

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Divinyl Polymerization of N, N'-Methylenebisacrylamide Initiated by Peroxydisulphate-Thiomalic Acid Redox System

K. Rathinamuthu^a; R. Victoria^b; S. Vaidyanathan^c; A. Gopaland^d

^a Department of Chemistry, Vivekananda College, Tiruvedakam, Madurai ^b Department of Chemistry, Lady Doak College, Madurai ^c Department of Physical Chemistry, Madurai Kamaraj University, Madurai ^d Department of Industrial Chemistry, Alagappa University, Karaikudi

To cite this Article Rathinamuthu, K. , Victoria, R. , Vaidyanathan, S. and Gopaland, A.(1997) 'Divinyl Polymerization of N, N'-Methylenebisacrylamide Initiated by Peroxydisulphate-Thiomalic Acid Redox System', International Journal of Polymeric Materials, 38: 1, 49 – 64

To link to this Article: DOI: 10.1080/00914039708031494

URL: <http://dx.doi.org/10.1080/00914039708031494>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Divinyl Polymerization of N, N'-Methylenebisacrylamide Initiated by Peroxydisulphate-Thiomalic Acid Redox System

K. RATHINAMUTHU^a, R. VICTORIA^b, S. VAIDYANATHAN^c
and A. GOPALAN^{d,*}

^a*Department of Chemistry, Vivekananda College, Tiruvedakam, Madurai-625 217;* ^b*Department of Chemistry, Lady Doak College, Madurai-625 002;* ^c*Department of Physical Chemistry, Madurai Kamaraj University, Madurai-625 021;* ^d*Department of Industrial Chemistry, Alagappa University, Karaikudi-623 003*

(Received 20 December 1996)

The kinetics of polymerization of N, N'-methylenebisacrylamide (MBA), a symmetrical non-conjugated divinyl monomer, initiated by a redox system potassium peroxydisulphate (PDS)-thiomalic acid (TMA) was studied in aqueous medium in the temperature range 35–50 °C. Rate of polymerization (R_p) and rate of disappearance of peroxydisulphate ($-R_{PDS}$) were followed. From the rate law for polymerization, a mechanism was proposed incorporating cyclopolymerization in the propagation in contrast to normal propagation in monovinyl polymerization. Rate parameters were evaluated and its significance discussed.

Keywords: Divinyl polymerization; N, N'-methylenebisacrylamide; initiation; redox system; rate of polymerization; reaction mechanism

INTRODUCTION

Cyclopolymerization of non-conjugated diolefins with radical initiation through redox systems were reported recently by Subbaratnam and coworkers [1–5]. Organic thiocarboxylic acids were effectively combined

* To whom correspondence can be made.

with $S_2O_8^{2-}$ to initiate vinyl polymerization [6–10]. Thiomalic acid finds application in the initiation of vinyl polymerization in combination with peroxydisulphate [11, 12]. The present work deals with the kinetics of peroxydisulphate-thiomalic acid redox initiated polymerization of N,N'-methylenebisacrylamide, a symmetrical non-conjugated divinyl monomer.

EXPERIMENTAL

Materials

N,N'-methylenebisacrylamide (Koch Light, England) was purified from acetone at 40 °C and used. Potassium peroxydisulphate (Sarabai M. Chemicals) and thiomalic acid (John Baker, USA) were used as such. All other reagents were of BDH and E. Merck AnalaR Grade and used without further purification.

Procedure

A typical polymerization procedure is as follows: The reaction mixture consisting of required concentration of N,N'-methylenebisacrylamide, sodium sulphate (to maintain ionic strength) and thiomalic acid was placed in a polymer tube of 80 ml capacity and deaerated for 20 minutes by passing oxygen free N_2 . Polymerization reaction time was taken from the time of addition of peroxydisulphate solution to the reaction mixture. Polymerization was allowed to continue at conditions without any gel formation [1–5, 13–14]. After a definite polymerization reaction time (varied with conditions), the polymerization was arrested by blowing air into the reaction mixture. The rate of polymerization, R_p was calculated by estimating the unreacted monomer by bromometry [15]. The rate of disappearance of peroxydisulphate ($-d[PDS]/dt$) was also followed under all polymerization conditions by estimating the unreacted peroxydisulphate by iodometry.

