

Redox-Initiated Graft Copolymerization onto Wool with Thiourea as Reductant. IV. Grafting of Vinyl Sulfone Dyes onto Wool Using Thiourea-H₂O₂ Redox System

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Synopsis

Wool samples were dyed with a vinyl sulfone dye in the presence of thiourea and H₂O₂ under a variety of conditions. Increasing the H₂O₂ concentration from 2.5 mmole/l. to 20 mmole/l. caused a significant enhancement in the rate of the dyeing, whereas increasing the thiourea concentration from 1.25 mmole/l. to 10 mmole/l. brought about an increase in the rate of dyeing. Further increase in the thiourea concentration (i.e., up to 15 mmole/l.) caused a significant decrease in the rate of dyeing. Raising the dyeing bath temperature from 30° to 70°C accelerated appreciably the rate of dye uptake. With respect to dye concentration, complete exhaustion occurred at dye concentrations of 0.5% and 1% (owf) when dyeing was performed at 70°C and pH 6 over a duration of 2 hr. This contrasts with 90% and 55% exhaustion for dye concentrations of 3% and 5% (owf), respectively. The rate of dyeing obtained at different pH's follows the order pH 2 > pH 4 > pH 6 > pH 8. A dye fixation of approximately 68%, 64%, and 50% could be achieved at pH 4, 6, and 8, respectively, if dyeing was performed at 70°C for 2 hr in a bath containing a dye concentration of 3% (owf) in the presence of thiourea (10 mmole/l.) and H₂O₂ (15 mmole/l.). The mechanism of dyeing is believed to be grafting by vinyl addition to wool radical formed under the influence of the decomposition products of thiourea and H₂O₂. Evidence of this mechanism is presented.

INTRODUCTION

A substantial amount of research in the area of chemical modification of wool through vinyl graft polymerization has been published during the last decade. Similar to vinyl polymerization, the grafting reaction involves three distinct steps, viz., initiation, propagation, and termination. Initiation entails formation of free radicals on the wool backbone which in the presence of the vinyl monomer initiates a chain. This is followed by many subsequent additions of monomer molecules to this initiated chain, thus propagating a grafted chain. Termination of the latter may occur by combination, disproportionation, chain transfer, initiator, or impurities.¹

Introduction of free radicals can be accomplished by physical or chemical activation of wool.²⁻⁴ Subjecting wool to high-energy radiation⁴⁻⁹ or low-energy radiation in the presence or absence of sensitizers^{7,10-15} produces wool macroradicals which are capable of initiating grafting. Similar wool radicals can be achieved under the action of redox systems,¹⁶⁻²⁰ ceric ion,^{21,22} periodate ion,²³ acetylonyl (acetonato) copper(II)-trichloroacetic acid complex,²⁴⁻²⁸ potassium permanganate,^{29,30} benzoyl peroxide,^{31,32} dimethylaniline-benzyl chloride mixture,³³ thiourea in acid medium,³⁴ and other redox systems such as Fe³⁺-thiourea,³⁵ ditertiary butyl peroxide-thiourea,³⁶ and hydrogen peroxide-thio-

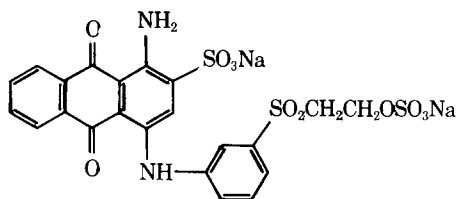
urea.³⁷ Creation of free radicals on the wool backbone via chain transfer has also been possible.³⁸

Though these wool macroradicals have extensively been used for grafting various vinyl monomers onto wool, their utilization in fixing dyes with activated double bonds on wool has not yet been thoroughly investigated. The only work relating to this subject was on the radiation-induced simultaneous graft copolymerization of acrylonitrile onto wool in the presence of a vinyl sulfone dye, using dimethylformamide (DMF) and DMF/water as solvents for the monomer.⁹

This work was undertaken with a view of investigating the possibility of fixing a dye with activated double bond on wool by means of chemical initiation. For this purpose, a vinyl sulfone dye was reacted with wool under various reaction conditions in the presence of the thiourea-H₂O₂ redox system.

