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Potassium persulphate-malonic acid redox pair initiated polymerization of methacrylamide

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Summary

The kinetics of aqueous polymerization of methacrylamide initiated by potassium persulphate-malonic acid redox pair has been investigated at 50 ± 1°C under nitrogen atmosphere. The initial rate of polymerization has been found to be square root dependence to the initial concentration of potassium persulphate and malonic acid. The order of reaction with respect to monomer has been found to be unity. The overall energy of activation has been found to be 66 ± 1 KJ/mol. The effect of addition of manganous sulphate and sulphuric acid has been investigated. On the basis of experimental results a suitable mechanism has been proposed.

Introduction

It has been reported by Dainton et al. [1] that persulphate ion itself is unable to initiate methacrylamide polymerization in comparison to acrylamide due to the steric hindrance rendered by methyl group present in methacrylamide but persulphate ion [2], [3] itself initiates methacrylamide polymerization at elevated temperatures. Similarly the recent studies [4], [5] also reveal that the persulphate ion in combination with different reducing agents can be used to initiate methacrylamide polymerization at room temperature. Therefore, all these earlier studies have prompted us to investigate the efficiency of persulphate ion in presence of malonic acid during the polymerization of methacrylamide.

Experimental

Methacrylamide (Fluka, A.G.) and malonic acid (A.G. Riedel) were purified by recrystallization from benzene-ethanol mixture and dried in vacuum over silica gel and the potassium persulphate (E. Merck) solution was prepared as reported elsewhere [2]. The rate of polymerization of methacrylamide has been followed by determining the rate of disappearanceof monomer at different intervals of time [6]. The viscometric average molecular weight of poly-

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methacrylamide in magnesium perchlorate solution has been determined by using following equation [7].

$$[\eta]_{25^\circ C} = 3.28 \times 10^{-4}\ \bar{M}_v^{0.55}$$

Results and Discussion

Ambiguities about the participation of peroxydisulphate ion through homolytic fission in initiation process have been clarified by comparing the results of other workers [8], where it is reported that uncatalysed symmetrical decomposition of persulphate requires 140 KJ/mol energy of activation which is very high in comparison to the present investigation (66± 1 KJ/mol). Therefore to explain the polymerization reaction in presence of peroxydisulphate ion-malonic acid redox pair, the following reaction steps have been proposed.

$$S_2O_8^{2-} + CH_2(COOH)_2 \xrightarrow{k_1} \dot{\bar{S}O_4} + \dot{C}H(COOH)_2 + HS\bar{O}_4 \qquad (1)$$

$$\left.\begin{array}{l} \dot{C}H(OOH)_2 + M \xrightarrow{k_i} \dot{M}_1 \\ \dot{\bar{S}O_4} + M \xrightarrow{k_i^*} \dot{M}_i \end{array}\right\} \quad \text{Initiation} \qquad (2)$$

$$\left.\begin{array}{l} \dot{M}_1 + M \xrightarrow{k_p} \dot{M}_2 \\ \dot{M}_{n-1} + M \xrightarrow{k_p} \dot{M}_n \end{array}\right\} \quad \text{Propagation} \qquad (3)$$

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_t} M_{n+m} \quad \text{Termination} \qquad (4)$$

Considering the above steps the rate of polymerization can be given by the following rate expression.

$$R_p = k_p \left\{\frac{k_1}{k_t}\right\}^{\frac{1}{2}} [M]\,[S_2O_8^{2-}]^{\frac{1}{2}}\,[CH_2(COOH)_2]^{\frac{1}{2}} \qquad (5)$$

and the kinetic chain length can be given as

$$\nu = k_p \frac{[M]}{2(k_1 k_t [S_2O_8^{2-}]\,[CH_2(COOH)_2])^{\frac{1}{2}}} \qquad (6)$$

It is evident from the equation (5) that the rate of polymerization is directly proportional to the concentration of monomer and square root in persulphate and malonic acid.

