

## Aqueous Polymerization of Acrylonitrile and Methyl Methacrylate by Cerium(IV)-Glycine Redox System Catalysed by Bromide Ion: A Kinetic Study

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Polymerization of acrylonitrile and methyl methacrylate monomers (M), initiated by a cerium(IV)-glycine redox system catalysed by bromide ion was investigated kinetically, over a temperature range of 35–50°C in aqueous medium under inert atmosphere. The incorporation of bromide ion, with cerium(IV)-glycine redox system and rate of polymerization ( $R_p$ ) has been studied at various concentrations of monomers and initiator. The polymerization exhibited a strong dependence on the concentration of bromide ion. The rate of polymerization,  $R_p \propto [M][Ce(IV)]^{1/2} [AH]^{1/2}[Br]^{1/2}$ . The influence of organic solvents and temperature on the rate of polymerization has also been investigated and energy of activation was calculated. On the basis of experimental results, a suitable kinetic scheme has been proposed and a rate expression has been derived.

### INTRODUCTION

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation status in aqueous medium can provide valuable information regarding the mechanistic details of the elementary steps<sup>1-7</sup>.  $\alpha$ -amino acids are the fundamental building blocks of proteins which take part in all life processes. The physical and chemical properties are due to the presence of both acidic and basic functional groups.

Among the large number of oxidants used halogens ( $Cl_2$  and  $Br_2$ )<sup>8</sup>, chloramine-T,<sup>8</sup>  $BrO_3^-$ ,<sup>8</sup>  $Fe^{3+}$ ,<sup>8</sup>  $S_2O_8^{2-}$ ,<sup>8</sup>  $MnO_4^-$ ,<sup>9</sup> and  $Co^{3+}$ ,<sup>10</sup> form good redox initiators in combination with glycine. There is a large induction period, when Ce(IV)-glycine redox system is used in polymerization studies. The increase of Ce(IV) concentration, shaking the reaction mixture or increasing the temperature, increases the induction period, decreases the initial rate and decreases the maximum conversion. However, if bromide ion is used as a catalyst, there is no induction period and the percentage conversion increases to about 85% within 1 h. Furthermore, glycine acts as chain modifier. Therefore no modifier needs to be added from the outside to regulate the molecular weight<sup>9</sup>.

### EXPERIMENTAL

Acrylonitrile and methyl methacrylate are purified by standard methods<sup>11</sup>.

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Ceric ammonium sulphate is dissolved in 1 M sulphuric acid to make a stock solution of 0.05 M ceric sulphate. This stock solution is used to prepare the polymerization recipe. A stock solution of glycine and potassium bromide is freshly prepared as and when required. All other chemicals used are of analytical grade and are used without further purification. Doubly distilled water is used to prepare all the solution.

### Kinetic measurement

Aqueous polymerization of purified acrylonitrile and methyl methacrylate is carried out at the required temperature under nitrogen atmosphere in pyrex glass vessels.

In a typical experiment, the reaction vessels containing appropriate quantities of water, sulphuric acid and ceric sulphate solution is flushed with nitrogen for 30 min. The vessels are then disconnected from each other after closing the stopcocks of the outlet and inlet tubes and placed inside a water bath set at the required temperature. After the vessels attain the bath temperature, required amounts of glycine and monomer (which are deaerated separately) are introduced quickly and the components are mixed by shaking. There is an induction period and the initiation of polymerization is indicated by the appearance of a haze in the initially clear solution. As the reaction progresses, the turbidity increases and ultimately the polymer precipitates out. It has been reported by Yuguchi and Watanabe<sup>12</sup> that stirring the reaction mixture hastens the precipitation of the polymer which is known to depress the rate of polymerization in heterogeneous system. The reaction medium is, therefore, left undisturbed in our study. For calculation of the rate of polymerization, the point of appearance of the turbidity is taken as the zero point. At definite intervals of time, the vessels are removed from the bath, opened and 50 cm<sup>3</sup> of hydroquinone solution (1.0%) introduced. The contents of the vessel are then poured into a large volume of ice-cold water and the precipitated polymer is filtered through a weighed, sintered (G-4) crucible, washed thoroughly with warm water and dried *in vacuo* to a constant weight.