EXPERIMENTAL

Materials. Merino wool fibers were purified by Soxhlet extraction with acetone for about 24 hr, followed by washing with cold, distilled water and air drying. The dye used was Remazol Brilliant Blue R (C.I. reactive blue 19) having the following structure:



The reactive side chain —SO₂CH₂CH₂OSO₃Na was converted into a vinyl sulfone —SO₂CH=CH₂ in the following manner: A solution of the dye (5 g) in water (100 ml) was adjusted to pH 12 by addition of 2*N* sodium hydroxide. After 10 min, virtually complete conversion into the corresponding vinyl sulfone had occurred, as shown by paper chromatography.³⁹ Hence, unless otherwise stated, the vinyl sulfone dye was used throughout this investigation.

Procedure. Reaction of the dye with wool in the presence of the thiourea-H₂O₂ redox system was carried out as follows: Wool sample was added to a dye bath containing the dye, H₂O₂, and thiourea. Temperature and pH of the dye bath were adjusted before introducing the sample. Dyeing was allowed to proceed for different lengths of time with occasional stirring. The experimental conditions used are detailed below.

Dye Uptake. Dye uptake was calculated as follows: Aliquots were withdrawn from the dye bath before addition of the wool sample and during the course of and at completion of dyeing, and the dye concentration of each aliquot was estimated colorimetrically.⁴⁰

Dye Fixation. The amount of dye covalently bound with wool was estimated as follows: The total dye on the wool sample was calculated from the degree of exhaustion of the dye bath. The unreacted dye was estimated by first soaking the dyed wool sample for several hours in a soap solution and then extracting the sample continuously with 50% DMF in a Soxhlet apparatus until no further

dye was removed. The dye present in the combined soap solution and DMF extract was then determined colorimetrically. The difference between the total dye on the wool sample and the dye in the mixture corresponds to the amount of covalently bound dye, namely, the amount of dye fixed on the wool.

RESULTS AND DISCUSSION

Since the primary objective of this work is to investigate the possibility of fixing dyes with activated double bonds on wool by means of chemical initiation, a dye having an activated vinyl moiety was applied to wool from a dye bath containing this dye, thiourea, and H_2O_2 . Thiourea and H_2O_2 form a redox system which has been used in initiating vinyl graft polymerization onto wool.³⁷ As is shown below, the rate of dyeing increases substantially in the presence of this free-radical redox catalyst, a point which can be attributed to opening of the structure of wool to dye as well as polymerization of the dye. Also, instead of polymerization of the dye, rather a free-radical addition of single dye molecules at reactive sites on the wool may be occurring. However, it might be considered that the mechanism of dye fixation is probably similar to that of graft polymerization of vinyl type compounds, i.e., formation of radicals on the wool backbone followed by vinyl addition and copolymerization. To substantiate this, dyeing was carried out under a variety of conditions. Variables studied include thiourea, H_2O_2 , and dye concentration; pH; reaction time; and temperature. As will be seen later, these variables considerably affect the dyeing rate curves in a manner similar to that observed with vinyl graft polymerization. Furthermore, evidence for covalent chemical fixation of the dye on wool could be envisaged from (a) the dye could not be removed by soaking in soap solution followed by extraction with DMF; (b) the dependence of the degree of dye fixation upon the presence of initiator components; and (c) the outstanding enhancement in dye fixation achieved after conversion of the side chain $-SO_2CH_2CH_2OSO_3Na$ to $-SO_2CH=CH_2$. Presented below are the pertinent results along with appropriate discussion.

