

CHAPTER-V

Redox Initiated Vinyl Polymerization Using Thiourea
as a Reductant

Introduction

Use of thiourea and N-substituted thiourea as redox component for initiation of aqueous vinyl polymerization is rather recent. Recently two groups of workers^{112, 113} have used these reducing agents with hydrogen peroxide (as the oxidant) for initiation of aqueous polymerization of acrylonitrile and suggested a tentative initiation mechanism on the basis of their kinetic results. In case of dye (eosin) sensitised aqueous photopolymerization of acrylamide in oxygen atmosphere, Dolzenne et al¹¹⁴ also used thiourea as the reductant and concluded that the initiating redox system actually consists of thiourea and hydrogen peroxide.

Recently the dye partition technique has been extended for the detection and estimation of amino bearing endgroups in polymers^{115, 116}. Use of thiourea as a reductant in redox initiated vinyl polymerization has a possibility of generating amino radicals. In fact quite a large number of oxidants have been found to be capable of forming redox initiation pairs with thiourea, with varying efficiencies, and special mention may be made of the redox pairs formed by the following oxidants:

- (a) Ferric chloride (Fe^{3+}) ;
- (b) Ethylene dibiguanide complex salts of tripositive silver (Ag^{3+}) ;
- (c) Hydrogen peroxide (H_2O_2);
- (d) Persulfate ($\text{S}_2\text{O}_8^{2-}$) and
- (e) Potassium bromate + hydrochloric acid ($\text{BrO}_3^- + \text{HCl}$)

Among these oxidants (a), (c) and (e) have no initiating capacity by themselves at room temperature, but (b) and (d) can do so only after prolonged induction period. The end-groups incorporated in the polymers initiated by the above mentioned redox initiators have been studied in details to throw some light about the mechanism of initiation in such redox initiating systems.

Experimental

All the reagents used were either B.D.H. or E. Merck analytical grade reagents. Dye samples used were obtained in purified form and were used without further purification other experimental details are given in the previous chapter.

The induction period was generally 0-15 mins. in case of redox pairs (a) to (d) in nitrogen atmosphere. But in presence of oxygen, induction period was rather prolonged. In case of (a), relatively high concentration of Fe^{3+} and thiourea were needed to initiate polymerization ; but at very

high Fe^{3+} concentration, induction period was quite prolonged and rate of polymerization was very slow. In case of (c) polymerization did not start at all if certain minimal concentration ($\sim 0.005 \text{ M}$) was not present in the system. Rate of polymerization was quite fast in all these cases and total yield was also quite high except in case of (b) where color of Ag(III) complex was discharged on addition of thiourea and polymerization stopped after some time (maximum yield, about 70%). In case of (e) induction period varied between 0 to 60 minutes, depending on the concentration of ingredients in the system.

MMA was photopolymerized in air flushed aqueous systems containing eosin and thiourea. Flasks containing all the ingredients were placed in front of 200 watt bulb for a few hours and temperature in the system increased to about $50-55^{\circ}\text{C}$ during this period. Induction period was quite prolonged. To maintain the pH of the medium at 9.2 and 8.0, borax and phosphate buffers were used respectively.

Results and Discussion

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 pairs. Polymers produced have been found to contain amino endgroups almost in all cases and results of these experiments have been tabulated in Table-XI.

TABLE XI

Aqueous Polymerization of Methyl Methacrylate Initiated by Redox Systems Containing Thiourea as the Reductant

at Room Temperature ($\sim 25-30^\circ\text{C}$)

System : MMA = 0.094 mole/litre ; Thiourea = 10^{-2} mole/litre ; N_2 atmosphere.

