PHOTOPOLYMERIZATION OF METHYL METHACRYLATE INITIATED BY POTASSIUM TRIS(OXALATO)FERRATE(III)

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Summary

The results of a kinetic study of the photopolymerization of methyl methacrylate by potassium tris(oxalato)ferrate(III) in aqueous sulphuric acid solution with light of wavelength 365 nm at 30 °C are presented. All reactions were carried out under completely deaerated conditions. The rate Rp of polymerization was followed by gravimetric estimation of the polymer formed and the rate of disappearance of the complex was followed by spectrocolourimetric estimation of the disappearing complex. Rp was found to be directly proportional to $[M]^{3/2}$, $[C]^{1/2}$ and $I^{1/2}$, where [M], [C] and I refer to the concentration of monomer, the concentration of complex and the light intensity respectively. The rate of complex disappearance was found to be directly proportional to [C] and I. A reaction scheme is presented and the corresponding kinetic expressions are derived.

1. Introduction

Photopolymerization has been widely used in imaging systems, such as photoresists, printing plates, proofing systems and holography, in laser-imaging systems and in non-imaging systems such as photocurable coatings and inks applications [1 - 4]. The first reference to image formation by photopolymerization was in 1945 when Gates proposed, in a British Patent [5], a process for forming shallow relief images in methyl methacrylate using a combination of light and heat. The initiation of polymerization in the presence of light using dyes and reducing agent systems was the subject of study for various workers [6, 7]. The majority of photochemical processes based on polymerization utilize radiant energy to initiate the polymerization via free-radical formation in the exposed areas. Metal complexes of copper(II), cobalt(III), iron(III), platinum(II), vanadium(V) and manganese(III) have been used as photoinitiators of vinyl polymerization

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by several workers [7]. Sahul *et al.* [8] have reported the photopolymerization of acrylamide in aqueous acid solution using potassium tris(oxalato)ferrate(III). This compound is well known as a chemical actinometer for measuring light intensities. The kinetic results, however, are usually valid only for the specific conditions described in each work. In this paper, we report the results of polymerization of methyl methacrylate in aqueous acidic solution photoinitiated by potassium tris(oxalato)ferrate(III) complex with light of wavelength 365 nm.

2. Experimental details

2.1. Materials

Methyl methacrylate (BDH) was purified by washing with 5 wt.% NaOH solution; it was then dried over anhydrous calcium chloride and distilled under reduced pressure. Potassium tris(oxalato)ferrate(III) was prepared by the procedure given by Hatchard and Parker [9]. All other chemicals were AnalaR grade. The irradiation source was a medium pressure 125 W 365 nm lamp (Philips, Holland).

2.2. Estimations

The kinetics of the reaction was followed by gravimetric determination of the rate $-d[M]/dt$ of monomer disappearance as the polymer precipitated in the aqueous medium; the Fe^{2+} production $d[Fe^{2+}]/dt$ was followed spectrocolourimetrically after converting the Fe^{2+} into Fe^{2+}–o-phenanthroline complex and measuring its absorption at 510 nm. $-d[M]/dt$ was assumed to be equal to the rate Rp of polymerization. The rate $-d[C]/dt$ of complex disappearance was equal to $d[Fe^{2+}]/dt$, since the photoredox reaction was the only reaction the complex underwent. Light intensities were measured as reported previously [9, 10]. The concentration $[M]$ of monomer, the concentration $[C]$ of complex and the light intensity I were varied in the following ranges: $[M]$, 0.1128 - 0.282 M; $[C]$, (3.0×10^{-5}) - (7.0×10^{-3}) M; I, (3.68×10^{-9}) - (10.41×10^{-9}) $Nh\nu$ l^{-1} s^{-1}. All experiments were conducted at 30 °C under deaerated conditions and at a pH of 0.7 ($\phi = 0.6$ [11]) obtained by adding aqueous sulphuric acid.