Effect of Thiourea Concentration

Dyeing rate curves for the vinyl sulfone dye obtained at different thiourea concentrations are shown in Figure 1. Wool samples were dyed with this dye at 70°C and pH 6 for different lengths of time using a material-to-liquid ratio of 1:100. The dyeing baths were prepared so as to give 3% (based on weight of fabric, owf) in the presence of different concentrations of thiourea (0–15 mmole/l.) and H_2O_2 (15 mmole/l.). It was observed that the color depth of the wool samples in the presence of thiourea, regardless of its concentration in the dye bath, is much higher than in its absence. However, the depth of color is dependent on the concentration of thiourea, decreasing as the concentration of thiourea increases. This indeed agrees with the results of Figure 1, where the loss in concentration of the dye bath was determined colorimetrically and the amount of the dye exhausted by the fiber from the dye bath (total dye uptake) was calculated.

The higher dye uptake in the presence of thiourea than in its absence implies that wool is perhaps more susceptible toward the dye in the presence of thiourea.

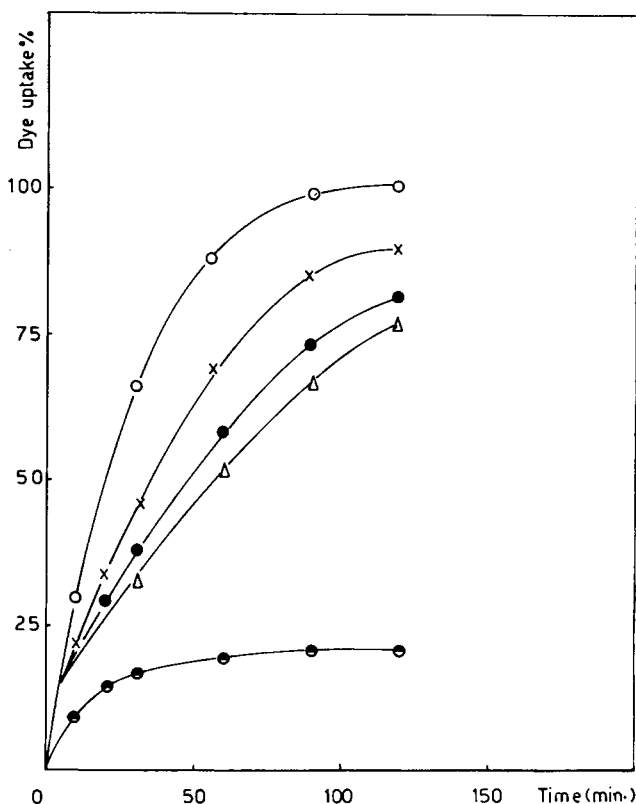


Fig. 1. Dyeing rate curves of vinyl sulfone dye obtained at different thiourea concentrations. Thiourea concentration: (●) 1.25 mmole/l.; (x) 2.5 mmole/l.; (○) 5 or 10 mmole/l.; (Δ) 15 mmole/l.; (●) no thiourea. Dye concentration, 3% (owf); pH, 6; temperature, 70°C; material:liquor ratio, 1:10.

This state of affairs could be associated with formation of wool macroradicals which are capable of initiating graft polymerization of the dye. Wool macroradicals might have been formed by (a) direct hydrogen abstraction from wool by the hydroxyl radicals and/or isothiocarbamide radicals resulting from reaction of H_2O_2 with thiourea³⁷; and (b) homolytic scission of the disulfide bonds through anisotropic swelling of wool at the temperature used (70°C) and/or under the influence of the initiator employed.^{32,34} In addition, thiourea reacts with wool to produce reduced wool. Previous reports^{24,29,37,38} have shown that reduced wool is more amenable to grafting than unreduced wool.

The decrease in dye uptake at higher thiourea concentration (i.e., 15 mmole/l.) suggests that some species must have been generated and is acting as an efficient radical scavenger. A similar trend was observed when cellulosic materials were grafted with 2-methyl-5-vinylpyridine using H_2O_2 -thiourea dioxide as initiator; the graft yield tends to decrease at higher concentration of thiourea dioxide.⁴¹

Effect of H_2O_2 Concentration

The dependence of the rate of dyeing wool with the vinyl sulfone dye on H_2O_2 concentration is shown in Figure 2. The dyeing conditions were similar to those described above, except that thiourea concentration was set at 10 mmole/l. while

