


CHAPTER-IV

Redox Initiating Systems Containing H₂O₂ as an Oxidant

Introduction

Hydrogen peroxide is a well-known oxidising agent. It either undergoes photolytic decomposition or it involves in redox reaction in conjunction with suitable reducing agents. Thereby generating initiating radicals for vinyl polymerization. Reducing agents such as Fe²⁺, reducing sulfoxy compounds, N₂H₄.H₂O etc. have already been used in redox combination with hydrogen peroxide¹⁰⁹. Hydroxylamine ($\begin{array}{c} \text{H} \\ \diagdown \\ \text{N} - \text{OH} \\ \diagup \\ \text{H} \end{array}$) is an interesting redox component as it has the possibility of acting both as an oxidant or a reductant. Hydroxyl amine in presence of strong reducing agents e.g. titanous or chromous ion, acts as an oxidant and Davis, Evans and Higginson¹¹⁰ showed that initiation was due to NH₂• radical. But hydroxylamine promotes polymerization in conjunction with peroxide compounds^{109, 111} and there it acts as reducing agent. But the mechanism of this redox reaction is not definitely known. So, we were interested in carrying out the endgroup analysis of polymers produced by redox initiation of hydrogen peroxide and hydroxylamine, and thus to gain insight into the mechanism of the redox reactions involved.

Hydroquinone, , again is another

interesting compound. It is a conventional inhibitor of free radical induced vinyl polymerization. But it has reducing potentialities too and it is quite possible that in presence of strong oxidising agents it may form effective redox initiation pair under suitable conditions. So hydrogen peroxide has been selected as the oxidising agent and its capability of forming redox initiation pairs with hydroquinone has been studied and the resultant polymers has been characterised with respect to their endgroups.

Experimental

The reagents viz. hydrogen peroxide, hydroxylamine hydrochloride, hydroquinone were all of analytical grade. The polymerization experiments were carried out under N₂ atmosphere at room temperature. The polymers thus obtained were subjected to endgroup analysis by dye-techniques, as described in a previous Chapter (Chapter II).

Results and Discussion

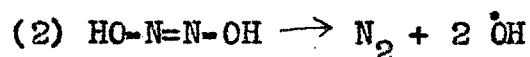
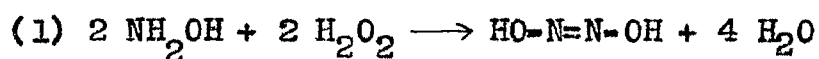
a) Hydroxylamine Hydrochloride-Hydrogenperoxide as Redox Initiator

Hydrogenperoxide along with hydroxylamine hydrochloride forms a redox pair which can initiate vinyl polymerization in dark at room temperature with negligible

induction period (2 to 3 mins.); the rate of polymerization was quite fast and D.P. of polymers formed was rather low. The results of endgroup analysis are presented in Table IX. The polymers were found to contain about two hydroxyl endgroups per chain and no amino or carboxylic endgroups have been detected. So it may be assumed that hydroxyl radicals are generated in the system which are subsequently incorporated in polymers chain. It is well-known that hydroxylamine in presence of oxidising agents forms hyponitrous acid, HO-N=N-OH, which is rather unstable and undergoes further oxidation, forming N₂ or N₂O.



Thus in presence of H₂O₂ the probable reaction mechanism may be as follows:



This mechanism, however, accounts for the generation of OH radicals as the only initiating species and formation of NH₂ radical is quite improbable. This has been amply justified by endgroup analysis results. Since hydroxyl endgroups are present to the extent of about two per chain, termination by combination or primary radical termination are the distinct possibilities.

TABLE-IX

Endgroup Analysis of Poly(methylmethacrylate) Initiated
by Hydroxylamine Hydrochloride-Hydrogenperoxide Redox
in Aqueous Systems

Systems : MMA = 0.094 m/l; H_2O_2 = 0.0176 m/l

Temp. $\sim 30^\circ C$;

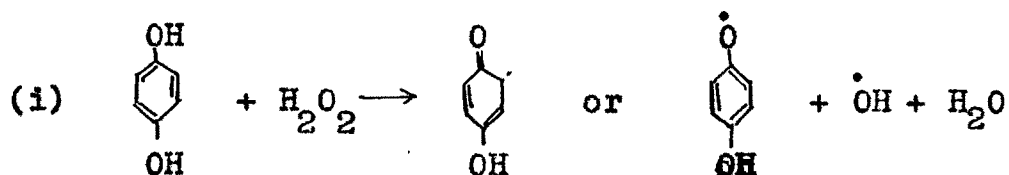
N_2 atmosphere

NH ₂ OH, HCl x 10 ² m/l	$[\eta]$	O.D. of 0.05% polymer solution with rhodamine reagent		Endgroup/Chain	
		Original*	Phthalated	COOH	OH
1.0	0.20	0.41	1.24	nil	2.09
2.0	0.17	0.42	1.23	nil	1.60
2.5	0.27	0.41	0.95	nil	1.80
5.0	0.26	0.43	1.07	nil	2.10
7.5	0.19	0.42	1.28	nil	2.09

