POLYMERIZATION OF VINYL MONOMERS

I. Dye-Reducing Agent Photosensitizing Systems

By M. Santappa, F.A.Sc. and A. I. Md. Sheriff

(*Department of Physical Chemistry, University of Madras, Madras-25*)

Abstract

A systematic study of the kinetics of photosensitized polymerization of vinyl monomers with the system Dye (erythrosin or acriflavine)-reducing agent (ascorbic acid), in the presence of oxygen and under buffered conditions (pH 6) in aqueous solution has been made. The determinations of the monomer disappearance, dye disappearance and of chainlengths of the polymers obtained against the different variables like light intensity, concentrations of monomer, dye, ascorbic acid, etc., have been made. A kinetic mechanism proposed for the overall reaction is discussed in the light of the experimental results and certain rate constants have also been evaluated.

I. Introduction

Oster[1] has reported that vinyl monomers can be photopolymerised using dye-reducing agent as a sensitizing system. Halogenated derivatives of fluorescein, acriflavine, riboflavine, etc., have been employed in combination with a mild reducing agent, such as ascorbic acid, thiourea, phenyl hydrazine hydrochloride, etc. It has been reported that the reduced form of the dye reacts with atmospheric oxygen to produce semiquinone form of the dye and hydroxyl radicals and the latter initiate the polymerization of vinyl monomers. Dye-sensitized polymerization of vinyl monomers in aqueous and non-aqueous solutions has been the subject of investigation for the past over a decade in U.S.A.,[7,8] Japan[2-6] and Belgium.[9-11] Divergent opinions have been expressed with regard to the nature of initiation of polymerization, the necessity or otherwise of oxygen, reducing agent, etc.[1-10] Some maintain that oxygen is not of primary importance in these systems for polymerization to occur[2,6,8] while others have emphasized the necessity for the optimum concentration of oxygen.[1,7,9,10] Among various methods of initiation

56

suggested, the following three types appear to be important: (i) direct energy transference between the excited dye and monomer,[12] (ii) production of radicals as a result of interaction of excited dye molecule and monomer,[2, 6, 7] (iii) production of radicals by the self-decomposition of the dye[5] or by the interaction of the dye with a third substance like oxygen, OH or the reducing agent.[1, 2(a), 8-10, 17] In the present work, a systematic study of the kinetics of vinyl polymerization, photosensitized by dye-reducing agent systems, has been made to get a clearer insight into various aspects on which discordant notes have been struck by various workers. Erythrosin and acriflavine have been used as dyes. Ascorbic acid has been used as a reducing agent. Methyl methacrylate has been employed as the vinyl monomer. Wavelengths in the region 400–550 mμ have been used for the excitation of the dyes. The polymerization has been conducted at 35° C.

II. EXPERIMENTAL

(a) Optional Arrangement

A high pressure mercury vapour lamp (250 Watt bulb type supplied by Pradip Lamp Works, Patna) with the necessary choke has been used as the light source. Wavelengths in the range 400–550 mμ have been isolated by suitable filter solution combinations[13] interposed between the light source and the reaction cell. The reaction cell is a cylindrical vessel (diameter 5·0 cm. and 4·6 cm. long with a capacity of about 80 c.c.) with both sides closed with pyrex glass plates and fitted on the top with two B-14 cones. The light from the source is collimated by a quartz condenser lens, passed through desired filter solutions and then allowed to fall on the reaction cell mounted inside a metal thermostat. The light intensity of the mercury vapour lamp is varied with a diaphragm.

(b) Reagents

All the reagents used in the preparation of solutions are either A.R.B.D.H. or G.R.E. Merck reagent grades. The dyes, supplied by B.D.H. and Magenta Chemicals, have been purified by recrystallization from ethanol. Water, doubly distilled over alkaline permanganate in an all-glass pyrex set-up and passed through a column of ' Biodeminrolit ' resin has been used in our experiments. The monomer methyl methacrylate, kindly supplied by Rhom and Haas, Philadelphia, U.S.A., has been purified chemically to remove the inhibitor and other basic impurities and then distilled thrice under reduced pressure in an atmosphere of nitrogen.

