PHOTO-INITIATED FREE RADICAL POLYMERIZATION OF METHYL ACRYLATE IN AQUEOUS SOLUTION[1]

C. Chaitanyan Menon and M. Santappa

ABSTRACT

Photo-initiated free radical polymerization of methyl acrylate in aqueous solution is described. Using mainly light of wavelength 3650 Å and the ion pairs $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ as photosensitizers the kinetics of polymerization were investigated by studying the effect of the variation of (i) intensity of light, (ii) concentration of monomer, (iii) fraction of light absorbed by the ion pair, and (iv) ferrous ion accumulating in, or initially added to, the system on (a) molecular weight of polymer, (b) the rate of disappearance of monomer, and (c) the rate of production of ferrous ion. The results have been analyzed in the light of a reaction scheme involving (1) a primary photochemical process and a dark back reaction, (2) initiation of polymerization by the primary product $Fe^{2+}OH$ or $Fe^{2+}Cl$, (3) dissociation of the primary product, (4) a secondary dark back reaction, (5) initiation by a free radical, (6) propagation, and (7) termination. Examination of the experimental results in the light of the reaction scheme indicated that the initiation of polymerization was due to OH or Cl free radicals formed by the dissociation of the primary product and that termination occurred by combination of growing polymer chains. Some expressions involving specific rate constants have been evaluated.

INTRODUCTION

Baxendale, Evans, and Park (1) have shown that the OH radicals produced in the reaction between hydrogen peroxide and ferrous ion initiate polymerization of vinyl monomers in aqueous solution. Rabinowitch and Stockmayer (2) have interpreted the spectra of ferric association complexes as "electron transfer spectra". The presence of "association complexes" or "ion-pair complexes" was also inferred by Fromherz and Lih (3) in their studies of lead halide solutions and by Davies and Wyatt (4) in investigations of numerous other salt solutions. Evans and Uri (5) have shown that atoms and free radicals produced by irradiation of ferric ion-pair complexes lead to polymerization of vinyl compounds in aqueous solution. These workers and Santappa (6, 7, 8, 9) have made systematic investigations of the polymerization of acrylonitrile and methyl methacrylate by the ion pairs $Fe^{3+}OH^-$, $Fe^{3+}Cl^-$, and $Fe^{3+}N_3^-$. Studies of the polymerization of methyl acrylate monomer even under thermal conditions have been very scanty because of the tough and elastic nature of the polymer formed under conditions of "auto-acceleration". Matheson and co-workers (10) have evaluated the specific rate constants for initiation, growth, and termination in the polymerization of this monomer. In this paper we wish to present in detail work on the polymerization of methyl acrylate by the ion-pair complexes $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$.

Light Absorption and Electron Transfer

It is assumed that the light absorption process is connected with an electron transfer:

$$Fe^{3+}X^- \xrightarrow{h\nu} Fe^{2+}X \quad (X = OH, Cl, etc.)$$
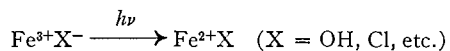
Dissociation of the complex $Fe^{2+}X$ into Fe^{2+} and X is expected (6) on energetic grounds. Radicals, X, thus produced lead to subsequent reactions like polymerization of vinyl compounds.
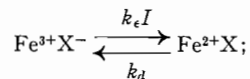
The Reaction Scheme
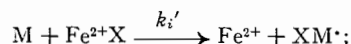
The following scheme includes those reactions which are likely to occur:
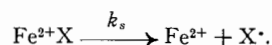
(1) Light absorption and primary dark back reaction:

$$Fe^{3+}X^- \underset{k_d}{\overset{k_\epsilon I}{\rightleftarrows}} Fe^{2+}X;$$

k_ϵ is the fraction of light absorbed by $Fe^{3+}X^-$ and I is the light intensity.

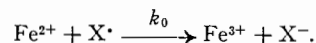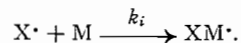(2) Initiation of polymerization by primary product $Fe^{2+}X$:

$$M + Fe^{2+}X \xrightarrow{k_i'} Fe^{2+} + XM^\cdot;$$

M represents vinyl monomer.