No. of experiment	Oxidant mole/l	Polymerization rate	Inhibition period (I.P.) min.	$[\eta]$	Endgroup expected	Endgroup found by dye techniques*	Remarks
1.	Acidified potassium bromate 10^{-2}	Very fast	12	0.90	Amino	Amino, sulfonate	Initiation with neutral bromate occurs with long I.P. (3-4 days). Oxidation of amino bearing endgroup to sulfoxy is a possibility
2.	Potassium permanganate (acidic & neutral) -do-	Moderate	20	0.30	Amino	Amino (trace) and sulfonate	MnO_2 separates out immediately. Oxidation of amino bearing endgroup to sulfoxy is a possibility
3.	Potassium persulfate -do-	Fast	12	0.94	Amino, and/or sulfonate	Amino, sulfonate and hydroxyl	Amino predominates
4.	Benzoyl peroxides** 10^{-3}	Very slow	20	-	-	-	Little polymerization propagation stops after sometime.

(contd.....)

TABLE XI (contd.,...)

No. of experiment	Oxidant	Oxidant mole/l	Polymerization rate	Inhibition period (I.P.) min.	$[\eta]$	Endgroup expected	Endgroup found by dye techniques*	Remarks
5.	m-Nitro benzoyl peroxide**	10^{-3}	Very slow	25	-	-	-	Little polymerization propagation stops after sometime
6.	Potassium dichromate	-do-	-	-	-	-	-	No initiation even with acid dichromate
7.	Potassium perchlorate	-do-	-	-	-	-	-	No initiation
8.	Potassium chlorate with/without acid	10^{-2}	-	-	-	-	-	-do-
9.	Hydrogen peroxide	10^{-2}	Very fast	10	0.10	Amino and/or hydroxyl	Amino and hydroxyl	Very low D.P.; hydroxyl predominant
10.	Ferric chloride	10^{-3}	Fast	25	0.94	Amino and/or chlorine	Amino	.

(contd.....)

TABLE XI (contd.....)

No. of experiment	Oxidant	Oxidant mole/l	Polymerization rate	Inhibition period (I.P.) min.	$[\eta]$	Endgroup expected by dye techniques*	Endgroup found by dye techniques*	Remarks
11.	Bromine	10^{-4}	Moderate	45	0.50	Amino and/or bromine	Amino	Bromine endgroup also may be present
12.	Ammoniacal silver nitrate	10^{-3}	-	-	-	-	-	Reduction to metallic silver takes place immediately
13.	Fehling's solution	10^{-2}	-	-	-	-	-	Slow reduction to cuprous state
14.	Erythrosin J***	10^{-5}	Moderate	30	0.42	Amino	Amino	
15.	Methylene blue***	10^{-4}	Slow	160	0.82	Amino	Amino	Inhibition period very long.

* Ref. 6, 7, 11 and 12

** Monomer solution of oxidation was used (oxidant being insoluble in water).

*** Exposed to 200 watt bulb.

Endgroup Analysis

The results of endgroup analysis of poly(methyl methacrylate) samples, initiated by redox pairs formed by oxidants Ferric chloride, ethylene dibiguanide complex salts of tripositive silver, hydrogen peroxide, persulfate, are presented in Table-XII. These results indicate that in case of oxidants ferric chloride and ethylene dibiguanide complex salts of tripositive silver, endgroups incorporated in polymers are mainly amino, with little or no hydroxyl endgroup and it appears that amino bearing radicals derived from thiourea are mainly responsible for both initiation and termination in these cases. In case of hydrogen peroxide, besides amino endgroups, hydroxyl endgroups are also found to be incorporated in polymers and relative extent of hydroxyl endgroups are much more than amino endgroups. These hydroxyl radicals are inevitably derived out of hydrogen peroxide, as also suggested by other workers^{112, 113}. In case of persulfate, polymers are found to contain amino, sulfate and occasionally hydroxyl endgroups to various extents. It appears that amino-bearing radicals are generated out of thiourea and sulfate and hydroxyl radicals are formed out of persulfate.

