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## RADIATION INDUCED POLYMERIZATION OF N,N'-METHYLENEBISACRYLAMIDE IN AQUEOUS SOLUTION

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### ABSTRACT

Gamma ray induced polymerization of N,N'-methylenebisacrylamide (MBA) in aqueous solution has been studied. Rates of polymerization have been determined as a function of dose, dose rate, and monomer concentration. Polymerization mechanism was found to be free radical with chain propagation step involving ring formation. About 90% conversion was achieved in 25 minutes of irradiation (dose rate  $1.54 \times 10^{18} \text{ eV dm}^{-3} \text{ s}^{-1}$ ) of MBA solution (36 mmol). The polymerization rates were found to vary from  $1.9 \times 10^{-4}$  to  $5.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  when the monomer concentrations were varied between 80–164 mmols. The value of the constant  $k_p/k_t^{1/2}$  was calculated to be 9.85 for the dose rate of  $1.54 \times 10^{18} \text{ eV dm}^{-3} \text{ s}^{-1}$ . The precipitated polymer showed mono disperse particles of diameter of about 170 nm. The polymer was found to be highly crosslinked and insoluble in any solvent.

### INTRODUCTION

N,N'-Methylenebisacrylamide (MBA), is a symmetrical divinyl monomer and is mostly used as a crosslinking agent in the polymer reactions. It generally produces a crosslinked insoluble polymer. It is further used as a vulcanization agent for urethane rubbers and in textile industry for improving surface properties. It also finds use in compositions for encapsulation of microorganisms and as a flocculating

agent in waste water treatment. Study of homo polymerization of the monomer using various redox systems has been reported [1-5]. The monomer can also be polymerized without crosslinking under certain conditions [6]. Photopolymerization of the monomer has also been reported by Suresh Babu *et al* [7]. Polymerization kinetics of MBA has been studied and mechanism of polymerization in all these systems has been found to be free radical with a novel chain propagation step involving ring formation [8-12]. However, radiation induced polymerization has not been studied so far.

The present work deals with the kinetics of gamma ray induced polymerization of MBA in aqueous solution.

## EXPERIMENTAL

The MBA used in these studies was obtained from M/S Aldrich Chemicals. It was purified by recrystallizing from acetone at 40°C and drying at 50°C under vacuum. Nanopure water required for the experiments was prepared by passing distilled water through Barnstead Nanopore cartridge filtration system. Different concentrations of MBA (80-170 mmol) solutions were made in nanopure water and 10 milliliters of these solutions were flushed with IOLAR grade nitrogen in capped tubes to remove dissolved oxygen. The tubes were irradiated by gamma radiations at  $28 \pm 1^\circ\text{C}$  using a cobalt-60 gamma cell fabricated in BARC. The dose rate of the gamma source was measured by using Fricke dosimeter;  $G(\text{Fe}^{+3}) = 15.6$ . The precipitated polymer was filtered and the concentration of the remaining monomer in the filtrate was determined by spectrophotometry ( $\gamma_{\text{max}}$  for the monomer = 225 nm) after properly diluting the monomer. The molar extinction coefficient  $\epsilon$  for the monomer was determined by measuring the absorbance of MBA solutions of known concentrations at 225 nm and found to be  $12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

The particle dimensions of the precipitated polymer was determined by BI-90 particle sizer.

Solutions of MBA containing different concentrations of oxygen were used for studying the effect of oxygen on polymerization. The concentration of the dissolved oxygen was determined by Dissolved Oxygen Meter, Model 5513-55 of Cole-Parmer Instrument Company.  $G(\text{Radical})$  value for the monomer was calculated from these studies.

## RESULTS AND DISCUSSION

N,N'-Methylenebisacrylamide has low solubility in water (175 mmols). Gamma irradiation of aqueous solution of MBA in low concentrations was found to produce a white flocculent polymer which is insoluble in the aqueous solution. The study of this system is interesting due to its heterogeneous nature affecting propagation and termination steps.

