



Aqueous Polymerization of Methyl Methacrylate Initiated by Manganese(III)- Glycine redox System in Aqueous Sulphuric acid Medium : a kinetic study.

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INTRODUCTION :

Redox polymerization of vinyl monomers initiated by transition metals in their higher oxidation states in an aqueous medium can provide valuable information regarding the mechanistic details of the elementary steps¹⁻¹¹. Alpha amino acids are the fundamental building blocks of proteins which take part in all life processes; their physical and the chemical properties are due to the presence of both acidic and basic functional groups. Glycine has been used in conjunction with a number of oxidizing agents, such as KMnO_4 ¹², halogens¹³, Chloramine-T¹³, Fe^{3+} ¹³, $\text{S}_2\text{O}_8^{2-}$ ¹³. The superiority of the system lies in the fact that no modifier needs to be added from outside to regulate the molecular weight of the polymer, because glycine itself acts as a modifier¹². This paper reports a kinetic study of a polymerization reaction of methyl methacrylate initiated by the manganese (III) – glycine redox system in aqueous sulfuric acid medium in the temperature range of 40-55°C. Several features, including the biological role of manganese, its ability to interact with a broad range of electron donors^{14,15}, the anomalous kinetic behavior associated with methyl methacrylate polymerization in aqueous medium¹⁶, and the importance of polymethyl methacrylate in the fibre industry, have stimulated the choice of this study. Electrochemically-generated manganese (III) sulphate in aqueous sulfuric acid has been employed in the present investigation.

EXPERIMENTAL :

Preparation of reagents: Methyl methacrylate(SISCOCHEM India) was purified by the method of Bamford and Jenkins¹⁷. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was an E. Merck GR Product. All other chemicals such as glycine, sodium bisulfate, sulphuric acid, sodium perchlorate, ferrous ammonium sulphate, sodium oleate, zinc sulfate, cetyl-trimethyl ammonium bromide and Triton-X-100 were of analytical grade.

Aqueous manganese (III) stock solutions were freshly prepared by electrolytic oxidation of an appropriate manganese (II) solution and used. The total manganese (II) concentration in the solution was determined by EDTA titration, while the manganese (III) concentration was determined by iodometry¹⁸. Triply distilled water was used throughout the experiment. Pure nitrogen, obtained by passing through a column of Fieser's solution and distilled water, was used for the deaeration of all experimental systems.

KINETIC MEASUREMENTS:

Reactions are performed under the inert atmosphere of nitrogen in pyrex glass vessels. In a typical kinetic run, a mixture of solutions containing requisite amount of the methyl methacrylate monomer [M], glycine, manganese(II), the acid (sulphuric acid + sodium bisulphate to maintain known acid concentration), sodium perchlorate (to maintain a constant ionic strength) and water (to keep the total volume constant) is thermally equilibrated in a water bath at a desired temperature. A wash bottle containing an aqueous solution of methyl methacrylate, whose concentration is the same as in the reaction vessel, is interposed between the nitrogen train and the reaction vessel to avoid any loss of monomer during deaeration. Oxygen free nitrogen is bubbled through the solution for a given period (ca. 30min) and then the solution of the oxidant manganese(III), is added. The reaction vessel is sealed with a rubber gasket. The reaction is arrested by adding a known amount of standard ferrous ammonium sulphate or by cooling the reaction mixture to 0°C and blowing air in. The rate of manganese(III) disappearance ($-R_m$) is followed spectrophotometrically at its max (490nm) by determining the concentration of manganese(III) before and after polymerization. The initial rate of polymerization (R_p) is determined gravimetrically. The molecular weights M of the purified samples of polymer is determined by the viscosity method using the equation, $[\eta] = (5.2 \times 10^{-3})M_v^{0.76}$ at 30°C for PMMA in benzene solvent.

RESULTS AND DISCUSSION:

The polymerization of methyl methacrylate initiated by manganese (III) – glycine redox systems takes place at a measurable rate at 40°C. Although no induction period is observed under deaerated conditions, there exists an induction period if the solution is not deaerated. Thus it is evident that the polymerization is initiated by free radicals formed in situ by the redox system. The steady state is attained within 60 minutes.

