

CHAPTER-III

Permanganate-E.D.T.A. and Permanganate-Oxalic
Acid as Redox Initiation Systems of Vinyl
Polymerization

Introduction

Permanganate cannot initiate aqueous vinyl polymerization by itself though it is reduced to Mn^{IV} stage in presence of the monomers and MnO_2 separates out. But if a reducing agent like oxalic acid is present in the system in sufficient excess for dissolution of MnO_2 , polymerization occurs and the colour of the solution changes from cherry red to yellow to practically colorless. Palit and Konar^{102,103} have studied the kinetics of the process, mentioned above and have concluded that as a result of the redox reaction between Mn^{4+} and oxalic acid carboxyl radicals, CO_2 and $Mn(III)$ oxalate complex are produced in the system. The cherry red $Mn(III)$ complex then decomposes slowly to form Mn^{2+} ions and carboxyl radicals and the latter initiates polymerization under favourable conditions. Since the initiating capacity of the system persists for quite a long time, even after complete decolorisation of the system, the generation of some sort of long-life free radical has been suspected; this is probably the case as "active" oxalic acid studied by Weiss¹⁰⁴.

It is rather well-known that ethylene diamine tetra-acetic acid is comparable to oxalic acid as regards to its reducing property. Besides, it has a strong complexing capacity with metal ions such as Ca, Mg, Zn, Mn etc. Yoshino et al¹⁰⁵ have actually been able to isolate a cherry red complex of Mn(III)-E.D.T.A. from a solution containing permanganate and E.D.T.A. and have also observed that the complex is transformed to colorless Mn(II)-E.D.T.A. form in presence of heat and light. So attempts have been made to use E.D.T.A. - KMnO_4 pair as a redox initiation system for aqueous polymerization of methyl methacrylate.

On addition of permanganate to an aqueous solution of monomer and sufficient excess of E.D.T.A. no precipitation of manganese dioxide occurs but a cherry-red colored solution is produced. This cherry-red colored solution is presumed to be due to Mn(III)-E.D.T.A. complex formation. This complex then acts as a slow and steady source of initiating free radicals, as indicated by the gradual color change of the medium to violet and light violet with progress of polymerization. Polymerization proceeds in precipitation phase and finally the solution becomes practically colorless as the whole Mn(III) is reduced to Mn(II) stage. The detailed kinetics of the process has been studied vis-a-vis endgroup analysis for elucidation of the mechanism involved. The endgroup analysis of the polymers initiated by permanganate-oxalic acid redox have also been carried out for the sake of

comparison of these two basically similar systems and to test the mechanism put forward by Palit and Konar¹⁰³ (based on kinetic study).

Comparative Study of Two Redox Initiating Systems
KMnO₄ - E.D.T.A. and KMnO₄ - Oxalic Acid

Kinetics of Polymerization

The results of kinetics of KMnO₄ - E.D.T.A. redox initiated aqueous polymerization of methyl methacrylate were presented in Table I and Figures V and VI. The yield curves (i.e. the % yield versus time in minutes) for varying initiator (KMnO₄) concentration at fixed monomer and activator (E.D.T.A.) concentration are given in Figure V. Logarithm of initial rate, R_p (in % yield per minute) versus logarithm of permanganate concentration has been plotted in Figure VI; the order of the reaction with respect to KMnO₄ comes out to be about 0.80. This probably indicates that termination in this system takes place both unimolecularly and through bimolecular collision between two chain radicals. This is in contrast with KMnO₄ - oxalic acid system where the KMnO₄(initiator) exponent changes from 1.0 to 0.5 with change in KMnO₄ concentration, as reported by Palit and Konar¹⁰³.