Among all the redox systems containing thiourea, acidified bromate-thiourea system merits special investigation due to the following features, viz., (i) the initiating efficiency is very high, probably highest of all the redox

TABLE- XII

Endgroup Analysis of Poly(methyl methacrylate) Obtained
by Aqueous Initiation with Redox Systems Containing
Thiourea as the Reductant

System : MMA = 0.094 mole/litre ;

Temperature ~ 25-30°C (unless otherwise mentioned) ;

N₂ atmosphere (" " ")

Thiourea m/l x 10 ²	Oxidant	Oxidant m/l x 10 ² [η]		Average number of endgroups per polymer chain		
				NH ₂	OH	SO ₄
1.0	FeCl ₃ , 6 H ₂ O	0.1	1.61	1.68	0.79	-
2.5	(a)	0.1	0.80	2.10	0.28	-
5.0		0.1	0.56	1.80	0.26	-
10.0		0.1	0.46	1.85	-	-
2.5		0.05	1.12	1.65	0.16	-
2.5		0.2	0.70	3.0	0.26	-
5.0		0.88	0.31	2.99	-	-
20.0		4.8	0.46	3.70	-	-
5.0 (O ₂ atm.)		0.1	0.87	1.79	-	-
2.5 (50°C)		0.1	1.08	1.45	-	-

(contd....)

TABLE- XII (contd....)

Thiourea m/l x 10 ²	Oxidant	Oxidant m/l x 10 ² [7]		Average number of endgroups per polymer chain		
				NH ₂	OH	SO ₄
	Ag ⁺ .C ₂ H ₄ (C ₂ H ₅ N ₃) ₂ ³⁺					
0.02	ClO ₄ ⁻	0.04	0.55	1.51	-	-
0.04	(b)	0.04	0.46	1.45	-	-
0.08		0.04	0.47	2.27	-	-
0.16		0.04	0.51	3.20	-	-
0.08		0.08	0.34	2.17	-	-
0.04 (O ₂ atm.)		0.04	0.66	1.80	-	-

0.1	H ₂ O ₂	1.0	0.78	0.11	0.93	-
0.5	(c)	1.0	0.36	0.24	0.99	-
1.0		1.0	0.27	0.35	1.02	-
0.5		5.0	0.28	0.13	1.55	-
5.0		2.0	0.33	0.18	0.74	-
5.0 (O ₂ atm.; light)		2.0	0.32	0.86	-	-
1.0 (O ₂ atm.)		2.0	0.23	0.31	-	-

0.5	K ₂ S ₂ O ₈	0.5	1.35	0.38	1.80	0.65
5.0	(d)	0.5	1.22	2.10	0.90	0.22
10.0		0.5	1.24	3.00	-	0.24
1.0		0.1	1.44	0.81	-	-
1.0		0.5	1.14	1.00	-	0.47
1.0		1.0	1.07	0.52	0.36	0.62

systems containing thiourea and inhibition period is practically undetectable in some cases : (ii) most of the water soluble vinyl monomers can be polymerized with it, with little or no induction period, even when they are stabilized with hydroquinone ; (iii) initiation does take place even at as low a temperature as 0°C and in the range of 5 to 19°C the rate is fairly high and (iv) the acidity of polymerization medium governs the endgroup profile of the resultant polymers ; initiating ability and rate of polymerization are also directly linked with it. The initiating power of the system becomes almost latent in the complete absence of acid and the span of inhibition period, which is a visible measure of initiating power, becomes shorter and shorter until it vanishes as the acid concentration is increased from 10^{-4} N to 0.1 N (Table XIII).

When acidity of the system is high ($[\text{Acid}] > 10^{-2}$ N), amino endgroups are not detected in polymers. On the contrary, sulfonate (non-hydrolyzable) endgroups are found to be incorporated in polymers indicating thereby that acidic sulfur atom is directly linked to the carbon atom of the polymer chain. In highly acidic medium, polymers are found to contain almost one sulfonate endgroup per chain. But sulfonate endgroup content gradually decreases with reduction of the acidity of the medium and below 10^{-2} N acid concentration, amino and/or sulfonate endgroups are detected in polymers (Table XIV).