Dependence of Rate on Initiator (Persulphate) Concentration

The observation of the results (Table 1) shows that on varying the concentration of persulphate from 0.66×10^{-3} mol.dm^{-3} to 2.0×10^{-3} mol.dm^{-3}, the initial rate of polymerization and maximum conversion increases but at still higher concentration of persulphate, the initial rate and maximum conversion shown a deviation which is an indicative to assume that persulphate ion itself is not efficient to generate the free radicals, therefore in the absence of sufficient amounts of malonic acid, the retardation in initial rate as well as in maximum conversion is obvious. The order of reaction with respect to persulphate has been found to be half (Fig. 1)

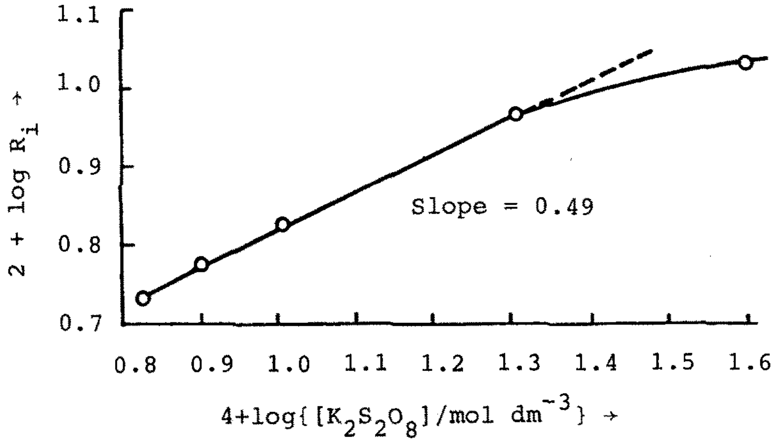

Fig.1 - [Methacrylamide] = 2.0 x 10^{-1} mol.dm^{-3}, [Malonic acid] = 1.3x10^{-3} mol.dm^{-3}, Temp.50°C.

Table 1

Effect of persulphate concentration variation on the rate of polymerization

$[K_2S_2O_8]$x 10^3 mol.dm^{-3}	% Conversion at different intervals of time (min)						[η]x10^{-2} dl/g at
	20	40	60	90	150	180	240 min
0.66	1.08	2.10	3.26	4.62	11.80	13.40	9.78
0.80	1.19	2.28	3.59	5.42	14.52	16.34	9.49
1.00	1.32	2.88	4.08	7.02	17.50	19.62	9.35
2.00	1.82	3.82	5.84	12.06	21.04	24.20	8.76
4.00	2.23	4.52	7.08	13.08	18.24	19.28	8.05

[Methacrylamide] = 2.0 x 10^{-1} mol.dm^{-3},[Malonic acid]=1.3x10^{-3} mol.dm^{-3}

R_i has been expressed as % conversion per minute for initial five per cent conversion. The square root dependence to persulphate concentration is an evidence to predict the bimolecular mode of termination as reported by other workers [3], [5]. Table 1 shows a linearly [9] between [intrinsic viscosity]$^{-1}$ vs[persulphate]which provides a reasonable support to assume direct proportionately between kinetic chain length (ν) and intrinsic viscosity [η], therefore it supports the validity of derived equation 6, and the proposed steps.

Dependence of Rate on Activator (Malonic Acid) Concentration

The results indicate (Table 2) that the initial rate of polymerization (R_i) increases at lower concentration (i.e.

from 0.6×10^{-3} mol.dm^{-3} to 1.66×10^{-3} mol.dm^{-3}) but shows a decreasing trend at higher concentration of malonic acid.

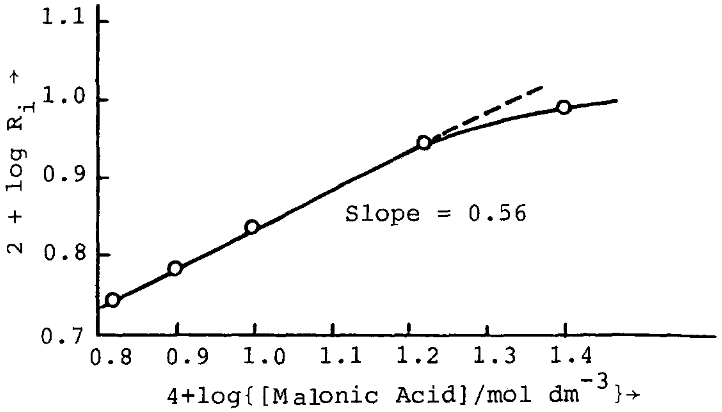

Fig. 2 - [Methacrylamide] = 2.0×10^{-1} mol.dm^{-3}, $[K_2S_2O_8]$ = 2.0×10^{-3} mol.dm^{-3}, Temp. 50°C.

