

Gel Free Polymerization of *N,N'*-Methylenebisacrylamide Initiated by a Peroxodiphosphate–Thioacetamide Redox System. A Kinetic Study

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ABSTRACT: The kinetics of polymerization of the divinyl monomer, *i.e.*, *N,N'*-methylenebisacrylamide has been studied employing a peroxodiphosphate–thioacetamide redox system under inert atmosphere at $40 \pm 1^\circ\text{C}$. The rate of polymerization R_p , was proportional to $[\text{Monomer}]^1$, $[\text{Thioacetamide}]^{1.0}$, and $[\text{Peroxodiphosphate}]^{0.5}$. Based on the experimental results, cyclopolymerization of the growing radicals and mutual termination has been proposed.

KEY WORDS Gel Free / Polymerization / *N,N'*-Methylenebisacrylamide / Peroxodiphosphate–Thioacetamide / Redox / Kinetics /

N,N'-Methylenebisacrylamide (MBA) has an industrial application as a crosslinking agent to increase the quality of naturally occurring fibres¹ by graft copolymerization. Butler and Ingley² however found that divinyl monomer can occasionally yield soluble, gel free polymers and they suggested a new type of alternating intra-inter molecular propagation for such cases: A variety of *N*-substituted diacrylamide and dimethacrylamides were cyclopolymerized through free radical initiators.^{3–7} Otsu and Ohya⁸ homopolymerized a large number of *N*-substituted dimethacrylamide derivatives and found that the cyclization process occurred through repeated intermolecular tail-tail (t-t) propagation with intramolecular head-head (h-h) cyclization. Recently the polymerization of this divinyl monomer has been reported by other workers.^{9–11} Such studies have prompted us to study the kinetics of polymerization of this monomer with redox system of peroxodiphosphate (PDP)-thioacetamide (RSH).

EXPERIMENTAL

Potassium peroxodiphosphate was generously provided by FMC Corporation and used as obtained. All other chemicals used were either E. Merck or Analar Grade. B.D.H. (British Drug House) products. *N,N'*-methylenebisacrylamide was recrystallized from acetone at 40°C and dried *in vacuo* over silica gel. The kinetics of the polymerization was followed as reported in our earlier communication.¹² The per cent conversion was calculated by the modified equation of Wallace and Young.¹³ Most of the reactions were carried out at $\text{pH} = 2.09$ and no induction period was observed for polymerization.

RESULTS AND DISCUSSION

Effect of Peroxodiphosphate Concentration on the Rate of Polymerization

The rate of polymerization (R_p) increases linearly with increase in peroxodiphosphate concentration within the range $(1.25 \times 10^{-3} - 10.0 \times 10^{-3}) \text{ mol dm}^{-3}$. The double logarithm-

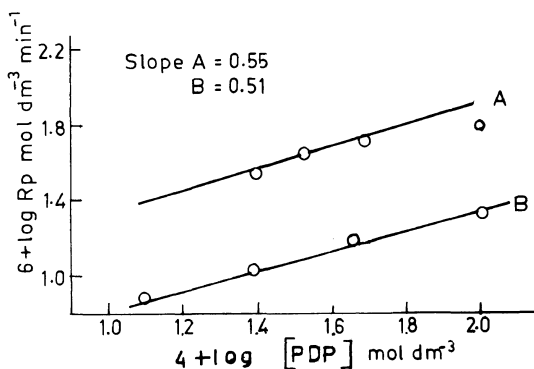


Figure 1. Dependence of the rate of polymerization on PDP concentration. Temp, 40°C; pH=2.09. [N,N'-MBA]: A = 5.0×10^{-3} mol dm⁻³; B = 6.0×10^{-3} mol dm⁻³. [Thioacetamide]: A = 4.0×10^{-3} mol dm⁻³; B = 3.0×10^{-3} mol dm⁻³.

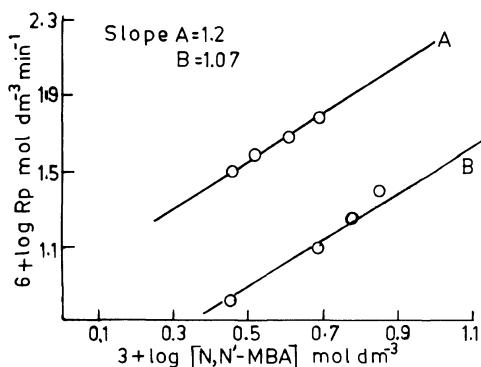


Figure 3. Dependence of the rate of polymerization on monomer concentration. Temp, 40°C; pH=2.09. [Thioacetamide]: A = 4.0×10^{-3} mol dm⁻³; B = 3.0×10^{-3} mol dm⁻³. [PDP]: A = 1.0×10^{-2} mol dm⁻³; B = 5.0×10^{-3} mol dm⁻³.