The rate of manganese(III) disappearance ($-R_m$) is first order with respect to manganese(III) and is independent of methyl methacrylate concentration. It depends on $[Mn(III)]$ and $[glycine]$. A plot of $-1/R_m$ versus $1/[glycine]$ is linear with an intercept on the rate axis, indicating Lineweaver – Burk kinetics for complex formation¹⁹ (Fig. 1a).

Effect of monomer concentration:

The effect of monomer concentration on polymerization rate (R_p) is studied in the region in the (0.0563- 0.1877 mol dm⁻³) The initial rate and percentage conversions are found to increase with the increase in monomer concentration. When the concentration of the monomer increased, the availability of monomer molecules in the propagation step increases, which obviously increases the rate of polymerization. The exponent with respect to monomer concentration is found to be 1.5(Fig.1b).

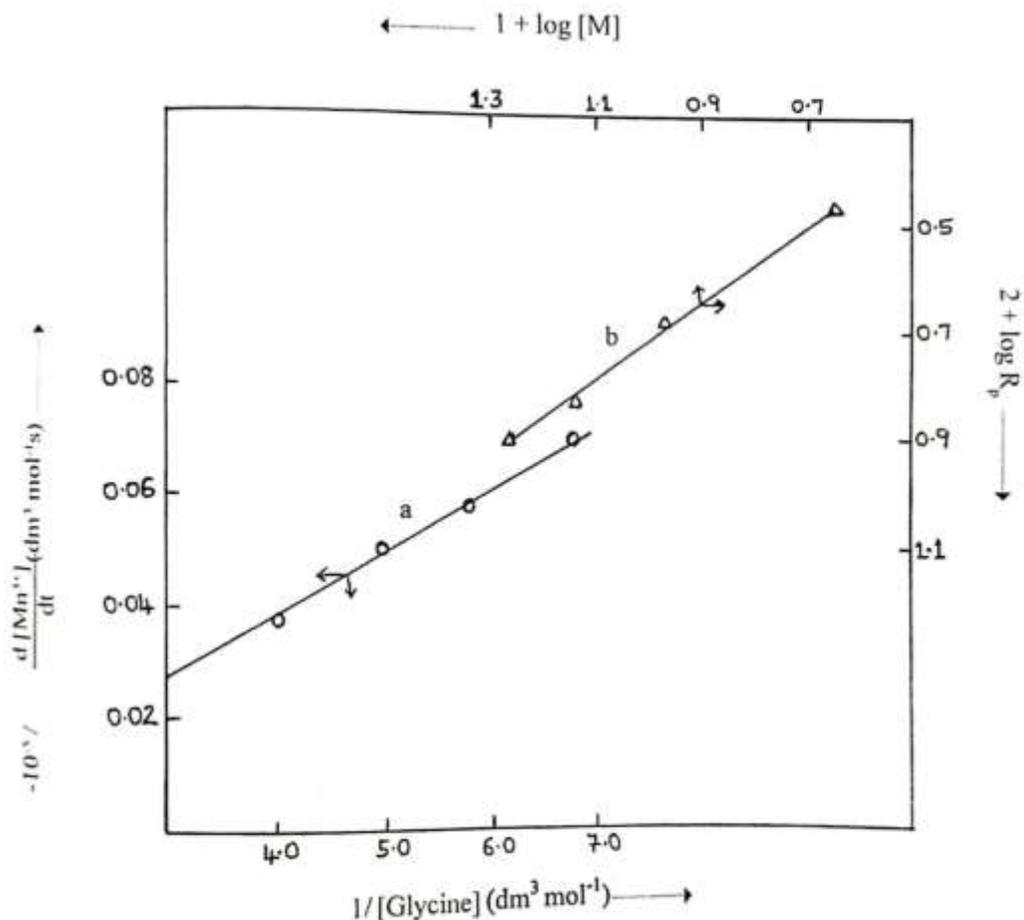


Fig.1(a) Plot of the reciprocal of the rate of Mn^{3+} disappearance versus $1/[Glycine]$, $[Mn^{3+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[Mn^{2+}] = 0.1 \text{ mol dm}^{-3}$, $[Glycine] = 0.15, 0.175, 0.2 \text{ and } 0.25 \text{ mol dm}^{-3}$, $[MMA] = 0.1314 \text{ mol dm}^{-3}$, $[H^+] = 1.5 \text{ mol dm}^{-3}$, $I = 7.0 \text{ mol dm}^{-3}$, $Temp = 313 \text{ K}$.

