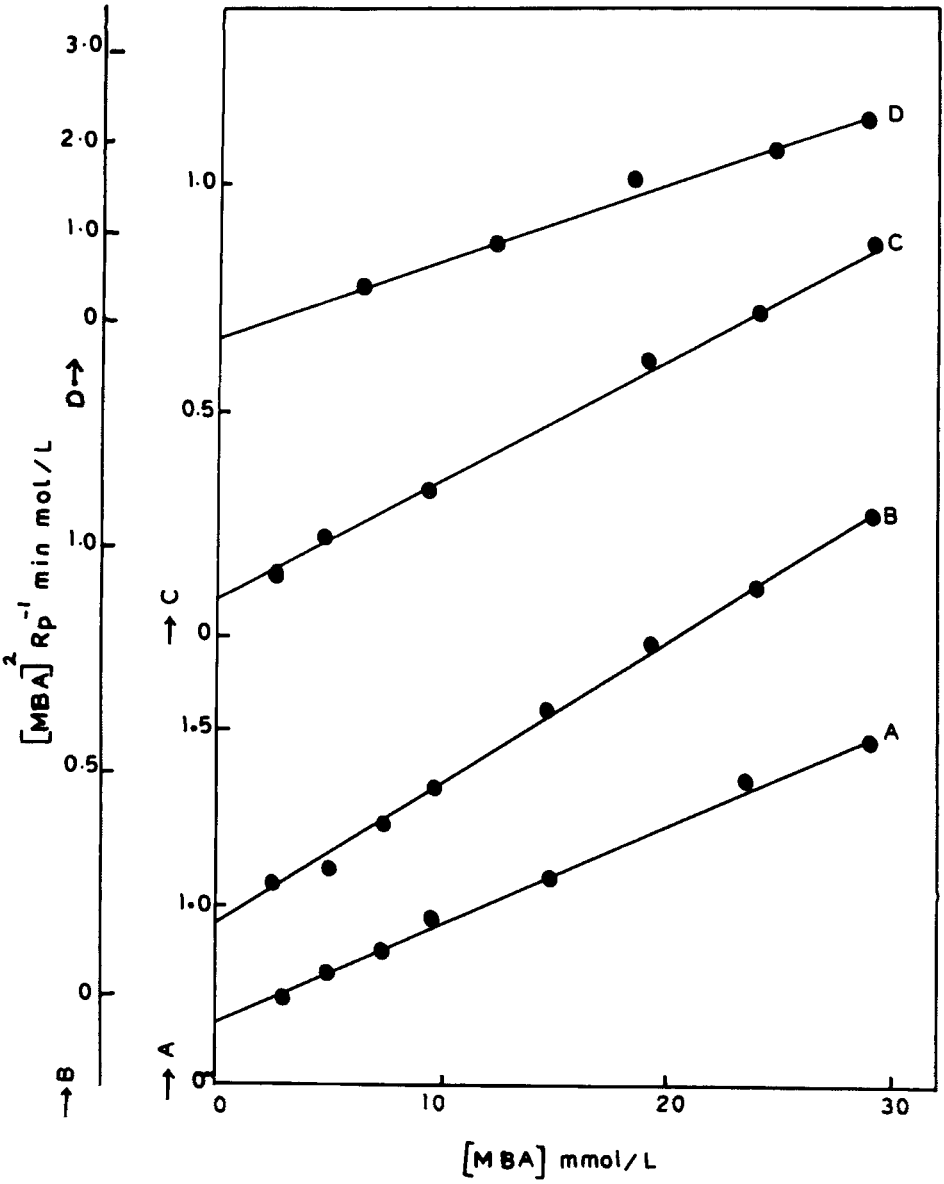

FIG. 3. Plots of R_p^{-1} [MBA]^2 vs [MBA]. Concentrations in mmol/L. (A) [TMA] = 10.0, [Mn(III)] = 0.508, temperature = 32°C. (B) [CAA] = 12.5, [Mn(III)] = 1.49, temperature = 30°C. (C) [MA] = 10.0, [Mn(III)] = 0.508, temperature = 26°C. (D) [MEK] = 5.0, [Mn(III)] = 2.29, temperature = 40°C.

and [MA] or [CAA] and the inverse first-order dependence on [Mn(III)] (Fig. 4A, 4B). For these systems, k_0 [Mn(III)] $\approx k_i$[MBA] and, as required by Eq. (5), the plots of $[MBA]^2 R_p^{-1}$ vs [MBA] become linear (Fig. 3B, 3C) and have an intercept. Such plots were obtained at different reductant concentrations, and the slopes and intercepts were again plotted against $[Red]^{-1}$. From the slopes and intercepts of these second plots, k_p/k_{t_1}, k_p/k_{t_2}, and k_0/k_i were calculated (Table 1).