(3) Separation of primary product:

$$Fe^{2+}X \xrightarrow{k_s} Fe^{2+} + X^\cdot.$$

(4) Secondary dark back reaction:

$$Fe^{2+} + X^\cdot \xrightarrow{k_0} Fe^{3+} + X^-.$$

(5) Initiation of polymerization by free radicals X:

$$X^\cdot + M \xrightarrow{k_i} XM^\cdot.$$

(6) Propagation of polymerization:

$$XM_n^\cdot + M \xrightarrow{k_p} XM_{n+1}^\cdot$$
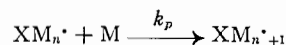
(7) Termination of polymerization with rate constant k_t.

EXPERIMENTAL

A 250 watt high pressure mercury vapor lamp (Gallenkamp, *dp* 7094) provided a bright source of light with the principal wavelengths 3650, 4046, 4358 Å, etc. The maximum arc brightness was 2×10^4 candles/cm². The lamp was a silica sphere mounted inside a metal shield 100 by 65 by 55 mm. fitted with a circular glass window. The lamp was stabilized by choke Z,1875, Gallenkamp *dp* 7094/1. For the 3130 Å line the light source was a 250 watt high pressure mercury vapor lamp supplied by B.T.H., U.K. The light from the lamps passed through a quartz condenser lens and the resulting parallel beam was passed through a series of filters to isolate the monochromatic lines. The principal line used was 3650 Å; lines at 3130, 4050, and 4350 Å were also used to some extent. The respective filters for the isolation of these lines are given by Bowen (11). The light beam consisting of the monochromatic line passed through an adjustable diaphragm into a thermostat fitted with quartz windows and filled with distilled water. At the center of the thermostat was mounted the cylindrical reaction cell with flat quartz plates at both ends and two outlet tubes provided with B 14 cones at the top. The diameter of the cell was 50 mm. and the length in the direction of the optical beam is 46 mm. All experiments were done at 30° C. ±0.1°, and the duration of irradiation was restricted to 1 hour. With $Fe^{3+}Cl^-$ initiator all the experiments were done at pH 1 but with $Fe^{3+}OH^-$ initiator most experiments were done at pH 2.

The lamp output was determined by chemical actinometry using uranyl oxalate (12). The light intensities used in our experiments range from 5×10^{-5} to 6×10^{-4} $Nh\nu$/hour.

The chemicals used were mostly B.D.H. Analar or Merck pure products. Methyl acrylate supplied by Rohm and Haas was repeatedly distilled in an atmosphere of nitrogen and preserved in a refrigerator. Ferric nitrate and ferric perchlorate (10^{-3} to 10^{-5} M) were used as sources of ferric ions whose concentration was determined by the standard procedure with Zimmerman–Reinhardt reagent. The concentration of ferrous ions (10^{-4} to 10^{-7} M) was determined colorimetrically with ortho phenanthroline as the coloring reagent. Purity of methyl acrylate was determined by the usual bromine addition method. The concentration of the monomer methyl acrylate used was 0.28 M for most of the experiments. The rate of disappearance of monomer was followed by weighing the amount of dried polymer.

The experimental conditions for the work closely follow those mentioned by Evans, Santappa, and Uri (6). The system monomer–initiator in aqueous medium was taken in the reaction cell and deaerated by passing oxygen free nitrogen for about one-half hour. The cell was then introduced into the thermostat kept at 30° C. ±0.1° and irradiated for about one hour. Turbidity occurred almost instantaneously when the cell was in the path of the light beam indicating the absence of any induction period. Polymer continuously precipitated. At the end of 1 hour, polymer was filtered off and the concentration of ferrous ions in the filtrate was determined colorimetrically.