**Determination of molecular weight,  $M_v$ :** The intrinsic viscosities ( $\eta$ ) of the purified samples of polymethyl methacrylate are determined using a Ubbelohde viscometer. The degree of polymerization  $P_n$  related to the intrinsic viscosity ( $\eta$ ) is given by the equation<sup>13</sup>  $\log P_n = 3.342 + 1.13 \log (\eta)$  for PMMA in benzene at 30°C. Polyacrylonitrile could not be dissolved in dimethyl formamide. Instead of dissolving it swelled into a gel-like structure. This may be either due to cross-linking in the polymer molecules or due to its very high molecular weight<sup>14</sup>.

**Ceric ion estimation:** Ceric ion concentrations at different intervals of time are determined by quenching the aliquots in suitable excess of ferrous ammonium sulphate, followed by back titration of the excess ferrous ions which ceric ammonium sulphate of known concentration using N-phenyl-anthranilic acid as indicator. The rate of  $d-[Ce(IV)]/dt$  is found to be first order with respect to  $[Ce(IV)]$  and also independent of monomer concentration. Earlier workers<sup>15</sup> have shown that Ce(IV) does not form kinetically detectable complexes with amino acids.

## RESULTS AND DISCUSSION

The polymerization of acrylonitrile and methyl methacrylate initiated by the Ce(IV)-glycine redox system catalysed by bromide ion takes place at a measurable rate in the temperature range 35–50°C. No induction period is observed under deaerated conditions.

**Effect of monomer concentration:** The rate of polymerization increases with monomer concentration. The order of reaction with respect to the monomer concentration is calculated from the plot of  $\log R_p$  versus  $\log$  (monomer). The order with respect to (acrylonitrile) was found to be unity in the concentration range (0.1517–0.6068 mol dm<sup>-3</sup>) (Fig. 1). The order with respect to methyl

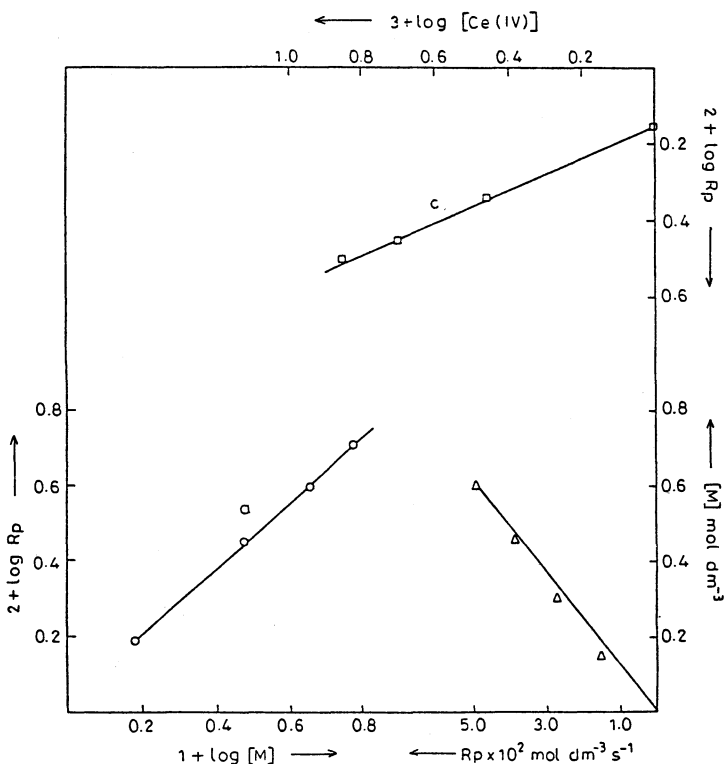


Fig. 1. (a) Plot of  $\log R_p$  versus  $\log [M]$ , (b)  $R_p$  versus  $[M]$

$[Ce(IV)] = 0.005 \text{ mol dm}^{-3}$ ,  $[gly] = 0.05 \text{ mol dm}^{-3}$ ,  
 $[Br^-] = 0.005 \text{ mol dm}^{-3}$ ,  $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$ ,  
 $[AN] = 0.1517, 0.3034, 0.4551, 0.6068 \text{ mol dm}^{-3}$ ,

