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POLYMERIZATION OF ACRYLAMIDE BY PEROXODIPHOSPHATE/DIFFERENT ACTIVATORS REDOX SYSTEM IN AN AQUEOUS MEDIUM

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ABSTRACT

The polymerization of acrylamide initiated by potassium peroxodiphosphate in combination with different activators (viz., sorbose and thiourea) was studied in an aqueous medium at 40 [illegible] 0°C in an inert atmosphere. The rate of polymerization was found to be first power to the monomer and half power to the initiator concentration. Sorbose and thiourea have half and unit orders, respectively. The overall energy of activation was found to be 38 ± 2 and 47 ± 2 kJ/mol for peroxodiphosphate/sorbose and peroxodiphosphate/thiourea redox systems, respectively. The effects of various additives, such as organic solvents, neutral salts, surfactants, and sulfuric acid, were studied. The viscometric-average molecular weight and the degree of polymerization were determined viscometrically.

INTRODUCTION

Potassium peroxodiphosphate (PDP) forms an efficient redox couple with various reducing agent such as hydroxy acids [1, 2], thio compounds [3, 4], metal ions [5, 6], bisulfite [7], etc. The half-order dependence with respect to initiator refers to the bimolecular termination of the growing polymer chain which has been reported by several workers [2–6]. Contrary to this, Hariharan and Meenakshi [1] reported that the rate of polymerization is independent of the PDP concentration and termination occurs by the participation of primary radicals as shown during a study of acrylonitrile polymerization initiated by the PDP-ascorbic acid redox pair.

The different views reported in the literature led us to study the polymerization of acrylamide initiated by PDP with two different activators: sorbose and thiourea.

EXPERIMENTAL

The method for purification of monomer, the course of the polymerization, and the measurement of intrinsic viscosity were followed as reported in our previous communications [3, 8].

RESULTS AND DISCUSSION

Rate Dependence on PDP Concentration

The results obtained in the absence of the activators clearly indicate that PDP alone is incapable of initiating the polymerization of acrylamide. The reaction proceeds with remarkable speed upon addition of the activators. The order of reaction with respect to PDP, calculated from a double lograthmic plot (Fig. 1) of rate of polymerization (R_p at 5% conversion) versus initial concentration of PDP was found to be half in both cases. Examination of Table 1 reveals that the intrinsic viscosity and viscometric-average molecular weight decrease on increasing the PDP concentration. This is due to the termination of propagating chain radicals rather than propagation resulting in a higher percent conversion with lower molecular weight polymer.

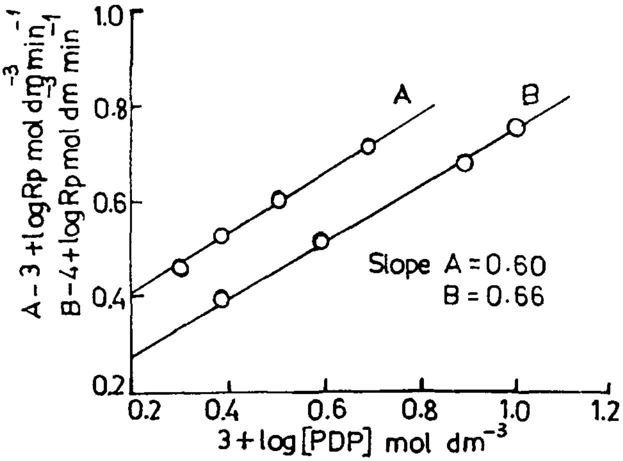


FIG. 1. Dependence of rate of polymerization on PDP concentration. Temperature = 40°C. A: [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [sorbose] = 2.0×10^{-2} mol·dm^{-3}. B: [Acrylamide] = 1.0×10^{-1} mol·dm^{-3}; [thiourea] = 1.6×10^{-2} mol·dm^{-3}; pH 2.0.

