

2. Bossolasco, M. and Elena, A., *Geofis. Pure Appl.*, 1960, 46, 167.
3. Skinner, N. J. and Wright, R. W., *J. Atmos. Terr. Phys.*, 1964, 26, 122.
4. Kotadia, K. M. and Patel, B. M., *Ibid.*, 1969; 31, 621.
5. Chakravarthy, S. C. and Rastogi, R. G., *Ind. J. Radio Space Phys.*, 1972, 1, 158.
6. Ganguly, S., *J. Atmos. Terr. Phys.*, 1975, 37, 177.
7. Chapman, S. and Bartels, J., *Geomagnetism*, Clarendon Press, Oxford, 1940.
8. Chakravarthy, S. C. and Rastogi, R. G., *Nature* 1969, 223, 939.
9. Rao, A. S. M.; *Ph.D. Thesis*, Andhra University, Waltair, 1967.
10. Chakravarthy, S. C. and Rastogi, R. G., *J. Atmos. Terr. Phys.*, 1970, 32, 945.
11. Chapman, S. and Westfold; *Ibid.*, 1956, 8, 1.
12. Rastogi, R. G., *Ibid.*, 1969, 31, 759.
13. Shrestha, K. L., *Ibid.*, 1971, 33; 213.
14. Rush, C. M., John, D. E. and Venkateswaran, S. V., *Radio Sci.*, 1970, 5; 1413.
15. Gnanalingam, S., *Proc. of 3rd International Symposium on Equatorial Aeronomy*, Vol. I, Physical Research Laboratory, Ahmedabad, 1969, p. 47.

#### A NEW INITIATING SYSTEM FOR THE VINYL POLYMERIZATION

THE initiation of vinyl polymerization in aqueous medium by redox catalysts has been the subject of extensive investigations and the mechanisms of several oxidation-reduction processes in solution involving electron transfer and leading to the formation of free radicals have been elucidated<sup>1</sup>. Redox systems comprising an oxidisable substrate and molecular oxygen<sup>2, 3</sup>, however, have not received much attention. Ascorbic acid has been used as reducing agent with several oxidants, *viz.*, H<sub>2</sub>O<sub>2</sub><sup>4</sup>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub><sup>5, 6</sup>, KMnO<sub>4</sub><sup>7</sup>, etc., to produce free radicals capable of initiating vinyl polymerization in aqueous media. Taqui Khan *et al.*<sup>8</sup>, in their study on the kinetics of the copper(II) ion catalysed oxidation of ascorbic acid (AA) by molecular oxygen, have observed the production of free radicals from the metal ascorbate oxygen complex. It is the aim of the present investigation to study the kinetics of the polymerization of vinyl monomers using AA-Cu(II) in the presence of molecular oxygen.

Methyl methacrylate (MMA) (Rohm and Haas) was freed from inhibitor with alkali, washed, dried over anhydrous sodium sulfate, distilled under reduced pressure and stored at 5°C. Ascorbic acid and copper sulfate were Analar grades and used without further purification. 2, 4-Dinitrophenyl hydrazine, thiourea and sulfuric acid were all BDH Analar grade samples. Water distilled thrice in an all-glass quick fit set-up was used for the polymerization reactions, and for solution preparations. Owing to its high oxidizing

nature to the atmospheric oxygen, freshly prepared ascorbic acid solutions were used for all polymerization reactions.

