

CHAPTER-VIII

Summary

General

Permanganate in redox combination with oxalic acid and E.D.T.A. have been used as initiators under varied conditions and the endgroups incorporated in the resulting polymers have been detected and estimated. The role of mechanism of initiation with hydrogen peroxide-hydroquinone and hydrogen peroxide-hydroxyl amine redox systems have been studied by analysis of endgroups in the resulting polymers. Thiourea has been used as a generator of amino bearing endgroup in vinyl polymerization in redox combination with various oxidising agents such as  $\text{FeCl}_3$ , hydrogen peroxide, acidified potassium bromate, persulphate etc. and the endgroups incorporated have been estimated to identify the nature of the initiating species. Attempts have been made to give the termination mechanism in methyl methacrylate and styrene polymerization with the help of endgroup studies. The incorporation of endgroups in different fractions of a fractionated polymer sample has been studied to give an idea about the endgroup profile in a fractionated polymer sample. The detection and estimation of polymer endgroups have been carried out by the application of two dye techniques, (1) the dye partition technique and (2) the dye interaction technique. The results provides strong and direct evidences to the nature

and identity of the initiating radicals. This again helps to throw some light on the mechanism of the chemical reactions undergone by the initiating species for the generation of free radical intermediates and on the mechanism of polymerization reaction.

Use of Permanganate-E.D.T.A. and Permanganate-Oxalic Acid  
as Redox Initiator of Vinyl Polymerization

Permanganate in redox combination with E.D.T.A. has been used as initiator of polymerization of methyl methacrylate and comparative studies regarding the kinetics and the endgroup picture have been made with the similar redox initiating system, permanganate-oxalic acid.

The permanganate-E.D.T.A. redox initiating system is basically similar to the well-known oxalic acid permanganate redox initiating system with the exception that the former is active even in fairly alkaline pH, whereas the latter operates only the acidity of the medium is maintained.

The permanganate exponent with respect to methyl methacrylate in permanganate-E.D.T.A. redox system has been found out. The exponent comes out to be 0.80 which indicates that termination in this system takes place both unimolecularly and through bimolecular collision between two chain radicals. This is in contrast with permanganate-oxalic acid redox

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Dye Techniques for Endgroup Analysis

Dye partition technique				Dye interaction technique			
Endgroup detected	Dye. reagent	Solvent for polymer	Results	Endgroup detected	Dye reagent	Solvent for polymer	Result
1a. Sulfate sulfonate for the like (anionic sulfoxy endgroups)	Aqueous methylene blue in 0.01M HCl solution	Chloroform	Chloroform layer turns blue	1. Carboxyl, hydroxyl trans-formed to carboxyl, sulfate, sulfonate (anionic acidic endgroups)	Rhodamine reagent in benzene	Benzene	Color changes from orange yellow to pink
b. Hydroxyl transformed to sulfate	-do-	-do-	-do-				
2a. Chlorine bromine (halogens) transformed to quaternary pyridinium halide endgroups	Aqueous disulfine blue in 0.01M HCl solution	-do-	-do-				
2b. Amino endgroups	-do-	-do-	-do-				

system where the permanganate (initiator) exponent changes from 1.0 to 0.5 with change in permanganate concentration, as reported by Palit and Konar.

The endgroups incorporated in permanganate-oxalic acid and permanganate-E.D.T.A. have been studied by the application of dye techniques. For permanganate-oxalic acid redox initiating systems experiments were performed two different monomer concentrations (0.062 and 0.094 mole/litre, respectively) where rates of polymerization are almost identical as reported earlier. Both carboxyl and hydroxyl endgroups were incorporated and the sum total of carboxyl and hydroxyl endgroups content generally lay between 1.5 to 2 per chain, although their respective proportion varied over a considerable range and, in a few cases, hydroxyl endgroup content was almost negligible. The endgroup picture in permanganate-E.D.T.A. redox is very similar to that of permanganate-oxalic acid redox initiating system.