Purification of polymethyl acrylate was effected by a solution of the polymer in a 1:1 volume mixture of acetone and chloroform, reprecipitation by addition of methanol, followed by drying at 60° C. to constant weight. Molecular weight, M, of polymethyl acrylate was determined by measuring the intrinsic viscosity, $[\eta]$, of the polymer in benzene solution and applying the relationship (13):

$$[\eta] = 1.282 \times 10^{-4} M^{0.7145}.$$

RESULTS

(a) Fraction of Light Absorbed, k_ϵ

It has been shown previously (7, 8, 9) that in ferric perchlorate solutions the ion pair $Fe^{3+}OH^-$ is the active species, the concentration of the species varying with pH. In the presence of chloride ions the species $Fe^{3+}Cl^-$ is also formed. When the system ferric ion pair – methyl acrylate in aqueous solution is irradiated there is a partial reduction of ferric ions to ferrous ions and polymerization of the monomer. Fig. 1 shows the dependence of the rate of formation of ferrous ion using the 3650 Å line at various fractions of light absorption, k_ϵ, arising from variations in the concentrations of $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$. Changes in the concentration of $Fe^{3+}OH^-$ were effected by changing the pH, and changes in the $Fe^{3+}Cl^-$ concentration were achieved by changing the ferric ion concentration of the system. It was further found that the rate of disappearance of monomer was a linear function of $k_\epsilon^{1/2}$ with $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ as initiators (Fig. 2). The chain length of polymethyl acrylate, produced by $Fe^{3+}OH^-$ initiator, was a linear function of $k_\epsilon^{-1/2}$ as seen in Fig. 3.

(b) Light Intensity, I

Fig. 4 shows the variation of the rate of formation of ferrous ion with light intensity for $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ initiators. It is observed that the relationship deviates from linearity at the high light intensities used in these experiments. A steady state kinetic analysis of the reaction scheme suggested above indicates that the deviations from linearity can be attributed to the condition $k_i[M] \gg k_0[Fe^{2+}]$ at high light intensities. Fig. 5 shows that the expected linearity between the rate of production of ferrous ion
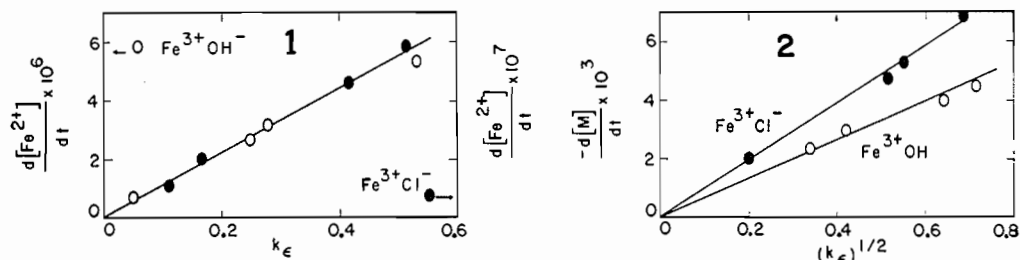
FIG. 1. Rate of production of ferrous ion as a function of fraction of light absorbed.
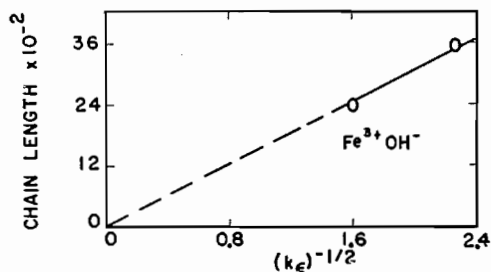FIG. 2. Rate of disappearance of methyl acrylate as a function of fraction of light absorbed.