Polymerization reactions were conducted at 40° ± 0.1°C, in pyrex glass reaction tubes with inlet and outlet arrangements. The concentration regions used in our study being, [Monomer] = 3.76–11.28 × 10<sup>-2</sup> M; [Cu(II)] = 0.8–20.0 × 10<sup>-5</sup> M; [AA] = 1.0–10.0 × 10<sup>-3</sup> M; [O<sub>2</sub>] = from zero partial pressure of oxygen to 100%. The O<sub>2</sub> concentration was varied by mixing with varying amounts of nitrogen. Polymerization did not occur with AA and oxygen, alone. Only in the presence of Cu(II) polymerization took place. In the presence of nitrogen (zero partial pressure of oxygen) negligible amount of polymer was formed, which may be due to the impurity in the nitrogen. Water and copper sulfate solution were taken in the reaction tube, and a stream of oxygen was passed through the solution for a specific period. The monomer was then added, followed by the AA solution, and immediately the oxygen supply was stopped. The polymerization was started with negligible induction period. Cooling in freezing mixture was adopted to arrest the reaction. Steady state rates were obtained within ten minutes with the conversion of monomer below 30%.

The rate of polymerization R<sub>p</sub>, (-d[M]/dt) was evaluated gravimetrically. The filtrate was used for the determination of AA disappearance (-d[AA]/dt) spectrophotometrically. Estimation of the dehydroascorbic acid was carried out as reported in the literature<sup>9</sup>. The values of chain length, *n*, were obtained by measuring the viscosity of solutions of poly (methyl methacrylate) PMMA in benzene at 25 ± 0.01°C and using the following relationship between the intrinsic viscosity [η] and the chain length *n*, given by Baxendale *et al.*<sup>10</sup> for PMMA

$$n = 2.81 \times 10^3 [\eta]^{1.32}$$

The influence of Cu(II) ion on the rate of polymerization was very interesting. In the lower concentration range, *i.e.*, below 3.0 × 10<sup>-5</sup> M the R<sub>p</sub> was increasing with increase in [Cu(II)]. The order with respect to Cu(II) in the range 0.8–2.4 × 10<sup>-5</sup> M was 0.5. In the higher concentration range of Cu(II) *i.e.*, above 6.0 × 10<sup>-5</sup> M, the rate of polymerization decreased with the increase in [Cu(II)]. Similar observation with respect to other metal ions<sup>11–13</sup> has been reported.

In the present investigation rate of polymerization was found to be proportional to [M]<sup>3/2</sup> at lower [Cu(II)] range, while it was proportional to [M]<sup>2</sup> at higher [Cu(II)]. The R<sub>p</sub> was found to be independent of ascorbic acid concentration above 1.1 × 10<sup>-3</sup> M. Similar observations have been reported by earlier workers<sup>5–7</sup>. Molecular oxygen increased the rate linearly.

Rise in temperature increased the rate, while increase in  $[H^+]$  decreased the rate of polymerization.

The rate of ascorbic acid disappearance was found to be independent of  $[M]$ , while it increased with increase in  $[Cu(II)]$ ,  $[AA]$  and  $[O_2]$ .

Direct dependence of chain length on  $[M]$  and inverse dependence on  $[Cu(II)]$  and  $[O_2]$  were observed. 'n' values were found to be unaffected by  $[AA]$ .

These observations may be accounted by the following tentative scheme for the polymerization of methyl methacrylate. The  $HO_2^{\cdot}$  and ascorbate anion radicals produced by the decomposition of the metal ascorbate oxygen complex may initiate the polymerization. The termination of the growing chains is by mutual combination at lower  $[Cu(II)]$  and by linear termination by  $Cu(II)$  ions at higher  $[Cu(II)]$ . Termination of the vinyl monomers by metal ions has been very well established<sup>3, 12-18</sup> both in aqueous and non-aqueous media. These two different modes of termination may result in the transient orders with respect to monomer at two different  $Cu(II)$  concentration ranges. The overall rate of polymerization may be expressed by the following relationships:

$$R_p \propto [M]^{3/2} [Cu^{2+}]^{0.5} [O_2] [AA]^0$$

at lower copper concentration range.

$$R_p \propto [M]^2 [O_2] [AA]^0 / [Cu^{2+}]$$

at higher copper concentration range

The rate of AA disappearance

$$-d[AA]/dt \propto [Cu^{2+}] [O_2] [AA]$$

and chain length 'n'

$$n \propto [M] / [O_2] [Cu^{2+}]$$

Further details with reaction mechanism will be published elsewhere. Studies with other metal ions are being carried out to arrive at the efficiency of these initiating systems.