Fig.1(b) $\log R_p$ versus $\log[M]$, $[Mn^{3+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[Mn^{2+}] = 0.1 \text{ mol dm}^{-3}$, $[Glycine] = 0.2 \text{ mol dm}^{-3}$, $[MMA] = 0.0563, 0.0939, 0.1314 \text{ and } 0.1690 \text{ mol dm}^{-3}$, $[H^+] = 1.5 \text{ mol dm}^{-3}$, $I = 7.0 \text{ mol dm}^{-3}$, $Temp = 313 \text{ K}$.

Effect of manganese (III) concentration:

The initial rate as well as the maximum conversion increases with increases in the manganese(III) concentration in the range $(2.5-10.0) \times 10^{-3} \text{ mol dm}^{-3}$. This is due to the fact that, increases in manganese(III) concentration increases the rate of production of primary radicals, and hence, the number of propagating polymer radicals, which in turn increases the polymerization rate and the, maximum conversion. The order with respect to manganese(III) concentration is found to be one half from a plot of $\log R_p$ Versus $\log [Mn(III)]$ (Fig.2a), which clearly indicates that termination occurs through bimolecular interaction of growing polymer chain radicals. The M_v decreases with increase of manganese(III) concentration, which can be explained with the fact that increasing concentration of manganese(III) provides more chance for premature termination of growing chain radicals, which in turn reduces the degree of polymerization^{20,21}.

Effect of glycine concentration:

The initial rate and limiting conversion is found to increase with concentration of glycine in the range $(0.152-0.25 \text{ mol dm}^{-3})$. When the initial concentration of glycine is increased, the rate increases due to the production of primary radical. The exponent of glycine concentration is found to be one half from the plot of

$\log R_p$ versus $\log [\text{glycine}]$. The decrease in M_v further supports the possibility of bimolecular termination by mutual combination of growing polymer chain radicals (Fig.2b).