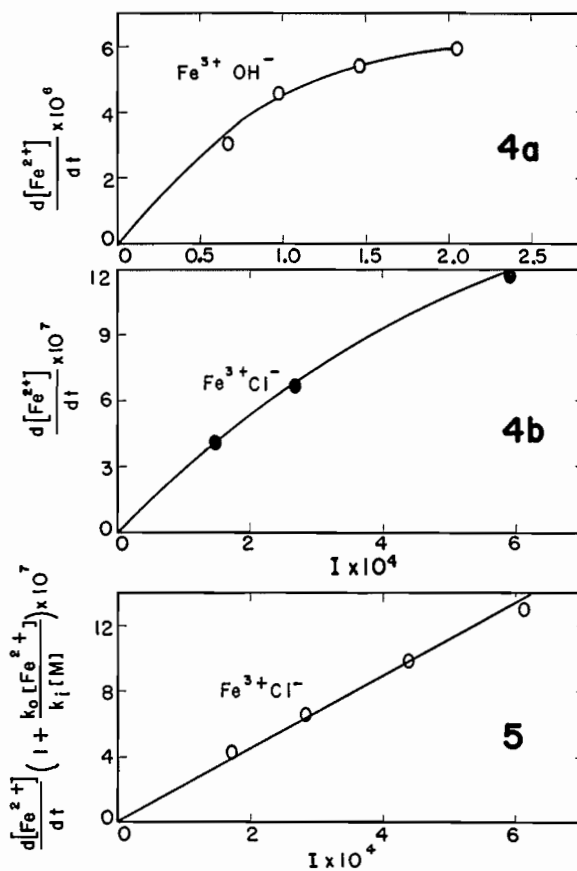FIG. 3. Chain length of polymethyl acrylate as a function of fraction of light absorbed.

FIG. 4. Rate of formation of ferrous ion as a function of light intensity.
FIG. 5. Rate of formation of ferrous ion, corrected for secondary dark back reaction, as a function of light intensity.

DETAILS OF EXPERIMENTAL CONDITIONS

For all experiments: wavelength = 3650 Å; temperature = 30° C.; time of experiment = 1 hour

	Figs. 1-3	Figs. 4-7	Figs. 8-10	Fig. 11		Fig. 12
$Fe^{3+}OH^-$ initiator						
Monomer	Methyl acrylate	Methyl acrylate	Methyl acrylate	Acrylonitrile	Methyl methacrylate	Methyl methacrylate
Intensity, $Nh\nu$/hr.	5.4×10^{-4}	0.52×10^{-4} to 2.1×10^{-4}	6.1×10^{-4}	5.95×10^{-5}	5.9×10^{-4}	5.9×10^{-5}
[Monomer], M	0.283	0.226	0.17 to 0.396	0.3 to 0.75	0.04 to 0.13	0.07
[Fe^{3+}], M	5×10^{-4}	1×10^{-3}	1×10^{-4}	1×10^{-3}	1×10^{-3}	1×10^{-3}
pH	1 to 2	2	2	1	1	1
						Mean [Fe^{2+}]0.85×10^{-5} to 3.5×10^{-5} M

	Figs. 1-3	Figs. 4-7	Figs. 8-10	Fig. 12
$Fe^{3+}Cl^-$ initiator				
Monomer	Methyl acrylate	Methyl acrylate		Methyl acrylate
Intensity, $Nh\nu$/hr.	4.2×10^{-4}	1.5×10^{-4} to 6.1×10^{-4}	2.3×10^{-4}	2.01×10^{-4}
[Monomer], M	0.283	0.283	0.17 to 0.396	0.226
[Fe^{3+}], M	2×10^{-4} to 8×10^{-4}	6×10^{-5}	2×10^{-3}	1×10^{-3}
[Cl^-], N	0.05	0.05	0.05	0.05
pH	1	1	1	1
				Mean [Fe^{2+}] 2.8×10^{-6} to 8.9×10^{-5} M

and light intensity is obtained when account is taken of the ferrous ions which are oxidized by chlorine atoms in the secondary dark back reaction. A linear dependence of the rate of disappearance of monomer on the square root of light intensity with $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ initiators could be obtained only at high intensities of light. At low intensities a strong tendency towards non-linearity (Fig. 6) indicated that the scattered light, which
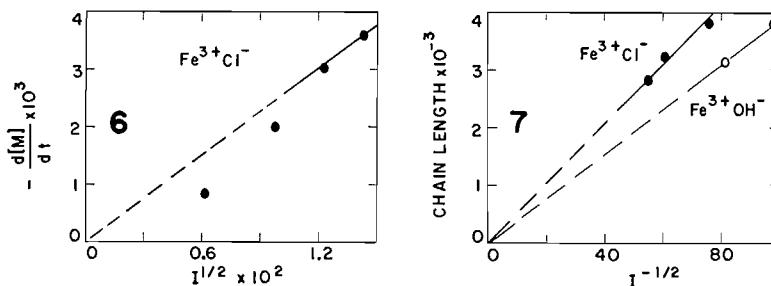

