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RADICAL POLYMERIZATION OF *N,N'*-METHYLENEBISACRYLAMIDE BY PEROXIDIPHOSPHATE- Ag^+ REDOX SYSTEM: A KINETIC STUDY

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ABSTRACT

The kinetics of aqueous polymerization of *N,N'*-methylenebisacrylamide (*N,N'*-MBA) was studied under an inert atmosphere within the 20–40°C temperature range. The rate of polymerization was found to be proportional to *N,N'*-MBA and square-root dependent to the concentration of Ag^+ and peroxidiphosphate. An intramolecular cyclization prior to propagation is proposed in the mechanism to explain the kinetic data. The overall energy of activation has been found to be 30.2 ± 0.1 kJ·mol⁻¹. On the basis of experimental results, a suitable scheme has been proposed and a rate expression has been derived.

INTRODUCTION

Peroxidiphosphate received little attention until Edward et al. published a number of reviews describing its potentiality as an initiator for polymerization processes. Surprisingly, the peroxidiphosphate was found to be a better initiator than peroxidisulfate, which is used frequently in vinyl polymerization. The peroxidiphosphate, in the presence of different reducing agents, has been used extensively in graft copolymerization [1, 2] and homopolymerization reactions [3, 4]. Very few investigations have been reported on homopolymerization of *N,N'*-methylenebis-

acrylamide (N,N' -MBA) using this oxidant alone or with other reducing agents. Normally, N,N' -MBA in the presence of a redox system yields crosslinked insoluble polymer, even at low concentrations of N,N' -MBA. Some recent studies reported in the literature [5, 6] indicate successful efforts were made to polymerize this monomer without forming any network structure. The growing importance of gel-free polymerization of N,N' -MBA has created interest in undertaking further studies of this fascinating problem.

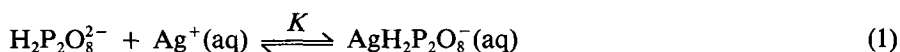
EXPERIMENTAL

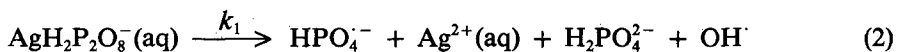
N,N' -Methylenebisacrylamide (Kotch-light) was recrystallized from acetone at 40°C. The AgClO_4 was prepared as described elsewhere [7]. Peroxidiphosphate was received as a gift sample from the FMC Corporation USA and was used without further purification. The rate of polymerization was determined as reported in our previous paper [8], and the percent conversion of monomer into polymer was calculated by modifying the equation of Wallace and Young [9]. Experiments involving silver perchlorate were protected from light. The ionic concentration in the reaction mixture was controlled using potassium sulfate as a neutral salt.

RESULTS AND DISCUSSION

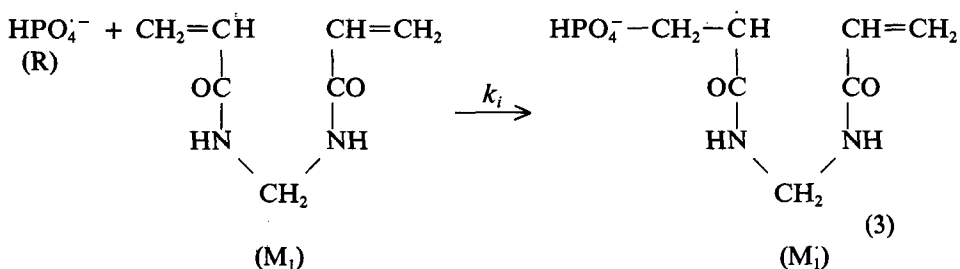
Preliminary experiments conducted using the peroxidiphosphate- Ag^+ system indicated that gel formation takes place at a higher concentration of the monomer in comparison with other conventional redox systems used in the vinyl polymerization process. During the optimization of concentration of the reactants, it was also found that the rate of polymerization of N,N' -MBA in the absence of Ag^+ is very slow, and that the total conversion into polymer does not exceed more than 20% of the initial concentration of monomer at 25°C. In addition to these observations it was also found that the induction period was very dominant when experiments were performed in the absence of the Ag^+ ion. To avoid the formation of a crosslinked network, the concentration of N,N' -MBA was not more than $40.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and reaction was followed until a gel appeared. Linear, isotactic poly- N,N' -MBA is water soluble, and it was subjected to spectral and endgroup analysis after the reaction mixture was purified. The IR spectrum of purified poly- N,N' -MBA had a prominent peak corresponding to the $-\text{P}-\text{O}-$ group, which supported the idea that initiation in the monomer takes place via phosphate ion radicals, as proposed in the scheme. The dye partition test [10] for the OH end group was applied in poly- N,N' -MBA. The negative test for the OH group precludes initiation through OH^\cdot radicals in the present system. On the basis of the experimental findings, the following scheme is proposed.

