Graft Copolymerization of Vinyl Monomers onto Modified Cotton. IX. Hydrogen Peroxide–Thiourea Dioxide Redox System Induced Grafting of 2-Methyl-5-vinylpyridine onto Oxidized Celluloses

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Synopsis

Cotton cellulose was independently oxidized with potassium periodate, potassium dichromate–sulfuric acid, and potassium dichromate–oxalic acid, and the resulting oxidized celluloses were further modified by treatment with chlorous acid or sodium borohydride. The various modified celluloses so obtained were grafted with 2-methyl-5-vinylpyridine using a thiourea–dioxide–H_2O_2 redox system. It was found that the initiation characteristics of the cellulose samples vary widely with the oxidizing agent used. Further modification of the oxidized celluloses by treating them with chlorous acid enhances considerably their susceptibility toward grafting. The opposite holds true when these oxidized celluloses were modified by sodium borohydride treatment. Excluding thiourea dioxide from the polymerization system offsets grafting onto cotton cellulose while considerable grafting takes place on the various oxidized celluloses and their further modified samples. The work was also extended to study the factors which affect the graft uptake, homopolymer formation, and total conversion. In addition, the reactions involved in initiation of grafting were elucidated.

INTRODUCTION

The graft polymerization of vinyl monomers onto chemically modified cellulose has been reported. These reports have dealt with graft polymerization onto cellulose xanthate using H_2O_2 as initiator,[1] phosphorylated cellulose using Fe^{2+}–H_2O_2 redox system,[2] and cyanoethylated cellulose using γ-irradiation[3] or ceric ion method for initiation.[4,5] The ceric ion method has been also used for vinyl graft polymerization onto partially carboxymethylated cellulose,[6] acrylamidomethylated cellulose,[7] acetylated cellulose,[8] carbamoylethylated cellulose,[7] crosslinked cellulose,[5,9] oxidized cellulose,[10–14] and cellulose bearing sulfur-containing groups,[15] carboxyethyl together with cyanoethyl[7] or carboxymethyl along with cyanoethyl.[7] Very recent work showed the feasibility of using dimethylaniline–benzyl chloride mixture for initiation of graft polymerization of methyl methacrylate onto partially carboxymethylated cotton.[16] Potassium permanganate[17] and azobisisobutyronitrile[18] have also been reported to initiate grafting of vinyl monomers onto modified celluloses. In addition, sodium periodate has been used as initiator for vinyl graft polymerization onto oxidized celluloses.[19]

The present work deals with graft polymerization of 2-methyl-5-vinylpyridine onto cotton cellulose, oxidized celluloses, and their further modified samples using a thiourea dioxide–H_2O_2 redox system with a view to finding (a) the feasibility of this redox system to initiate grafting, (b) the factors affecting the magnitude of polymerization, (c) the behavior of the oxidized celluloses before

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and after being treated with chlorous acid or sodium borohydride toward grafting, and (d) the effect of excluding thiourea dioxide from the polymerization system on the graft uptake.

EXPERIMENTAL

Purified Cellulose

Egyptian cotton slivers were purified by a mild alkaline scouring (2% NaOH and 0.2% wetting agent, on weight of material) for 5 hr at 110°C and 6–10 lb/in.^{2} using a liquor ratio of 10:1.

Preparation of Oxidized Cellulose

Periodate-Oxidized Cellulose. The purified cellulose was immersed in an aqueous solution of potassium metaperiodate (0.01M) at 30°C for 24 hr, keeping a liquor ratio of 50:1.
Potassium Dichromate–Sulfuric Acid-Oxidized Cellulose. Oxidation of the purified cellulose was carried out with 0.1N potassium dichromate and 0.2N sulfuric acid at 30°C for 24 hr using a liquor ratio of 50:1.
Potassium Dichromate–Oxalic Acid-Oxidized Cellulose. Purified cellulose was stepped in an aqueous solution containing oxalic acid (2N) and potassium dichromate (2N) for 4 hr at 30°C using a liquor ratio of 50:1.
Treatment of Oxidized Cellulose with Sodium Borohydride Solution[20]. The various oxidized celluloses mentioned above were treated with unbuffered sodium borohydride solutions at 30°C for 24 hr, using a liquor ratio of 50:1.
Treatment of Oxidized Cellulose with Chlorous Acid[21,22]. The oxidized samples were treated with 0.2N sodium chlorite solutions in 1M acetic acid at 30°C for 72 hr. After all the treatments described above were completed, the samples were washed with several portions of distilled water in each case till free from the impurities and dried at ambient temperature before analyzing.

Analysis of Oxidized Celluloses

The copper number of these celluloses was determined according to a reported method.[23] For the determination of carboxyl groups, all the oxidized celluloses were rendered cation free by steeping them in a 0.5N hydrochloric acid at 30°C for 2 hr, followed by washing free of acid and drying at ambient temperature. The carboxyl content was determined by a method described elsewhere.[24]

Vinyl Monomer

2-Methyl-5-vinylpyridine (MVP) was the monomer used for graft polymerization. It was distilled under reduced pressure before use.