FIG. 6. Rate of disappearance of methyl acrylate as a function of light intensity.
FIG. 7. Chain length of polymethyl acrylate as a function of light intensity.

would have made a considerable contribution to the rate of monomer disappearance, could not be neglected. Further, such behavior was not observed with other monomers previously studied (7, 8, 9) but appeared to be characteristic of polymethyl acrylate. However, linear functions of chain length vs. reciprocal square root of light intensity were obtained with both $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ initiators as illustrated in Fig. 7.

(c) Monomer Concentration, [M]

It has been observed (7) with monomers like acrylonitrile and methyl methacrylate that an accurate investigation of the dependence of the rate of production of ferrous ion on monomer concentration was difficult because of interactions of free radicals with impurities (9), especially at low concentrations of monomer. With methyl acrylate and $Fe^{3+}OH^-$ initiator there was a regular variation of the rate of production of ferrous ion with monomer concentration whereas with $Fe^{3+}Cl^-$ initiator the rate of production of ferrous ion was insensitive to changes in the monomer concentration. Fig. 8 shows the
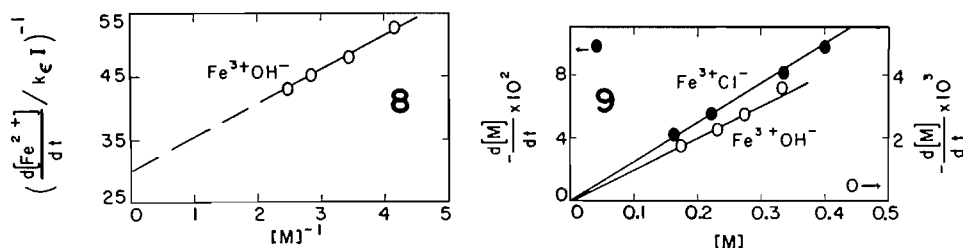

FIG. 8. Quantum yield for production of ferrous ion as a function of concentration of methyl acrylate.
FIG. 9. Rate of disappearance of methyl acrylate as a function of concentration of methyl acrylate.

linear relationship, with $Fe^{3+}OH^-$ initiator, between reciprocal quantum yield for ferrous ion production, $1/\gamma$, and reciprocal monomer concentration, $1/[M]$, where

$$\gamma = \frac{d[Fe^{2+}]/dt}{k_\epsilon I} .$$

Plots of rate of disappearance of monomer vs. monomer concentration (Fig. 9) and of

chain length vs. monomer concentration (Fig. 10) were linear with both $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ initiators. The dependence of the rate of polymerization on monomer concentration for methyl methacrylate and acrylonitrile monomers and $Fe^{3+}OH^-$ initiator, hitherto not reported, has also been studied and is illustrated in Fig. 11.
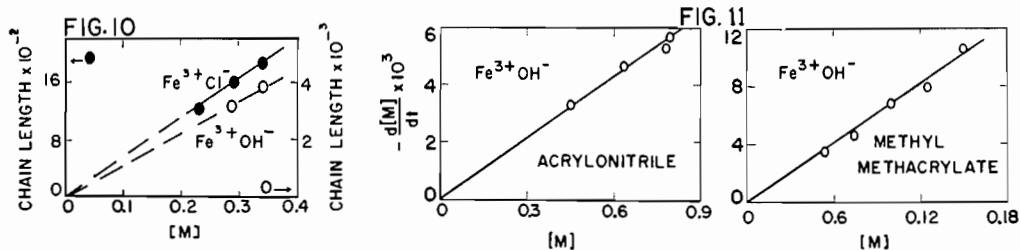

FIG. 10. Chain length of polymethyl acrylate as a function of concentration of monomer.
FIG. 11. Rates of polymerization of acrylonitrile and methyl methacrylate with $Fe^{3+}OH^-$ initiator as functions of concentration of monomer.

