

# The Study of Polymerization Kinetics of Methacrylamide by Oxidation: Reduction System Using Potassium Permanganate/Glycine in Aqueous Medium

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**ABSTRACT:** The polymerization kinetic of methacrylamide with the  $\text{KMnO}_4$ /glycine redox system has been investigated volumetrically at  $35 \pm 0.1^\circ\text{C}$  under nitrogen atmosphere in aqueous sulfuric acid medium in a dimethylsulfoxide/ $\text{H}_2\text{O}$  mixture (5% v/v). The rates of polymerization were found to obey the following equation:  $\bar{R}_p \propto [\text{Methacrylamide}]^{1.08}[\text{Glycine}]^{0.44}[\text{KMnO}_4]^{0.46}$ . A glycine end group containing polymethacrylamide was prepared by the  $\text{MnO}_4^-$ /glycine redox system under mild conditions. The

reaction proceeded with radical mechanism and the overall energy of activation ( $E_a$ ) was calculated to be 29.87 kJ/mol from the Arrhenius plot in the temperature range 25–50°C. Molecular weight of the polymer was determined by viscometry. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3918–3924, 2003

**Key words:** activation energy; calculation; kinetics (polymerization); radical polymerization

## INTRODUCTION

Various redox systems have been used successfully for the polymerization of organic vinyl monomers in aqueous media.<sup>1–10</sup> The interaction between the oxidizing and reducing agent proceeds with the formation and free radical mechanism.<sup>11</sup> In the polymerization of acrylamide, acrylonitrile, methacrylamide, methyl methacrylamide, and vinylacetate, the manganese dioxide is produced by the reaction between monomer and permanganate. Mn(VII) reacts with the reducing agent to yield highly reactive Mn(III) ions. These Mn(III) ions then generate active free radicals with the reducing agent.<sup>11</sup> Some hydroxy carboxylic acids such as malic,<sup>12</sup> tartaric,<sup>13</sup> citric,<sup>14</sup> lactic,<sup>15</sup> glyceric,<sup>16</sup> oxalic,<sup>1</sup> and  $\beta$ -hydroxybutyric<sup>17</sup> acids, and also some amino acids such as L-cystein<sup>18</sup> and glycine,<sup>11</sup> were used for the polymerization of acrylamide with permanganate in aqueous medium. The glycine end group containing polyacrylamide prepared by Ce(IV)/glycine or  $\text{MnO}_4^-$ /glycine redox systems, were used for the construction of immunologically active high molecular structures containing weakly bound structures destroyed at physiological conditions.<sup>19–20</sup> In the present article, the potassium permanganate/

glycine redox system was used to polymerize methacrylamide and the kinetics of polymerization of the monomer with this redox pair has been studied.

## EXPERIMENTAL

All chemicals used for preparation of solutions were products of E. Merck and Analar, B.D.H., and of G.R. grade. Methacrylamide (E. Merck) was recrystallized from methanol and dried in vacuum over phosphorous pentoxide. All the solutions were prepared using double-distilled water. The rate of monomer disappearance was followed by estimation of double bond monomer concentration after the polymerization by bromometry using the following equation given by Wallace et al.<sup>21</sup>:

$$\% \text{ conversion} = \frac{N(V_2 - V_1)M}{20w}$$

where  $N$  is the normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, and  $V_1$  and  $V_2$  are the volumes of this solution used at zero and different time intervals, respectively.  $M$  is the molecular weight of methacrylamide, and  $w$  is its weight in the sample.

Polymerization of methacrylamide was carried out in a Pyrex vessel equipped with gas inlet and outlet tubes. Calculated amounts of glycine solution, sulfuric acid, purified monomer solution, and dimethylsulfoxide (DMF)/ $\text{H}_2\text{O}$  (5% v/v), to make a final volume of 95 mL were taken in reaction vessel. Shielded from

