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Potassium peroxodiphosphate–cysteine hydrochloride redox-couple-initiated polymerization of methacrylamide in an aqueous medium

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The kinetics of the aqueous polymerization of methacrylamide has been studied under an inert atmosphere employing the potassium peroxodiphosphate–cysteine hydrochloride redox pair. The order with respect to monomer and activator has been found to be unity and initiator showed half order. The polymethacrylamide samples collected under different kinetic conditions have been used for the determination of intrinsic viscosity $[\eta]$, viscometric average molecular weight $\bar{M}_V$ and degree of polymerization $\bar{P}_n$.

(Keywords: PDP–Cys.HCl redox couple; methacrylamide; kinetics)

INTRODUCTION

Potassium peroxodiphosphate has been used along with various activators[1–3] but a literature survey shows that no attempt has been made to study the kinetics of aqueous polymerization of methacrylamide initiated by the potassium peroxodiphosphate–cysteine hydrochloride (PDP–Cys.HCl) redox system.

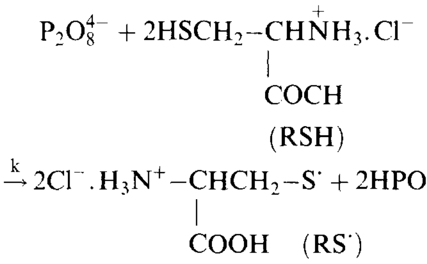
EXPERIMENTAL

Methacrylamide (Fluka A-G) was purified as reported elsewhere[4]. PDP was received as a gift sample from FMC, New York, and was used as supplied. All other chemicals used were of AnalaR (BDH) grade. The kinetics of polymerization was followed bromometrically[5]. The $\bar{M}_V$ was determined by dissolving the polymethacrylamide sample in magnesium perchlorate solution and by using the equation given by Chatterjee *et al.*[6].

RESULTS AND DISCUSSION

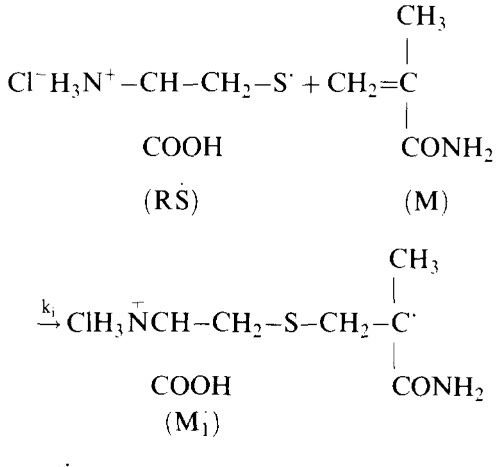
On the basis of experimental results the following steps have been proposed in order to ascertain the kinetic behaviour of methacrylamide polymerization initiated by the PDP–Cys.HCl redox pair and to elucidate possible anomalies, if any.

Primary radical formation



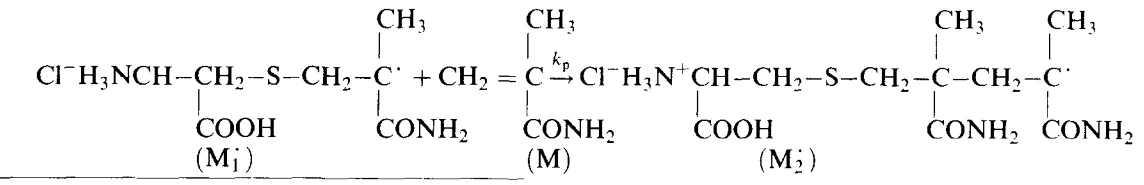
$$\mathrm{P_2O_8^{4-} + 2HSCH_2\text{–}\underset{\underset{(RSH)}{COCH}}{CH}\overset{+}{N}H_3.Cl^-} \xrightarrow{k} \mathrm{2Cl^-.H_3N^+\text{–}\underset{COOH}{CH}CH_2\text{–}S^{\cdot} + 2HPO_4^{2-}}\ \ (\mathrm{RS^{\cdot}}) \quad (1)$$

