Kinetics of perphosphate-initiated polymerization of acrylamide with different activators

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The kinetics of aqueous polymerization of acrylamide was studied under an inert atmosphere at 30 ± 1°C using perphosphate as initiator with different activators such as mercaptosuccinic acid and cysteine hydrochloride. The order with respect to perphosphate and acrylamide is found to be one-half and unity, respectively, in both redox systems. Mercaptosuccinic acid has half-order dependence on the rate of polymerization, whereas cysteine hydrochloride has first-order dependence. The overall energy of activation is 42.5 ± 2 kJ mol^{-1} and 38.3 ± 1 kJ mol^{-1} for perphosphate/mercaptosuccinic acid and perphosphate/cysteine hydrochloride redox systems, respectively. Polyacrylamide samples collected under different kinetic conditions are used for the determination of the intrinsic viscosity.

(Keywords: kinetics; perphosphate; mercaptosuccinic acid; cysteine hydrochloride; polymerization; acrylamide)

INTRODUCTION

Potassium perphosphate has been used extensively in grafting processes[1,2] by many workers owing to its unique nature of giving high percentage grafting. At the same time, the growing importance of acrylamide in different fields prompted us to study the kinetics of homopolymerization of acrylamide using perphosphate ion as initiator. However, recently potassium perphosphate has been employed by some workers for the homopolymerization of acrylonitrile[3,4], methyl methacrylate[5] and *N*,*N*′-methylenebisacrylamide[6–8] along with different activators.

EXPERIMENTAL

Acrylamide was purified by crystallization from methanol and dried in a vacuum desiccator over silica gel. Solutions of other chemicals were prepared by weighing and by dissolving in triply distilled water. All the chemicals used were of Analar (B.D.H.) grade. Potassium perphosphate was received from F.M.C. Corporation, New York, as a gift and was used after recrystallization from distilled water. The kinetics of the polymerization reaction was followed as reported in earlier communications[9,10]. The intrinsic viscosity of the samples was determined by using the method reported elsewhere[9,10].

RESULTS AND DISCUSSION

On the basis of the observed experimental results, the following two kinetic schemes were proposed for the polymerization of acrylamide using different redox systems.

Scheme A: perphosphate/mercaptosuccinic acid-initiated polymerization of acrylamide

Radical formation

$$P_2O_8^{4-} + RSH \xrightarrow{k} R\dot{S} + HPO_4^{2-} + P\dot{O}_4^{2-} \quad (1)$$

Initiation

$$P\dot{O}_4^{2-} + M \xrightarrow{k_i'} \dot{M}_1 \quad (2)$$

$$R\dot{S} + M \xrightarrow{k_i''} \dot{M}_1 \quad (3)$$

Propagation

$$\dot{M}_1 + M \xrightarrow{k_p} \dot{M}_2$$

$$\dot{M}_{n-1} + M \xrightarrow{k_p} \dot{M}_n \quad \text{etc.} \quad (4)$$

Termination

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_t} M_{n+m} \quad (5)$$

The proposed steps lead to the following rate expression:

$$R_p = k_p(k/k_t)^{1/2}[M][P_2O_8^{4-}]^{1/2}[RSH]^{1/2} \quad (6)$$

The kinetic chain length is given as:

$$v = k_p[M]/2(kk_t[P_2O_8^{4-}][RSH])^{1/2} \quad (7)$$

where M and RSH are given after equation (13).

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Scheme B: perphosphate/cysteine hydrochloride-initiated polymerization of acrylamide

Radical formation

$$P_2O_8^{4-} + 2RSH \xrightarrow{k} 2R\dot{S} + 2HPO_4^{2-} \quad (8)$$

Initiation

$$R\dot{S} + M \xrightarrow{k_i} \dot{M}_1 \quad (9)$$

Propagation

$$\dot{M} + M \xrightarrow{k_p} \dot{M}_2$$
$$\dot{M}_{n-1} + M \xrightarrow{k_p} \dot{M}_n \quad \text{etc.} \quad (10)$$

Termination

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_t} M_{n+m} \quad (11)$$

The following rate expression was derived from the above scheme:

$$R_p = k_p(k/2k_t)^{1/2}[M][P_2O_8^{4-}]^{1/2}[RSH] \quad (12)$$

The kinetic chain length is:

$$v = k_p[M]/(2kk_i[P_2O_8^{4-}])^{1/2} \quad (13)$$

In these equations, M = monomer and RSH = mercaptosuccinic acid or cysteine hydrochloride as the case may be.