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light and kept in a thermostat at  $35 \pm 0.1^\circ\text{C}$ . The content of the vessel were freed from dissolved oxygen by passing a stream of oxygen-free nitrogen gas. The reaction mixture was shaken to ensure effective mixing. After 1 h, polymerization was initiated by adding a calculated amount of potassium permanganate solution. At various time intervals the sample was drawn from the reaction mixture and injected into a known excess ice methanol. The polymer was precipitated and isolated. The rates of polymerization were followed volumetrically by the bromometry method.  $V_p$  was taken as the slope of the curve giving percentage of conversion vs time in the linear part of it. The polymethacrylamide samples were purified by twice precipitating from methanol and were dried under vacuum. The viscosity of very dilute aqueous solution of the polymer was measured automatically using the Schott Gerate, model AVS 400, viscometer at  $25^\circ\text{C}$ . The viscometer average molecular weight has been calculated from the equation given by the Mark-Houwink equation <sup>22</sup>:

$$[\eta]_{25^\circ\text{C}} = K[M]^\alpha$$

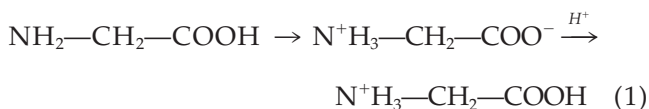
taking  $K=6.8 \times 10^{-4}$ ,  $\alpha=0.8$ , where the concentration of polymethacrylamide is in g/100 mL.

### RESULTS AND DISCUSSION

#### Mechanism

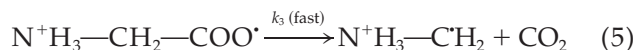
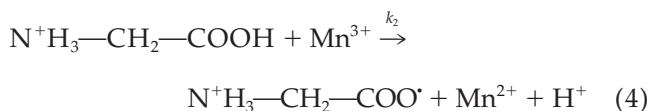
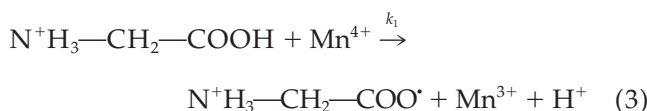
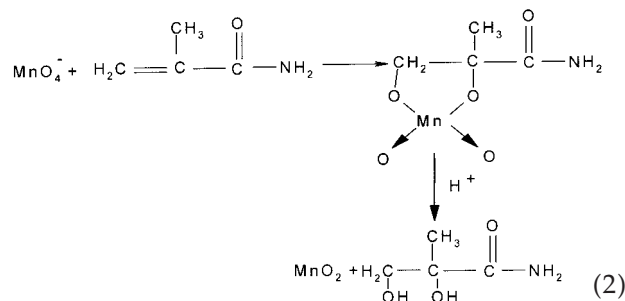
##### Free radical formation

The following mechanism has been suggested for the vinyl polymerization of methacrylamide initiated by potassium permanganate in aqueous sulfuric acid medium:



In the potassium permanganate/glycine redox system, the permanganate first reacts with methacrylamide and produces immediately a brownish black homogeneous solution due to the formation of manganese dioxide (step 2), which disappears slowly in presence of protonated glycine to produce highly reactive  $\text{Mn}^{3+}$  ions and free radicals ( $\text{N}^+\text{H}_3\text{—CH}_2\text{—COO}^\bullet$ ) (step 3). This manganese (III) ions further reacts with another molecule of protonated glycine to produce  $\text{Mn}^{2+}$  ions and free radicals ( $\text{N}^+\text{H}_3\text{—CH}_2\text{—COO}^\bullet$ ) (step 4). These free radicals

can be converted quickly to another type of free radical ( $\text{N}^+\text{H}_3\text{—CH}_2^\bullet$ ) by releasing of  $\text{CO}_2$  molecules (step 5).

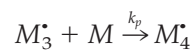


The free radicals thus generated attack at the double bond of methacrylamide to initiate the polymerization of this monomer. Taking the free radicals  $\text{N}^+\text{H}_3\text{—CH}_2^\bullet$ , the following kinetic scheme can be proposed:

##### Initiation



##### Propagation



⋮

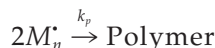


The rate of polymerization is a sum of many individual propagation steps and the constant ( $k_p$ ) for all propagation steps are more or less the same. There-

fore, the rate of polymerization can be expressed by the following equation:

$$V_p = k_p[M] \sum_{n=1}^{\infty} [M_n^{\bullet}]$$

Termination



The 0.5 power of rate of polymerization with respect to initiator confirms the bimolecular termination. Molecular weight of the polymer was measured by viscometry and high molecular weight polymer was obtained, which confirms the exponent 0.5 with respect to initiator. This may be due to the termination of the growing polymer chain by mutual combination.