Initiation



$$\underset{(\mathrm{R\dot{S}})}{\mathrm{Cl^-H_3N^+\text{–}\underset{COOH}{CH}\text{–}CH_2\text{–}S^{\cdot}}} + \underset{(\mathrm{M})}{\mathrm{CH_2{=}\overset{CH_3}{\underset{CONH_2}{C}}}} \xrightarrow{k_i} \underset{(\mathrm{M_1^{\cdot}})}{\mathrm{Cl\overset{+}{H_3}N\underset{COOH}{CH}\text{–}CH_2\text{–}S\text{–}CH_2\text{–}\overset{CH_3}{\underset{CONH_2}{C^{\cdot}}}}} \quad (2)$$

Propagation



$$\underset{(\mathrm{M_1^{\cdot}})}{\mathrm{Cl^-H_3N\underset{COOH}{CH}\text{–}CH_2\text{–}S\text{–}CH_2\text{–}\overset{CH_3}{\underset{CONH_2}{C^{\cdot}}}}} + \underset{(\mathrm{M})}{\mathrm{CH_2 = \overset{CH_3}{\underset{CONH_2}{C}}}} \xrightarrow{k_p} \underset{(\mathrm{M_2^{\cdot}})}{\mathrm{Cl^-H_3N^+\underset{COOH}{CH}\text{–}CH_2\text{–}S\text{–}CH_2\text{–}\overset{CH_3}{\underset{CONH_2}{C}}\text{–}CH_2\text{–}\overset{CH_3}{\underset{CONH_2}{C^{\cdot}}}}} \quad (3)$$

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$$\mathrm{M}_2^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_3^{\cdot} \qquad (4)$$

$$\mathrm{M}_{n-1}^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_n^{\cdot} \qquad (5)$$

Termination

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_t} M_{n+m} \qquad (6)$$

The following rate expression can be derived from the above scheme:

$$R_p = k_p(k/2k_t)^{1/2}[\mathrm{M}][\mathrm{PDP}]^{1/2}[\mathrm{RSH}] \qquad (7)$$

The kinetic chain length can be written as:

$$\nu = k_p[\mathrm{M}]/(2kk_t)[\mathrm{PDP}]^{1/2}[\mathrm{RSH}] \qquad (8)$$

All the observed experimental results are satisfactorily explained by the above rate expression (7).

Rate dependence on initiator concentration

The order of reaction with respect to PDP is found to be 0.68 and 0.65 for conditions A and B respectively, which deviate from the ideal value of 0.50 (*Figure 1*). This indicates that termination of the growing chain radical is predominantly due to mutual combination of polymer chain radicals[7,8] along with little primary radical termination[9]. On the other hand, $[\eta]$, $\bar{M}_V$ and $\bar{P}_n$ decrease with the increase of PDP concentration (*Table 1*), which can be explained by the fact that propagating chain radicals undergo termination rather than propagation[10].

Rate dependence on activator concentration

The order of reaction with respect to Cys.HCl has been found to be unity for both conditions A and B (*Figure 2*), which can be explained by the fact that the polymerization is initiated only by the cysteine radical produced by the interaction between Cys.HCl and PDP. The sharp i.r. absorption spectral band at 704 cm^{-1} (for $-CH_2-S-CH_2-$ group) in the resulting polymer clearly indicates the presence of $-CH_2-S-CH_2-$ group. On the other hand $[\eta]$, $\bar{M}_V$ and $\bar{P}_n$ increase with the decrease of Cys.HCl concentration (*Table 2*), which is in accordance with equation (8).

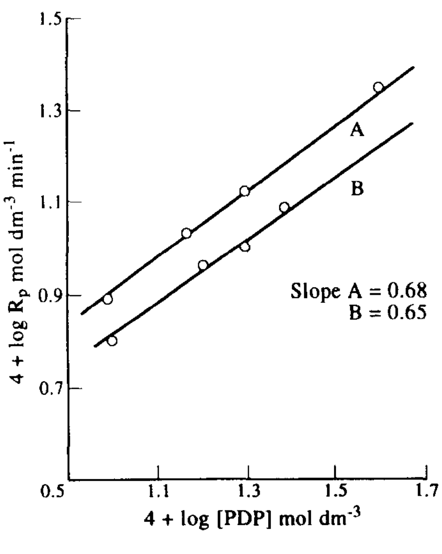

Figure 1 Plot of R_p vs. PDP concentration, at temp. = 45°C; [methacrylamide] = 2.0 × 10^{-1} mol dm^{-3} (A), 1.51 × 10^{-1} mol dm^{-3} (B); [cys.HCl] = 1.0 × 10^{-2} mol dm^{-3} (A), 1.50 × 10^{-2} mol dm^{-3} (B)