TABLE XIII

Aqueous Polymerization of Methyl Methacrylate by Thiourea-Acidified Bromate Redox System at Room Temperature (~ 25-30°C)

System : MMA = 0.094 mole/litre ; N₂ atmosphere

Thiourea mole/l x 10 ²	KBrO ₃ mole/l x 10 ²	HCl mole/l x 10 ²	Inhibition period, min.	Dye Partition Technique for		Amino endgroup with disulfine. blue.	
				Sulfonate endgroup with methylene blue	Sulfonate endgroup per chain		
				O.D. of 0.1% polymer solution at 660 m μ	O.D. of 0.1% polymer solution at 660 m μ	Amino endgroup per chain	
1.0	1.0	10.0	Nil	0.34	1.55	1.22	-
1.0	1.0	1.0	12	0.90	0.11	0.34	0.67
1.0	1.0	0.1	40	1.05	-	-	0.70
1.0	1.0	0.01	60	1.41	0.11	0.61	0.44
1.0	0.1	1.0	15	1.88	-	-	0.35
1.0	0.01	1.0	60	Very little polymerization	-	-	-
0.1	1.0	1.0	15	0.39	0.48	0.47	-
0.01	1.0	1.0	17	1.07	0.20	0.71	-

TABLE-XIV

Effect of Acid Concentration on the Aqueous Polymerization of Methyl Methacrylate by Thiourea-Acidified Bromate Redox System at Room Temperature ($\sim 25-30^\circ\text{C}$)

System : Thiourea = $\text{KBrO}_3 = 10^{-2}$ mole/litre ;

MMA = 0.094 mole/litre ; N_2 atmosphere

HCl mole/l $\times 10^2$	Inhibition period (I.P.) min.	$[\eta]$	Dye Partition Techniques for Endgroup Analysis			Sulfoxy Amino (nonhydro- lyzable)	Endgroup/Chain
			O.D. of 0.1% polymer solution with disulfine blue at 630 $m\mu$	with methylene blue at 660 $m\mu$			
10.0	Nil	0.34	-	1.55	1.22	-	-
7.0	1-2	0.25	-	1.54	0.83	-	-
5.0	2	0.37	-	0.67	0.61	-	-
4.0	5	0.38	-	0.86	0.78	-	-
2.0	10	0.68	-	0.16	0.34	-	-
1.0	12	0.90	0.67	0.11	0.34	1.83	1.83
0.1	40	1.05	0.70	-	-	2.34	2.34

Nature of Primary Radicals

(i) Sugimura et al¹¹³ found that both urea and guanidine are incapable of forming redox pairs with H_2O_2 and concluded that N-bearing groups in thiourea do not take any part in radical generation. They also studied the initiating efficiencies of thiourea and a number of N-substituted thiourea in presence of H_2O_2 and suggested that isothiurea, $HS-C(:NH).NH_2$, a thiol, which exists in tautomeric equilibrium with thiourea in aqueous solution, is the reductant. When it takes part in reduction, the reactive H atom attached to sulfur may be removed and primary isothiocarbamido radical, $\dot{S}-C(:NH).NH_2$, may be generated.

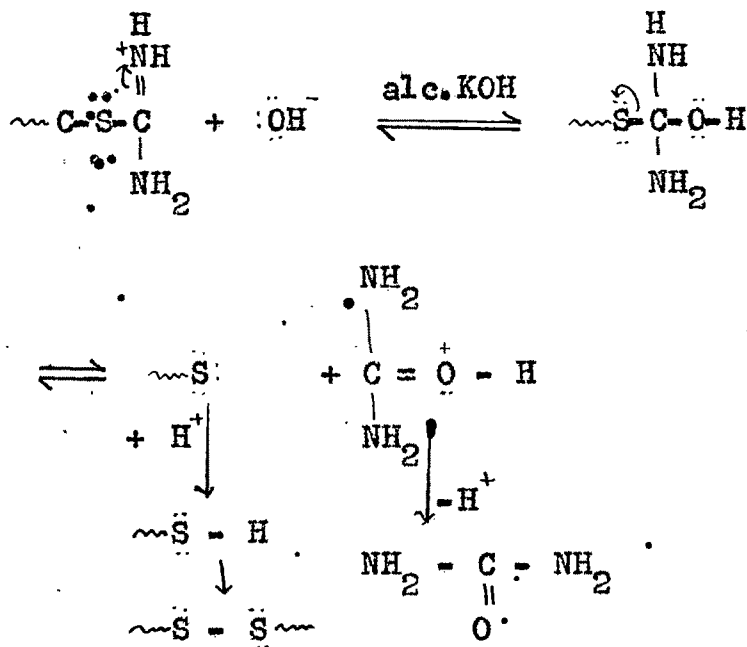
(ii) Oxidation of thiourea with acid-permanganate is known to generate formamidine disulfide¹¹⁷ $NH_2.C(:NH).S.S.C(:NH).NH_2$, and the initiating capability of this redox pair suggests that intermediate isothiocarbamido radicals might be formed during this redox reaction. If this isothiocarbamido radical initiates polymerization, the resultant amino bearing polymeric endgroup should be represented as $\sim C-S-C(:NH).NH_2$.

