Cyclopolymerization of Divinylmonomer with A Novel Redox Pair of Mn(VII)-Tetramethylethylenediamine†

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Kinetics of cyclopolymerization of *N,N'*-methylenebisacrylamide (MBA) was studied with a novel redox pair of Mn(VII)-tetramethylethylenedi- amine in a homogeneous gel free state under varying conditions of concentration, temperature, ionic strength and pH. Polymerization of N,N'-methylenebisacrylamide was carried out in acid medium at low concentrations with Mn(VII)-tetramethylethylenediamine as redox initiator at 50 ºC. The dependence of the rate of polymerization various experimental conditions, such as different concentrations of monomer, Mn(VII), tetramethylethylenediamine and different ionic strength at different temperature were studied. The rate of polymerization was found to be independent of ionic strength and pH. The rate of polymerization showed an increase with increase in temperature. The rate of polymerization was found to depend on [monomer]¹ and independent of [Mn(VII)] and [tetramethylethylenediamine] over a range. A polymerization mechanism involving cyclopolymerization mechanism was addressed. Evaluation of composite rate constant is in good agreement with the suggested mechanism. Under steady state conditions the rate of cyclo-polymerization is: $R_p = k_p k_d / k_t \times MBA$.

Key Words: Cyclopolymerization, Non conjugated divinyl monomer, *N,N'*-Methylenebisacrylamide, Mn(VII)-tetramethyl-ethylenediamine couple.

INTRODUCTION

A new technology development needs to study kinetics of cyclopolymerization. Bulk synthesis of polymer involves various kinetic factors. Kinetics studies play a major role in synthesis in the formation of physical gel[1]. Tetramethyl-ethylenediamine (TMEDA) being a bidentate ligand is a well known complexing agent and effectively employed as a catalyst for the polymerization of monovinyl and divinyl monomers in electrophoretic experiments in the formation of gels[2]. A number of redox systems involving Mn(VII) with organic substrates as reductants[3-7] had been widely studied in our laboratory for the cyclopolymerization of non-conjugated divinyl monomer, *viz. N,N'*-methylenebisacrylamide (MBA), in continuation of our earlier work with kinetic study of polymerization of acrylic acid with $S_2O_8^{2-}$- tetramethylethyl-enediamine couple[8], we were interested in studying the cyclopolymerization of *N,N'*-methylenebisacrylamide with the above said couple under homogeneous gel free condition and the kinetic results are presented here.

EXPERIMENTAL

N,N'-Methylenebisacrylamide (Koch light) was recrystal-lized from acetone at 40 ºC. Tetramethylethylenediamine (Loba chemie) and AnalaR grade $KMnO_4$ (SDS) were used as such without further purification. Water, twice distilled over alkaline permanganate was used to prepare all solutions. Polymerization was carried out by a procedure described earlier[9,10]. The rate of monomer disappearance was determined by estimating the unreacted monomer by bromometry[11] at different time intervals and after attainment of a steady state. Most of the reactions were carried out with [H⁺] = 0.01 mol L⁻¹ and at ionic strength of 0.031 mol L⁻¹.

RESULTS AND DISCUSSION

The rate of polymerization (R_p) in the monomer concen-tration range of 5 to 20 mmol L⁻¹ was found to depend on the first power of [MBA] (Fig. 1) and independent of [Mn(VII)] and [TMEDA] (Tables 1 and 2). R_p was found to be independent of ionic strength. The activation energy for the polymerization

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reaction of the above system was computed to be 23.03 kcal mol^{-1} from the Arrhenius plot of log R_p *versus* T^{-1}. From the kinetic results of our earlier studies with Mn(VII) as oxidant along with many reducing agents we were able to observe Mn(VII) to produce Mn(III) in its active form as Mn(OH)$^{2+}$ to interact with the monomer as well as reductant forming complexes, which in turn decomposed to produce radicals, leading to polymerization[3-7].