All the following observed results are explained satisfactorily by the above rate expressions.

Rate dependence on potassium perphosphate

A plot of log(initial rate of polymerization R_p at 5 min) *versus* log(initial concentration of perphosphate) (*Figure 1*) exhibits the half-order perphosphate dependence on the rate of polymerization of acrylamide. However, the lower order (0.5) at higher concentrations of perphosphate is attributed to the increasing rate of oxidation and termination of radicals which are supposed to be involved in the polymerization reaction. Since the order with respect to perphosphate was found to be one-half, the termination of growing chain radicals is due to mutual combination of polymer chain radicals[9-15]. The decrease in intrinsic viscosity with increasing concentration of perphosphate (*Table 1*) can be explained by the fact that the propagating chain radicals undergo a termination process rather than propagation[14], which results in a higher percentage conversion and lower molecular weight of the polymer formed.

Rate dependence on activator concentration

The order with respect to mercaptosuccinic acid and cysteine hydrochloride, calculated with the help of plots of log R_p (R_p at 5 min) and log[activator] (*Figure 2*), was found to be one-half and unity, respectively. The initial rate of polymerization (R_p at 5 min) increases linearly

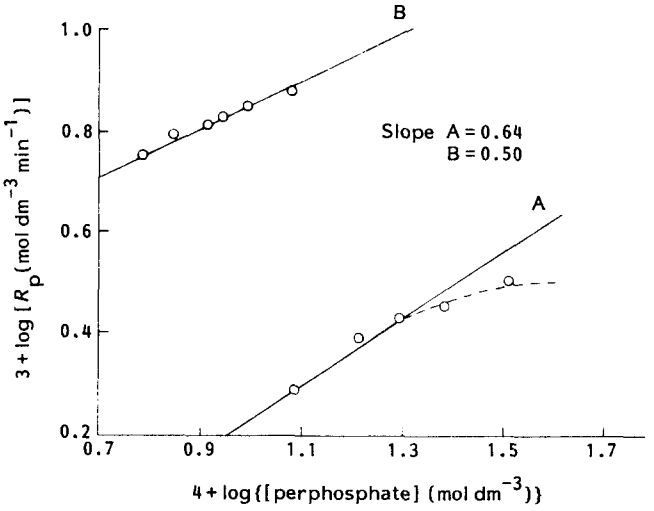


Figure 1 Plot of R_p vs. $[P_2O_8^{4-}]$: temp.$_{A\&B}$ = 30°C; $[acrylamide]_{A\&B} = 2.0 \times 10^{-1}$ mol dm^{-3}, $[MSA]_A = 3.33 \times 10^{-3}$ mol dm^{-3}, [cysteine hydrochloride] = 2.0×10^{-3} mol dm^{-3}

Table 1 Rate dependence on varying the concentration of initiator

	[Perphosphate] × 10^3 (mol dm^{-3})	Conversion (%) at different times (min)							$\bar{M}_v$	$[\eta] \times 10^2$ (dl g^{-1})
		5	10	15	20	25	30	35		
A	3.33	3.50	8.60	13.20	18.40	24.20	29.60	35.40	–	5.80
	2.50	3.00	7.50	11.20	16.20	21.80	25.60	30.00	932	6.20
	2.00	2.60	6.20	9.80	14.00	18.80	22.00	26.80	1144	7.10
	1.66	2.30	5.80	9.00	12.60	16.00	19.20	22.00	1371	8.00
	1.25	2.00	4.60	7.80	10.20	14.20	16.80	18.00	1894	9.90