RESULTS

Polymerization was found to occur only in the presence of both redox components. This indicates that polymerization does not take place by

peroxydisulphate alone. The kinetic results obtained with respect to rate of polymerization (R_p) and rate of peroxydisulphate disappearance ($-R_{PDS}$) are presented here to arrive at a suitable mechanism for the polymerization.

Effect of Monomer Concentration on R_p

R_p was followed in the monomer concentration range 1.96×10^{-3} to $7.82 \times 10^{-3} \text{ mol l}^{-1}$ while keeping all the other parameters such as $[PDS]$, $[TMA]$, μ and temperature as constant.

The plot of R_p vs $[M]$ (Fig. 1, Plot A) was drawn and found to be linear with negligible intercept. This points out the first power dependence of R_p on $[M]$. This first power dependence was further confirmed by following R_p for varying $[M]$ in another set of experimental conditions and with the plot of R_p vs $[M]$ (Fig. 1, Plot B).

Effect of PDS Concentration on R_p

The effect of $[PDS]$ on R_p was studied and R_p remained constant with increase of $[PDS]$ (Tab. I). This indicates the zero order dependence of R_p on $[PDS]$.

Effect of TMA Concentration on R_p

R_p was followed for varying $[TMA]$ in the range 1.04 to $6.24 \times 10^{-4} \text{ mol l}^{-1}$ while keeping $[M] = 2.99 \times 10^{-2} \text{ mol l}^{-1}$, $\mu = 0.60 \text{ mol l}^{-1}$, $[PDS] = 5.12 \times 10^{-3} \text{ mol l}^{-1}$ and $T = 35^\circ\text{C}$. R_p was found almost constant with $[TMA]$ indicating the independency of R_p on $[TMA]$ (Tab. I).

Effect of Temperature and Ionic Strength on R_p

The temperature was varied from 30°C to 50°C . R_p value was found to increase with increase in temperature. The Arrhenius plot of $\log R_p$ vs $1/T$ (Fig. 2A) was drawn. From the slope of the plot the overall activation energy was calculated and found to be 36.4 kJ mol^{-1} . The effect of temperature on R_p was also observed under a different set of experimental conditions. The plot of $\log R_p$ vs $1/T$ (Fig. 2B) was found to be linear one. From the slope of the plot also the activation energy was calculated and found to be close to the above value.

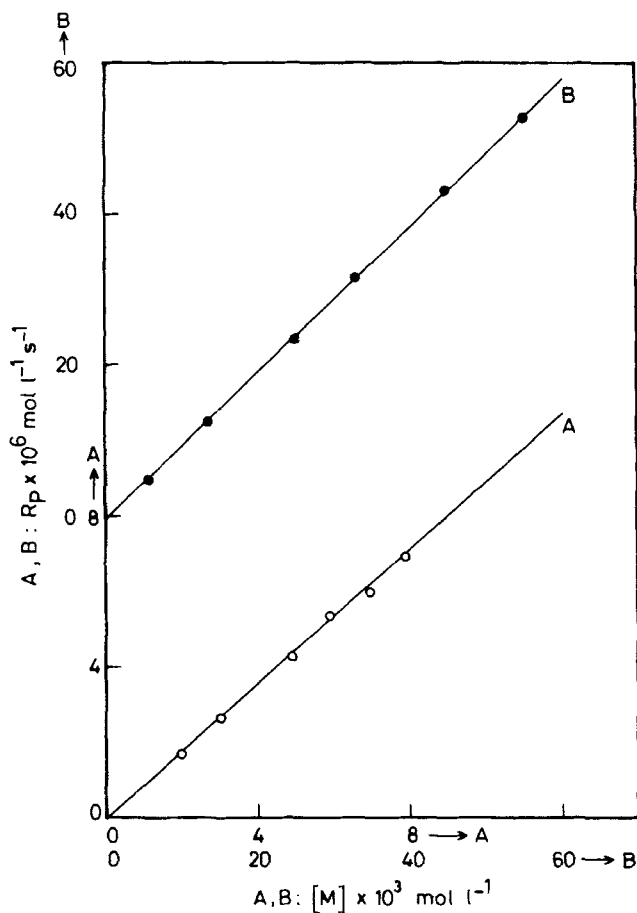


FIGURE 1 Effect of $[M]$ on R_p : $[PDS] = 5.12 \times 10^{-3} \text{ mol l}^{-1}$ (A); $1.02 \times 10^{-3} \text{ mol l}^{-1}$ (B). $[TMA] = 4.16 \times 10^{-4} \text{ mol l}^{-1}$ (A); $2.08 \times 10^{-4} \text{ mol l}^{-1}$ (B). $\mu = 0.60 \text{ mol l}^{-1}$ (A, B). Temp = 35°C (A, B).