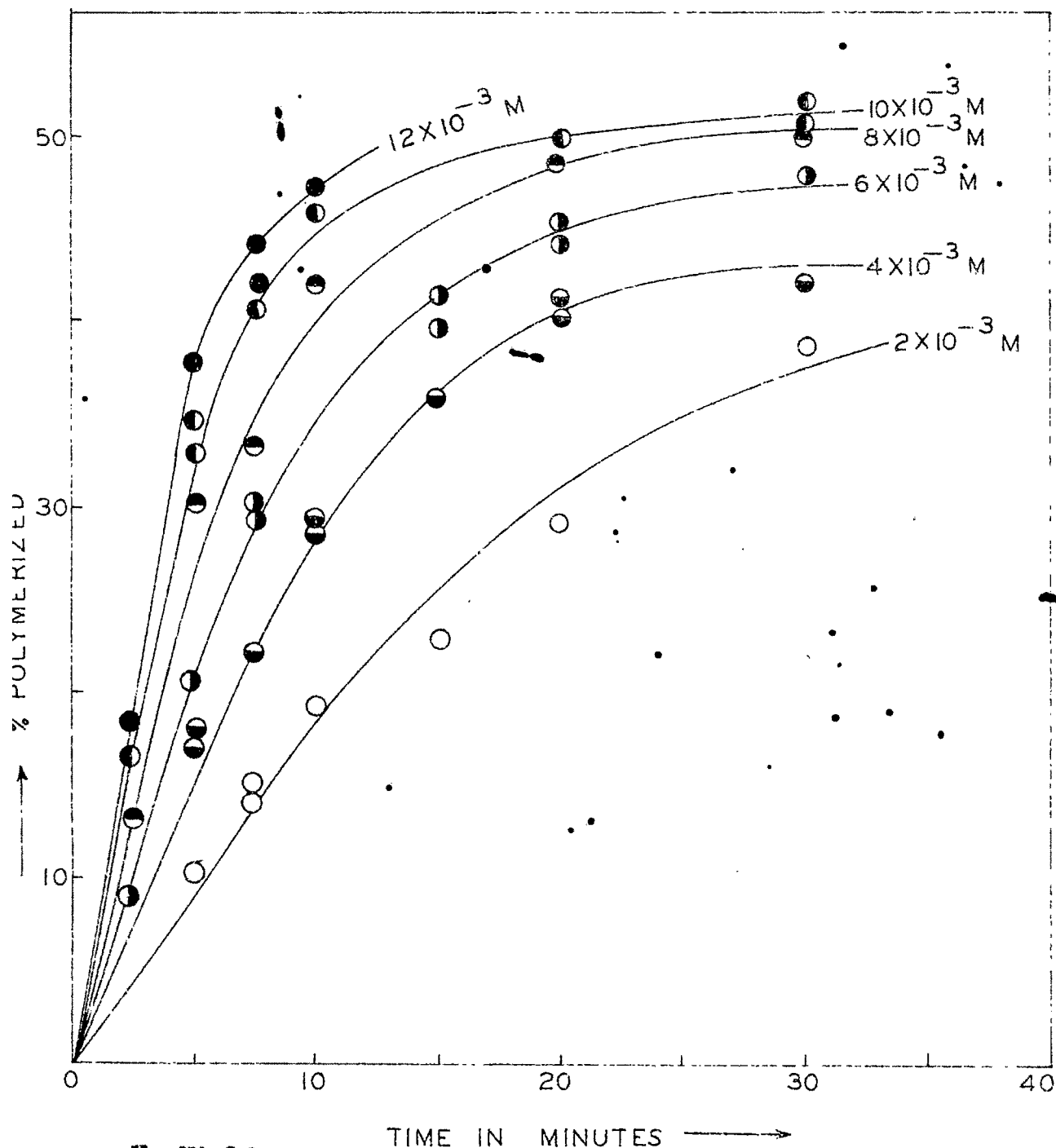


FIG. V- Yield curve in aqueous polymerization of MMA (0.094 m/l) with permanganate - E.D.T.A. initiation at E.D.T.A. concentration of 4×10^{-2} M and varying concentrations of permanganate. Temp. = $35 \pm 0.2^{\circ}\text{C}$.