Table 1 Effect of PDP concentration on η, $\bar{M}_V$ and $\bar{P}_n$

[PDP] × 10^3 (mol dm^{-3})	η × 10^2 (dl g^{-1})	M_V	$\bar{P}_n$
4.0	13.2	54 450	640.58
2.0	14.3	62 950	740.58
1.5	15.2	70 310	827.17
1.0	16.3	79 800	938.82

Temp. = 45°C; [methacrylamide] = 2.0 × 10^{-1} mol dm^{-3}; [Cys.HCl] = 1.0 × 10^{-2} mol dm^{-3}

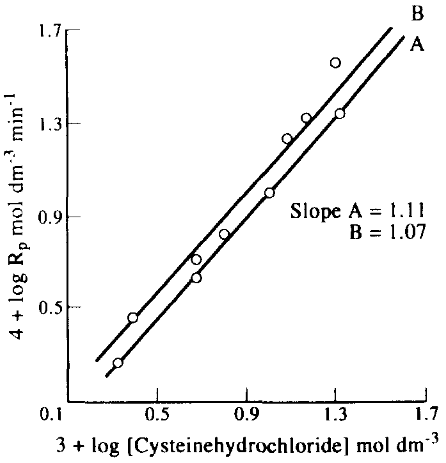

Figure 2 Plot of R_p vs. Cys.HCl concentration, at temp. = 45°C; [methacrylamide] = 2.0 × 10^{-1} mol dm^{-3} (A), 1.5 × 10^{-1} mol dm^{-3} (B); [PDP] = 1.0 × 10^{-2} mol dm^{-3} (A), 8.0 × 10^{-3} mol dm^{-3} (B)

Table 2 Effect of Cys.HCl concentration on η, $\bar{M}_V$ and P_n

[Cys.HCl] × 10^3 (mol dm^{-3})	η × 10^2 (dl g^{-1})	$\bar{M}_V$	$\bar{P}_n$
20.0	9.17	28 050	330.00
12.5	10.0	32 810	386.00
10.0	10.3	34 990	411.64
5.0	11.36	41 020	482.58
2.5	12.04	45 710	537.76

Temp. = 45°C; [methacrylamide] = 2.0 × 10^{-1} mol dm^{-3}; [PDP] = 1.0 × 10^{-2} mol dm^{-3}

Rate dependence on monomer concentration

The order of reaction with respect to methacrylamide has been found to be unity for both conditions A and B (*Figure 3*). The values of $[\eta]$, $\bar{M}_V$ and $\bar{P}_n$ also increase with the increase of methacrylamide concentration (*Table 3*) as required by equation (8).

Rate dependence on temperature

The overall energy of activation has been found to be 41.54 ± 1 and 43.39 ± 1 kJ mol^{-1} for conditions A and B respectively from the plot of log R_p *versus* T^{-1} (*Figure 4*). On the other hand, $[\eta]$, $\bar{M}_V$ and $\bar{P}_n$ decrease gradually with the increase of temperature (*Table 4*). This can be attributed to the increase of termination rate as compared to propagation, which may be due to bimolecular termination. At higher temperatures, the viscosity decreases, thus increasing the mobility of growing chain radicals, and hence there may be enhancement of bimolecular termination.