The ionic strength was varied from 0.12 to 0.84 mol l^{-1} and R_p was found to remain constant with increase of ionic strength (Tab. I).

Effect of $[M]$ on $-R_{PDS}$

The rate of disappearance of peroxydisulphate, $-R_{PDS}$ was studied separately during monomer variations. $-R_{PDS}$ did not vary much with

TABLE I Effect of [PDS], [TMA] and ionic strength (μ) on R_p
 Temperature = 35°C

	(a)		(b)		(c)
[PDS] $\times 10^3$ mol l ⁻¹	$R_p \times 10^5$ mol l ⁻¹ s ⁻¹	[TMA] $\times 10^4$ mol l ⁻¹	$R_p \times 10^5$ mol l ⁻¹ s ⁻¹	μ mol l ⁻¹	$R_p \times 10^5$ mol l ⁻¹ s ⁻¹
2.56	2.64	1.04	2.20	0.12	1.70
7.68	2.64	2.08	2.20	0.24	1.63
10.2	2.66	3.12	2.20	0.36	1.42
12.8	2.66	4.16	2.20	0.48	1.40
15.4	2.66	5.20	2.20	0.72	1.35
17.9	2.64	6.24	2.20	0.84	1.38

(a), (c): [M] = 2.93×10^{-2} mol l⁻¹; (b): [M] = 2.99×10^{-2} mol l⁻¹; (a), (b): $\mu = 0.60$ mol l⁻¹; (a), (c): [TMA] = 4.17×10^{-4} mol l⁻¹; (b), (c): [PDS] = 5.12×10^{-3} mol l⁻¹.

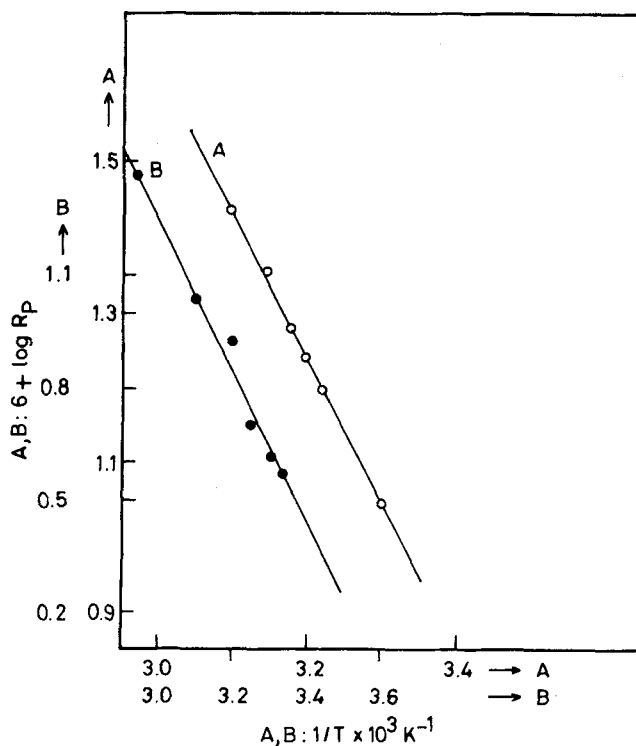


FIGURE 2 Effect of Temperature on R_p : [M] = 2.93×10^{-2} mol l⁻¹ (A); 1.96×10^{-2} mol l⁻¹ (B). [PDS] = 5.00×10^{-3} mol l⁻¹ (A); 1.11×10^{-3} mol l⁻¹ (B). [TMA] = 4.12×10^{-4} mol l⁻¹ (A); 2.04×10^{-4} mol l⁻¹ (B). $\mu = 0.60$ mol l⁻¹ (A, B)

change in monomer concentrations indicating the independency of $-R_{\text{PDS}}$ on monomer concentration (Tab. II).

Effect of [PDS] on $-R_{\text{PDS}}$

It was observed that $-R_{\text{PDS}}$ increases with increase in [PDS]. The plot of $-R_{\text{PDS}}$ vs [PDS] (Fig. 3) is a linear one and passing through the origin and shows the first power dependence of $-R_{\text{PDS}}$ on [PDS].