A5

(c) *Estimations*

The course of the reaction has been followed by determining the rate of monomer disappearance by the weight of the polymer produced. The rate of dye disappearance has been followed spectrophotometrically by taking advantage of the maximum absorption and obedience to Beer's law by both dyes (for erythrosin $\lambda_{max.}$ is at 537 mμ and for acriflavine $\lambda_{max.}$ is at 456 mμ.). The absorption measurements have been made in the Hilger-Watts U.V. Spectrophotometer H-700 type. The chainlengths of the polymers are determined viscometrically by using the equation due to Baxendale, Bywater and Evans[16]

$$n = 2 \cdot 81 \times 10^3 \, [\eta]^{1 \cdot 32}$$

at 25° C. for polymethylmethacrylate in benzene. The polymers are purified by reprecipitation with suitable solvents and the viscosity measurements of polymer solutions in benzene are made in a PCL Ubbelohde type viscometer in a thermostat at 25° C. The light intensity has been determined by using potassium ferri-oxalate as the chemical actinometer.[14]
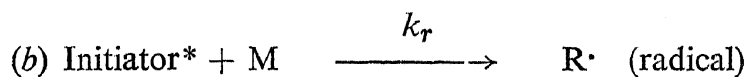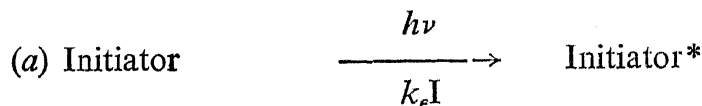
A typical experiment with details of procedure for various measurements is briefly described:

The system dye-reducing agent-vinyl monomer in aqueous solution buffered at pH = 6 (with phosphate buffer) is taken in the reaction cell which is mounted inside a thermostat (35° C.). The cell is then irradiated with the suitable monochromatic radiation when initiation of polymerization without induction period is observed. After irradiation of the system for about 30–45 minutes the reaction cell is taken out of the thermostat and the precipitated polymer is filtered off, dried at 60° C. and then rate of monomer disappearance is computed. The filtrate has been used for determining the rate of dye disappearance. Some of the experiments have been carried out under deaerated conditions for comparison. It is observed that the rate of polymerization has been found to be enhanced in the undeaerated systems when compared to the rate of polymerization obtained in the deaerated systems. Similar view has been expressed by Ai Watanabe[2(a)] in the study of photopolymerization of acrylonitrile sensitized by acriflavine-stannous chloride system. The deaeration of the reaction mixture has been done by passing oxygen-free nitrogen (Fieser's solution[15]) through the system before irradiation.
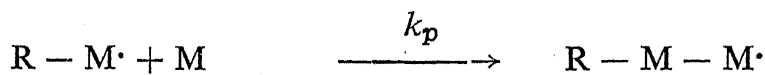
III. Kinetic Scheme

A *prima facie* kinetic scheme consists of the following steps:—

1. *Initiation*:

   (a) Initiator $\xrightarrow[k_e I]{h\nu}$ Initiator*

   (b) Initiator* + M $\xrightarrow{k_r}$ R· (radical)

   (c) R· + M $\xrightarrow{k_i}$ R — M·.

2. *Propagation*:

   R — M· + M $\xrightarrow{k_p}$ R — M — M·

   R — M — M· + M $\xrightarrow{k_p}$ R — M$_3$·

   .... etc.

   .... etc.

3. *Termination*:

   R — M$_n$· + ·M$_m$ — R $\xrightarrow{k_t}$ R — (M)$_{n+m}$—R

4. *Deactivation*:

   R· $\xrightarrow{k_d}$ S.