3. Results and discussion

3.1. Kinetics

The steady state for the reaction was reached in about 20 min (Fig. 1, curve A) with approximately 20% conversion. Rp was found to be proportional to $[M]^{3/2}$ (Fig. 1, curves B and C) under constant $[C] = 1.0 \times 10^{-3}$ M for plot B and $[C] = 5.0 \times 10^{-4}$ M for plot C and light intensity $I = 1.408 \times 10^{-8}$ $Nh\nu$ l^{-1} s^{-1}. Rp was proportional to $[C]^{1/2}$ in the concentration range (3.0×10^{-5}) - (2.0×10^{-4}) M (Fig. 2, curve E) under constant $[M] = 0.282$ M
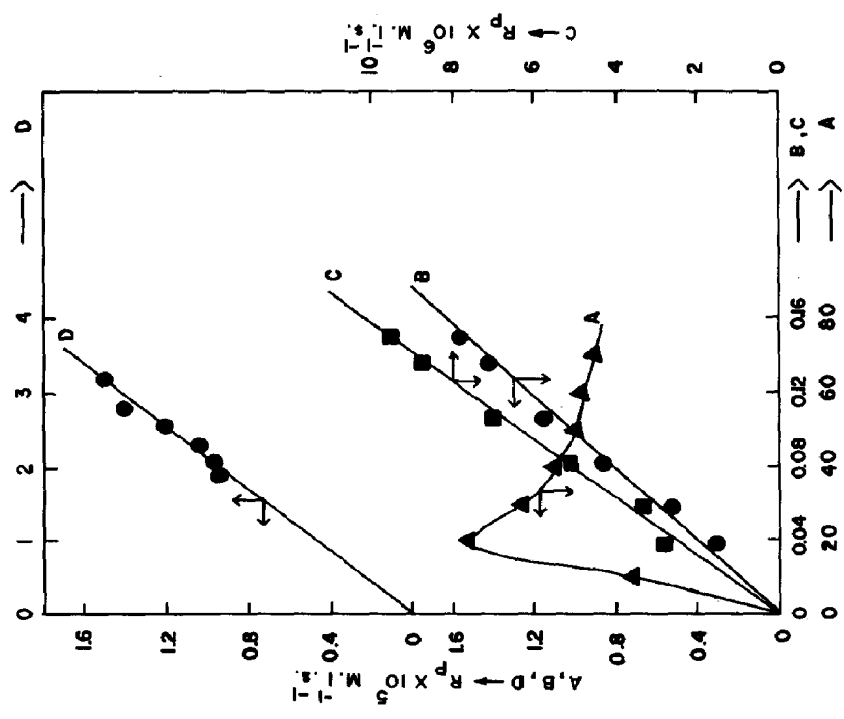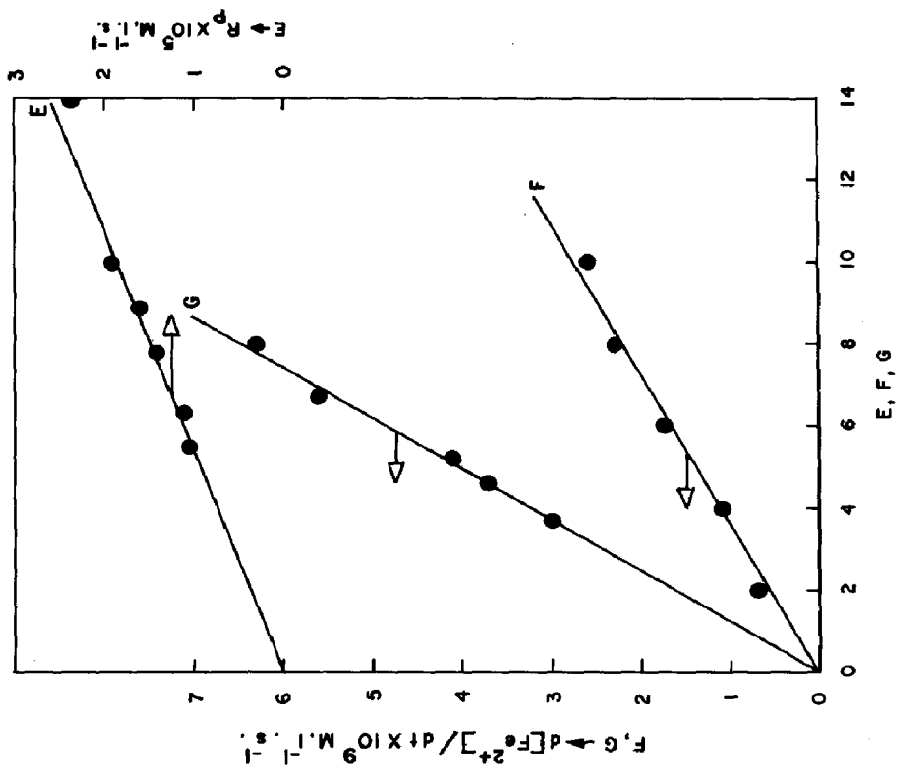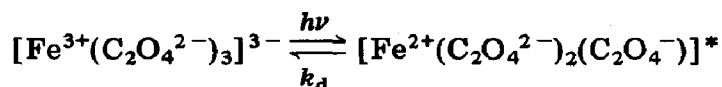
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Fig. 1. Curve A, plot of R_p against time in minutes; curve B, plot of R_p against $[M]^{1.5}$ ((mol l^{-1})$^{1.5}$) at $[C] = 1.0 \times 10^{-3}$ M; curve C, plot of R_p against $[M]^{1.5}$ ((mol l^{-1})$^{1.5}$) at $[C] = 5.0 \times 10^{-4}$ M; curve D, plot of R_p against $I^{0.5} \times 10^{4.5}$ (($Nh\nu$ l^{-1} s^{-1})$^{0.5}$).