TABLE 1. Dependence of Viscosity and Molecular Weight on Initiator Concentration[a]

[PDP] × 10^{-3} mol·dm^{-3}		[η] × 10^2 dL/g		$\overline{M}_v$	
A	B	A	B	A	B
5.0	10.0	31.8	4.0	11,090	480
3.3	5.0	54.2	5.5	24,890	788
2.5	2.5	65.4	6.2	33,040	932
2.0	1.25	71.3	7.1	67,670	1145

[a] A: [Acrylamide] = 2.0 × 10^{-1} mol·dm^{-3}; [sorbose] = 5.0 × 10^{-2} mol·dm^{-3}; temperature = 30°C. B: [Acrylamide] = 2.0 × 10^{-1} mol·dm^{-3}; [thiourea] = 2.0 × 10^{-2} mol·dm^{-3}; temperature = 30°C; pH 2.0.

Rate Dependence on Activator Concentration

The double lograthmic plot (Fig. 2) between rate of polymerization (at 5% conversion) and activator concentration shows half and unit orders with respect to sorbose and thiourea, respectively.

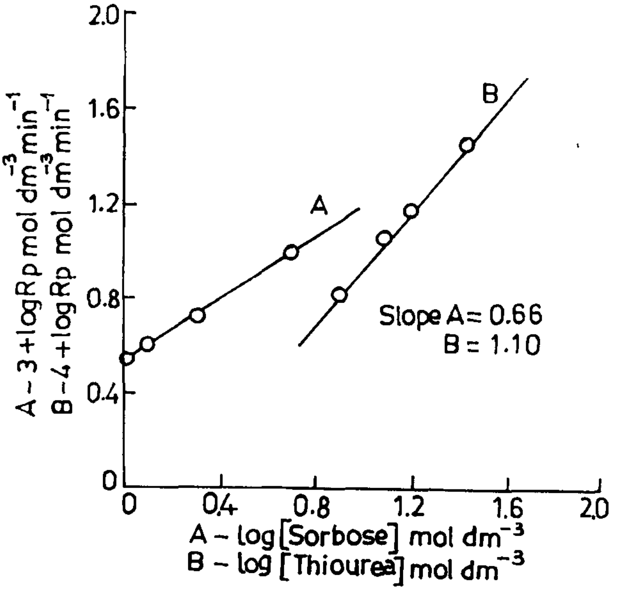


FIG. 2. Dependence of rate of polymerization on activator concentration. Temperature = 40°C. A: Sorbose – [acrylamide] = 2.0 × 10^{-1} mol·dm^{-3}; [PDP] = 5.0 × 10^{-3} mol·dm^{-3}. B: Thiourea – [acrylamide] = 2.0 × 10^{-1} mol·dm^{-3}; [PDP] = 1.0 × 10^{-2} mol·dm^{-3}; pH 2.0.

TABLE 2. Dependence of Viscosity and Molecular Weight on Activator Concentration[a]

[Sorbose] × 10^2 mol·dm^{-3}, A	[Thiourea] × 10^2 mol·dm^{-3}, B	[η] × 10^2 dL/g		$\overline{M}_v$	
		A	B	A	B
5.0	2.0	31.8	4.0	11,090	480
2.0	1.6	39.2	5.1	15,240	693
1.25	1.2	46.4	6.4	19,630	977
1.00	0.8	60.9	7.5	29,650	1230

[a] A: [Acrylamide] = 2.0 × 10^{-1} mol·dm^{-3}; [PDP] = 5.0 × 10^{-3} mol·dm^{-1}; B: [Acrylamide] = 2.0 × 10^{-1} mol·dm^{-3}; [PDP] = 1.0 × 10^{-2} mol·dm^{-3}; temperature = 30°C; pH 2.0.

Decreases in the intrinsic viscosity and average molecular weight (Table 2) can be predicted by considering the bimolecular mode of termination of growing chain radicals as reported by other workers [9, 10].

