

# Kinetics of Radical Polymerization of *N*-vinylpyrrolidone by Peroxidiphosphate–Ag<sup>+</sup> System

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## SYNOPSIS

The kinetics of aqueous polymerization of *N*-vinylpyrrolidone (*N*-VP) was carried out using potassium peroxidiphosphate–Ag<sup>+</sup> system under nitrogen atmosphere at 25°C. The rate of polymerization was directly proportional to the concentration of the *N*-vinylpyrrolidone and showed a half-order with respect to the concentration of the peroxidiphosphate (H<sub>2</sub>P<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and Ag<sup>+</sup> ions. The value of  $k_p/(k_t)^{1/2}$  was computed and its value found to increase on increasing the temperature of the reaction mixture. The energy of activation ( $E_a$ ) was found to be  $65.8 \pm 0.1$  kJ mol<sup>-1</sup> within the temperature range from 20 to 50°C. Viscometric average molecular weight of polyvinylpyrrolidone was determined by measuring intrinsic viscosity of the polymer samples collected at different kinetic conditions. The effect of various additives was also studied. A suitable mechanism of polymerization has been proposed and a reaction rate law was derived considering experimental results. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polyvinylpyrrolidone has been extensively used in the pharmaceutical and cosmetics industries. The cationic polymerization of *N*-vinylpyrrolidone leads to the formation of oligomers.<sup>1</sup> Hence studies dealing with radical polymerization of *N*-vinylpyrrolidone (*N*-VP) become more important from the application point of view of the polymer formed in this reaction. Senogles et al.<sup>2,3</sup> have reported the kinetics of polymerization of *N*-VP in the presence of the Azobisisobutyronitrile (AIBN) and persulfate initiators. The polymers formed in the organic solvent using peroxides as initiators were found to be of low molecular weight due to facile chain transfer reactions to the solvents. This monomer has been used successfully to grafting on polytetrafluoroethane-hexafluoropropylene films.<sup>4</sup> Similarly studies dealing with copolymerization of *N*-VP and  $\alpha$ -haloacrylic acid were also reported.<sup>5</sup> The literature survey reveals that no serious attempt has been made to investigate the kinetic scheme of radical polymerization of *N*-VP in the presence of redox system. Hence in this study an effort has been made to study the

kinetics of polymerization of *N*-VP in presence of peroxidiphosphate and Ag<sup>+</sup> ions.

## EXPERIMENTAL

*N*-vinylpyrrolidone (Fluka) was distilled under reduced pressure and dried by calcium hydride. The fraction boiling at 60°C was used for the radical polymerization. The peroxidiphosphate was received as a gift sample from FMC Corporation (USA) and used without further purifying. The silver perchlorate was prepared as reported elsewhere.<sup>6</sup> The rate of polymerization was followed by estimating the monomer concentration using iodometry. The polymer samples were dissolved in sodium acetate and viscometric average molecular weight was determined by using the following relationship:<sup>7</sup>

$$[\eta]_{25^\circ\text{C}} = 8.86 \times 10^{-5} \bar{M}_v^{0.74}$$

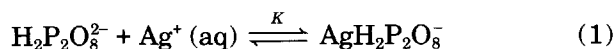
## RESULTS AND DISCUSSION

The prepared poly-*N*-vinylpyrrolidone has an unusual property in the sense that it has solubility both in water as well as in organic solvents. The aqueous solution of the poly-*N*-vinylpyrrolidone also showed

