Polymerization of N,N'-methylenebis-acrylamide initiated by Ce^{IV}–thiourea redox system*

S. Paulrajan, A. Gopalan and N. R. Subbaratnam
Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India
and K. Venkatarao
Department of Physical Chemistry, University of Madras, A. c. College Campus, Madras 600 025, India
(Received 23 July 1982)

The kinetics of polymerization of the symmetrical non-conjugated divinyl monomer N,N'-methylenebisacrylamide has been studied using Ce^{IV}–thiourea redox system as initiator. The rate of polymerization, R_p is proportional to $[Ce^{IV}]^{1/2}$, $[thiourea]^{1/2}$ and $[monomer]^{3/2}$. A cyclopolymerization mechanism fits in with the experimental results.

INTRODUCTION

Monovinyl polymerizations involving initiation with ceric ion and organic substrates are well known[1-5]. The use of thiourea as a component of redox initiation with ceric ion has recently been attempted for monovinyl monomers[6,7]. We report here our findings on the kinetics of polymerization of a non-conjugated divinyl monomer, N,N'-methylenebisacrylamide with Ce^{IV}–thiourea redox initiating system. We are prompted to take up this work because of the significantly new results obtained by us on KMnO$_4$–H$_2$C$_2$O$_4$ redox initiation for this type of monomer[8]. Normally divinyl monomers give rise to cross-linked insoluble polymers, but occasionally they yield soluble, gel-free polymers also. For such cases Butler and Angley[9] have proposed a novel chain propagation mechanism known as 'cyclopolymerization'. Ce^{IV}–thiourea redox-initiated polymerization of the divinylmonomer is explained here through such a cyclopolymerization mechanism.

EXPERIMENTAL

N,N'-methylenebisacrylamide (Koch-Light) was recrystallized from acetone at 40°C.[8] Ceric ammonium sulphate (E. Merck) and thiourea (E. Merck) were used without further purification. Water, doubly distilled over alkaline permanganate and deionized, was used to prepare the reagents. The nitrogen gas used was purified by passing through Fieser solution.

Polymerization was carried out in a reaction tube of 100 ml capacity. An aliquot of 20 ml of the reaction mixture containing monomer, ceric ion and the neutral salt was de-aerated for 30 min. The polymerization was started by adding thiourea. The rate of monomer disappearance, R_p, was estimated at different time intervals by bromometry[10]. The reactions were carried out in low monomer concentrations and in 0.5 M sulphuric acid. Ionic strength and temperature were maintained as 2.0 M and 35°C respectively for most of the reactions.

At high conversions (>50%) the polymer was precipitated out by adding acetone to the reaction mixture and dried at 60°C for 2 h. The polymer was tested for residual unsaturation by bromometry[11].
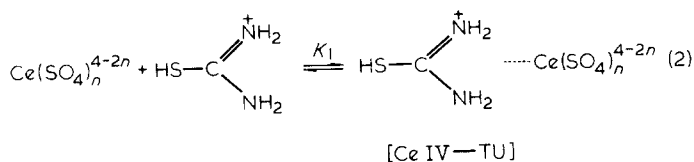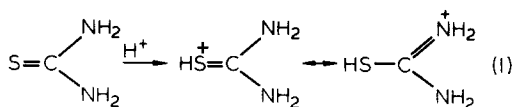
RESULTS AND DISCUSSION

Ceric ion by itself was not found to initiate polymerization during this study. The disappearance of the yellow colour after adding thiourea (TU) within a few seconds indicated the steady-state attainment of polymerization without an induction period.

The steady-state rate of polymerization, R_p, was found to depend on $[M]^{3/2}$ in the monomer concentration range $(8-80) \times 10^{-3}$ mol l^{-1} (*Figure 1*). Ceric ion concentration was varied in the range $(0.765-15.3) \times 10^{-4}$ mol l^{-1} and a plot of R_p vs. $[Ce^{IV}]^{1/2}$ (*Figure 1*) gave a straight line, indicating the dependence of R_p on $[Ce^{IV}]$ as 1/2. Thiourea showed a half-order dependence on R_p in the concentration range $(1.0-50.0) \times 10^{-4}$ mol l^{-1} (*Figure 1*).
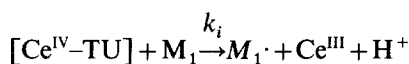
Experiments have also been done at higher concentrations of thiourea $(>50.0 \times 10^{-4}$ mol l^{-1}). R_p now falls drastically with increasing [TU] (*Table 1*). Temperature was varied from 30° to 50°C. The overall activation energy was ~ 11.3 kcal mol^{-1} in that range (*Figure 2*). Ionic strength and H$^+$ ion concentrations did not affect R_p.