(c) Plot of  $\log R_p$  versus  $\log [Ce(IV)]$

$[Ce(IV)] = 0.001, 0.003, 0.005 \text{ and } 0.007 \text{ mol dm}^{-3}$ ,  
 $[gly] = 0.05 \text{ mol dm}^{-3}$ ,  $[Br] = 0.005 \text{ mol dm}^{-3}$ ,  
 $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$ ,  $[AN] = 0.3034 \text{ mol dm}^{-3}$ ,  
 $I = 4.0 \text{ mol dm}^{-3}$ ,  $temp. = 318 \text{ K}$

methacrylate concentration is found to be also unity in the concentration range (0.0470–0.094 mol dm<sup>-3</sup>) (Fig. 4). At a higher methyl methacrylate concentration the rate decreases<sup>16</sup>, probably because of increase in viscosity of the medium due to the solubility of the polymer in the monomer, rendering the diffusion of the ions difficult through the medium. An order of reaction higher than unity is indicative of the occurrence of cage effect<sup>17–20</sup>.

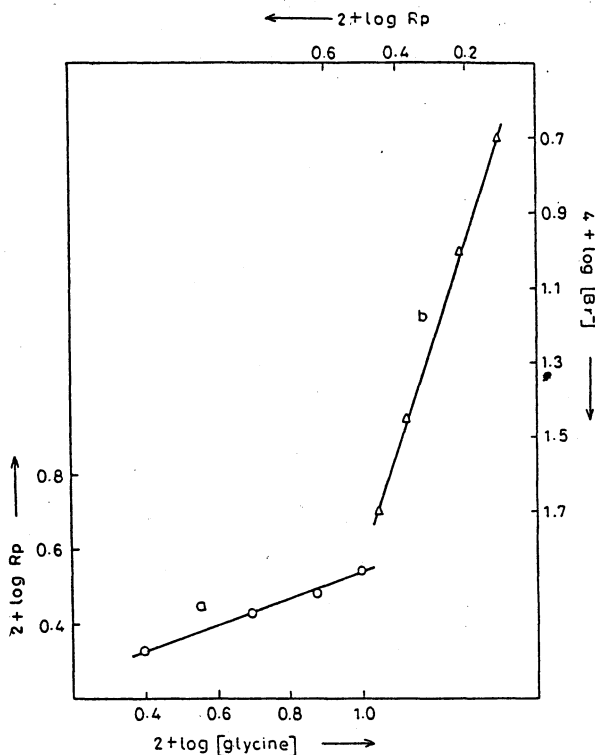


Fig. 2. (a) Plot of  $\log R_p$  versus  $\log [\text{gly}]$

$[\text{Ce(IV)}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{gly}] = 0.025, 0.05, 0.076$  and  $0.10 \text{ mol dm}^{-3}$ ,  $[\text{Br}^-] = 0.005 \text{ mol dm}^{-3}$ ,

$[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{AN}] = 0.3034 \text{ mol dm}^{-3}$ ,

$I = 4.0 \text{ mol dm}^{-3}$ , temp. = 318 K

(b) Plot of  $\log R_p$  versus  $\log [\text{Br}^-]$

$[\text{Ce(IV)}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{gly}] = 0.05 \text{ mol dm}^{-3}$ ,

$[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{AN}] = 0.3034 \text{ mol dm}^{-3}$ ,

$[\text{Br}^-] = 0.0005, 0.0010, 0.003, 0.005 \text{ mol dm}^{-3}$ ,

$I = 4.0 \text{ mol dm}^{-3}$ , temp. = 318 K

The kinetic chain length of polymethyl methacrylate increases with increase in the concentration of methyl methacrylate.

**Effect of Ce(IV) concentration:** The rate of polymerization increases with increase in the concentration of cerium(IV), probably due to an increase in the concentration of active species. The order of reaction with respect to  $[\text{Ce(IV)}]$  is found to be 0.5 in the concentration range (0.0006–0.007 mol dm<sup>-3</sup>) (Fig. 1 and 4). This also clearly indicates that the termination occurs through bimolecular interaction of growing polymer chain radicals<sup>21–23</sup>.