Radical formation:

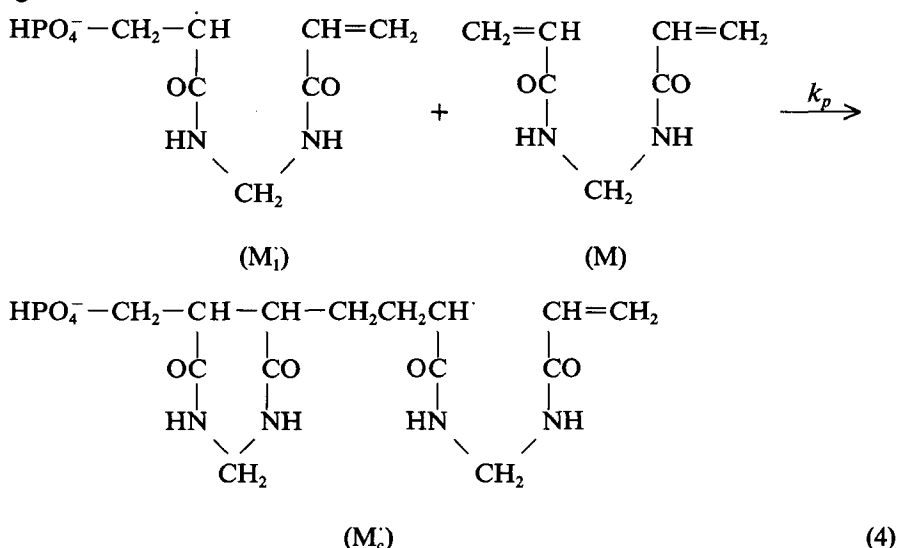




Initiation:



Propagation:



Termination:



In order to study the effect of concentration and physical conditions on the polymerization process, the following variations were tried and the results are discussed.

Effect of Monomer

The initial rate of polymerization and maximum percent conversion were measured on varying the initial concentration of *N,N'*-methylenebisacrylamide from 8 to $40.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ while keeping the concentration of silver perchlorate and

peroxidiphosphate constant. The order with respect to monomer, calculated from the slope of a log-log plot (Fig. 1), was found to be unity. On increasing the concentration of the monomer beyond $40.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, the reaction mixture became heterogeneous within a few minutes owing to the formation of a polymer network. Therefore, all studies were carried out at low concentrations of the monomer. At a high concentration ($>40.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) of the monomer, the reaction order was more than unity, which might be due to the existence of the cage effect, as suggested by Riggs et al. [11] for the acrylamide-persulfate system. The monomer molecules which were activated by hydrogen phosphate ion radicals (HPO_4^-) in Step 3 form seven-membered rings by reacting with the next monomer unit (Step 4) during the chain propagation step. The seven-membered ring formed in the cyclization step is assumed to be stable due to the presence of the two carbonyl groups in the ring which reduce the ring strain [12]. The observed high reactivity of N,N' -MBA in comparison with acrylamide and related vinyl monomers further suggests that cyclization of the pendant bulky group might be the reason for its high reactivity in comparison with acrylamide and methacrylamide which contain bulky pendant groups like $-\text{NH}_2$ and $-\text{CH}_3$. These groups can not be cyclized, and their steric hindrance in the propagation steps of the polymerization process ultimately slows down the rate of polymerization. The absence of the characteristic peak corresponding to a double bond in the IR spectrum of poly(N,N' -MBA) provides further evidence of a cyclization step in the chain propagation reaction, as