The 'Initiator' is assumed to be a transient complex comprising, dye-monomer-reducing agent as a 'cluster' and a photosensitizing agent. It can be easily shown that the light absorption fraction by the cluster, $k_{\epsilon(cluster)}$ is related to light absorption fraction by the entire system, $k_{\epsilon(total)}$:

$$k_{\epsilon(cluster)} = k_{\epsilon(total)} \left[\frac{K\,[AA]\,[M]}{1 + K\,[AA]\,[M]} \right]$$

$$= k_{\epsilon(total)}\,K\,[AA]\,[M]$$

if it is assumed that $k_{\epsilon(cluster)}$ is equal to $k_{\epsilon(dye)}$ and the equilibrium,

Dye + M + AA $\underset{}{\overset{K}{\rightleftharpoons}}$ Cluster to be present. $K\,[AA]\,[M] \ll 1$ under our experimental conditions. [AA] = Ascorbic acid; [M] = monomer.

A6

IV. RESULTS AND DISCUSSION

(a) Rate of Monomer Disappearance

Making the usual assumptions for stationary state kinetics for micro- and macro-radicals and also constancy of k_p and k_t with chain growth it is easy to deduce the expression for rate of monomer disappearance:

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{\frac{1}{2}}} [M]^2 \left[\frac{k_i k_{\epsilon(total)} K [AA] I}{k_d}\right]^{\frac{1}{2}}$$

provided $k_i [M] \ll k_d$. It has been experimentally observed with both erythrosin and acriflavine dye systems that the rates are proportional to (i) second power of monomer concentration (Fig. 1, Plots A, B, C); (ii) square root of ascorbic acid concentration (Fig. 2, Plot A) and square root of the incident light intenisty (Fig. 3, Plots A, B). From the slopes of all these plots

$$\frac{k_p}{k_t^{\frac{1}{2}}} \left[\frac{k_i k_{\epsilon(total)} K}{k_d}\right]^{\frac{1}{2}}$$