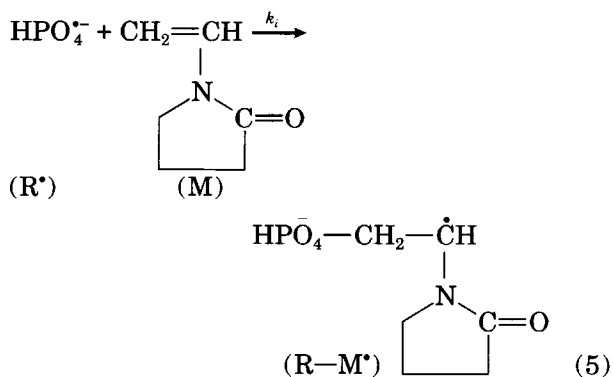
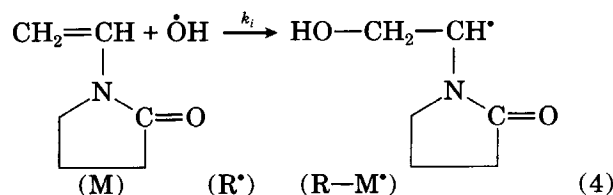
an unusual behavior in that its viscosity is not affected by the addition of the electrolyte, as is observed with other polymer solutions. The free radical polymerization of *N*-VP in nonaqueous solvent generally gives low molecular weight polymers, and this prompted the study of the polymerization reaction in the aqueous medium. Peroxidiphosphate has been used successfully to initiate the vinyl polymerization reactions in the presence and absence of  $\text{Ag}^+$  ions.<sup>8,9</sup> In the present study it has been observed that peroxidiphosphate alone does not initiate the polymerization of *N*-VP at the ambient temperature, but in the presence of the  $\text{Ag}^+$  ions the reaction occurred at a faster rate even at low temperature. These observations suggested the participation of the  $\text{Ag}^+$  ions in the decomposition of peroxidiphosphate to generate the primary free radicals ( $\text{HPO}_4^{\cdot-}$ ). The peroxidiphosphate combines with  $\text{Ag}^+$  ions in the solution and forms an unstable complex [Eq. (1)]. This complex decomposes instantaneously into phosphate ion radicals ( $\text{HPO}_4^{\cdot-}$ ) and a phosphate salt of  $\text{Ag}$ (II) [Eq. (2)]. This silver salt is water soluble and remains in the reaction mixture without further transformation and decomposition. It is also presumed that this salt of  $\text{Ag}$ (II) acts as a cocatalyst in activating the reactivity of the monomer through interaction of  $\text{Ag}$ (II) with the lone pairs of the nitrogen in *N*-VP. This interaction of  $\text{Ag}$ (II) and the inductive effect of the carbonyl group of the monomer reduces the negative charge of the vinyl group, which is generated during the attack of the phosphate ion radical at the monomer molecule. The rate of polymerization was found to increase on increasing the ionic strength ( $\mu$ ) of the medium, which has supported the idea of metal ion interaction with the monomers, thus considering experimental observations. The following reaction steps have been proposed for the polymerization reaction of *N*-VP.

## Mechanism

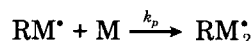
### Free Radical Formation



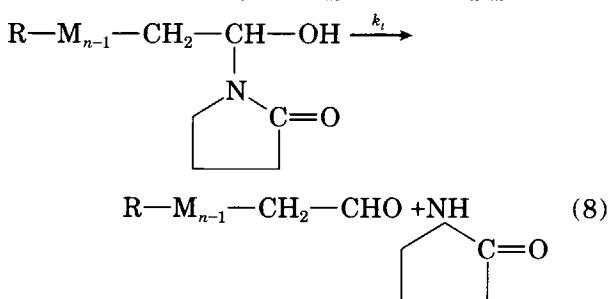
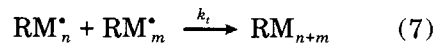
### Initiation



### Propagation



### Termination



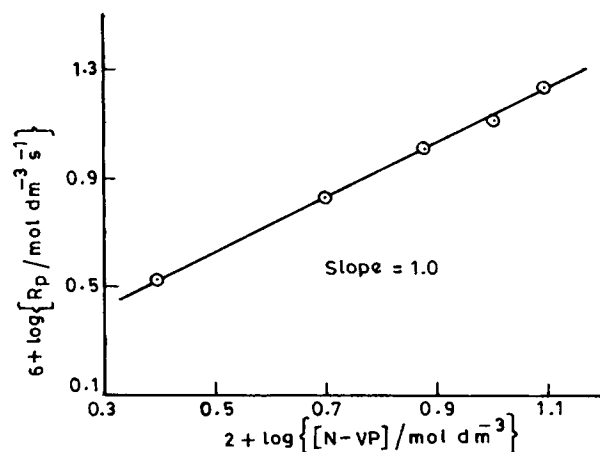
The above reaction scheme is proposed on the basis of the experimental results recorded under different kinetic conditions. The participation of  $\dot{\text{O}}\text{H}$  radicals in the initiation [Eq. (4)] and termination [Eq. (8)] as shown in the scheme has been excluded<sup>10</sup> on the basis of negative end group test for the  $-\text{OH}$  and  $-\text{CHO}$  groups performed on poly-*N*-vinylpyrrolidone. These observations have also supported discarding the formation of  $\dot{\text{O}}\text{H}$  radicals in Eq. (3). The IR spectrum of the poly-*N*-vinylpyrrolidone has given a stretching frequency corresponding to  $-\text{O}-\text{P}-$  group in the polymer, hence suggesting the exclusive initiation by phosphate ion radicals [Eq. (5)]. Comparing the reaction rate of *N*-VP with *N,N'*-methylenebisacrylamide, it has been found that the rate of polymerization of the *N*-VP is low. This might be due to the steric hinderances created by the pendant group present in the propagating chain. To determine the rate dependence on various reactants, the rate of polymerization has been studied on varying initial concentration of the monomer, peroxidiphosphate and  $\text{Ag}^+$  ions. The effect of various additives has been studied to explain the mechanism of the polymerization.