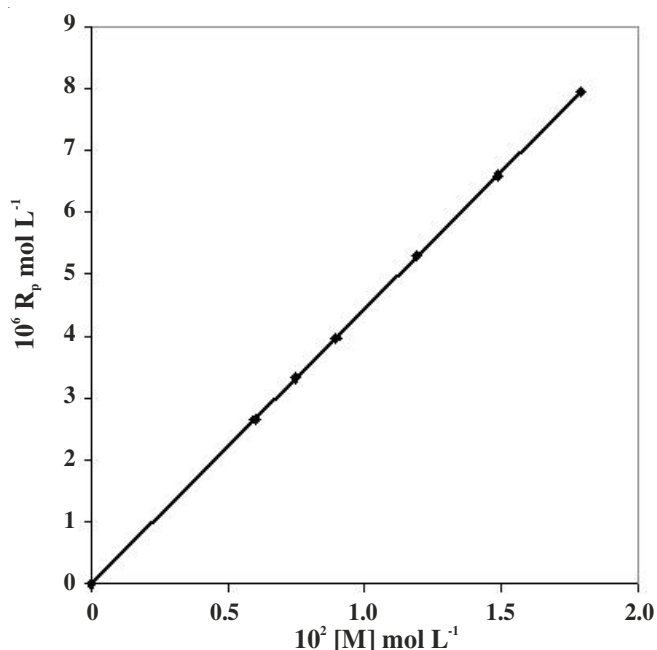
Fig. 1. Dependance of MBA on R_p; [Mn(VII)] = 2.5 × 10^{-4} mol L^{-1}, [TMEDA] = 1.32 × 10^{-3} mol L^{-1}, [H$^+$] = 0.01 mol L^{-1}, I = 0.031 mol L^{-1}, t = 50 ºC; composite rate constant K_p/k_d = 4.08 s^{-1}

However in the present investigation, from the results of kinetic study we were able to note interestingly that Mn(VII)

TABLE-1
EFFECT OF [MBA] ON R_p
[Mn(VII)] = 2.5 × 10^{-4} mol L^{-1}; [TMEDA] = 1.32 × 10^{-3} mol L^{-1};
[H$^+$] = 0.01 mol L^{-1}; I = 0.031 mol L^{-1}; t = 50 ºC

[M] × 10^2 mol L^{-1}	log [M] + 3	R_p × 10^6 mol s^{-1}	log R_p + 6
0.597	0.7759	2.65	0.4232
0.747	0.8733	3.32	0.5211
0.896	0.9523	3.95	0.5965
1.19	1.0755	5.30	0.7242
1.49	1.1731	6.59	0.8188
1.79	1.2528	7.96	0.9009

TABLE-2
EFFECT OF R_p ON [Mn(VII)] AND [TMEDA]

Effect of [Mn(VII)] on R_p [M] = 0.65 × 10^{-2} mol L^{-1} [TMEDA] = 1.32 X 10^{-3} mol L^{-1} [H$^+$] = 0.01 mol L^{-1} I = 0.031 mol L^{-1}; t = 50 ºC		Effect of [TMEDA] on R_p [M] = 1.19 X 10^{-2} mol L^{-1} [Mn(VII)] = 2.5 × 10^{-4} mol L^{-1} [H$^+$] = 0.01 mol L^{-1} I = 0.031 mol L^{-1}	
[Mn(VII)] × 10^4 (mol L^{-1})	R_p × 10^6 (mol L^{-1})	[TMEDA] × (10^3 mol L^{-1})	R_p × 10^6 (mol s^{-1})
2.5	2.85	0.66	5.10
5.0	2.84	0.99	5.30
7.5	2.86	1.32	5.29
10.0	2.83	1.98	5.31
15.0	2.85	2.64	5.32
20.0	2.84	3.96	5.31

itself could form a complex with the catalyst (TMEDA), which acts as a reductant. This complex in its turn decomposes to produce initiating free radicals as detailed below.

