The aqueous polymerization of acrylamide, initiated by potassium persulphate-cysteine hydrochloride redox couple has been studied under nitrogen atmosphere at $30^\circ \pm 0.1^\circ$. The initial rates of polymerization have been found to be proportional to nearly half the power of catalyst concentration in the range of $0.4 \times 10^{-3}$ to $2.2 \times 10^{-3}$ mole litre$^{-1}$ and to the first power of monomer concentration in $0.8 \times 10^{-3}$ to $1.2 \times 10^{-1}$ mole litre$^{-1}$ respectively. The rate also appears to increase with increasing concentration of the activator from $1.0 \times 10^{-3}$ to $7.0 \times 10^{-3}$ mole litre$^{-1}$. The energy of activation has been estimated to be 9.92 kcal mol$^{-1}$. Addition of NaCl, NaF and ($\text{CH}_3$)$_2\text{NI}$ lowers the initial rate of polymerization while MnSO$_4$ increases it. The presence of Na$_2\text{C}_2\text{O}_4$, $\text{E}_2\text{C}_2\text{O}_4$, and ($\text{NH}_4$)$_2\text{C}_2\text{O}_4$ shows inhibition towards acrylamide polymerization. Water soluble aliphatic alcohols have been observed to retard the monomer conversion to polymer.

Materials and Methods

Acrylamide (HPCI, Japan) was purified by recrystallization from methanol. Potassium persulphate, cysteine hydrochloride and other reagents used were all of (BDH) AR grade.

The desired volumes of acrylamide and cysteine hydrochloride solutions of known concentration were placed in the reaction vessel, maintained at $30^\circ \pm 0.1^\circ$ in a thermostat. A regulated current of purified dry nitrogen gas was bubbled through the above monomer/activator mixture for 1 hr and to this was added requisite volume of standard persulphate solution (nitrogen was passed throughout the experimental run). An aliquot (5 ml) of this mixture was immediately withdrawn and introduced directly into a leak-proof iodine flask containing a known volume of ice-cooled standard brominating reagent. Several such samples of the reaction mixture were taken out and treated as before to quench the acrylamide polymerization at required stages. The course of polymerization was followed by quantitative estimation of the unchanged double bond character in the unpolymerized monomer at different time intervals. This was done as follows:

An appropriate volume of one molar sulphuric acid was added to each one of the above samples collected and shaken intermittently for 30 min. A suitable excess of potassium iodide solution was then added carefully and the iodine liberated was quickly titrated with a standard solution of thiosulphate to the starch end point. The percentage conversion of the monomer to polymer was calculated from the established relation of Misra and Narain:

$$\% \text{ conversion} = \frac{N(V_2 - V_1)M}{20W}$$

in which $N$ is the normality of hypo solution, $V_1$ and $V_2$ are the volumes of this solution used in the titration at zero and different times respectively, $M$ is the molecular weight of acrylamide and $W$ being its weight in the sample analysed.

Further, the measurements showed a significant increase of the viscosity of monomer-redox system during the course of polymerization. Thick white and rigid polyacrylamide samples were isolated by the addition of methanol at suitable occasions to ensure the smooth progress of polymerization.

Results and Discussion

Probable mechanism — A mechanism of redox initiation leading to a smooth polymerization of aqueous vinyl monomers by bromate/cysteine couple has been recently suggested by Palit et al. The
free radical nature of polymerization has been suitably confirmed by the use of dye partition technique.

From a close similarity of the present redox to the one utilized by Palit et al. a tentative initiation step (1), therefore, may be suggested:

\[
2\text{HSCH}_2\text{CH(COOH)}\text{NH}_2 + \text{KS}_2\text{O}_8 \rightarrow 2\text{SCH}_2\text{CH(COOH)}\text{NH}_2 + 2\text{KHSO}_4
\]  

Fig. 1 - Effect of \(\text{K}_2\text{S}_2\text{O}_8\) concentration at fixed concentrations of cysteine hydrochloride \((5\cdot0 \times 10^{-3} \text{ mole litre}^{-1})\) and acrylamide \((1\cdot0 \times 10^{-3} \text{ mole litre}^{-1})\) at 30° on per cent conversion

The growing radical chains with time as depicted by step (2) on mutual termination would create an heterogeneous environment due to polyacrylamide formation, as has been amply supported by viscosity measurements.