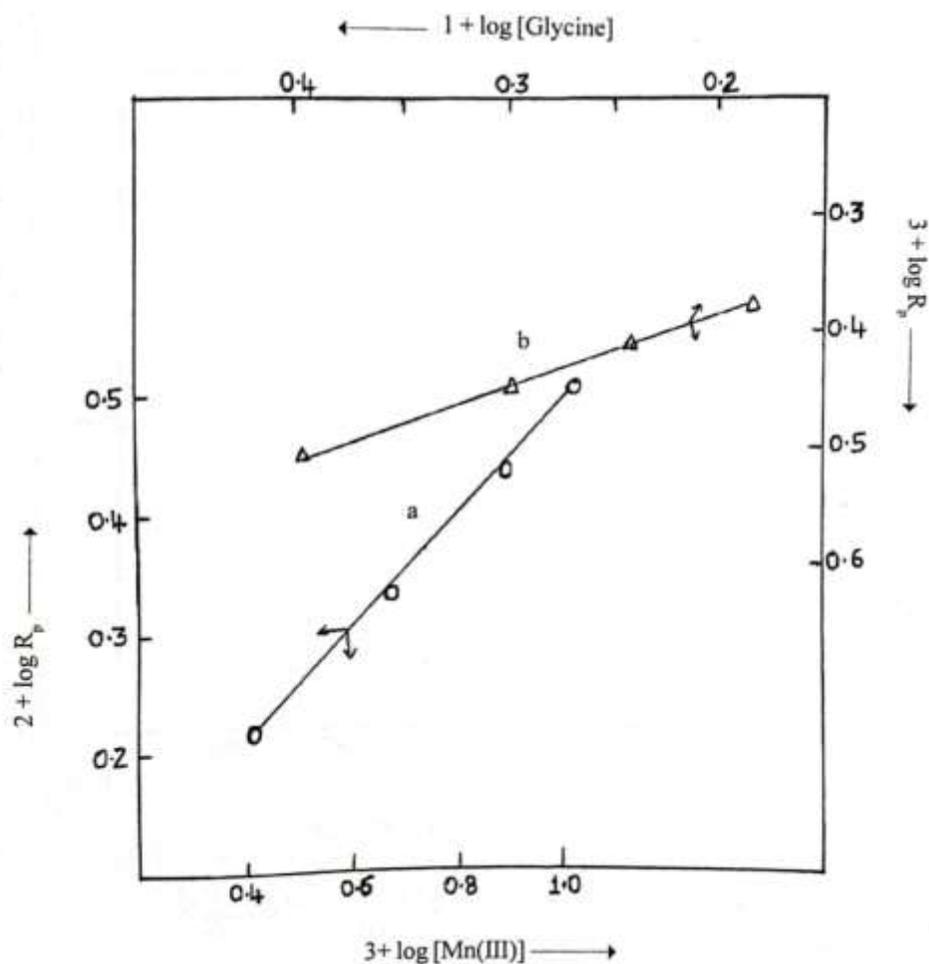


Fig.2(a) Plot of $\log R_p$ versus $\log [\text{Mn}^{3+}]$, $[\text{Mn}^{3+}] = 2.5 \times 10^{-3}, 5.0 \times 10^{-3}, 7.5 \times 10^{-3}$ and $10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}] = 0.1 \text{ mol dm}^{-3}$, $[\text{Glycine}] = 0.2 \text{ mol dm}^{-3}$, $[\text{MMA}] = 0.1314 \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.5 \text{ mol dm}^{-3}$, $I = 7.0 \text{ mol dm}^{-3}$, $\text{Temp} = 313 \text{ K}$.

Fig.2(b) Plot of $\log R_p$ versus $\log [\text{Glycine}]$, $[\text{Mn}^{3+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}] = 0.1 \text{ mol dm}^{-3}$, $[\text{Glycine}] = 0.152, 0.175, 0.2$ and 0.25 mol dm^{-3} , $[\text{MMA}] = 0.1314 \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.5 \text{ mol dm}^{-3}$, $I = 7.0 \text{ mol dm}^{-3}$, $\text{Temp} = 313 \text{ K}$.

Effect of H^+ ion concentration:

Kinetic measurements are performed in H_2SO_4 - NaHSO_4 solutions of different H^+ ion concentration. The effective hydrogen ion concentrations are evaluated from the calibration plot of Kemp and Waters²². The rate of polymerization decreases with an increase in H^+ ion concentration indicating that the hydrolyzed species of manganese(III) is more reactive than unhydrolyzed species, and also that the unprotonated form of glycine is more reactive than the protonated form. The order with respect to H^+ ion concentration is found to be unity from the plot of $\log R_p$ versus $\log [\text{H}^+]$ (Fig.3b).