may be obtained for both the dye systems. The dependence of rate on the second power of the monomer concentration may be attributed to participation of monomer in the formation of initiator with low initiator's efficiency. The high molecular weights of the polymers formed support such conclusions. Similar observations have been made by Delzenne, DeWinter, Toppet and Smets[10] and G. K. Oster, G. Oster, and G. Prati[7] who have made use of the systems, eosin-thiourea-acrylamide and riboflavine-acrylamide respectively. The dependence of rate on ascorbic acid concentration appears to be critical. For concentrations of ascorbic acid $> 1\cdot4 \times 10^{-2}$ M the rates have been found to become constant. A similar behaviour of the reducing agent has been reported by Koizumi and Watanabe[2(a)] in their study on the polymerization of acrylonitrile sensitized by acriflavine-stannous chloride system. Delzenne *et al.*[10] and Gozo Takayama[4] (photopolymerization of vinyl acetate in methanol sensitized by acriflavine-ascorbic acid system) have reported actual decrease in the rate for concentrations of ascorbic acid $> 1\cdot35 \times 10^{-3}$ M. We have as yet no convincing explanation as to why ascorbic acid at higher concentrations brings in the phenomenon of constancy or even lowering in the rates. The square root dependence of rate on ascorbic acid concentration and incident light intensity clearly shows that the termination is mutual type. In our systems, we find both reducing agent and an optimum concentration of oxygen are necessary for polymerization to occur.
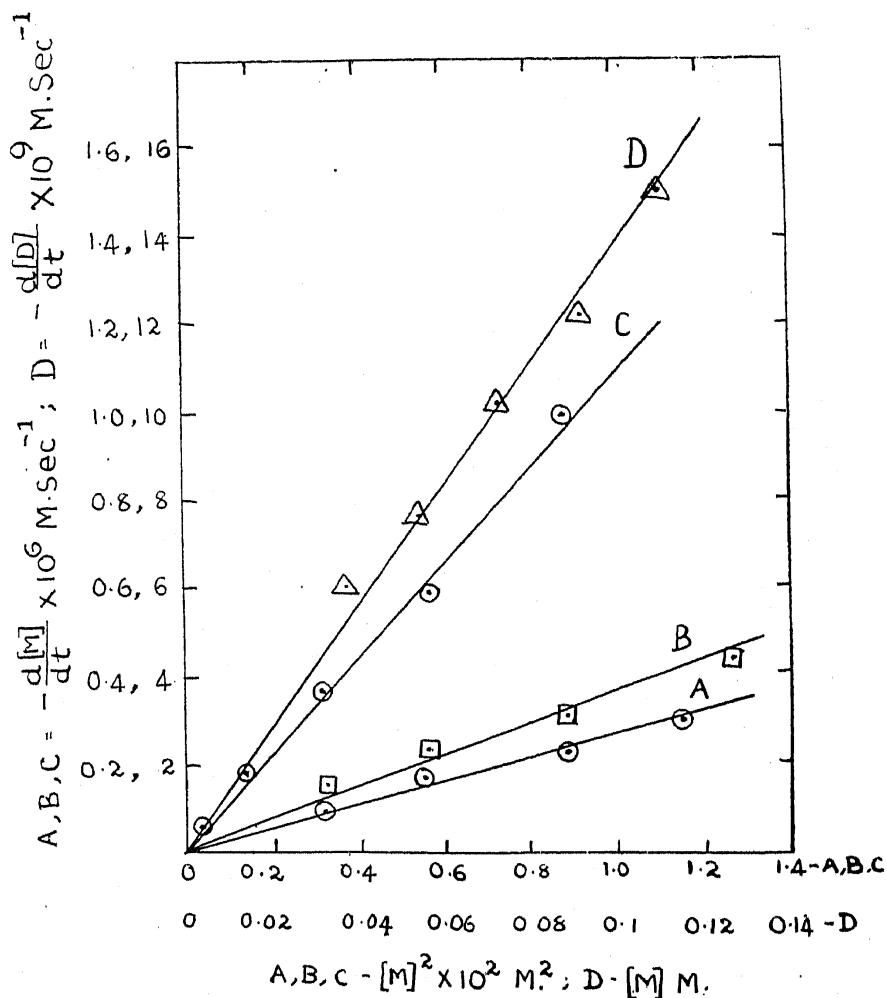
FIG. 1. Plots of rates of monomer disappearance and dye disappearance *versus* square of the monomer concentrations and first power of the monomer concentrations respectively, Monomer: Methyl methacrylate. Temp.: $35°$ C. $\lambda = 435\,m\mu$. (A, D), Acriflavine-ascorbic acid system; (B, C) Erythrosin-ascorbic acid system.

(*b*) *Rate of Dye Disappearance*

The expression for the rate of dye disappearance:

$$-\frac{d\,[D]}{dt} = k_{\epsilon(total)}\,K\,[AA]\,[M]\,I$$

may be derived. The rate of dye disappearance has been observed to be proportional to first powers of (i) ascorbic acid concentration (Fig. 2, Plots B, C), (ii) light intensity (Fig. 3, Plots C, D), (iii) monomer concentration (Fig. 1, Plot D), and (iv) light absorption fraction (total) for both the dye systems. Our observations with regard to dye fading are in accord with those