**Catalyst dependence** - It is evident that the catalyst \((\text{K}_2\text{S}_2\text{O}_8)\) in the presence of the activator cysteine, \(\text{HSCH}_2\text{CH(COOH)}\text{NH}_2\), generates the carboxamidothiole free radicals to propagate the acrylamide \((\text{H}_2\text{C} = \text{CHCONH}_2)\) polymerization. At fixed concentrations of the activator and the monomer, the initial rates of polymerization and corresponding conversions are found to increase with increasing concentration of the catalyst (Fig. 1).

At a fixed concentration of the activator, varying amounts of persulphate obviously generate different amounts of active primary radicals. Since, the initial rate of polymerization depends on the population of such active species, an increasing trend of initial rates should be observed with an increasing concentration of persulphate, as is obvious from Fig. 1.

The order of reaction with respect to [catalyst] has been determined graphically from a double logarithm plot. Fig. 2 presents log \(R_i\) \((R_i\) is obtained from the slope of time vs conversion curves of Fig. 1 at zero time and expressed in percentage polymerization min\(^{-1}\)) plot against the corresponding logarithm of oxidant concentration, \(I\) (in mole litre\(^{-1}\)). The catalyst exponent is found to be 0.47 in the concentration range of \(0.4 \times 10^{-3}\) to \(2.2 \times 10^{-2}\) mole litre\(^{-1}\). Thus, the rate of redox polymerization is dependent on the square root of catalyst concentration, indicating a bimolecular mechanism of termination step.

**Activator dependence** — The results of the percentage polymerization of acrylamide at varying concentrations of cysteine hydrochloride, recorded in Table 1, show that with increasing concentration of cysteine hydrochloride from \(1.0 \times 10^{-3}\) to \(7.0 \times 10^{-3}\) mole litre\(^{-1}\), the rate as well as limiting conversion increase simultaneously. Usually, in common redox initiated vinyl polymerization an increase in the activator concentration results in a corresponding increase in the population of primary free radicals thereby leading to an enhancement of the polymerization rate. However, in the present case, an abrupt decrease in both the initial rate and maximum conversion is observed on increasing the activator concentration above \(7.0 \times 10^{-3}\) mole litre\(^{-1}\). This fact may be explained as follows:

At relatively higher concentration of the activator either persulphate or its lower fragments tend to

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**Table 1** — The Rates of Polymerization of Varying Concentrations of Cysteine Hydrochloride

(Recipe: \([\text{H}_2\text{C} = \text{CHCONH}_2]\) = \(1.0 \times 10^{-3}\) mole litre\(^{-1}\) and \([\text{K}_2\text{S}_2\text{O}_8]\) = \(1.0 \times 10^{-3}\) mole litre\(^{-1}\); Temp. = 30°±0.1°)

<table>
<thead>
<tr>
<th>Conc. of cysteine.HCl (\times 10^3) (mole litre(^{-1}))</th>
<th>Polymerization (%) at different times (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>1.0</td>
<td>20:50</td>
</tr>
<tr>
<td>5.0</td>
<td>23:28</td>
</tr>
<tr>
<td>7.0</td>
<td>24:64</td>
</tr>
<tr>
<td>9.0</td>
<td>11:52</td>
</tr>
</tbody>
</table>
generate 'inhibiting oxygen' appreciably in the presence of excess of hydrogen ions (H3O+), derived from cysteine hydrochloride. Thus, beyond an optimum concentration of activator, the growing chain radicals are ruptured to suppress the overall rate of polymerization as is, indeed, the case at 9·0 × 10^{-3} mole litre^{-1}. Such a trend is not unique and is analogous to the earlier reports^{1-2,6-11} in the domain of other redox polymerizations of several monomers.