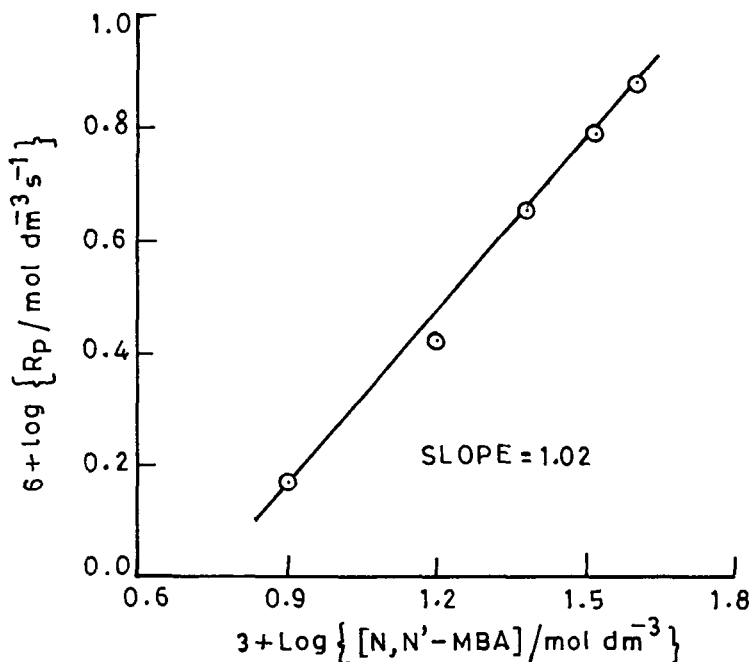


FIG. 1. Rate dependence on monomer concentration. $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 7.5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $[\text{Ag}^+] = 5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $\mu = 0.2 \text{ mol} \cdot \text{dm}^{-3}$, 298 K.

suggested by Marvel [13] and Butler et al. [14–17] for nonconjugated dienes separated by a few carbon atoms. Evidence of cyclization as an important step in the propagation of *N,N'*-MBA was found by calculating the value of the $k_p/(k_t)^{1/2}$ ratio under different experimental conditions and comparing them with the reported values of such vinyl monomers as acrylamide and methacrylamide. The results given in Table 1 clearly indicate that the $k_p/(k_t)^{1/2}$ ratio for *N,N'*-MBA is higher than for acrylamide and methacrylamide. Butler et al. [18] also compared the $k_p/(k_t)^{1/2}$ values of divinyl monomers with other monomers to support the existence of a cyclization step in the propagation reactions of divinyl monomers. They consider this step an important factor in increasing the initial rate and maximum conversion of divinyl monomers. In this intra-intermolecular mechanism, a primary free radical is first formed by the interaction of free radicals (Step 3). Then propagation takes place through intramolecular cyclization and intermolecular addition of the next monomer. In this process a radical is formed at the end of the added monomer which remain uncyclized until further interaction occurs with the next monomeric unit. This mode of propagation is responsible for the generation of a linear, gel-free, soluble polymer from *N,N'*-MBA, found to be predominant in the presence of peroxidiphosphate as an oxidant. *N,N'*-MBA is a symmetrical, nonconjugated diene. Termination is assumed to take place through mutual interactions of the growing radicals, as suggested by Gibbs et al. [19].

Effect of Peroxidiphosphate

The concentration of peroxidiphosphate was varied from 2.5 to 15.0×10^{-3} mol·dm⁻³ while keeping the concentration of the other reactants constant in order to study its effect on the rate of polymerization of *N,N'*-MBA. The reaction rate was not affected substantially by the absence of the Ag⁺ ion, which suggests that the Ag⁺ ion helps in the decomposition of the peroxidiphosphate ion to generate free radicals. The order of reaction with respect to peroxidiphosphate was determined by the slope value of a log-log plot (Fig. 2) and found to be 0.52. The half-order dependence of the rate on peroxidiphosphate indicates that termination

TABLE 1. Comparison of the Ratio of Propagation and Termination Rate Constant $k_p/(k_t)^{1/2}$ of *N,N'*-MBA^a

$[N,N'\text{-MBA}] \times 10^3$ mol·dm ⁻³	$[H_2P_2O_8^{2-}] \times 10^3$ mol·dm ⁻³	$[Ag^+] \times 10^4$ mol·dm ⁻³	Temp., °C	$k_p/(k_t)^{1/2}$ mol ⁻¹ ·dm ³ ·s ^{-1/2}
8.0	7.5	5.0	25	2.11
16.0	7.5	5.0	25	2.11
20.0	2.5	5.0	25	2.15
20.0	10.0	5.0	25	2.14
20.0	7.5	2.0	25	2.13
20.0	7.5	6.0	25	2.12
24.0	7.5	5.0	20	1.78
24.0	7.5	5.0	40	3.17

^a $k_p/(k_t)^{1/2}$ for acrylamide = $0.42 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1/2}$.