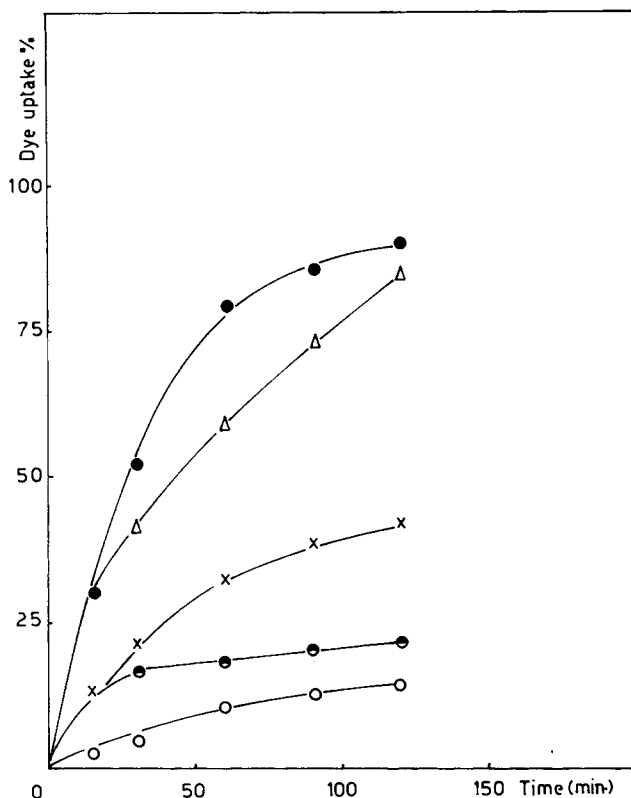


Fig. 2. Dyeing rate curves of vinyl sulfone dye obtained at different H_2O_2 concentrations. H_2O_2 concentration: (○) 2.5 mmole/l.; (x) 5 mmole/l.; (Δ) 10 or 15 mmole/l.; (●) 20 mmole/l.; (●) without thiourea. Dye concentration, 3% (owf).

the concentration of H_2O_2 varied from 0 to 20 mmole/l. Visual assessment of the depth of color revealed that the latter was appreciably higher if H_2O_2 was included in the dyeing system. Furthermore, the depth of color was more intense the higher the H_2O_2 concentrations.

In accordance with these observations are the results of dye uptake (Fig. 2). As is evident, the dye uptake in the presence of H_2O_2 , particularly at higher concentration, is outstandingly higher than in its absence. This could be explained on the basis of an increase in the speed of initiating graft polymerization of the dye with increasing concentration of the peroxide owing to which, within the time studied, newer initiating chains can be formed and the growing polymer chains have more time for growth.

Effect of Dye Concentration

Dyeing baths were prepared so as to give dye concentrations of 0.5%, 1%, 3%, and 5% (owf). Besides the vinyl sulfone dye, the dyeing bath contained thiourea (10 mmole/l.) and H_2O_2 (15 mmole/l.). For each dye concentration dyeing was carried out at 70°C and pH 6 for different periods of time ranging from 10 to 120 min using a material-to-liquor ratio of 1:100. It was observed that the depth of color increases as the dye concentration in the dyeing bath (i.e., the % dye concentration) increases.