observed by others. Shepp, Chaberek and Mac Neil,[8] in their study on the thionine sensitized polymerization of acrylamide, have reported that the rate of dye fading is directly proportional to the light intensity and the reciprocal of the rate of dye fading is proportional to the reciprocal of the monomer concentration. Toppet $et\ al.$[11] have reported in their study on the polymerization of acrylamide sensitized by eosin that the rate of photoreduction of the dye is directly proportional to the monomer concentration and light intensity. From the slopes of plots (Figs. 1–3) the equilibrium constant, $K = 4 \cdot 824 \times 10^{-3}$ for erythrosin cluster and $4 \cdot 737 \times 10^{-3}$ for acriflavine cluster have been computed.
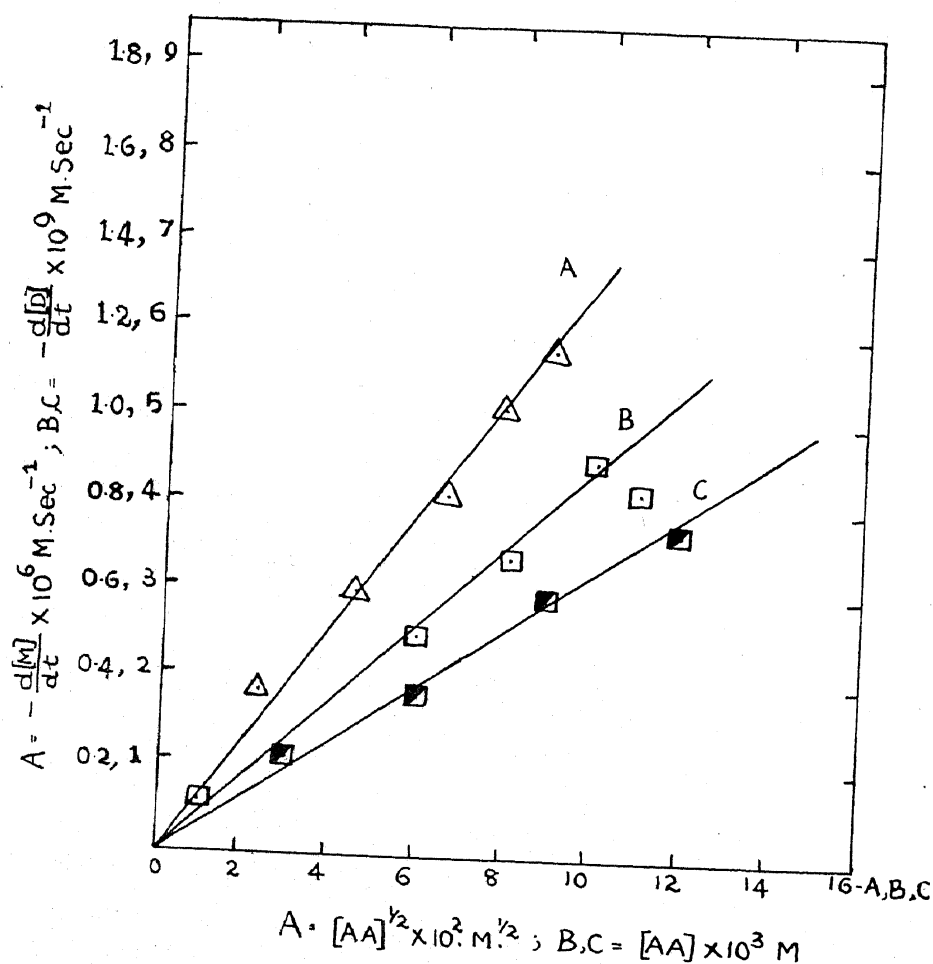