### Effect of Monomer Concentration

The rate of polymerization was measured within the concentration range of  $2.5\text{--}12.5 \times 10^{-2} \text{ mol dm}^{-3}$  of *N*-VP at  $25^\circ\text{C}$ . The graph between  $\log R_p$  versus  $\log [\text{Monomer}]$  was linear (Fig. 1), which indicated first-order dependence on monomer concentration. However, at higher concentration ( $> 12.5 \times 10^{-2} \text{ mol dm}^{-3}$ ), the rate of polymerization was slowed down. This decreasing trend at higher concentration might be due to the solvent properties of the *N*-VP thereby termination steps predominate.<sup>11</sup> The intrinsic viscosity  $[\eta]$  and viscometric average molecular weight were found to increase on increasing the concentration of the monomer (Table I).

### Effect of Peroxidiphosphate Concentration

The effect of peroxidiphosphate concentration on the rate of polymerization of *N*-VP has been recorded by varying its concentration from  $4.0$  to  $20.0 \times 10^{-3} \text{ mol dm}^{-3}$ . It has been observed that in the absence of the  $\text{Ag}^+$  ion, the initial rate and maximum yield were very low, which has suggested the participation of  $\text{Ag}^+$  ions in the decomposition of the peroxidiphosphate. The rate dependence on peroxidiphosphate concentration has been determined by drawing a plot (Fig. 2) between  $\log R_i$  versus  $\log [\text{H}_2\text{P}_2\text{O}_8^{2-}]$ , which has given the slope a value equal to 0.5. This half-order dependence on peroxidiphosphate has clearly suggested that phosphate ion radicals are formed through the decomposition of the peroxidiphosphate in the presence of the  $\text{Ag}^+$  ions. These phosphate ion radicals ( $\text{HPO}_4^{\cdot-}$ ) participate in the initiation step of the polymerization.

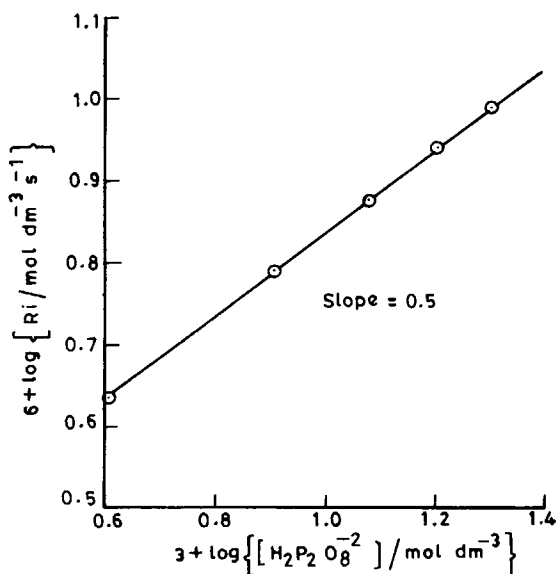


**Figure 1** Dependence of polymerization rate on concentration of *N*-VP.  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. =  $298 \text{ K}$ .

**Table I** Variation of  $[\eta]$  and  $\bar{M}_v$

|   |                             |             |
|---|-----------------------------|-------------|
| $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$ , $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. = $298 \text{ K}$ |                             |             |
| $[\text{N-VP}] \cdot 10^2 / \text{mol dm}^{-3}$   | $[\eta] / \text{dl g}^{-1}$ | $\bar{M}_v$ |
| 2.5   | 0.138                       | 20,500      |
| 7.5   | 0.311                       | 62,000      |
| 12.5  | 0.452                       | 103,000     |
| $[\text{N-VP}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. = $298 \text{ K}$                          |                             |             |
| $[\text{H}_2\text{P}_2\text{O}_8^{2-}] \cdot 10^3 / \text{mol dm}^{-3}$   | $[\eta] / \text{dl g}^{-1}$ | $\bar{M}_v$ |
| 4   | 0.228                       | 40,413      |
| 12  | 0.150                       | 23,259      |
| 20  | 0.125                       | 18,021      |
| $[\text{N-VP}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ , $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. = $298 \text{ K}$     |                             |             |
| $[\text{AgClO}_4] \cdot 10^4 / \text{mol dm}^{-3}$  | $[\eta] / \text{dl g}^{-1}$ | $\bar{M}_v$ |
| 2.0   | 0.323                       | 65,000      |
| 6.0   | 0.212                       | 36,800      |
| 10.0  | 0.105                       | 14,200      |
| $[\text{N-VP}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ , $\mu = 0.2 \text{ mol dm}^{-3}$                               |                             |             |
| Temp./K   | $[\eta] / \text{dl g}^{-1}$ | $\bar{M}_v$ |
| 293   | 0.227                       | 40,320      |
| 303   | 0.169                       | 26,880      |
| 313   | 0.101                       | 13,440      |