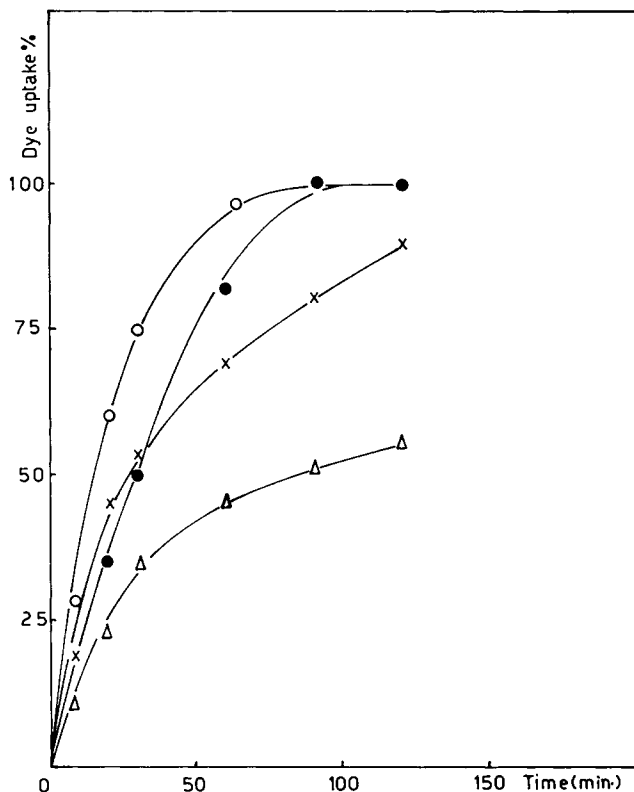


Fig. 3. Dyeing rate curves of the vinyl sulfone dye obtained at different dye concentrations. Dye concentration (owf): (O) 0.5%; (●) 1%; (x) 3%; (Δ) 5%. Thiourea concentration, 10 mmole/l.; H_2O_2 concentration, 15 mmole/l.; temperature, 70°C; pH, 6; material:liquor ratio, 1:100.

Figure 3 shows that within 2 hr the dye uptake corresponds to complete exhaustion when dye baths having dye concentration of 0.5% and 1% (owf) were used. This contrasts with dye uptakes which correspond to exhaustion of 90% and 55% for dye concentrations of 3% and 5% (owf), respectively. Despite the relatively lower dye uptake observed with the dye bath of 5% (owf), its dyeings showed much deeper color than the corresponding dyeings obtained with a dye bath of 1% (owf) which showed dye uptake of complete exhaustion. It is understandable that percentage dye uptake on the fiber from the dye bath is related to the amount of dye originally added to the dye bath. Hence, the results of Figure 3 agree with the observation that the depth of color increases as the dye concentration in the dye bath increases within the range studied.

The considerable decrease in the amount of dye taken up by the fiber from the dye bath when using higher dye concentration, i.e., 5% (owf), could be associated with homopolymerization of the dye. Homopolymerization seems to perform two functions: (a) decreasing the amount of dye available for exhaustion by the fiber; and (b) impeding diffusion of the dye into the fibers perhaps through deposition on the fiber surface. Both functions would certainly lead to lower exhaustion (Fig. 3).

Effect of Temperature

To investigate the effect of temperature on the rate of dyeing, wool samples were dyed with the vinyl sulfone dye at pH 6 and at different temperatures, viz., 30°, 40°, 60°, and 70°C, for varying lengths of time using a material-to-liquor ratio of 1:100. The dye bath was prepared so as to give 3% (owf) in the presence of thiourea (10 mmole/l.) and H₂O₂ (15 mmole/l.). Figure 4 shows the dyeing rate curves obtained at the four temperatures studied.

It is clear (Fig. 4) that the rate of dyeing is much higher at 70°C than at 30°C; the dye uptake follows the order 70°C > 60°C > 40°C > 30°C. This is rather expected since increasing the temperature is accompanied by (a) enhancement in wool swellability; anisotropic swelling of wool may lead to homolytic scission of the disulfonide bonds thereby producing wool radicals that are capable of initiating graft polymerization of the dye; (b) increasing the rate of diffusion of the dye from the aqueous phase to fiber phase; (c) accelerating reaction of thiourea with H₂O₂ thus increasing the free-radical species in the reaction medium; (d) enhancing reaction of the free-radical species, i.e., the hydroxyl and isothiocarbamide radicals, with wool to bring about wool macroradicals; (e) accentuating the initiation and propagation steps; (f) facilitating nucleophilic addition of hydrogen atoms from the amino and hydroxyl groups in the wool to the double bond of the dye, though the contribution of this addition reaction in the dye fixation seems to be minor (see below).