Initiator

The thiourea dioxide–hydrogen peroxide (H_2O_2) redox system was used for graft polymerization of MVP on the said substrates. Thiourea dioxide was prepared according to a reported method.[25]

Graft Polymerization Procedure

Unless otherwise stated, the graft polymerization reaction was carried out as follows: Conditioned cellulose sample (1 g) was steeped in 50 ml of a solution containing known concentrations of thiourea dioxide (TUO), H_2O_2, and MVP at pH 6. The flask was immediately stoppered and kept in a thermostatted water bath for periods varying from 0 to 120 min. During the reaction, the cellulosic material was kept well immersed in the solution. After the desired reaction time, the contents of the flask were filtered on a sintered glass crucible, washed with water, dried in an oven at 105°C for 5 hr, cooled to room temperature, and weighed. The samples was then repeatedly Soxhlet extracted with methanol, dried as described above, and weighed.

The percentages of the graft uptake, homopolymer, and total conversion were calculated as follows:

$$\% \text{ graft uptake} = \frac{\text{dry wt. of grafted sample} - \text{dry wt. of original sample}}{\text{dry wt. of original sample}} \times 100$$

$$\% \text{ homopolymer} = \frac{\text{dry wt. of homopolymer}}{\text{wt. of monomer used}} \times 100$$

$$\% \text{ total conversion} = \frac{\text{wt. of graft uptake} + \text{wt. of homopolymer}}{\text{wt. of monomer used}} \times 100$$

The term percent polymer, which is shown in Figures 7–10, is used in this paper to refer to either the graft uptake, homopolymer, or total conversion.

RESULTS AND DISCUSSION

Chemical Modification of Cellulose Via Oxidation

It is well known that the oxidation of cellulose results in creation of different functional groups on its molecule. Among these groups are alkali-sensitive reducing groups, enediol groups, carboxyl groups, and lactones. The carboxyl groups are formed in different positions of the anhydroglucose units of cellulose macromolecules. Reduction of the aldehyde, keto, enediol, and lactone groups can be brought about by sodium borohydride, whereas oxidation of aldehyde groups can be effected by chlorous acid. Hence, it is possible to obtain chemically modified cellulose by subjecting purified cellulose to selected oxidizing agents, followed by borohydride or chlorous acid treatments. In this way different functional groups in certain positions in the anhydroglucose units of cellulose macromolecules will be formed.

Oxidation of the purified cellulose was performed using three oxidizing agents as described in the experimental section; the reducing and acidic properties of these oxidized celluloses were determined before and after borohydride or chlorous acid treatment. The results obtained are summarized in Table I.

Previous studies[21] have shown that chlorous acid can be used for oxidation of free aldehydic groups present in oxidized celluloses without attacking the cellulose at other sites. Hence the effect of chlorous acid treatment is to produce carboxyl groups in the reducing type of oxidized cellulose. As is evident (Table I), chlorous acid oxidizes most of the reducing groups (assessed in terms of copper number), producing a substantial amount of acidic groups. That is, not all the

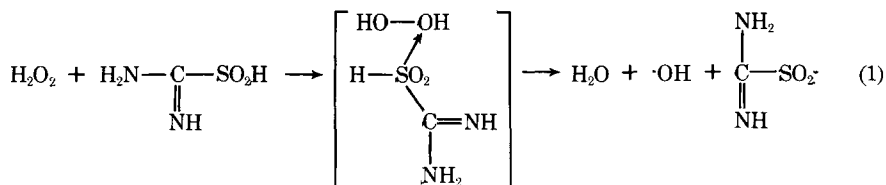<div align="center">Table I
Properties of Oxidized Celluloses</div>

Substrate	Copper number	Carboxyl content, meq/100 g
1. Potassium periodate-oxidized cellulose	9.3	9.47
2. Potassium periodate-oxidized cellulose treated with chlorous acid	1.68	20.50
3. Potassium periodate-oxidized cellulose treated with borohydride	0.5	1.32
4. Potassium dichromate–sulfuric acid-oxidized cellulose	0.36	1.84
5. Potassium dichromate–sulfuric acid-oxidized cellulose treated with chlorous acid	0.40	3.47
6. Potassium dichromate–sulfuric acid-oxidized cellulose treated with borohydride	0.28	1.32
7. Potassium dichromate–oxalic acid-oxidized cellulose	3.2	2.37
8. Potassium dichromate–oxalic acid-oxidized cellulose treated with chlorous acid	1.15	4.47
9. Potassium dichromate–oxalic acid-oxidized cellulose treated with borohydride	0.16	1.58

reducing groups in the oxidized celluloses are converted to carboxyl groups during the chlorous acid treatment.
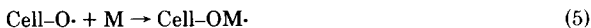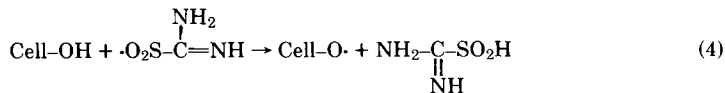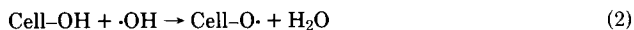
On the other hand, the effect of sodium borohydride treatment is to bring about a significant decrease in the copper number and a substantial decrease in the carboxyl groups (Table I). The significant decrease in copper number is rather expected since most, if not all, the reducing groups present in the oxidized celluloses are removed by the borohydride treatment, whereas the decrease in carboxyl groups after the borohydride treatment suggests (a) that the calcium acetate method[24] gives the total number of acidic groups, including the lactones, if present in the oxidized celluloses, and (b) that a certain amount of acidic groups, which are free carboxyl groups, remain unaffected by the borohydride treated with borohydride shown in Table I may be taken as representing free carboxyl groups present therein.

