Kinetics of Reactions between Chloride Radicals from Photo-excited Ion-pair $Fe^{+3}Cl^-$ and Vinyl Monomers in Aqueous Solution

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ABSTRACT

Using the System, Ion-pair $Fe^{3+}Cl^-$ Vinyl monomer, in aqueous solution a new method of photo-polymerization of vinyl monomers is described. Light absorption by the photochemically active ion-pair $Fe^{+3}Cl^-$, leads to an electron transfer reaction involving reduction of the cation and oxidation of Cl^- to a free radical Cl which initiates polymerization. Kinetics of the reaction were followed by a study of the dependence of (a) light absorption fraction by the ion-pair, (b) light intensity, (c) concentration of monomer, (d) initially added ferrous and (e) quantum yields with regard to ferrous production and monomer disappearance upon (i) Rate of ferrous ion production, (ii) overall rate of Polymerization and (iii) chain-length of polymers. A prima facie reaction scheme was put forward. Examination of the experimental results in the light of the suggested scheme revealed that Cl radicals initiated polymerization and recombination of the active chain endings terminated Polymerization.

Rabinowitch and Stockmayer (1942) in their investigation on the ferric 'association' or 'ion-pair' complexes indicated that a solution of ferric chloride contained in addition to the neutral species $Fe(Cl)_3$, the ion pairs, $Fe^{3+}OH^-$, $Fe^{3+}Cl^-$, $Fe^{3+}Cl_2^{2-}$, $Fe^{3+}Cl_3^{3-}$, $Fe^{3+}Cl_4^{4-}$, $Fe^{3+}Cl_5^{5-}$, $Fe^{3+}Cl_6^{6-}$, etc. The yellow-green-brown colours of ferric chloride solutions were attributed to the presence of one or all the ion pairs. They interpreted the absorption spectra of $Fe^{3+}X^-$ ($X = OH$, Halide ion, etc.) as electron transfer spectra $Fe^{3+}X^- \xrightarrow{h\nu} Fe^{2+}X$, and the difference in the maxima of any two spectra corresponded to the difference in the electron affinities plus solvation energies of the respective anions. Rabinowitch (1942) therefore predicted occurrence of free radicals

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or atoms during irradiation of aqueous ferric halide solutions. Evans and Uri (1949) showed that such free radicals initiated polymerization of Vinyl compounds. Evans, Santappa and Uri (1951) have briefly reported on the polymerization of Vinyl compounds in aqueous solution. This paper (Santappa, 1951) presents a detailed Kinetic behaviour of the ion-pair $Fe^{3+}Cl^-$ as a photosensitizer in the polymerization of vinyl monomers, chiefly methylmethacrylate, acrylonitrile and to some extent methacrylic acid.

EXPERIMENTAL

Optical arrangements :—The light source was a 250 watt high pressure B.T.H. mercury vapour lamp, the size of the arc being 3.75 mm. $\times 1.5$ mm. The beam was rendered parallel by a condenser lens and then passed through suitable filters (1946) to isolate 313 mμ or 365 mμ. The monochromatic light beam was then used to irradiate the system $Fe^{3+}Cl^-$ (Ferric perchlorate + perchloric acid + hydrochloric acid) and vinyl monomer contained in a cell (capacity 75 ml, 50 mm. diameter and 46 mm. optical depth) which was mounted in a thermostat at $25 \pm 0.1°$ C.

Purity of reagents :—Ferric perchlorate was prepared from precipitated brown ferric oxide and perchloric acid. Monomers were purified after removal of stabilizers by repeated distillation in an atmosphere of nitrogen. Feiser's (1924) solution was used for deoxygenating nitrogen which was used to deaerate the solutions before irradiation.

Estimations and determinations :—Ferric ion concentration was determined by Zimmer Mann-Reinhardt standard procedure. Ferrous ion (dFe^{+2}/dt) was determined colorimetrically with O-Phenanthroline in Hilger Spekkar Colorimeter. Rate of monomer disappearance (dM/dt) was determined either by the weight of the purified and dried polymer or by the determination of monomer concentration before and after irradiation of the solution. Chain lengths of methyl methacrylate polymers (n) were determined viscometrically according to Baxendale, ByWater & Evan's (1946) method. Light absorption fraction (k_ε) by the complex $Fe^{3+}Cl^-$ could be calculated (1954) or measured spectrophotometrically. The lamp output or intensity of light (I) was determined actinometrically (Bowen, 1946) using uranium oxalate solution. Variation of light intensity was achieved by using an Iris

diaphragm in front of the lamp. Concentration of methyl methacrylate or methacrylic acid (M) was determined by bromine addition and after adding potassium iodide, titration against standard sodium thiosulphate.

