

Permanganate-EDTA & Permanganate-Oxalic Acid as Redox Initiators

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Manuscript received 29 May 1964

Permanganate in the presence of EDTA has been found to form a redox initiator 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 latter operates only if the acidity of the medium is maintained. The order of the reaction of KMnO_4 -EDTA redox initiated aqueous polymerization of methyl methacrylate, with respect to KMnO_4 , is found to be 0.80. This probably indicates that termination in this system takes place both unimolecularly and through bimolecular collision between two chain radicals. In both the initiator systems, hydroxyl and carboxyl endgroups have been found to be incorporated in the resultant polymer to the extent of about 1.5-2 per chain.

IN a system containing a vinyl monomer, ethylenediamine tetraacetic acid (EDTA) and potassium permanganate in aqueous solution, Mn (VII) is rapidly reduced through Mn (IV) to Mn (III) stage and this is complexed by EDTA. Initiation can now take place either by the Mn (III) complex itself or by the Mn (III)-EDTA redox couple¹. This latter system is basically similar to the well-known oxalic acid-permanganate redox initiation system, studied by Palit and Konar^{2,3}. Some results with regard to its kinetic behaviour and endgroup picture are reported in this communication and these have been compared with the behaviour of oxalic acid-permanganate redox initiator.

Materials and Methods

Reagents — Disodium salt of EDTA (Trade name Titriplex III, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$), oxalic acid and potassium permanganate were analytical reagents (E. Merck). Both potassium permanganate and EDTA assayed to more than 99 per cent purity. Cetyl trimethyl ammonium bromide (CTAB) used as emulsifier was of 97 per cent purity. Monomers styrene and methyl methacrylate (MMA) were purified by usual procedures and the middle fraction of the vacuum distillate of the monomer was stored at 5-10°C. in a refrigerator.

Preparation and purification of polymers — Aqueous polymerization of freshly distilled methyl methacrylate was carried out either in a constant temperature bath or at room temperature under an atmosphere of purified nitrogen^{2,4}. The induction period was usually about 10 min. or less but it increased to as high as 30 to 40 min. at high oxalic acid concentration (40 to 50 millimoles/litre). The overall yield was rather low, being about 30-50 per cent in 1 hr. In any case, polymerization was generally allowed to proceed for only 45 min. to 1 hr after initiation in order to maintain a standard condition of polymerization and to restrict the hydrolysis of ester units of poly(methyl methacrylate) in acidic

medium to a negligible extent. Otherwise, carboxyl units generated in the polymer due to the ester hydrolysis might interfere with the independent estimation of carboxyl endgroups, incorporated in the polymer chain during initiation or termination step. EDTA or oxalic acid was taken in sufficient excess to avoid precipitation of MnO_2 . In case of KMnO_4 -EDTA redox, polymerization could be carried out even at pH 10. At very high pH values (approximately in *N*/5 NaOH medium), however, $\text{Mn}(\text{OH})_2$ precipitated out. This is in contrast with the behaviour of KMnO_4 -oxalic acid redox, where the acidity of the medium was essential for polymerization to occur.

The polymerization rate was measured by a gravimetric method³ at $35 \pm 0.2^\circ\text{C}$. Polymerization was forcibly terminated at different intervals by introduction of oxygen and results of duplicate runs were generally within ± 2 units of per cent yield.

Freshly distilled styrene monomer was emulsified by using cetyl trimethyl ammonium bromide (CTAB) as the emulsifier and was polymerized in an atmosphere of purified nitrogen. Polymerization was allowed to proceed nearly to completion and polymer was collected by breaking the emulsion with acetone.

Polymers formed either in aqueous or emulsion phase were washed repeatedly with warm distilled water and dried in an air oven at 45-50°C. These polymers were subjected to rigorous purification by repeated precipitation following the standard procedure⁵ to make these polymers suitable for endgroup estimation by the dye interaction technique.

Endgroup Analysis by Dye Interaction Method

Determination of carboxyl endgroup — The sensitive dye reagent⁵ was prepared by quick extraction of a concentrated aqueous solution (pH 10) of calcozine rhodamine 6Gx dye with benzene. This orange-yellow dye extract was mixed with an equal volume of purified polymer solution of known concentration

in benzene and the resultant colour change of the dye due to carboxyl endgroups was measured in a Hilger spectrophotometer at 515 m μ using 1 cm. cells. The optical density of blank dye was maintained at 0.40 ± 0.005 for easy comparison. The extent of carboxyl endgroup in the polymer was measured with the help of a calibration curve using formic acid as the basis of comparison⁵.