Effect of [TMA] on $-R_{\text{PDS}}$

The effect of [TMA] on $-R_{\text{PDS}}$ was found (Tab. II). $-R_{\text{PDS}}$ was unaffected by the change in [TMA].

DISCUSSION

In free radical polymerization of symmetrical divinyl monomers like acrylic anhydride, divinyl formal etc. kinetic relationships between rate of polymerization and the concentration of the components were obtained with the involvement of inter-intramolecular propagation step in the mechanism [3, 4, 13–17].

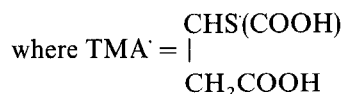
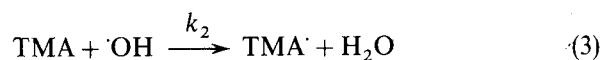
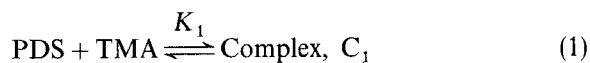
The observation of zero order dependence for both the redox components is quite contrast to the earlier observations in the polymerization of *N,N'*-methylenebisacrylamide [2–5]. The square root order dependence on both the redox components or zero order dependence on one of the redox components was found earlier [1–5, 12–14]. This new observation, therefore, requires a difference in the initiation or termination path. Hence the following proposal of the mechanism is given to explain the present investigation.

MECHANISM

Primary Reaction and Initiation

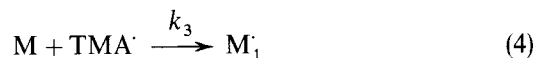
The complex formation by direct interaction between PDS and TMA is proposed as a possible precursor reaction to the primary radical production as given earlier on systems in vinyl polymerization [10, 11]. The

redox complex on decomposition can produce free radical capable of initiating polymerization.



Initiation may take place by the following reaction steps.

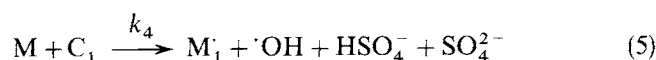
i) Initiation by primary organo thio radical



where



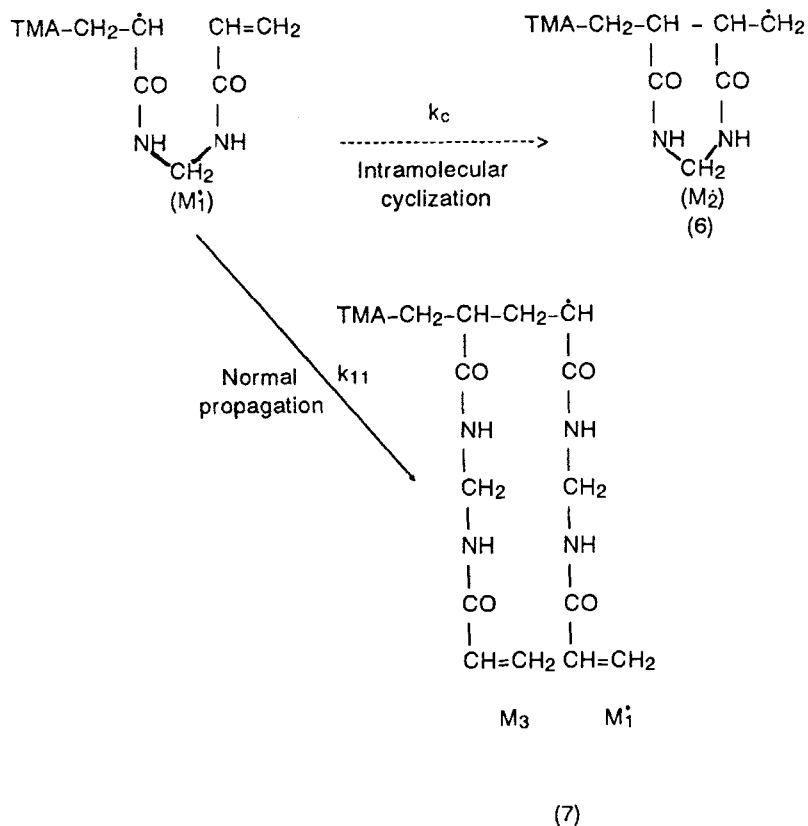
ii) Direct interaction between complex (C_1) and monomer (M) giving M_1



Propagation

There can be two competing reactions for propagation after the production of M_1 (i) Intramolecular cyclization of M_1 between the radical part

and the double bond present in the same repeating unit forming a new cyclized radical M_2 (ii) Normal intermolecular propagation as in monovinyl propagation forming a radical M_1 containing the unreacted pendant double bond (M_3).