Fig. 2. Curve E, plot of R_p against $[C]^{0.5} \times 10^3$ ((mol l^{-1})$^{0.5}$); curve F, rate of Fe^{2+} ion production against $[C] \times 10^4$ (mol l^{-1}); curve G, rate of Fe^{2+} ion production against $I \times 10^9$ ($Nh\nu$ l^{-1} s^{-1}).

and $I = 1.408 \times 10^{-8}$ $Nh\nu$ l^{-1} s^{-1}. Rp also depended on the square root of I (Fig. 1, curve D) under constant $[M] = 0.282$ M and $[C] = 1.0 \times 10^{-3}$ M. The rate $d[Fe^{2+}]/dt$ of Fe^{2+} ion production was found to be directly proportional to $[C]$ (Fig. 2, curve F) and I (Fig. 2, curve G).
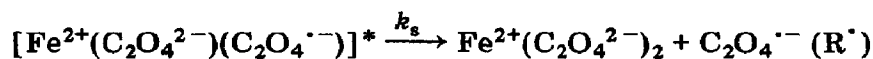
3.2. Reaction scheme

The ferrioxalate complex has been reported to undergo a photoredox reaction quite similar to the reactions of ion pairs such as $Fe^{3+}OH^-$, $Fe^{3+}Cl^-$ etc. [12, 13] yielding oxalato free radical. It was established [11, 14] that on light absorption the ferrioxalate complex decomposed to yield Fe^{2+} and CO_2. Parker and Hatchard [15] studied the photolysis of the complex, in which it was postulated that the primary photochemical process involved an electron transfer from the oxalato ligand to the central Fe^{3+} ion, resulting in the formation of Fe^{2+} and a free radical. The free radicals subsequently underwent other modes of reaction. The formation of free radicals was further supported by proton magnetic resonance studies [16]. The presence of oxygen dissolved in the system caused induction periods. Polymerization occurred almost immediately when the reaction mixture was deaerated and irradiated with light of wavelength 365 nm. Based on the kinetic orders obtained, the following reaction scheme may be considered.
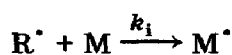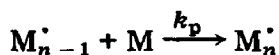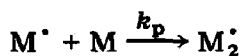
(1) Primary photoreaction:

$$[Fe^{3+}(C_2O_4{}^{2-})_3]^{3-} \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} [Fe^{2+}(C_2O_4{}^{2-})_2(C_2O_4{}^-)]^*$$

(2) Decomposition of the reduced complex:

$$[Fe^{2+}(C_2O_4{}^{2-})(C_2O_4{}^{\cdot-})]^* \xrightarrow{k_s} Fe^{2+}(C_2O_4{}^{2-})_2 + C_2O_4{}^{\cdot-} \ (R^\cdot)$$

(3) Initiation:

$$R^\cdot + M \xrightarrow{k_i} M^\cdot$$

(4) Propagation:

$$M^\cdot + M \xrightarrow{k_p} M_2^\cdot$$

$$M_{n-1}^\cdot + M \xrightarrow{k_p} M_n^\cdot$$

(5) Termination:

$$M_n^\cdot + M_m^\cdot \xrightarrow{k_t} \text{polymer}$$
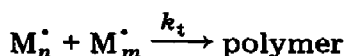
Termination occurred by mutual annihilation of two polymer radicals. The dependence of Rp on $[C]^{1/2}$ and $I^{1/2}$ further lends support to the occurrence of mutual termination. The primary light-absorbing species is the complex since $-d[Fe^{2+}]/dt$ is directly proportional to both $[C]$ and I.