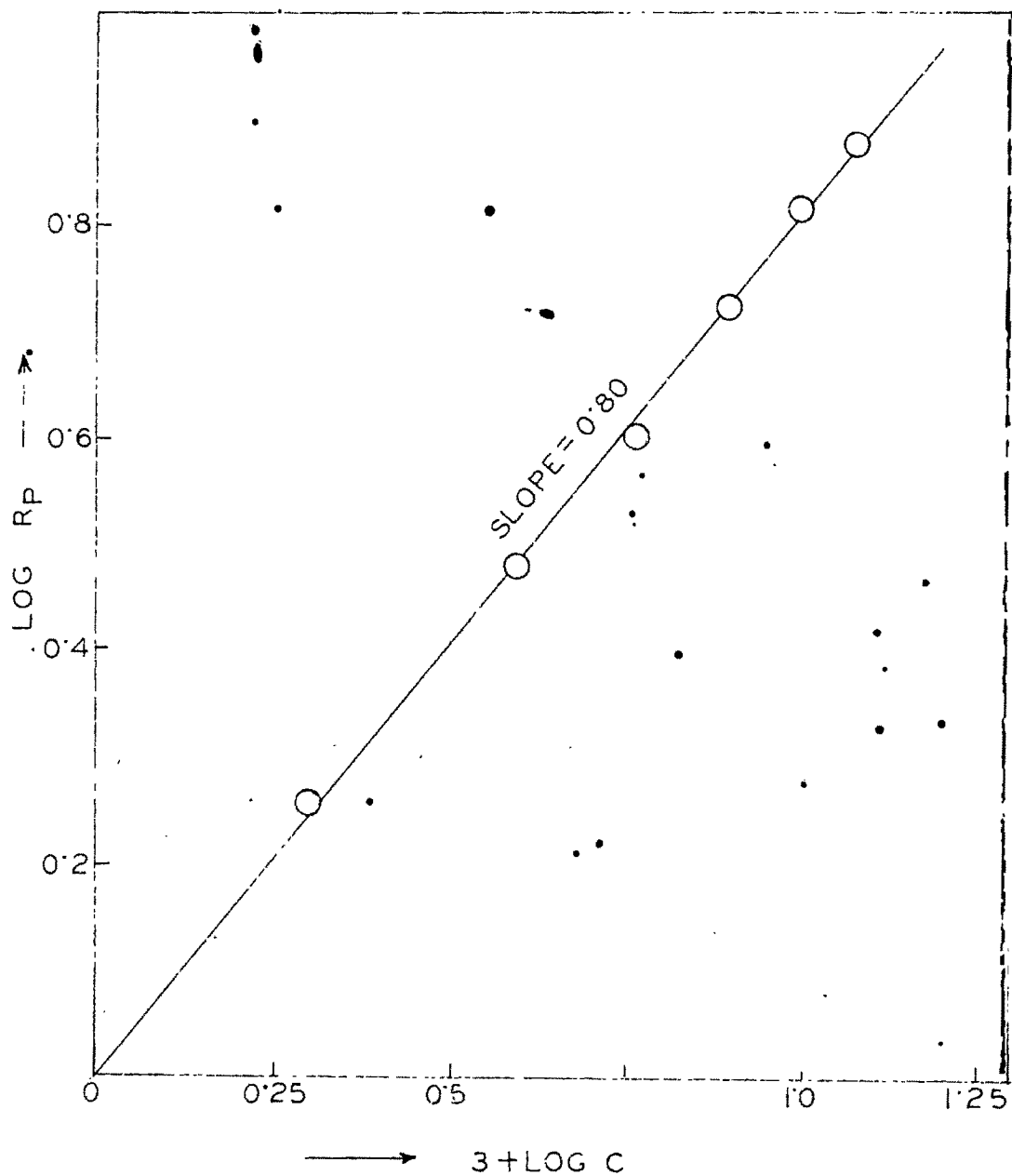


FIG. VI

Plot of the logarithm of initial rate, " R_p "
(in % polymerized/min) Vs. the logarithm of
catalyst concentration " c " (in m/l)

TABLE-I

Variation of the Rate of Polymerization of Methyl-
methacrylate with Initiator (KMnO₄) Concentration
in Aqueous Medium

System : MMA - 0.094 mole/litre ; Temp : 35 ± 0.2° C
 N₂ Atmosphere ; E.D.T.A. = 4 x 10⁻² mole/litre

KMnO ₄ m/l c x 10 ³	3 + log c	Rate of polymeriza- tion from initial slope. • R _p (% yield/minute)	log R _p	Initiator exponent
2.0	0.301	1.8	0.255	
4.0	0.602	3.0	0.477	
6.0	0.778	4.0	0.60	
8.0	0.903	5.3	0.721	0.80
10.0	1.0	6.5	0.813	
12.0	1.079	7.5	0.875	

Results of variation of E.D.T.A. concentration under otherwise constant conditions are shown in Figure VII. The rate of polymerization definitely shows some variation with variation of E.D.T.A. concentration, but in a peculiar way. As E.D.T.A. concentration is increased, rate of polymerization tends to increase, but on the otherhand, corresponding lowering of pH of the medium tends to reduce the rate. However, with increasing E.D.T.A. concentration, overall yield decreases, although initial rate may be relatively high. Similar observation was also made by Palit and Konar¹⁰³ in KMnO_4 - oxalic acid system.