Rate Dependence on Monomer Concentration

Figure 3 shows the order of reaction with respect to acrylamide is unity in both cases. The order below unity at higher concentrations of acrylamide in the case of the PDP/sorbose redox pair can be assumed to be due to the fact that an excess of monomer acts as a good solvent and increases the probability of binary collisions necessary for termination by increasing the mobility of the growing chains

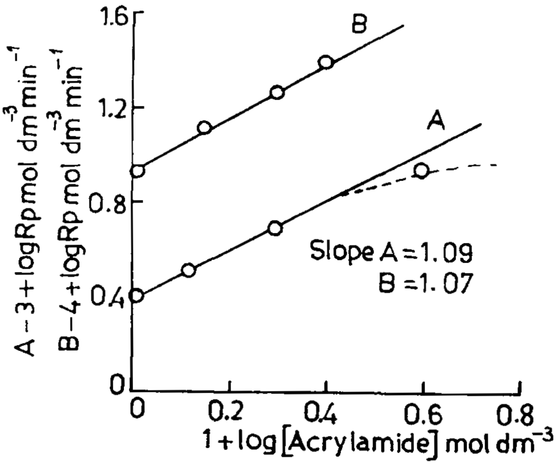


FIG. 3. Dependence of rate of polymerization on monomer concentration. Temperature = 40°C. A: [Sorbose] = 2.0 × 10^{-2} mol·dm^{-3}; [PDP] = 5.0 × 10^{-3} mol·dm^{-3}. B: [Thiourea] = 2.0 × 10^{-2} mol·dm^{-3}; [PDP] = 1.0 × 10^{-2} mol·dm^{-3}; pH 2.0.

TABLE 3. Dependence of Viscosity and Molecular Weight on Monomer Concentration[a]

[Acrylamide] × 10 mol·dm^{-3}		$[\eta] \times 10^2$ dL/g		$\overline{M}_v$	
A	B	A	B	A	B
4.0	2.5	37.7	5.6	14,450	809
2.0	2.0	31.8	4.0	11,090	480
1.33	1.5	23.4	3.6	6,918	409
1.0	1.0	14.0	3.1	3,199	326

[a] A: [Sorbose] = 5.0×10^{-2} mol·dm^{-3}; [PDP] = 5.0×10^{-3} mol·dm^{-3}; temperature = 30°C. B: [Thiourea] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 1.0×10^{-2} mol·dm^{-2}; temperature = 30°C; pH 2.0.

[11-13]. It may also be due to the fact that the rate of propagation becomes diffusion controlled at higher monomer concentrations, and the water-soluble polyacrylamide formed in the system interferes with the normal course of propagation [14]; hence, the rate of polymerization decreases.

The results in Table 3 indicate that the intrinsic viscosity and average molecular weight increase linearly with an increase in acrylamide concentration.

Rate Dependence on Temperature

The energies of activation are found to be 38 ± 2 and 47 ± 2 kJ·mol^{-1} (Fig. 4) for the PDP/sorbose and PDP/thiourea redox systems, respectively, clearly indicating that polymerization takes through a free radical mechanism.

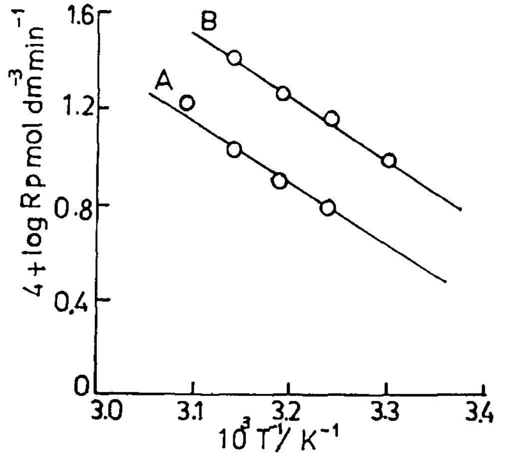


FIG. 4. Dependence of rate of polymerization on temperature. A: [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [sorbose] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 5.0×10^{-3} mol·dm^{-3}. B: [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [thiourea] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 1.0×10^{-2} mol·dm^{-3}; pH 2.0.