Grafting Studies

It is understandable that the presence of a reducing agent such as thiourea dioxide as a cocatalyst with H_2O_2 will accelerate decomposition of the latter to produce free radicals due to one electron transfer with concomitant cleavage of the O–O bond under the attack of this nucleophile. The reactions involved may be presented as follows:

$$H_2O_2 + H_2N-\underset{\underset{NH}{\|}}{C}-SO_2H \longrightarrow \left[\begin{array}{c} HO-OH \\ \nearrow \\ H-SO_2 \\ \searrow \\ C=NH \\ | \\ NH_2 \end{array}\right] \longrightarrow H_2O + \cdot OH + \underset{\underset{NH}{\|}}{\overset{\overset{NH_2}{|}}{C}}-SO_2^- \quad (1)$$

From eq. (1) it is reasonable to assume that polymerization onto cellulose (Cell–OH) can be initiated by the hydroxyl radical, eqs. (2) and (3), or the thiourea dioxide radical, eqs. (4) and (5), or both:

$$\text{Cell–OH} + \cdot\text{OH} \rightarrow \text{Cell–O}\cdot + H_2O \tag{2}$$

$$\text{Cell–O}\cdot + M \rightarrow \text{Cell-OM}\cdot \tag{3}$$

$$\text{Cell–OH} + \cdot O_2S\text{–}\overset{\overset{\displaystyle NH_2}{|}}{C}\text{=NH} \rightarrow \text{Cell–O}\cdot + NH_2\text{–}\underset{\underset{\displaystyle NH}{\|}}{C}\text{–}SO_2H \tag{4}$$

$$\text{Cell–O}\cdot + M \rightarrow \text{Cell-OM}\cdot \tag{5}$$

where M is the vinyl monomer to be grafted. Subsequent addition of monomer molecules to the initiated monomer on cellulose, eqs. (3) and (5), leads to propagation of a grafted chain on the cellulose backbone. Indeed, this is found to be true, as is seen from the results presented below.

Nature of The Substrate

The purified cellulose, the various oxidized celluloses, and their further modified samples were grafted with MVP (8%) by H_2O_2 (25 mmole/l.) and thiourea dioxide (10 mmole/l.) for different lengths of time. The polymerization reaction was carried out at 70°C and pH 6 using a material-to-liquor ratio of 1:50. Figures 1, 2, and 3 show the results obtained.

It is seen in Figure 1 that grafting proceeds initially fast, slows down with time, and then levels off. It is also seen that both the initial rate and the extent of grafting after a reaction time of 2 hr depend upon the type of the oxidized cellulose. The initial rate of grafting follows the order potassium dichromate–sulfuric acid–oxidized cellulose > potassium periodate-oxidized cellulose > purified cellulose > potassium dichromate–oxalic acid-oxidized cellulose. Whereas maximum grafting (i.e., the percent graft uptake after 2 hr) follows the order purified cellulose > potassium dichromate-sulphuric acid oxidized cellulose > periodate oxidized cellulose > potassium dichromate-oxalic acid oxidized cellulose.

This indicates that the oxidized state of cellulose varies widely with the oxidizing agent used, and such variation is probably responsible for the characteristic behavior of each sample during polymerization.
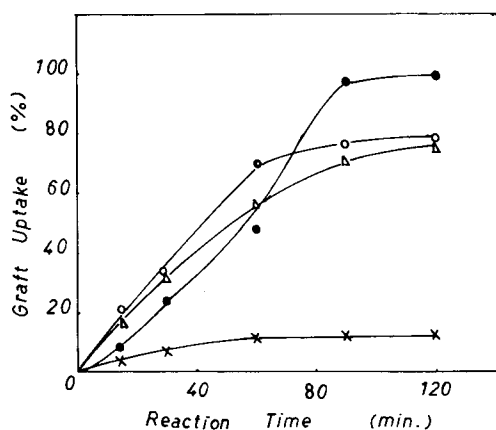

Fig. 1. Rate curves for graft polymerization of MVP on chemically modified celluloses: (●) unmodified cellulose; (X) dichromate–oxalic acid-oxidized cellulose; (O) dichromate–sulfuric acid-oxidized cellulose; (Δ) periodate-oxidized cellulose; [TUO], 10 mmole/l.; [H_2O_2], 25 mmole/l.; [MVP], 8%; pH, 6; temperature, 70°; material:liquor ratio, 1:50.
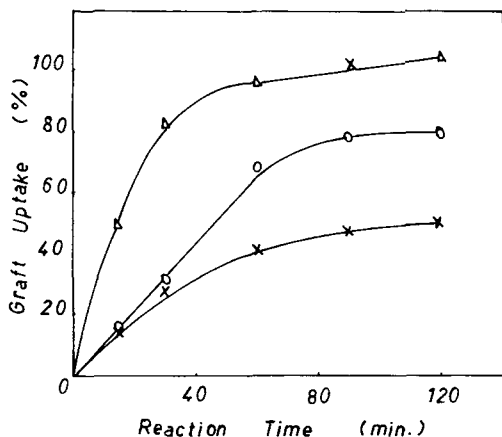
Fig. 2. Rate curves of graft polymerization of MVP on oxidized celluloses, after being treated with chlorous acid: (△) chlorous acid-treated periodate-oxidized cellulose; (○) dichromate–sulfuric acid-oxidized cellulose treated with chlorous acid; (×) dichromate–oxalic acid-oxidized cellulose treated with chlorous acid; [TUO], 10 mmole/l.; [H₂O₂], 25 mmole/l.; [MVP], 8%; pH, 6; temperature, 70°C; material:liquor ratio, 1:50.
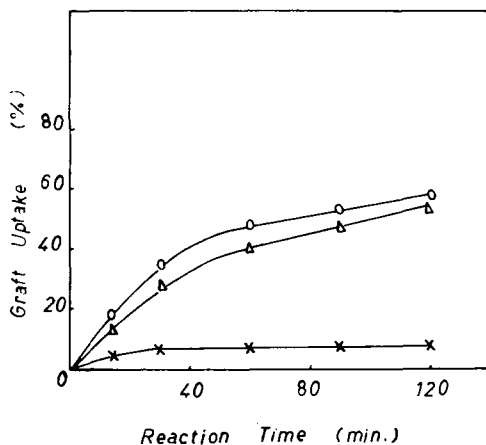