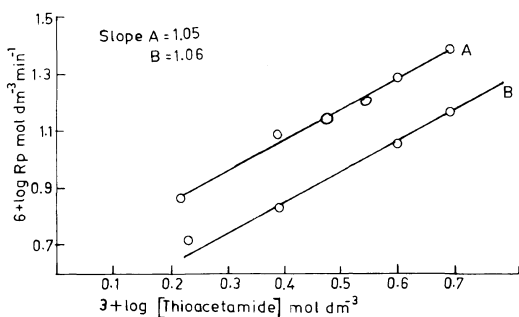


Figure 2. Dependence of the rate of polymerization on thioacetamide concentration. Temp, 40°C; pH=2.09. [N,N'-MBA]: A = 5.0×10^{-3} mol dm⁻³; B = 6.0×10^{-3} mol dm⁻³. [PDP]: A = 1.0×10^{-2} mol dm⁻³; B = 5.0×10^{-3} mol dm⁻³.

mic plot of R_p vs. initial [peroxodiphosphate] (Figure 1) show that the exponent of the peroxodiphosphate concentration is half, hence confirming termination^{14,15} occurs through bimolecular interaction of propagating chain radicals.

Dependence of Activator Concentration on the Rate of Polymerization

The rate of polymerization increases with increase in concentration of thioacetamide from (1.66×10^{-3} — 5.0×10^{-3}) mol dm⁻³. The exponent of the thioacetamide concentration was found to be unity (Figure 2) which confirms

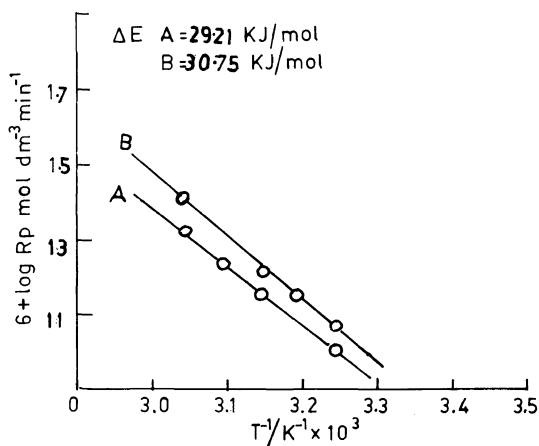


Figure 4. Temperature effect on the rate of polymerization. pH=2.09. [N,N'-MBA]: A = 5.0×10^{-3} mol dm⁻³; B = 6.0×10^{-3} mol dm⁻³. [Thioacetamide]: A = 4.0×10^{-3} mol dm⁻³; B = 3.0×10^{-3} mol dm⁻³. [PDP]: A = 8.0×10^{-3} mol dm⁻³; B = 4.0×10^{-3} mol dm⁻³.

that polymerization process is initiated by thioacetamide radical.

Dependence of Rate of Reaction on Monomer Concentration

Due to low solubility of monomer in water (3.0 g l^{-1}) and to obtain the soluble polymer during polymerization process, our study was restricted to (2.85×10^{-3} — 7.0×10^{-3}) mol dm⁻³ range of [M]. The rate of polymeriza-

tion is proportional to the concentration of monomer. Precipitation of the polymer occurred at more than 70% conversion of monomer and hence the experiments were performed below 70% conversion. The exponent to the concentration of monomer is little more than unity (Figure 3) which refers to the occurrence of the cage effect^{16,17} thought little.