(iii) Our dye-partition technique using disulfine blue dye reagent also indicates the presence of such an

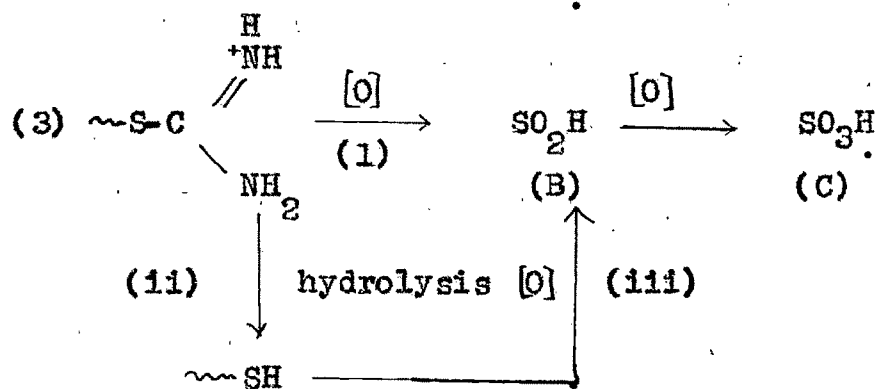
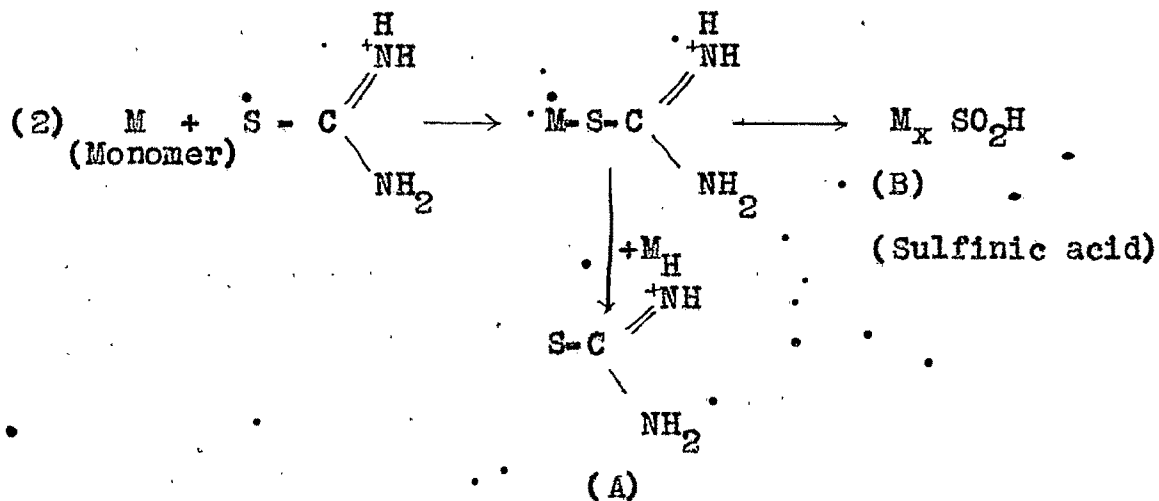
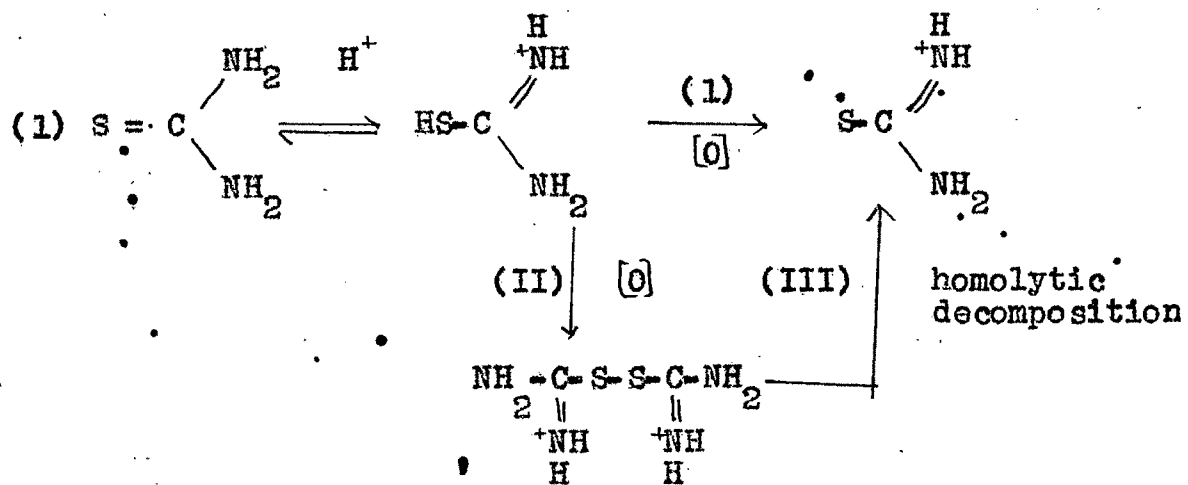
endgroup, though it is very difficult to predict at this stage whether both NH and NH₂ groups would give response to our dye-partition technique. If the radical end was on N and not on S, then the endgroup should have been $\sim\text{NH.C}(\text{:S}).\text{NH}_2$, which is very similar to $\sim\text{NH.C}(\text{:O}).\text{NH}_2$ endgroup present in polyacrylamide ; but the later is found to be insensitive to disulfine blue dye reagent.