Determination of hydroxyl (OH) endgroup — Hydroxyl endgroup in polymers was converted to dye responsive carboxyl (COOH) group by heating the polymer (0.1-0.2 g.) with phthalic anhydride (0.5 g.) in pyridine (10 ml.) solution under reflux^{4,6,7} on a water bath for 6 hr. The polymer was then purified by following a specified procedure and was put to dye interaction test using rhodamine reagent. An increased response after phthalation indicated the presence of hydroxyl endgroup in the polymer.

Determination of intrinsic viscosity and molecular weight of polymers — The reduced viscosity (η_{sp}/C) of each polymer sample was obtained by measuring its viscosity in benzene solution at $35^\circ \pm 0.1^\circ\text{C}$. The intrinsic viscosity $[\eta]$ for each polymer was then obtained by usual method of extrapolation. The number average molecular weight (\bar{M}_n) was calculated from the respective $[\eta]$ values with the use of the following equations:

$$\bar{M}_n = 2.81 \times 10^5 \times [\eta]^{1.32} \text{ for poly (methyl methacrylate)}^8$$

$$\bar{M}_n = 1.84 \times 10^5 \times [\eta]^{1.40} \text{ for polystyrene}^9$$

Results and Discussion

On addition of permanganate to an aqueous solution of a monomer and sufficient excess of EDTA, no precipitation of manganese dioxide occurs but a cherry red coloured solution is produced. This

cherry red coloured solution is presumed to be due to Mn (III)-EDTA complex formation. Yoshino *et al.*¹⁰ have been able to isolate such a complex from this solution. This complex then acts as a slow and steady source of initiating free radicals, as indicated by the gradual colour change of the medium to violet and light violet with progress of polymerization. Polymerization proceeds in precipitation phase and finally the solution becomes practically colourless as the whole of Mn (III) is reduced to Mn (II) stage. Yoshino *et al.*¹⁰ also observed that the complex is transformed to colourless Mn (II)-EDTA form in presence of heat or light.

Kinetics of polymerization — The results of experiments on the kinetics of KMnO_4 -EDTA redox initiated aqueous polymerization of methyl methacrylate are presented in Figs. 1 and 2. The yield curves (i.e. percentage yield versus time in minutes) for varying initiator (KMnO_4) concentration at fixed monomer and activator (EDTA) concentration are given in Fig. 1. Logarithm of initial rate, R_p (in per cent yield/min.) versus logarithm of KMnO_4 concentration has been plotted in Fig. 2; the order of the reaction with respect to KMnO_4 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 KMnO_4 -oxalic acid system where the KMnO_4 (initiator) exponent changes from 1.0 to 0.5 with change in KMnO_4 concentration as reported by Palit and Konar³.

The results of experiments on the variation of EDTA concentration, under otherwise constant conditions, are presented in Fig. 3. The rate of polymerization definitely shows some variation with

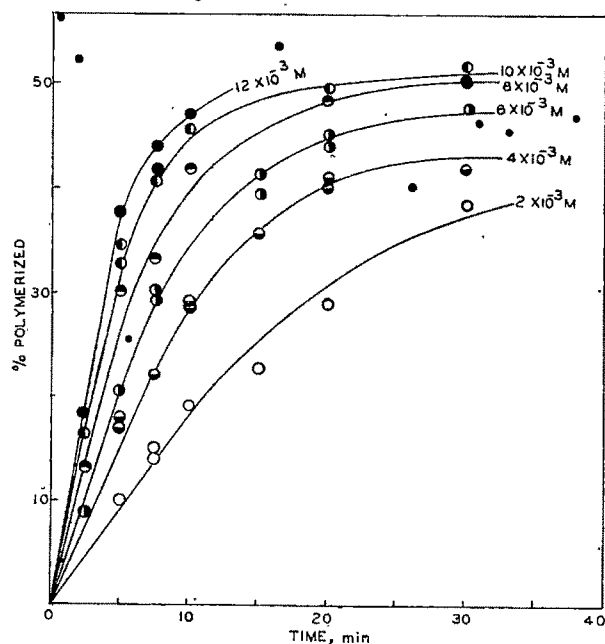


Fig. 1 — Yield-time curve in aqueous polymerization of MMA (0.094 mole/litre) with permanganate-EDTA initiation at EDTA conc. of $4 \times 10^{-2} M$ and varying concentrations of KMnO_4 ; temp. $35^\circ \pm 0.2^\circ\text{C}$.