Experimental Results :— (i) Light Absorption fraction (k_ε) by the ion pair: k_ε and dFe/dt. The concentration of $Fe^{3+}Cl^-$ and therefore the value of k_ε depends on the equilibrium $Fe^{3+}Cl^- + OH^-$; $\rightleftharpoons Fe^{3+}Cl^- + OH^-$; in other words k_ε is dependent on ferric ion concentration. Table 1 gives variation k_ε with $[Fe^{3+}]$ as well as variation of dFe^{+2}/dt and dM/dt with k_ε.

TABLE 1.

Data for k_ε and dFe^{+2}/dt; [Methylmethacrylate] $= 0\cdot1$ M; [HCl] $= 0\cdot05$N; Time of irradiation $= 1\cdot00$ hr.;

I, Intensity of light $= 6\cdot5 \times 10^{-5}$ N$h\nu$/hr.

Data for k and dM/dt; [Methylmethacrylate] $= 0\cdot08$ M;

I $= 3\cdot8 \times 10^{-5}$ N$h\nu$/hr.

$[Fe^{3+}]$	k_ε	$k^{\frac{1}{2}}_\varepsilon$	dFe^{2+}/dt (moles/hr) $\times 10^6$	dM/dt (moles/hr) $\times 10^3$
5×10^{-3}	$0\cdot88$		$9\cdot8$	
2×10^{-3}	$0\cdot87$		$9\cdot5$	
10^{-3}	$0\cdot86$	$0\cdot93$	$8\cdot3$	$3\cdot2$
5×10^{-4}	$0\cdot75$		$6\cdot5$	
2×10^{-4}	$0\cdot46$		$4\cdot0$	
10^{-4}	$0\cdot24$	$0\cdot49$	$1\cdot6$	$2\cdot8$
5×10^{-5}	$0\cdot15$	$0\cdot39$	$0\cdot9$	$1\cdot9$
2×10^{-5}	$0\cdot09$	$0\cdot3$	$0\cdot8$	$1\cdot1$

(b) k_e and dM/dt: Variation of dM/dt for Methylmethacrylate with $[Fe^{3+}]^{\frac{1}{2}}$ is given in Table 2 for two intensities.

TABLE 2

Intensity $Nh\nu/hr.$ $\times 10^5$	$[Fe^{3+}]^{\frac{1}{2}}$ $\times 10^3$	dM/dt (moles/hr.) $\times 10^3$
11·2	100	3·5
	31·6	3·05
	10·0	2·8
	6·33	1·9
	4·47	1·6
	3·16	1·0
	2·0	0·55
	1·4	0·25
6·8	31·6	2·04
	10	2·15
	6·33	1·42
	4·47	0·86
	3·16	0·62
	2·0	0·35

(c) k_e & Chain length (n): Fig. 1 graph A shows the linear variation of (n) against $k_e^{-\frac{1}{2}}$. $k_p/k_i^{\frac{1}{2}} = 1·3 - 1·4$ has been evaluated from the graph A. (For significance of k_p & k_i see reaction scheme under discussion).

(ii) *Light intensity* (I): I and dFe^{2+}/dt; Results between light intensity and dFe^{2+}/dt show that for higher intensities, say

above 5×10^{-5} Nhν/hr., rate of ferrous ion falls. This falling off of ferrous is due to dark back reaction between ferrous ions and chloride radicals. It will be seen in the discussion part that when this dark back reaction is taken into account the actual rate of ferrous production will be $dFe^{2+}/dt \left[1 + \dfrac{k_o[Fe^{2+}]}{k_i[M]} \right]$ where k_o & k_i are rate constants for dark back reaction and initiation of polymerization respectively and $[Fe^{2+}]$ is called 'mean ferrous'—this will be discussed at great length elsewhere in this paper but it will be sufficient at this stage to say that there was a more regular variation between I and $dFe^{2+}/dt \left[1 + \dfrac{k_o[Fe^{2+}]}{k_i[M]} \right]$ (Table 3) than between I and dFe^{+2}/dt.

TABLE 3

$[Fe^{3+}]_o = 4 \times 10^{-5}$ M; [HCl] $= 0.05$ N; pH $= 1.3$

Intensity (Nhν/hr) $\times 10^5$	dFe^{2+}/dt (moles/hr) $\times 10^6$	Mean (Fe^{2+}) (molar) $\times 10^6$	dFe^{2+}/dt ($\times 10^6$)
8	0.97	6.94	1.50
6.8	0.80	5.72	1.16
5.4	0.69	4.93	0.96
3.3	0.45	3.22	0.57
2.04	0.30	2.15	0.35
1.23	0.20	1.43	0.23
0.63	0.155	1.11	0.17

(b) I & dM/dt: dM/dt was found to depend on the square root of the intensity of light (Table 4).