The initiation and termination mechanisms would be the same for monovinyl and divinyl polymerization[12]. Non-conjugated divinyl monomers differ from the monovinyl one only in the propagation step. A novel chain propagation mechanism seems to be involved[9]. We propose here a kinetic scheme involving cyclopolymerization as the propagation step to derive the rate expression:
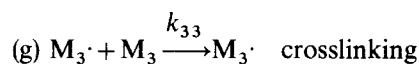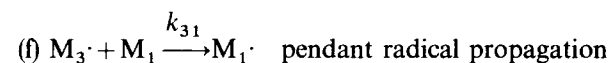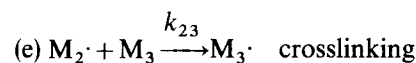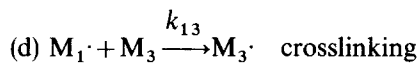
[Chemical scheme (I): protonation and rearrangement of thiourea]

$$S=C\diagup{NH_2}\diagdown{NH_2} \xrightarrow{H^+} HS\overset{+}{=}C\diagup{NH_2}\diagdown{NH_2} \rightleftharpoons HS-C\diagup{\overset{+}{N}H_2}\diagdown{NH_2} \quad (1)$$

$$Ce(SO_4)_n^{4-2n} + HS-C\diagup{\overset{+}{N}H_2}\diagdown{NH_2} \underset{K_1}{\rightleftharpoons} HS-C\diagup{\overset{+}{N}H_2}\diagdown{NH_2}\cdots Ce(SO_4)_n^{4-2n} \quad (2)$$

$$[Ce\ IV-TU]$$

(I) *Initiation*

$$[Ce^{IV}-TU]+M_1 \xrightarrow{k_i} M_1{}^{\cdot}+Ce^{III}+H^+$$

(II) *Propagation*

(a) $M_1{}^{\cdot} \xrightarrow{k_c} M_2{}^{\cdot}$ cyclization

(b) $M_1{}^{\cdot}+M_1 \xrightarrow{k_{11}} M_1{}^{\cdot}$ linear propagation

(c) $M_2{}^{\cdot}+M_1 \xrightarrow{k_{21}} M_1{}^{\cdot}$ propagation

(d) $M_1{}^{\cdot}+M_3 \xrightarrow{k_{13}} M_3{}^{\cdot}$ crosslinking

(e) $M_2{}^{\cdot}+M_3 \xrightarrow{k_{23}} M_3{}^{\cdot}$ crosslinking

(f) $M_3{}^{\cdot}+M_1 \xrightarrow{k_{31}} M_1{}^{\cdot}$ pendant radical propagation

(g) $M_3{}^{\cdot}+M_3 \xrightarrow{k_{33}} M_3{}^{\cdot}$ crosslinking

(III) *Termination*

$$M_2{}^{\cdot}+M_2{}^{\cdot} \xrightarrow{k_t} polymer$$
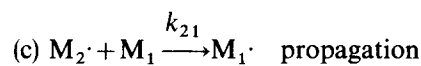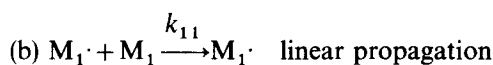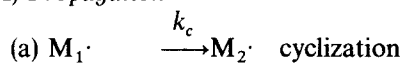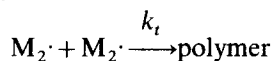
Here M_1 could be either of the double bonds of the previously unreacted symmetrical monomer. $M_1{}^{\cdot}$ is the radical produced when M_1 is attacked by a radical. $M_2{}^{\cdot}$ is the radical formed when $M_1{}^{\cdot}$ cyclizes. M_3 may be taken as a pendant double bond present in $M_1{}^{\cdot}$ with capability of acting as a new site for further radical attack. $M_3{}^{\cdot}$ may be taken as the radical produced when M_3 is attacked by another radical. The reactions under the categories of 'pendant double bond propagation' and 'crosslinking' take place when the pendant double bond M_3 reacts with radicals.