The half-order dependence on  $\text{H}_2\text{P}_2\text{O}_8^{2-}$  concentration also supports the view that termination exclusively takes place via mutual combination of the growing chains. The IR studies of the polyvinylpyrrolidone has also supported the idea that  $\text{HPO}_4^{\cdot-}$  radicals initiate the polymerization. At higher concentration of the peroxidiphosphate, the initial as well as the maximum yield was found to decrease. This retardation effect of peroxidiphosphate at its higher concentration might be due to the excess production of the primary free radicals that ultimately participate in the immature termination of the propagating chain radicals. There is another reason that peroxidiphosphate might have oxidized the reactive species of the mixture; hence retardation in rate as well as in maximum yield is obvious. It is also assumed that at higher concentrations of peroxidiphosphate, deactivation of primary free radicals takes place through oxygen that is produced in a

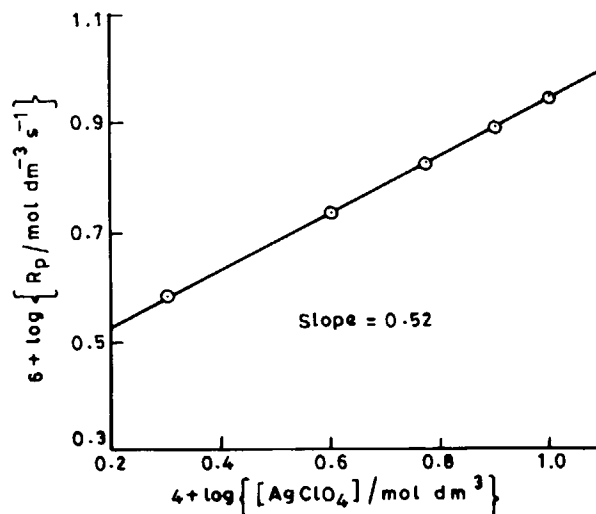


**Figure 2** Dependence of polymerization rate on peroxidiphosphate concentration.  $[N\text{-VP}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. = 298 K.

side reaction. Thus retardation of initial rate at higher concentration of the peroxidiphosphate may be due to either one of the factors as discussed above. The molecular weight ( $\bar{M}_v$ ) is found to decrease on increasing the concentration of the peroxidiphosphate (Table I).

#### Effect of Silver Perchlorate ( $\text{AgClO}_4$ ) Concentration

The effect of concentration variation of  $\text{Ag}^+$  ions on the rate of polymerization of  $N\text{-VP}$  has been studied at constant ionic strength ( $\mu = 0.2 \text{ mol dm}^{-3}$ ). The order with respect to  $\text{Ag}^+$  ions is found to be 0.52 (Fig. 3), which clearly suggests that  $\text{Ag}^+$  ions do not participate in termination process otherwise the order would have been equal to 1. These  $\text{Ag}^+$  ions only help in the decomposition of the peroxidiphosphate molecules. The literature survey reveals that  $\text{Ag}^+$  ions were normally used to increase,<sup>12,13</sup> the rate of polymerization of different vinyl monomers and they do not participate in the termination steps. In the present scheme it has been assumed that the  $\text{Ag}^+$  ions are oxidized to  $\text{Ag(II)}$  in reaction step 2 [Eq. (2)] and remain in the solution as silver phosphate. These  $\text{Ag(II)}$  ions interact with the nitrogen atom of the monomer and reduce the negative charge from the propagating end of the growing chains, which ultimately enhances the rate of polymerization. The interaction of  $\text{Ag(II)}$  with the  $\text{N}_2$  atom has been proposed on the basis of the positive salt effect ob-