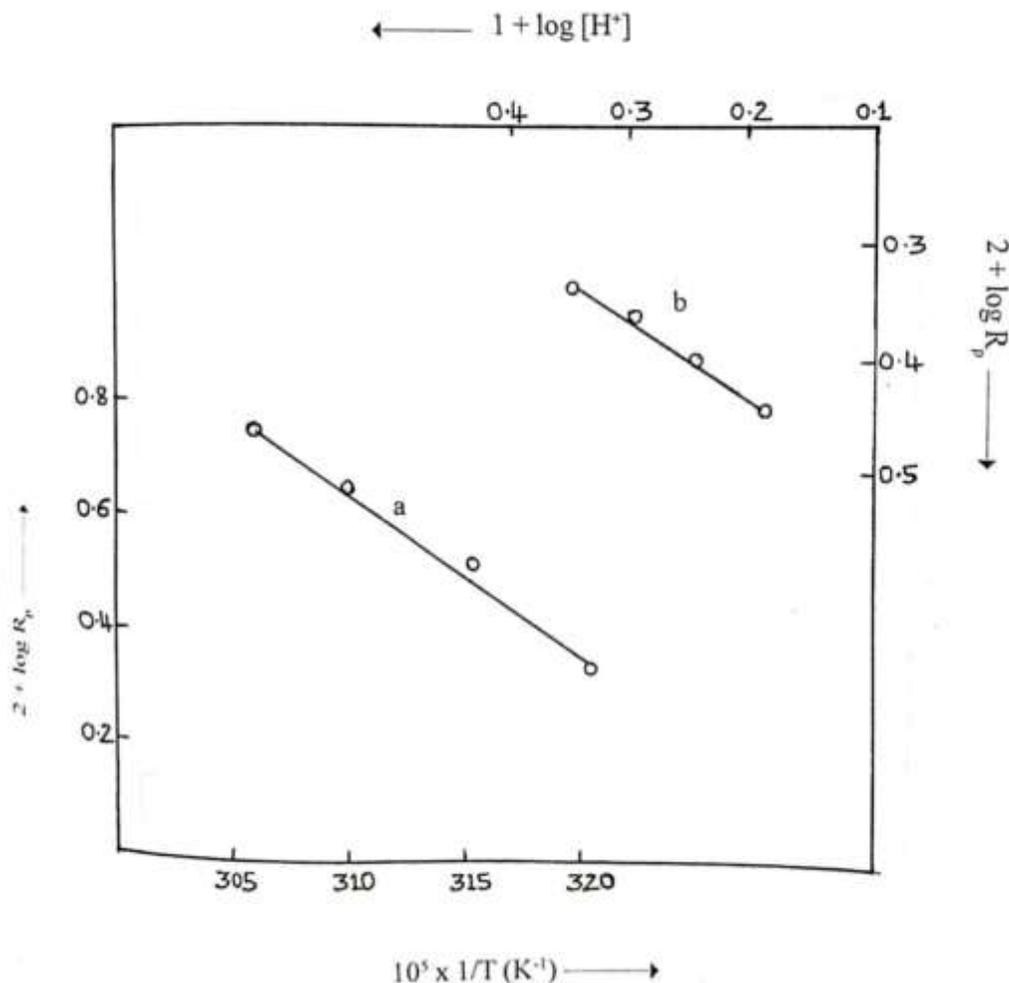


Fig.3(a) Plot of $\log R_p$ versus $1/T$, $[Mn^{3+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[Mn^{2+}] = 0.1 \text{ mol dm}^{-3}$, $[Glycine] = 0.2 \text{ mol dm}^{-3}$, $[MMA] = 0.1314 \text{ mol dm}^{-3}$, $I = 7.0 \text{ mol dm}^{-3}$, Temp = 313, 318, 323 and 328K.

Fig.3(b) Plot of $\log R_p$ versus $\log [H^+]$, $[Mn^{3+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[Mn^{2+}] = 0.1 \text{ mol dm}^{-3}$, $[Glycine] = 0.2 \text{ mol dm}^{-3}$, $[MMA] = 0.1314 \text{ mol dm}^{-3}$, $[H_2SO_4] + [NaHSO_4] = 3.545 \text{ mol dm}^{-3}$, $I = 7.0 \text{ mol dm}^{-3}$, Temp = 313K.

Effect of organic solvents:

Addition of water miscible – organic solvents (5% v/v) such as MeOH, EtOH and DMF to the reaction mixture depresses the initial rate as well as the maximum conversion. This is probably due to the decrease in the area of shielding of a strong hydration in the aqueous medium, resulting in the termination of radical end of the growing chain, or due to the increase in the regulated rate of production of primary radicals caused by the solvent, which renders the termination rate to be relatively fast compared to the growth of the polymer chains, as shown by Schulz et al²³. Konar and palit²⁴ have made similar observation even with the homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking the polymer chain is not rigid causing a premature mutual combination of the polymer chains.

Effects of surfactants on the rate:

Addition of anionic surfactant, sodium oleate increases the R_p above and below the CMC value. The cationic surfactants like, cetyl trimethyl ammonium bromide decreases the rate above and below the CMC value. In contrast, the non-ionic surfactants like Triton X-100 have no effect on the rate. Hydrophobic interactions and electrostatic attractions are mainly responsible for the enhancement or the inhibition of the rate of polymerization.

Effect of ionic strength (I):

The rate of polymerization decreases when the ionic strength of the medium increased by varying NaClO_4 concentration, showing a negative salt effect. But when the ionic strength is varied by using ZnSO_4 , there is an increase in the rate of polymerization due to the catalyzing effect of SO_4^{2-} .

Effect of added salts:

Manganese(II) is the reduced product of the oxidant and its effect on reaction is investigated. As the initial concentration of manganese(II) is increased, the rate of polymerization progressively decreases. This indicates that Mn(IV) is not involved in the oxidation reaction.

The effect of complexing agents like pyrophosphate, fluoride and chloride ions on the rate of reaction are also investigated. Addition of sodium pyrophosphate, sodium chloride or sodium fluoride had a retardation effect. This may be attributed to the displacement of co-ordinate sulphate ligand leading to the establishment of a new Mn(III)-Mn(II) couple with $\text{P}_2\text{O}_7^{4-}$, F^- , Cl^- as ligands such redox couples have lower redox potentials, thereby decreasing the rate. This also means that Mn(III) is the reactive species under experimental conditions.