In the presence of acid, thiourea exists in the mono-protonated form[13] (step (1)). Various ceric species like $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ are reported to be active in sulphuric acid medium[14]. Agarwal and Kapoor[15], and also King and Pandov[16], concluded that the complexes having more sulphato groups are less reactive towards organic substrates. Complex formation as a precursor to electron transfer has been suggested by Krishna and Tewari[17]. Thiourea being in protonated form disfavours the approach of positively charged ceric species. Neutral and negatively charged ceric species can however form a 1:1 adduct, the state at which electron transfer is much more facilitated (step (2)).

We propose here the interaction between ceric–thiourea adduct and monomer as the initiation step (I).

During the interaction a thiocarbamido free radical is transferred onto the monomer which gets converted to $M_1{}^{\cdot}$. This is in agreement with experimentally observed order-3/2 dependence of R_p on monomer concentration (*Figure 1*).

Now there can be two competing pathways for propagation: (i) intramolecular cyclization where $M_1{}^{\cdot}$ cyclizes to give $M_2{}^{\cdot}$ as in II(a) and (ii) intermolecular propagation where $M_1{}^{\cdot}$ reacts with another monomer unit M_1 giving $M_1{}^{\cdot}$ radical with pendant double bonds M_3 as in II(b):

The ease of intramolecular cyclization depends on the monomer structure and on the stability of the ring formed during cyclization. The monomer in the present study being a symmetrical non-conjugated diolefin, both the double bonds have the same reactivity. Formation of a
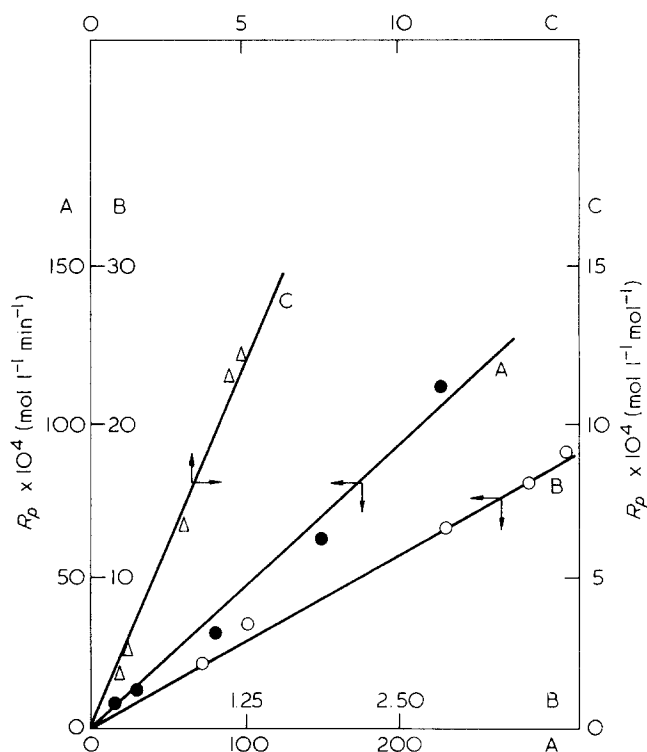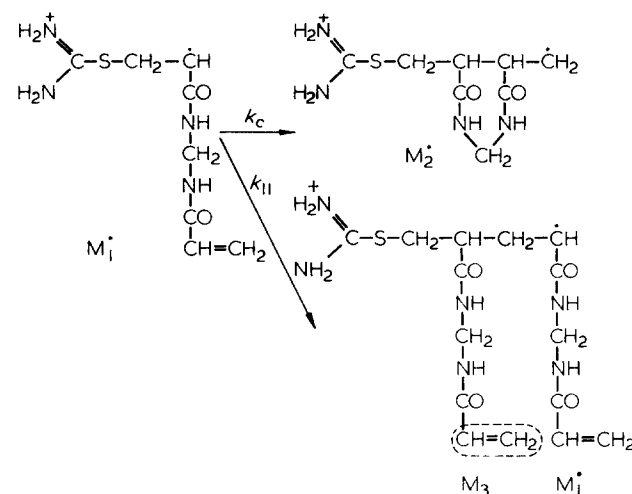
[Chemical scheme for $M_1{}^{\cdot}$, $M_2{}^{\cdot}$ and M_3 showing the cyclization (k_c) and linear propagation (k_{11}) pathways]

[Graph: Dependences of R_p with three sets of axes labelled A, B, C. Vertical axes labelled $R_p \times 10^4$ (mol l^{-1} min^{-1}) on left and $R_p \times 10^4$ (mol l^{-1} mol^{-1}) on right. Curves labelled A, B, C.]