The simplest case of radiation induced polymerization in solution corresponds to a system in which the solvent does not interfere with the reaction steps in the polymerization but acts solely as an inert diluent. With radiation, however, such a situation can never arise since the solvent gets radiolyzed forming additional free radicals which may contribute to chain initiation and termination reactions. Moreover, energy transfer reactions from monomer to solvent and vice versa may also take place thus affecting the kinetics of polymerization. Based on simple dilution theory where effective energy transfer processes do not take place and assuming radical mechanism for radiation induced polymerization, the rate of polymerization in solution is given by A. Shapiro [13] as

$$R_{p,sol} = k_p \times k_t^{1/2} \times I^{1/2} \times (\phi_m [M] + \phi_s [S])^{1/2} [M] \quad (1)$$

where  $\phi_m$  and  $\phi_s$  are the rate constants of free radical production in the monomer and solvent respectively expressed per unit of exposure dose.

$\phi_m [M]$  can be expressed as

$$\begin{aligned} & G \text{ of M} \times \text{No. of electrons in molecule M} \times \text{Conc. of M} \\ &= \frac{\hspace{10em}}{100 \times \text{electron density of Fricke solution}} \end{aligned}$$

$$\begin{aligned} \text{Elec. density of Fricke solution} &= 100 \times \{ [H_2O] \times \text{No of electrons in } H_2O + \\ & [H_2SO_4] \times \text{No of elec. in } H_2SO_4 \} \times 6.023 \times 10^{23} \\ &= 100 \times ( 55.5 \times 10 + 0.4 \times 50 ) \times 6.023 \times 10^{23} \\ &= 3.47 \times 10^{28} \end{aligned}$$

For MBA monomer,

$$\phi_{mba} \times [MBA] = \frac{G_{mba} \times 82 \times [MBA]}{3.47 \times 10^{28}} = 0.24 \times 10^{-26} \times \frac{G_{mba}}{[MBA]}$$

For water solvent

$$\phi \text{H}_2\text{O} \times [\text{H}_2\text{O}] = \frac{3.3 \times 10 \times 55.55}{3.47 \times 10^{28}} = 5.29 \times 10^{-26}$$

R<sub>p</sub> sol then becomes equal to

$$= k_p/k_t^{1/2} \times I^{1/2} \times 10^{-13} \times (0.24 \times G_{\text{mba}} \times [\text{MBA}] + 5.29)^{1/2} [\text{MBA}]$$

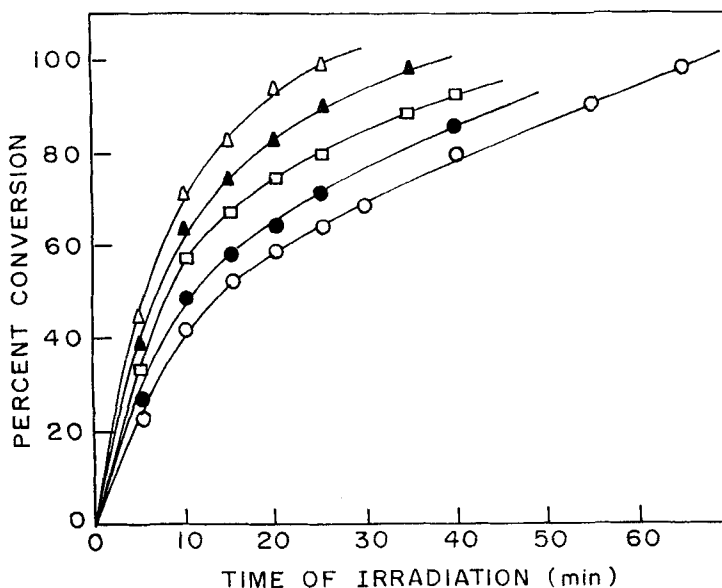
where I stands for Fricke dose rate in electron volts per litre per second. Assuming G radical values for organic molecules to be about 10 for the acrylamide type of molecules, the first term in the bracket could be neglected compared to the second term which contains very high concentration of water molecules (55 moles) compared to the monomer concentration (~150 mmols) Hence, the contribution of the H· and OH· radicals produced from water molecules by gamma radiation will have a significant role in the initiation as well as termination reactions of polymerization. The final equation used for the polymerization studies in aqueous solution then reduces to

$$\begin{aligned} R_p &= k_p/k_t^{1/2} \times I^{1/2} \times 10^{-13} \times (5.29)^{1/2} \times [\text{MBA}] \\ &= k_p/k_t^{1/2} \times I^{1/2} \times 10^{-13} \times 2.3 \times [\text{MBA}] \end{aligned} \quad (2)$$