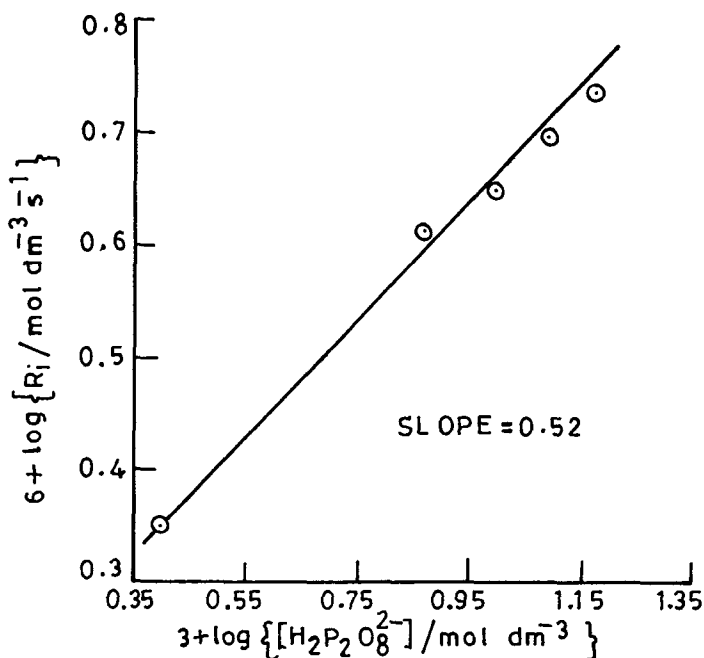
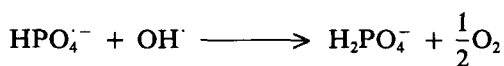


FIG. 2. Rate dependence on peroxidiphosphate concentration. $[N,N'$ -MBA] = $2.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, $[Ag^+] = 5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $\mu = 0.2 \text{ mol} \cdot \text{dm}^{-3}$, 298 K.

occurs through a mutual combination of the growing chains. At higher peroxidiphosphate concentrations, the initial rate as well as the maximum yield decrease. This retardation might be due to (1) excess production of primary free radicals which terminate the propagating chain radicals as well as other active radicals of the system, (2) peroxidiphosphate might have oxidized the reactive species of the system, (3) at higher concentration ($> 15.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) of the peroxidiphosphate, the following side reaction might generate oxygen, and if this affects growth of the chain and primary radicals, then the rate as well the maximum conversion will decrease.



Effect of Ag^+

The initial rate of polymerization was studied on varying the concentration of Ag^+ from 2 to $8.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ at constant temperature and ionic strength. The order of reaction was found to be 0.51 (Fig. 3). This rate dependence on Ag^+ excludes the participation of Ag^+ ions in the chain termination step; otherwise, the order would have been unity.