SCHEME: Propagation possibilities

The relative probabilities of these two modes will depend on certain factors. The ease of intramolecular cyclization depends on the structure of the monomer. If five or six membered rings are formed on cyclization, highly cyclized polymers are formed because strain is reduced on ring or loop formation [18]. If seven or higher membered rings are formed on cyclization, the number of cyclized units in the polymer chain was found

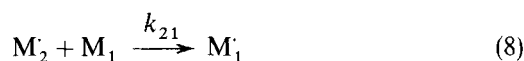
to be low. The observation made by Zeigler and Holl [19] revealed, however, that the substitution of carbonyl group or oxygen for a methylene group reduces the strain in the ring by reducing the number of interfering hydrogens. The ring in M_2 is seven membered in the present case, containing two carbonyl groups thereby contributing to lowering of strain. The probability of cyclization, therefore, is enhanced.

The presence of pendant group hinders monovinyl type intermolecular propagation in divinyl polymerization. With increase in length of the pendant group, its bulkiness increases so providing more shielding to the radical. Probability for linear propagation decreases with a lowered interaction. Further, the monomer concentration taken in our studies is very low and therefore M_1 will have relatively little opportunity for linear propagation with other monomer molecules as against intramolecular cyclization. The production of M_1 with M_3 can lead to gel formation, if normal linear propagation dominates. The gel-free nature of polymerization also disfavours the above possibility.

Hence reaction $M_1 + M_1 \xrightarrow{k_{11}} M_1$ is assumed not to occur. Here, M_1 is either of the double bonds of previously unreacted symmetrical monomer and M_1 is the initial radical derived from the attack of a radical on M_1 .

There is another intermolecular propagation in which the cyclized radical M_2 reacts with M_1 . Since there is no steric hindrance in the cyclized radical for the approach of the monomer, this reaction can take place at a greater rate and no pendant groups to prevent this propagation. Because of low probability for linear propagation and production of pendant double bond (M_3), all reactions involving M_3 and M_3 radical can be neglected.

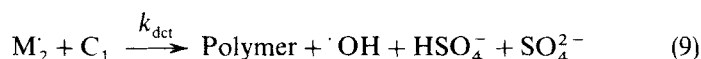
A final picture of the propagation steps now emerges from these considerations. The first step is the intramolecular cyclization and the second is the intermolecular propagation through cyclized radical which reacts with monomer and the sequence repeats itself. Hence, in the present study after the production of M_1 , the propagation is considered through cyclopolymerization



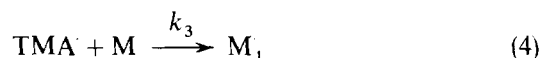
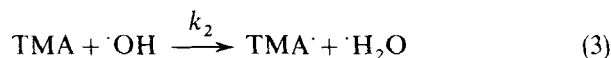
Termination

For symmetrical non-conjugated diolefins, when cyclization is the preferred path, termination takes place mainly between cyclized M_2 radicals [20]. If this kind of termination is dominant in the system under investigation, the rate expression derived would lead to a linear plot of R_p vs $[M]$ with $[PDS]^{1/2}$ and $[TMA]^{1/2}$. This is not the case in the present work. This necessitates consideration of a different type of termination as given below.

New Termination Path with Degradative Chain Transfer



The formed $\cdot\text{OH}$ can now reinitiate polymerization through steps (3) and (4).

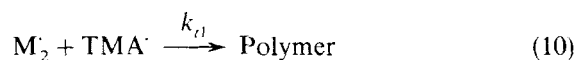


The M_1 radical can now propagate through steps 6 and 8.

Propagation

As mentioned above.

The final maturation of growing M_2 radical may now take place through linear termination by primary radical.



Under steady state conditions, if a rate expression is derived with the possibilities in mind the rate can be obtained as

$$R_p = \frac{k_{21}k_1[M]^1[PDS]^0[TMA]^0}{2k_{det}} \quad (\text{E } 12)$$

(The manner of arriving at the expression for R_p is given in Appendix I).

For the proposed reaction mechanism, $-R_{PDS}$ can also be derived as

$$-R_{PDS} = 3/2 k_1 [PDS]_T [M]^0 [TMA]^0 \quad (E 15)$$

(For derivation, see Appendix II).

