Studies of Some Radical Transfer Reactions. II.[†] Electron Transfer Reactions Involving Halide and Oxalate Ions with OH Radicals during the Aqueous Polymerization of Methylmethacrylate

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Hydroxyl radicals (OH·) in solution may possible participate in electron transfer reactions with some anions (X^-) present in the same medium, thereby losing their radical nature and being replaced by new radicals (X·) derived from the anions in question:

$$OH\cdot + X^- \rightarrow OH^- + X\cdot$$

In polymerization experiments in such systems, the occurrence of the above type of radical transfer reactions may easily be traced by the analysis of the polymer endgroups. The present paper will report the results of our investigation of such reactions involving halide (F^-, Cl^- and Br^-) and oxalate ions with OH· radicals in aqueous media, based on the analysis of the endgroup of the polymethylmethacrylate prepared in such systems.

Experimental

The aqueous polymerization of purified methylmethacrylate (MMA) was carried out in Pyrex flasks under a nitrogen atmosphere at room temperature; it was initiated by OH radicals derived either by the photolysis of H_2O_2 in ultraviolet light or by redox reaction with Fe^{2+} ions in the dark. Sodium fluoride, potassium chloride and potassium bromide were separately added at varied concentrations in the polymerization media. The PMMA samples obtained after the completion of polymerization were filtered, washed, and then dried in an air oven at 45°C.

The polymers were then heated with pyridine in sealed tubes in order to transform any halogen atom endgroups presumably incorporated in them to quaternary pyridinium halide endgroups. The quaternised polymers were then properly purified of pyridine and dried. Tests for halogen in the polymers were then carried out by the dye-partition technique, using an aqueous disulfine blue reagent. Quantitative analysis was carried out spectrophotometrically.[1)] The determination of the carboxyl endgroup in polymers obtained in the presence of oxalate ions was carried out by the dye interaction test using a Rhodamine reagent.[2)]

Results and Discussion

The hydrogen peroxide-initiated polymerization of MMA in the presence of the halide salts in aqueous media proceeds with certain characteristics, the polymers being obtained in a coarse precipitated form. The increase in the salt concentration results in an increase in the induction period, probably due to some replacement of the active OH· radicals by the less active halogen atoms according to the above reaction. The increase in salt concentration also leads to an appreciable decrease in the yield of the polymer. No polymerization occurs in the presence of potassium iodide, probably because of the fast oxidation of the iodide ion by the active OH· radicals with the liberation of iodine, which acts as a strong inhibitor. The general features of polymerization in the presence of oxalate ion in aqueous media are more or less the same as in presence of F^-, Cl^- or Br^- ions.

The polymers obtained with the use of H_2O_2 as the initiator in aqueous media have been found, by the application of the sensitive dye technique,[3)] to bear an OH endgroup only to the extent of about 1 per chain. However, when prepared in the presence of the halide ions (F^- Cl^- and Br^-), they also give a positive response to the dye partition

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1) M. N. Saha, P. Ghosh and S. R. Palit, *J. Polymer Sci.*, **A2**, 1365 (1964).

2) S. R. Palit and P. Ghosh, ibid., **58**, 1225 (1962).

3) P. Ghosh, A. R. Mukherjee and S. R. Palit, ibid., **A2**, 2807 (1964).

Table I.* Endgroup results of PMMA obtained by aqueous photoinitiation with H_2O_2 in presence of halide ions

[MMA] = 0.094 mol./l.

Concn. of H_2O_2 mol./l.	Concn. of halide ion mol./l.	$[\eta]$[a] of the polymer	OH/ chain	Halogen chain	Total endgroup/ chain	$\frac{[\text{Hal}]}{[\text{OH}]+[\text{Hal}]}$ %
	[NaF]			[Fluorine]		
0.05	0.0	0.81	1.05	0.0	1.05	0.0
0.05	0.012	0.75	1.20	0.15	1.35	11.1
0.05	0.024	0.70	1.13	0.10	1.23	8.1
0.05	0.047	0.65	1.20	0.15	1.35	11.1
0.05	0.119	0.53	1.14	0.16	1.30	12.3
0.05	0.238	0.40	1.00	0.07	1.07	6.5
0.05	1.190	0.35	1.08	0.05	1.13	4.6
	[KCl]			[Chlorine]		
0.05	0.134	0.38	1.21	0.06	1.27	5.3
0.05	0.402	0.36	1.13	0.07	1.20	6.0
0.05	0.938	0.30	1.00	0.03	1.03	3.7
	[KBr]			[Bromine]		
0.02	0.0	1.09	1.20	0.0	1.20	0.0
0.02	0.42	1.02	1.29	0.090	1.38	6.5
0.02	0.89	0.90	1.30	0.098	1.39	7.0
0.02	1.26	0.82	1.26	0.060	1.32	4.5
0.02	1.68	0.64	1.31	0.056	1.36	4.1
0.05	4.20	0.35	1.22	0.12	1.34	8.9
0.05	5.88	0.28	1.04	0.07	1.11	6.7
0.05	7.56	0.24	0.96	0.053	1.01	5.2