(d) Quantum Yields for Production of Ferrous Ion

The maximum quantum yields for production of ferrous ion at 30° C., measured at monomer concentrations corresponding to their solubility in the aqueous medium, were found to depend on the initiating species and the wavelength of the radiation (Table I). With $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ initiators the quantum yields were practically equal at 3130 and 3650 Å but dropped off steeply when the limit of the visible was reached. It is, however, of interest that γ_{max} reported (9) for $Fe^{3+}OH^-$ (0.05) and $Fe^{3+}Cl^-$ (0.13) in the presence of methyl methacrylate and acrylonitrile were not realized in the presence of methyl acrylate. The quantum yields with regard to monomer disappearance were found to depend on monomer concentration, light intensity, etc.

(e) Effect of Initially Added Ferrous Ion and Ferrous Ion Formed During the Reaction

The rate of increase of ferrous ion concentration was found to be considerably reduced by (i) initially added ferrous ions and (ii) ferrous ions accumulating in the course of the reaction. The reciprocal rate of formation of ferrous ion with $Fe^{3+}Cl^-$ initiator was found to vary linearly with the mean ferrous ion concentration in the system. Linear relationships were also observed in the plots of reciprocal rate of increase of ferrous ion concentration vs. mean ferrous ion concentration with the systems $Fe^{3+}OH^-$ – methyl methacrylate and $Fe^{3+}Cl^-$ – methyl acrylate (Fig. 12). The mean ferrous ion concentration was taken to be the sum of the initial ferrous ion concentration and half the increase in concentration of ferrous ions resulting from the reaction.

DISCUSSION

Application of stationary state kinetics to the reaction scheme leads to the following expression for the rate of formation of ferrous ion:

$$\frac{d[Fe^{2+}]}{dt} = \frac{k_\epsilon I}{k_d + k_s + k_i'[M]} \left(\frac{k_s k_i[M]}{k_0[Fe^{2+}] + k_t[M]} + k_i'[M] \right).$$

The fact that the quantum yield for ferrous ion production reached a constant value below unity at the highest monomer concentration provides evidence that the undissociated complex, $Fe^{2+}X$, does not initiate polymerization directly, or, more accurately,

that $k_i'[M] \ll k_s$. The above equation can therefore be simplified to:

$$[1] \qquad \frac{d[Fe^{2+}]}{dt} = \frac{k_s k_\epsilon I}{k_d + k_s} \left(\frac{k_i[M]}{k_i[M] + k_0[Fe^{2+}]} \right).$$

Thus when OH or Cl free radicals initiate polymerization the quantum yield, defined by $(d[Fe^{2+}]/dt)/k_\epsilon I$, has, according to equation [1], the maximum value $k_s/(k_d + k_s)$.
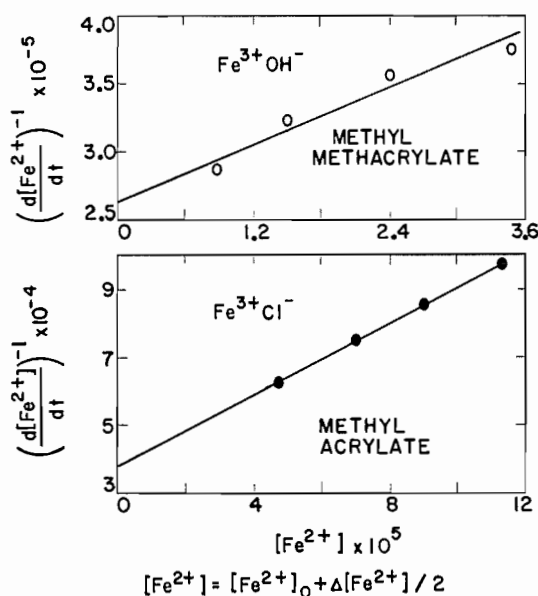

FIG. 12. Rate of accumulation of ferrous ion as a function of mean concentration of ferrous ion.