### Rate expression

The concentration of primary free radicals  $N^+H_3-CH_2-COO^{\bullet}$  and  $N^+H_3-CH_2^{\bullet}$  as well as of growing radicals  $M_n^{\bullet}$  can be given as follows by applying the steady state assumption:

$$\begin{aligned} \frac{d[M_1^{\bullet}]}{dt} &= k_i[N^+H_3-CH_2^{\bullet}][M] - k_p[M_1^{\bullet}][M] \\ &\quad - 2k_t[M_1^{\bullet}]\{[M_1^{\bullet}] + [M_2^{\bullet}] + \dots + [M_n^{\bullet}]\} \end{aligned}$$

In the above mechanism,  $M_1^{\bullet}$  may react with another  $M_1^{\bullet}$ , or with  $M_2^{\bullet}$ , or with  $M_3^{\bullet}$ , or... or with  $M_n^{\bullet}$  and terminate to the chain-propagate reactions.

$$\begin{aligned} \frac{d[M_1^{\bullet}]}{dt} &= k_i[NH_3^+-C^{\bullet}H_2][M] - k_p[M_1^{\bullet}][M] \\ &\quad - 2k_t[M_1^{\bullet}] \sum_{n=1}^{\infty} [M_n^{\bullet}] = 0 \end{aligned}$$

$M_2^{\bullet}$  may react with  $M_1^{\bullet}$ , or with  $M_2^{\bullet}$ , or with  $M_3^{\bullet}$ , ... or with  $M_n^{\bullet}$ :

$$\begin{aligned} \frac{d[M_2^{\bullet}]}{dt} &= k_p[M_1^{\bullet}][M] - k_p[M_2^{\bullet}][M] \\ &\quad - 2k_t[M_2^{\bullet}] \sum_{n=1}^{\infty} [M_n^{\bullet}] = 0 \end{aligned}$$

And in the total case, for the radicals  $M_n^{\bullet}$ , we get

$$\frac{d[M_n^{\bullet}]}{dt} = k_p[M_{n-1}^{\bullet}][M] - 2k_t[M_n^{\bullet}] \sum_{n=1}^{\infty} [M_n^{\bullet}] = 0$$

From the sum of all these equations, we can derived the following relation:

$$\begin{aligned} &k_i[N^+H_3-CH_2^{\bullet}][M] \\ &\quad - 2k_t\{[M_1^{\bullet}] + [M_2^{\bullet}] + [M_3^{\bullet}] + \dots + [M_n^{\bullet}]\} \sum_{n=1}^{\infty} [M_n^{\bullet}] = 0 \\ &\quad \sum_{n=1}^{\infty} \end{aligned}$$

or

$$k_i[N^+H_3-CH_2^{\bullet}][M] - 2k_t \left( \sum_{n=1}^{\infty} [M_n^{\bullet}] \right)^2 = 0$$

or

$$\sum_{n=1}^{\infty} [M_n^{\bullet}] = \left( \frac{k_i[N^+H_3-C^{\bullet}H_2][M]}{2k_t} \right)^{1/2}$$

We know that

$$V_p = k_p[M] \sum_{n=1}^{\infty} [M_n^{\bullet}]$$

Hence

$$V_p = k_p[M] \left( \frac{k_i[N^+H_3-C^{\bullet}H_2][M]}{2k_t} \right)^{1/2} \quad (I)$$

The rate of polymerization can be derived by using eq. (I) and also determining the concentration of free radicals by applying the steady-state treatment.

The rate of production of free radical  $N^+H-CH_2^{\bullet}$  on applying the steady-state treatment is given as

$$\begin{aligned} \frac{d[N^+H_3-C^{\bullet}H_2]}{dt} &= k_2[N^+H_3-CH_2-COO^{\bullet}] \\ &\quad - k_t[M][N^+H_3-C^{\bullet}H_2] = 0 \end{aligned}$$

or

$$[N^+H_3-C^{\bullet}H_2] = \frac{k_3[N^+H_3-CH_2-COO^{\bullet}]}{k_t[M]} \quad (II)$$