FIG. 2. Plots of rates of monomer disappearance and dye disappearance $versus$ square root of ascorbic acid concentrations and first power of ascorbic acid concentrations respectively. Temp.: 35° C. $\lambda = 435\ m\mu$. (A, B), Acriflavine-ascorbic acid system; (C), Erythrosin-ascorbic acid system. Monomer: Methyl methacrylate.
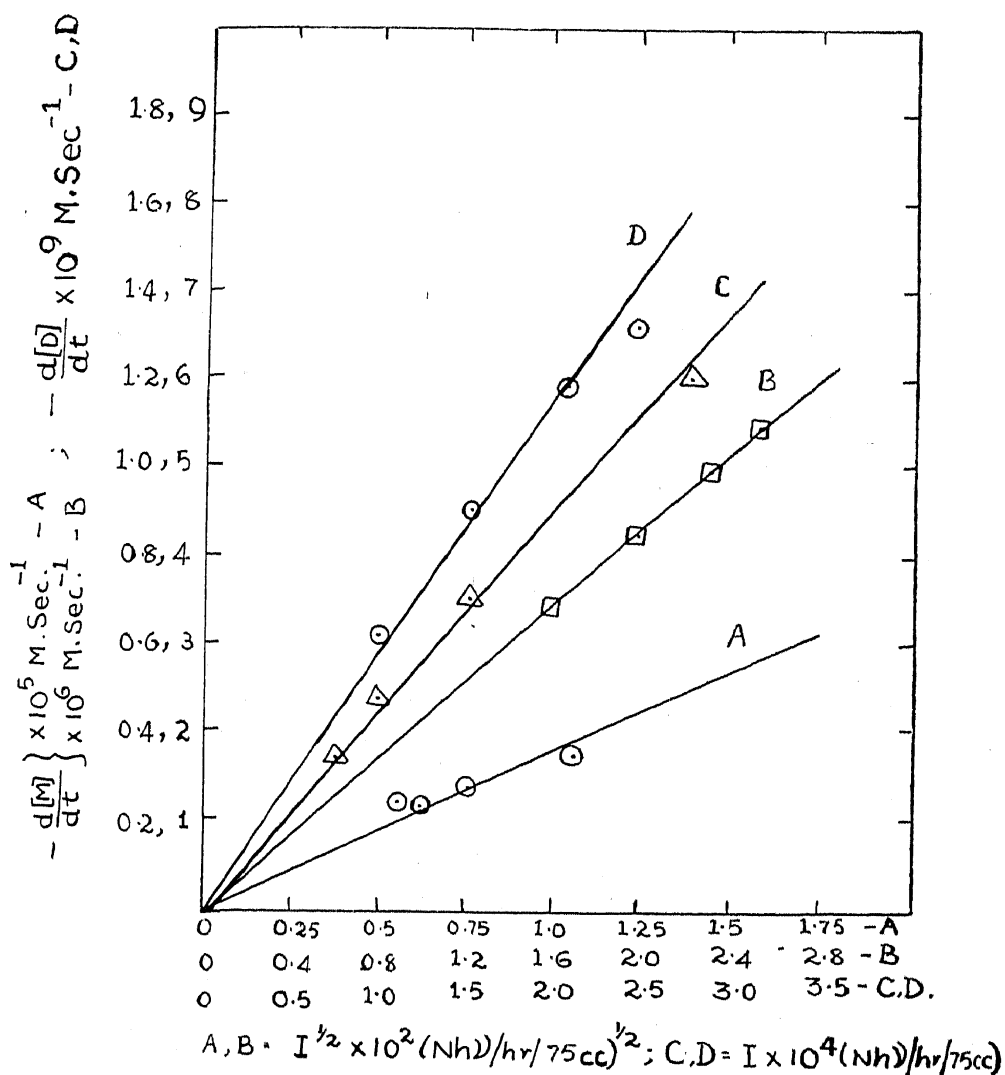
FIG. 3. Plots of rates of monomer disappearance and dye disappearance *versus* square root of light intensities and first power of light intensities respectively. Monomer: Methyl methacrylate. Temp.: 35°C. λ = 435 mμ (A, C), Erythrosin-ascorbic acid system; (B, D), Acriflavine-ascorbic acid system.

(c) Chainlengths

On the basis of mutual type of termination the expression for chainlengths may be derived:

$$n = \frac{k_p}{k_t^{\frac{1}{2}}} \left[\frac{k_d}{k_i k_{e(\text{total})} K} \right]^{\frac{1}{2}} \frac{1}{[\text{AA}]^{\frac{1}{2}} I^{\frac{1}{2}}} \cdot$$

The equation demands an inverse proportionality between chainlength and square roots of both ascorbic acid concentration and light intensity (Fig. 4,