(iv) We have failed to detect the presence of amino groups in such polymers by I.R. technique, evidently due to their very low concentration.

(v) Mondal et al¹¹⁸ in our laboratory have shown that on treating benzene or acetone solution of such polymers with alcoholic KOH under very mild conditions, response to disulfine blue dye reagent disappears. In most cases the molecular weight of the treated polymers increases considerably. A polymer of the same starting molecular weight and having carboxyl endgroups, on similar treatment, does not show any significant change in molecular weight. This indicates a hydrolytic cleavage of the terminal $\sim\text{S-C}$ bond during this treatment with subsequent removal of amino group bearing part from the polymer chain¹¹⁹. Increase in molecular weight may be due to disulfide formation, as indicated below:-



(vi) The general features of acidic thiourea-bromate redox initiation system and endgroup analysis of resultant polymers indicate a complex and quite different initiation mechanism. It has been reported earlier that sulfonic acid¹²⁰⁻¹²³ are produced by disproportionation of sulfinic acids, and the latter are excellent low temperature catalysts for vinyl polymerization^{124, 125}. Initiating efficiency of sulfonic acids is rather controversial. Since notable features of acidic thiourea-bromate initiation (as mentioned before) show close resemblance to sulfinic acid initiation, the following tentative reaction mechanism has been elicited for this system.



Polymer (A) would give response for amino endgroups and polymer (B) for nonhydrolysisable sulfonate endgroups. (B), which

is a sulfinic acid, may be responsible for initiation as well. Formation of formamidine sulfinic and sulfonic acids during oxidation of thiourea has been reported by earlier workers also^{126,127}. The variation of average sulfonate endgroup content of polymers (Table-XIV) may be explained in terms of either incomplete oxidation of amino bearing endgroups (equation 3) or participation of both isothiocarbamido radical and sulfinic acid in initiation (equations 1 and 2).