Sulphate ions had catalytic effect on the rate of polymerization. Added $[\text{SO}_4^{2-}]$ was varied between $(1.68-1.92 \text{ mol dm}^{-3})$ at constant ionic strength, $[\text{H}^+]$ and temperature. The rate of polymerization increased gradually. This behavior has been explained with the aid of additional equilibrium.



This brings down the effective $[\text{H}^+]$ in the reaction mixture, thereby increasing the rate of reaction.

Effect of temperature:

The rate of polymerization increases with temperature. At a higher temperature the maximum conversion decreases. The energy of activation is calculated from the Arrhenius plot of $\log R_p$ versus $1/T$ in the temperature range $40-55^\circ\text{C}$ is $52.65 \pm 0.5 \text{ kJ mol}^{-1}$. The overall thermodynamic parameters are, $G^\ddagger = 196.70 \text{ kJ mol}^{-1}$, $H^\ddagger = 49.73 \text{ kJ mol}^{-1}$, $S^\ddagger = -469.58 \text{ JK}^{-1} \text{ mol}^{-1}$ (Fig. 3a). Δ

Mechanism and the rate law:

It has been assumed that manganese(III) species present in sulphuric acid are $\text{Mn}^{3+}(\text{aq})$, $\text{Mn(OH)}^{2+}(\text{aq})$ and MnSO_4 . Since the effect of HSO_4^- ion on the reaction under investigation is negligible, the role of MnSO_4 is ruled out. Therefore a combined role of $\text{Mn}^{3+}(\text{aq})$ and $\text{Mn(OH)}^{2+}(\text{aq})$ can be envisaged as observed in many manganese(III) reactions. In fact $\text{Mn(OH)}^{2+}(\text{aq})$ should be considered as more reactive in view of the decrease in rate with increase in $[\text{H}^+]$.

Amino acids exist as cations $\text{RCH}^+(\text{NH}_3)\text{COOH}$ in the strongly acidic medium. The most likely reaction mechanism, which can satisfactorily explain the observed data, is as below,

$$d/dt[\text{complex}] = k_1[\text{Mn}^{3+}] [\text{AH}^+] - k_{-1}[\text{complex}]x [\text{H}^+] - k_2[\text{complex}] = 0 \dots\dots\dots(11)$$

$$[\text{complex}] = k_1[\text{Mn}^{3+}] [\text{AH}^+] /k_2 + k_{-1} [\text{H}^+] \dots\dots\dots(12)$$

$$-d[\text{Mn}^{3+}]/dt = k_1k_2 [\text{Mn}^{3+}] [\text{AH}^+] /k_2 + k_{-1} [\text{H}^+] \dots\dots\dots(13)$$

$$d/dt [\text{R}\cdot] = k_2[\text{complex}] - k_{-2}[\text{R}\cdot][\text{Mn}^{2+}][\text{H}^+] - k_0[\text{R}\cdot][\text{Mn}^{3+}] - k_i[\text{R}\cdot][\text{M}] = 0 \dots\dots\dots(14)$$

$$[\text{R}\cdot] = k_1k_2 [\text{Mn}^{3+}] [\text{AH}^+] / \{ k_2 + k_{-1} [\text{H}^+] \} \{ k_{-2}[\text{Mn}^{2+}][\text{H}^+] + k_0[\text{Mn}^{3+}] - k_i[\text{M}] \} \dots\dots\dots(15)$$

Since the propagation is the stage that involves the major consumption of the monomer, the rate of monomer loss can be expressed in terms of propagation only:

$$R_p = -d[\text{M}] / dt = k_p[\text{RM}\cdot_x] [\text{M}] \dots\dots\dots(16)$$

Based on the usual assumption that the radical reactivity is independent of the radical chain length, the rate of polymerization becomes,

$$R_p = k_p [\text{RM}\cdot_x] [\text{M}] \dots\dots\dots(17)$$

In the over all polymerization, the rate of initiation and the rate of termination become equal, resulting in a steady concentration of free radicals.

$$k_i[\text{R}\cdot][\text{M}] = k_t [\text{R}\cdot\text{M}\cdot_x]^2 \dots\dots\dots(18)$$

$$[\text{R}\cdot\text{M}\cdot_x] = (k_i / k_t)^{1/2} [\text{R}\cdot]^{1/2}[\text{M}]^{1/2} \dots\dots\dots(19)$$

