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Mineral Acids as Photoinitiators of Vinyl Polymerization in Aqueous Media

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A few mineral acids, namely hydrochloric, hydrobromic and sulfuric acid, have been used as photoinitiators for the polymerization of methyl methacrylate in aqueous media in the presence of ultraviolet light. The endgroups incorporated in the resulting polymers have been determined by the application of the sensitive "Dye Techniques" lately developed in our laboratory. On the basis of the endgroup results, attempts have then been made to explain the mechanism of such polymerization, and also the nature of the initiating species involved.

Mineral acids have been used as the initiators of vinyl polymerization to a very limited extent; a few of the instances quoted in the literature[1,2] are supposed to proceed through an ionic mechanism. The present communication will describe the use of some mineral acids, viz., hydrochloric, hydrobromic and sulfuric acids, as photoinitiators for the aqueous polymerization of methyl methacrylate. The endgroups incorporated in the resulting polymers have been determined by the application of the "Dye Techniques"[3] lately developed in our laboratory in order to get an idea of the nature of the initiating species involved in such processes.

Experimental

Purified methyl methacrylate (MMA) was used as the monomer. The acids employed as initiators were of an analytical grade and were free of traces of iron.

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1) M. J. Hayes and D. C. Pepper, a) *Trans. Faraday Soc.*, **57**, 432 (1961); b) *Proc. Roy. Soc.*, **A263**, 63 (1961); c) *Proc. Chem. Soc.*, **1961**, 228.

2) D. C. Pepper and P. J. Reilly, *J. Polymer Sci.*, **58**, 639 (1962).

3) S. R. Palit, a) *Chem. & Ind.*, **1960**, 1531; *Makromol. Chem.*, **36**, 89 (1959); **38**, 96 (1960).

Polymerization experiments were carried out in clean pyrex conical flasks in a nitrogen atmosphere in the presence of ultraviolet light, without any filter, and at a temperature of 30°C, the concentration of the monomer being kept at 0.094 mol./l. in all the experiments. The induction period for the polymerization varied from about half an hour to about 3 hr., depending on the nature and concentration of the acids empolyed as initiators. Polymers were obtained as a coarse precipitate after the polymerization was over. The polymers were then washed free of acid, dried in an air oven at 45°C, and purified by repeated reprecipitations from a benzene solution by a mixture of alcohol and petroleum ether.

The purified polymers were then subjected to the "Dye Tests" in order to determine the endgroups incorporated in them. The halogen endgroups were determined by the application of the "Dye partition test" using a Disulfine blue reagent after the quaternisation of the polymers with pyridine.4) The sulfate endgroup was estimated by the "Dye partition test" employing a methylene blue reagent.5)

Results and Discussion

The usual features of these polymerization, e. g., the initiation of polymerization only in the presence of light, a fairly long induction period, the polymerization over a considerable period of time (about 2—5 hr.), and the complete inhibition of the polymerization in the presence of oxygen, are suggestive of a typical radical polymerization process.

Initiation by Halo Acids.—Both hydrochloric and hydrobromic acid could initiate the polymerization of MMA in the presence of ultraviolet light, while hydroiodic acid failed to do so under identical conditions, probably because of the strong inhibitive action of the iodine liberated. The polymers obtained with both hydrochloric and hydrobromic acid were found to bear halogen endgroups to a varying extent (about 0.3 to 0.8 per chain) (Table I). This definitely indicates that some of the polymer chains are initiated by halogen atoms generated in the systems by the photolysis of the halo acids or, more precisely, by that of the halide ions in question; thereby they appear as polymer endgroups. The generation of halogen atoms probably takes place by the following mechanism:

$$HX \rightleftarrows H^+ + X^-$$

$$X^- + HOH \xrightarrow{h\nu} X\cdot + H\cdot + OH^- \quad [X=Cl \text{ or } Br]$$

It appears, therefore, that both the radicals, X· (Cl· in the case of hydrogen chloride and Br· in the case of hydrogen bromide) and the hydrogen atom (H·), may bring about the initiation of polymerization. (It has been indicated by Dainton6) that the hydrogen atom (H) produced by irradiation with X-ray or γ-ray can initiate the polymerization of acrylonitrile in aqueous media.)