Effect of Oxygen

All these redox systems can also initiate polymerization in oxygen flushed closed systems with prolonged induction period. But if oxygen is slowly bubbled in any of these systems, polymerization does not start. This indicates that oxygen is an inhibitor for these systems, as also for many other typical free radical initiated systems. But when present in limited quantity, it is rather quickly consumed giving products which probably do not inhibit the process. The endgroup picture does not suffer any significant change in presence of oxygen (Table-XII). In case of photosensitized eosin - thiourea system, oxygen, however, has been claimed to be a necessary constituent of the redox initiating system¹¹⁴.

Effect of pH of the Medium

Normally with thiourea as a reductant, polymerization either proceeds very slowly as does not proceed at all in alkaline medium. For example, with H_2O_2 - thiourea redox initiating system polymerization does not start at all in alkaline medium at room temperature. But Bonwini et al¹¹² have reported that polymerization occurs with hydrogen peroxide-thiourea redox system in alkaline medium at 60°C. They also polymerized acrylonitrile in both acid and alkaline medium with thiourea- Fe^{3+} -hydrogen peroxide redox system at 60°C. On the other hand, thiourea probably loses its reducing property to a great extent in alkaline medium as shown by the fact that while it can reduce selenium dioxide to metallic selenium in acid medium, almost quantitatively, it practically fails to do so in alkaline medium. It is therefore more likely that the initiating power obtained by Bonwini in alkaline medium is unconnected directly with the presence of thiourea and is due to decomposition of hydrogen peroxide at such a high temperature; also the possibility of independent redox reaction between Fe^{3+} - H_2O_2 in the acrylonitrile system cannot be ruled out.

However, MMA could be polymerized in air-flushed closed systems with prolonged induction period at pH 8 and 9.2 using photosensitized eosin - thiourea redox system¹¹⁴ as initiator; but very little or no amino endgroups were

found to be incorporated in resultant relatively high molecular weight polymers. Similar experiments, when carried out in acid or neutral medium produced polymers of relatively low molecular weight and of very high amino endgroup content (Table-XV). The reason for incorporation of quite a large number of amino endgroups in that case is still obscure. The presence of any hydroxyl endgroup in both these types of polymers could not be established by the application of dye techniques (the applicability of pyridine-phthalic anhydride technique in these cases is, however, rather subject to large error due to the presence of large number of rhodamine-responsive groups in the original polymers.

Thus the comparison of results presented in Table-XII and Table-XV together with the fact that in thiourea-hydrogen peroxide redox initiation system a minimal concentration (~ 0.005 M) of hydrogen peroxide is essential, indicate that in no way the thiourea-eosin system resembles the thiourea-hydrogen peroxide and thus the participation of H_2O_2 in the initiation mechanism of thiourea-eosin system as presumed by Dolzenne¹¹⁴ could not be established by our work.

Mechanism

In conformity with the results of endgroup analysis, redox reaction (a) and (b) may be represented as,

TABLE- XV

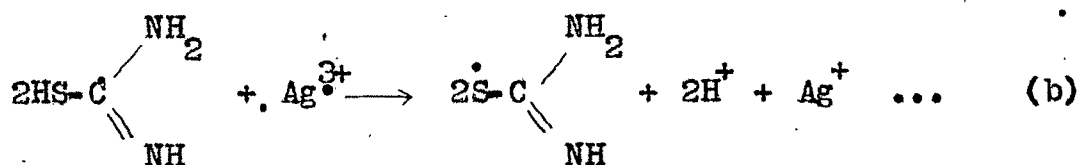
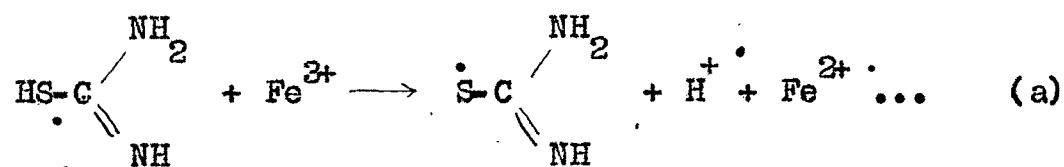
Endgroup Analysis of Poly(methyl methacrylate) Obtained
by Aqueous Photoinitiation with Eosin and Thiourea