	[Perphosphate] × 10^3 (mol dm^{-3})	Conversion (%) at different times (min)								$\bar{M}_v$	$[\eta] \times 10^2$ (dl g^{-1})
		5	10	15	20	25	30	35	45		
B	12.50	18.60	33.80	45.40	53.60	58.80	64.20	67.40	70.20	2535	12.0
	11.11	17.80	29.80	40.00	48.40	53.60	58.40	61.00	64.00	–	14.0
	10.00	16.20	27.40	36.20	44.40	50.00	54.60	57.20	58.80	3202	15.0
	8.33	15.60	25.60	34.40	41.20	46.80	49.60	52.60	55.40	3846	15.8
	6.25	13.40	21.60	29.80	34.60	38.40	41.60	43.50	45.00	5456	19.9

[Acrylamide] = 2.00×10^{-1} mol dm^{-3}
[Cysteine hydrochloride]$_B$ = 2.0×10^{-3} mol dm^{-3}
[Mercaptosuccinic acid]$_A$ = 3.33×10^{-3} mol dm^{-3}

with the initial concentration of activator but at higher concentration it decreases considerably due to the insufficient amount of perphosphate to produce the required number of free radicals to maintain linearity.

The decrease in intrinsic viscosity with increasing mercaptosuccinic acid concentration (*Table 2*) can be explained by considering the bimolecular mode of termination[15,16]. Contrary to this, intrinsic viscosity increases linearly with the concentration of cysteine hydrochloride up to a certain extent. The deviation from linearity at higher concentration of cysteine hydrochloride might be due to the termination of growing chain radicals by primary free radicals (*Table 2*).

Rate dependence on acrylamide concentration

With both redox systems the order with respect to acrylamide was found to be unity (*Figure 3*) with the help of graphs of log(rate of polymerization R_p at 10 min) *versus* log(initial concentration of acrylamide). The order below unity at higher concentration of acrylamide can be explained by considering the assumption[17-19] that excess of monomer acts as a good solvent, which increases the mobility of the growing chains, and thus increases the probability of binary collisions necessary for termination, and hence decreases the rate.

The results in *Table 3* show that the intrinsic viscosity increases with the concentration of acrylamide but at higher concentration of acrylamide it does not show very much change. The aforesaid assumption[17] can satisfactorily explain this observation.

The calculated activation energies (*Figure 4*) are $42 \pm 2\,kJ\,mol^{-1}$ and $38.29 \pm 1\,kJ\,mol^{-1}$ for perphosphate/mercaptosuccinic acid and perphosphate/cysteine hydrochloride systems, respectively. The results in *Table 4* reveal that the intrinsic viscosity decreases with temperature. This can be explained by assuming that the decreasing viscosity of a medium with temperature favours the termination of growing chain radicals, and consequently gives a low-molecular-weight polymer.

In view of the kinetic parameters and the corresponding rates of polymerization with respect to perphosphate/mercaptosuccinic acid and perphosphate/cysteine hydrochloride systems, the latter system was found to be different in giving higher-molecular-weight polymer (*Table 1*) even at low concentrations of

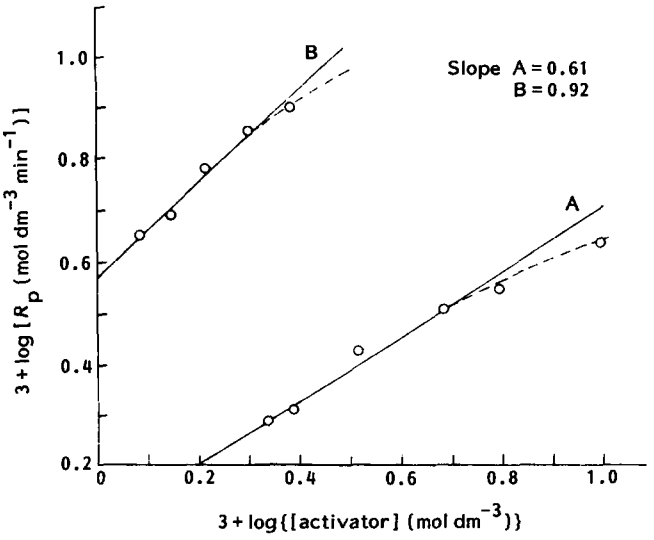


Figure 2 Plot of R_p vs. [activator]: temp.$_{A\&B}$ = 30°C; [acrylamide]$_{A\&B} = 2.0 \times 10^{-1}$ mol dm^{-3}, [perphosphate]$_A = 2.0 \times 10^{-3}$ mol dm^{-3}, [perphosphate]$_B = 10.0 \times 10^{-4}$ mol dm^{-3}