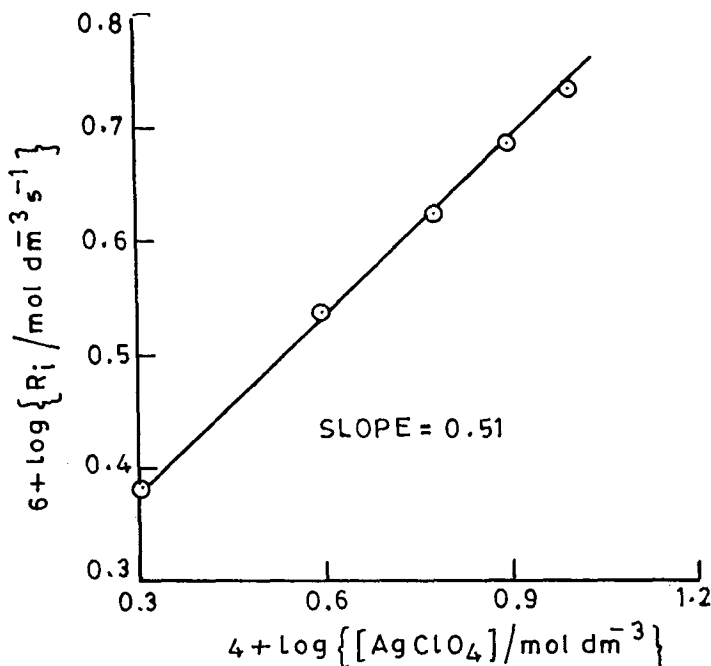


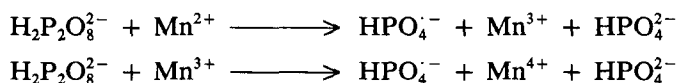
FIG. 3. Rate dependence on silver ion concentration. $[N,N'$ -MBA] = 2.0×10^{-2} mol·dm⁻³, $[H_2P_2O_8^{2-}] = 7.5 \times 10^{-3}$ mol·dm⁻³, $\mu = 0.2$ mol·dm⁻³, 298 K.

Effect of Temperature

The rate of polymerization of *N,N'*-MBA was found to increase with an increase in the temperature of the reaction. However, it decreases substantially at very high temperatures (>40°C), which may be due to the dominance of the termination step over the initiation and propagation steps at higher temperatures. The activation energy was calculated from a log k_p vs $1/T$ plot (Fig. 4), and it was found to be 30.25 ± 0.1 kJ·mol⁻¹. This activation energy is low in comparison to other water-soluble vinyl monomers reported in the literature.

Effect of Addition of Manganous Sulfate (MnSO₄), Acid (HCl), Complexing Agent (NaF), and Salt (K₂SO₄)

Upon the addition of manganous sulfate (1.0×10^{-4} mol·dm⁻³) to the reaction mixture in the presence of Ag⁺ ion, the initial rate of polymerization and maximum percent yield were found to increase substantially (Fig. 5). The increase caused by Mn²⁺ may be due to the formation of highly reactive Mn³⁺ ions [20] through the following reactions:



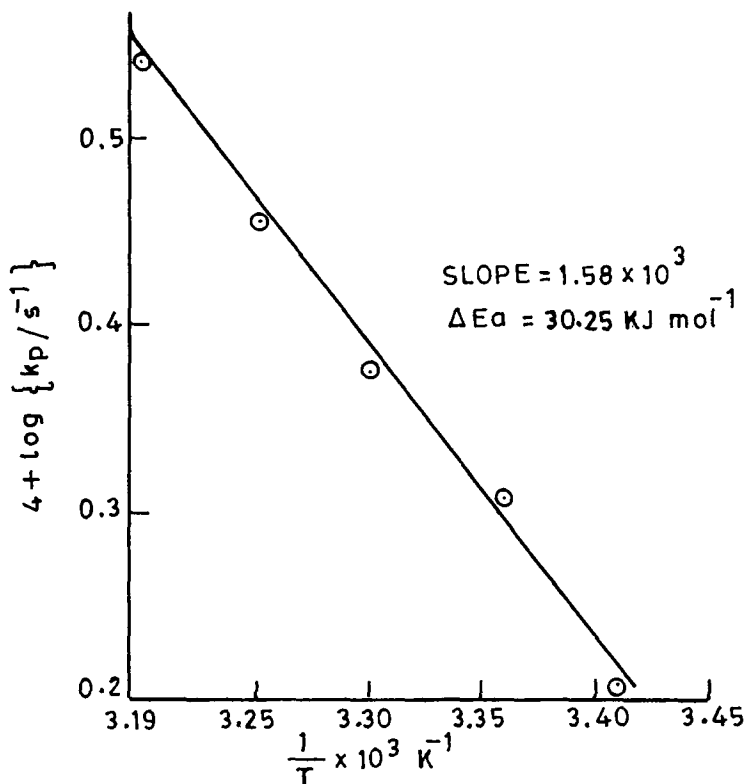


FIG. 4. Effect of temperature. $[N,N'\text{-MBA}] = 2.4 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 7.5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{Ag}^+] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, $\mu = 0.2 \text{ mol}\cdot\text{dm}^{-3}$.