Fig. 3. Rate curves of grafting polymerization of MVP on oxidized celluloses treated with borohydride: (△) periodate-oxidized cellulose treated with borohydride; (○) dichromate–sulfuric acid-oxidized cellulose treated with borohydride; (×) dichromate–oxalic acid-oxidized cellulose treated with borohydride; [TUO], 10 mmole/l.; [H₂O₂], 25 mmole/l.; [MVP], 8%; pH, 6; temperature, 70°C; material:liquor ratio, 1:50.

Figure 2 shows the rate of grafting of the three oxidized celluloses after being treated with chlorous acid. It is clear that regardless of the oxidized cellulose used, the rate of grafting enhances substantially after treatment of the oxidized cellulose with chlorous acid. Since the latter oxidizes most of the reducing groups (assessed in terms of copper number in Table I) to carboxyl groups, there is indication that creation of carboxyl groups in the cellulose molecules increases the effectiveness of cellulose for graft polymerization with MVP. It is very likely that the presence of carboxyl groups (after ionization) increases the negative surface potential of the substrate thereby making it easier for the positively charged MVP monomer to approach the proximity of the substrate.

Evidence supporting the favorable effect of the presence of carboxyl groups

in the cellulose molecules on grafting is obtained from the behavior of oxidized celluloses treated with borohydride. In the latter, most of the carboxyl groups in the original oxidized celluloses are removed. As can be seen in Figure 3, the rate and extent of grafting for these substrates (oxidized cellulose treated with borohydride) are much lower than those for the corresponding oxidized celluloses.

Graft Polymerization in The Absence of Thiourea Dioxide

In the foregoing section, all the polymerization reactions were carried out using H_2O_2 together with thiourea dioxide. Here, attempts were made to omit thiourea dioxide from the polymerization system. Hence, graft polymerization of MVP (8%) on the purified cellulose, the various oxidized celluloses, and their further modified samples was performed using only H_2O_2 (25 mmole/l.) as initiator. The polymerization was conducted at 70°C and pH 6 for different periods of time using a material-to-liquor ratio of 1:50. The results obtained are shown in Figures 4, 5, and 6.

The data of Figure 4 reveal clearly that no grafting occurs on the purified cellulose in the absence of thiourea dioxide. With the oxidized celluloses, on the other hand, substantial grafting could be achieved; the magnitude of grafting relies on the oxidized agent used. Potassium periodate-oxidized cellulose proves to be the best substrate amenable for grafting with MVP using H_2O_2 as initiator, whereas potassium dichromate–oxalic acid-oxidized cellulose is the least. The percent graft uptake obtained with potassium dichromate–sulfuric acid-oxidized cellulose stands in a midway position.

The percent graft uptake follows the same order mentioned above, even after the oxidized celluloses were treated with either chlorous acid (Fig. 5) or borohydride (Fig. 6). Hence it is obvious that the graft polymerization characteristics of cellulose samples can be improved significantly by proper selection of the type of preoxidation.

That grafting failed to occur on the purified cellulose while taking place on
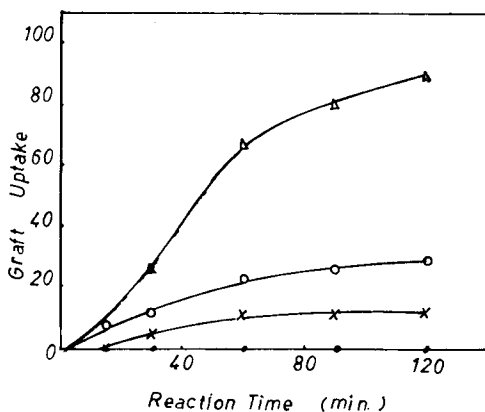