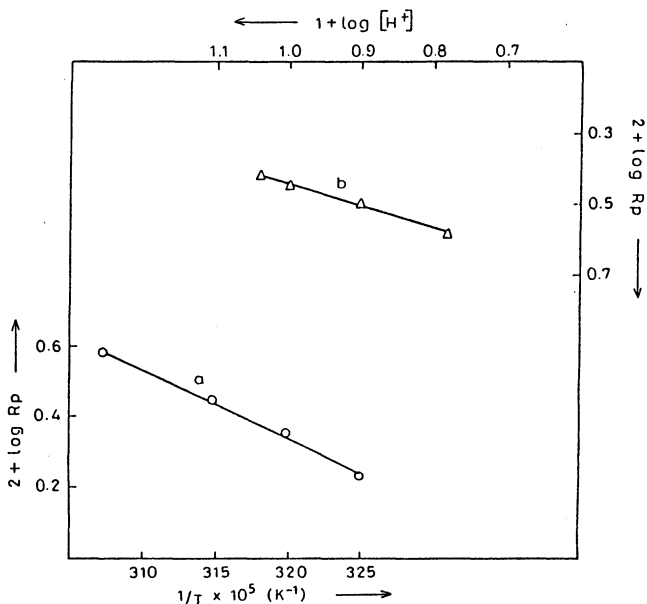


Fig. 3. (a) Plot of  $\log R_p$  versus  $1/T$

$[\text{Ce(IV)}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{gly}] = 0.05 \text{ mol dm}^{-3}$ ,  
 $[\text{Br}^-] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$   
 $[\text{AN}] = 0.3034 \text{ mol dm}^{-3}$ ,  $I = 4.0 \text{ mol dm}^{-3}$ ,  
 temp. = 308, 312, 318 and 323 K

(b) Plot of  $\log R_p$  versus  $\log [\text{H}^+]$

$[\text{Ce(IV)}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{gly}] = 0.005 \text{ mol dm}^{-3}$ ,  
 $[\text{Br}^-] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 0.6, 0.8, 1.0$  and  
 and  $1.1 \text{ mol dm}^{-3}$ ,  $[\text{AN}] = 0.3034 \text{ mol dm}^{-3}$ ,  
 $I = 4.0 \text{ mol dm}^{-3}$ , temp. 318 K

The molecular weight  $M_v$  of polymethyl methacrylate decreases with increase in  $[\text{Ce(IV)}]$ . This can be explained by the fact that increasing the concentration of Ce(IV) provides more chances for premature termination of growing chain radicals, which reduce the degree of polymerization<sup>24, 25</sup>.

**Effect of glycine concentration:** Increase of glycine concentration increases the rate gradually. The order of reaction with respect to  $[\text{glycine}]$  is found to be fractional from a plot of  $\log R_p$  versus  $\log [\text{glycine}]$  in the concentration range (0.026–0.10 mol dm<sup>-3</sup>). At higher concentration of glycine the rate decreases due

to chain transfer of glycine. The molecular weight  $M_v$  of the polymer (polymethyl methacrylate) also decreases with increase in [glycine] (Figs. 2 and 5).