The Mn^{3+} ions generate free radicals which ultimately increase the rate of polymerization. The polymerization process of N,N' -MBA was also studied in the presence of different concentrations of the acid. The results, given in Fig. 5, clearly indicate an increasing effect of acid at low concentrations ($3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$). A substantial decrease in rate and in maximum conversion were observed at higher acid concentrations ($>2.0 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$). It has been assumed that peroxidiphosphate forms a variety of species depending upon the acid concentration. At low acid concentration an active species of peroxidiphosphate ($\text{H}_3\text{P}_2\text{O}_8^-$) is formed, as suggested by Edward [21]. This species interacts with other species of the peroxidiphosphate and generates free radicals in the reaction mixture. Hence, the rate of polymerization increases at low acid concentrations but at high acid concentrations ($>2.0 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$) the oxidizing power of the peroxidiphosphate ion decreases [22] due to the interaction of acid anions with peroxidiphosphate ions. Therefore the initial rate and the maximum conversion were decreased. There is also the possibility that protonation of peroxidiphosphate takes place at high acid concentrations. This ultimately converts peroxidiphosphate oxygen into hydroxide ion, thereby decreasing the potential of peroxidiphosphate to generate primary free radicals.

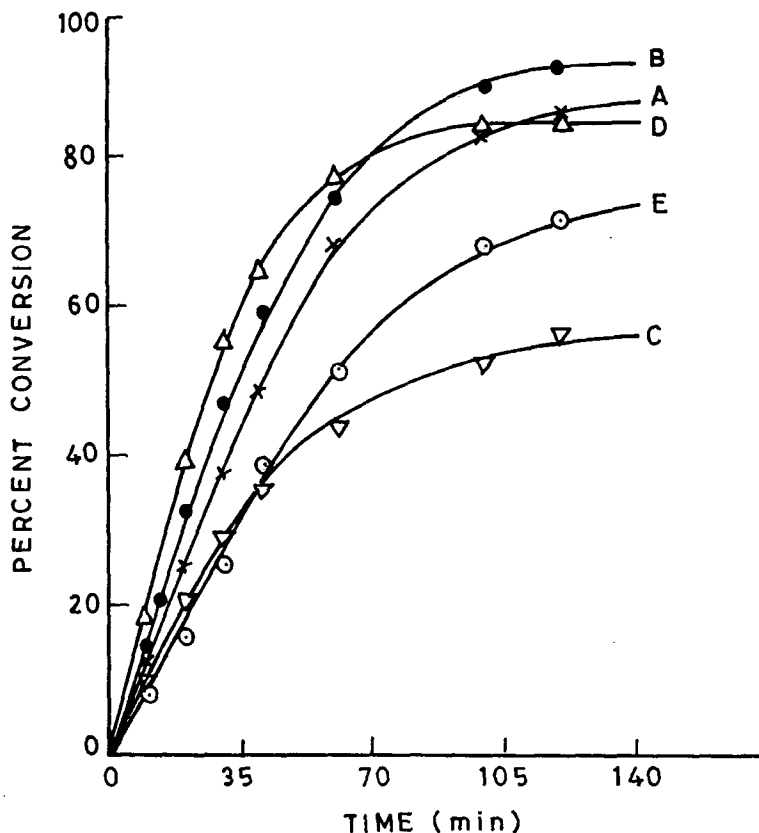


FIG. 5. Effect of additives. (A) Control, $[N,N'\text{-MBA}] = 2.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 7.5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{Ag}^+] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, $\mu = 0.2 \text{ mol}\cdot\text{dm}^{-3}$, 298 K. (B) $[\text{MnSO}_4] = 1.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$. (C) $[\text{NaF}] = 1.2 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$. (D) $[\text{HCl}] = 3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$. (E) $[\text{HCl}] = 25.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$.

Upon adding sodium fluoride to the reaction mixture (Fig. 5), both the initial rate and the maximum conversion decrease. The fluoride ion (F^-) generated in the system forms a stable complex with the Ag^+ ion, hence the decomposition of peroxidiphosphate is prevented, which results in a decrease in the initial rate and the maximum conversion of N,N' -MBA.

To observe the effect of ionic strength (μ) on the rate of polymerization, experiments were performed by using a neutral salt (K_2SO_4) to control the ionic strength of the medium. The results, given in Table 2, show a negative salt effect on the rate of polymerization.