Equation [1] was applied to the experimental results in the following ways:

(i) The variation of $d[Fe^{2+}]/dt$ with k_ϵ for both the complexes was found to be linear (Fig. 1).

(ii) The influence of ferrous ion produced during the course of the reaction or of ferrous ion initially added has been tested by plotting $(d[Fe^{2+}]/dt)^{-1}$ against $[M]^{-1}$ and against $[Fe^{2+}]$ (Figs. 12 and 8). From the slopes of these plots the ratio k_0/k_i was evaluated. The value of the ratio for the system methyl acrylate – $Fe^{3+}OH^-$ is 1.26×10^4 while for methyl acrylate – $Fe^{3+}Cl^-$ it is 3.8×10^3. The intercepts of these graphs give the values of $k_s/(k_d + k_s)$ as 0.024 for $Fe^{3+}OH^-$ and 0.14 for $Fe^{3+}Cl^-$. These values are of the expected orders of magnitude, though it may be noted that $\gamma = k_s/(k_d + k_s) = 0.14$ for $Fe^{3+}Cl^-$ is not in accord with the value 0.078 determined by direct measurement of $d[Fe^{2+}]/dt$ at maximum concentration of monomer (Table I). In view of the fact that small experi-

TABLE I

QUANTUM YIELDS FOR FERROUS ION PRODUCTION WITH
$Fe^{3+}OH^-$ AND $Fe^{3+}Cl^-$ INITIATORS

Wave length, angstroms	Quantum yield	
	$Fe^{3+}OH^-$	$Fe^{3+}Cl^-$
3130	0.033	0.078
3650	0.022	0.075
4050	0.015	0.044
4360	0.017	0.047

mental errors in the determination of mean ferrous ion concentration introduce large errors in the graphical evaluations of k_0/k_t and $k_s/(k_d+k_s)$ the estimation of these quantities must be regarded as only approximately correct. The value of $k_s/(k_d+k_s)$ for $Fe^{3+}Cl^-$ may be considered higher than the correct value by a factor of 2.

It may be stated here that the quantum yields for ferrous ion production higher than our values have been reported by Baxendale and Magee (14) and by Dainton (15) in their works on the reactions of organic free radicals with species involving ferrous and ferric ions. Baxendale's values (14) for quantum yields for ferrous ion production in the oxidation of benzene with $Fe^{3+}OH^-$ as the active species are higher than ours by a factor of six. On the other hand the quantum yields reported by Baxendale are higher than ours only by a factor of two when we consider our quantum yields with $Fe^{3+}Cl^-$ as the active species. Baxendale's work (14) is connected with the oxidation of benzene by OH radicals from $Fe^{3+}OH^-$ in homogeneous medium whilst our work is connected with the reaction of OH radicals with vinyl monomer in a medium where the polymer continuously precipitates. We venture to suggest that the decrease in the quantum yields for ferrous ion production in our system may be due to the following reasons. Firstly we have not considered the reaction step,

$$H_2O + Ph \cdot + Fe^{3+} \longrightarrow PhOH + Fe^{2+} + H^+,$$
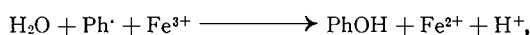
suggested by Baxendale because such a step with reference to our reaction system would mean that the rate of polymerization would be proportional to the first power of light intensity. On the other hand we have observed in our polymer reactions that the rate of polymerization is always proportional to the light intensity raised to the power half which means that the termination involves two chain radicals but never a chain radical and an ion like Fe^{3+} or an ion pair like $Fe^{3+}X^-$ (X = Cl or OH), as suggested by Baxendale (14), or $FeCl_3$ molecule and a chain radical as suggested by Bamford (16).