The intrinsic viscosity and the viscosity average molecular weight decrease linearly with temperature (Table 4). The decrease in viscosity results in enhancement of the frequency of the termination process by coupling of radical chain ends.

Rate Dependence on Additives

The rate of polymerization of acrylamide has also been studied in the presence of various additives such as organic solvents, neutral salts, surfactants, and sulfuric acid.

The addition of water-miscible organic solvents has a retarding effect on the rate of polymerization in both cases (Fig. 5) due to the increase in the area of shielding [15] of a strong hydration layer in aqueous medium, resulting in termination of a radical end of a growing chain, and also due to the transfer of macroradical chains to these solvents, which forms sluggish radicals incapable of re-initiating polymerization. The order of depression of the rate of polymerization was found to be methanol < ethanol < propanol < butanol.

The addition of salts (viz., LiCl, NaCl, KCl, and Na_2SO_4) causes a depression in the rate of polymerization in both cases (Fig. 6) and is in the order of increasing ionic radii (i.e., LiCl < NaCl < KCl) for alkali metal chlorides. This is due to the increasing accessibility of cations with size toward the growing polymer chain radical to form a ion-radical pair and primary radical; hence, the rate is reduced. For the addition of Na_2SO_4, depression is due to thickening of the medium or to the process of salting out, which interferes in the course of the reaction, resulting in premature termination of the growing chain as reported by Misra et al. [16].

The addition of an anionic surfactant, i.e., sodium oleate or sodium lauryl sulfate, above its CMC value enhances the rate of polymerization [17] in both cases (Fig. 7). The dissociation of anionic surfactants generates negatively charged ionic micelles which exert a repelling force between the growing polymer chains, which decreases the possibility of termination. Contrary to this, the addition of a cationic surfactant, i.e., cetyltrimethylammonium bromide (CTAB), opposes the production of negatively charged ion radical and favors the mutual interaction of cationic micelles with the growing polymer chain, which results in a depression in the rate of polymerization [18].

TABLE 4. Dependence of Viscosity and Molecular Weight on Temperature[a]

Temperature, °C		$[\eta] \times 10^2$ dL/g		$\overline{M}_v$	
A	B	A	B	A	B
35	25	46.4	5.42	19,630	760
40	30	31.8	4.0	11,090	480
45	40	21.2	2.7	5,998	272
50	45	15.8	1.1	3,846	67

[a] A: [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [sorbose] = 5.0×10^{-2} mol·dm^{-3}; [PDP] = 5.0×10^{-3} mol·dm^{-3}. B: [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [thiourea] = 2.0×10^{-2} mol·dm^{-1}; [PDP] = 1.0×10^{-2} mol·dm^{-3}; pH 2.0.

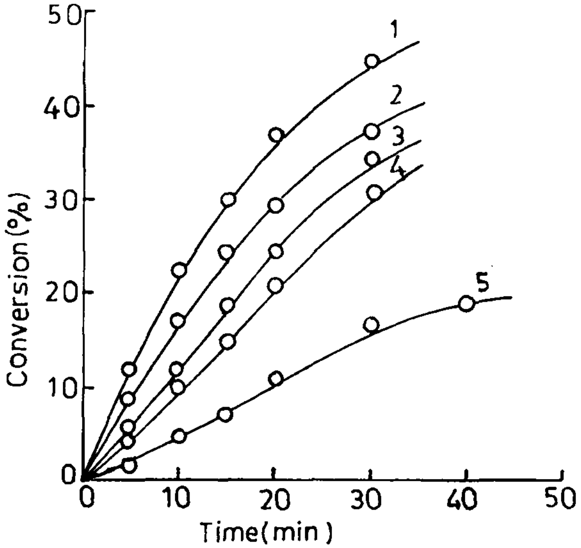


FIG. 5. Effect of organic solvents on rate of polymerization. Temperature = 40°C. [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [sorbose] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 5.0×10^{-3} mol·dm^{-3}. [Solvents] = 1 M: (1) Blank, (2) methanol, (3) ethanol, (4) propanol, (5) butanol.