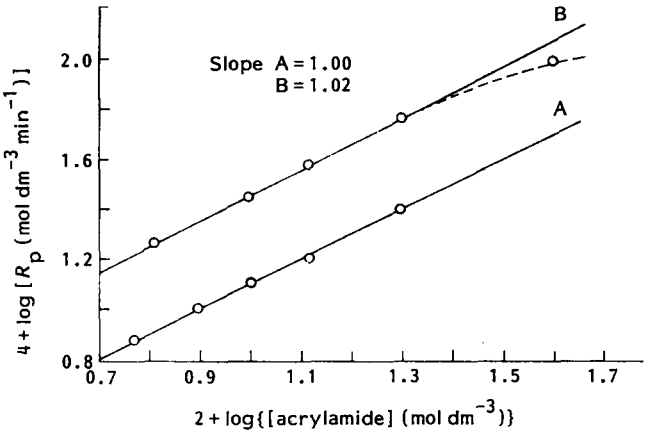


Figure 3 Plot of R_p vs. [acrylamide]: temp.$_{A\&B}$ = 30°C; [perphosphate]$_A = 2.0 \times 10^{-3}$ mol dm^{-3}, [perphosphate]$_B = 10.0 \times 10^{-4}$ mol dm^{-3}, [mercaptosuccinic acid]$_A = 3.33 \times 10^{-3}$ mol dm^{-3}, [cysteine hydrochloride]$_B = 20.0 \times 10^{-3}$ mol dm^{-3}

Table 2 Rate dependence on varying the concentration of activator

	[Mercaptosuccinic acid] $\times 10^3$ (mol dm^{-3})	Conversion (%) at different times (min)							$\bar{M}_v$	$[\eta] \times 10^2$ (dl g^{-1})
		5	10	15	20	25	30	35		
A	10.00	5.60	11.00	16.20	21.60	25.80	29.40	31.20	926	6.17
	5.00	3.80	8.60	14.20	18.60	23.00	27.80	30.20	1001	6.50
	4.00	3.20	7.20	11.20	16.80	21.40	25.20	28.60	–	
	3.33	3.00	6.00	9.60	13.80	17.60	22.20	25.40	1144	7.10
	[Cysteine hydrochloride] $\times 10^3$ (mol dm^{-3})	Conversion (%) at different times (min)							$\bar{M}_v$	$[\eta] \times 10^2$ (dl g^{-1})
		5	10	15	20	25	30	35	45	
B	2.50	17.80	29.80	40.00	48.40	53.60	58.40	61.00	64.00	3883	15.90
	2.00	14.20	26.00	35.00	42.20	51.60	52.00	55.40	60.40	3202	14.00
	1.66	11.20	20.40	30.20	37.40	43.80	46.80	49.00	53.60	2664	12.40
	1.42	9.20	16.40	24.20	31.40	36.00	41.00	44.60	48.60	2222	11.00

[Acrylamide]$_{A\&B} = 2.0 \times 10^{-1}$ mol dm^{-3}
[Perphosphate]$_A = 2.0 \times 10^{-3}$ mol dm^{-3}
[Perphosphate]$_B = 10.0 \times 10^{-4}$ mol dm^{-3}