Figure 1   Dependences of R_p: on A[M]$^{3/2}$, ●, [Ce^{IV}]=3.83×10^{-4} mol l^{-1}, [TU]=2.0×10^{-3} mol l^{-1}; B[Ce^{IV}]$^{1/2}$, ○, [M]=2.0 ×10^{-2} mol l^{-1}, [TU]=2.0×10^{-3} mol l^{-1}; and on C [TU]$^{1/2}$, ▲, [M]=2.0×10^{-2} mol l^{-1}, [Ce^{IV}]=3.83×10^{-4} mol l^{-1}, μ=2.0 mol l^{-1}, t=35°C, [H$^+$]=0.5 mol l^{-1}

Table 1 Effect of higher [TU] (>0.005 mol l^{-1}) on R_p for the polymerization of *N,N'*-methylenebisacrylamide ([M] = 2.0 x 10^{-2} mol l^{-1}; [Ce^{IV}] = 3.83 x 10^{-4} mol l^{-1}; t = 35°C; μ = 2.0 mol l^{-1}; [H$^+$] = 0.5 mol l^{-1})

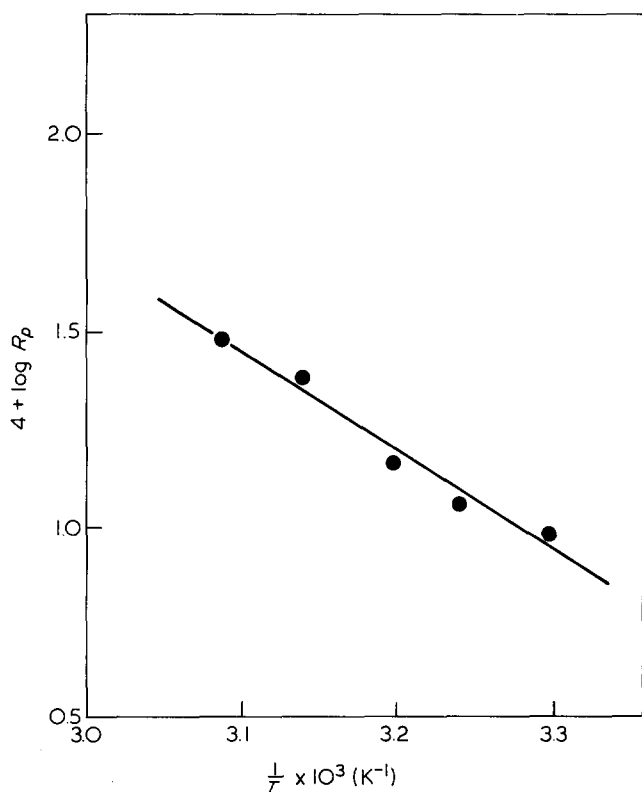| [TU] x 10^4 (mol l^{-1})	R_p x 10^4 (mol l^{-1} min^{-1})
75	12.80
100	11.80
200	7.73
400	4.91
500	2.72

Figure 2 Plot of log R_p versus $1/T$ for the polymerization of *N,N'*-methylenebisacrylamide. [M] = 2.0 x 10^{-2} mol l^{-1}, [Ce^{IV}] = 3.83 x 10^{-4} mol l^{-1}, [TU] = 2.0 x 10^{-3} mol l^{-1}, μ = 2.0 mol l^{-1}, [H$^+$] = 0.5 mol l^{-1}

seven-membered ring during cyclization has been suggested recently for this monomer[8]. Formation of normally stable five- or six-membered ring during cyclization of monomer unit is well known[18]. For monomers that can form seven- or higher membered rings on cyclization the number of cyclized units in the polymer chain was found to be low. An observation by Zeigler and Holl[19] revealed, however, that the substitution of carbonyl or oxygen for a methylene group reduces the strain by decreasing the number of interfering hydrogens. In the present case, the ring formed is seven-membered containing two carbonyl groups and thereby contributing to lowering of strain. The probability of cyclization is therefore enhanced.

The monovinyl type linear propagation II(b) would be a sterically hindered step because of the long pendant group which provides a shielding effect for the approach of another monomer molecule to M$_1$·. When the polymer formed was actually tested for the presence of pendant double bonds by bromometry[11], no double bond was found. Therefore step II(a) is preferred to step II(b). All reactions involving M$_3$ and M$_3$· arise only if reaction in step II(b) takes place. In view of the low probability of step II(b), such reactions can be ruled out.