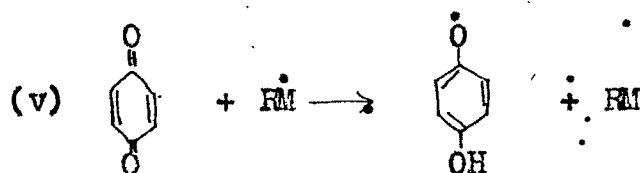
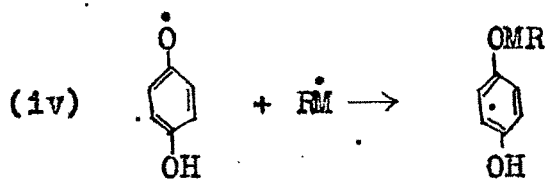
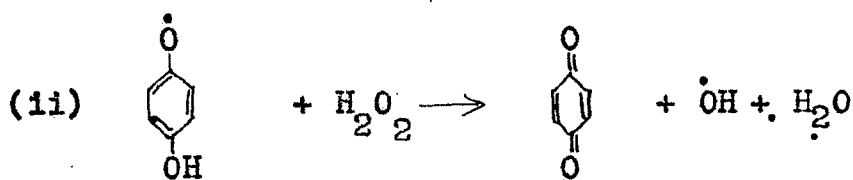
* 0.2% polymer solution used.

b) Hydroquinone-Hydrogenperoxide as Redox Initiator

Hydroquinone forms an effective redox initiation pair with hydrogen peroxide in dark at room temperature. The polymerization proceeds in course coagulum phase. The induction period varies from 2 to 3 mins. to about 1 hr. depending upon the hydrogenperoxide-hydroquinone molar concentration ratio. The lower is the hydrogenperoxide-hydroquinone molar ratio, the higher is the induction period and lower is the rate of polymerization. Thus presence of excess of hydrogenperoxide in the system is a necessary criterion for initiation of polymerization by this redox pair. In case of insufficient hydrogenperoxide, the quinone, formed due to partial oxidation of hydroquinone acts as an inhibitor thereby increasing the I.P. and lowering the R_p to indefinite extent and polymerization may not start at all in some cases. The degree of polymerization (D.P.) of the polymers formed are very low in all these cases. In order to explain the initiation and termination reaction the following mechanism may be proposed



In presence of excess H_2O_2




Thus excess hydrogenperoxide is expected to facilitate continuation of polymerization by ensuring profuse supply of hydroxyl radicals. The lower degree of polymerization can be explained on the basis of quick formation of the growing polymer radical by the  radical and quinone formed during the process (Reactions iv and v). The endgroup analysis shows the presence of hydroxyl endgroup to an extent of about one per chain (Table X) and it appears that termination is probably due to disproportionation or unimolecular. But we are not sure whether the product in reaction iv will give

TABLE-X


Endgroup Analysis of Poly(methylmethacrylate) Initiated
by Hydroquinone-Hydrogenperoxide Redox in Aqueous
Systems

System : MMA - 0.094 mole/litre

Temp. ~ 30°C ; N₂ atmosphere

Hydroquinone x 10 ² m/l	Hydrogen peroxide x 10 m/l	$[\eta]$	O.D. of 0.05% polymer solu- tion with rhodamine re- agent		Endgroup/Chain		
			Origi- nal*	Phtha- lated	CQOH	OH	Total
0.1	1.32	0.18	0.449	0.745	0.08	1.11	1.19
1.0	1.32	0.12	0.461	1.411	0.08	1.38	1.46
2.5	1.32	0.095	0.495	1.720			
5.0	1.32	0.10	0.556	1.413	0.16	1.89	1.05
5.0	1.76	0.135	0.532	1.063	0.14	0.66	0.80

* 0.2% polymer solution used.

response for both the hydroxyl endgroups in our dye technique (dye technique may not account for phenolic OH). So, we cannot say anything definitely about termination mechanism. Thus in presence of excess hydrogenperoxide, the probability of inhibition by  is remote, as it is expected to be rapidly oxidised to quinone. Here quinone formed is probably the main inhibiting species in the polymerization process.