Again, the rate production of free radical  $N^+H_3-CH_2-COO^{\bullet}$  on applying the steady-state treatment is given as

$$\begin{aligned} \frac{d[\text{N}^+\text{H}_3\text{—CH}_2\text{—COO}^*]}{dt} &= k_1[\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}][\text{M}_n^{4+}] \\ &+ k_2[\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}][\text{M}_n^{3+}] \\ &- k_3[\text{N}^+\text{H}_3\text{—CH}_2\text{—COO}^*] = 0 \end{aligned}$$

or

$$[\text{N}^+\text{H}_3\text{—CH}_2\text{—COO}^*] = \frac{[\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}]\{k_1[\text{M}_n^{4+}] + k_2[\text{M}_n^{3+}]\}}{k_3} \quad \text{(III)}$$

On substituting the value of  $[\text{N}^+\text{H}_3\text{—CH}_2\text{—COO}^*]$  from eq. (III) into eq. (II), we have

$$[\text{N}^+\text{H}_3\text{—C}^*\text{H}_2] = \frac{[\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}]\{k_1[\text{M}_n^{4+}] + k_2[\text{M}_n^{3+}]\}}{k_i[M]} \quad \text{(IV)}$$

On substituting the value of  $[\text{N}^+\text{H}_3\text{—CH}_2^*]$  from eq. (IV) into eq. (I), we get the following expression:

$$V_p = k_p[M] \left( \frac{k_i[\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}]^{1/2} \times \{k_1[\text{M}_n^{4+}] + k_2[\text{M}_n^{3+}]\}[M]}{2k_i k_i[M]} \right)^{1/2}$$

or

$$V_p = \frac{k_p}{(2k_i)^{1/2}} [M][\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}]^{1/2} \times \{k_1[\text{M}_n^{4+}] + k_2[\text{M}_n^{3+}]\}^{1/2}$$

Since both  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  ions are derived from  $\text{KMnO}_4$ , the term  $\{k_1[\text{Mn}^{4+}] + k_2[\text{Mn}^{3+}]\}$  is supposed to be equivalent to  $[\text{KMnO}_4]$ . Thus, finally, we get the expression:

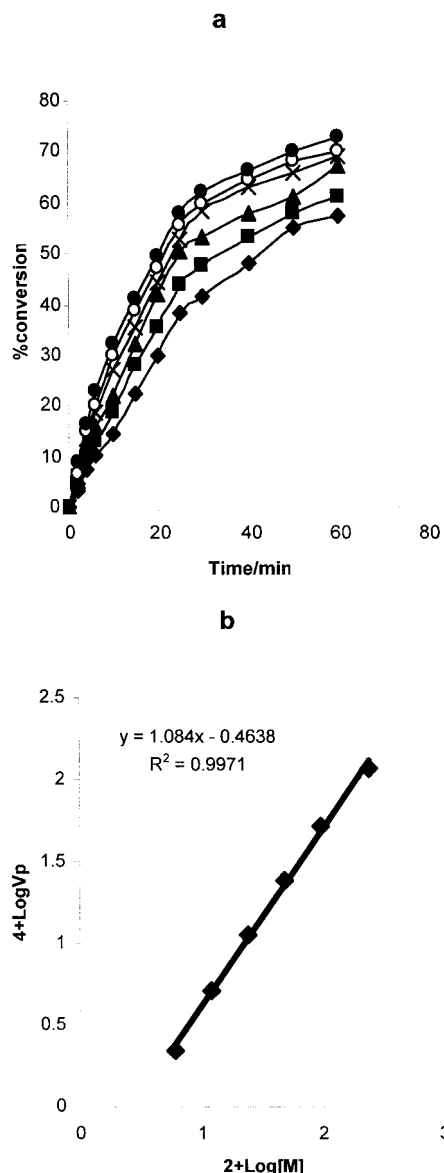
$$V_p = k[M][\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}]^{1/2}[\text{KMnO}_4]^{1/2}$$

This expression confirms all the experimental observations to a satisfactory extent.

Addition of *P*-benzoquinone as radical scavenger, completely retarded this polymerization reaction, which confirms a free radical mechanism for the polymerization reaction.

