



Aqueous Polymerization of Divinyl Monomers Initiated by Mn(III)-Amino Acid Chelating Agents†

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The polymerization kinetics of *N,N*-methylenebisacrylamide initiated by the redox pairs trisacetatomanganese(III) dehydrate-ethylenediaminetetracetic acid and trisacetatomanganese(III) dehydrate - nitrilotriacetic acid in dilute sulphuric acid medium was investigated. The rate of polymerization R_p , was proportional to $[MBA]^{1.1}$, $[EDTA]^{0.4}$ and inverse dependence to $[Mn(III)]$ for MBA-Mn(III)-EDTA system and $[MBA]^{1.1}$, $[NTA]^{0.7}$ and inverse dependence to $[Mn(III)]$ for MBA-Mn(III)-NTA system. The rate of manganic ion disappearance R_m , was directly proportional to $[Mn(III)]$ and $[Red]$ but independent of monomer for both the systems. Both R_p and R_m were not affected by the changes in $[H^+]$, ionic strength, added Mn(II) and R_p decreased with the addition of sodium nitrate. The activation energy was evaluated by using Arrhenius plot. Suitable mechanism has been proposed to explain the observed kinetic data.

Key Words: Divinyl monomer, Cyclopolymerization, Mn(III)-amino acid chelating agents, Rate of manganic ion disappearance.

INTRODUCTION

The non conjugated divinyl monomer *N,N'*-methylenebisacrylamide is a well known cross linking agent, the polymer of which has the major application in the gel electrophoresis. While plenty of redox systems were employed on monovinyl monomers, not many works had been done on MBA in the past¹⁻³.

Hence in our laboratory, trisacetatomanganese(III) dihydrate has been coupled with the chelating agents, ethylenediaminetetracetic acid (EDTA) and nitrilotriacetic acid (NTA). These redox pairs were employed in the aqueous polymerization of monovinyl monomers acrylamide, acrylic acid and a non-conjugated divinyl monomer, *N,N'*-methylenebisacrylamide. The present paper deals with the kinetics of *N,N'*-methylenebisacrylamide initiated by the redox pairs, trisacetatomanganese(III) dehydrate-ethylenediaminetetr-acetic acid and trisacetatomanganese(III) dehydrate-nitrilotri-acetic acid in dilute sulphuric acid medium. From the experimental results, a suitable reaction scheme has been proposed and kinetic parameters were evaluated.

EXPERIMENTAL

The reagents used were purified by standard methods. The polymerization reaction was carried out in nitrogen atmosphere. The rate of monomer disappearance R_p was determined

by bromometry and the rate of manganic ion disappearance R_m was determined by cerimetry.

RESULTS AND DISCUSSION

$$\text{Rate of polymerization, } R_p = \frac{-d[M]}{dt}$$

In both *N,N'*-methylenebisacrylamide-Mn(III)-EDTA and *N,N'*-methylenebisacrylamide-Mn(III)-NTA systems, the rate of polymerization depended on $[M]^{1.1}$ was well indicated by the plots of R_p vs. $[M]^{1.1}$ passing through the origin (Fig. 1). The rate of polymerization R_p , showed an order of 0.4 with respect to $[EDTA]$ in the case of MBA-Mn(III)-EDTA (Fig. 2) and 0.6 with respect to $[NTA]$ in the case of MBA-Mn(III)-NTA system. In both the systems, R_p showed an inverse dependence to $[Mn(III)]$ (Fig. 3). R_p was unaffected by the changes in $[H^+]$, ionic strength and added Mn(II) in both the systems in the observed range. In both the systems, R_p was found to be increased with increasing temperature.

$$\text{Rate of manganic ion disappearance, } R_m = \frac{-d[Mn(III)]}{dt}$$

At constant $[Red]$, $[H^+]$, ionic strength and temperature, a first order dependence with respect to $[Mn(III)]$ was observed. R_m increased with $[Red]$ and lineweaver-Burck plots of R_m^{-1} vs. $[Red]^{-1}$ were produced definite intercepts on the Y axis

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(Fig. 4). The rate was unaltered by the changes in $[H^+]$, ionic strength and added $Mn(II)^{4-6}$.