Complexation:

$$\text{Mn(VII)} + \text{TMEDA} \underset{}{\overset{K}{\rightleftharpoons}} \text{Complex} \qquad (1)$$
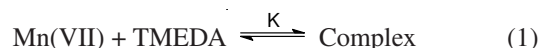
Formation of free radicals:

$$\text{Complex} \xrightarrow{k_d} \text{R}\hat{} \qquad (2)$$

whre, R$\hat{}$ is the initiating free radical.

Initiation:

$$\text{MBA} + \text{R}\hat{} \xrightarrow{k_i} \text{M}_1\hat{} \qquad (3)$$

Radical oxidation:

$$\text{R}\hat{} + \text{Mn(VII)} \xrightarrow{k_0} \text{Products} \qquad (4)$$

Propagation:

$$\left.\begin{array}{c} \text{M}_1^{\bullet} \xrightarrow{k_c} \text{M}_2^{\bullet} \\ \text{M}_2^{\bullet} + \text{MBA} \xrightarrow{k_p} \text{M}_n^{\bullet} \end{array}\right\} \qquad (5)$$
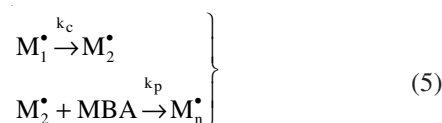
Termination:

Linear termination by interaction with metal ion-reductant complex.

$$\text{M}_2\hat{} + [\text{Mn(VII) Red] complex} \xrightarrow{k_t} \text{Polymer} \qquad (6)$$

Under steady state conditions the rate of cyclopolymerizarion

$$R_p = \frac{k_p k_d}{k_t} \text{MBA}$$

[MBA]$^{-1}$ R_p is found to be invariant for different variations of [monomer] at different conditions of [oxidant] and [reductant] (Table-2), which is in agreement with the above sequence of reaction mechanism. The complex kinetic rate parameter, $k_p k_d/k_t$ could be arrived as 4.3 × 10^{-4} s^{-1} approximately from the plots of R_p *versus* [MBA] passing through the origin (Table-1; Fig. 1).

Evidence for cyclopolymerization: Cyclopolymerization of this non-conjugated divinyl monomer had been widely studied with different types of initiators in our laboratory[3-7]. A detailed analysis of the cyclopolymerization in terms of the supporting evidences and the structure of the polymer units were reported. One of the convincing evidences for the cyclopolymerization is the comparison between the rate of polymerization of MBA and that of monovinyl monomer and the rate of polymerization under identical conditions is much greater for the non-conjugated divinyl monomer, MBA than that for analogous monovinyl monomers which confirms involvement of cylcopolymerization with MBA (Table-3).

TABLE-3
REACTIVITY OF MONOMERS
[M] = 1.19 × 10^{-2} mol L^{-1} [H$^+$] = 0.01 mol L^{-1}
[Mn(VII)] = 2.5 × 10^{-4} mol L^{-1} I = 0.031 mol L^{-1}
[TMEDA] = 1.32 × 10^{-3} mol L^{-1}; t = 50 ºC

Monomer	R_p × 10^7 (mol^{-1} s^{-1})
Acrylamide	24.6
Methacrylamide	11.5
MBA	52.9

The polymer solution formed is found to have no unsaturation which again confirms the involvement of both

the double bonds in the propagation step, otherwise known as cyclopolymerization. An attempt was made in our laboratory to analyze the IR and NMR spectra of the polymer formed which gave the conclusive evidence for the seven membered cyclized ring units in polymer[12] as detailed below.

The IR spectral details of the polymer and monomer are given in Table-4 and Fig. 2. The absorption at 1700 cm^{-1} due to carbonyl function is not affected in the polymer and in the monomer, MBA. However the absence of -CH=CH$_2$ stretching frequency at 1630 cm^{-1} in the polymer which well pronounced in the monomer is of significance. This observation clearly indicates the cyclization propagation sequence (Fig. 3 step III or IV) and not through intermolecular addition propagation as observed with monovinyl monomers (Fig. 3 step II), in which case the pendant double bonds could be detected. It is also noted that the polymers formed do not consume bromine by addition as decided by brommetric estimations.