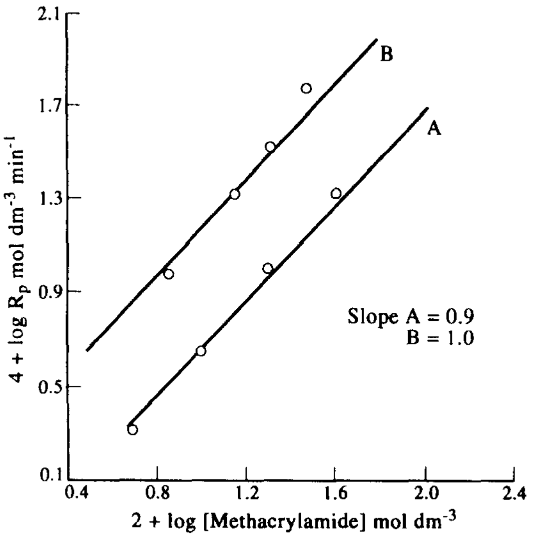

Figure 3 Plot of R_p vs. methacrylamide concentration, at temp. = 45°C: [Cys.HCl] = 1.0×10^{-2} mol dm^{-3} (A), 1.5×10^{-2} mol dm^{-3} (B); [PDP] = 1.0×10^{-2} mol dm^{-3} (A), 8.0×10^{-2} mol dm^{-3} (B)

Table 3 Effect of monomer concentration on η, $\bar{M}_V$ and $\bar{P}_n$

[Methacrylamide] $\times 10^2$ (mol dm^{-3})	$\eta \times 10^2$ (dl g^{-1})	$\bar{M}_V$	$\bar{P}_n$
4.0	12.8	51 400	604.00
2.0	10.3	34 990	411.00
1.0	9.1	27 670	325.00
0.5	8.4	24 150	282.00

Temp. = 45°C; [PDP] = 1.0×10^{-2} mol dm^{-3}; [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}

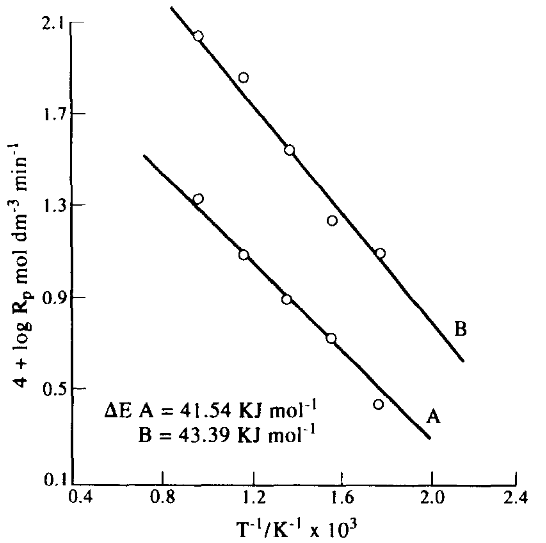

Figure 4 Temperature effect on R_p: [methacrylamide] = 2.0×10^{-1} mol dm^{-3} (A), 1.51×10^{-1} mol dm^{-3} (B); [Cys.HCl] = 1.0×10^{-2} mol dm^{-3} (A), 1.50×10^{-2} mol dm^{-3} (B); [PDP] = 1.0×10^{-2} mol dm^{-3} (A), 8.0×10^{-3} mol dm^{-3} (B)

Table 4 Effect of temperature on η, $\bar{M}_V$ and $\bar{P}_n$

Temperature (°C)	$\eta \times 10^2$ (dl g^{-1})	$\bar{M}_V$	$\bar{P}_n$
35	12.1	46 450	546.4
40	11.2	40 360	474.8
45	10.3	34 990	411.4
50	9.3	28 770	338.4
55	8.25	23 120	272.0

[Methacrylamide] = 2.0×10^{-1} mol dm^{-3}; [PDP] = 1.0×10^{-2} mol dm^{-3}; [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}

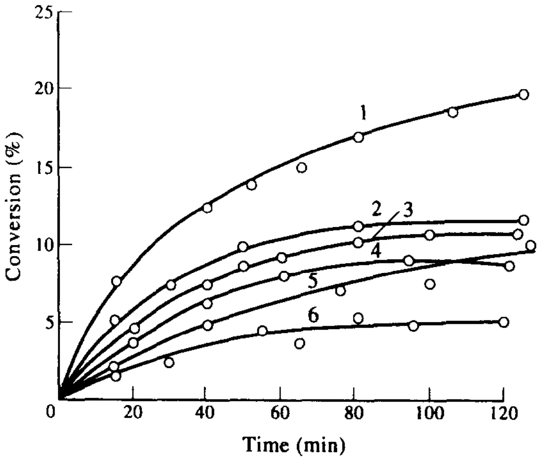

Figure 5 Percentage conversion as a function of time, at temp. = 45°C: [methacrylamide] = 2.0×10^{-1} mol dm^{-3}, [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}, [PDP] = 1.0×10^{-2} mol dm^{-3}, [solvent] = 1 M. Solvents used: 1, controlled experiment; 2, methanol; 3, ethanol; 4, propanol; 5, dimethylformamide; 6, butanol