* Similar trend of result was also obtained using Fe^{2+}/H_2O_2 system as the source of hydroxyl radicals.

a) The intrinsic viscosity $[\eta]$ of the polymers, obtained by the usual extrapolation method was transformed to the number average molecular weight ($\overline{M}_n$) by the application of the following equation.

$$\overline{M}_n = 2.81\times10^5\times[\eta]^{1.32} \quad \text{(PMMA in benzene)}$$

Table II. Endgroup results of PMMA obtained by aqueous photoinitiation with H_2O_2 in presence of oxalate ions

[MMA] = 0.094 mol./l.

Concn. of H_2O_2 mol./l.	Concn. of Na-oxalate mol./l.	$[\eta]$ of the polymer	OH/ chain	Carboxyl/ chain	Total endgroup/ chain	$\frac{[\text{COOH}]}{[\text{OH}]+[\text{COOH}]}$ %
0.0176	0.00074	1.06	1.18	0	1.18	0.0
0.0176	0.0037	1.04	1.23	0	1.23	0.0
0.0176	0.0074	1.01	1.26	0.06	1.32	4.5
0·0176	0.0370	0.95	1.11	0.11	1.22	9.0
0.0176	0.0740	0.881	1.15	0.20	1.35	14.8

test with aqueous disulfine blue reagents for halogen atom endgroups (transformed to quaternary halide groups) (Table I). For quantitative purposes, it is assumed that the different pyridinium halides (fluoride, chloride and bromide) groups are all equally responsive to the appropriate dye test; the spectrophotometric determinations are based on a comparison of the experimental optical density values with the same calibration curve of a particular model compound. There is, of course, some uncertainty about the quantitative values for halogen contents in the polymers, as these are highly contingent upon the very slow and sluggish process of quaternisation,[4,5] which is slower and more sluggish than usual in the present case as the concentration of halogens, (appearing only at chain ends) in the polymer is extermely low. The process of quaternisation may be completed to varying extents in different samples. Due to these limitations, a proper order in halogen content in the polymers as determined from any consideration is probably far from expectation; in fact, none is realised by our experiments. However, qualitatively the dye techniques employed for the endgroup characterisation of the polymers obtained

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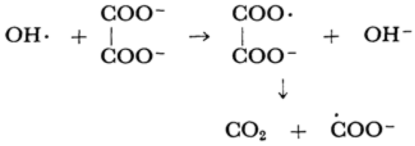
[4] R. M. Fuoss and U. P. Strauss, ibid., **3**, 246 (1948).

[5] R. M. Fuoss and M. Watanabe, ibid., **48**, 5 (1960).

in the present set of experiments give a simple and sound demonstration of the radical transfer reaction between OH· radicals and F^-, Cl^- and Br^- ions in aqueous media.

It is known that chloride ions inhibit the reactions of OH· radicals, and this can be explained on the basis of radical ion transfer reaction under discussion.6-9) Expectedly, the effect is greater with bromide ion. However, with fluoride ions with a very high affinity for electrons, a similar effect appears to be much less favoured,10) if not improbable. A fairly positive test for fluorine-atom endgroups in polymers prepared in the presence of fluoride ions indicates, however, the occurrence of the electron transfer reaction between the OH· radical and the F^- ion.

Much as hadide ions, oxalate ions also take part in electron transfer reaction with OH· radicals; this is clearly indicated by the presence of carboxyl endgroups in the respective polymers (Table II). The generation of carboxyl radicals probably occurs by means of the following mechanism:



$$\mathrm{OH}\cdot + \begin{array}{c}\mathrm{COO}^-\\ |\\ \mathrm{COO}^-\end{array} \rightarrow \begin{array}{c}\mathrm{COO}\cdot\\ |\\ \mathrm{COO}^-\end{array} + \mathrm{OH}^-$$

$$\downarrow$$

$$\mathrm{CO}_2 + \dot{\mathrm{C}}\mathrm{OO}^-$$

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7) A. O. Allen, *J. Phys and Colloid Chem.*, **52**, 479 (1948).

8) I. M. Kolthoff and A. I. Medalia, *J. Am. Chem. Soc.*, **71**, 3777, 3784 (1949).

9) W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462, 591 (1951).

10) N. Uri, *Chem Revs.*, **50**, 375 (1952).

11) J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).