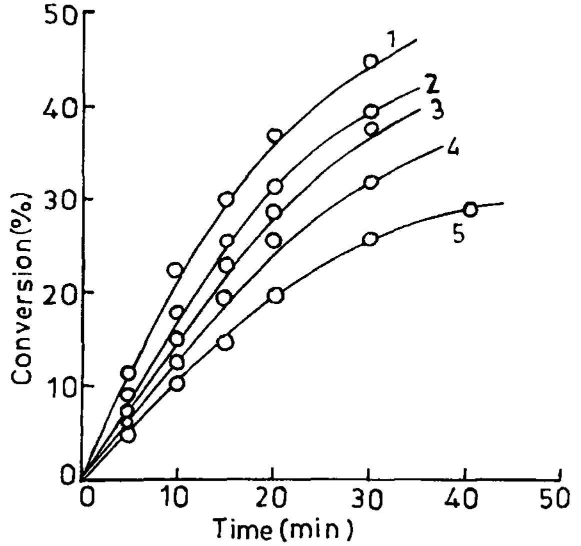


FIG. 6. Effect of inorganic salts on rate of polymerization. Temperature = 40°C. [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [sorbose] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 5.0×10^{-3} mol·dm^{-3}. [Salts] = 2.0×10^{-2} mol·dm^{-3}: (1) Blank, (2) LiCl, (3) Na_2SO_4, (4) NaCl, (5) KCl.

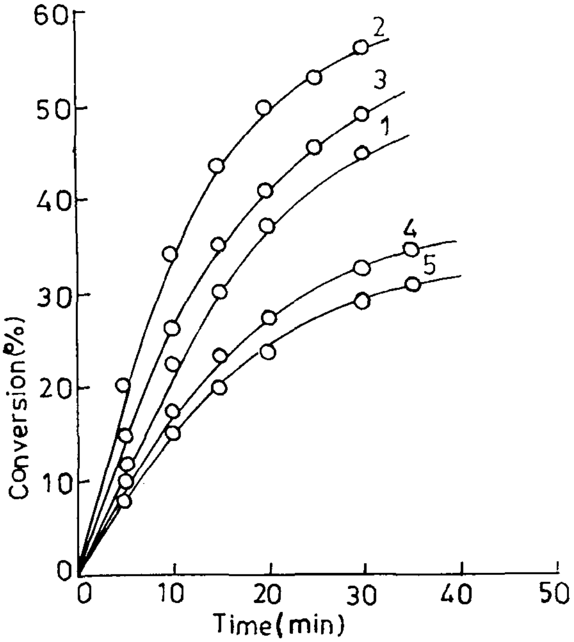


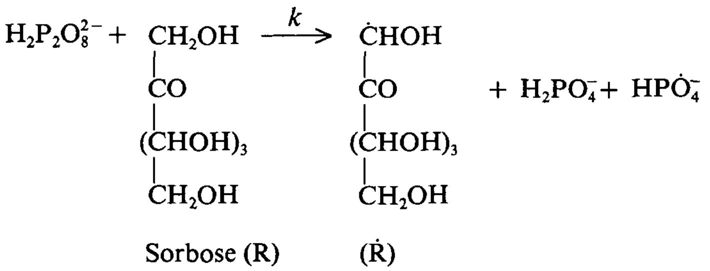
FIG. 7. Effect of surfactants on rate of polymerization. Temperature = 40°C. [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [thiourea] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 5.0×10^{-3} mol·dm^{-3}. (1) Blank, (2) sodium oleate (5.0×10^{-4} mol·dm^{-3}), (3) sodium lauryl sulfate (5.0×10^{-4} mol·dm^{-3}), (4) CTAB (1.0×10^{-3} mol·dm^{-3}), (5) CTAB (2.0×10^{-3} mol·dm^{-3}).