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1. Uri, N., *Chem. Revs.*, 1952, 50, 375.
2. Sully, B. D., *J. Chem. Soc.*, 1950, Part II, 1498.
3. Menon, C. C. and Kapur, S. L., *J. Polym. Sci.*, 1951, 54, 45.
4. Kureha Chemical Works Ltd., Brit. Pat. 895, 1962, p. 153.
5. Csuros, Z., Gara, M. and Czurkovic, I., *Acta Chim. Acta Sci. Hung.*, 1961, 29, 207.
6. Mishra, G. S. and Gupta, C. V., *Makromol. Chem.*, 1973, 165, 205.

7. Shukla, J. S. and Misra, D. C., *J. Polym. Sci.*, 1973, 11, 751.
8. Taqui Khan, M. M. and Mortell, A. E., *J. Am. Chem. Soc.*, 1967, 89, 4176.
9. Roe, J. H., *Methods of Biochemical Analysis*, Vol. 1, Interscience Publishers Inc., New York, N.Y., 1954, pp. 115.
10. Baxendale, J. H., Bywater, S. and Evans, M. G. *J. Polym. Sci.*, 1946, 1, 237.
11. Anuradha Rout, Swoyam P. Rout, Baishnab, C. Singh and Santappa, M., *Makromol. Chem.*, 1977, 178, 639.
12. Jijie, K., Santappa, M. and Mahadevan, V., *J. Polym. Sci.*, 1966, 4, 393.
13. Viswanathan, S. and Santappa, M., *Ibid.*, 1971, 9, 1685.
14. Dainton, F. S. and Seaman, P. H., *Ibid.*, 1959, 39, 279.
15. Watanabe, M. and Kiuchi, H., *Ibid.*, 1962, 58, 103.
16. Anantanarayanan, V. S. and Santappa, M., *Indian J. Chem.*, 1964, 2, 330.
17. Bamford, C. H., Jenkins, A. D. and Johnston, R., *Nature*, 1956, 177, 992.
18. Succubai, S., and Santappa, M., *J. Polym. Sci.*, 1969, 7, 643.

#### PHYTOCHEMICAL STUDIES ON CASSIA SIAMEA LEAVES

IN view of the popular use of *Cassia siamea* leaves to cure skin diseases and to reduce swellings<sup>1</sup> a detailed chemical examination was taken up. There was only one report of chemical investigation of *Cassia siamea* leaves in which Hussaniali-Walji *et al.*<sup>2</sup> reported only barakol, a novel dioxaphenylene derivative.

The powdered leaves were completely extracted with alcohol and the total alcoholic extract was concentrated to a small bulk and fractionated with petroleum ether, ether and ethyl acetate.

The petroleum ether extract was saponified and chromatographed over alumina when two crystalline substances were obtained. Of the two, one was wax m.p. 84-86°. The second crystalline component was obtained as shining plates from acetone m.p. 139°,  $[\alpha]_D^{20} - 35.7$  C<sub>29</sub>H<sub>50</sub>O; acetate, m.p. 126° ( $\alpha$ )<sub>D</sub><sup>20</sup> - 40.7° C<sub>31</sub>H<sub>52</sub>O<sub>2</sub>. The identity of the compound was established by m.m.p. and TLC comparison and identical I.R. spectra with authentic  $\beta$ -sitosterol.

The residue from the ether extract gave positive colour reactions for flavonoids. This residue was macerated with 5% dilute hydrochloric acid. The acid solution was neutralised and the residue was extracted with chloroform and crystallised from methanol when lemon yellow refracting needles were obtained, m.p. 165°; C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>. Survey of literature indicated this compound could be barakol and hence the derivatives reported for barakol were attempted.