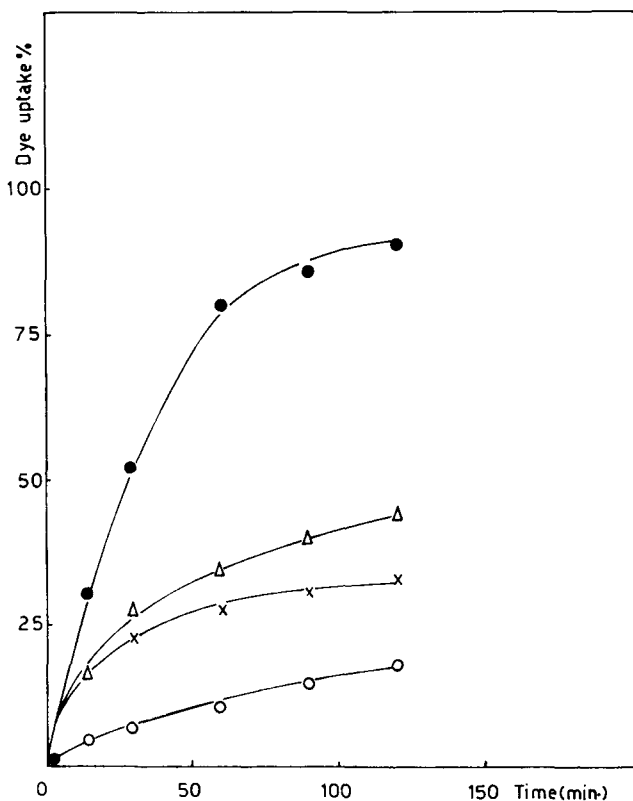
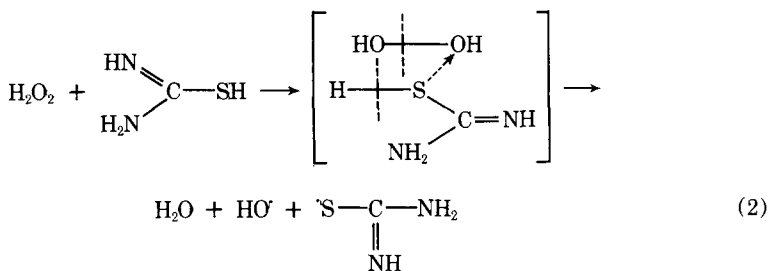
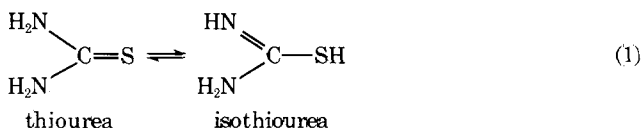


Fig. 4. Dyeing rate curves of the vinyl sulfone dye obtained at different dyeing temperatures. Temperature: (O) 30°C; (x) 40°C; (Δ) 60°C; (\bullet) 70°C. Dyeing concentration (owf), 3%; H₂O₂ concentration; 15 mmole/l.; thiourea concentration, 10 mmole/l.; pH 6; material:liquor ratio, 1:100.

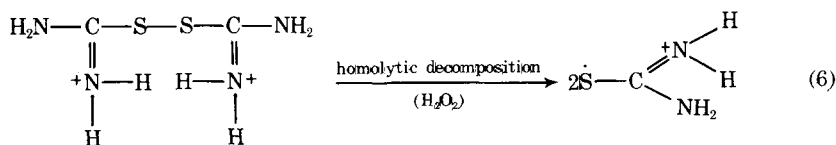
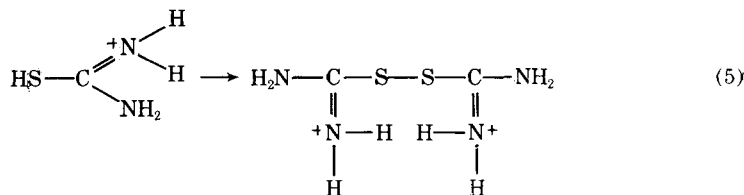
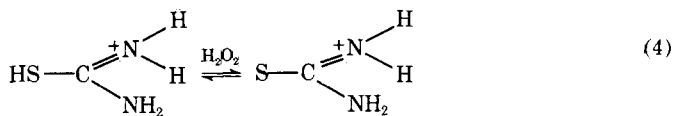
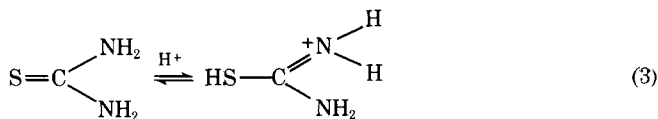
The effect of all these functions taken together is certainly higher dyeing. Indeed, samples dyed at 70°C acquire much deeper color than the corresponding dyeings for other temperatures within the range studied.