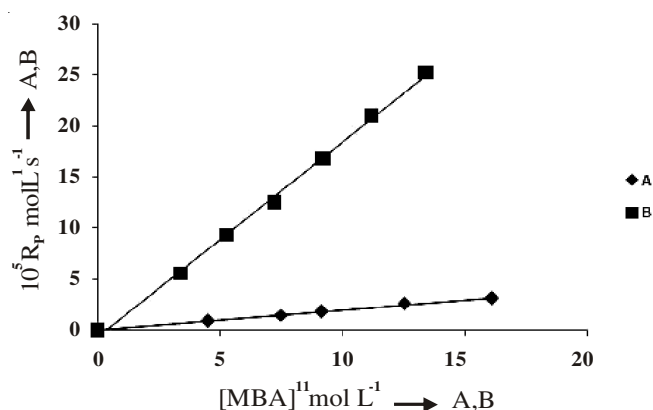


Fig. 1. (A) Dependence of R_p on $[MBA]$; $[EDTA]=1.00 \times 10^{-6}$, $[Mn(III)]=1.20 \times 10^{-2}$; (B) Dependence of R_p on $[MBA]$; $[NTA]=1.25 \times 10^{-3}$, $[Mn(III)]=8.03 \times 10^{-3}$

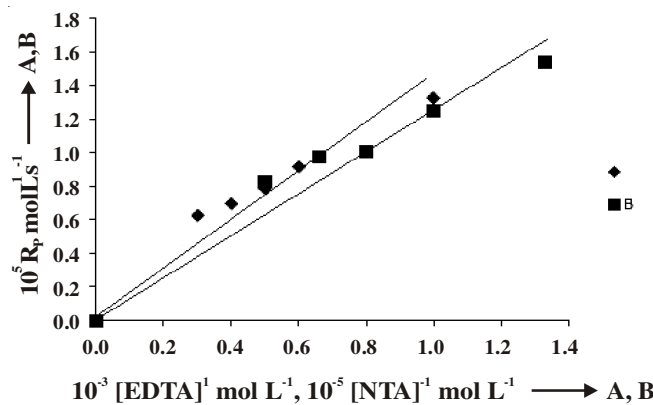


Fig. 2. (A) Dependence of R_p on $[EDTA]$; $[MBA]=1.16 \times 10^{-2}$, $[Mn(III)]=2.27 \times 10^{-2}$; (B) Dependence of R_p on $[NTA]$; $[MBA]=13.2 \times 10^{-3}$, $[Mn(III)]=1.03 \times 10^{-2}$

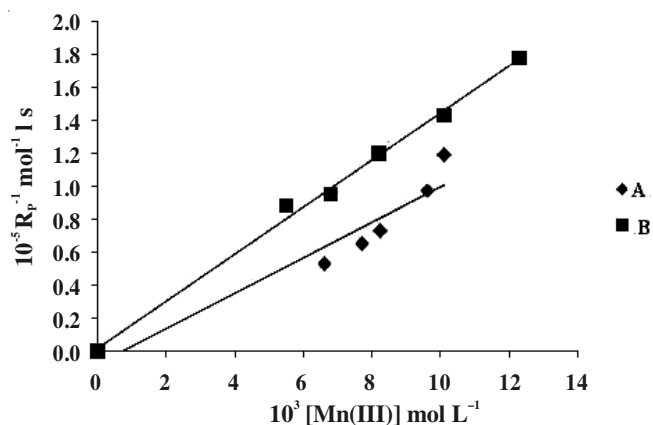


Fig. 3. (A) Dependence of R_p on $[Mn(III)]$; $[MBA]=15.30 \times 10^{-2}$, $[EDTA]=1.00 \times 10^{-3}$; (B) Dependence of R_p on $[Mn(III)]$; $[MBA]=11.60 \times 10^{-2}$, $[NTA]=1.00 \times 10^{-3}$

Mechanism and rate law: Based on the above observation and applying steady state approximations, the following rate expressions were arrived at.

$$R_p = \frac{k_p k_i k_d K[Red][M]^2}{k_t (k_i [M] + k_0 [Mn(III)] (1 + K[Red]))} \quad (1)$$

R_m in the presence of monomer is given by the relation.