Effect of additives

The retarding effect on the rate of polymerization on addition of water-miscible organic solvents is due to the fact that these solvents decrease the area of shielding[11] of the strong hydration layer in the aqueous medium and also decrease interchain hydrogen bonding between polymethacrylamide chains, resulting in an increase in mutual termination of the polymer chain. The retarding effect increases from methanol to butanol (*Figure 5*), which are in order of decreasing dielectric constant. Similar results have also been observed by other workers[12].

Both anionic and cationic detergents reduce the rate of polymerization (*Figure 6*). The value of R_p decreases, due to the positively charged micelles produced by cationic detergent (cetyltrimethylammonium bromide, CTAB), which favours the orientation of growing polymer for termination. The retarding effect of cations may also be due to specific ion-pair bonding of $P_2O_8^{4-}$ anion with cation, which lowers the rate of primary radical generation. On the other hand, the dissociation of anionic detergents (sodium lauryl sulfate, SLS) provides negatively charged micelles, which probably exert a repelling force between $P_2O_8^{4-}$ anion and negatively charged ionic micelles, thus lowering the rate of primary radical generation. Hence a retarding effect is observed.

The retarding effect (*Figure 7*) due to addition of inorganic salts can be explained as follows:

(A) In the case of alkali-metal chloride the basic character of alkali-metal ion increases, i.e. ionic radius increases from Li to K.

(B) In the case of neutral salts (NH_4Cl and Na_2SO_4) the decrease in the rate may be due to thickening of the medium, or the process of salting out causes interference with the usual reaction, resulting in premature termination of the growing chain.

Similar results have also been reported by others[13].

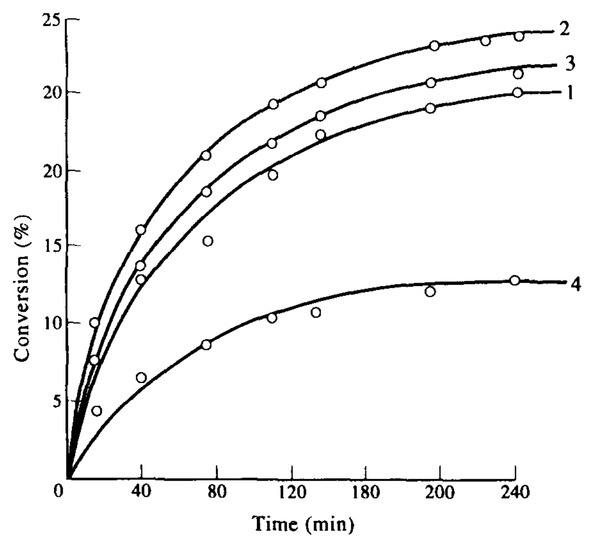

Figure 6 Effect of detergent concentration on R_p, at temp. = 45°C: [methacrylamide] = 2.0×10^{-1} mol dm^{-3}, [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}, [PDP] = 1.0×10^{-2} mol dm^{-3}. Detergents used: 1, controlled experiment; 2, sodium lauryl sulfate (1×10^{-2} mol dm^{-3}); 3, sodium oleate (1.0×10^{-3} mol dm^{-3}); 4, cetyltrimethylammonium bromide (1.0×10^{-3} mol dm^{-3})