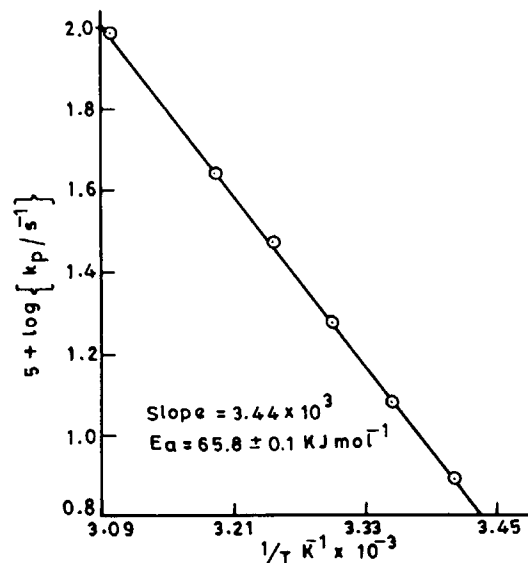


**Figure 3** Dependence of polymerization rate on  $\text{Ag}^+$  ion concentration.  $[N\text{-VP}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. = 298 K.

served in the presence of other cations. The intrinsic viscosity  $[\eta]$  and  $\bar{M}_v$  were found to decrease on increasing the concentration of the silver perchlorate (Table I).

#### Effect of Temperature

The rate of polymerization of  $N\text{-VP}$  has also been studied as a function of temperature, and energy of activation ( $E_a$ ) has been calculated by drawing an

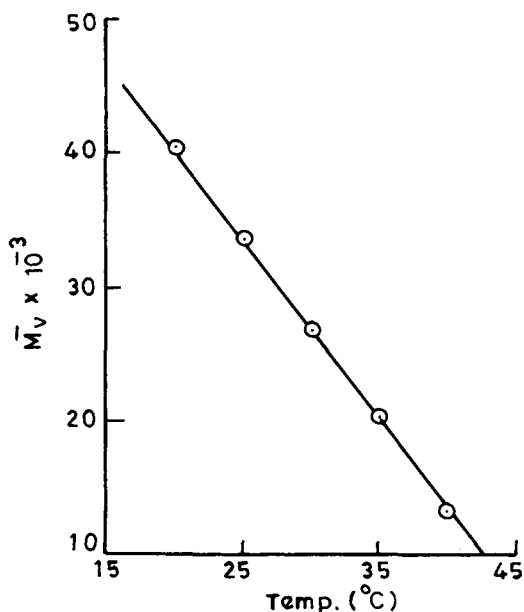


**Figure 4** Effect of temperature.  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[N\text{-VP}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $\mu = 0.2 \text{ mol dm}^{-3}$ .

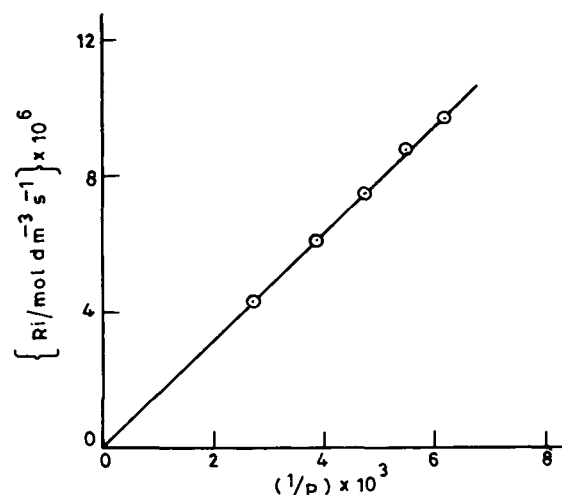
Arrhenius plot (Fig. 4). The energy of activation within the temperature range from 20 to 50°C was found to be  $65.8 \pm 0.1 \text{ kJ mol}^{-1}$ . This energy is slightly higher than the other vinyl monomers,<sup>14</sup> which may be due to steric hinderance offered by the bulky group (pyrrole group) present in the monomer. On increasing the temperature, the rate of monomer disappearance has increased, but the molecular weight of the polyvinylpyrrolidone was found to decrease linearly (Fig. 5). This linear decrease in molecular weight can be assumed due to the premature termination of the growing chain of the polymer. At low temperature the propagating chain grows to its maximum size, but as the temperature is increased the average life of the propagating chain radical is reduced. Hence polyvinylpyrrolidone molecules were of low molecular weight.

### Degree of Polymerization (*P*)

The degree of polymerization (*P*) has been determined by determining average molecular weight of the polyvinylpyrrolidone. The value of degree of polymerization (*P*) is found to decrease linearly on increasing the initial concentration of the peroxidiphosphate. A linear plot (Fig. 6) between initial rate of polymerization (*R<sub>i</sub>*) versus reciprocal of degree of polymerization ( $1/P$ ) was obtained.