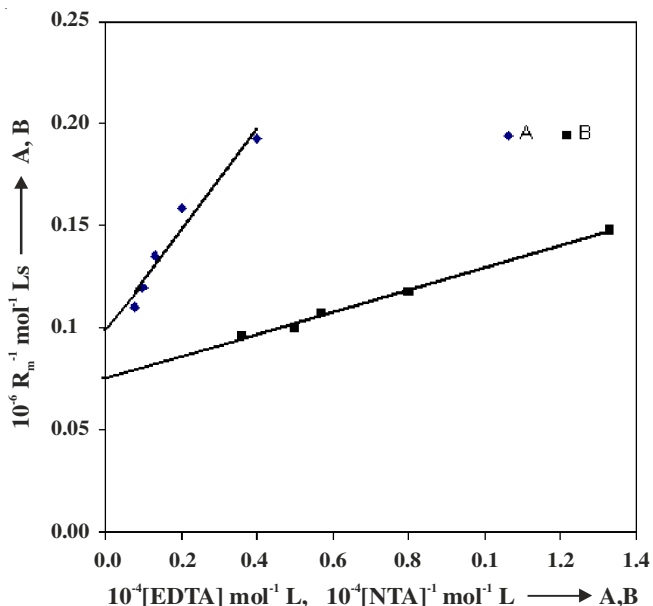


Fig. 4. Line weaver-Burk plot: (A) Dependence of $10^6 R_m^{-1} L s$ vs. $10^{-4} [EDTA] \text{ mol}^{-1} L$; $[Mn(III)]=11.1 \times 10^{-3} \text{ mol}^{-1} L$, $[H^+]=0.05 \text{ mol}^{-1} L$, $I=0.025 \text{ mol}^{-1} L$, $t=50?$; (B) Dependence of $10^6 R_m^{-1} L s$ vs. $10^{-4} [NTA] \text{ mol}^{-1} L$; $[Mn(III)]=15.7 \times 10^{-3} \text{ mol}^{-1} L$, $[H^+]=0.05 \text{ mol}^{-1} L$, $I=0.025 \text{ mol}^{-1} L$, $t=50?$

$$R_m = \frac{2k_d K[Mn(III)][Red]}{1 + K[Red]}$$

Propagation in MBA cyclopolymerization: To explain the experimental observation that certain 1,6-dienes were giving rise to non-cross linked gel-free polymers, Butler *et al.*⁷, proposed cyclopolymerization mechanism involving the formation of cyclic units along the polymer backbone and by an alternating intramolecular-intermolecular propagation reaction. The first step is the intramolecular cyclization of M^0 1 to give M^0 2, the seven membered cyclized radical. The second step is the intermolecular propagation through cyclized radicals reacting with monomer to yield M^n and the sequence repeats itself. The scheme is similar to the one suggested by Gibbs⁸, for the polymerization of symmetrical non conjugated diolefins, where k_c is the rate constant for intramolecular cyclization reaction and k_p is that for intermolecular propagation reaction (Fig. 5).

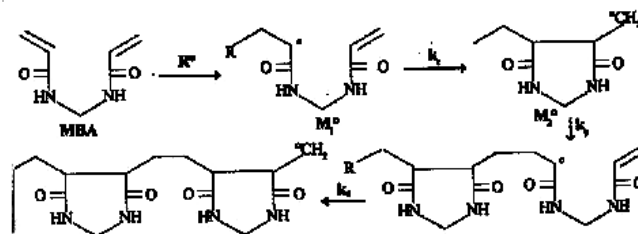


Fig. 5. Intramolecular cyclization reaction

Evidence for cyclopolymerization: Butler and Kimura observed that R_p values of divinyl monomer compared with those of monovinyl analogues were considerably higher by a factor of two to ten. This was interpreted in terms of cyclopolymerization of the divinyl monomers in contrast to monovinyl propagation of their monovinyl counterparts.

Following these lines of experiments, the rate of polymerization of MBA was measured under identical experimental conditions along with those of two analogous monovinyl monomers, acrylamide (AM) and methacrylamide (MAM). AA being a monovinyl analogue of MBA was chosen to show the effect of - substitution on R_p . The order of magnitude of R_p values was found to be $MBA > AM > MAM$ (Table-1). The observed higher R_p for MBA than acrylamide and methacrylamide is in the light of differences in the propagation mechanism between the two monomers. MBA undergoes cyclo-polymerization in contrast to the monovinyl linear propagation for acrylamide and methacrylamide.

TABLE-1
EFFECT OF R_p ON MONOMERS

10^{-2} [M] mol L ⁻²	AM $10^6 R_p$ mol L ⁻²	MAM $10^6 R_p$ mol L ⁻²	MBA $10^6 R_p$ mol L ⁻²
17.0	1.30	0.80	9.25
23.0	1.66	1.15	16.9
29.0	3.50	2.00	23.0

The higher rate of polymerization of MBA confirms the involvement of cyclo-polymerization in these systems.