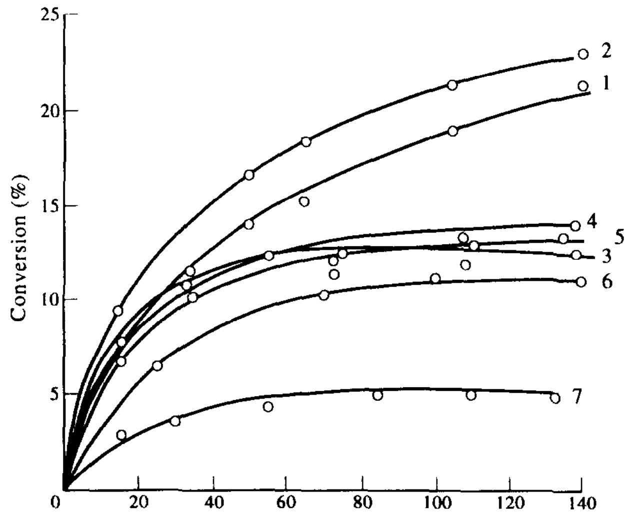

Figure 7 Effect of inorganic salts on R_p, at temp. = 45°C: [methacrylamide] = 2.0×10^{-1} mol dm^{-3}, [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}, [PDP] = 1.0×10^{-2} mol dm^{-3}, [salt] = 2.0×10^{-2} mol dm^{-3}. Salts used: 1, controlled experiment; 2, $MnSO_4$; 3, NH_4Cl; 4, KCl; 5, LiCl; 6, NaCl; 7, Na_2SO_4

The rate of polymerization increases with the addition of $MnSO_4$ (*Figure 7*) where Mn^{2+} is easily oxidized to Mn^{3+} by the interaction of PDP, which in turn produces free radicals[14-16] by the interaction of Cys.HCl as:

$$P_2O_8^{4-} + Mn^{2+} \rightarrow Mn^{3+} + P^{\cdot}O_4^{2-} + PO_4^{3-}$$

$$P^{\cdot}O_4^{2-} + Mn^{2+} \rightarrow Mn^{3+} + PO_4^{3-}$$

$$Mn^{3+} + RSH \rightarrow Mn^{2+} + RS^{\cdot}$$

where RSH = Cys.HCl and $RS^{\cdot}$ = cysteine free radical.

On the other hand, the addition of $CuSO_4$ decreases the R_p (*Figure 8*), which is due to formation of Cu^{2+} radical pair[17]. The retarding effect is also observed by the addition of NaF, which can be explained by the fact that NaF, being a complexing agent (*Figure 9*), lowers the effective concentration of PDP[18].

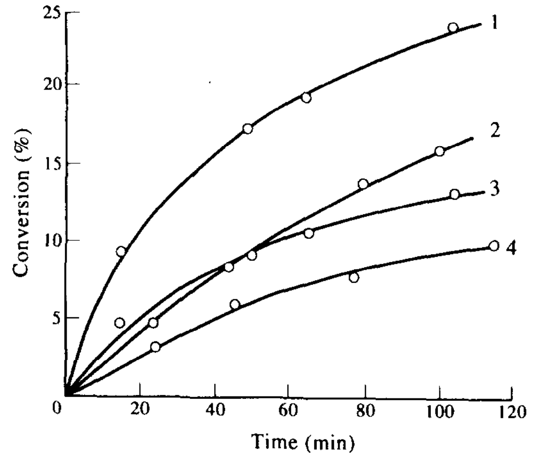

Figure 8 Effect of concentrations of complexing agent and transition-metal ion on R_p, at temp. = 45°C: [methacrylamide] = 2.0×10^{-1} mol dm^{-3}, [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}, [PDP] = 1.0×10^{-2} mol dm^{-3}. Curves: 1, controlled experiment; 2, [NaF] = 0.5×10^{-3} mol dm^{-3}; 3, [$CuSO_4$] = 1.0×10^{-3} mol dm^{-3}; 4, [NaF] = 1.0×10^{-3} mol dm^{-3}