TABLE I. ENDGROUP ANALYSIS OF POLYMETHYL METHACRYLATE OBTAINED BY THE AQUEOUS PHOTOINITIATION WITH MINERAL ACIDS

Initiator concn. (normality)	$[\eta]$a) of the polymer	Average halogen or sulfate endgroup/chain
[HCl]		[Cl]
0.012	2.85	0.80
0.024	2.65	0.50
0.036	2.53	0.50
0.048	2.40	0.27
0.096	2.10	trace
0.120	1.80	trace
0.240	Polymer is almost insoluble in benzene and chloroform.	
[HBr]		[Br]
0.012	3.60	—
0.030	2.68	0.31
0.060	1.70	0.38
0.120	1.60	0.34
0.180	1.50	0.29
0.360	1.00	0.23
0.600	0.91	0.40
$[H_2SO_4]$		[Sulfate]
0.036	1.00	0.11
0.072	0.90	0.18
0.180	0.84	0.12
0.360	0.80	0.15
0.720	Polymer is almost insoluble in benzene and chloroform.	

a) Number average molecular weight ($\overline{M}_n$) of the polymers was obtained viscometrically by the application of the following equation9):

$$\overline{M}_n=2.81\times10^5\times[\eta]^{1.32}$$
(for P. MMA in benzene)

The hydroxyl endgroups in these polymers could not be determined by the application of "dye techniques" due to the extensive hydrolysis of the ester units to a carboxyl group, a process which rendered the polymer increasingly insoluble in benzene and chloroform. The determination of the halogen endgroup in the polymer by the above spectrophotometric method is based on the process of quaternisation, which is extremely slow and sluggish at the end of the reaction,7) especially when the quantity of halogen is extremely low, as in the case of the polymer endgroup. This leads to some uncertainty as to the quantitative values obtained herein; hence, there is hardly any order in the endgroup values obtained. However, allowing for these uncertainties, it can be easily demonstrated that the polymers obtained by using

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

5) P. Ghosh, S. C. Chadha, A. R. Mukherjee and S. R. Palit, ibid., **A2**, 4433 (1964).

6) F. S. Dainton, *Nature*, **160**, 268 (1947).

7) a) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948); b) R. M. Fuoss, M. Watanabe and B. D. Coleman, ibid., **48**, 5 (1960).

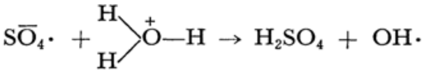
hydrogen chloride and hydrogen bromide as photoinitiators incorporate halogen endgroups at least in part.

Initiation by Sulfuric Acid.—The polymers obtained with sulfuric acid as a photoinitiator have been found to incorporate sulfate endgroups to an average extent of about only 0.1 to 0.2 per chain (Table I); this is indicative of initiation by sulfate ion radicals, at least in part. The generation of sulfate ion radicals may take place in the following way:

$$H_2SO_4 \rightleftarrows 2H^+ + SO_4^{2-}$$

$$SO_4^{2-} + HOH \xrightarrow{h\nu} S\overline{O}_4\cdot + H\cdot + OH^-$$

Both $S\overline{O}_4\cdot$ and $H\cdot$ may initiate the polymer chain and may, thereby, appear as polymer endgroups. The ability of $S\overline{O}_4\cdot$ to initiate the vinyl polymerization has been widely studied.5,8) It is also probable that, due to the acidity of the medium, sulfate ion radicals react readily with water to generate hydroxyl radicals, e. g.;



$$S\overline{O}_4\cdot + H_2\overset{+}{O}{-}H \rightarrow H_2SO_4 + OH\cdot$$

This reaction probably occurs more readily at higher concentrations of acids.5) However, the hydroxyl endgroups in these polymers could not be examined because of a difficulty similar to that indicated in the case of halo acids.

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8) I. M. Kolthoff, A. I. Medalia and H. P. Raaen, *J. Am. Chem. Soc.*, **73**, 1733 (1951).

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