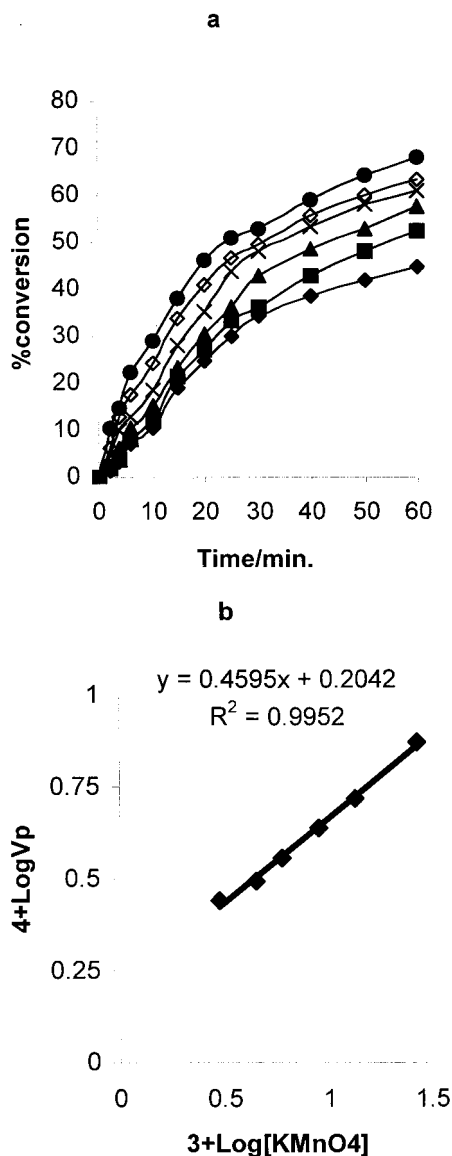
**Effect of monomer concentration on reaction rate**

The study of polymerization at different intervals of time on varying the concentration of monomer in the range of 0.06 to 1.92 mol/L [Fig. 1(a)] shows that the initial rate and maximum conversion increases with



**Figure 1** (a) Plot of initial course of polymerization of methacrylamide for various initial concentration of monomer at fixed  $[\text{KMnO}_4]=9.00 \times 10^{-3}$  mol/L,  $[\text{glycine}]=4.50 \times 10^{-2}$  mol/L,  $\text{pH}=2.5$ ,  $35 \pm 0.1^\circ\text{C}$ . ( $\blacklozenge$ ) 0.06, ( $\blacksquare$ ) 0.12, ( $\blacktriangle$ ) 0.24, ( $\times$ ) 0.48, ( $\circ$ ) 0.96, and ( $\bullet$ ) 1.92 mol/L. (b) Logarithmic plot of the initial rate of polymerization ( $V_p$  in % conversion per minute) vs the initial concentration of monomer, slope=1.08.

increasing concentration of monomer. As the concentration of the monomer is increased, a large number of monomer units become available for production of more free radicals—thus the rate of polymerization increases. The  $\text{Log } V_p$ , i.e., percent conversion per minute at the 25th minute vs  $\text{Log}[M]$  plot [Fig. 1(b)] indicates that the order with respect to the monomer is 1.08, which confirms the first power dependence of the rate on monomer concentration.