The longer spread of the initial linear portion of the yield time curve and the slower rate of polymerization in case of Mn(III)-E.D.T.A. complex, compared to Mn(III)-oxalic acid complex indicate greater stability of the former under identical conditions. But the difference between these two complexes is only of degree and not of kind, because in both cases, Mn(III) is finally reduced to Mn(II) stage and the solution becomes colorless.

Endgroup Analysis

Result of endgroup analysis of poly(methyl methacrylate) obtained by aqueous initiation with KMnO_4 -oxalic acid redox and KMnO_4 -E.D.T.A. redox are presented in Tables II and III respectively. All the polymer samples exhibit a positive response (faint or intense depending on

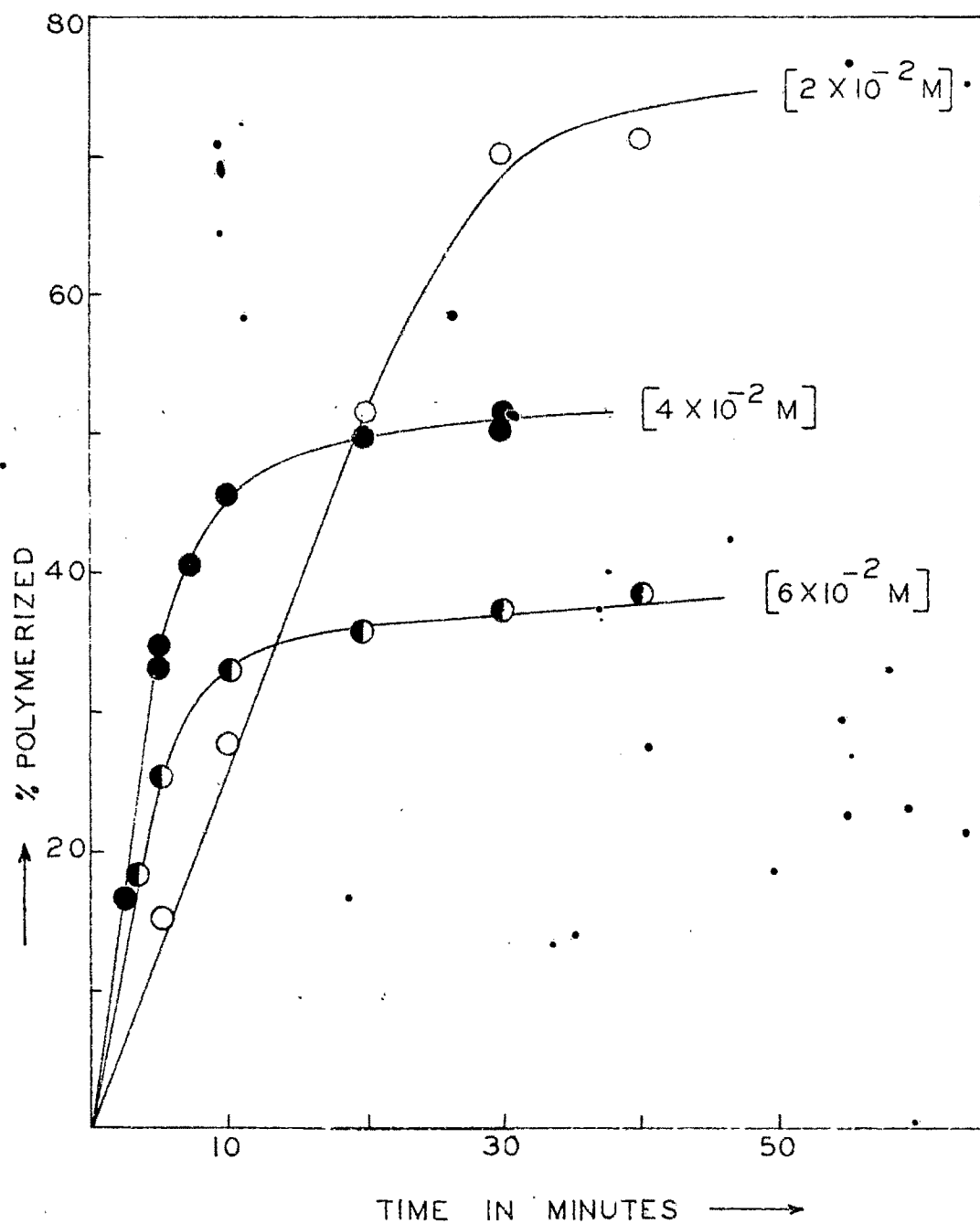


FIG. VII

Yield curve in aqueous polymerization of MMA (0.094 M/l) with permanganate - E.D.T.A. initiation at KMnO_4 concentration of 1×10^{-2} M and varying concentrations of E.D.T.A.