It is interesting to note that all the experimental observations such as first power dependence of R_p on $[M]$ (Fig. 1), zero order dependences on $[PDS]$ (Tab. I) and $[TMA]$ (Tab. I) are clearly accounted for in (E 12). The results with $-R_{PDS}$ are in agreement with (E 15) (Tab. II, Fig. 3). These two facts support the proposed mechanism.

Evaluation of Rate Parameters

The expression for the rate of polymerization, as in (E 12) is utilized for the evaluation of composite rate constant $k_{21} k_1 / k_{dc}$. From the slope of the plots of R_p vs $[M]$, and the constancy of R_p during $[PDS]$ and $[TMA]$ variations the composite rate constant is calculated as $8.22 \times 10^{-3} \text{ s}^{-1}$ at 35°C .

$-R_{PDS}$ expression as in (E 15) is used to find k_1 . From the slope of the plot $-R_{PDS}$ vs $[PDS]$ (Fig. 3), k_1 value was calculated as $4.76 \times 10^{-4} \text{ s}^{-1}$ at 35°C .

The value of decomposition constant (k_1) of the PDS-TMA complex is found to be far high than that of the self decomposition of the PDS ($\sim 10^{-8} \text{ s}^{-1}$). This strongly supports that the radical generation is only

TABLE II Effect of $[M]$ and $[TMA]$ on $-R_{PDS}$

$\mu = 0.60 \text{ mol l}^{-1}$		Temperature = 35°C	
	(a)		(b)
$[M] \times 10^3$ mol l^{-1}	$-R_{PDS} \times 10^6$ $\text{mol l}^{-1} \text{ s}^{-1}$	$[TMA] \times 10^4$ mol l^{-1}	$-R_{PDS} \times 10^6$ $\text{mol l}^{-1} \text{ s}^{-1}$
1.96	4.37	1.04	3.62
2.93	4.37	2.08	3.62
4.90	4.37	3.12	3.62
5.87	4.37	4.16	3.62
6.84	4.37	5.20	3.62
7.82	4.37	6.24	3.62

(a), (b): $[PDS] = 5.12 \times 10^{-3} \text{ mol l}^{-1}$; (a): $[TMA] = 4.16 \times 10^{-4} \text{ mol l}^{-1}$;
(b): $[M] = 2.99 \times 10^{-2} \text{ mol l}^{-1}$.

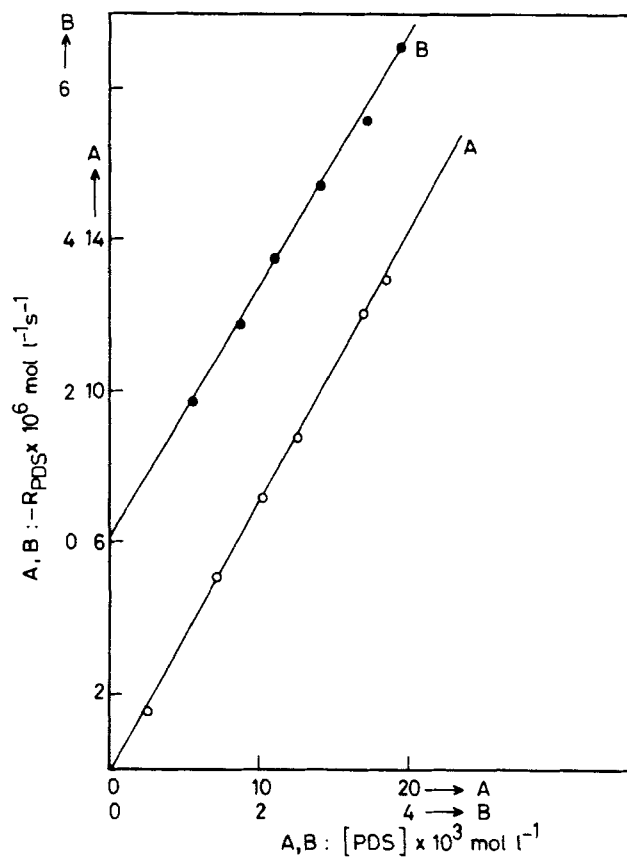


FIGURE 3 Effect of $[PDS]$ on $-R_{PDS}$: $[M] = 2.93 \times 10^{-2} \text{ mol l}^{-1}$ (A); $3.86 \times 10^{-2} \text{ mol l}^{-1}$ (B). $[TMA] = 4.17 \times 10^{-4} \text{ mol l}^{-1}$ (A); $2.08 \times 10^{-4} \text{ mol l}^{-1}$ (B). $\mu = 0.60 \text{ mol l}^{-1}$ (A, B). Temp = 35 °C (A, B)

through the decomposition of the complex as described in the selected mechanism for polymerization. Using $k_{21} k_1 / k_{\text{det}}$ and k_1 values, k_{21} / k_{det} value is calculated as 3.50.