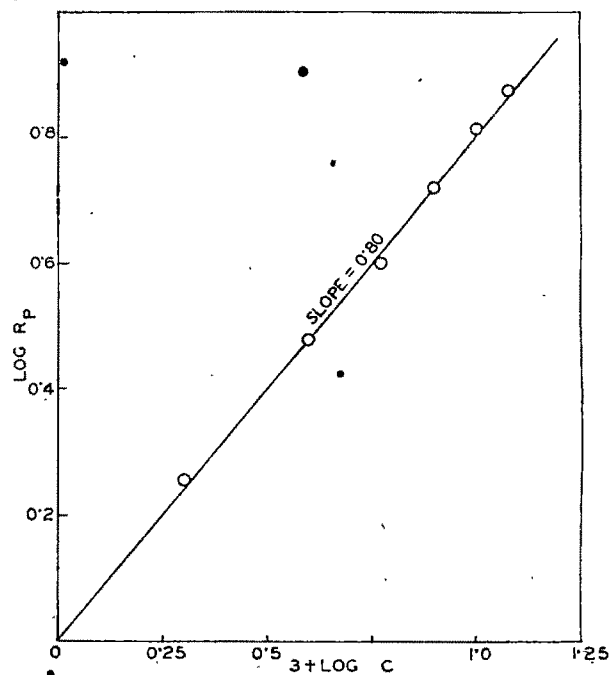


Fig. 2 — Plot of $\log R_p$ (in per cent polymerized/min.) versus $\log C$ (catalyst conc. in mole/litre)

EDTA concentration, but in a peculiar way. As EDTA concentration is increased, rate of polymerization tends to increase; but on the other hand, corresponding lowering of *pH* of the medium tends to reduce the rate. However, with increasing EDTA concentration, overall yield decreases, although initial rate may be relatively high. Similar observation was also made by Palit and Konar³ 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)-EDTA complex, compared to Mn (II)-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 is finally reduced to Mn (II) stage and the solution becomes colourless.

Endgroup analysis—The results of endgroup analysis of poly(methyl methacrylate) obtained by aqueous initiation with KMnO_4 -oxalic acid redox and KMnO_4 -EDTA redox are presented in Tables 1 and 2 respectively. All the polymer samples exhibit a positive response (faint or intense depending on initiator concentration) to rhodamine reagent, presumably due to presence of carboxyl endgroups in them.

Palit and Konar² detected carboxyl endgroups in poly(methyl methacrylate) polymers initiated by KMnO_4 -oxalic acid redox and attributed it to the initiation by active oxalic acid radicals (carboxyl