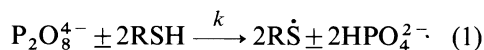
Effect of Temperature on the Rate of Polymerization

As the temperature is increased from 35°C to 55°C the rate of production of free radicals

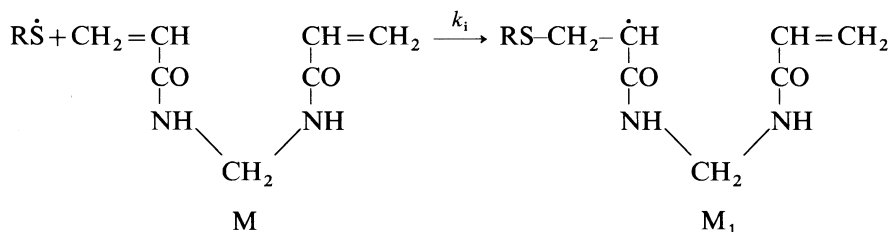
also increased with causes the increase in rate of polymerization (Figure 4). The energy of activation was found to be $30.75 \pm 2 \text{ k J mol}^{-1}$ which is clearly indicative of the fact that reaction proceeds through radical mechanism.

On the basis of kinetic results, the following reaction steps have been proposed:

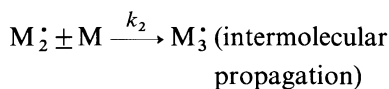
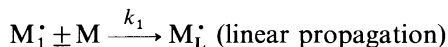
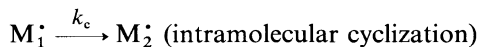
Radical formation



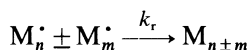
Initiation



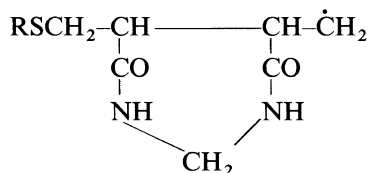
Propagation



Termination



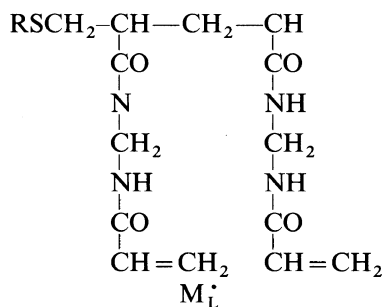
Thus $\text{M}_2\dot{\text{S}}$ represents



Most of the radicals formed in step,¹ by intraction of thioacetamide with peroxydisphosphate, are thought to be the dominating species responsible for polymerization of

N,N'-methlenebisacrylamide by undergoing cyclization prior to the combination of the next incombng fresh monomer molecules. $\text{M}_1\dot{\text{S}}$ is more likely to cyclize and give radical $\text{M}_2\dot{\text{S}}$ since the monomer is a symmetrical non conjugated diolefin having double bond at the terminal position.^{8,9} The cyclopropagation of $\text{M}_1\dot{\text{S}}$ may be explained by a similar argument made by Otsu and Ohya⁸ in their cyclopropagation studies on *N*-substituted dimethylacrylamide derivatives. The head-head intramolecular cyclization followed by tail-tail intermolecular propagation may give rise to soluble polymer of *N,N'*-methlenebisacrylamide with a seven membered cyclized unit in it. Similar results have also been reported by others.^{8,9} Formation of normally stable five or six membered ring during cyclization of monomer unit is well known.¹⁸ An observation of Zeigler and Hall¹⁹ revealed however, that the substitution of carbonyl or oxygen for a methylene groups reduces the strain by decreasing the number of interfering hydrogens. The assumption of proposing a seven membered ring during

polymerization is based on the fact that it is a less strained ring amongst the medium size rings, according to Baeyer's strain theory, therefore the stability of the ring is supposed to be higher in this case. The proof of the cyclization during the polymerization process can be provided by the IR spectra of the polymer. The IR spectra of the pure *N,N'*-methylenebisacrylamide shows the presence of an amide absorption band at 1623 cm^{-1} whereas the spectra of poly(*N,N'*-methylenebisacrylamide) showed the characteristic absorption band at 1670 cm^{-1} for C=O group present in the cyclized ring containing more than six members.²⁰ Therefore, the IR spectra clearly support the idea of ring formation during the polymerization process. During cyclization the reactive centre is created at the terminal carbon atoms of the second vinyl group, so reducing the chances of participation of the second ethylenic group into the cross linking process.



Resulting poly(*N,N'*-methylenebisacrylamide) was actually tested for the presence of double bond bromometrically²¹ no double bond was found.