Table 3 Rate dependence on varying the concentration of monomer

	[Acrylamide] × 10^1 (mol dm^{-3})	Conversion (%) at different times (min)							$\bar{M}_v$	$[\eta] \times 10^2$ (dl g^{-1})
		5	10	15	20	25	30	35		
A	4.00	5.80	12.40	20.45	25.60	30.00	34.20	37.00	1536	9.80
	2.00	5.50	6.20	17.50	22.00	26.20	30.20	33.20	1444	7.10
	1.33	5.30	6.60	16.50	21.19	25.39	27.19	28.20	794	5.58
	0.80	5.80	6.75	16.50	21.80	26.00	27.00	28.80	–	
B	2.00	18.20	30.00	41.20	48.00	55.70	59.60	63.50	3202	1.40
	1.00	17.80	29.80	40.00	48.40	53.40	61.00	64.00	1218	0.74
	0.80	16.20	27.50	39.80	49.00	53.60	58.80	62.50	–	
	0.66	10.46	29.76	39.76	47.13	55.71	60.20	65.45	573	0.45

Temp.$_{A\&B}$ = 30°C
[Perphosphate]$_A$ = 2.0×10^{-3} mol dm^{-3}
[Perphosphate]$_B$ = 10.0×10^{-4} mol dm^{-3}
[Mercaptosuccinic acid]$_A$ = 3.33×10^{-3} mol dm^{-3}
[Cysteine hydrochloride]$_B$ = 20.0×10^{-3} mol dm^{-3}

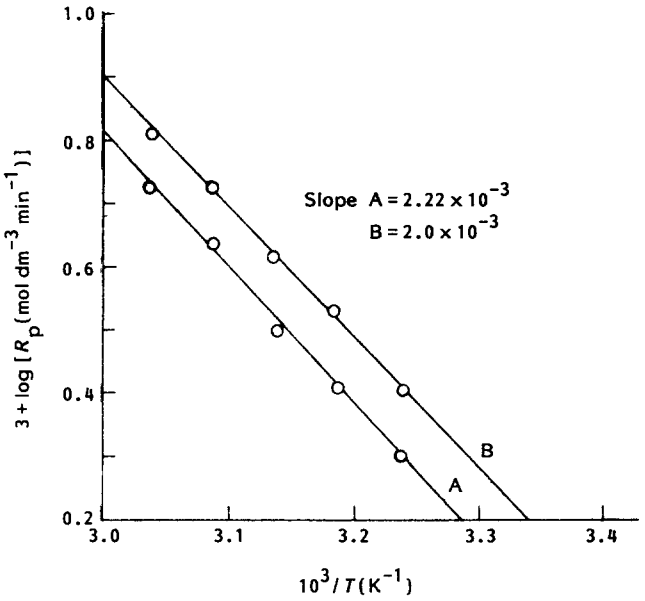


Figure 4 Plot of R_p vs. $1/T$: [acrylamide]$_{A\&B}$ = 2.0×10^{-1} mol dm^{-3}, [perphosphate]$_A$ = 2.0×10^{-3} mol dm^{-3}, [perphosphate]$_B$ = 11.1×10^{-4} mol dm^{-3}, [mercaptosuccinic acid]$_A$ = 3.3×10^{-3} mol dm^{-3}, [cysteine hydrochloride]$_B$ = 2.5×10^{-3} mol dm^{-3}

reactants when compared with the former. The molecular weights of samples have been calculated as reported elsewhere[9,10].

Effect of addition of additives

The rate of polymerization of acrylamide has been studied in the presence of various additives, such as inorganic salts, detergent, alcohols and sulphuric acid. A retarding effect on the rate of polymerization was observed on addition of water-miscible organic solvents. This is due to the fact that these solvents decrease the area of shielding[20] of a strong hydration layer in aqueous medium and also decrease the interchain hydrogen bonding between polyacrylamide chains, resulting in an increase in the mutual termination of polymer chains. The retarding effect increases prominently from methanol to butanol (methanol < ethanol < propanol < butanol), which are in the order of decreasing dielectric constant (*Figure 5*).