### Effect of Concentration on R<sub>p</sub>

Figure 1 shows typical polymerization curves showing the effect of dose and concentration on the conversion. The curves show no induction periods. It is observed that more than 90% conversion was achieved in 60 minutes of irradiation of MBA solution (170 mM) for dose rate 0.037 MRads/hr, whereas for lower concentrations the conversions reached a higher value much earlier. In all these cases, the conversions were found to increase linearly up to about 10-15% and decreased afterwards indicating reduction in the rates of polymerization due to reduced monomer concentrations afterwards.

The rates of conversion of MBA in aqueous solution are observed to be the fastest in radiation-chemical polymerizations of acrylamide. Polyacrylamide, however, is water-soluble, whereas poly-MBA immediately precipitates from the aqueous phase and steady state kinetics may not apply in this case. The rates of polymerizations of MBA were found to increase with an increase in monomer concentration as is obvious from Equation 2 of the solution polymerization. The graphs of log R<sub>p</sub> vs log M are linear. However, the average exponent of the monomer was

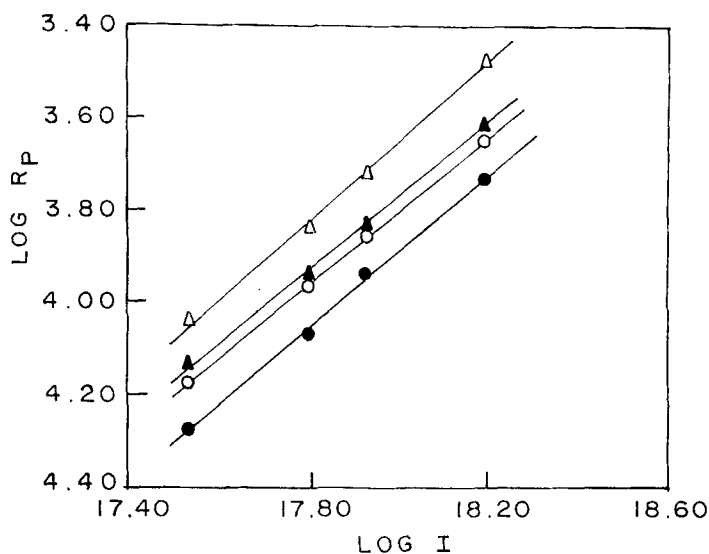


**Figure 1.** Graphs of conversion vs time of irradiation for different concentrations of MBA.  $\Delta$  - 36 mM.  $\Delta$  - 80 mM.  $\square$  - 117 mM.  $\bullet$  - 165 mM,  $\circ$  - 175 mM. Dose rate =  $6.4 \times 10^{17} \text{ ev dm}^{-3} \text{ S}^{-1}$

found to be 0.7 instead of 1. This deviation was attributed to the heterogeneous nature of the system and also to the very low concentration used in this study when steady state kinetics may not be applicable.

### Effect of Dose Rate

Figure 2 shows the plots of  $\log R_p$  vs.  $\log I$  for different monomer concentrations. The plots are linear indicating radical mechanism of polymerization. For radical radical termination reaction, the dose rate exponent is expected to be 1/2. However, if the polymer is insoluble in the monomer or in the solvent, this rule no longer holds good and the rate of polymerization is proportional to  $I^n$  where  $0.5 < n < 1$ . For MBA, the exponent has been observed to be 0.84. Polymer of MBA formed by radiation precipitates immediately on formation. In addition, the monomer concentration ( $\sim 100$  mmoles) is many orders of magnitudes lower compared to the concentration of the solvent water (55 moles), with the result that the radical radical termination reaction of the polymeric radicals is hindered and the termination is mostly by the abundantly available ( $\text{H}^\bullet$  and  $\text{OH}^\bullet$  radicals from water



**Figure 2.** Graphs of  $\log R_p$  vs  $\log I$  for different concentrations of M13A.  $\Delta$ -175 mM.  $\Delta$  - 117 mM. O - 105 mM.  $\bullet$  - 80 mM.

