



Kinetics of Polymerization of Methacrylic Acid Monomer Initiated by Peroxo Disulphate – N,N,N',N'-Tetramethylethylenediamine

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ABSTRACT

The polymerization of vinyl monomer, Methacrylic acid (MAA) was carried out in acid medium under varying conditions of concentration, temperature, ionic strength and pH with potassium peroxodisulphate (PPS) – N,N,N',N'- tetramethylethylenediamine (TMEDA) couple as redox initiator at 50°C. The rate of polymerization, R_p was proportional to $[MAA]^{1.5}$, $[PPS]^{0.5}$ and independent of TMEDA. R_p was found to be insensitive to change in $[H^+]$ and also ionic strength. R_p showed an increase with increase in temperature. The activation energy E_a for the overall rate of polymerization has been found to be $10.4 \text{ k Cal.mol}^{-1}$. The value of composite rate constant was found to be approximately constant, $4.06 \times 10^{-6} \text{ mol L}^{-2} \text{ s}^{-2}$. Under steady state conditions the rate of polymerization is $R_p = (2kp^2k_3/k_{t1}) [MAA]^{1.5} [PPS]^{0.5} [TMEDA]^0$

Keywords: Methacrylicacid, Potassium peroxodisulphate, N,N,N',N'-tetramethylethylenediamine, rate of polymerization.

INTRODUCTION

The decomposition of peroxodisulphate in aqueous medium under varying pH were done by Chandra Singh et al [1] and the polymerization of vinyl monomers using peroxodisulphate alone were studied by Venkatarao et al [2-6] and also coupled with reducing agents [7,8] TMEDA is widely used as catalyst along with $S_2O_8^{2-}$ ion for the preparation of electrophoretic gel which finds extensive applications in biology. Polymethylacrylicacid polymer hydrogel capsules is mainly act as a therapeutic cargo in biomedical engineering [9-11]. The present paper deals the kinetics of polymerization of methacrylic acid initiated by redox pairs, potassium peroxodisulphate (PPS) and , N,N,N',N'-tetramethylethylenediamine in acid medium. From the experimental results, a suitable reaction scheme has been derived and kinetic parameters were evaluated.

MATERIALS AND METHODS

Methacrylic acid (Riedel,F.R.G) was twice distilled in the presence of ferrous sulphate and copper powder at reduced pressure (50°C/7mmHg). N,N,N',N'-tetramethylethylenediamine (TMEDA) (Loba chemie)

was used as such without purification. Potassium peroxydisulphate (E.Merc G.R.,F.R.G) was twice recrystallized from double distilled water. For adjusting ionic strength, a stock solution of NaClO_4 was prepared by carefully neutralizing a standard solution of HClO_4 (E.Merc.G.R) with NaOH (E.Merc,G.R), the neutralization being checked by a pH meter. The rate of polymerization was followed by estimating monomer disappearance by bromometry [12-14].

RESULTS AND DISCUSSION

The rate of monomer disappearance taken to be equal to the rate of polymerization (R_p) was found to be depend on $[\text{MAA}]^{1.5}$ (Fig.1), $[\text{PPS}]^{0.5}$ and independent of $[\text{TMEDA}]$ (table 1) under steady state condition. The dependence of R_p on $[\text{MAA}]^{1.5}$ and $[\text{PPS}]^{0.5}$ explains clearly that the initiation was by direct interaction between monomer and $\text{S}_2\text{O}_8^{2-}$ while termination was by the mutual interaction of polymer radicals. R_p was found to be insensitive to change in $[\text{H}^+]$ and also ionic strength variation.

Effect of temperature: R_p showed an increase with increase in temperature. The activation energy for the overall rate of polymerization has been calculated from the Arrhenius plot and found to be $10.4\text{ k Cal. mol}^{-1}$.

Effect of composite rate constant: The value of composite rate constant $k_p^2 k_6 / k_{t1}$, is evaluated and found to be approximately constant, $4.06 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-2}$.

Reaction Mechanism and rate law: The following mechanistic sequences of reaction was found to explain the kinetics of TMEDA catalysed polymerization of MAA by peroxydisulphate ion.