It is more likely that normal monovinyl type of linear propagation does not take place because of bulky pendent group capable of causing steric hindrance to M_1^\cdot for the approach of another monomer unit. Therefore cyclization of M_1^\cdot is more probable and cyclized radical can now add another monomer unit to give M_2 which then cyclized to repeat the sequence as suggested by Marvel²² and Butler *et al.*²³

Table I. Comparison of overall rate of polymerization^a

Monomer (M)	$[\text{M}] \times 10^3$	$R_p \times 10^4$
	mol dm^{-3}	$\text{mol dm}^{-3} \text{ min}^{-1}$
<i>N,N'</i> -Methylenebisacrylamide	6.6	17.4
Acrylamide	6.6	1.50
Methacrylamide	6.6	0.95

^a [Thioacetamide] = $3.0 \times 10^{-3} \text{ mol dm}^{-3}$; [PDP] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; pH = 2.09.

The observed square root dependence of [Peroxydiphosphate] (Figure 1) that termination occurs by mutual combination of growing macro-radicals. This view is further supported by the work of other workers²⁴ that for a symmetrical nonconjugated diolefin when cyclization in the preferred path, termination is predominantly by mutual interaction of two growing macro-radicals. On comparison the rate of polymerization of *N,N'*-methylenebisacrylamide with monomer like acrylamide (AM) and methacrylamide (MAM) it follows the sequence



This fact supports that cyclopolymerization occurs in propagation step as proposed.

Effect of Additives

The rate of polymerization of *N,N'*-methylenebisacrylamide has been studied in presence of various additives such as alcohols, inorganic salts, detergents, transition metal ions, and sulphuric acid. The addition of water soluble organic solvents decreases the rate of polymerization and maximum conversion. The effect can be explained on the basis that these organic solvents namely methanol, ethanol, propanol, butanol, dimethylformamide (DMF) and acetone decreases the area of shielding²⁵ of a strong hydration layer in aqueous medium, therefore the total effect is the termination of radical end of growing chains. Since the

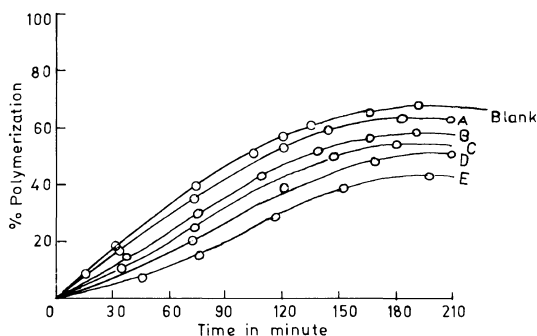


Figure 5. Effect of organic solvents on R_p , $[N,N'$ -MBA] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; [Thioacetamide] = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$; [PDP] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$; [Solvents] = 1 M; temp, 40°C ; pH = 2.09; A = methanol; B = propanol; C = butanol; D = DMF; E = acetone.

retarding effect of alcohols increases prominently from methanol to butanol, which may also be due to the decreasing dielectric constant of the alcohols. The alcohols may also increase the rate of termination by decreasing the interchain hydrogen bonding between the poly(N,N' -methylenebisacrylamide) chains. The acetone and DMF also retard the rate of polymerization. The retarding effect increases sharply from methanol to butanol (Figure 5)

Methanol < Ethanol < Propanol <
Butanol < DMF < Acetone

On addition of alkali metal chloride such as KCl, NaCl, LiCl, and Na_2SO_4 decreases the rate of polymerization. The retarding effect of these salts can be explained as—

(1) In case of alkali metal chlorides, the basic character of the alkali metal ion increases *i.e.*, ionic radii increases from Li to K.

(2) In case of neutral salts like NaCl, KCl, and Na_2SO_4 the depression (Figure 6) in the rate may be due to the thickening of the medium or the process of salting out causes interference with usual reaction resulting in the premature termination of growing chain. Similar results have also been reported by other workers.²⁶

Both cationic and anionic detergents reduce the rate of polymerization. The positively

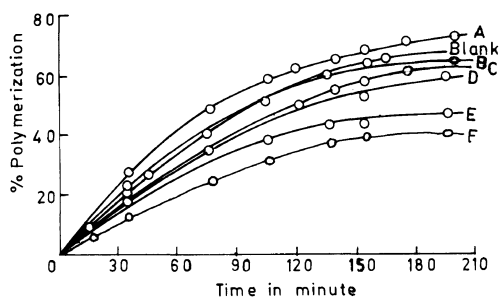


Figure 6. Effect of Inorganic salts and transition metal ions on R_p , $[N,N'$ -MBA] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; [Thioacetamide] = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$; [PDP] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$; [Salts] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$; [Metal ions] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$; temp, 40°C ; pH = 2.09; A = MnSO_4 ; B = AgNO_3 ; C = Na_2SO_4 ; D = LiCl; E = NaCl; F = KCl.