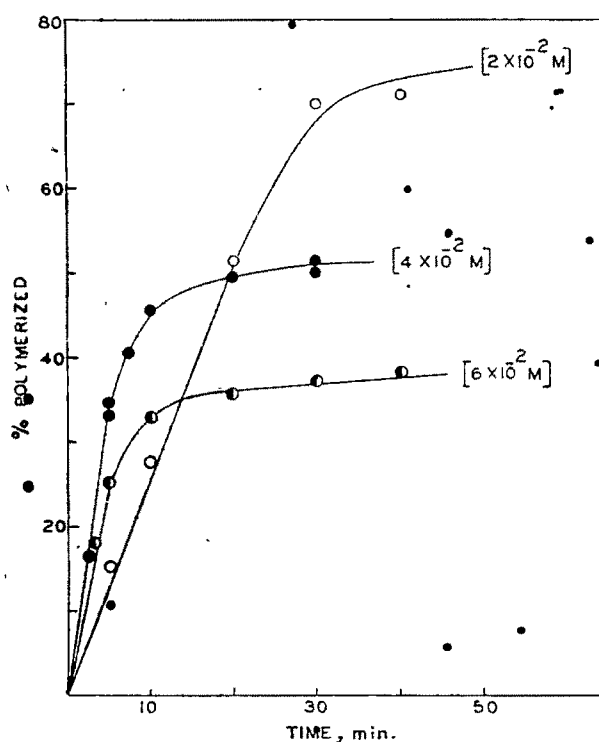


Fig. 3 — Yield-time curve in aqueous polymerization of MMA (0.094 mole/litre) with permanganate-EDTA initiation at KMnO_4 conc. of $1 \times 10^{-2} M$ and varying concentrations of EDTA

TABLE 1 — ENDGROUP ANALYSIS OF POLY(METHYL METHACRYLATE) INITIATED BY KMnO_4 -OXALIC ACID REDOX AT TWO DIFFERENT MONOMER CONCENTRATIONS

(Experimental conditions: N_2 atmosphere; aqueous polymerization; temp., 25-30°C.)

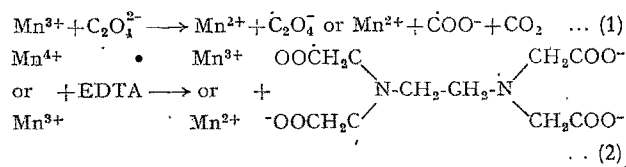
KMnO_4 mole/litre $\times 10^4$	Oxalic acid mole/litre $\times 10^3$	[η]	OD of 0.025% polymer soln with rhodamine reagent		Endgroup/chain		
					COOH	OH	Total
			Original	Phthalated			
METHYL METHACRYLATE CONC., 0.094 MOLE/LITRE							
0.2	5.0	1.70	0.44	—	1.5	—	—
0.5	5.0	1.10	0.465	0.495	1.5	0.60	2.10
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
METHYL METHACRYLATE CONC., 0.062 MOLE/LITRE							
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 2 — ENDGROUP ANALYSIS OF POLY(METHYL METHACRYLATE) INITIATED BY KMnO_4 -EDTA REDOX(Experimental conditions: N_2 atmosphere; MMA conc., 0.094 mole/litre; aqueous polymerization; temp., 25-30°C.)

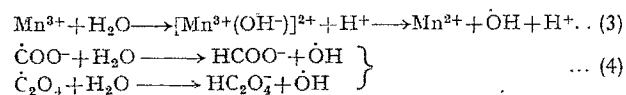
KMnO ₄ mole/litre $\times 10^3$	EDTA mole/litre $\times 10^2$	[η]	OD of 0.05% polymer soln with rhodamine reagent		Endgroup/chain		
			Original	Phthalated	COOH	OH	Total
3.0	4.0	1.10	0.465	0.56	0.75	1.17	1.92
4.0	4.0	0.85	0.47	0.58	0.60	1.00	1.60
5.0	2.5	0.85	0.505	0.64	0.90	1.10	2.0
5.0	3.0	0.60	0.54	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
12.5	4.0	0.40	0.80	0.92	1.28	0.40	1.68
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	0.57	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

bearing radical generated according to Launer-Yost mechanism^{11,12}). In the present study the polymers were subjected to quantitative estimation of both carboxyl and hydroxyl endgroups. Experiments were performed at two different monomer concentrations (0.062 and 0.094 mole/litre respectively) where rates of polymerization are almost identical as reported by Palit and Konar³. The sum total of carboxyl and hydroxyl endgroup content in all these polymers generally lay between 1.5 and 2.0 per chain, but their respective proportion varied over a considerable range and, in a few cases, hydroxyl endgroup content was almost negligible (Table 1). This endgroup picture is very similar to that of KMnO_4 -EDTA redox initiated polymers (Table 2).

The above results lead to the conclusion that both carboxyl bearing as well as OH radicals are present in the system and take part in initiation and termination. The carboxyl bearing radical may be generated by the oxidation of oxalic acid or its anion in case of KMnO_4 -oxalic acid redox and by oxidation of EDTA in case of KMnO_4 -EDTA redox (Eqs. 1 and 2) and the course of oxidation may follow the well-known Launer-Yost mechanism^{11,12}.