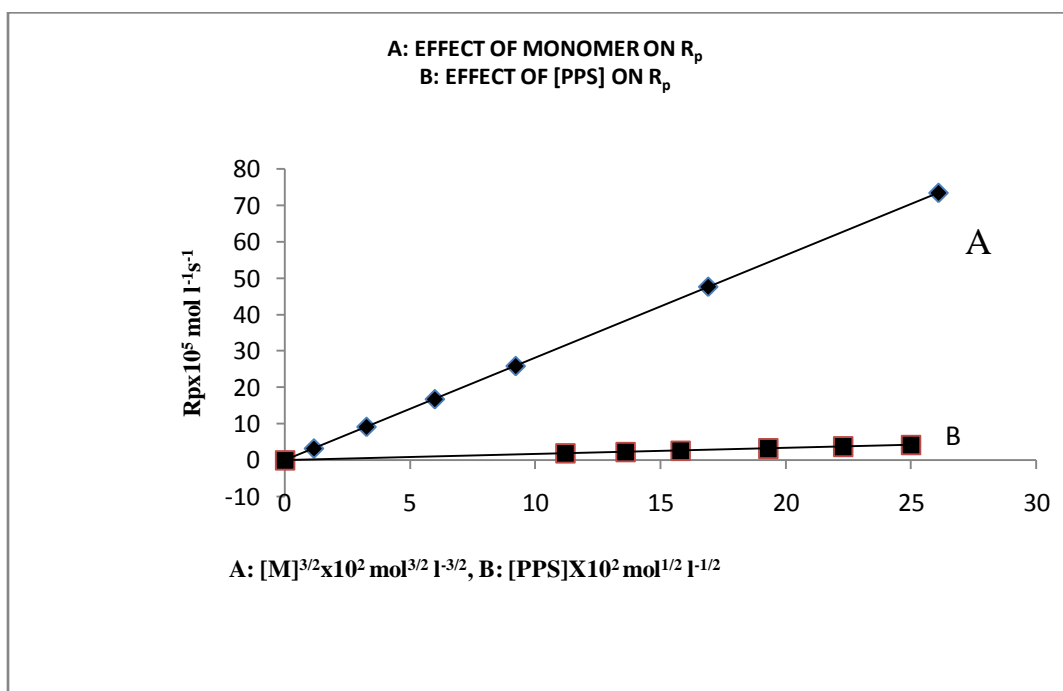
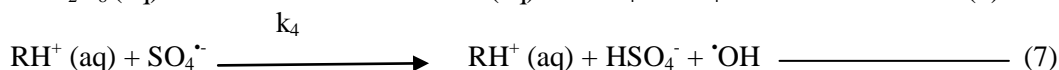
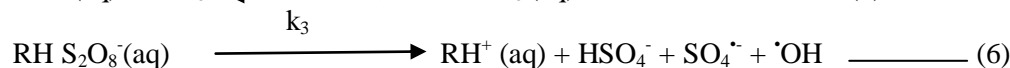
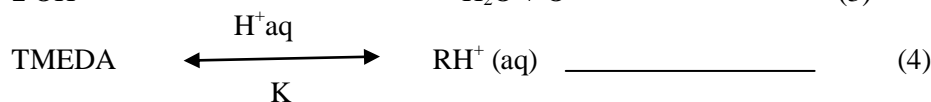
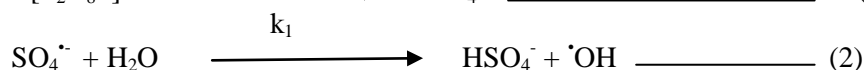
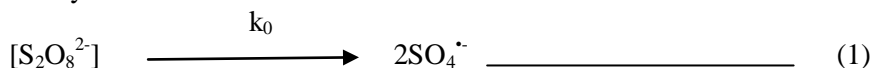
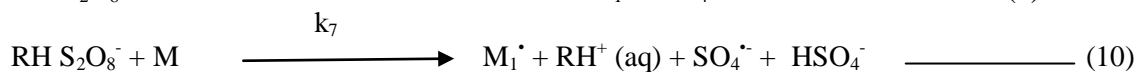