(c) I & (n): Chain length of the polymer varied with the reciprocal of the square root of light intensity (Graph B) (Fig. 1). $k_p/k_t^{\frac{1}{2}}$ has been evaluated as ≈ 1.0.

TABLE 4

$[HCl] = 0.05$ N; pH $= 1.3$; [Acrylonitrile] $= 1.0$ M;

[Methylmethacrylate] $= 0.1$ M.

$[Fe^{3+}]_0^{1/2}$	$(Nh\nu/hr)^{1/2}$ Intensity $\times 10^3$	dM/dt (moles/hr.) $\times 10^3$	
		Methylmetha-crylate.	Acrylo-nitrile
4×10^5	8.22	2.09	1.7
„	5.75	2.10	1.18
„	4.53	1.60	0.97
„	2.50	0.80	0.45
„	1.25	0.42	—
2×10^5	10.58	1.7	—
„	8.90	1.5	—
„	6.10	1.0	—
„	1.97	0.25	—
10^2	11.5	3.5	—
„	8.37	2.2	—
„	4.42	1.25	—
„	2.62	0.50	—

(iii)   *Change of monomer concentration* [M]; [M] & $d\mathrm{Fe}^{2+}/dt$:
An accurate investigation of $d\mathrm{Fe}^{+2}/dt$ with [M] proved difficult
because at very low monomer concentrations or even in the
absence of any monomer the rate of ferrous production was more
or less as high as at higher monomer concentrations. This is to
be attributed to reactions of traces or organic impurities in distilled
water or the reagents in the System with the Chloride radicals.
This aspect of impurities which Kolthoff & Medalia (1949) as well

as Barb, Baxendale, Hargrave (1951) have recognised in the System, Fe^{2+}—H_2O_2—substrate, has been dealt with elsewhere by the author (1954) at greater length as applied to our system $Fe^{3+}X^-$—Vinylmonomer. The results for invariability of dFe^{2+}/dt with type and concentration of monomer at all pHs but variation with intensities or concentration of ferric ion are given in Table 5.

TABLE 5

[Fe³⁺]	Intensity (Nhν/hr) × 10⁵	[Monomer]	pH.	$\dfrac{dFe^{2+}}{dt}$ (moles/hr) × 10⁶
10^{-2}	·13·2	Acrylonitrile 1·0; 0·8-0·02 M and also nil monomer.	2; 1·7; 1·5-0·8	16-17
10^{-3}	6·9	„	„	8- 9
„	„	Methylmethacrylate 0·1 to 10 M as well as nil mono-mer.	„	8- 9
4×10^{-5}	„	„		0·6-0·8

(b)   [M] and dM/dt: dM/dt varied more regularly with [M] (Table 6). With regard to both dM/dt as well as dFe^{+2}/dt with [M] behaviour of methacrylic acid has been found to differ slightly from methylmethacrylate or acrylonitrile. This anamolous behaviour of methacrylic acid is perhaps due to its poly-electrolyte character. Fig. 2 Graphs A & B indicate that dM/dt varies more regularly with [M] rather than [M²] for acrylonitrile and Graph C represents the anamolous behaviour of methacrylic acid.

(c)   [M] and (n): The result for variation of (n) with [M] are given in Table 7 (Graph C Figure 1) and $k_p/k_t^{\frac{1}{2}}$ has been evaluated as 1-1·2.

TABLE 6

Monomer	[M] molar	dM/dt (moles/hr) $\times 10^3$	$(dFo^{2+}/dt) \times 10^6$
Acrylonitrile	1·0	2·99	0·7 to 0·8
	0·6	1·72	"
	0·3	0·72	"
	0·1	0·31	"
	0·05	0·12	"
Methylmethacrylate	$7·6 \times 10^{-2}$	1·42	"
	$4·6 \times 10^{-2}$	0·74	"
	$3·0 \times 10^{-2}$	0·55	"
	$1·9 \times 10^{-2}$	0·30	"
	$9·7 \times 10^{-3}$	0·16	"
	$5·0 \times 10^{-3}$	0·075	"
Methacrylic acid	$9·5 \times 10^{-3}$	0·09	1·1 to 1·2
	$1·4 \times 10^{-2}$	0·15	"
	$5·9 \times 10^{-2}$	1·09	"
	0·12	2·19	"
	0·28	2·97	"
	0·43	"	"
	0·70	"	"
	0·9	"	"
	5·0	8·4	"

TABLE 7

$[Fe^{+3}] = 10^{-4}M$; $k_c = 0\cdot24$; $I = 6\cdot8 \times 10^{-5} Nh\nu$ units/hr.