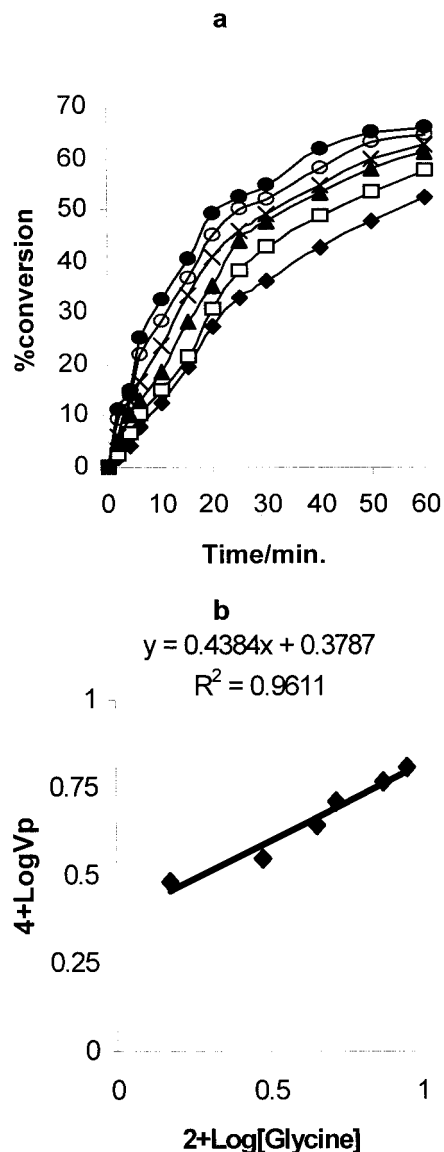


**Figure 2** (a) Plot of initial course of polymerization of methacrylamide for various initial concentration of  $\text{KMnO}_4$  at fixed  $[M]=0.12$  mol/L,  $[\text{glycine}]=4.50 \times 10^{-2}$  mol/L,  $\text{pH}=2.5$ ,  $35 \pm 0.1^\circ\text{C}$ . ( $\blacklozenge$ )  $3.00 \times 10^{-3}$ , ( $\blacksquare$ )  $4.50 \times 10^{-3}$ , ( $\blacktriangle$ )  $6.00 \times 10^{-3}$ , ( $\times$ )  $9.00 \times 10^{-3}$ , ( $\circ$ )  $1.35 \times 10^{-2}$ , and ( $\bullet$ )  $2.70 \times 10^{-2}$  mol/L. (b) Logarithmic plot of the initial rate of polymerization ( $V_p$  in % conversion per minute) vs the initial concentration of  $\text{KMnO}_4$ , slope=0.46.

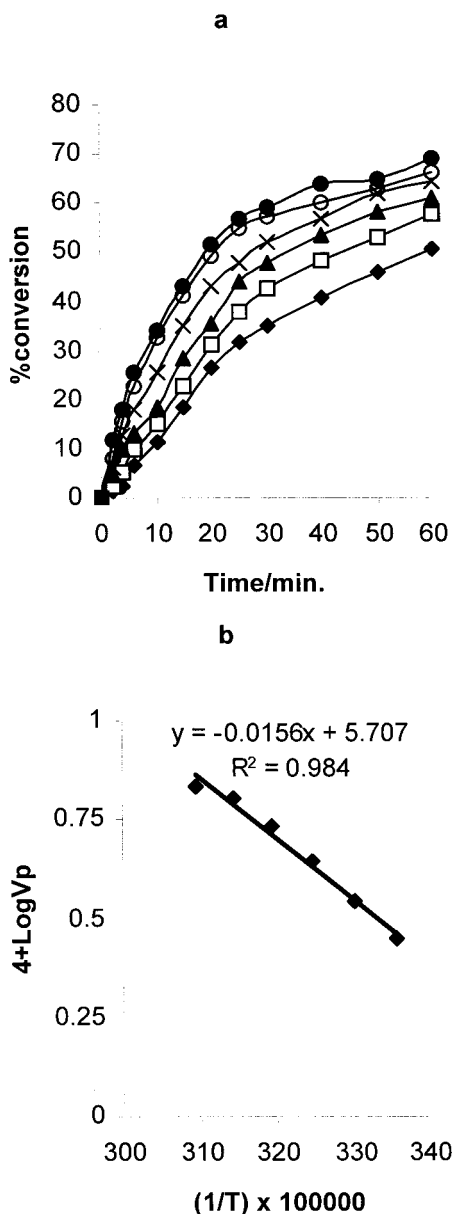
#### Effect of potassium permanganate concentration on reaction rate

The effect of  $\text{KMnO}_4$  concentration on the rate of polymerization was studied by varying the concentration of potassium permanganate in the range of  $3.00 \times 10^{-3}$  to  $2.70 \times 10^{-2}$  mol/L. Figure 2(a) shows how the rate of polymerization and percentage conversion changed with respect to the concentration of  $\text{KMnO}_4$ . On increasing the  $\text{KMnO}_4$  concentration, the initial rate and percentage conversion increases. This may be

due to the fact that when the  $\text{KMnO}_4$  concentration is increased, the rate of production of primary radicals, the number of free radicals, and hence the number of propagating polymer radicals increase, which obviously results in an increase in the polymerization rate and the percentage conversion. The rate of polymerization has been found to show 0.46 power dependence on the  $\text{KMnO}_4$  concentration [Fig. 2(b)], which indicates the order of reaction with respect to the  $\text{KMnO}_4$  concentration to be 0.5. The 0.5 power also confirms the existence of a bimolecular mechanism for