Fig. 4. Rate curves for graft polymerization of MVP on modified cellulose in absence of TUO: (△) periodate-oxidized cellulose; (○) dichromate–sulfuric acid-oxidized cellulose; (×) dichromate–oxalic acid-oxidized cellulose; (●) unmodified cellulose; [H_2O_2], 25 mmole/l.; [MVP], 8%; pH, 6; temperature, 70°C; material:liquor ratio, 1:50.
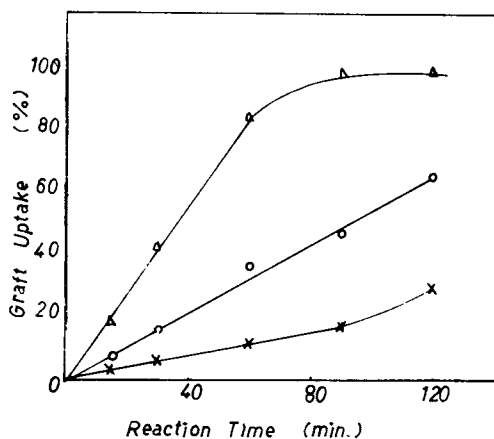
Fig. 5. Rate curves for graft polymerization of MVP in absence of TUO on oxidized celluloses treated with chlorous acid: (△) periodate-oxidized cellulose; (O) dichromate–sulfuric acid-oxidized cellulose; (×) dichromate–oxalic acid-oxidized cellulose; [H_2O_2], 25 mmole/l.; [MVP], 8%; pH, 6; temperature, 70°C; material:liquor ratio, 1:50.
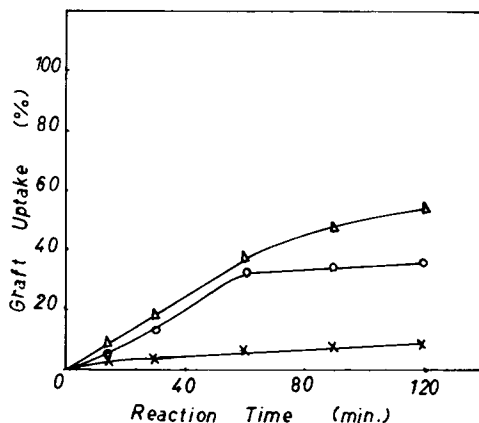

Fig. 6. Rate curves for graft polymerization of MVP in absence of TUO on oxidized celluloses treated with borohydride: (△) periodate-oxidized cellulose treated with borohydride; (O) dichromate–sulfuric acid-oxidized cellulose treated with borohydride; (×) dichromate–oxalic acid-oxidized cellulose treated with borohydride; [H_2O_2], 25 mmole/l.; [MVP], 8%; pH, 6; temperature, 70°C; material:liquor ratio, 1:50.

oxidized celluloses suggests that H_2O_2-oxidized celluloses form a very effective redox system for graft polymerization. Besides this, the oxidized celluloses contain ionizable carboxyl groups which facilitate attraction of the monomer to the vicinity of the cellulose. Thus it is not surprising that with some substrates, in particular, the periodate-oxidized cellulose, grafting initiated by H_2O_2 produces graft uptakes which are comparable to those brought about by grafting initiated by the H_2O_2–thiourea dioxide redox system.

Thiourea Dioxide Concentration

Graft polymerization of MVP onto potassium dichromate–sulfuric acid-oxidized cellulose was carried out at 70°C for 2 hr using the H_2O_2–thiourea dioxide redox system for initiation. The concentration of H_2O_2 in the polymerization

system was set at 25 mmole/l., whereas the thiourea dioxide concentration varied from 0 to 40 mmole/l. Figure 7 shows variation of the graft uptake with concentration of thiourea dioxide. It is clear that considerable grafting does occur even in the absence of thiourea dioxide, indicating formation of cellulose macroradicals capable of graft initiation. These cellulose macroradicals may be generated via decomposition of H_2O_2 in the presence of oxidized cellulose to yield hydroxyl radicals. That is, oxidized cellulose and H_2O_2 form an effective redox system for graft polymerization onto cellulose. As was shown above, H_2O_2 alone is not able to induce grafting of MVP onto unoxidized cellulose.

It is also seen in Figure 7 that increasing thiourea dioxide concentration upto 10 mmole/l. brings about a significant enhancement in the graft uptake. Beyond this concentration, the graft uptake drops sharply. In other words, a thiourea dioxide concentration of 10 mmole/l. constitutes the optimal concentration of grafting under the condition studied.

The significant decrease in grafting when higher thiourea dioxide concentrations were used could be interpreted in terms of a faster rate of termination probably due to an abundance of free-radical species in the polymerization system. It is also possible that at higher concentrations of thiourea dioxide, the latter acts as radical scavenger. A third possibility is that the homopolymerization reaction exceeds the grafting reaction at higher concentrations of thiourea dioxide. There is, however, little reason to believe that one of the three possibilities is operating to the exclusion of the other, though data presented below is not in favor of the third possibility.

The effect of thiourea dioxide concentration on the homopolymerization and total conversion is shown in Figure 7. Similar to grafting, both homopolymer and total conversion increase as the thiourea dioxide increases, attain maxima, and then fall at higher concentrations. But maximum homopolymer is achieved upon using about 3 mmole/l., in contrast to 10 mmole/l. for maximum grafting and maximum total conversion. Since the total conversion is the sum of monomer converted to graft as well as homopolymer, this finding implies that grafting is more favored than homopolymerization at concentrations higher than 3.3 mmole/l. This, indeed, unvalidates the third possibility suggested above for explaining the fall in grafting at higher concentrations of thiourea dioxide.
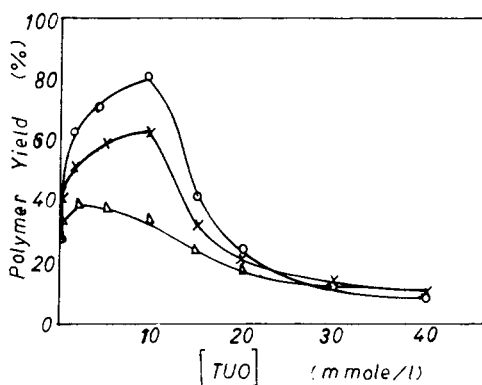

Fig. 7. Effect of thiourea dioxide concentration on graft uptake, homopolymer, and total conversion: (O) % graft uptake; (△) % homopolymer; (X) total conversion; [MVP], 8%; [H_2O_2], 25 mmole/l.; pH, 6; temperature, 70°C; reaction time, 2 hr; material:liquor ratio, 1:50.