TABLE-II

Endgroup Analysis of Poly(methylmethacrylate) Initiated
by KMnO_4 - Oxalic Acid Redox

System : MMA - 0.094 mole/litre ; N_2 atmosphere ;
Aqueous Polymerization ; Temp.: 25-30°C

KMnO_4 m/l $\times 10^4$	Oxalic acid m/l $\times 10^3$	$[\eta]$	O.D. of 0.025% polymer solu- tion with rhodamine reagent		Endgroup/Chain		
			original	phtha- lated	COOH	OH	Total
0.2	5.0	1.70	0.44	-	1.5	-	-
0.5	5.0	1.10	0.465	0.495	1.5	0.60	2.10
1.0	5.0	0.70	0.495	0.55	1.20	0.80	2.0
2.0	5.0	0.50	0.602	-	1.71	-	-
5.0	5.0	0.35	0.69	0.74	1.54	0.28	1.82
5.0	10.0	0.31	0.57	0.75	0.76	0.84	1.60
5.0	20.0	0.40	0.55	0.67	0.94	0.76	1.70
5.0	30.0	0.53	-	0.64	-	-	2.16
10.0	5.0	0.22	0.80	1.02	1.15	0.65	1.80
20.0	5.0	0.20	0.81	1.15	1.00	0.90	1.90
20.0	10.0	0.15	1.02	1.49	1.10	0.87	1.97

TABLE-III

Endgroup Analysis of Poly(methylmethacrylate) initiated
by KMnO_4 - E.D.T.A. Redox

System : MMA - 0.094 mole/litre ; N_2 atmosphere ;
Aqueous Polymerization ; Temp.: 25-30°C

KMnO_4 m/l $\times 10^3$	E.D.T.A. [2] m/l $\times 10^2$	O.D. of 0.05% polymer solution with rhodamine reagent	Endgroup/Chain				
			Original	Phthalated	COOH	OH ⁻ Total	
2.0	4.0	1.25	0.44	0.53	0.50	1.38	1.88
3.0	4.0	1.10	0.465	0.56	0.75	1.17	1.92
4.0	4.0	0.85	0.47	0.58	0.60	1.00	1.60
5.0	2.5	0.85	0.505	0.64	0.90	1.10	2.0
5.0	3.0	0.60	0.54	0.77	0.74	1.22	1.96
5.0	4.0	0.75	0.585	-	1.35	-	-
10.0	4.0	0.49	0.665	0.84	1.10	0.70	1.80
12.0	4.0	0.40	0.80	0.92	1.28	0.40	1.68

initiator concentration) to rhodamine reagent, presumably due to the presence of carboxyl endgroups in them. Palit and Konar¹⁰² detected carboxyl endgroups in poly(methylmethacrylate) polymers initiated by KMnO_4 - oxalic acid redox and attributed it to the initiation by active oxalic acid radicals (carboxyl bearing radical generated according to Launer and Yost.^{106, 107} mechanism). In the present study the polymer is subjected to quantitative estimation of both carboxyl and hydroxyl endgroups. Experiments were performed at two different monomer concentrations (0.094 and 0.062 moles/litre respectively) (Tables II and IV) where rates of polymerization are almost identical as reported by Palit and Konar¹⁰³. The sum total of carboxyl and hydroxyl endgroup content in all these polymers generally lay between 1.5 to 2.0 per chain, but their respective proportion varied over a considerable range, and in a few cases, hydroxyl content was almost negligible. This endgroup picture is very similar to KMnO_4 - E.D.T.A. redox initiated polymers (Table III).