Effect of pH

Previous work⁴² has shown that the reducing properties of thiourea are higher at low pH values. Hence, its reaction with H₂O₂ to generate free radicals capable of initiating graft polymerization of the vinyl sulfone dye onto wool as well as its reaction with the latter to bring about reduced wool with higher susceptibility toward grafting will be pH dependent. Reaction of thiourea with H₂O₂ may be represented as follows⁴³:



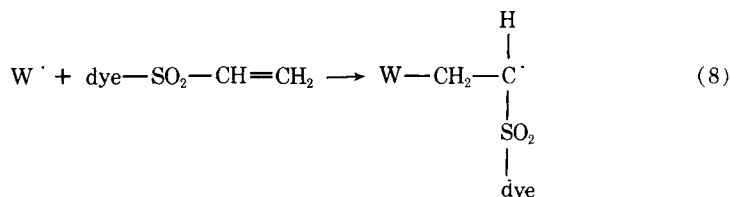
At low pH values eq. (1) is very likely to shift to the right-hand side. Also, decomposition of the complex formed between the peroxide and thiourea, eq. (2), proceeds much faster in the acidic side than in the alkaline side.³⁷ It is rather possible that the following sequences of reactions take place at low pH values^{37,42}:



Obviously, besides the participation of the hydroxyl and isothiocarbamide radical, eq. (2), in producing wool radicals, free radicals formed according to eqs. (4) and (6) may contribute to such an interaction. Thus,



where WH is wool, R \cdot represents the free-radical species shown in eqs. (2), (4), and (6), and W \cdot represents the wool radical. In the presence of the vinyl sulfone dye (dye—SO₂—CH=CH₂), the wool radical initiates graft polymerization of the dye via addition to the double bond of the dye substituent, eq. (8):



From the above discussion, one could assume that dyeing of wool with the vinyl sulfone dye in the presence of thiourea and H₂O₂ would be much favored on the acidic side than on the alkaline side. To check the validity of this, wool samples were dyed at different pH's ranging from 2 to 8. Regardless of the pH used, dyeing was performed in a dyeing bath of a dye concentration of 3% (owf) at 70°C in the presence of thiourea (10 mmole/l.) and H₂O₂ (15 mmole/l.) for varying lengths of time using a material-to-liquor ratio of 1:100. As shown in Figure 5, the rate of dyeing is dependent on the pH value over the range of 2–8; the rate of dyeing decreases as the pH increases. This and the observations that the depth of the color for samples dyed on the acidic side is much higher than that of the corresponding depth for samples dyed in the alkaline side would validate the above assumption.

Effect of Time

The effect of time on the dye uptake may be realized from figures 1–5. All these figures show one common feature: the dye uptake proceeds initially at a fast rate and decreases with time to a slower rate; levelling off occurs only in cases where dye uptake which corresponds to complete exhaustion could be attained. It is thus clear that slowing down of dye uptake with time is due to depletion in both dye and initiator (thiourea and H₂O₂) concentrations as dyeing continues, being dependent upon the pH and temperature of dyeing.