Hydrogen Peroxide Concentration

Figure 8 shows the graft uptake as a function of H_2O_2 concentration when graft polymerization of MVP onto potassium dichromate–sulfuric acid-oxidized cellulose was carried out in the presence of thiourea dioxide (10 mmole/l.) at 70°C for 2 hr. As is evident, increasing the H_2O_2 concentration from 0 to 30 mmole/l. is accompanied by a significant increase in the graft uptake. Thereafter, grafting decreases as H_2O_2 concentration increases.

These finding could be explained as follows. In the presence of thiourea dioxide, H_2O_2 decomposes to yield hydroxyl and thiourea dioxide radicals as shown above, eq. (1). These free radicals may participate in (a) the direct abstraction of hydrogen atom from cellulose backbone to bring about cellulose macroradical capable of initiating grafting, (b) the termination process with the growing polymer chains, (c) the combination of free-radical species, in particular, hydroxyl and thiourea dioxide radicals, to yield $H_2N-C=NHSO_3H$, (d) the termination process with cellulose macroradicals, and (e) decomposition of H_2O_2 by the hydroxyl radical to give ultimately nacent oxygen.[26-28] At lower H_2O_2 concentrations, the effect of (a) seems to prevail over the combined effect of (b), (c), (d), and (e), thereby increasing grafting. The opposite holds true at higher H_2O_2 concentration where the combined effect of (b), (c), (d), and (e) is more pronounced than (a). As a result, lower grafting occurred.

The amount of homopolymer formed during graft polymerization of MVP onto the oxidized cellulose in question using different concentrations of H_2O_2 along with constant concentration of thiourea dioxide is given in Figure 8. It is seen that the homopolymer increases as the H_2O_2 concentration increases, attains a maximum, and then falls at higher H_2O_2 concentrations, similar to grafting. However, the fall in the homopolymer is not as sharp as in the case of grafting. Furthermore, maximum homopolymerization took place at an H_2O_2 concentration of 40 mmole/l., whereas maximum grafting occurred at a range of H_2O_2 concentration of 25–30 mmole/l. Difference in the ability of the H_2O_2–thiourea dioxide redox system in initiating and terminating the graft and homopolymer would account for this.
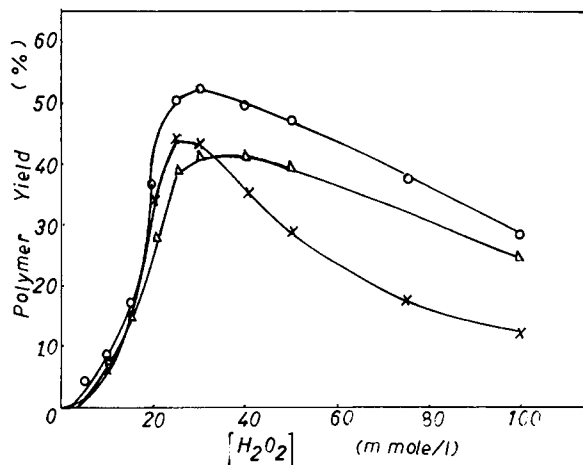

Fig. 8. Variation of graft uptake, homopolymer, and total conversion with H_2O_2 concentration: (×) % graft uptake; (△) % homopolymer; (○) total conversion; [MVP], 8%; [TUO], 10 mmole/l.; pH, 6; temperature, 70°C; reaction time, 2 hr; material:liquor ratio, 1:50.

Figure 8 shows variation of the total conversion of MVP monomer to its polymer with H_2O_2 concentration. It is obvious that the total conversion shows a trend which is similar to that of grafting, but the decrease in its magnitude at higher H_2O_2 concentration is not as sharp as in grafting. This is rather expected since the extent of homopolymer is not lowered outstandingly by increasing H_2O_2 concentration within the range studied. Naturally, the magnitude of homopolymer is reflected on the magnitude of total conversion.

Monomer Concentration

The effect of MVP concentration on the extent of grafting is illustrated in Figure 9, where monomer concentration ranging from 2% to 12% is plotted against the graft uptake. The polymerization reaction was performed on potassium dichromate–sulfuric acid-oxidized cellulose at 70°C for 2 hr using an H_2O_2 concentration of 25 mmole/l. together with a thiourea dioxide concentration of 10 mmole/l. The data indicate that there is a significant enhancement in the graft uptake when the MVP concentration increases from 2% to 6%, and no improvement in grafting could be achieved upon raising the monomer concentration to 8%. Above this concentration, the graft uptake tends to be considerably lower. The same trend was also observed with respect to homopolymer and total conversion (Fig. 9).