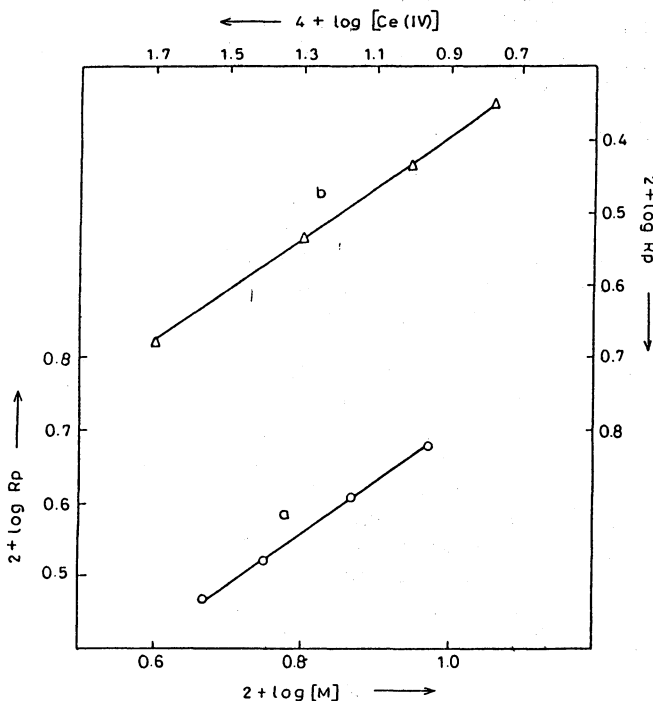


Fig. 4. (a) Plot of  $\log R_p$  versus  $\log [M]$

$[Ce(IV)] = 0.005 \text{ mol dm}^{-3}$ ,  $[gly] = 0.05 \text{ mol dm}^{-3}$ ,  
 $[Br^-] = 0.005 \text{ mol dm}^{-3}$ ,  $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$ ,  
 $[MMA] = 0.0470, 0.0564, 0.0752 \text{ and } 0.0940$

(b) Plot of  $\log R_p$  versus  $\log [Ce(IV)]$

$[Ce(IV)] = 0.0006, 0.001, 0.003, 0.005 \text{ mol dm}^{-3}$ ,  
 $[gly] = 0.05 \text{ mol dm}^{-3}$ ,  $[Br^-] = 0.005 \text{ mol dm}^{-3}$ ,  
 $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$ ,  $[MMA] = 0.0940 \text{ mol dm}^{-3}$ ,  
 $I = 4.0 \text{ mol dm}^{-3}$ ,  $\text{temp.} = 318 \text{ K}$

**Effect of bromide ion concentration:** Cerium(IV) reactions are found to be catalysed by bromide ion<sup>26,27</sup>. The rate of polymerization increases with increase in  $[Br^-]$  which may be due to increase in the rate of oxidation resulting in an increased production of primary radicals. The order of reaction with respect to bromide ion is found to be 0.5 from a plot of  $\log R_p$  versus  $\log [Br^-]$  (Figs. 2 and 5) in the concentration range (0.0005–0.005  $\text{mol dm}^{-3}$ ).

**Effect of  $H^+$  concentration and ionic strength:** The rate of polymerization decreases with increase in  $[H^+]$  (Figs. 3 and 6) and ionic strength. Sodium bisulphate is used to maintain the ionic strength. All these observations could be explained on the assumption that the reactive species is the ceric sulphate molecule<sup>28</sup>. In solutions of ceric ammonium sulphate in sulphuric acid the following equilibria are recognised.

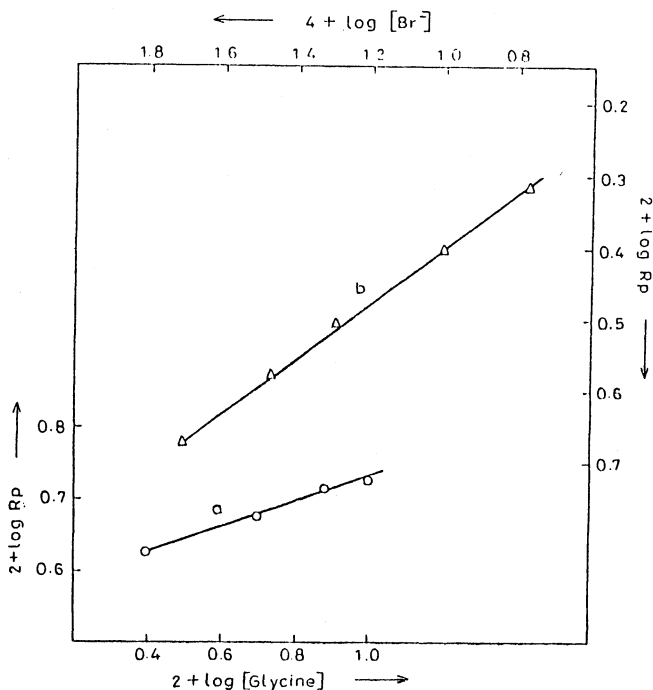
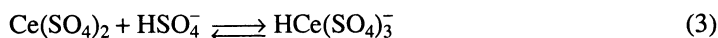
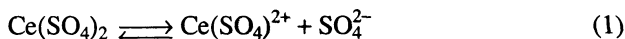