The results of NMR analysis of the polymer also support the cyclization propagation (step III or IV) rather than the vinyl propagation (step II) as proved by the absence of any signal at 6.15 δ due to the pendant CH$_2$ = CH- in the polymer (Fig. 4). In the cyclopolymerization of acrylic anhydrides[13-15], the difference in the chemical shift for methylenic protons in the six membered rings and that for the two intermittent methylenic
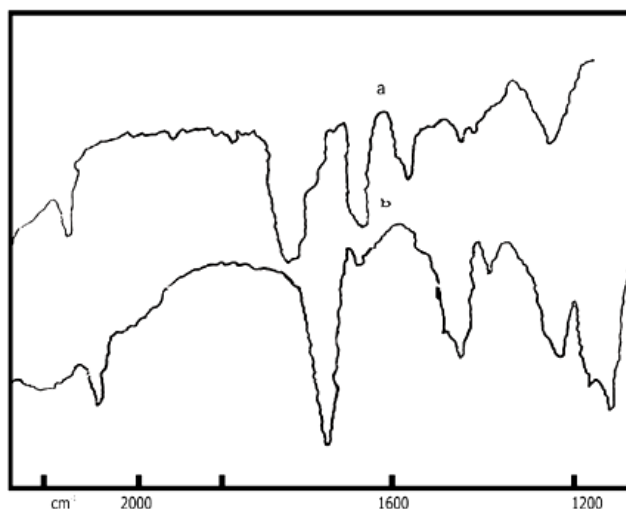

Fig. 2. IR Spectra (a) poly MBA (b) MBA

protons in the five membered rings were differentiated, recorded and ratio of HH/HT intramolecular cyclization was also calculated.

On this basis, similar observation could be expected in cyclopolymerization of MBA also. The observed NMR spectra of MBA polymer is shown in Fig. 4. For comparison the NMR

TABLE-4
SPECTRAL DATA OF MBA AND POLY MBA

Sample	Fig. 2. IR cm^{-1}			Fig. 4. NMR ? value			
	CO	-CH=CH$_2$	-CH$_2$-	-CH=CH$_2$	-CH$_2$-	-CH=CH$_2$	-NH-
MBA	1725 (W) 1680 (S)	1630 (S)	1400	6.2	2.0		9.8
Poly MBA	1740 (W) 1670 (S)		1300		2.2	4.0	9.8
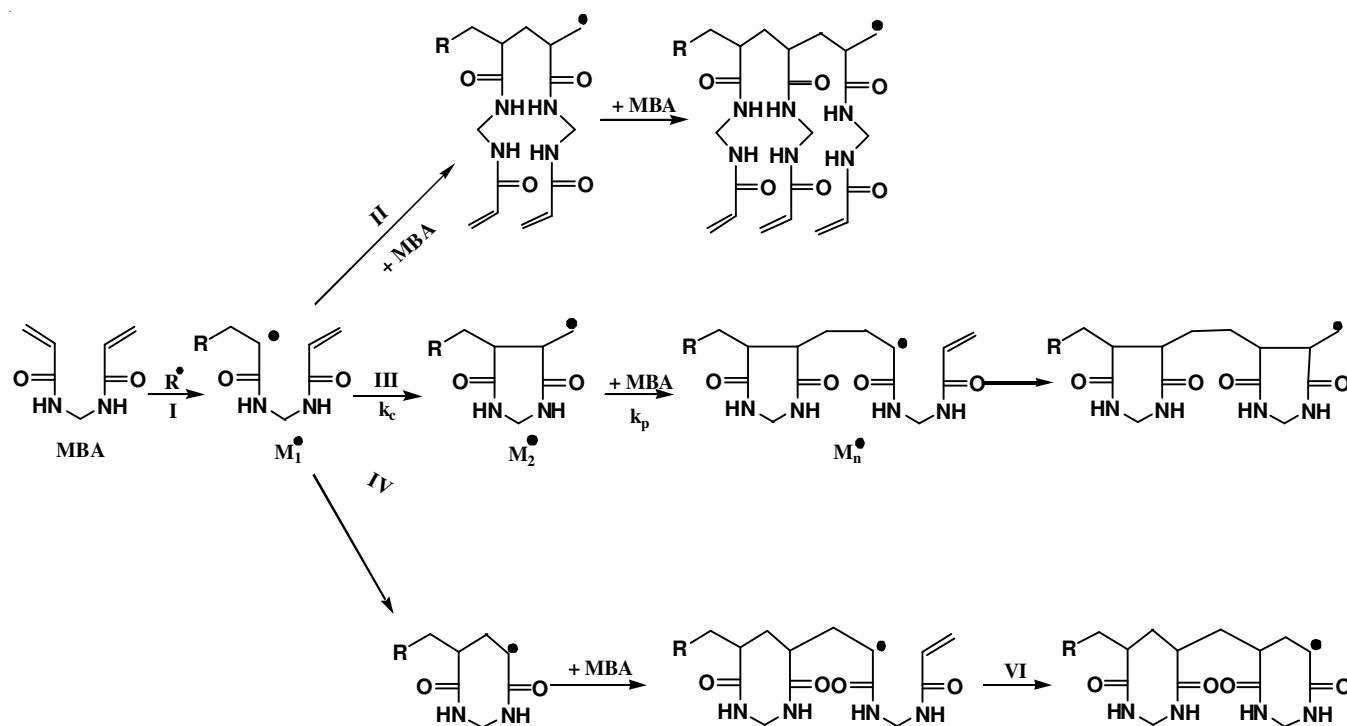
Step I : Initiation by free radical generated by the decomposition of redox pair complex; **Step II** : Vinyl propagation by intermolecular HT addition; **Step III** : Cyclopolymerization by HH intramolecular addition giving seven membered ring unit; **Step IV** : Cyclopolymerization by HT intra and intermolecular addition propagation giving eight membered ring unit