This could be explained if one assumes that the MVP monomer in the aqueous reaction medium is present in three forms, viz., soluble, highly dispersed, and insoluble forms. It might also be considered that the soluble and most probably the highly dispersed forms are amenable for polymerization. Data of current work suggest that the magnitude of these two monomer forms enhances by in-
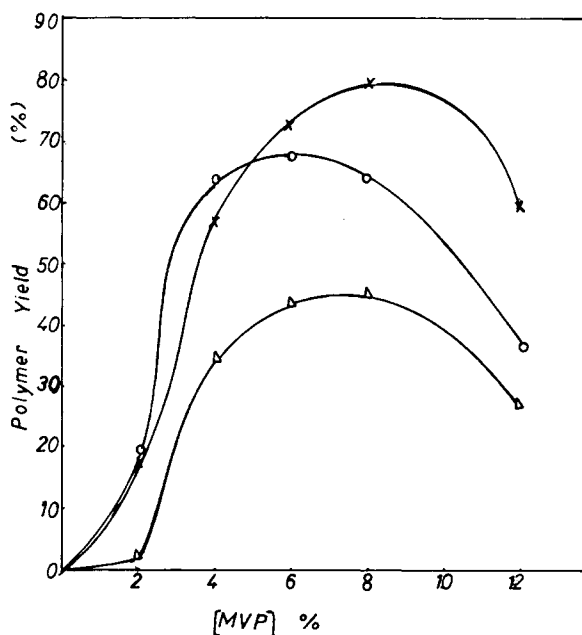
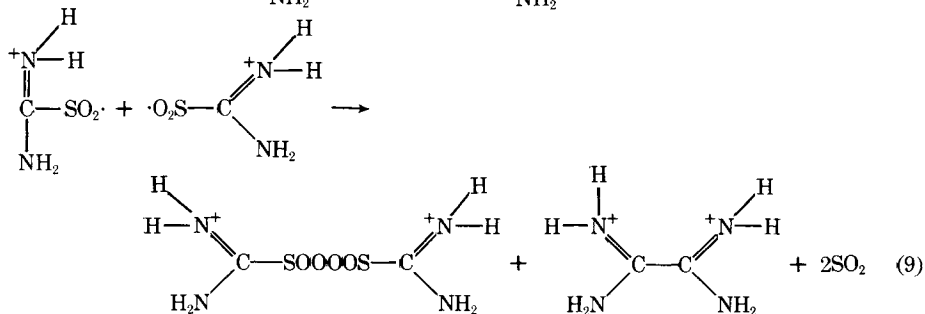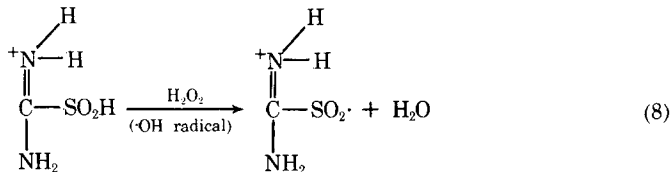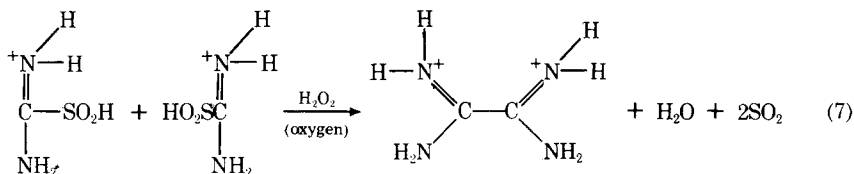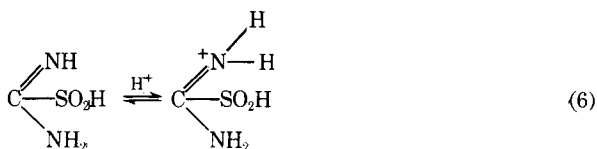Fig. 9. Influence of monomer concentration on percentages graft uptake, homopolymer, and total conversion: (×) % graft uptake; (△) % homopolymer; (○) % total conversion; [TUO], 10 mmole/l.; [H_2O_2], 25 mmole/l.; pH, 6; temperature, 70°C; reaction time, 2 hr; material:liquor ratio, 1:50.

creasing the monomer concentration up to a range of 6%–8%, thereby accentuating grafting. Beyond this concentration range, the insoluble monomer form dominates and leads to lower grafting.

pH of the Reaction

To investigate the effect of pH, graft polymerization of MVP onto potassium dichromate–sulfuric acid-oxidized cellulose was carried out at various pH's ranging from 4 to 9. Hydrochloric acid and triethylamine were used for pH adjusting. Concentrations of MVP, H_2O_2, and thiourea dioxide were set at 8%, 25 mmole/l., and 10 mmole/l., respectively. Polymerization was conducted at 70°C for 2 hr using a material-to-liquor ratio of 1:50. Results of this investigation are shown in Figure 10. It is clear that grafting increases considerably as the pH increases, attains a maximum at pH 6, and then falls at higher pH values. The same situation was encountered with homopolymer and total conversion.

At lower pH, it is possible that the following sequence of reactions takes place:

$$
\begin{array}{c}
\underset{\overset{|}{NH_2}}{\overset{\diagup NH}{C}}\!\!-\!SO_2H \xrightarrow[\ ]{H^+} \underset{\overset{|}{NH_2}}{\overset{\diagup \overset{\displaystyle H}{\overset{|}{N}}-H}{C}}\!\!-\!SO_2H \qquad (6)
$$

$$
\underset{\overset{|}{NH_2}}{\overset{\overset{\displaystyle H}{\overset{|}{{}^+N}}-H}{C}}\!\!-\!SO_2H \; + \; HO_2S\underset{\overset{|}{NH_2}}{\overset{\overset{\displaystyle H}{\overset{|}{{}^+N}}-H}{C}} \xrightarrow[\text{(oxygen)}]{H_2O_2} \underset{H_2N}{\overset{H-{}^+N}{\diagdown}}\!\!C\!-\!C\underset{NH_2}{\overset{{}^+N-H}{\diagup}} \; + \; H_2O \; + \; 2SO_2 \qquad (7)
$$