System : MMA = 0.094 mole/litre ; O₂ atmosphere*

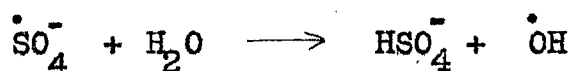
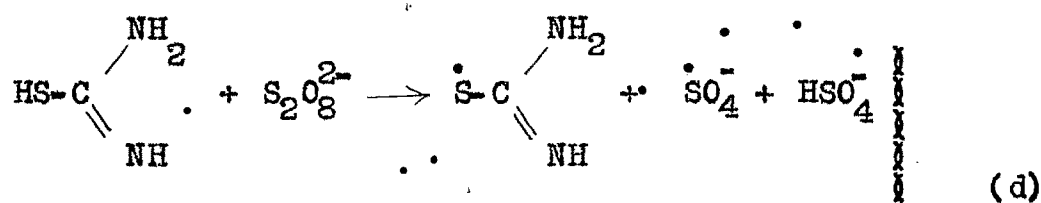
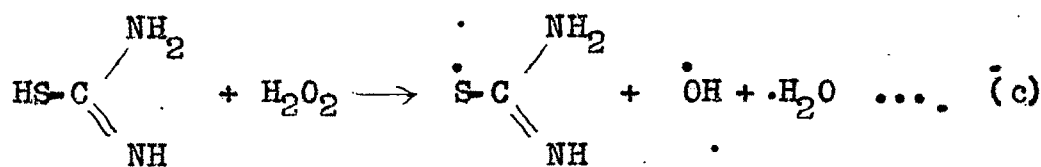
Thiourea mole/l x 10 ²	Eosin mole/l x 10 ⁴	pH of the medium	[η]	O.D. of 0.01% polymer soln. with disulfine blue at 630 m	Amino** endgroups- chain
1	1.0	5-6	0.44	0.54	6.0
5	1.0	"	0.40	0.50	4.70
10	1.0	"	0.43	0.40	4.05
5	0.5	"	0.33	0.68	4.87
5	0.2	"	0.37	0.43	3.65
5	1.0	9.2	0.80	0.01	0.25
1	1.0	9.2	0.73	0.04	0.92
5	1.0	8.0	0.65	0.01	0.19
1	1.0	8.0	1.40	0.01	0.48

* Samples were placed in front of a 200 watt lamp for a few hours ; temperature increased to about 55°C during polymerization.

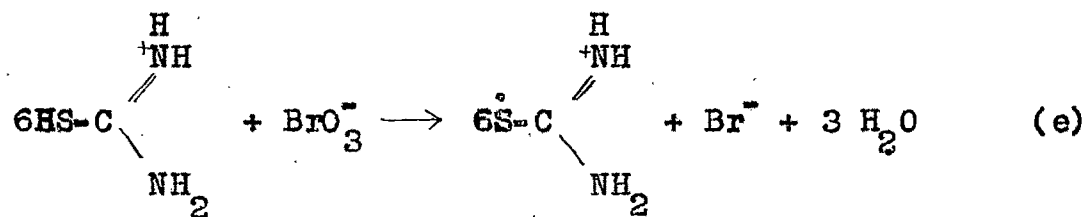
** We failed to detect any hydroxyl endgroup in these polymers by our dye technique.



In cases of (c) and (d), corresponding redox reaction may be represented as,



The proposed tentative initiation mechanism for acidic bromate-thiourea redox system has already been discussed and initial radical generation reaction may be represented as



It may be seen that isothioureia, which exists only ⁱⁿ aqueous solution, takes part in all these redox reactions. So, it is apparent that reducing property of thioureia should operate only in systems containing water, partly or wholly.