Thus,

$$R_p = k_p(k_i/k_t)^{1/2} \{ [\text{M}]^{3/2} [k_1k_2[\text{Mn}^{3+}][\text{AH}^+]/\{k_2+k_{-1}[\text{H}^+]\} \{ k_{-2}[\text{Mn}^{2+}][\text{H}^+] + k_0[\text{Mn}^{3+}] - k_i[\text{M}] \}]^{1/2} \} \dots\dots\dots(20)$$

$$R_p = k_p(k_1k_2k_i/k_t)^{1/2} \{ [\text{M}]^{3/2} [\text{Mn}^{3+}]^{1/2} [\text{AH}^+]^{1/2} / \{ k_2 + k_{-1}[\text{H}^+] \}^{1/2} \{ k_{-2}[\text{Mn}^{2+}][\text{H}^+] + k_0[\text{Mn}^{3+}] + k_i[\text{M}] \}]^{1/2} \} \dots\dots\dots(21)$$

Thus the dependence of R_p on $[\text{M}]^{1.5}$, $[\text{Mn}^{3+}]^{1/2}$, $[\text{AH}]^{1/2}$, $[\text{H}]$, $[\text{Mn}^{2+}]^{-0.5}$, all of which are observed, are consistent with the experimental results. The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence of the existence of transient radical intermediates generated in redox reactions. It also enables the identification of these radicals as end groups of the polymer.

CONCLUSION:

Kinetics of polymerization of methyl methacrylate by Mn(III) –glycine studied. The Mn(III) – glycine the reactive species appears to be the hydrolyzed form of Mn(III) and the rate of polymerization decreases with H^+ ions concentration. The IR spectrum of polymethyl methacrylate of Mn(III) – glycine system shows at 3500 cm^{-1} for $-\text{NH}_2$ group and 1600 cm^{-1} for N-H bending. A sharp peak at 2960 cm^{-1} for C-H stretching and at 1750 cm^{-1} for C=O stretching.(Fig.4).

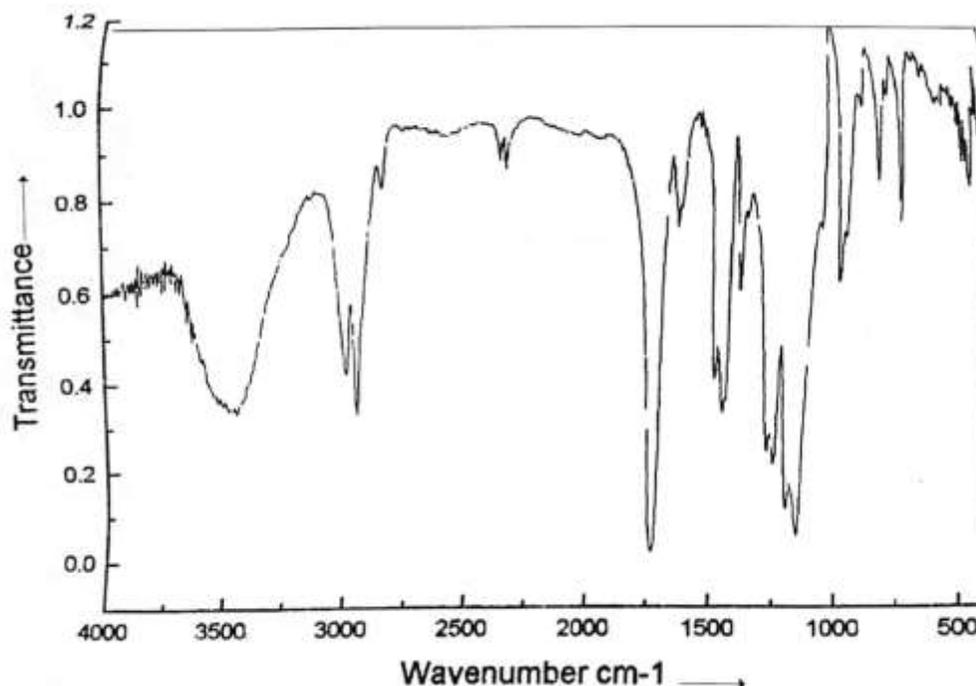


Fig. 4. IR Spectrum of the polymer sample of polymethyl methacrylate formed by the manganese(III)-glycine redox system.

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