Since there is uncertainty as regards the presence of carboxyl endgroups in poly(methyl methacrylate), it being liable to acid hydrolysis experiments have been performed with styrene in emulsion phase in case of KMnO_4 - oxalic acid redox - initiation where no such possibility exists. The endgroup picture was found to be almost the same as in the case of poly(methyl methacrylate) (Table V). A strikingly

TABLE-IV

Endgroup Analysis of Poly(methylmethacrylate) Initiated
by KMnO_4 - Oxalic Acid Redox

System : MMA - 0.062 mole/litre ; N_2 atmosphere ;
• Aqueous Polymerization ; Temp. : 25-30°C

KMnO_4 m/l $\times 10^4$	Oxalic acid m/l $\times 10^3$	$[\eta]$	O.D. of 0.025% polymer solution with rhodamine reagent		Endgroup/Chain		
			Original	Phthalated	COOH	OH	Total
0.2	5.0	1.30	0.44	-	1.07	-	-
0.5	5.0	0.95	0.465	0.505	1.30	0.80	2.10
1.0	2.0	0.66	0.505	0.533	1.28	0.32	1.60
1.0	5.0	0.67	0.505	0.55	1.28	0.48	1.76
1.0	10.0	0.70	0.483	0.52	1.10	0.55	1.65
1.0	20.0	0.90	0.475	0.495	1.35	0.35	1.70
1.0	40.0	1.0	0.467	0.505	1.40	0.84	2.24
1.0	45.0	1.20	0.455	-	1.40	-	-
1.0	50.0	1.25	0.478	-	2.25	-	-
2.0	5.0	0.42	0.555	0.625	1.08	0.47	1.55
3.0	5.0	0.35	0.65	0.80	1.33	0.77	2.10
4.0	5.0	0.32	0.76	0.80	1.68	0.20	1.88
5.0	5.0	0.27	0.89	0.92	1.95	0.15	2.0

TABLE-V

Endgroup Analysis of Polystyrene Initiated by KMnO_4 -Oxalic Acid Redox in Emulsion Phase

System : Styrene = 0.174 mole/litre ;
 Cetavlon = 2% by weight
 Temp.: 25-30°C ; N_2 atmosphere

KMnO_4 m/l $\times 10^4$	Oxalic acid m/l $\times 10^3$	[η]	O.D. of 0.025% polymer solution with Rhodamine reagent		Endgroup/Chain		
			Orig- nal	Phthalaed	COOH	OH	Total
5.0	5.0	1.75	0.47	0.61	0.55	1.05	1.60
5.0	3.0	1.90	0.52	-	1.0	-	-
5.0	1.0	3.60	0.48	0.493	1.65	0.27	1.92
1.0	5.0	3.90	0.47	-	1.63	-	-

different result was obtained when KMnO_4 -E.D.T.A. redox initiated polymerization of MMA was carried out in almost neutral medium (by addition of alkali), where any question of hydrolysis does not arise. The overall endgroup content (OH + COOH) decreased considerably in these polymers with increasing pH, due to lesser incorporation of hydroxyl endgroup but carboxyl endgroup content was found to be almost one per chain in all samples (Table VI). This might indicate that hydroxyl radical generating steps are not much favoured under alkaline conditions. The results also clearly show that methyl methacrylate units suffered almost no hydrolysis under our experimental conditions and so our main results were not affected by any disturbing hydrolytic side reaction.

Palit and Konar¹⁰³ pointed out that at high concentration of oxalic acid, carboxyl endgroups tend to disappear as generation of "active" oxalic acid was forcibly suppressed under this condition. Launer and Yost^{106,107} also made a similar assumption. But during the present investigation no positive evidence could be gathered which could justify these statements. In fact carboxyl endgroup content instead of decreasing was found to increase somewhat with increase in oxalic acid to permanganate ratio in the system (Table II). The gradual increase in degree of polymerization (D.P.) of the polymer with increase in oxalic acid concentration at a fixed oxalic acid concentration corroborates Palit and Konar¹⁰³ earlier findings. The error

TABLE-VI

Endgroup Analysis of Poly(methylmethacrylate) Initiated
by KMnO_4 - E.D.T.A. Redox at Different pH of the Medium

System : MMA - 0.094 mole/litre ; N_2 atmosphere ;
Aqueous Polymerization ; Temp.: 25-30°C

KMnO_4 m/l $\times 10^3$	E.D.T.A. m/l $\times 10^2$	[η]	O.D. of 0.05% polymer solution with rhodamine reagent		Endgroup/Chain		
			Original	Phtha- lated	COOH	OH	Total
5.0 (pH=4.54)	4.0	0.75	0.585	-	1.35	-	-
5.0 (pH=5.37)	4.0	0.58	0.585	0.715	0.96	0.68	1.64
5.0 (pH=5.87)	4.0	0.50	0.75	0.66	0.70	0.42	1.12
5.0 (pH=9.16)	4.0	0.53	0.58	0.62	0.86	0.20	1.06

in Palit and Konar¹⁰² finding, as regards in carboxyl endgroup content at high oxalic acid concentration may be traced back to the increase in D.P. of the resultant polymers and their decreased response to dye test.