Monomer = Methylmethacrylate.

[M] molar	Chain length (n)	
	Measured	Calculated
0·095	2588	2180
0·075	1778	1634
0·05	1038	1090
0·025	496	457
0·005	327	109

(iv)   Effect of Ferrous accumulated in the reaction or ferrous initially added:

It was found that dFe^{+2}/dt decreased as the mean time interval or 'mean ferrous ion' increased. 'Mean ferrous ion' may be computed from (1) ferrous ion accumulating in the reaction at a particular intensity over an interval of time or (2) ferrous accumulating at different intensities for the same time interval or (3) ferrous initially added. The decrease of dFe^{+2}/dt must be attributed to dark back reaction between Fe^{+2} and Cl giving $Fe^{+3}Cl^{-}$. Mean $[Fe^{+2}]$ is taken as ferrous present before irradiation of the System plus half ferrous produced during irradiation. From the values of mean $[Fe^{+2}]$, $[M]$ and dFe^{+2}/dt, values for k_o/k_t as well as $k_s/k_s + k_d$ for methylmethacrylate and acrylonitrile could be calculated—(Table 8). (For significance of k_o, k_t, k_s, k_d, see reaction scheme under discussion). The decrease of dFe^{+2}/dt with (a) time, (b) increase of mean ferrous ion from initially added ferrous and (c) increase of mean ferrous at different intensities are represented by Graphs A, B and C respectively in Fig. 3.

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TABLE 8

For Methylmethacrylate, $I = 4.8 \times 10^{-5} Nh\nu/\text{hr}$, and

For Acrylonitrile, $I = 6.9 \times 10^{-5} Nh\nu/\text{hr}$.

Monomer	Initially added $[Fe^{2+}]$ (molar) $\times 10^5$	Fe^{2+} (molar) $\times 10^5$ (accumulated)	Fe^{2+} (molar) $\times 10^5$ produced	Mean Fe^{2+} (molar) $\times 10^5$	$\dfrac{dFe^2}{dt} \times 10^6$	$\dfrac{k_o}{k_i}$	$\dfrac{k_s}{k_s + k_d}$
0.1 M. Methylmethacrylate ..	nil	18.2	55.5	46	4.35	48	0.11
1.0 M. Acrylonitrile ..	0		5.6	2.8	1.82		
	5		3.7	6.8	1.51		
	7.5		3.9	9.45	1.37	6×10^3	0.13
	10		3.7	11.85	1.3		
	25 20						

Ferrous produced very small in comparison with initially added Fe^{++}

(v) *Quantum yield*:—Quantum yield $\gamma_{Fe^{+2}}$ with regard to dFe^{2+}/dt in case of $Fe^{3+}Cl^-$ was found to vary with $[Fe^{3+}]$, attaining a maximum value of 0.13. This value was found to be independent of type and concentration of the monomers as well as wavelengths $313\ m\mu$ or $365\ m\mu$ though it dropped steeply in the visible. Quantum yield (γ_M) with regard to dM/dt was found to depend on (i) the type and concentration of the monomer, (ii) light intensity. Results for $\gamma_{Fe^{+2}}$ and γ_M are given in Table 9.
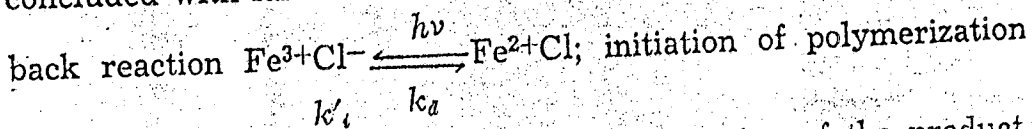
TABLE 9

$[Fe^{3+}]$	Monomer	Intensity $Nh\nu/hr$ $\times 10^5$	$\gamma_{Fe^{+2}}$	γ_M
10^{-2}	Methylmethacrylate (0.1 M)	13.2	0.13	26.5
10^{-2}	"	6.9	0.13	
10^{-3}	"	13.2	0.12	26.8
10^{-3}	"	6.9	0.12	42
10^{-4}	"	13.2	0.10	88
10^{-4}	"	6.9	0.10	130
4×10^{-5}		13.2	0.09	113
"	"	6.9	0.1	137
"	Methylmethacrylate (0.005 M)	6.9	0.10	7.3
"	Acrylonitrile 1.0 M	6.9	0.1	290
	0.05 M	"	0.1	12
"	Methacrylic acid 1.0 M	"	0.1	300
	0.009	"	0.1	8