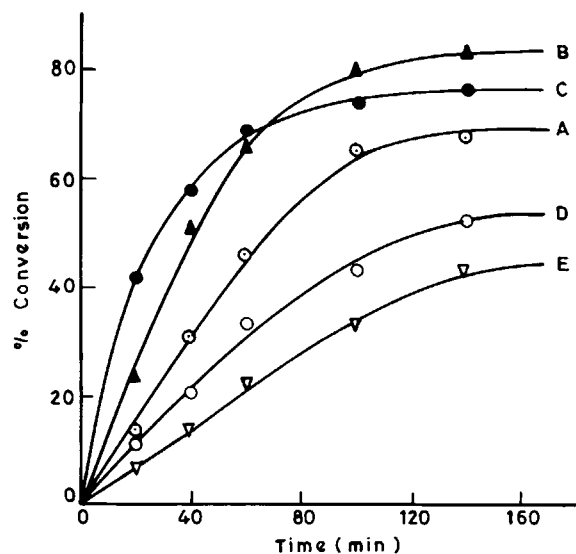
**Figure 5** Effect of temperature on molecular weight.  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{N-V-P}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $\mu = 0.2 \text{ mol dm}^{-3}$ .



**Figure 6** Dependence of degree of polymerization (*P*).  $[\text{N-V-P}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $\mu = 0.2 \text{ mol dm}^{-3}$ , Temp. = 298 K.

### Effect of Surfactants, Complexing Agent, and Acid

The suspension polymerization is an industrially important method for the production of various useful vinyl polymers. Studies relating the importance and use of various surfactants are available in the literature. Despite this there still exists a gap in our knowledge related to the effect of the detergent on the medium and the proper choice of the surfactants. These surfactants are selected on the basis of trial and error. In view of these, the rate of polymerization of *N*-VP has been studied in the presence of the cationic and anionic detergents. The results obtained in the presence of the detergents were compared with the control experiment (Fig. 7). The observation of the results given in the Figure 7 clearly indicated that both surfactants have increased the rate of polymerization as well as the maximum yield. The concentration of the studied surfactants was kept above their critical micelles concentration (CMC) value. The anionic surfactant (sodium oleate) was found to be more efficient in increasing the initial rate of polymerization than the cationic detergent, i.e., cetyltrimethylammonium bromide. This effect may be due to the negative charge on the micelles formed by the anionic detergent. The increasing effect of the detergents on the rate of polymerization might be due to peptization action of the detergents. There may be another possibility that the presence of surfactants enhances the rate of decomposition of the peroxidiphosphate as suggested by Capek et al.<sup>15</sup> Thus either one of the factors may be responsible for increasing the rate of polymerization by the surfactants.



**Figure 7** Effect of additives. (A):  $[N\text{-VP}] = 5.0 \times 10^{-2}$  mol dm $^{-3}$ ,  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3}$  mol dm $^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4}$  mol dm $^{-3}$ , Temp. = 298 K,  $\mu = 0.2$  mol dm $^{-3}$ . (B)  $[\text{CTAB}] = 8.0 \times 10^{-4}$  mol dm $^{-3}$ , (C) [sodium oleate] =  $2.0 \times 10^{-4}$  mol dm $^{-3}$ , (D)  $[\text{NaF}] = 1.5 \times 10^{-2}$  mol dm $^{-3}$ , (E)  $[\text{HCl}] = 2.5 \times 10^{-2}$  mol dm $^{-3}$ .

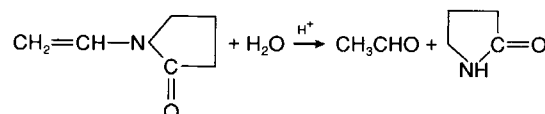
The effect of the addition of a complexing agent on the rate of polymerization has been studied and results are given in Figure 7. The observation of the results clearly indicated that in the presence of sodium fluoride both initial rate and maximum yield have decreased substantially. This decreasing effect of sodium fluoride may be assumed due to the complexation of the fluoride ions with the silver ion, thus slowing down the decomposition of the peroxidiphosphate, which ultimately resulted in a decrease in rate of polymerization and maximum yield. The effect of ionic strength on the rate of polymerization has been studied by adding neutral salt ( $\text{K}_2\text{SO}_4$ ) in the solution and recording the rate of polymerization and maximum yield. It has been observed that on increasing the ionic strength of the medium, the rate of polymerization has been increased (Table II). The rate of polymerization has

**Table II** Effect of Ionic Strength ( $\mu$ ) on  $R_p^a$

| $R_p \times 10^6 / \text{mol dm}^{-3} \text{ s}^{-1}$ | $\mu / \text{mol dm}^{-3}$ |
|---|----------------------------|
| 6.15  | 0.20                       |
| 8.22  | 0.35                       |
| 10.00   | 0.50                       |