The OH radical may be generated either by oxidation of water by Mn (III) (Eq. 3) or by abstraction of hydrogen from water by the carboxyl bearing radicals (Eq. 4).



That the hydroxyl endgroup incorporated in polymers come from water in case of the above-

mentioned redox initiation has been conclusively proved by changing the solvent. When solution polymerization of MMA in presence of KMnO_4 -oxalic acid redox is carried out in ethylene carbonate solvent (a solvent having no transferring capacity), only carboxyl endgroup (with complete exclusion of hydroxyl endgroup) is found to be incorporated to an extent of about one per chain (Palit, S. R. *et al.*, unpublished data).

In order to avoid any vitiation of the result due to hydrolysis of the monomer units in acidic medium, as may happen to some extent with methyl methacrylate, experiments were performed with styrene in emulsion phase in case of KMnO_4 -oxalic acid redox initiation. Endgroup picture was found to be almost the same as in the case of poly(methyl methacrylate). A strikingly different result was obtained when KMnO_4 -EDTA redox initiated polymerization of methyl methacrylate was carried out in almost neutral medium (by addition of alkali), where any question of hydrolysis did 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 the samples (Table 2). This suggests that the hydroxyl radical generating steps are not much favoured under alkaline conditions. These results also clearly show that methyl methacrylate units suffer almost no hydrolysis under the experimental conditions employed and the main results obtained are not affected by any disturbing hydrolytic side reaction.

Launer and Yost¹¹ theorized that at higher ratio of oxalic acid to permanganate, the production of carboxyl radical is suppressed and this has been to some extent corroborated by Palit and Konar's² qualitative observations. The results of the present experiments, however, are contrary to those expected from the ideas of Launer and Yost. In fact carboxyl endgroup content instead of decreasing has been found to increase somewhat with increase in oxalic acid to permanganate ratio in the system (Table 1).

TABLE 3 — ENDGROUP ANALYSIS OF POLY(METHYL METHACRYLATE) INITIATED BY KMnO_4 -OXALIC ACID AND KMnO_4 -EDTA REDOX AT DIFFERENT TEMPERATURES.

(Experimental conditions: N_2 atmosphere; aqueous polymerization)

Temp. °C.	[η]	OD of 0.05% polymer soln with rhodamine reagent		Endgroup/chain		
		Ori-ginal	Phthalated	COOH	OH	Total
MMA, 0.062 MOLE/LITRE; KMnO_4 , 1×10^{-4} MOLE/LITRE; OXALIC ACID, 5×10^{-3} MOLE/LITRE						
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
MMA, 0.094 MOLE/LITRE; KMnO_4 , 5×10^{-3} MOLE/LITRE; EDTA, 3×10^{-2} MOLE/LITRE						
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

The gradual increase in degree of polymerization (DP) of the polymer with increase in oxalic acid concentration at a fixed initiator concentration, as shown in Table 1, corroborates Palit and Konar's³ earlier findings. The error in Palit and Konar's² finding as regards decrease in carboxyl endgroup content at high oxalic acid concentration may be traced to the increase in DP of the resultant polymers and their decreased response to dye test.

Effect of temperature—It is generally observed in case of precipitation phase aqueous polymerization that at a fixed initiator and activator concentration, [η] gradually increases with increase of polymerization temperature, attains a maximum value at a

certain temperature (optimum) and then again decreases at higher temperatures. KMnO_4 -oxalic acid redox initiated system also behaves in a similar fashion³ and the optimum temperature is found to be about 50-55°C. (Table 3). But a strikingly different observation has been made in the case of KMnO_4 -EDTA redox initiated system where change of polymerization temperature is found to have little effect on [η] of the polymer formed (Table 3). This point requires closer study for a suitable explanation.

As regards endgroup picture, increase of polymerization temperature results in increased amount of carboxyl endgroup incorporation in KMnO_4 -oxalic acid redox initiated poly(methyl methacrylate) (Table 3). This might be due to a little hydrolysis of the monomer units under more severe experimental conditions. In case of KMnO_4 -EDTA redox initiated polymerization, however, endgroup picture has been found to remain almost unchanged (Table 3) under these conditions.

Acknowledgement

Thanks are due to the Council of Scientific & Industrial Research, New Delhi, for granting financial aid to one of the authors (A.R.M.).

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