For the system MBA-Mn(III)-TMA, an order of 1.7 with respect to [MBA] (Fig. 2D) could be explained by assuming that k_0 [Mn(III)] $> k_i$[MBA], which is in agreement with the calculated ratio of these rates (Table 1). R_p followed an inverse first-order dependence with respect to [Mn(III)] (Fig. 4C), and plots of R_p^{-1} vs $[TMA]^{-1}$ had an intercept on the rate axis. Values of $[MBA]^2 R_p^{-1}$ were obtained at different [TMA]'s and plotted against [MBA]. Contrary to the previous systems, the slopes of these plots were constant for different [TMA]'s, which indicates that k_p/k_{t_1} makes little contribution (Eq. 5). The termination could be mainly by the linear Mn(III)-TMA complex interacting with polymer radicals. Neglecting the terms involving k_{t_1}/k_p in Eq. (5) leads to

$$[MBA]^2 R_p^{-1} = \frac{k_{t_2}[MBA]}{k_p k_d} + \frac{k_{t_2}(k_0/k_i)[Mn(III)]}{k_p k_d}.$$

From the slope and intercept of the plots of $[MBA]^2 R_p^{-1}$ vs [MBA] (Fig. 3A), k_p/k_{t_1} and k_0/k_i values were calculated (Table 1).

The activation energies for the polymerization reactions were also calculated (Table 1).

Neither R_p nor R_m was affected by changes in $[H^+]$, ionic strength, or of added [Mn(II)].

CONCLUSIONS

We have discussed in detail the cyclopolymerization sequence followed by this divinyl monomer in our previous reports [4, 5]. That a similar mechanism was operative in the present system is evidenced by the homogeneous gel-free polymerization, by the enhanced rate of polymerization compared to the monovinyl monomers, and by the lack of residual unsaturation in the polymer obtained on precipitation. However, with the reductants GLY [4] or EG and ME [5] we observed mutual termination of growing polymer radicals. But in this study with CAA, MAL, MEK, or TMA as re-