Fig. 5. (a) Plot of  $\log R_p$  versus  $\log [\text{gly}]$   
 $[\text{Ce(IV)}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{gly}] = 0.026, 0.050,$   
 $0.076, 0.10 \text{ mol dm}^{-3}$ ,  $[\text{Br}^-] = 0.005 \text{ mol dm}^{-3}$ ,  
 $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{MMA}] = 0.0940 \text{ mol dm}^{-3}$ ,  
 $I = 4.0 \text{ mol dm}^{-3}$ ,  $\text{temp.} = 318 \text{ K}$   
 (b) Plot of  $\log R_p$  versus  $\log [\text{Br}^-]$   
 $[\text{Ce(IV)}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{gly}] = 0.005 \text{ mol dm}^{-3}$   
 $[\text{Br}^-] = 0.0006, 0.001, 0.003 \text{ and } 0.005 \text{ mol dm}^{-3}$   
 $[\text{MMA}] = 0.0940 \text{ mol dm}^{-3}$ ,  $I = 4.0 \text{ mol dm}^{-3}$ ,  
 $\text{Temp.} = 318 \text{ K}$ ,  $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$



The decrease in rate by increases of  $[\text{H}_2\text{SO}_4]$  and  $[\text{NaHSO}_4]$  may be due to the depletion of  $\text{Ce}(\text{SO}_4)_2$  by the above equilibria.

**Effect of Organic solvents:** Water miscible organic solvents such as DMF, methanol and ethanol (5% v/v) depress the rate of polymerisation. This is probably due to decrease in the area of shielding of a strong hydration layer in the aqueous medium resulting in the termination of the 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 as

compared to the growth of the polymer chains as shown by Schulze *et al.*<sup>29</sup> It may also be due to a change in the termination rate arising from a change in the degree of occlusion of the radical.

**Effect of temperature:** The rate of polymerization increases with increase in temperature (Figs. 3 and 6). The energy of activation is found to be 81.1 kJ mol<sup>-1</sup>, for acrylonitrile polymerization and 27.66 kJ mol<sup>-1</sup> for methyl methacrylate polymerisation.

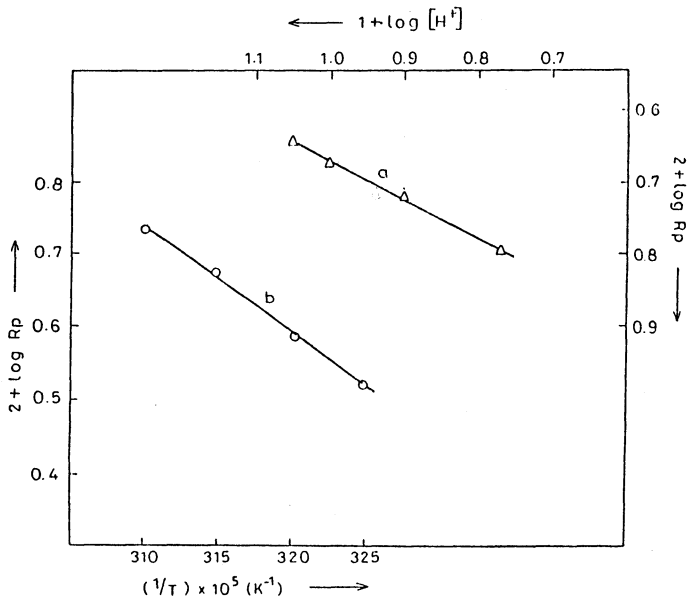


Fig. 6. (a) Plot of  $\log R_p$  versus  $1/T$

$[Ce(IV)] = 0.005 \text{ mol dm}^{-3}$ ,  $[gly] = 0.05 \text{ mol dm}^{-3}$ ,  
 $[Br^-] = 0.005 \text{ mol dm}^{-3}$ ,  $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$ ,  
 $[MMA] = 0.0940 \text{ mol dm}^{-3}$ ,  $I = 4.0 \text{ mol dm}^{-3}$ ,  
 Temp. = 308 K