DISCUSSION

The energetics of the light absorption process $Fe^{3+}Cl^- \overset{h\nu}{\rightleftharpoons} Fe^{2+}Cl$ have been well discussed by Rabinowitch and Stockmayer (1942) and subsequently by Evans & Uri (1949). It has also been sug-

gested by Evans, Santappa and Uri (1951) that after optical tran-sition in $Fe^{3+}X^-$ ($X = OH$, Cl, etc.) according to Franck Condon principle, $Fe^{2+}X$ (*aq*) would be left in non-equilibrium configura-tion especially of the hydration shell and would therefore dosso-ciated into Fe^{+2} plus X with a repulsion energy of ~ 50 kcal. X radicals thus produced lead to polymerization of Vinyl com-pounds. The experimental data presented may now be examined in the light of the following reaction scheme which is assumed and then the modes of initiation and terminating mechanisms may be concluded with fair certainty. Light absorption and primary dark back reaction $Fe^{3+}Cl^- \underset{k'_i}{\overset{h\nu}{\rightleftharpoons}} \overset{k_d}{} Fe^{2+}Cl$; initiation of polymerization by $Fe^{2+}Cl$; $Fe^{2+}Cl \rightarrow Fe^{2+} + Cl-M-$; Separation of the product, $Fe^{2+}Cl \overset{k_s}{\rightarrow} Fe^{2+} + Cl$ and second dark back reaction, $Fe^{+2} + Cl \overset{k_o}{\rightarrow} Fe^{+3} + Cl^-$, k_i, k_p, k_{t1}, k_{t2}, k_t, are the rate constants for initiation by Cl radicals, propagation, termination by the radical $Fe^{2+}Cl$, ter-mination by the Cl radicals and termination by recombination of active endings respectively.

Assuming stationary concentrations for the radicals, $Fe^{2+}Cl$, Cl and the radical chains $Cl- (M)_n -$ where $M =$ Monomer and $n = 1$ to ∞, it can be shown if (i) $Fe^{2+}Cl$ initiates as well as ter-minates (disproportionation) the chains, then,

$$dFe^{2+}/dt = \frac{k_\varepsilon I k'_i [M]}{k_d} \text{ and } dM/dt = k_p k'_i [M]^2/k_{t1}$$

(ii) $Fe^{2+}Cl$ initiates and termination is by recombination, then dFe^2/dt is same as in (i) but $dM/dt = k_p[M]^{3/2}\{k'_i k_\varepsilon I/k_t k_d\}^{\frac{1}{2}}$

(iii) Cl radicals initiate as well as terminate (dispropor-tionation) the chains then,

$$dFe^{2+}/dt = \frac{k_s k_\varepsilon I}{k_d + k_s} \left\{ \frac{k_i[M]}{k_i[M] + k_o[Fe^{+2}]} \right\} .$$

and $dM/dt = k_p k_i [M]^2/k_{t2}$

(iv) Cl radical initiates but termination is by recombination then, dFe^2/dt is same as in (iii) but $dM/dt = \frac{k_p[M]}{k_t^{\frac{1}{2}}} \left(\frac{K_s k_\varepsilon I}{k_s + k_d} \right)^{\frac{1}{2}}$

If $Fe^{2+}Cl$ initiates polymerization then according to (i) or (ii)

quantum yield for ferrous ion must go on increasing as the concentration of monomer increases and must not attain a constant value below unity. On the other hand if Cl radicals initiate, then, according to (iii) or (iv) quantum yield for ferrous must go on increasing as the concentration of the monomer is increased and when $k_t[M] \gg k_o[Fe^{2+}]$, $\gamma_{Fe^{+2}}$ becomes independent of monomer concentration and is represented by a constant quantity, $k_s/(k_s + k_d)$. In our experiments with $Fe^{3+}Cl^-$ a constant quantum yield of $\sim 0\cdot10$ to $0\cdot13$ was obtained (Table 3, this value being almost independent of type and concentration of monomer. That $\gamma_{Fe^{+2}}$ is as high even in the absence of any monomer must be attributed to the reaction of Chloride radicals with organic impurities in the system and any possibility of photo-oxidation of water at the wave lengths and intensities of lights used in the experiments, must be very remote if not completely excluded. Therefore rate of ferrous production will be correctly represented by (iii) or (iv),

$$dFe^{2+}/dt = \frac{k_s k_\varepsilon \; I}{k_d + k_s} \left\{ \frac{k_t[M]}{k_t[M] + k_o[Fe^{2+}]} \right\}$$

The applicability of this equation was further confirmed by
(1) a regular variation of dFe^{2+}/dt with k_ε (Table 1).