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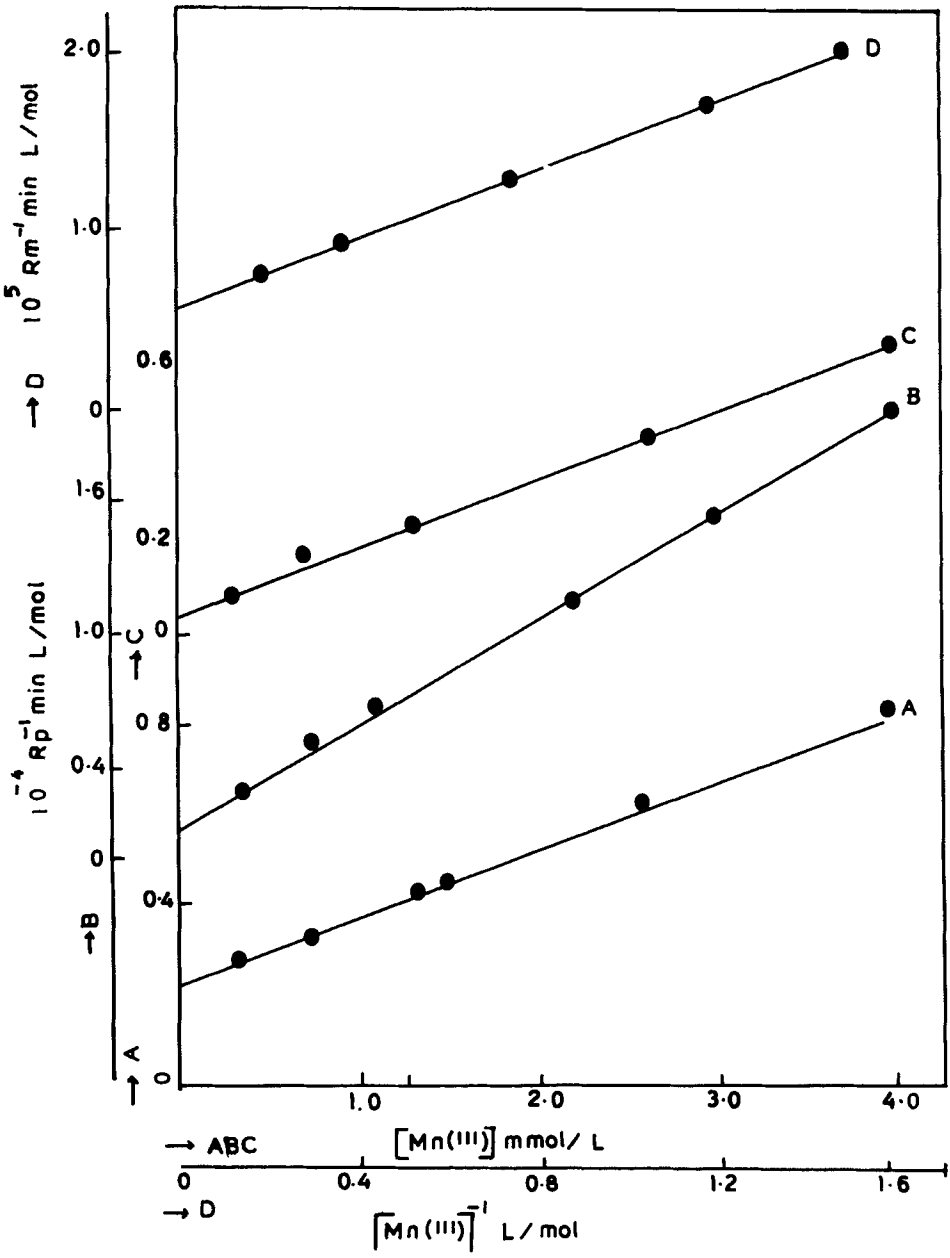

FIG. 4. A, B, and C are plots of R_p^{-1} vs [Mn(III)]. D is plots of R_m^{-1} vs $[\mathrm{Mn(III)}]^{-1}$. Concentrations in mmol/L. (A) [MA] = 10.0, [MBA] = 4.74, temperature = 36°C. (B) [CAA] = 12.5, [MBA] = 9.53, temperature, = 36°C. (C, D) TMA = 10.0, [MBA] = 18.97, temperature = 36°C.

ductants, we observe linear termination of polymer radicals with metal ion or metal ion-reductant complex, which may be attributed to the difference in the equilibrium constants of the various intermediate complexes proposed.

REFERENCES

[1] A. Gopalan, P. Venuvanalingam, S. P. Manickam, and N. R. Subbaratnam, *J. Macromol. Sci.–Chem., A23,* 117 (1986).
[2] A. Gopalan, P. Venuvanalingam, S. P. Manickam, K. Venkatarao, and N. R. Subbaratnam, *Eur. Polym. J., 18,* 531 (1982).
[3] S. Paulrajan, A. Gopalan, K. Venkatarao, and N. R. Subbaratnam, *Polymer, 24,* 906 (1983).
[4] S. Ratnasabapathy, N. Marisami, S. P. Manickam, K. Venkatarao, and N. R. Subbaratnam, *J. Macromol. Sci.–Chem., A25,* 83 (1988).
[5] S. Ratnasabapathy, N. Marisami, S. P. Manickam, K. Venkatarao, and N. R. Subbaratnam, *Ibid., A25,* 97 (1988).
[6] A. Jayakrishnan and V. Mahadevan, *Makromol. Chem., 181,* 1181 (1980).
[7] P. Elayaperumal, T. Balasubramanian, and M. Santappa, *Ibid., 178,* 2271 (1977).
[8] P. Elayaperumal, T. Balakrishnan, and M. Santappa, *J. Madras Univ., B, 46*(1), (1983).

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