**Figure 3** (a) Plot of initial course of polymerization of methacrylamide for various initial concentration of glycine at fixed  $[M]=0.12$  mol/L,  $[\text{KMnO}_4]=9.00 \times 10^{-3}$  mol/L,  $\text{pH}=2.5$ ,  $35 \pm 0.1^\circ\text{C}$ . ( $\blacklozenge$ )  $1.50 \times 10^{-2}$ , ( $\square$ )  $3.50 \times 10^{-2}$ , ( $\blacktriangle$ )  $4.50 \times 10^{-2}$ , ( $\times$ )  $6.00 \times 10^{-2}$ , ( $\circ$ )  $7.50 \times 10^{-2}$ , and ( $\bullet$ )  $9.00 \times 10^{-2}$  mol/L. (b) Logarithmic plot of the initial rate of polymerization ( $V_p$  in % conversion per minute) vs the initial concentration of monomer, slope=0.44.



**Figure 4** (a) Plot of initial course of polymerization of methacrylamide varying temperature at fixed  $[M]=0.12$  mol/L,  $[\text{KMnO}_4]=9.00 \times 10^{-3}$  mol/L,  $[\text{glycine}]=4.50 \times 10^{-2}$  mol/L,  $\text{pH}=2.5$ ,  $35 \pm 0.1^\circ\text{C}$ . ( $\blacklozenge$ ) 25, ( $\square$ ) 30, ( $\blacktriangle$ ) 35, ( $\times$ ) 40, ( $\circ$ ) 45, and ( $\bullet$ )  $50^\circ\text{C}$ . (b) Logarithmic plot of the initial rate of polymerization vs  $(1/T) \times 10^5$  (in K). Energy of activation  $E_a=29.87$  kJ/mol.

the termination reaction half-order correlation between the rate and the  $\text{KMnO}_4$  concentration has also been observed by other workers, who studied with other vinylic monomers like acrylamide.<sup>16,23,24</sup>

#### Effect of glycine concentration on reaction rate

The initial rate of polymerization and the percentage of conversion are found to increase with increasing

concentration of glycine in the studied range of  $1.50 \times 10^{-2}$  to  $9.00 \times 10^{-2}$  mol/L [Fig. 3(a)]. When the initial concentration of glycine is increased, the number of initiating species (free radicals) increases, which results in both the initial rate of polymerization and percentage conversion. The order of reaction with respect to glycine concentration, calculated from the slope of the logarithmic plot of  $V_p$  (in % conversion/min) vs the initial concentration of glycine, has been found to be 0.44 [Fig. 3(b)], thus showing a half-order dependence of the rate of polymerization of glycine concentration.

#### Effect of temperature on reaction rate

The effect of temperature has been studied between 30 and  $50^\circ\text{C}$ . The initial rate, as well as percentage conversion, increases with increasing temperature [Fig. 4(a)]. This increase is probably due to the rise in the active center formation and chain propagation. From the Arrhenius plot of  $\text{Log} V_p$  vs  $1/T$  (slope =  $-E_a/R$ ) [Fig. 4(b)], the overall energy of activation ( $E_a$ ) was calculated to be 29.87 kJ/mol. A lower energy of activation allows the redox polymerization to be carried out under mild conditions.

#### CONCLUSION

Metacrylamide is polymerized in a nitrogen atmosphere by the redox system of potassium permanganate/glycine via a free-radical mechanism. The polymerization reaction with respect to monomer is 1.08, and the reaction orders related to the potassium permanganate and glycine concentrations are 0.46 and 0.44, respectively, which indicates bimolecular mechanism for the termination reaction. On the basis of the results obtained, a suitable reaction mechanism is suggested and the following rate equation is derived:

$$V_p = k[M]^{1.08}[\text{N}^+\text{H}_3\text{—CH}_2\text{—COOH}]^{0.44}[\text{KMnO}_4]^{0.46}$$

From the Arrhenius plot, the overall energy of activation ( $E_a$ ) has been calculated to be 29.87 kJ/mol in the investigated range of temperatures.

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