Secondly Baxendale has produced evidence that the secondary back reaction $Fe^{2+}+OH \longrightarrow Fe^{3+}+OH^-$ is negligible in his reaction system. On the other hand the existence of this back reaction in photochemical polymerization in aqueous medium using ion pairs as photosensitizers is well established in our system and others already reported (6, 7, 8, 9). The fall in dFe^{2+}/dt with time as well as the influence of initially added Fe^{2+} on dFe^{2+}/dt have provided strong evidence in favor of such a reaction. Baxendale and Magee (14) are unable to account for the imbalance between ferrous ion produced and the oxidation products of benzene but they are of the opinion that the consumption of free radicals by impurities in the system is of no importance; however, we have strong evidence in favor of the consumption of radicals by impurities in our system involving polymer formation (17).

(iii) The influence of light intensity was assessed by plotting $(dFe^{2+}/dt)(1+(k_0[Fe^{2+}])/k_t[M]$ against the light intensity (Fig. 5), with k_0/k_t values obtained by the procedure described above.

In accordance with the reaction scheme the rate of disappearance of monomer when $k_t[M] \gg k_0[Fe^{2+}]$ is:

[2]
$$\frac{-dM}{dt} = \frac{k_p}{k_t^{\frac{1}{2}}} \left(\frac{k_s k_\epsilon I}{k_d+k_s}\right)^{\frac{1}{2}} [M] \, .$$

Figs. 2, 6, and 9 confirm the linear relationship between $-dM/dt$ and (a) $k_\epsilon^{1/2}$, (b) $I^{1/2}$, and (c) [M]. Termination of active polymer by OH or Cl free radicals would lead to $-dM/dt$ dependent on $[M]^2$ and independent of I. Experimental results thus appear to support the mechanism of termination by interaction of active polymer ends.

If termination of polymer by recombination is assumed the chain length, n, is given by:

[3a]
$$n = \frac{2k_p}{k_t^{\frac{1}{2}}}\left(\frac{k_d+k_s}{k_s k_\epsilon I}\right)^{\frac{1}{2}}[M]$$

or by

[3b]
$$n = -(2dM/dt) \div (dFe^{2+}/dt).$$

Values of n found by viscosity measurements are compared with those calculated from equation [3b] in Table II. The satisfactory agreement between the observed and

TABLE II

CHAIN LENGTH OF POLYMETHYL ACRYLATE INITIATED
BY $Fe^{3+}OH^-$ AND $Fe^{3+}Cl^-$

	Chain length $\times 10^{-3}$	
Initiator	Calculated (Equation 3b)	Observed (viscometry)
$Fe^{3+}Cl^-$	0.69	0.94
	0.93	1.24
	3.30	3.93
$Fe^{3+}OH^-$	1.60	1.62
	1.91	2.36
	3.17	3.46

calculated chain lengths is strong evidence in support of the recombination mechanism for termination of polymer. The applicability of equation [3a] to the experimental results has been tested by plotting (a) n vs. [M] (Fig. 10), (b) n vs. $k_\epsilon^{-1/2}$ (Fig. 3), and (c) n vs. $I^{-1/2}$ (Fig. 7), all of which gave linear relationships.

Finally, from the previous estimates of $k_s/(k_d+k_s)$, values of $k_p/k_t^{1/2}$ were calculated by various methods. The results are recorded in Table III. These values of $k_p/k_t^{1/2}$

TABLE III

$k_p/k_t^{1/2}$ VALUES (LITER/MOLE)$^{-1/2}$ SEC.$^{-1/2}$ FOR METHYL ACRYLATE POLYMERIZATION

Initiator	Method						Mean
	$-dM/dt$ vs. [M]	$-dM/dt$ vs. $k_\epsilon^{1/2}$	$-dM/dt$ vs. $I^{1/2}$	n vs. $k_\epsilon^{-1/2}$	n vs. $I^{-1/2}$	n vs. [M]	
$Fe^{3+}OH^-$	0.432	0.402	0.392	0.77*	0.757*	0.453	0.42
$Fe^{3+}Cl^-$	0.272	0.276	0.145	0.123	0.6*	0.782*	0.20

*Not used in calculating mean.

relate to aqueous solution and it does not appear profitable to make comparisons with values reported for bulk or solution polymerization because of various factors, as yet unknown, operating in aqueous medium.

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