It has been observed in the PDP/thiourea redox system that the reaction ceases in the absence of sulfuric acid. Hence, the reaction has been carried out in an optimum concentration of acid. The variation of sulfuric acid shows that on increasing the concentration of the acid, the rate of polymerization decreases (Fig. 8). It is therefore presumed that the protonated form of the peroxodiphosphate ion [19] is an active species which interacts with the unprotonated form of thiourea to give the primary thiocarbamido free radical.

A plausible mechanism suggested for the present study may be outlined as follows.

Scheme A: PDP/sorbose-initiated polymerization of acrylamide.

Radical formation:



$$H_2P_2O_8^{2-} + \underset{\text{Sorbose (R)}}{\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}} \xrightarrow{k} \underset{(\dot{R})}{\begin{array}{c} \dot{C}HOH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}} + H_2PO_4^- + HP\dot{O}_4^- \qquad (1)$$

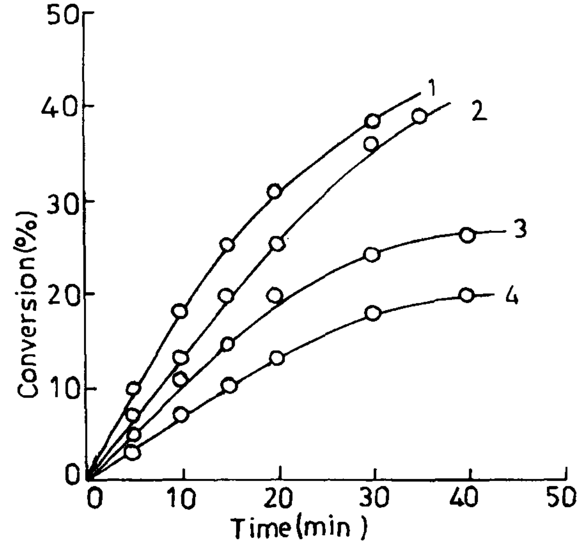


FIG. 8. Effect of sulfuric acid on rate of polymerization. Temperature = 40°C. [Acrylamide] = 2.0×10^{-1} mol·dm^{-3}; [thiourea] = 2.0×10^{-2} mol·dm^{-3}; [PDP] = 1.0×10^{-2} mol·dm^{-3}. [H_2SO_4]: (1) 1.0×10^{-2} N, (2) 2.5×10^{-2} N, (3) 5.0×10^{-2} N, (4) 8.0×10^{-2} N.

Initiation:

$$\dot{R} + M \xrightarrow{k_1} M_1^{\cdot}$$

$$M + H\dot{P}O_4^{-} \xrightarrow{k_1'} M_1^{\cdot} \qquad (2)$$

Propagation:

$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$$

$$M_{n-1}^{\cdot} + M \xrightarrow{k_p} M_n^{\cdot} \qquad (3)$$

Termination:

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_t} M_{n+m} \qquad (4)$$

It is well known that when the exponent of the initiator concentration is 0.5, bimolecular termination takes place.

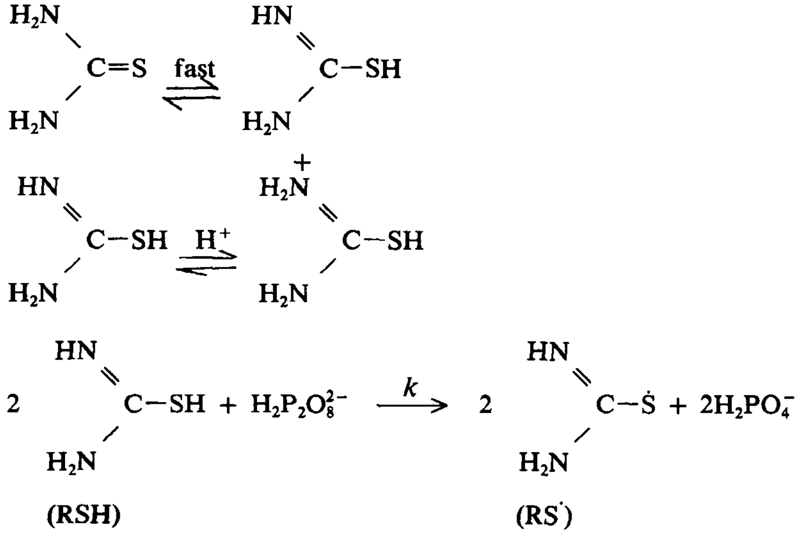
The following rate expression can be derived from the proposed steps:

$$R_p = k_p \left(\frac{k}{2k_t} \right)^{1/2} [M][H_2P_2O_8^{2-}]^{1/2} [\text{sorbose}]^{1/2} \qquad (5)$$

and the kinetic chain length is given by

$$\nu = \frac{k_p[\mathrm{M}]}{2(kk_t[\mathrm{P_2O_8^{4-}}][\mathrm{sorbose}]^{1/2}} \tag{6}$$

Scheme B: PDP/thiourea-initiated polymerization of acrylamide.
Primary radical formation:



$$\mathrm{(H_2N)_2C{=}S} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{HN{=}C(SH)NH_2} \tag{7}$$

$$\mathrm{HN{=}C(SH)NH_2} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{H_2\overset{+}{N}{=}C(SH)NH_2} \tag{8}$$

$$2\ \underset{\text{(RSH)}}{\mathrm{HN{=}C(SH)NH_2}} + \mathrm{H_2P_2O_8^{2-}} \xrightarrow{k} 2\ \underset{(\mathrm{RS^{\cdot}})}{\mathrm{HN{=}C(\dot{S})NH_2}} + \mathrm{2H_2PO_4^-} \tag{9}$$

Initiation:

$$\mathrm{R\dot{S}} + \mathrm{M} \xrightarrow{k_i} \mathrm{M_1^{\cdot}} \tag{10}$$

Propagation:

$$\mathrm{M_1^{\cdot}} + \mathrm{M} \xrightarrow{k_p} \mathrm{M_2^{\cdot}}$$

$$\mathrm{M_{n-1}^{\cdot}} + \mathrm{M} \xrightarrow{k_p} \mathrm{M_n^{\cdot}} \tag{11}$$

Termination:

$$\mathrm{M_n^{\cdot}} + \mathrm{M_m^{\cdot}} \xrightarrow{k_t} \mathrm{M_{n+m}} \tag{12}$$

Considering the above steps, the following rate expression can be derived:

$$R_p = k_p\left(\frac{k_1}{2k_t}\right)^{1/2} [\mathrm{M}][\mathrm{H_2P_2O_8^{2-}}]^{1/2}[\mathrm{RSH}] \tag{13}$$

and kinetic chain length will be

$$\nu = \frac{k_p[\mathrm{M}]}{2(k_1k_t)^{1/2}[\mathrm{H_2P_2O_8^{2-}}]^{1/2}[\mathrm{RSH}]} \tag{14}$$

Equations (5), (6), (13), and (14) explain the observed experimental results.

The participation of thiourea in the unprotonated form (Step 9) is favored because the rate of polymerization decreases with increasing hydrogen ion concentration (Fig. 8). As the hydrogen ion concentration increases, the equilibrium in Step (8) shifts to the right-hand side, i.e., more protonated thiourea is formed, thereby decreasing the concentration of unprotonated thiourea, and hence the rate decreases. If protonated thiourea is involved in Step (9), the rate of polymerization should increase with increasing concentration of hydrogen ion.

CONCLUSION

The rate of polymerization has been found to be directly proportional to monomer and thiourea concentrations. PDP and sorbose concentrations show a half-order dependence. The intrinsic viscosity and the viscosity-average molecular weight increase with an increase in the concentration of monomer and decrease with an increase in the concentration of activator and initiator in both redox systems. Similarly, an increase in the temperature causes decreases in the intrinsic viscosity and the viscosity-average molecular weight.

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