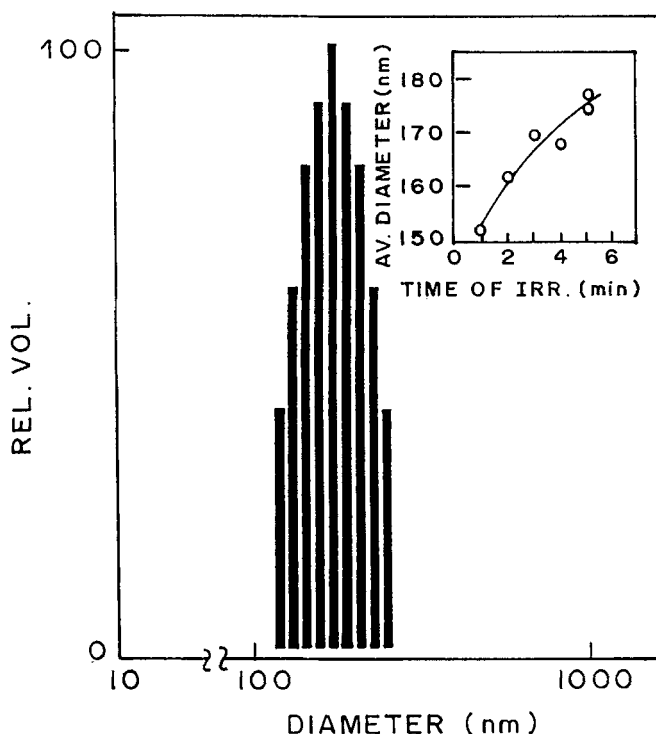
molecules produced by radiation. Similar behavior is observed in the case of radiation induced polymerization of acrylonitrile [14] where polyacrylonitrile is insoluble in the monomer and  $R_p$  is proportional to the dose rate to the power of 0.8. However, if the same polymerization is carried out in dimethyl formamide in which the polymer is soluble, the exponent was found to be 0.55 [14].

### The $k_p/k_t^{1/2}$ Value

The ratio of  $k_p/k_t^{1/2}$  is an important kinetic parameter in polymerization reactions, the knowledge of which can throw light on the relative rates of polymerizations of vinyl monomers. The ratio can be calculated from  $k_p/k_t^{1/2} = R_p/R_i^{1/2} [M]$ , if the rate of initiation or GR of the monomer is known. The ratio can also be calculated if the rates of polymerizations are known at different dose rates and monomer concentrations. From Table 1, the average value of the constant (average of the last four readings) was found to be 9.85 at the highest dose rate of  $1.54 \times 10^{18}$  eV dm<sup>-3</sup> s<sup>-1</sup>. The first value 49 appears to be too high and could not be explained.

### Particle Formation

Radiation induced polymerization of MBA gives a very good means of obtaining highly crosslinked even diameter particles with a narrow distribution [15].



**Figure 3.** Particle size distribution of poly MBA [MBA] = 7mM. Dose rate =  $1.2 \times 10^{18} \text{ ev dm}^{-3} \text{ S}^{-1}$

Figure 3 shows a typical graph of particle dimension vs. time of irradiation. The particle dimensions of the precipitated polymer as determined by BI-90 particle sizer showed mono disperse particles of an average diameter of about 170 nm. The variation of the particle dimensions with dose was found to be small. The particles were spherical and highly crosslinked since they were not found to be soluble in any solvent.