References

- [1] Gopalan, A., Venuvanalingam, P., Manickam, S.P., Venkatarao, R. and Subbaratnam, N. R. (1982). *Eur. Polym. J.*, **18**, 531.
- [2] Gopalan, A., Sugantha Esther, C., Ananthanarayanan, L. and Venkatarao, K. (1992). *J. Polym. Material*, **9**, 137.

- [3] Paulrajan, S., Gopalan, A., Venkatarao, K. and Subbaratnam, N. R. (1983). *Polymer*, **24**, 906.
- [4] Gopalan, A., Paulrajan, S., Venkatarao, K. and Subbaratnam, N. R. (1985). *J. Polym. Sci. Polym. Chem.*, Ed. **23**, 1861.
- [5] Subbaratnam, N. R., Venkatarao, K., Manickam, S. P., Venuvanalingam, P. and Gopalan, A. (1986). *J. Macromol. Sci.-Chem.*, **A 23** (1), 117.
- [6] Misra, G. S. and Bhasilal, N. M. (1978). *Eur. Polym. J.*, **14**, 901.
- [7] Misra, G. S. and Bhasilal, N. M. (1978). *J. Macromol. Sci.-Chem.*, **A 12**, 1275.
- [8] Shukla, J. S., Tiwari, R. K. and Sharma, G. K. (1983). *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2665.
- [9] Hussain, M. M. and Misra, S. N. (1978). *Macromol. Chem.*, **179**, 295.
- [10] Misra, G. S. and Dubey, S. L. (1979). *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 1393.
- [11] Misra, G. S. and Dubey, S. L. (1979). *Colloid Polym. Sci.*, **257** (2), 156.
- [12] Seetharaman, S., Hariharan, S. S., Gopalan, A. and Subbaratnam, N. R. (1989). *Polym. Commun.*, **30**, 136.
- [13] Ratnasabapathy, S., Marisamy, N., Manickam, S. P., Venkatarao, K. and Subbaratnam, N. R. (1988). *J. Macromol. Sci. -Chem.*, **25**, 83.
- [14] Ratnasabapathy, S., Marisamy, N., Manickam, S. P., Venkatarao, K. and Subbaratnam, N. R. (1988). *J. Macromol. Sci. -Chem.*, **25**, 97.
- [15] Mino, G., Kaizerman, S. and Rasmussen, E. (1959). *J. Polym. Sci.*, **38**, 393.
- [16] Mercier, J. and Smets, G. (1963). *J. Polymer Sci.*, **A 1**, 1491.
- [17] Minoura, Y. and Mitoh, M. (1965). *J. Polymer Sci.*, **A 3**, 2149.
- [18] Gibbs, W. E. and Barton, J. M. (1967). *Vinyl Polymerization* (Ed. by George, E. Ham), Vol. 1, Marcel Dekker Inc., New York, (59).
- [19] Zeigler, K. and Holl, H. (1937). *Ann.*, **528**, 143.
- [20] Butler, G. B. and Angelo, R. (1957). *J. Am. Chem. Soc.*, **79**, 3128.

APPENDIX I

Derivation for rate of polymerization, R_p :

Applying steady state principle

$$-\frac{d[\text{TMA}^*]}{dt} = K_1 k_1 [\text{PDS}] [\text{TMA}] + 2k_2 [\text{TMA}^*] [\text{OH}^*] - 2k_3 [\text{M}] [\text{TMA}^*] - k_{t1} [\text{M}_2^*] [\text{TMA}^*] = 0 \quad (\text{E } 1)$$

$$-\frac{d[\text{OH}^*]}{dt} = K_1 k_1 [\text{PDS}] [\text{TMA}] + K_1 k_4 [\text{M}] [\text{PDS}] [\text{TMA}] + K_1 k_{\text{det}} [\text{M}_2^*] [\text{PDS}] [\text{TMA}] - 2k_2 [\text{TMA}^*] [\text{OH}^*] = 0 \quad (\text{E } 2)$$