(2) Variation of mean Fe^{2+} with dFe^{2+}/dt (Table 8) according to the equation $1/(dFe^{2+}/dt) = \dfrac{k_s + k_d}{k_s \; k_\varepsilon \; I} \left(1 + \dfrac{k_o \, [Fe^{2+}]}{k_t[M]} \right)$ from which (a) k_o/k_t for methylmethacrylate = 48; for acrylonitrile = 6×10^3 and (b) $\dfrac{k_s}{k_s + k_d} \approx 0\cdot10$ to $0\cdot13$ have been calculated.

And (3) non-uniform variation of dFe^{2+}/dt with light intensity because of secondary dark back reaction at higher light intensities. But with $dFe^{2+}/dt \left(1 + \dfrac{k_o \, (Fe^{2+})}{k_t[M]} \right)$ which takes into account the dark back reaction uniform variation could be observed even at higher light intensities (Table 3). It is therefore concluded that Cl radicals initiate polymerization.
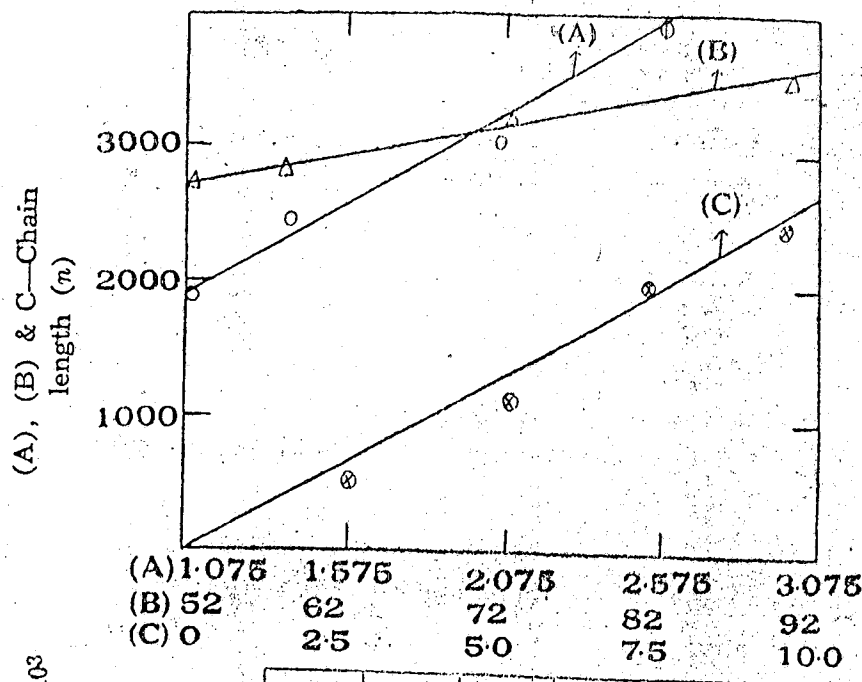
Fig. 1.

(A) $(k_\varepsilon)^{-1/2}$;

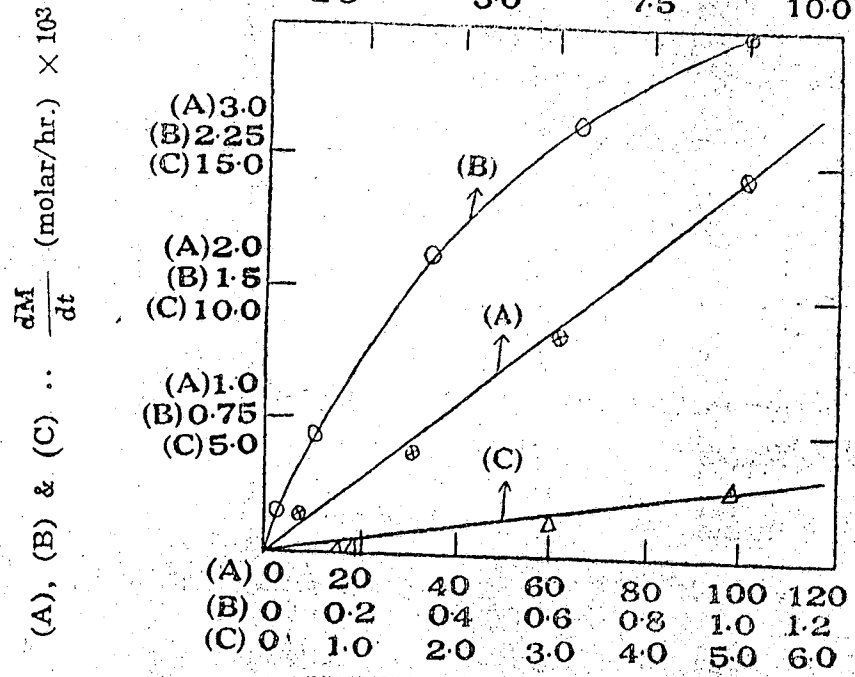(B) (Intensity)$^{-1/2}$, $\times 10^{-2}$;