The polymer chain grows by the propagation reaction II(c). Here M$_2$· (the cyclized radical) reacts with M$_1$. This can take place at a fairly fast rate because there is no steric hindrance in the cyclized radical for the approach of another monomer as it does not contain any pendant group. From the above considerations, the propagation step for this polymerization can be envisaged as follows. After intramolecular cyclization an intermolecular propagation follows where the cyclized radical reacts with another monomer molecule and the sequence repeats itself.

For a symmetrical non-conjugated diolefin when cyclization is the preferred path, termination would be predominantly by the mutual interaction of M$_2$· radicals[20]. Taking this mutual termination as the final step along with the initiation and propagation mechanisms suggested now, a rate expression is derived under steady state:

$$R_p = -\frac{d[M_1]}{dt} = 2k_{21}\left(\frac{k_iK_1}{k_t}\right)^{1/2}[M]^{3/2}[Ce^{IV}]^{-3/2}[TU]^{1/2}$$

In the above expression the experimentally observed dependences [monomer$^{3/2}$, [Ce^{IV}]$^{1/2}$ and [thiourea]$^{1/2}$ are accounted for. The overall rate constant $k_{21}(k_iK_1/k_t)^{1/2}$ is calculated to be 77 mol$^{3/2}$ l$^{3/2}$ s^{-1}.

The decrease in R_p with increase in thiourea at high concentrations (*Table 1*) may be explained in a manner analogous to the one reported for monovinyl polymerization[21]. Thiourea molecule as such enters in the propagation step at high concentration giving a radical incapable of adding further monomer units. This leads to the reduced polymerization rate.

ACKNOWLEDGEMENT

REFERENCES

1 Katai, A., Kulshereshta, V. K. and Marchessault, R. H. *J. Polym. Sci. C* 1963, **2**, 403
2 Subramanian, S. V. and Santappa, M. *J. Polym. Sci. A1* 1968, **6**, 493
3 Lalitha, J. and Santappa, M. *Vignana Parished Ansandhan Patrika* 1961, **4**, 139
4 Sahar, S. K. and Chaudhri, A. K. *J. Ind. Chem. Soc.* 1965, **42**, 735
5 Mohanty, N., Pradhan, P. and Kanhetra, M. C. *Eur. Polym. J.* 1980, **16**, 451
6 Pramanick, D. and Chatterjii, A. K. *Eur. Polym. J.* 1980, **16**, 451
7 Pramanick, D. and Chatterjii, A. K. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 311
8 Gopalan, A., Venuvanalingam, P., Manickam, S. P., Venkatarao, K. and Subbaratnam, N. R. *Eur. Polym. J.* 1982, **18**, 531
9 Butler, G. B. and Ingley, F. L. *J. Am. Chem. Soc.* 1951, **73**, 894
10 Mino, G., Kaizerman, S. and Rassmussen, E. R. *J. Polym. Sci.* 1959, **58**, 343
11 Holt, T. and Simpson, W. *Proc. R. Soc. (London) A* 1956, **238**, 154
12 Gibbs, W. E. *J. Polym. Sci. A* 1964, **2**, 4815
13 Rout, A., Rout, S. P., Singh, B. C. and Santappa, M. *Eur. Polym. J.* 1977, **13**, 497
14 Hardwick, T. J. and Robertson, E. *Can. J. Chem.* 1951, **29**, 828
15 Agarwal, O. P. and Kapoor, R. C. *J. Pract. Chem.* 1963, **20**, 81
16 King, E. L. and Pandov, M. L. *J. Am. Chem. Soc.* 1963, **75**, 3063
17 Krishna, B. and Tewari, K. C. *J. Chem. Soc.* 1961, **1**, 3097
18 Gibbs, W. I. and Barton, J. A. in 'Vinyl Polymerisation', Vol. 1 (Ed. G. E. Hame), Marcel Dekker, New York, 1967, p. 59
19 Zeigler, K. and Holl, H. *Ann.* 1957, **528**, 143
20 Butler, G. B. and Angleo, R. *J. Am. Chem. Soc.* 1957, **79**, 3128
21 Pramanick, D. and Chatterjii, A. K. *Eur. Polym. J.* 1980, **16**, 875