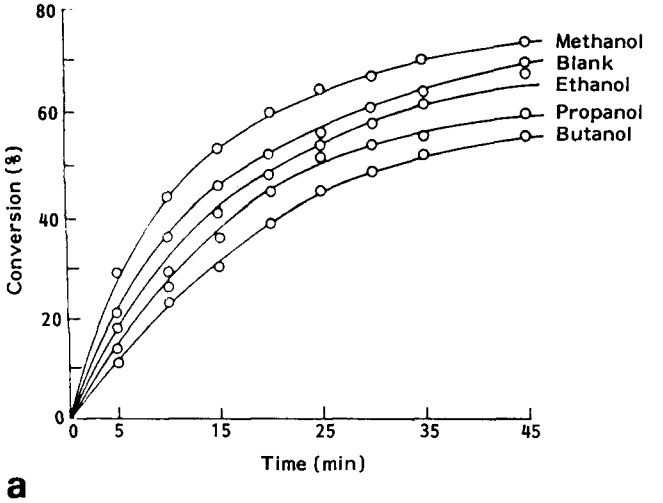
Table 4 Intrinsic viscosity and molecular weight as functions of temperature

Temp. (°C)	A		B	
	$[\eta] \times 10^2$ (dl g^{-1})	$\bar{M}_v$	$[\eta] \times 10^2$ (dl g^{-1})	$\bar{M}_v$
35	8.0	1371	15.4	3699
40	7.1	1144	14.0	3202
45	6.2	932	12.9	2029
50	5.0	672	11.4	2345
55	3.9	461	10.10	11925

[Acrylamide]$_{A\&B}$ = 2.0×10^{-1} mol dm^{-3}
[Perphosphate]$_A$ = 2.0×10^{-3} mol dm^{-3}
[Perphosphate]$_B$ = 10.0×10^{-4} mol dm^{-3}
[Mercaptosuccinic acid]$_A$ = 3.33×10^{-3} mol dm^{-3}
[Cysteine hydrochloride]$_B$ = 2.0×10^{-3} mol dm^{-3}

The effect of an anionic detergent like sodium oleate or sodium laurylsulphate above its critical micelle concentration (c.m.c.) increases the initial rate of polymerization of acrylamide initiated by perphosphate/mercaptosuccinic acid (*Figure 6*) and the maximum yield. However, a cationic detergent like cetyltrimethylammonium bromide (CTAB) above its c.m.c. decreases the initial rate and maximum conversion effectively, as reported by Hussain *et al.*[21]. On the other hand, the rate of polymerization of acrylamide initiated by perphosphate/cysteine hydrochloride decreases with the addition of an anionic detergent, contrary to the results of Hussain *et al.*[21] (*Figure 7*).

Manganous sulphate has also shown extraordinary behaviour. On addition of manganous sulphate the initial rate and maximum conversion decrease in the perphosphate/mercaptosuccinic acid redox system. Since Mn^{2+} forms complexes easily with hydroxy acids, which lowers total activator concentration, retardation was observed. On the other hand, it enhances the rate of polymerization in perphosphate/cysteine hydrochloride-initiated polymerization of acrylamide, which may be due to oxidation of Mn^{2+} to Mn^{3+} by perphosphate. The Mn^{3+} abstracts hydrogen atoms from the organic substrate to produce free radicals, and therefore increases the rate of polymerization. Addition of $AgNO_3$ accelerates the reaction in the perphosphate/mercaptosuccinic acid system. Ag^+ is oxidized to Ag^{2+} by perphosphate ions and radicals are produced by the