Figure 1

Table -1

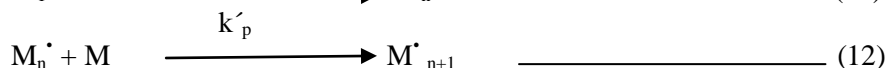
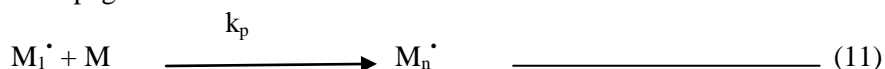
A: EFFECT OF MONOMER ON R _p [PPS]=3.75X10 ⁻² mol l ⁻¹ [TMEDA]=1.32X10 ⁻³ mol l ⁻³ [H ⁺]=0.05 mol l ⁻¹ I=0.21 mol l ⁻¹ T=50°C			B: EFFECT OF [PPS] ON R _p [M]=15.3X10 ⁻² mol l ⁻¹ [TMEDA]=1.32X10 ⁻³ mol l ⁻³ [H ⁺]=0.05 mol l ⁻¹ I=0.21 mol l ⁻¹ T=50°C			EFFEC OF [TMEDA} ON R _p [M]=20.43X10 ⁻² mol l ⁻¹ [PPS]=3.75X10 ⁻³ mol l ⁻³ [H ⁺]=0.05 mol l ⁻¹ I=0.21 mol l ⁻¹ T=50°C	
[M]x10 ² mol l ⁻¹	[M] ^{3/2} x10 ² mol ^{3/2} l ^{-3/2}	R _p x10 ⁵ mol l ⁻¹ s ⁻¹	[PPS]X10 ² mol l ⁻¹	[PPS]X10 ² mol ^{1/2} l ^{-1/2}	R _p x10 ⁵ mol l ⁻¹ s ⁻¹	[TMEDA]X10 ³ mol l ⁻¹	R _p x10 ⁵ mol l ⁻¹ s ⁻¹
5.11	1.15	3.24	1.25	11.2	1.88	0.66	25.9
10.2	3.25	9.19	1.87	13.6	2.30	1.32	25.7
15.3	5.98	16.8	2.50	15.8	2.65	1.65	25.6
20.4	9.21	25.9	3.75	19.3	3.25	2.64	25.8
30.6	16.9	47.7	5.00	22.3	3.76	3.30	25.9
40.9	26.1	73.5	6.25	25.0	4.20	3.96	25.7

1. Primary reactions

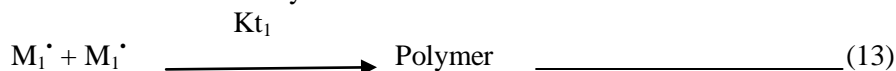
2. Initiation by S₂O₈²⁻

Initiation by SO₄^{·-} has not been considered because the reaction between RH⁺(aq) and SO₄^{·-} was considered to be fast, similar to the fast reaction between Ag⁺(aq) catalyst and SO₄^{·-} as already reported [15].

3. Propagation



4. Mutual termination by combination of chain radicals



Based upon the above sequence of reaction scheme, we get the following rate expression, assuming steady state principle for the concentration of free radicals.

$$R_p = (2k_p^2 k_3 / k_{t1}) [MAA]^{1.5} [PPS]^{0.5} [TMEDA]^0$$

APPLICATIONS

These studies are useful to suggest the mechanism of reaction in polymerisation

CONCLUSIONS

The kinetics of methacrylic acid initiated by the redox pairs, potassium peroxodisulphate - N,N,N',N'-tetramethylethylenediamine in perchloric acid medium was studied. From the experimental results, a suitable reaction scheme which involves the direct interaction of $S_2O_8^{2-}$ with the monomer in the initiation step and mutual termination has been proposed. The rate of polymerization of was found to depend on the $[MAA]^{1.5}$, $[PPS]^{0.5}$ and $[TMEDA]^0$. The activation energy for the polymerization reaction was 10.4 kCal. mol^{-1} . The value of composite rate constant $2k_p^2 k_3 / k_{t1}$ was found to be constant.

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