Plots A, B, C, D). We wish to emphasize that these plots of chainlengths are to be treated with caution in as much as the polymers obtained experimentally are heterogeneous type. The relationship,

$$- \frac{\frac{d\,[M]}{dt}}{n} = [M]^2 \frac{k_i k_{e\,(total)}}{k_d} K \, [AA]\, I$$

has been made use of for the evaluation of
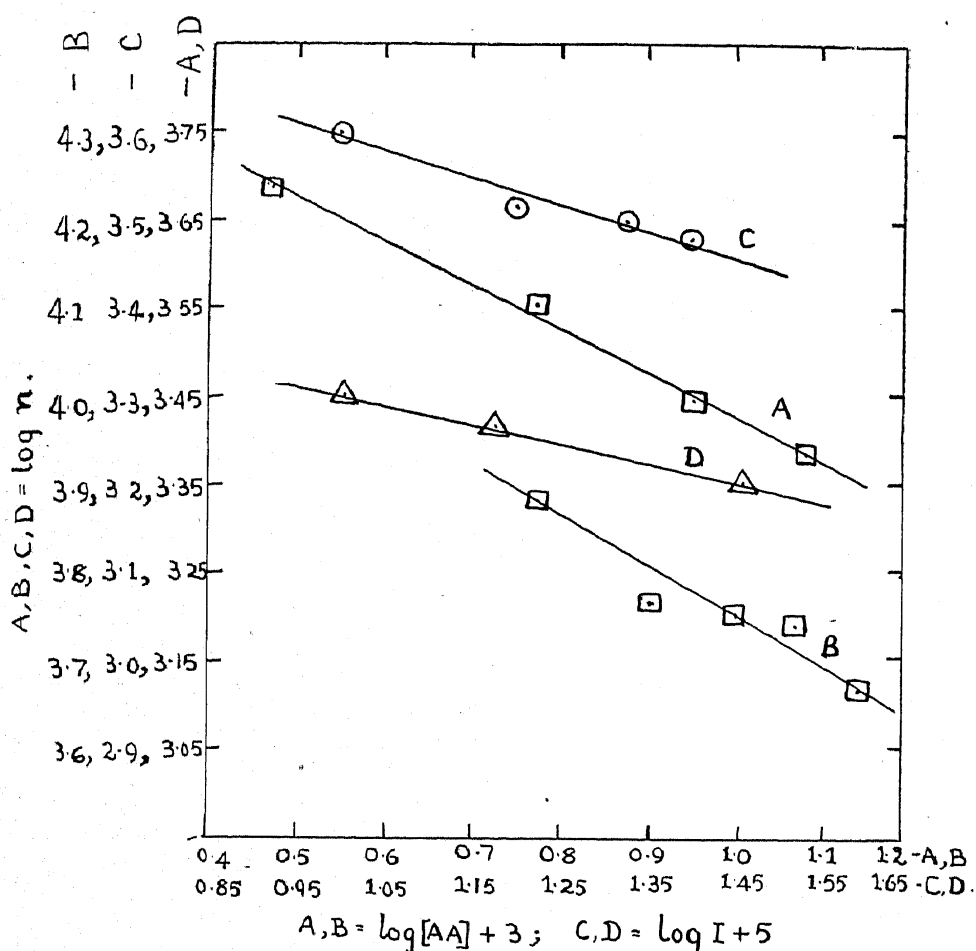
$$\frac{k_i k_{e\,(total)}}{k_d} K$$

Fig. 4. Plots of log of chainlengths vs. log of ascorbic acid concentrations and log of incident light intensities. Monomer: Methyl methacrylate. Temp.: 35° C. $\lambda = 435\,m\mu$. (A, C), Erythrosin-ascorbic acid system; (B, D), Acriflavine-ascorbic acid system.