Dye Fixation

Wool samples were dyed with the vinyl sulfone dye in dye baths of 3% concentration (owf) at different pH's in the presence of either thiourea, H₂O₂, or both at 70°C for 2 hr using a material-to-liquor ratio of 1:100. In another series of experiments dyeing with the original dye (sulfatoethyl sulfone dye) was carried out in the presence of thiourea together with H₂O₂ under similar conditions. The total dye on the wool samples was calculated from the degree of exhaustion of the dye baths, whereas the unreacted dye was determined by washing in soap

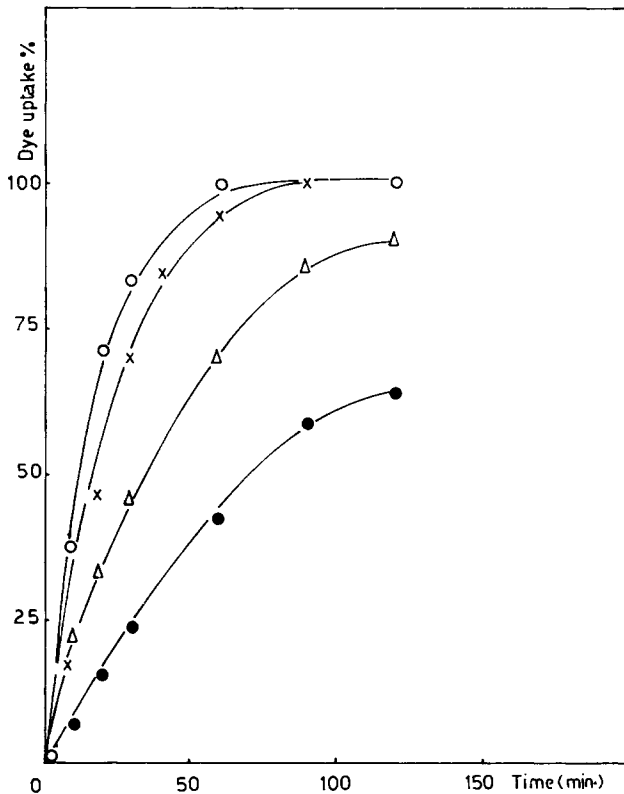


Fig. 5. Dyeing rate curves of vinyl sulfone dye obtained at different pH values: (O) pH 2; (x) pH 4; (Δ) pH 8. Dye concentration, 3% (owf); thiourea concentration, 10 mmole/l.; H_2O_2 concentration, 15 mmole/l.; temperature, 70°C; material:liquor ratio, 1:100.

TABLE I
Fixation of Vinyl Sulfone dye on Wool Fibers Under Various Conditions^a

Dyeing bath composition	Dye fixation ^b		
	pH 4	pH 6	pH 8
Dye + thiourea + H_2O_2	68.3 (9.83)	63.7 (12.1)	50.5 (14.58)
Dye + thiourea	12.5	14.1	17.9
Dye + H_2O_2	13.8	16.2	17.9

^a Thiourea concentration, 10 mmol/l.; H_2O_2 concentration, 15 mmol/l.; temperature, 70°C; reaction time, 2 hr; material-to-liquor ratio, 1:100. Values in parentheses represent dye fixation for the original dye i.e., Remazol Brilliant Blue R, before converting the sulfatoethyl sulfone substituent to the vinyl sulfone.

^b As percentage of the total dye exhausted from the dye bath by the wool samples.

solution followed by DMF extraction as described earlier. The amount of reacted dye (dye fixation) was estimated by difference. The results obtained are given in Table I.

It is obvious (Table I) that the vinyl sulfone dye yields significant fixation, approximately amounting to 68%, 64%, and 50% for dyeings at pH 4, 6, and 8, respectively. This contrasts with approximately 10%, 12%, and 13% fixation at the same pH's but by using the original dye. The fact that the original dye contains masked vinyl groups which could not react with the wool radical ac-

counts for this contrast. In addition, fixation of the original dye occurs essentially via nucleophilic addition reaction, whereas fixation of the vinyl sulfone dye is very likely to occur through both graft polymerization and addition reactions. However, contribution of the former reaction in dye fixation seems to be very great since the fixation decreases significantly upon exclusion of thiourea or H_2O_2 from the dyeing bath.

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Reviewed November 18, 1976

Revised May 12, 1977