Equating the rate of formation and disappearance of chain radical

$$\begin{aligned} \frac{d[M_2]}{dt} &= 2k_3[M][TMA\cdot] + K_1k_4[M][PDS][TMA] \\ &- K_1k_{\text{det}}[M_2][PDS][TMA] - k_{t1}[M_2][TMA\cdot] = 0 \end{aligned} \quad (\text{E } 3)$$

Adding (E 1) (E 2) and (E 3)

$$\begin{aligned} K_1k_1[PDS][TMA] + k_{t1}[M_2][TMA\cdot] \\ + K_1k_4[M][PDS][TMA] = 0 \end{aligned} \quad (\text{E } 4)$$

Adding (E 1) and (E 2)

$$\begin{aligned} 2K_1k_1[PDS][TMA] + K_1k_4[M][PDS][TMA] \\ + K_1k_{\text{det}}[M_2][PDS][TMA] - 2k_3[M][TMA\cdot] \\ - k_{t1}[M_2][TMA\cdot] = 0 \end{aligned} \quad (\text{E } 5)$$

Subtracting (E 3) from (E 5) and rearranging,

$$[TMA\cdot] = \frac{K_1[PDS][TMA](k_1 + k_{\text{det}}[M_2])}{2k_3[M]} \quad (\text{E } 6)$$

Substituting (E 6) in (E 4) we get,

$$k_1 + k_4[M] = k_{t1}[M_2] \left(\frac{k_1 + k_{\text{det}}[M_2]}{2k_3[M]} \right) \quad (\text{E } 7)$$

Under the conditions $k_1 \gg k_4[M]$, (E 7) becomes and on rearranging

$$k_{t1}k_{\text{det}}[M_2]^2 + k_1k_{t1}[M_2] - 2k_1k_3[M] = 0 \quad (\text{E } 8)$$

Taking positive root of the expression (E 8)

$$[M_2] = \frac{k_1}{2k_{\text{det}}} \left(1 + \frac{8k_3 k_{\text{det}} [M]}{k_1 k_{t1}} \right)^{1/2} \quad (\text{E 9})$$

and on binominal expansion under

$$\frac{8k_3 k_{\text{det}} [M]}{k_1 k_{t1}} \ll 1, \quad (\text{E 9}) \text{ becomes,}$$

$$[M_2] = \frac{k_1}{2k_{\text{det}}} \quad (\text{E 10})$$

$$\text{Knowing, } R_p = k_{21} [M_2] [M], \quad (\text{E 11})$$

$$R_p = \frac{k_{21} k_1 [M]}{2k_{\text{det}}} \quad (\text{or}) \quad R_p = \frac{k_{21} k_1 [M]^1 [PDS]^0 [TMA]^0}{2k_{\text{det}}} \quad (\text{E 12})$$

APPENDIX II

Derivation for rate of disappearance of peroxydisulphate, $-R_{\text{PDS}}$:

The total [PDS] can be given by $[PDS]_T = [PDS]_{\text{eq}} (1 + K_1 [TMA])$

$$\text{On rearranging } [PDS]_{\text{eq}} = \frac{[PDS]_T}{1 + K_1 [TMA]}$$

$$\begin{aligned} -R_{\text{PDS}} = -\frac{d[PDS]}{dt} &= 3/2 K_1 k_1 [PDS]_{\text{eq}} [TMA] \\ &+ K_1 k_4 [PDS]_{\text{eq}} [M] [TMA] \end{aligned} \quad (\text{E 13})$$

Substituting the value of $[PDS]_{\text{eq}}$ in (E 13)

$$-R_{\text{PDS}} = -\frac{d[PDS]}{dt}$$

$$= \frac{3/2 K_1 k_1 [\text{PDS}]_T [\text{TMA}] + K_1 k_4 [\text{PDS}]_T [\text{M}] [\text{TMA}]}{1 + K_1 [\text{TMA}]} \quad (\text{E } 14)$$

Under condition $1 \ll K_1 [\text{TMA}]$ and when the second term is neglected, the (E 14) is reduced to

$$-R_{\text{PDS}} = 3/2 k_1 [\text{PDS}]_T \quad (\text{or}) \quad 3/2 k_1 [\text{PDS}]_T [\text{M}]^0 [\text{TMA}]^0 \quad (\text{E } 15)$$