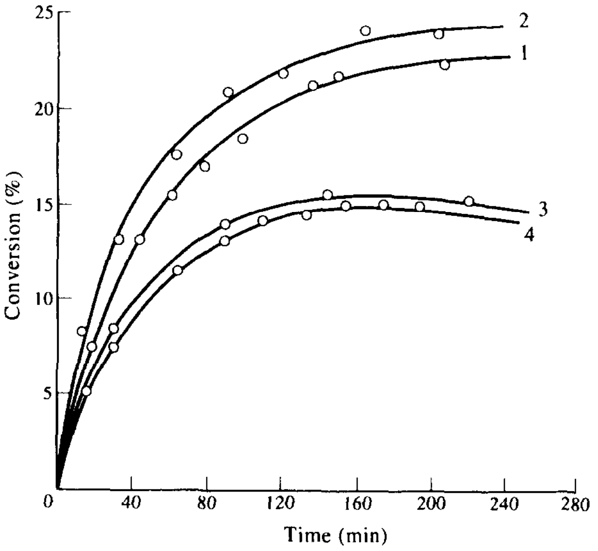

Figure 9 Effect of pH on R_p, at temp. = 45°C: [methacrylamide] = 2.0×10^{-1} mol dm^{-3}, [Cys.HCl] = 1.0×10^{-2} mol dm^{-3}, [PDP] = 1.0×10^{-2} mol dm^{-3}. Curves: 1, no addition of H_2SO_4; 2, pH 2.69; 3, pH 3.0; 4, pH 3.30

As the concentration of hydrogen ion increases (pH decreases) the formation of $HP^{\cdot}O_4^{-}$ and $P^{\cdot}O_4^{2-}$ radical ion increases, which enhances the R_p:

$$P_2O_8^{4-} + H^{+} \rightarrow HP^{\cdot}O_4^{-} + P^{\cdot}O_4^{2-}$$

CONCLUSION

R_p increases with the increase of [PDP], [Cys.HCl] and [methacrylamide] respectively, as expected by the following equation:

$$R_p = k_p(k/2k_t)^{1/2}[M][PDP]^{1/2}[RSH]$$

The energy of activation being 41.54 ± 1 kJ mol^{-1} is indicative of free-radical polymerization of methacrylamide by PDP–Cys.HCl system. The addition of organic solvent, detergent and inorganic salts shows decreasing effect on R_p while the $MnSO_4$ and H_2SO_4 (H^+) addition shows increasing effect on R_p.

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REFERENCES

1 Baral, N., Pati, N. C., Nayak, P. L. and Desh, S. B. *J. Macromol. Sci., Chem. (A)* 1983, **18**, 1123

2 Gopalan, A., Paulrajan, S., Venkatarao, K. and Subharathan, N. R. *Eur. Polym. J.* 1983, **19**, 817

3 Sarasvathi, S. and Venkatarao, K. *Makromol. Chem. Rapid Commun.* 1981, **2**, 219

4 Behari, K., Agrawal, U. and Das, R. *Polymer* 1993, **34**, 4557

5 Wallace, R. A. and Young, D. G. *J. Polym. Sci. (A1)* 1966, **4**, 1179

6 Chatterjee, S. K., Prokopova, E. and Bohdanecky, M. *Eur. Polym. J.* 1978, **14**, 665

7 Mishra, G. S. and Bajpai, U. D. N. *J. Macromol. Sci., Chem. (A)* 1979, **13** (8), 1135

8 Flory, P. J. 'Principles of Polmer Chemistry', Cornell University Press, Ithaca, NY, 1967, p. 309

9 Deb, P. C. and Meyerhoff, G. *Eur. Polym. J.* 1974, **10**, 709

10 Behari, K., Gupta, K. C. and Verma, M. *Angew. Makromol. Chem.* 1985, **67**, 130

11 Lange, N. A. 'Handbook of Chemistry', McGraw-Hill, New York, 1967, p. 1234

12 Palit, S. R. and Konar, R. S. *J. Polym. Sci.* 1962, **58**, 85; Thomas, W. H., Gleason, E. A. and Mino, G. *J. Polym. Sci.* 1957, **24**, 43

13 Mishra, G. S., Shukla, J. S. and Narain, H. *Makromol. Chem.* 1968, **119**, 74

14 Okomoto, T., Takahashi, M. and Inaki, Y. *Angew. Makromol. Chem.* 1974, **38**, 81

15 Waters, W. A. and Littler, J. A. 'Oxidation in Organic Chemistry' (Ed. K. B. Wiberg), Academic Press, London, 1965, p. 3

16 Pradhan, A. K., Pati, N. C. and Nayak, P. L. *J. Macromol. Sci., Chem. (A)* 1982, **18** (3), 395

17 Manickahra, S. P., Subhrathan, N. R. and Venkatarao, K. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 1679

18 Rebellow, J. J. *Makromol. Chem.* 1975, **176**, 2203