Table 2
Effect of malonic acid concentration variation on the rate of polymerization

[Malonic acid]$\times10^3$ mol.dm^{-3}	% conversion at different intervals of time (min)						$[\eta]\times10^2$ dl/g at
	20	40	60	90	150	180	240 min
0.66	1.10	2.02	3.54	5.06	11.43	14.41	8.64
0.80	1.24	2.82	3.86	5.52	13.21	16.22	8.12
1.00	1.38	3.02	4.22	6.23	20.24	23.46	7.91
1.66	1.98	3.56	5.36	12.10	27.70	30.24	7.07
2.50	2.09	4.18	6.60	15.32	26.92	27.82	6.54

[Methacrylamide] = 2.0×10^{-1} mol.dm^{-3},

$[K_2S_2O_8]$ = 2.0×10^{-3} mol.dm^{-3}.

The malonic acid generate free radicals at active methylene group by interacting with persulphate ion (Step 1) at lower concentration of malonic acid but at higher concentration of malonic acid, the effective concentration of persulphate is reduced as reported by Kolthoff et al. [8] due to the formation of bisulphate ion and sulphurtetraoxide. The order with respect to malonic acid has been found to be half (Fig. 2).

Dependence of Rate on Monomer (Methacrylamide) Concentration

The rate of propagation (R_p) increase linearly (Table-3)

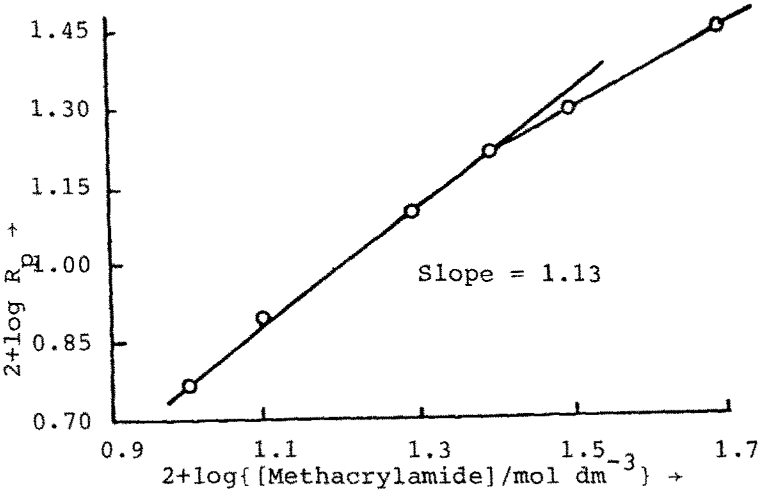

Fig. 3 - $[K_2S_2O_8] = 2.0 \times 10^{-3}$ mol. dm^{-3},
[Malonic acid] = 1.3×10^{-3} mol.dm^{-3},Temp.50°C

in the concentration range of methacrylamide from 1.0×10^{-1} mol.dm^{-3} to 2.5×10^{-1} mol.dm^{-3} but deviation occurs from linearity at higher concentration. The order with respect to methacrylamide has been found to be unity (Fig. 3), where R_p is the per cent conversion per minute at 30th minute. The deviation from linearity at higher concentration of methacrylamide can be presumed due to increase in viscosity of the medium as suggested by Suen et al. [10]. The viscometric results shown in the Table 3 indicate that at higher concentra-

Table 3
Effect of methacrylamide concentration variation on the rate of polymerization

[Methacrylamide]x10 mol.dm^{-3}	% conversion at different intervals of time (min)						$[\eta] \times 10^2$ dl/g at 240 min
	20	40	60	90	150	180	
1.00	1.21	2.43	4.13	6.82	11.24	12.48	0.90
1.25	1.84	3.88	5.64	10.82	14.42	15.02	0.98
2.00	3.20	7.08	12.00	17.12	22.82	24.02	3.07
2.50	4.02	9.42	16.14	21.32	26.12	27.22	4.51
3.33	5.70	11.15	21.01	26.33	30.62	32.44	6.11
5.00	9.18	16.36	24.42	25.00	28.42	28.92	8.04

$[K_2S_2O_8] = 2.0 \times 10^{-3}$ mol.dm^{-3},

[Malonic acid] = 1.3×10^{-3} mol.dm^{-3}.