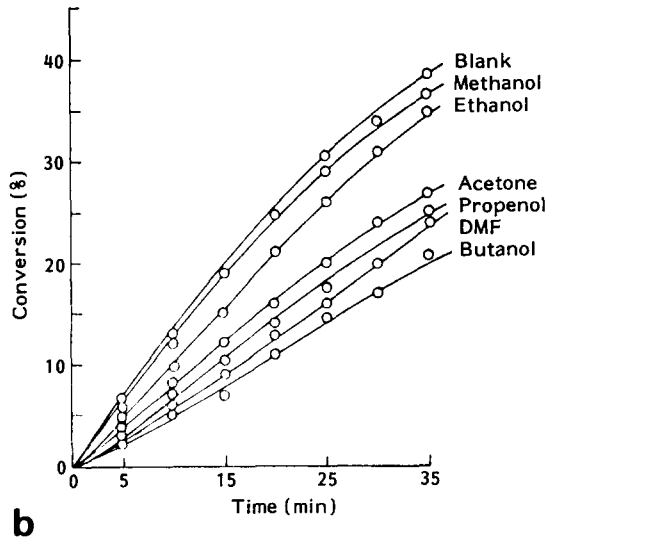


Figure 5 Percentage conversion as a function of time: (a) temp. = 40°C;
[acrylamide] = 2.0×10^{-1} mol dm^{-3},
[perphosphate] = 10.0×10^{-4} mol dm^{-3},
[cysteine hydrochloride] = 2.0×10^{-3} mol dm^{-3},
[solvents] = 10.0×10^{-1} mol dm^{-3}.
(b) Temp. = 40°C; [acrylamide] = 2.0×10^{-1} mol dm^{-3},
[perphosphate] = 2.0×10^{-3} mol dm^{-3},
[mercaptosuccinic acid] = 3.3×10^{-3} mol dm^{-3},
[solvents] = 10.0×10^{-1} mol dm^{-3}

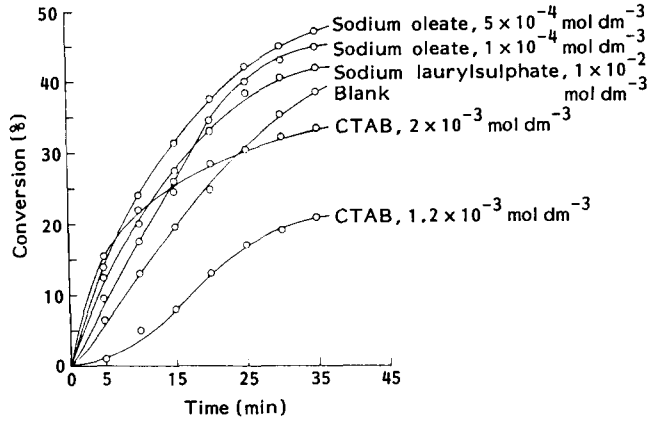


Figure 6 Percentage conversion as a function of time: temp. = 40°C;
[acrylamide] = 2.0×10^{-1} mol dm^{-3},
[perphosphate] = 2.0×10^{-3} mol dm^{-3},
[mercaptosuccinic acid] = 3.3×10^{-3} mol dm^{-3}

interaction with mercaptosuccinic acid and monomer (*Figure 8*). Hence an accelerating effect was observed. Contrary to this $AgNO_3$ decreases the rate of perphosphate/cysteine hydrochloride redox system. This retarding effect may be due to formation of complexes between Ag^+ and cysteine hydrochloride.

The addition of alkali-metal chlorides such as LiCl, NaCl and KCl (LiCl < NaCl < KCl) depresses the rate of polymerization of acrylamide initiated by perphosphate/mercaptosuccinic acid due to the increased size of cation (*Figure 8*) whereas in the case of the perphosphate/cysteine hydrochloride system these alkali chlorides enhance the rate of polymerization (KCl < NaCl < LiCl). Complex formation occurs between the propagating radicals and chloride ions to give a mesomeric structure which has enhanced reactivity (*Figure 9*).

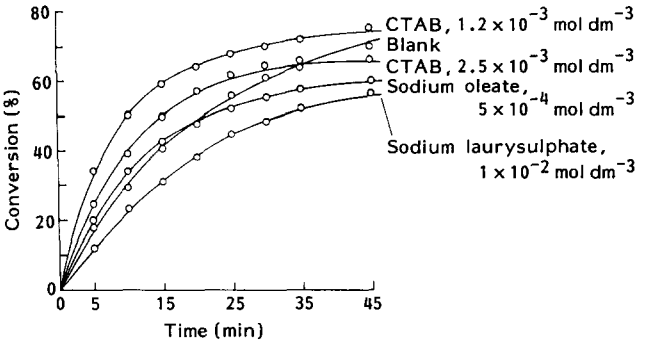


Figure 7 Percentage conversion as a function of time: temp. = 40°C;
[acrylamide] = 2.0×10^{-1} mol dm^{-3},
[perphosphate] = 2.0×10^{-3} mol dm^{-3},
[cysteine hydrochloride] = 2.0×10^{-3} mol dm^{-3}