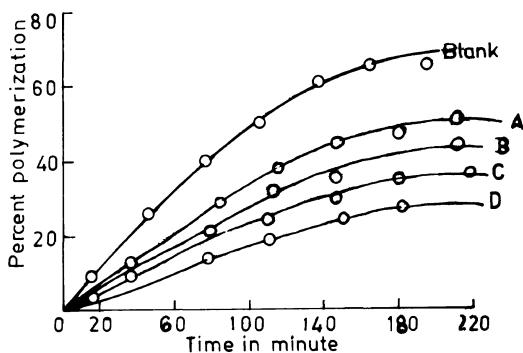


Figure 7. Effect of detergents on R_p , $[N,N'$ -MBA] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; [Thioacetamide] = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$; [PDP] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$; temp, 40°C ; pH = 2.09; A [Sodium lauryl sulphate] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$; B [Sodium oleate] = $1.4 \times 10^{-3} \text{ mol dm}^{-3}$; C [CTAB] = $0.5 \times 10^{-3} \text{ mol dm}^{-3}$; D [CTAB] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$. ([CTAB], cetyltrimethylammonium bromide)

charged micelles produced by the cationic detergents (CTAB) favours the orientation of growing polymer for termination, hence the rate of polymerization decreases. The retarding effect of cation may also be explained by specific ion pair binding of anion $\text{P}_2\text{O}_8^{4-}$ with cation, which lowers the rate of primary radical generation. The dissociation of anionic detergents provides negatively charged ionic micelles that probably exert a repelling force between anion $\text{P}_2\text{O}_8^{4-}$ and negatively charged ionic micelles which lowers the rate of primary

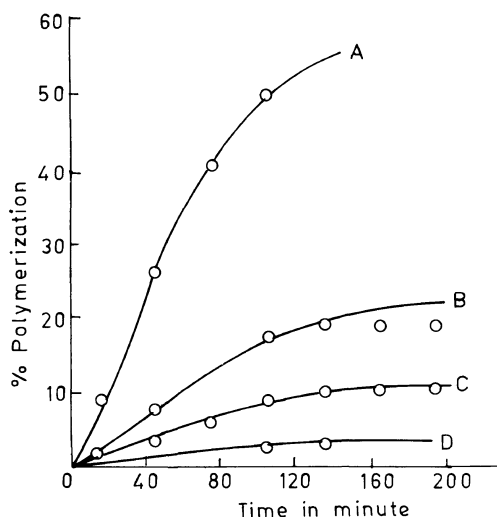
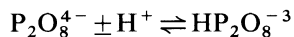


Figure 8. Effect of pH on R_p . $[N,N'$ -MBA] = 5.0×10^{-3} mol dm $^{-3}$; [Thioacetamide] = 4.0×10^{-3} mol dm $^{-3}$; [PDP] = 1.0×10^{-2} mol dm $^{-3}$; temp, 40°C; pH A = 2.09; B = 2.30; C = 2.60; D = 3.0.

radical generation, hence retarding effect is observed (Figure 7).

Addition of $MnSO_4$ and $AgNO_3$ enhances the rate of polymerization due to the fact that Mn^{2+} and Ag^{\pm} is easily oxidised to $Mn^{3\pm}$ and $Ag^{+\pm}$ which are strong oxidising agents, hence more of the thioacetamide is oxidised giving more radicals which are capable of increasing the rate of polymerization (Figure 6).

The rate of polymerization increases with increase in the concentration of H^+ ions. Figure 8, which can be explained by the fact that $P_2O_8^{4-}$ forms protonated species.²⁷



This protonated species of PDP is supposed to be active species in the studied pH range and $HP_2O_8^{-3}$ interacts with thioacetamide giving radicals which causes enhancement in the rate of polymerization.

On the basis of the experimental results, the following rate expression has been derived by considerations of steps

$$R_p = k_p \left[\frac{k}{2k_t} \right]^{1/2} [M][P_2O_8^{4-}]^{1/2} [RSH]$$

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Polymerization of MBA by Redox System

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