and substitution of $k_{e\,(total)}\,K$ (from plots of $- d\,[D]/dt$ versus [AA] or [M] or (I) into this gives the values for k_i/k_d. With the known values of k_i/k_d,

and $k_{\epsilon(total)}$ K, and from the slopes of the plots of $-d[M]/dt$ *versus* $[M]^2$ or $I^{\frac{1}{2}}$ or $[AA]^{\frac{1}{2}}$, etc., the values of $k_p/k_t^{\frac{1}{2}}$ have been computed. For erythrosin sensitized system $k_p/k_t^{\frac{1}{2}} = 1 \cdot 378$ and for acriflavine sensitized system $k_p/k_t^{\frac{1}{2}} = 1 \cdot 424$. Our values for the rate constants are found to be in accord with the values reported by other workers using $Fe^{3+} Cl^{-}$[18], ferric citrate-oxalate complexes,[19] uranyl ions,[20] $Fe^{3+} OH^{-}$[21], etc., as photoinitiators in the vinyl polymerization.

V. ACKNOWLEDGMENT

REFERENCES

1. Oster, G. .. *Nature*, 1954, **173**, 300.

———— .. *Photo. Eng.*, 1953, **4**, 173.

2. Koizumi, M. and Watanabe, Ai. *Bull. Chem. Soc., Japan*, 1955, **28**, 136.

———— *Ibid.*, 1955, **28**, 141.

Watanabe, Ai. .. *Ibid.*, 1959, **32**, 557.

(a) ———— and Koizume, M. *Ibid.*, 1961, **34**, 1036.

Watanabe, Ai. .. *Ibid.*, 1962, **35**, 1562.

3. Hiroo Oba and Isamu Fujita *Kobunshi Kagaku*, 1958, **15**, 445.

4. Gozo Takayama .. *Ibid.*, 1960, **16**, 644.

5. Hajimi Miyama .. *J. Chem. Soc., Japan*, Pure Chem. Sec., 1955, **76**, 1013.

———— .. *Ibid.*, 1956, **77**, 691.

6. Fukuo Takemura .. *Bull. Chem. Soc., Japan*, 1962, **35**, 1074.

———— .. *Ibid.*, 1962, **35**, 1078.

7. Oster, G. K., Oster, G. and Prati, G. *J. Amer. Chem. Soc.*, 1957, **79**, 595.

8. Shepp, A., Cheberek, S. and Mac Neil, R. *J. Phys. Chem.*, 1962, **66**, 2563.

9. Delzenne, G., Toppet, S. and Smets, G. *J. Polymer. Sci.*, 1960, **48**, 347.

———— .. *Bull. Soc. Chim. Belges*, 1962, **71**, 857.

10. ————, DeWinter, W., Toppet, S. and Smets, G. *J. Polymer. Sci.*, 1964, **2**, 1069.

11. Toppet, S., Delzenne, G. and Smets, G.   *Ibid.,* 1964, **2,** 1539.

12. Ueberreiter, K. and Sorge, G.   *Z. Elektrochem.,* 1953, **57,** 795.

13. Bowen, E. J.   .. *Chemical Aspects of Light,* University Press, London, Oxford 1946, p. 279.

14. Hatchard, C. G. and Parker, C. A.   *Proc. Roy. Soc., London,* 1956, **235 A,** 518.

15. Fieser, L. F.   .. *J. Amer. Chem. Soc.,* 1924, **46,** 2639.

16. Baxendale, J. H., Bywater, S. and Evans, M. G.   *J. Polymer. Sci.,* 1946, **1,** 237.

17. Md. Sheriff, A. I. and Santappa, M.   *Curr. Sci.,* 1964, **33,** 302.

18. Evans, M. G., Santappa, M. and Uri, N.   *J. Polymer. Sci.,* 1951, **7,** 243.

19. Subramaniam, R. V. and Santappa, M.   *Makromol. Chem.,* 1956, **22,** 147.

20. Mahadevan, V. and Santappa, M.   *J. Polymer. Sci.,* 1961, **50,** 361.

21. Atkinson, B. and Cotton, G. R.   *Trans. Faraday Soc.,* 1958, **54,** 877.