### Effect of Oxygen

The polymerization of MBA was found to be highly sensitive to the presence of oxygen i.e. a slight presence of oxygen in the solution was found to inhibit polymerization indicating radical nature of polymerization. From the graph of conversion vs time of irradiation for 170 mmol of MBA containing 0.6 mmols of dissolved oxygen induction period was found to be 33 minutes. The threshold dose required to consume all dissolved oxygen was calculated from this induction period



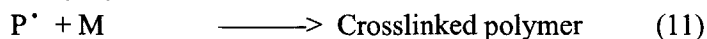
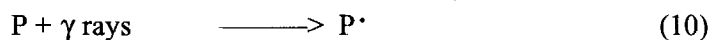
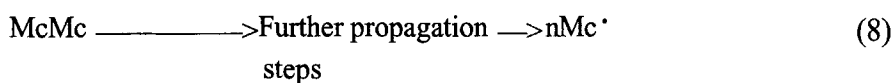
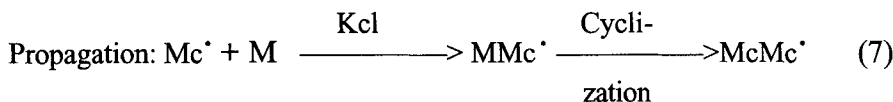
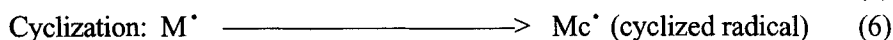
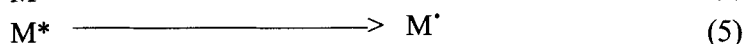
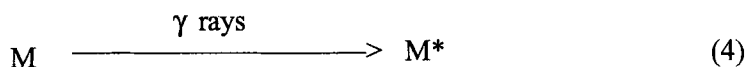
to be  $3.05 \times 10^{21} \text{ eV dm}^{-3}$ . From the threshold dose, G radical was calculated to be 11.8 ( $G_R = 100 \times [\text{O}_2] \times 6.023 \times 10^{23} \text{ threshold dose in eV per dm}^3$ ). This gives a broad idea of the total initiating radicals available for every 100 electron volts of gamma energy deposited in the matrix. They could be  $\text{H}^\bullet$  and  $\text{OH}^\bullet$  radicals from water molecules in addition to the radicals from the monomer formed by gamma radiation. The resulting monomer radical can be shown to be



In the earlier studies of chemically photopolymerization of MBA [6, 8, 10, 16, 17], initiated and intramolecular cyclization of the initiating radical forming a seven-membered ring was proposed. In our studies on pulse radiolysis of aqueous solution of MBA [18], we have given direct evidence of cyclization of this monomer radical prior to propagation. The rate constant  $K_{cl}$  for the first propagation step was also calculated to be  $6 \pm 0.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [15]. The study has confirmed that linear monovinyl-type propagation is sterically hindered due to long pendant groups with double bonds as proposed by R. Das *et al* [17]. MBA polymer obtained by gamma irradiation was found to be insoluble in pyridine water mixture which is the solvent for MBA polymer [6]. It was found to be insoluble in any other solvent indicating its highly crosslinked nature and the absence of any double bonds (IR of the polymer sample did not show any band corresponding to the double bond). The cyclized radical species propagates the chain with the addition of monomer units. Though linear propagation without ring formation is hindered, propagation after ring formation appears to form gel-free polymer soluble in pyridine-water in the case of chemically initiated polymerizations as observed by other workers. This is indicative of the fact that in radiation induced polymerization, part of the monomer acts as a crosslinking agent during polymerization. MBA, a divinyl monomer containing two double bonds can very efficiently crosslink the two growing chains. The reduction in the rate of polymerization with time (Figure 1) could be attributed to the participation of the monomer forming crosslinks. Secondly, radiation can produce radical sites on the precipitated polymer molecules which can act as termination centres for producing crosslinks.

Based on the above results, mechanism of polymerization initiated by gamma rays could be written in simple form as follows:





From the above results, it is observed that the free radical mechanism is followed in the polymerization reaction and that the kinetics is generally governed by Equation 2. The deviations from the ideal behavior could be explained from the basic heterogeneous nature of the system and the role played by abundant radicals (about 18 times) produced by water compared to those produced by the monomer.