Fig. 3. Propagation sequences

spectra of polymethacrylate and polymethylmethacrylate are also indicated (as model compounds) in Fig. 5, where total HT addition involving six membered rings and 30 % HH cyclization were reported[16]. By analysis of these spectral data it is clear that the MBA undergoes a total cyclopolymerization and it could be only seven membered rings with two intermittent methylenic groups (Fig. 3, Step III) constituting the polymer and this conclusion supports our earlier prediction of this type of cyclic units.
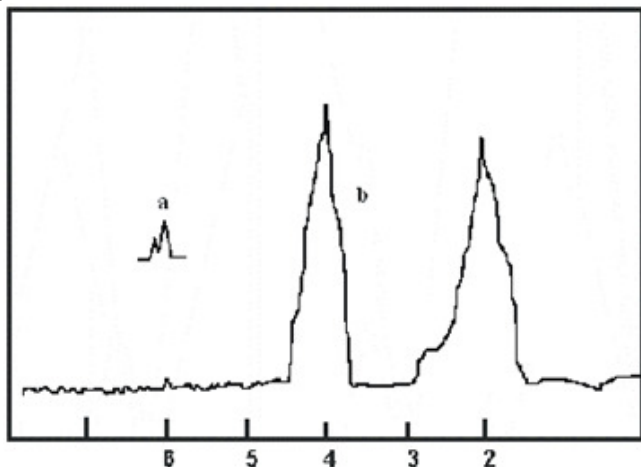