$$
\underset{\overset{|}{NH_2}}{\overset{\overset{\displaystyle H}{\overset{|}{{}^+N}}-H}{C}}\!\!-\!SO_2H \xrightarrow[\text{(·OH radical)}]{H_2O_2} \underset{\overset{|}{NH_2}}{\overset{\overset{\displaystyle H}{\overset{|}{{}^+N}}-H}{C}}\!\!-\!SO_2\cdot \; + \; H_2O \qquad (8)
$$

$$
\underset{\overset{|}{NH_2}}{\overset{\overset{\displaystyle H}{\overset{|}{{}^+N}}-H}{C}}\!\!-\!SO_2\cdot \; + \; \cdot O_2S\!\!-\!\underset{NH_2}{\overset{{}^+N-H}{\diagup}}\!\!C \longrightarrow
$$

$$
\underset{H_2N}{\overset{H-{}^+N}{\diagdown}}\!\!C\!-\!SOOOOS\!-\!C\underset{NH_2}{\overset{{}^+N-H}{\diagup}} \; + \; \underset{H_2N}{\overset{H-{}^+N}{\diagdown}}\!\!C\!-\!C\underset{NH_2}{\overset{{}^+N-H}{\diagup}} \; + \; 2SO_2 \qquad (9)
$$

Thus, instead of creating more active species, thiourea dioxide is converted to isothiourea dioxide which undergoes reaction with the decomposition products of H_2O_2 to give ultimately inactive species, as shown in eqs. (7) and (9). At higher pH values the concentration of active species capable of initiating polymerization seems also to decrease because thiourea dioxide probably looses its reducing
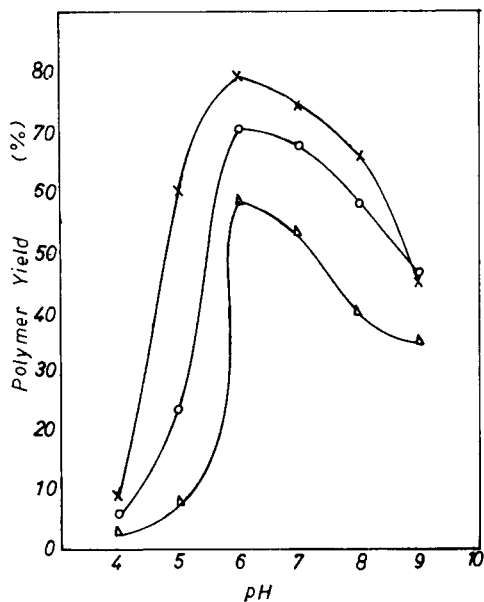
Fig. 10. Percentages graft uptake, homopolymer, and total conversion as functions of pH of the polymerization medium: (×) % graft uptake; (△) % homopolymer; (○) % total conversion; [TUO], 10 mmole/l.; [H$_2$O$_2$], 25 mmole/l.; [MVP], 8%; temperature, 70°C; reaction time, 2 hr; material:liquor ratio, 1:50.
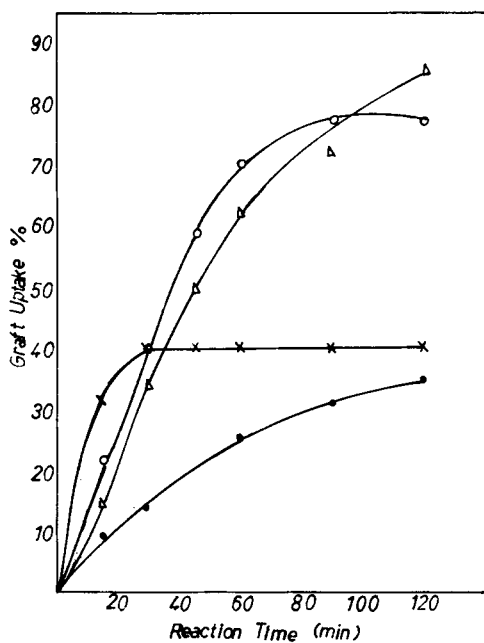

Fig. 11. Effect of temperature on the rate of grafting reaction: (△) 60°C; (×) 80°C; (○) 70°C; (●) 40°C; [TUO], 10 mmole/l.; [H$_2$O$_2$], 25 mmole/l.; [MVP], 8%; pH, 6; material:liquor ratio, 1:50.

action in the alkaline pH's, similar to thiourea.[29]   This would account for the decreased grafting observed at lower and higher pH values.   At pH 6, on the other hand, formation of isothiourea dioxide, eq. (6), will be at minimum.   Consequently, the sequence of the reactions shown in eqs. (1)–(5) would be favored thereby leading to increased grafting.

Reaction Temperature

Figure 11 shows the effect of temperature on grafting of MVP onto potassium dichromate–sulfuric acid-oxidized cellulose using H_2O_2 (25 mmol/l.) and thiourea dioxide (10 mmole/l.) as a co-catalyst.   The polymerization reaction was carried out for 2 hr at 70°C and pH 6 using a material-to-liquor ratio of 1:50.   As can be seen, grafting proceeds initially fast, then slows down with time at 40° and 60°C within the 2-hr reaction time studied.   The same holds true for grafting at 70° and 80°C, but after the initial fast rate reaction does level off after 90 and 30 min, respectively.   However, the maximum graft uptake obtained at 70°C is significantly higher than at 80°C.   This could be accounted for by faster rate of termination at 80°C.   In accordance with this is the order of graft yield obtained after 2 hr at the four temperatures; the graft uptake follows the order 60°C > 70°C > 80°C > 40°C.

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