Evaluation of rate parameters: It can be seen from eqn. (1), R_p would follow an order between 1 and 2 depending on the relative rates of monomer initiation, ($k_i/[M]$) and the rate of primary radical oxidation, ($k_o/[Mn(III)]$). R_p should depend on $[M]$ and should be independent of $[Mn(III)]$ if $k_i [M]$ is $> k_o [Mn(III)]$. Likewise if $k_o [Mn(III)] > k_i [M]$, a second order dependence of R_p on $[MBA]$ would result. On the otherhand, if $k_o [Mn(III)]$ is approximately = $k_i [M]$ then as per equation (1), R_p would follow an order between 1 and 2 with respect to $[M]$ and a fractional order with respect to $[Red]$, as was found in the MBA-Mn(III)-EDTA, MBA-Mn(III)-NTA systems. This is also substantiated by the calculated values of k_o/k_i from eqn. (1), k_p/k_{t1} , k_p/k_{t2} were calculated and tabulated (Table-2). From the plots of R_m^{-1} vs. $[Red]^{-1}$, the unimolecular decomposition constant (k_d) and the formation constant of the complex (K) were evaluated (Fig. 3) and tabulated (Table-2).

TABLE-2
CONSTANT VALUES FOR THE SYSTEMS
MBA-Mn(III)-EDTA AND MBA-Mn(III)-NTA

System	K (mol ⁻¹ L)	K_a s ⁻¹	k_p/k_{t1}	k_p/k_{t2}	k_o/k_i
MBA-Mn(III)-EDTA	3.26×10^3	8.84×10^{-4}	7.80	1.49	1.56
MBA-Mn(III)-NTA	1.05×10^3	1.22×10^{-3}	1.95	2.42	2.82

The higher value of the formation constant K, indicates the strong complex formation between Mn(III) and the reductants EDTA and NTA. The enhanced stability may be ascribed to the strong coordinating ability of these chelating agents⁹. The formation of five membered rings has been shown to be the most stable chelates of aliphatic amino acids^{10,11}. EDTA and NTA formed five membered rings with Mn(III). Such ring

formation has been reported with Ce(IV)¹. The complex formation constants of these systems are larger than those obtained from other Mn(III)-reducing agent systems (Table-3).

TABLE-3
COMPLEX FORMATION CONSTANT VALUES FOR THE
POLYMERIZATION OF VINYL MONOMERS USING Mn(III)-
ORGANIC SUBSTRATES REDOX SYSTEMS

Monomers	Organic substrates	K (mol ⁻¹ L)
³¹ Acrylonitrile	Cyclohexanone	16.68
³¹ Acrylonitrile	DMSO	2.57
³¹ Methylmethacrylate	Glycerol	10.20
³¹ Methylmethacrylate	Fructose	80.00
³² N,N'-Methylene bisacrylamide	Cynoacetic acid	34.70
³² N,N'-Methylene bisacrylamide	Ethylene glycol	6.20
³² N,N'-Methylene bisacrylamide	Thiomalic acid	210.00
N,N'-Methylene bisacrylamide	EDTA	3260.00
N,N'-Methylene bisacrylamide	NTA	1050.00

Variation of R_m with reductant concentration indicates the complex formation prior to electron transfer. This is further confirmed by Lineweaver-Burck plots. Participation of Mn(III) or Mn(III)-red complex in the termination was confirmed by the inverse dependence of R_p with $[Mn(III)]$. Increase of ionic strength and $[H^+]$ showed negligible effect on R_p and R_m , which is common in free radical Polymerization.

Effect of temperature: In the present systems, R_p increased with increase of temperature. A rise in the rate of active centre formation and chain propagation increases the overall rate of conversion of monomer into polymer. Activation energy calculated by using Arrhenius lots were 28.8 kJ/mol and 17.8 kJ/mol for the systems MBA-Mn(III)-EDTA and MBA-Mn(III)-NTA respectively.

Conclusion

Both of these systems followed a similar mechanism, initiation by the primary radical R_0 and propagation by cyclo-polymerization. The initiation and termination mechanism would be the same for monovinyl and divinyl polymerization. Non-conjugated divinyl monomers differ from the monovinyl one only in the propagation step. Participation of Mn(III) or Mn(III)-red complex in the termination was confirmed by the inverse dependence of R_p with $[Mn(III)]$.

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