Fig. 4. H NMR spectra (a) $CH_2=CH_2$ protons in MBA (b) poly MBA in CDCl$_3$ at 100 ºC
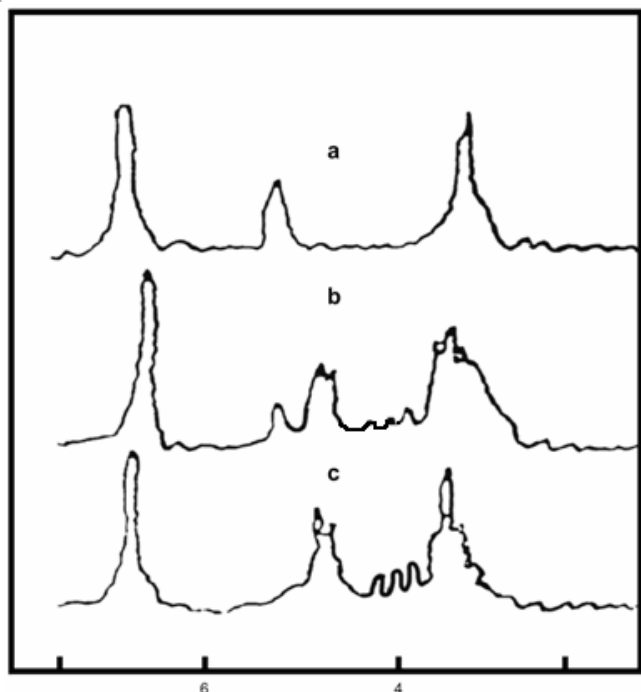

Fig. 5. H NMR spectra model compounds (a) for pure HH (b) for pure HT and (c) 30/70 HH/HT addition propagations

Conclusion

In this study, the use of novel redox pair of Mn(VII)-tetramethylethylenediamine as initiator for cyclopolymerization has been reported. The rate of polymerization was found to depend on the first power of [MBA] and independent of [Mn(VII)] and [TMEDA]. The activation energy for the polymerization reaction was 23.03 kcalmol^{-1}. The divinyl monomer MBA undergoes a total cyclopolymerization and it could be only seven membered rings with two intermittent methylenic groups constituting the polymer.

REFERENCES

1. S. Park, T. Okada, D. Takeuchi and K. Osakada, *Chem. Eur. J.*, **16**, 8565 (2010).
2. A. Gopalan, A. Venuvanalingam S.P. Manickam, K. Venkatrao and N.R. Subbaratnam, *Eur. Polym. J.*, **18**, 531 (1982).
3. S. Ratnasabapathy, N. Marisamy, S.P. Manickam, K. Venkatrao and N.R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25**, 83 (1988).
4. S. Ratnasabapathy, N. Marisamy, S.P. Manickam, K. Venkatrao and N.R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25**, 97 (1988).
5. S. Ratnasabapathy, N. Marisamy, S.P. Manickam, K. Venkatrao and N.R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25**, 943 (1988).
6. M. Umayavalli, V. Gopalakrishnan, S. Ratnasabapathy and S.P. Manickam, *Polym. Int.*, **38**, 363 (1995).
7. S. Paulrajan, A. Gopalan, K. Venkatrao and N.R. Subbaratnam, *Polymer*, **24**, 906 (1983).
8. A. Gopalan, S. Paulrajan, K. Venkatrao and N.R. Subbaratnam, *Eur. Polym. J.*, **19**, 817 (1983).
9. G. Mino, S. Kaizmann and E. Rasimussin, *J. Polym. Sci.*, **58**, 393 (1959).
10. S. Ratnasabapathy and S.P. Manickam, *Macromolecules,* Proc. Int. Symp. Trivandrum., India, Allied Publishers, New Delhi, Vol. 1, p. 476 (1995).
11. S. Ratnasabapathy and S.P. Manickam, Polymer Science, Contemporary Themes, Tata MC.Graw Hill Edn., New Delhi, **1**, 127 (1991).
12. G.C. Corfield, *Chem. Soc., Rev.*, **1**, 523 (1972).
13. K. Hatada, Y. Okamoto, K. Ohta and H. Yuki, *J. Polym. Sci.,* **14**, 51 (1976).
14. T. Ohya and T. Otsu, *J. Polym. Sci.,* **20**, 3533 (1980).
15. P. Timy, J. Sharanappa, T. Nandibewoor and S.M. Tuwar, *J. Soln. Chem.*, **35**, 51 (2006).
16. T. Parthsarathy and V. Uma, *J. Chem. Sci.*, **116**, 115 (2004).