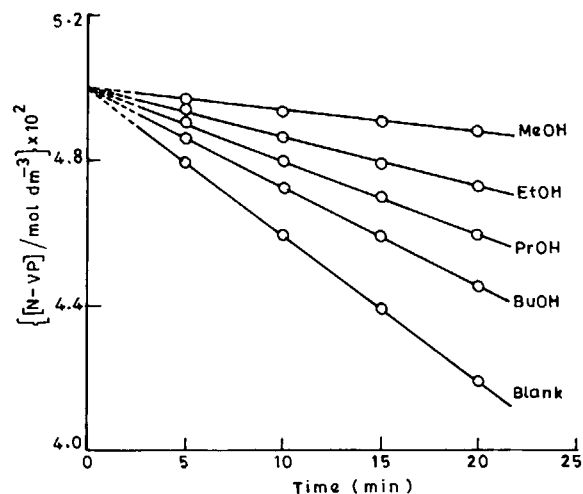
<sup>a</sup>  $[N\text{-VP}] = 5.0 \times 10^{-2}$  mol dm $^{-3}$ ,  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 8.0 \times 10^{-3}$  mol dm $^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4}$  mol dm $^{-3}$ , Temp. = 298 K.

been studied in presence of hydrochloric acid ( $2.5 \times 10^{-2}$  mol dm $^{-3}$ ). On comparing the results obtained in the presence of acid with the blank experiments, it has become clear that the rate of polymerization and maximum percent yield decreased to a greater extent by the addition of the acid. This retardation effect of the acid can be explained by assuming a change in the nature of the peroxidiphosphate and *N*-VP. It is reported<sup>16</sup> that the presence of acid decomposes the *N*-VP into acetaldehyde and pyrrolidone as given below:



Similarly the interaction of the acid anions with the peroxidiphosphate ion decreases the oxidizing power of the peroxidiphosphate,<sup>17</sup> which results in a substantial decrease in the rate of the polymerization.

At high concentration of the acid ( $> 1.5 \times 10^{-1}$  mol dm $^{-3}$ ), the peroxidiphosphate gets protonated and converts peroxidiphosphate oxygen into hydroxide ion, which results in an overall decrease in the primary radicals in the reaction mixture. Since the rate of polymerization has been found to decrease even at very low concentration of the acid ( $< 1.5 \times 10^{-1}$  mol dm $^{-3}$ ), therefore it may be assumed that the decrease in the initial rate as well as in the max-



**Figure 8** Retardation effect of water-soluble alcohols. Blank- $[N\text{-VP}] = 5.0 \times 10^{-2}$  mol dm $^{-3}$ ,  $[\text{AgClO}_4] = 5.0 \times 10^{-4}$  mol dm $^{-3}$ ,  $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 10.0 \times 10^{-3}$  mol dm $^{-3}$ ,  $\mu = 0.2$  mol dm $^{-3}$ , Temp. = 298 K.  $[\text{MeOH}]$ ,  $[\text{EtOH}]$ ,  $[\text{PrOH}]$ ,  $[\text{BuOH}] = 0.1$  mol dm $^{-3}$ .

**Table III Retardation Constant (*I*) for Various Alcohols<sup>a</sup>**

| Alcohols | [Alcohol] × 10/mol dm <sup>-3</sup> | <i>I</i> |
|----------|-------------------------------------|----------|
| Methanol | 1.0                                 | 2.15     |
| Ethanol  | 1.0                                 | 0.95     |
| Propanol | 1.0                                 | 0.46     |
| Butanol  | 1.0                                 | 0.22     |

<sup>a</sup> [N-VP] = 5.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [AgClO<sub>4</sub>] = 3.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>P<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = 10.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, μ = 0.2 mol dm<sup>-3</sup>, Temp. = 298 K.

imum yield may be due to the decomposition of the monomer rather than the transformation of the peroxidiphosphate in the solution.