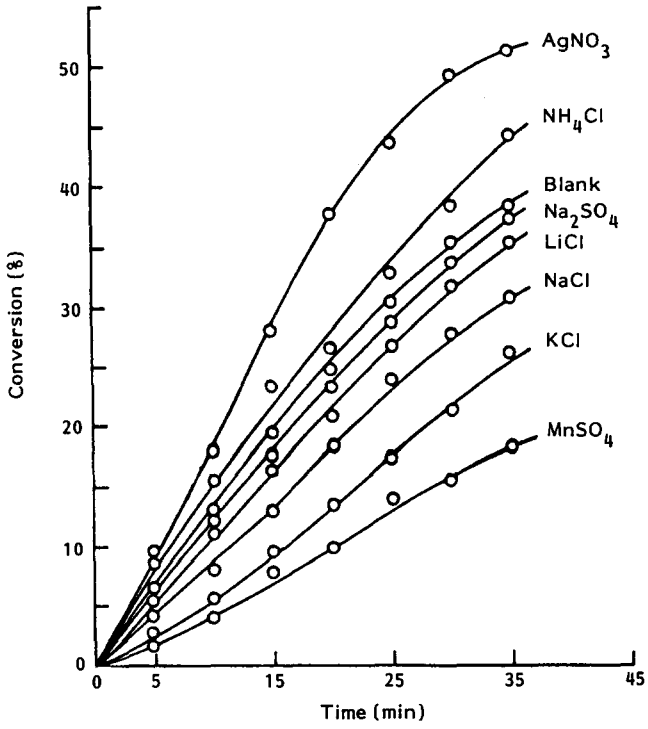


Figure 8 Percentage conversion as a function of time: temp. = 40°C;
[acrylamide] = 2.0×10^{-1} mol dm^{-3},
[perphosphate] = 2.0×10^{-3} mol dm^{-3},
[mercaptosuccinic acid] = 3.3×10^{-3} mol dm^{-3},
[salts] = 2.0×10^{-2} mol dm^{-3}

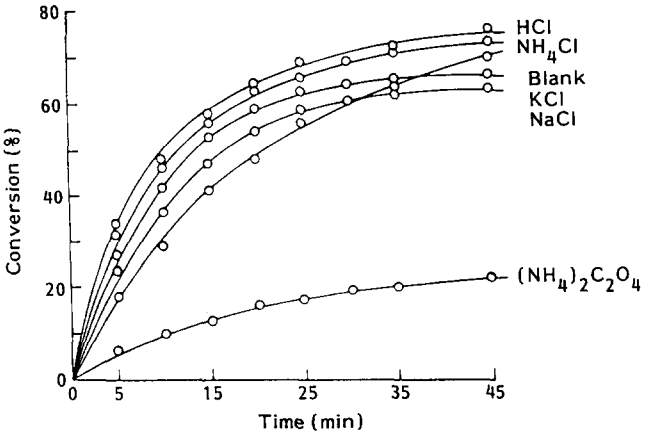


Figure 9 Percentage conversion as a function of time: temp. 40°C; [acrylamide] = 2.0×10^{-1} mol dm^{-3}, [perphosphate] = 10.0×10^{-4} mol dm^{-3}, [cysteine hydrochloride] = 2.0×10^{-3} mol dm^{-3}, [salts] = 2.0×10^{-2} mol dm^{-3}

The rate of polymerization increases with the decrease in concentration of hydrogen ions. This can be explained as:

$$P_2O_8^{4-} + H^+ \rightarrow HP\dot{O}_4 + P\dot{O}_4^{2-}$$

$$P_2O_8^{4-} + 2H^+ \rightarrow 2HPO_4^{2-}$$

So at higher concentration of acid, perphosphate decomposes asymmetrically resulting in the formation of inactive ions. Morgan[22] has given a similar explanation for the retarding effect of H^+ ions on persulphate-initiated vinyl polymerization.

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