Effect of Addition of Surfactants and Alcohols

The polymerization of N,N' -MBA was also studied in the presence of anionic (sodium oleate) and cationic (cetyltrimethylammonium bromide-CTAB) detergents. The results were compared with control experiments (Table 3). The concentrations

TABLE 2. Effect of Ionic Strength (μ) on R_p ^a

$R_p \times 10^6, \text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$	$\mu, \text{mol} \cdot \text{dm}^{-3}$
3.83	0.2
3.15	0.4
2.80	0.6

^a $[N,N'$ -MBA] = $2.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, $[\text{H}_2\text{P}_2\text{O}_8^{2-}]$
 = $7.5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $[\text{Ag}^+] = 5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$,
 298 K.

of the detergents were kept above their cmc values. The results reveal that both surfactants show an increasing trend in the rate of polymerization. However, the anionic detergent (sodium oleate) was found to be more effective in increasing the initial rate of polymerization. This might be due to the negative charge on the micelles generated by sodium oleate. The increasing effect of surfactants in general is due to their peptization action which prevents the macroradicals from coalescing. The addition of methanol and butanol to the reaction mixture shows a prominent retarding effect (Table 3) on both the initial rate and the maximum yield. This retardation behavior of the alcohols in the present system might be due to the formation of additional free radicals by the interaction of peroxidiphosphate and the added alcohols. These excess free radicals take an active part in the premature termination of the primary and growing free radicals of the system, which results in an overall decrease in the rate of polymerization.

Thus, on the basis of experimental observations and considering the kinetic scheme proposed in Steps (1)–(7), the rate law is

$$R_p = k_p \left(\frac{k_1 K}{2k_t} \right)^{1/2} [\text{H}_2\text{P}_2\text{O}_8^{2-}]^{1/2} [\text{Ag}^+]^{1/2} [N,N'\text{-MBA}] \quad (8)$$

and the kinetic chain length (ν) is

TABLE 3. Effect of Additives on R_p ^a

Additives	% Conversion at different intervals of time (min)						
	10	20	30	40	60	100	120
Control	12.0	24.5	36.5	48.0	68.0	83.0	84.0
[CTAB] = 8.0×10^{-4} $\text{mol} \cdot \text{dm}^{-3}$	14.0	31.0	44.0	55.0	72.0	90.0	92.0
[Sodium oleate] = $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$	18.0	35.0	60.0	74.0	82.5	85.0	86.0
[Methanol] = 5% v/v	8.0	18.0	27.5	35.0	50.0	67.0	71.0
[Butanol] = 5% v/v	4.0	12.0	13.0	24.5	35.5	50.5	58.5

^a $[N,N'$ -MBA] = $2.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, $[\text{H}_2\text{P}_2\text{O}_8^{2-}] = 7.5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$,
 $[\text{Ag}^+] = 5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $\mu = 0.2 \text{ mol} \cdot \text{dm}^{-3}$, 298 K.

$$r = \frac{k_p[N,N'\text{-MBA}]}{(2k_t k_i K)^{1/2} [\text{Ag}^+]^{1/2} [\text{H}_2\text{P}_2\text{O}_8^{2-}]^{1/2}} \quad (9)$$

The values of rate constant k_p , k_t and $k_p/(k_t)^{1/2}$ were found to be $1.9 \times 10^{-4} \text{ s}^{-1}$, $8.19 \times 10^9 \text{ mol}^2 \cdot \text{dm}^{-6} \cdot \text{s}^{-1}$ and $2.11 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1/2}$, respectively. The value of $k_p/(k_t)^{1/2}$ was found to increase on increasing the temperature (Table 1), which might be due to the predominant increase in the value of k_p in comparison to k_t . The ratio $k_p/(k_t)^{1/2}$ was found to be useful to support the existence of a cyclization step in the propagation step of N,N'-MBA. Rate expression (8) explained the experimental results to a great extent, hence the steps proposed in this scheme might be correct.

CONCLUSION

The polymerization of N,N'-methylenebisacrylamide in the presence of peroxodiphosphate-Ag⁺ occurred instantaneously through an intra-intermolecular mechanism. The rate of polymerization of N,N'-methylenebisacrylamide was found to be higher than that of other vinyl monomers. The usefulness of this system lies in the fact that the polymerization of N,N'-methylenebisacrylamide proceeds without forming crosslinked insoluble polymer, even at a substantial concentration of the monomer.

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