**Monomer dependence** — The effect of acrylamide concentration on its conversion to polyacrylamide is depicted in Fig. 3. It may be seen from Fig. 3 that the conversion increases progressively with an increase of monomer concentration. The rate in terms of percentage conversion at a definite time (say, at 5 min) is found to be a function of monomer concentration, as is shown in Fig. 4.

The percent conversion of monomer to polymer increases with increasing [monomer]. The rate is found to be directly proportional to the first power of acrylamide concentration in the concentration range 0·8 × 10^{-3} to 1·2 × 10^{-3} mole litre^{-1}.

**Temperature dependence** — A rise in polymerization temperature results in the enhancement of initial rate, whereas the percent conversion tends to decrease above 30°. This is due to the fact that at higher temperatures and at later stages, the involvement of active polymerizing free radicals in side reactions become more pronounced, causing thereby a decrease in percent conversion. Similar observations have been recorded by previous investigators on different redox polymerizations^{3,4,6-13}.

The energy of activation has been obtained graphically from the linear plot of log $R_t$ vs $1/T$ within the temperature range of 298°K to 318°K. The value, thus determined is 9·02 kcal mole^{-1} which is lower than many redox polymerizations of acrylamide^{2-3,8-12}. This, perhaps points to a promising role of persulphate/cysteine redox pair in dealing with aqueous polymerization of acrylamide. It is also interesting to note that a high yield of polyacrylamide is obtained using the present redox couple, as compared to other thiols^{8-14} coupled with persulphate under identical conditions.

**Effect of added salts** — Addition of salts, e.g. NaCl, NaF, (CH3)4NI, MnSO4 and the oxalates affect both the initial rate and maximum conversion appreciably. It may be seen from Fig. 5 that the initial rate as well as the maximum conversion are lower in the presence of NaCl, NaF and (CH3)4NI in comparison to the blank polymerization. In view of a high dielectric constant of the medium, the existence of the aqueous ionic species^{1-4,6-12} in the system are prone to interfere with the normal propagation process, resulting into premature termination of growing polymer chains. Thus the progress of polymerization is appreciably hindered by the added halides. (CH3)4NI appears to be the best depressant of rate and conversion among the studied 1:1 electrolytes.

MnSO4 increases the initial rate at lower limiting conversion. Mn^{2+} ions associated with an autocatalysing action on the course of initiation step appears to be a plausible explanation to this trend. This is in agreement with earlier findings of similar nature^{1-2,8,11,13}.

The interesting role of Na2C2O4, K2C2O4 and (NH4)2C2O4 towards the usual conversion of monomer to polymer shows a complete arrest of redox polymerization. Similar inhibiting effect of the oxalate ions as additives has also been observed.
in the case of acrylamide polymerization, initiated by persulphate mercaptoethylamine and persulphate thioglycollic acid couples.

Effect of added alcohols — The effect of water miscible aliphatic alcohols has been studied. It is observed that methanol, ethanol and propanols tend to suppress both the initial rate and conversion progressively, the decreasing order being methanol > ethanol > propanol > isopropanol. This trend is well supported by several studies in a variety of redox polymerizations. Moreover, the structure difference of isopropanol and propanol leads to polymerization to different extents. Similar results in decreasing the degree of polymerization (DP) of acrylonitrile by alcoholic addition have been reported by Katayama and Saito. It is, therefore, clear that the presence of an alcohol in the medium probably creates a condition under which the polymer is incapable of attaining a substantial dimension of its own. The addition of alcohol to the aqueous polymerizing media has been shown to weaken the interchain hydrogen bonding which helps in interlocking the polyacrylamide chains. In the presence of alcohol, therefore, there is a tendency towards mutual termination so as to influence the kinetics significantly. According to Kern and coworkers, the presence of an alcohol enhances the regulated rate of generation of primary free radicals which renders the termination rate relatively faster in comparison to propagation rate of polymer chains.

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References