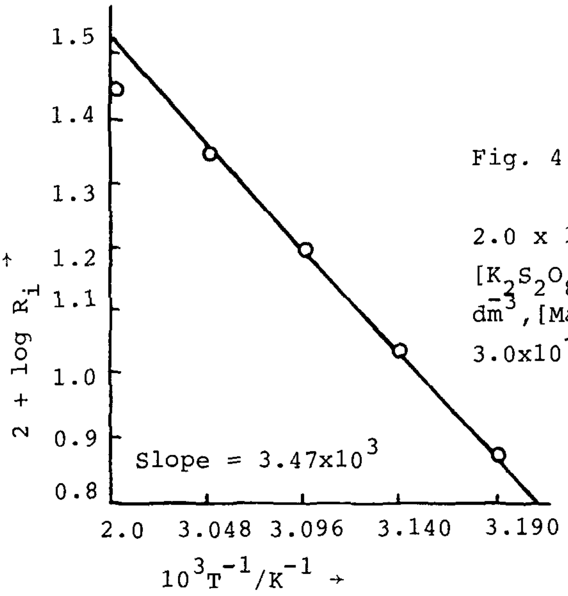

Fig. 4 - [Methacrylamide] = 2.0×10^{-1} mol.dm^{-3}, [$K_2S_2O_8$]=2.0×10^{-3}mol.dm^{-3}, [Malonic acid] = 3.0×10^{-3} mol.dm^{-3}.

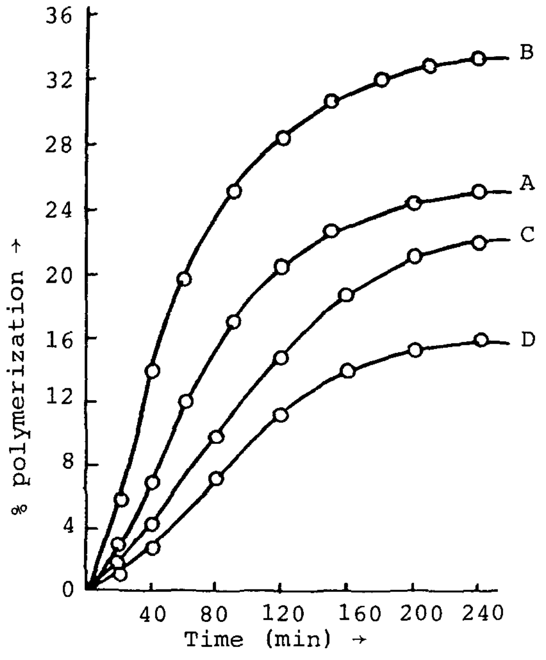

Fig. 5 - [Methacrylamide]=2.0×10^{-1} mol.dm^{-3}, [$K_2S_2O_8$] =2.0×10^{-3}mol.dm^{-3}, [Malonic acid] = 2.0×10^{-3}mol.dm^{-3}, Temp.50°C. A= Blank, B=[$MnSO_4$]=1.0×10^{-2} mol.dm^{-3}, C-[H_2SO_4]=1.0×10^{-2} mol.dm^{-2}, D-[H_2SO_4]=2.0×10^{-2} mol.dm^{-3}.

tion of methacrylamide the intrinsic viscosity shows deviation from linearity which can be explained by considering the theory of Norrish et al. [11] where it is assumed that excess of methacrylamide function as a solvent for polymethacrylamide molecules.

Effect of Temperature and Additives

The initial rate of polymerization (R_i) increase on increasing the temperature upto 55°C. The energy of activation has been found to be 60 ± 1 KJ/mol (Fig. 4). The addition of small amounts of manganous sulphate (Fig. 5) increases the initial rate and maximum conversion which can be assumed due to the oxidation of manganese (II) into the manganese (III). Since it is reported that manganese (III) can generate radicals with malonic acid through hydrogen atom abstraction [12] from active methylene group, therefore the increasing effect of manganous sulphate concentration on the rate of polymerization can be explained due to the formation of radicals by the interaction of Mn(III) and malonic acid. The addition of sulphuric acid (Fig. 5) decreases the initial rate of polymerization and maximum conversion which can be explained due to the formation of sulphurteraoxide and bisulphate ion.

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