(C) $[M] \times 10^2$.

(A), (B) & C—Chain length (n)

(A) 1·075	1·575	2·075	2·575	3·075
(B) 52	62	72	82	92
(C) 0	2·5	5·0	7·5	10·0

Fig. 2.

(A) .. $[M]$ (molar) $\times 10^2$;

(B) .. $[M]^2$ (molar)^2

(C) (molar) $\times 10^3$

(A), (B) & (C) .. $\dfrac{dM}{dt}$ (molar/hr.) $\times 10^3$

(A) 3·0 (B) 2·25 (C) 15·0

(A) 2·0 (B) 1·5 (C) 10·0

(A) 1·0 (B) 0·75 (C) 5·0

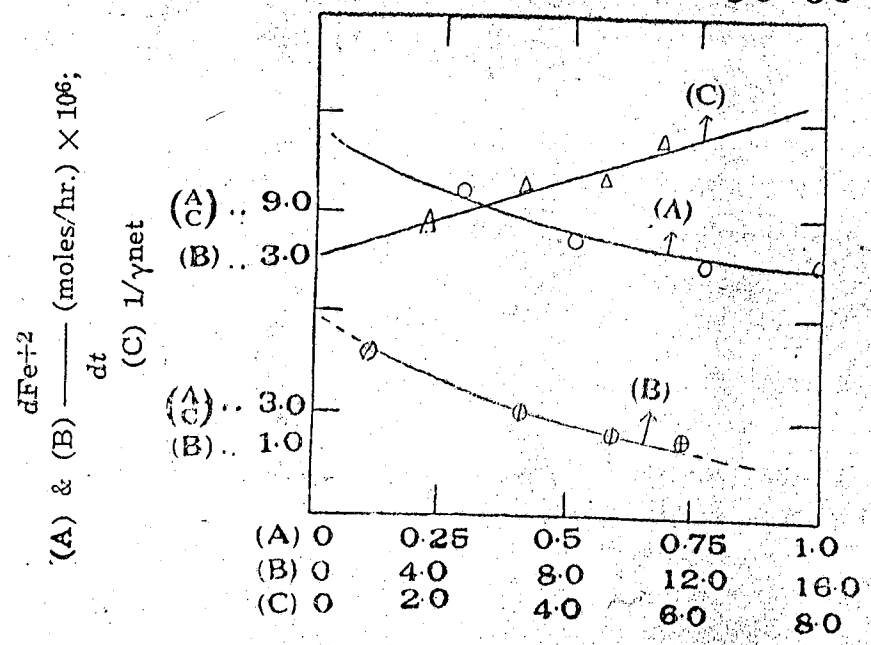|						
(A) 0	20	40	60	80	100	120
(B) 0	0·2	0·4	0·6	0·8	1·0	1·2
(C) 0	1·0	2·0	3·0	4·0	5·0	6·0

Fig. 3.

(A) Meantime on hours;

(B) Mean Fe^{+2} from initially added Fe^{+2};

(C) Mean Fe^{+2} from different intensities.

(A) & (B) $\dfrac{dFe^{+2}}{dt}$ (moles/hr.) $\times 10^6$;

(C) $1/\gamma_{net}$

$\begin{pmatrix} A \\ C \end{pmatrix}$ .. 9·0

(B) .. 3·0

$\begin{pmatrix} A \\ C \end{pmatrix}$ .. 3·0

(B) .. 1·0

(A) 0	0·25	0·5	0·75	1·0
(B) 0	4·0	8·0	12·0	16·0
(C) 0	2·0	4·0	6·0	8·0

LEGENDS FOR THE FIGURES

Fig. 1. Curve A shows the variation of chainlength (n) of methylmethacrylate polymer with the reciprocal of square root of light absorption fraction $(k\epsilon^{-1/2})$ for the ion-pair $Fe^{+3}Cl^{-}$.