Styrene was polymerized in emulsion phase with permanganate-oxalic acid redox to avoid the error which may come due to the hydrolysis of methyl methacrylate in acidic medium. The endgroup picture was found to be the same as in the case of poly(methyl methacrylate). But different results were obtained in case of permanganate-E.D.T.A. redox initiated polymerization of MMA carried out in almost neutral medium. The overall endgroup content decreases considerably

with the increase in pH of the medium, due to lesser incorporation of hydroxyl endgroups.

#### Redox Initiating Systems Containing $H_2O_2$ as an Oxidant

Hydrogen peroxide in redox combination with hydroxylamine hydrochloride and hydroquinone have been used as initiators of polymerization and the endgroup pictures have been studied.

In case of hydrogen peroxide-hydroxylamine redox initiation two hydroxyl endgroups per chain of the polymer formed have found to be incorporated. Possible mechanism for initiation has been given.

In case of hydrogen peroxide-hydroquinone redox initiated polymerization, the molar ratio of hydrogen peroxide-hydroquinone has been found to be the main criterion. The presence of excess hydrogen peroxide is essential for effective initiation. One hydroxyl endgroup per chain has found to be incorporated in the resulting polymers.

#### Redox Initiated Polymerization Using Thiourea as a Reductant

Altogether fifteen reagents have been tested as oxidants in conjunction with thiourea as reductant and quite a few of them have been found to form redox initiation pair. The endgroups incorporated have been studied to give an idea about the nature and identity of the initiating radicals.

In presence of ferric chloride or ethylene dibiguanide complex salts of tripositive silver as an oxidant the endgroups incorporated are mainly amino. But in presence of hydrogen peroxide or persulfate as an oxidant, besides amino endgroups fragments of oxidants are also incorporated as endgroups in polymers.

Among all the redox systems containing thiourea, acidified bromate-thiourea redox system is the most interesting. It forms a very efficient redox initiating system with thiourea as is evidenced by its capability of polymerizing hydroquinone stabilized water soluble vinyl monomers at very low temperature ( $\sim 0^{\circ}\text{C}$ ) and with quite fast a rate.

In highly acidic medium ( $[\text{Acid}] > 10^{-2}\text{N}$ ) sulfonate and not amino endgroups are found to be incorporated in polymers. But sulfonate endgroup content gradually decreases with reduction of the acidity of the medium and below  $10^{-2}\text{N}$  acid concentration, amino and/ or sulfonate endgroups are detected in polymers.

All these redox systems can also initiate polymerization in presence of oxygen with prolonged induction period. The endgroup picture does not suffer any significant change in presence of oxygen.

Evidences so far collected indicate the generation of  $\dot{\text{S}}\text{-C}(\text{:NH})\text{.NH}_2$  radicals in the system of oxidation of

isothiourea,  $\text{HS-C(:N).NH}_2$  and these are incorporated in polymers as endgroups. Suitable initiation mechanism has been suggested in each case.

Use of  $\gamma\gamma'$ -Azo( $-\gamma$ -cyano-n-valeric Acid) for Generation of Carboxyl Bearing Radicals

$\gamma\gamma'$ -Azo( $-\gamma$ -cyano-n-valeric acid) has been used as initiator for solution polymerization of MMA and styrene using dimethylformamide and ethylene carbonate as solvents. Results of endgroup analysis show that about one endgroup per chain of polymer formed is incorporated in case of ethylene carbonate as solvent but lower (e.g. less than one) in case of dimethyl formamide. In case of dimethyl formamide its chain transferring capacity influence in termination thereby reducing the endgroup incorporation. Termination mechanism has been suggested for polymerization of methyl methacrylate and styrene.

Endgroup Profile of Fractionated Polymers

The number average molecular weight of different fraction of a few polymers, containing reactive endgroups has been determined by viscometry and osmometry as well, and endgroup contents per polymer chain have been calculated by utilising their molecular weight value. The results

show that the endgroup content per chain monotonically decrease with decrease in molecular weight of fraction concerned. The reason for such a monotonic decrease in endgroup profile is still obscure and tentative mechanism has been suggested for termination in polymerization processes.