### Effect of Alcohols

The effect of addition of the alcohols on the rate of polymerization has been studied by taking equimolar concentration (0.1 mol dm<sup>-3</sup>) of the alcohols in the reaction mixture. The initial rate and maximum percent yield were found to decrease in the presence of the alcohols. However, the decreasing effect of the studied alcohols was different. To compare the effect of the added alcohols and to calculate the value of the retardation constant (*I*), a graph has been made (Fig. 8) between the remaining concentration of the monomer and the time of the polymerization. The observation of the results clearly indicated that the rate of monomer disappearance has substantially decreased in the presence of the methanol. There is a gradual decrease in the retarding efficiency from

methanol to butanol. The decreasing trend in the presence of the alcohols is predominantly due to the transfer of the growing macroradical chain to the added alcohols through hydrogen abstraction from the alcohols. During chain transfer reaction, a solvent radical is generated that is generally incapable of initiating the polymerization reaction. This is the reason that the polymerization of the *N*-VP in organic solvents produces the oligomers. The retarding constants (*I<sub>s</sub>*) for the studied alcohols were calculated with the intercept of the graph drawn between monomer concentration and polymerization time (Fig. 8). The values of these retardation constants are given in Table III. The order of numerical value of the retardation constant (*I*) and the observed retardation effect of the solvents (Fig. 8) has been found to be same, i.e.,



Thus considering experimental observations and the kinetic scheme proposed in Eqs. (1)–(8), the rate expression for the polymerization of *N*-VP in presence of peroxidiphosphate and Ag<sup>+</sup> ion is derived as

$$R_p = k_p \left( \frac{k_1 K}{k_t} \right)^{1/2} [\text{H}_2\text{P}_2\text{O}_8^{2-}]^{1/2} [\text{AgClO}_4]^{1/2} [\text{N-VP}] \quad (9)$$

and the kinetic chain length (*ν*) would be

$$\nu = \frac{k_p [\text{N-VP}]}{(k_t k_1 K)^{1/2} [\text{AgClO}_4]^{1/2} [\text{H}_2\text{P}_2\text{O}_8^{2-}]^{1/2}} \quad (10)$$

**Table IV Comparison of the Kinetic Parameter  $k_p/(k_t)^{1/2}$  of *N*-VP<sup>a</sup>**

| [N-VP].10 <sup>2</sup> /mol dm <sup>-3</sup> | [H <sub>2</sub> P <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ].10 <sup>3</sup> /mol dm <sup>-3</sup> | [AgClO <sub>4</sub> ].10 <sup>4</sup> /mol dm <sup>-3</sup> | Temp. (°C) | $k_p/(k_t)^{-1/2}$ mol dm <sup>3</sup> S <sup>-1/2</sup> |
|--|---|---|------------|--|
| 2.5  | 10.0  | 5.0   | 25         | 0.66   |
| 7.5  | 10.0  | 5.0   | 25         | 0.66   |
| 12.5   | 10.0  | 5.0   | 25         | 0.66   |
| 5.0  | 4.0   | 5.0   | 25         | 0.66   |
| 5.0  | 12.0  | 5.0   | 25         | 0.66   |
| 5.0  | 20.0  | 5.0   | 25         | 0.66   |
| 5.0  | 8.0   | 2.0   | 25         | 0.65   |
| 5.0  | 8.0   | 6.0   | 25         | 0.66   |
| 5.0  | 8.0   | 10.0  | 25         | 0.67   |
| 5.0  | 8.0   | 5.0   | 30         | 1.03   |
| 5.0  | 8.0   | 5.0   | 40         | 2.39   |
| 5.0  | 8.0   | 5.0   | 50         | 5.31   |

<sup>a</sup>  $k_p/(k_t)^{1/2}$  for acrylamide and *N,N'*-methylenebisacrylamide were 0.42 and 2.11 mol<sup>-1</sup> dm<sup>3</sup> S<sup>-1/2</sup>, respectively.

the observed kinetic data were in good agreement with rate expression (9) and (10). The values of  $k_p$ ,  $k_t$ , and  $k_p/(k_t)^{1/2}$  were found to be  $1.37 \times 10^{-4} \text{ S}^{-1}$ ,  $4.31 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6} \text{ S}^{-1}$ , and  $0.66 \text{ mol}^{-1} \text{ dm}^3 \text{ S}^{-1/2}$ , respectively. These values are given in Table IV. The value of  $k_p/(k_t)^{1/2}$  was almost constant during concentration variation of monomer, silver perchlorate, and peroxidiphosphate but was found to increase on increasing the temperature from 20 to 50°C. The value of kinetic parameter  $k_p/(k_t)^{1/2}$  was found to be comparable with that of acrylamide and methacrylamide as expected on the basis of the structural criteria reported in the literature.<sup>18,19</sup> On comparing the value of this parameter of *N*-VP with the *N,N'*-methylenebisacrylamide, it has been observed that the value of this parameter is higher with *N,N'*-methylenebisacrylamide.<sup>8</sup> These observations have further supported the idea of cyclization step in the polymerization of divinylmonomers.<sup>20</sup>

The author is thankful to University of Roorkee and DST New Delhi for financial support.

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Received October 14, 1993

Accepted January 19, 1994