TABLE 1

Rate Rp of polymerization of methyl methacrylate initiated by potassium tris(oxalato)-ferrate(III) at $\lambda = 365$ nm

Complex concentration ($\times 10^{-4}$ M)	Rp $\times 10^5$ (mol l^{-1} s^{-1})
4	1.9044
6	1.7379
10	1.5481
20	1.2019
30	1.1053
40	0.9488
50	0.8922
60	0.8323
70	0.7957

[M] = 0.282 M; $I = 1.408 \times 10^{-8}$ $Nh\nu$ l^{-1} s^{-1}.

When complex concentrations above 2.0×10^{-4} M were used for the reaction, Rp exhibited a decreasing trend as illustrated in Table 1. Hence it is likely that at a higher concentration of the complex the termination of the polymer chain occurs through interaction between the molecules of the complex. Similar trends at high complex concentrations have been reported in the literature [8, 17, 18]. Rp has been reported to be proportional to the square root of the complex concentration in the concentration range (2.0×10^{-6}) - (3.0×10^{-4}) M for the photopolymerization of acrylamide [8] after which Rp decreased. Attempts were made to polymerize methyl methacrylate using a complex concentration below 3.0×10^{-5} M under our experimental conditions. The very slight traces of polymer formed were, however, practically irrecoverable.

Steady state kinetic treatment of the above-mentioned reaction scheme gives the kinetic expressions

$$Rp = \frac{-d[M]}{dt} = \frac{k_p}{k_t^{1/2}} \left(\frac{k_s}{k_d + k_s} \right)^{1/2} [M]^{3/2}[C]^{1/2}I^{1/2}$$

$$\frac{-d[C]}{dt} = \frac{d[Fe^{2+}]}{dt} = \left(\frac{k_s}{k_d + k_s} \right) [C]I$$

Our studies on the photopolymerization of methyl methacrylate by ferrioxalate complex provides further evidence for the production of significant concentrations of $C_2O_4^-$ radical anions, and today photopolymerization is probably the most widely studied system of photochemical image formation.

References

1 A. B. Cohen, *Ind. Res.*, (December, 1976) 39.
2 P. Walker, V. J. Webers and G. A. Thommes, *J. Photogr. Sci.*, *18* (1970) 150.
3 R. J. Povinelli (ed.), *Proc. Semin. on Applications of Photopolymers*, Society of Photographic Science and Engineering, 1970.
4 S. P. Pappas (ed.), *UV Curing: Science and Technology*, Technology Marketing Corporation, Connecticut, 1978.
5 W. E. F. Gates, *Br. Patent 566,795* (1945).
6 R. J. Allen and S. Chaberek, *Photogr. Sci. Eng.*, *9* (1965) 148.
7 M. K. Mishra, *J. Macromol. Sci. C*, *22* (3) (1982/83) 409.
8 K. Sahul, L. V. Natarajan and Q. Anwaruddin, *J. Polym. Sci. Lett. Ed.*, *15* (1977) 605.
9 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, *235* (1956) 518.
10 H. A. Taylor, in J. M. Fitzgerald (ed.), *Analytical Photochemistry and Photochemical Analysis*, Dekker, New York, 1971, pp. 110 - 111.
11 G. B. Porter, W. Doering and S. Karanka, *J. Am. Chem. Soc.*, *84* (1962) 4027.
12 N. Uri, *Chem. Rev.*, *50* (1952) 375.
13 F. S. Dainton, *J. Chem. Soc. (Spec. Publ.)*, *1* (1954) 18.
14 W. W. Wendlandt and E. L. Simmons, *J. Inorg. Nucl. Chem.*, *28* (1966) 2420.
15 C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, *63* (1959) 22.
16 D. J. R. Ingram, W. E. Hodgson, C. A. Parker and W. T. Rees, *Nature*, *176* (1955) 1227.
17 G. A. Delzenne, *J. Polym. Sci., Part C*, *16* (1967) 1027.
18 M. Aslam, Q. Anwaruddin and L. V. Natarajan, *Polym. Photochem.*, *5* (1984) 41.