It is almost a general observation in case of precipitation phase aqueous polymerization that at a fixed initiator and activator concentration, $[\eta]$ gradually increases with increase of polymerization temperature, attains its maxima at a certain temperature (optimum) and then again it decreases at higher temperature. Permanganate-oxalic acid redox initiated system was found to behave in a similar fashion and the optimum temperature was found to be about 50-55°C (Table VII). But a strikingly different observation was made in case of permanganate-E.D.T.A. redox initiated system where change of polymerization temperature was found to have very little effect in D.P. of the polymer formed (Table VIII).

As regards endgroup picture, increase of polymerization temperature resulted in increased amount of carboxyl endgroup incorporation in permanganate - oxalic acid redox initiated poly(methyl methacrylate) (Table VII). This might be due to a little hydrolysis of the monomer units under more severe conditions. In case of permanganate - E.D.T.A. redox initiated polymerization, however, endgroup picture was found to remain almost unchanged (Table VIII).

TABLE-VII

Endgroup Analysis of Poly(methylmethacrylate) Initiated
by KMnO_4 - Oxalic Acid Redox at Different Temperatures

System : Aqueous Polymerization ; N_2 atmosphere

MMA = 0.062 mole/litre ;

KMnO_4 = 1×10^{-4} mole/litre ;

Oxalic acid = 5×10^{-3} mole/litre

Temperature °C	[η]	O.D. of 0.05% polymer solu- tion with rhodamine re- agent		Endgroup / Chain		
		Original	Phtha- lated	COOH	OH	Total
25-30	0.67	0.61	0.70	1.28	0.48	1.76
35	0.70	0.66	0.73	1.75	0.43	2.18
40	0.79	0.65	0.78	2.00	0.95	2.95
45	0.94	0.64	0.73	2.34	0.91	3.25
50	1.10	0.70	-	3.60	-	-
55	1.30	0.62	-	3.20	-	-
60	1.20	0.54	0.60	1.90	0.80	2.70

TABLE-VIII

Endgroup Analysis of Poly(methylmethacrylate) Initiated
by KMnO_4 - E.D.T.A. Redox at Different Temperatures

System : Aqueous Polymerization ; N_2 atmosphere

MMA = 0.094 mole/litre ;

KMnO_4 = 5×10^{-3} mole/litre ;

E.D.T.A. = 3×10^{-2} mole/litre

Temperature °C	[η]	O.D. of 0.05% polymer solu- tion with rhodamine reagent		Endgroup / Chain		
		Original	Phtha- lated	COOH	OH	Total
25-30	0.60	0.54	0.77	0.74	1.22	1.96
40	0.55	0.655	-	1.25	-	-
45	0.53	-	-	-	-	-
50	0.50	0.58	-	0.76	-	-
55	0.45	0.61	0.85	0.78	0.89	1.67
60	0.36	0.635	0.90	0.66	0.72	1.38

redox initiation has been conclusively proved by changing the solvent when solution polymerization of methyl methacrylate in presence of permanganate - oxalic acid redox is carried out in ethylene carbonate medium (a solvent having almost zero transfer constant) only carboxyl endgroup (with complete exclusion of hydroxyl endgroup) is found to be incorporated to an extent of about one per chain¹⁰⁸.

Conclusion

It has been found out that permanganate in presence of E.D.T.A. form a redox initiating system for aqueous vinyl polymerization. The system is basically similar to the well-known oxalic acid-permanganate redox initiation system with the exception that while the former is active even in fairly alkaline pH, the later operates only if the acidity of the medium is maintained. The $KMnO_4$ exponent with respect to methyl methacrylate in $KMnO_4$ - E.D.T.A. system has been found out to be 0.80 in contrast with $KMnO_4$ - oxalic acid system where $KMnO_4$ exponent changes from 1.0 to 0.5 with change in $KMnO_4$ concentration as reported by Palit and Konar¹⁰³. As regards endgroup incorporation in case of these two initiator system, both hydroxyl and carboxyl endgroups

have been found to be incorporated in the resultant polymer to an extent of about 1.5 - 2 per chain.