(b) Plot of  $\log R_p$  versus  $\log [H^+]$

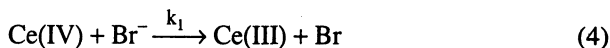
$[Ce(IV)] = 0.005 \text{ mol dm}^{-3}$ ,  $[gly] = 0.05 \text{ mol dm}^{-3}$ ,  
 $[Br^-] = 0.005 \text{ mol dm}^{-3}$ ,  $[H_2SO_4] = 0.6, 0.8, 1.0 \text{ and } 1.1 \text{ mol dm}^{-3}$   
 $[MMA] = 0.0940 \text{ mol dm}^{-3}$ ,  $I = 4.0 \text{ mol dm}^{-3}$ ,  
 Temp. = 318 K

As the temperature increases, the rate of production of primary radicals also increases thus causing an increase in the rate of polymerization. An increase in temperature causes a decrease in the chain length which may be due to an increase in the mobility of growing chain radicals in the system, leading to their efficient termination.

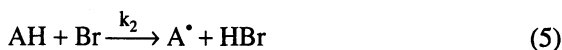
### Mechanism and rate law

The following reaction scheme may be used to explain satisfactorily the observed kinetic results.

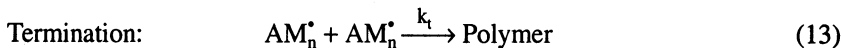
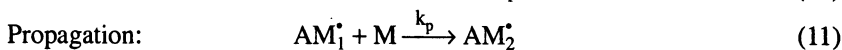
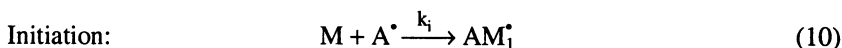




The Br atom is an efficient hydrogen atom abstractor<sup>30</sup>.



As the [acid] is increased, the acid forming hydrolysis<sup>8,30</sup> of Br<sub>2</sub> is suppressed and polymerization through the following steps may be suppressed.



Applying steady state principles,

$$d[\text{A}^\bullet]/dt = k_2[\text{AH}][\text{Br}] - k_i[\text{A}^\bullet][\text{M}] = 0 \quad (14)$$

$$[\text{A}^\bullet] = k_2[\text{AH}][\text{Br}]/k_i[\text{M}] \quad (15)$$

$$d[\text{Br}]/dt = k_i[\text{Ce(IV)}][\text{Br}^-] - k_2[\text{AH}] \quad (16)$$

Since propagation is the stage which involves the major consumption of the monomer, the rate of monomer loss can be expressed essentially in terms of propagation only.

$$R_p = k_p[\text{AM}_1^\bullet][\text{M}] \quad (17)$$

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

$$R_p = k_p[\text{AM}_n^\bullet][\text{M}] \quad (18)$$

In the overall polymerization the rate of initiation and the rate of termination becomes equal, resulting in a steady-state concentration of free radicals.

$$k_i[\text{A}^\bullet][\text{M}] = k_t[\text{AM}_n^\bullet]^2 \quad (19)$$

$$[\text{AM}_n^\bullet] = (k_i/k_t)^{1/2} [\text{A}^\bullet]^{1/2} [\text{M}]^{1/2} \quad (20)$$

$$R_p = k_p(k_i/k_t)^{1/2} [\text{M}]^{3/2} [\text{A}^\bullet]^{1/2} \quad (21)$$

$$= \frac{k_p(k_1 k_2 k_i)^{1/2}}{k_t} \frac{[\text{M}][\text{Ce(IV)}]^{1/2} [\text{AH}]^{1/2} [\text{Br}^-]^{1/2}}{k_i^{1/2} (k_3 + k_2) [\text{AH}]^{1/2}} \quad (22)$$

$$= \frac{k_p(k_1 k_2)^{1/2}}{k_t} \frac{[\text{M}][\text{Ce(IV)}]^{1/2} [\text{AH}]^{1/2} [\text{Br}^-]^{1/2}}{(k_3 + k_2) [\text{AH}]^{1/2}} \quad (23)$$

The dependence of  $R_p$  on  $[M]$ ,  $[Ce(IV)]^{1/2}$ ,  $[Br^-]^{1/2}$ ,  $[AH]^{1/2}$  all of which are realised, is inconsistent with the above scheme. The low energy of activation is an indication of the high reactivity of the initiator, thus providing direct experimental evidence for the existence of transient radical intermediates formed *in situ* by the redox system.

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