## CONCLUSION

Aqueous solution of N,N'-Methylenebisacrylamide under polymerization by free radical mechanism producing highly crosslinked white flocculent polymer which is insoluble in the bulk matrix. Rates of polymerizations are of the order of  $10^{-4}$  moles  $\text{dm}^{-3} \text{ s}^{-1}$ . The value of the constant  $k_p/k_t^{1/2}$  was found 19.85 for the dose rate of  $1.54 \times 10^{18}$  eV  $\text{dm}^{-3} \text{ s}^{-1}$ . The precipitated polymer showed mono disperse particles of diameter about 170 nm. The monomer exponent 0.7 calculated from this graph is indicative of a more contribution from the solvent molecules in the polymerization reaction.

## LIST OF SYMBOLS USED IN THE PAPER

- (1) GR = Number of radicals formed per 100 eV of absorbed dose.
- (2)  $\lambda_{\text{max}}$  = Wavelength where monomer absorption is maximum
- (3)  $\epsilon$  = Extinction coefficient  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

- (4)  $R_{p, \text{sol}}$  = Rate of polymerization in solution  $\text{mol dm}^{-3} \text{s}^{-1}$ .  
(5)  $k_p, k_t$  = Rate constants for propagation and termination reactions in polymerization  
(6)  $R_i$  = Rate of initiation in polymerization

## REFERENCES

- [1] A. Gopalan, P. Venuvanalingam, S. P. Manickam, K. Venkatrao, and N. R. Subbaratnam, *Eur. Polym. J.*, **18**, 531 (1982).  
[2] S. Paulrajan, A. Gopalan, K. Venkatrao, and N. R. Subbaratnam, *Polymer*, **24**, 906 (1983).  
[3] T. Parthasarathy, K. Nageswar Rao, B. Sethuram, and T. Navneeth Rao, *J. Polym. Mater.*, **3**, 191 (1986).  
[4] N. R. Subbaratnam, S. P. Manickam, P. Venuvanalingam, and A. Gopalan, *J. Macromol. Sci.-Chem.*, **A23**, 117 (1986).  
[5] K. Behari, Uma Agrawal, and Rina Das, *J. Polym. Sci. Part A: Poly. Chem.*, Vol. 31, 1444 (1993).  
[6] B. Suresh Babu, K. Nageswar Rao, B. Sethuram, and T. Navaneeth Rao, *J. Macromol. Sci.-Chem.*, **A25(l)**, 109 (1988).  
[7] B. Suresh Babu, Bhagavanthu, K. Nageswar Rho, and B. Sethuram, *J. Polym. Mater.*, **13**, 121 (1996).  
[8] K. Behari, G. D. Raja, and K. C. Gupta, *Polym. Commun.*, **30(12)**, 372 (1989).  
[9] S. Rathnasabhpathy, N. Marisami, S. P. Manickam, K. Venkatrao, and N. R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25(l)**, 83 (1988).  
[10] S. Rathnasabhpathy, N. Marisami, S. P. Manickam, and N. R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25**, 97 (1988).  
[11] A. Gopalan, S. Paulrajan, K. Venkatrao, and N. R. Subbaratnam, *Euro. Polym. J.*, **19**, 817 (1983).  
[12] A. Gopalan, P. Venuvanalingam, S. P. Manickam, K. Venkatarao, and N. R. Subbaratnam, *Eur. Polym. J.*, **18**, 531 (1982).  
[13] A. Shapiro, "Radiation Chemistry of Polymeric Systems", p. 13 1, Interscience Publishers, John Wiley & Sons, Inc., 1962.  
[14] A. Shapiro, M. Magat, A. Prevot-Bemas, and J. Sebban, *J. Chim. Phys.*,  
[15] Yukihiro Naka and Yamamoto Yukihiro, *Chemistry-Letters, Tokyo*, **12**, 2263 (1993).

- [16] R. Das, K. Behari, and U. Agrawal, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 1449 (1993).
- [17] R. Das, K. Behari, and U. Agrawal, *Polym. Intern.*, **31**, 235 (1993).
- [18] M. S. Panajkar, S. N. Guha, and C. Gopinathan, *J. Macromol. Sci.-Pure Appl. Chem.*, **A32(1)**, 143 (1995).

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