Curve B shows the linear variation of chainlength of methylmethacrylate polymer with reciprocal square root light intensity $(I^{-1/2})$ when $Fe^{+3}Cl^{-}$ has been used.

Curve C shows the dependence of chainlength of methylmethacrylate polymer on the concentration of methylmethacrylate monomer with $Fe^{+3}Cl^{-}$ ion pair; $I = 6 \cdot 8 \times 10^{-5} Nh\nu/hr.$ and $[Fe^{+3}] = 10^{-4}M.$

Fig. 2. Graph A shows the linear relation between rate of monomer disappearance and first power of monomer concentration for the System $Fe^{+3}Cl^{-}$—acrylonitrile; $[Fe^{+3}] = 4 \times 10^{-5}M;$ $[HCl] = 0 \cdot 5$ N; $I = 6 \cdot 8 \times 10^{-5} Nh\nu/hr.$

Graph B shows the non-linear relation between rate of monomer disappearance and square of monomer concentration ceteris paribus as graph A.

Graph C represents the relation between dM/dt and $[M]$ and tendency for anamolous behaviour for higher concentration of methacrylic acid.

Fig. 3. Curve A shows the gradual decrease in the rate of ferrous ion production as the mean time interval increases;

$[Fe^{+3}] = 10^{-2}M;$ Intensity $= 7 \cdot 7 \times 10^{5} Nh\nu/hr.;$

[Acrylonitrile] $= 1 \cdot 2$ M.

Curve B shows the decrease of rate ferrous ion production with the increase of 'mean ferrous ion'; $[Fe^{3+}] = 10^{-4}M;$

Intensity $= 6 \cdot 9 \times 10^{-5} Nh\nu/hr;$ Acrylonitrile; pH $= 1 \cdot 3.$

Fig. 3. Graph C represents the linear relation between $1/\gamma$ net and 'mean ferrous ion' calculated from different intensities; $[Fe^{+3}] = 4 \times 10^{-5}M;$ Methylmethacrylate; pH $= 1 \cdot 3.$

To decide the question whether terminating mechanism is one of (a) disproportionation by the radicals $Fe^{2+}Cl$ or Cl or (b) recombination of active endings, we have to consider four equations for dM/dt under (i), (ii), (iii) and (iv). It was easy to conclude that termination was by recombination of active endings when Cl radicals initiated the chains and results confirmed the equation under (iii)

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

The following arguments could be adduced in support of the recombination mechanism. Regular variation of (1) $k_e^{\frac{1}{2}}$ with dM/dt (Table 1); (2) I with dM/dt (Table 4) and (3) $[M]$ with dM/dt (Table 6). From (1), (2), (3) by making use of known values $k_s/(k_s+k_d)$ as well as k_e I it was possible to calculate the values of $k_p/k_t^{\frac{1}{2}}$ for, acrylonitrile $= 0.156$; methylmethacrylate $= 1.0$ and for methacrylic acid $= 1.56$. It was also found by chlorine estimation of the polymethylmethacrylate that two chlorine atoms were present for each chain.

Further evidence for the terminating mechanism could be obtained by a knowledge of variation of chain-length of methylmethacrylate polymer with k_e I and $[M]$. If termination is by disproportionation then Chain length (n) would be represented by the ratio, $n = \frac{dM}{dt}/$ birth rate of the chains or $(dM/dt)\frac{dFe^{+2}}{dt}$.

On the other hand for termination by combination, $n = \frac{dM}{dt}/\frac{1}{2}$ birth rate of the chains or $\frac{dM}{dt}/\frac{1}{2}\frac{dFe^{+2}}{dt}$

Variations of chain length of polymethylmethacrylate with $[M]$, $K_e^{-\frac{1}{2}}$ as well as $I^{-\frac{1}{2}}$ were observed (Fig. 1). From the graphs in Fig. 1 with 'n' as a function of $K_e^{-\frac{1}{2}}$, $I^{-\frac{1}{2}}$ and $[M]$ values of $K_p/K_t^{\frac{1}{2}}$ have been evaluated as $1.2 - 1.3$ for methylmethacrylate. Further, the measured chain lengths of methyl methacrylate polymer from viscosities using Baxendale, Bywaters and Evans' Equation, could be compared with (n) calculated from the equation given above for chain length (Table 7). The foregoing discussion proves that termination is by recombination of the active endings.

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