

Redox-Initiated Vinyl Graft Polymerization Onto Wool with Thiourea as the Reductant. I. Grafting of Methyl Methacrylate with the Hydrogen Peroxide-Thiourea Catalyst System

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Synopsis

The interaction of methyl methacrylate with wool under the catalytic influence of the hydrogen peroxide-thiourea redox system was studied under a variety of conditions. The degree of grafting depends upon the method employed; it is advantageous to first immerse wool in thiourea solution, monomer and hydrogen peroxide being then subsequently applied. Increasing the hydrogen peroxide concentration from 4 to 8 mmole/l. causes a significant enhancement in the graft yield. The latter remains practically unchanged upon further increment in hydrogen peroxide concentration within the range studied, i.e., up to 12 mmole/l. This was also observed with respect to thiourea concentration. On the other hand, increasing monomer concentration is accompanied by a significant increase in the graft yield. The polymerization reaction is temperature dependent; at the three temperatures examined, the graft yields follow the order $80^\circ > 60^\circ > 40^\circ\text{C}$. The rate of grafting is also dependent on the pH of the reaction medium over the range of 2 to 8, being decreased as the pH increased. Furthermore, the presence of traces of cupric ions in the polymerization system accentuates the graft formation. The alkali solubility as well as the urea bisulfite solubility of wool grafted with poly(methyl methacrylate) are much lower than those of physical mixtures of wool and poly(methyl methacrylate). This demonstrates that grafting of poly(methyl methacrylate) into wool has occurred.

INTRODUCTION

Chemical modification of wool by grafting has received considerable attention in recent years. With the wide variety of vinyl and other available monomers today, grafting promises to be a potentially powerful method for producing substantial modification in wool properties. This field of research has thus evoked considerable academic and practical interest.¹

Vinyl graft copolymerization onto wool is usually accomplished by free-radical or radical ion-initiation systems. Hence the primary step involves creation of free-radical sites on the wool backbone, probably through abstraction of hydrogen from thiol, amino, or hydroxyl groups in the wool molecule. This can be achieved by high-energy irradiation²⁻⁵ low-energy

irradiation in the presence and absence of sensitizer,⁵⁻⁷ and redox systems.^{8,9} Free radicals can also be produced by the use of powerful oxidizing agents such as ceric ions which attack the wool directly.^{10,11} Moreover, production of the free radicals on the wool backbone has been possible by copper (II) complexes formed through complexation of bis(acetylacetonato)copper(II) with trichloroacetic acid or ammonium trichloroacetate.¹²⁻¹⁵ Recently, grafting has been initiated by free radicals formed on wool under the catalytic influence of the permanganate¹⁶ and periodate.¹⁷ Initiation of free radicals on wool via chain transfer process has also been reported.¹⁸

During the last few years, the use of thiourea and N-substituted thioureas as redox components for initiation of aqueous vinyl polymerization has been examined. Bonvicini and Caldo¹⁹ and Sugimura et al.²⁰ have used these reducing agents with hydrogen peroxide as the oxidant for initiation of aqueous polymerization of acrylonitrile. Mukherjee et al.²¹ have used thiourea as reductant with a number of oxidants such as ferric chloride (Fe^{3+}), ethylene dibiguanide complex salts of tripositive silver (Ag^{3+}), hydrogen peroxide, persulfate, and bromate plus hydrochloric acid for initiation of aqueous polymerization of methyl methacrylate. These redox systems have been disclosed to be quite effective in initiating vinyl polymerization. However, the capability of these systems to initiate grafting of vinyl monomers on wool has not as yet been reported.

In this laboratory, there is a research program to investigate the vinyl graft polymerization onto wool using different oxidants, e.g., hydrogen peroxide, persulfate, periodate, permanganate, bromate, ferric salts, etc., as catalyst and thiourea as cocatalyst. The presence of thiourea in the initiation system would be expected to perform the following functions: (a) production of reduced wool with higher susceptibility toward grafting, (b) decomposition of the oxidant takes place to an appreciable extent, (c) creation of isothiocarbamido radicals which may participate in formation of wool macroradicals, and (d) lowering the extent of oxidant attack on wool, thereby reducing the extent of wool damage. This paper presents results of studies of graft polymerization of methyl methacrylate onto wool fibers using the hydrogen peroxide-thiourea 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.

Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution; it was then dried with anhydrous sodium sulfate and distilled under reduced pressure in nitrogen before use.

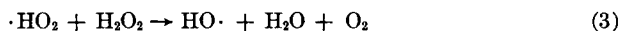
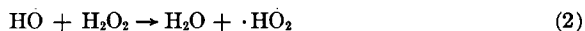
Hydrogen peroxide was pure grade chemicals. Thiourea was also grade chemical.

Procedure

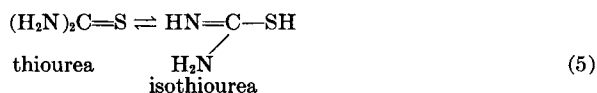
The polymerization reaction was performed as follows: A 50-ml portion of hydrogen peroxide solution (4–12 mmoles/l.) at a specific temperature (60°C) was taken in a 70-ml glass-stoppered Erlenmeyer flask. The required quantities of freshly distilled monomer (0.2–0.6 mole/l.) and thiourea (0.4 mmole/l.) were then added, followed immediately by wool (1 g). The flasks were stoppered and kept in a thermostatic water bath for different lengths of time (15–120 min) with occasional shaking. During the reaction, the wool fibers were kept well immersed in the solution. The fibers were then removed, washed well with water, given a light soaping to remove the loosely adhered homopolymers, washed, and dried. At this point, the samples were repeatedly extracted with acetone till constant weight was obtained. Calculation of the percentage grafting was based on dry weight.

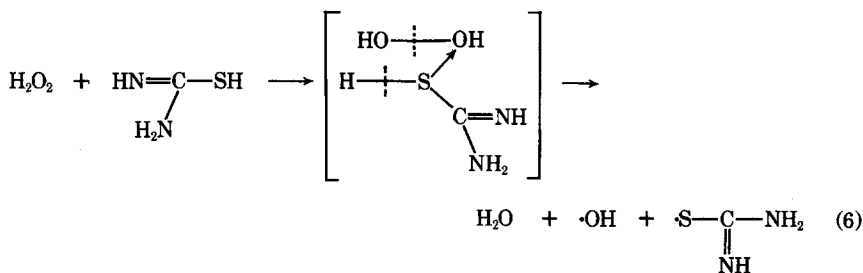
RESULTS AND DISCUSSION

To start with, attempts were made to initiate graft polymerization of methyl methacrylate (2 ml) onto wool fibers (1 g) by the use of hydrogen peroxide having a concentration ranging from 4 to 12 mmoles/l. as initiator. A material-to-liquor ratio of 1:50 was used. No polymerization occurred at low temperature (30°C), even if the reaction was allowed to proceed for 12 hr. A graft yield never exceeding 4% could be achieved with this system when the temperature was raised to 60°C. This implies that H₂O₂ had interacted with wool not as a hydroxyl radical formed via a transfer of electron from wool but essentially via nascent oxygen. That is, H₂O₂ decomposes to $\dot{O}H$ radicals at elevated temperature, i.e., 60°C. However, instead of attacking the wool to produce wool macroradical, the $\dot{O}H$ radicals further decompose H₂O₂ to give ultimately nascent oxygen as shown below:^{22–24}

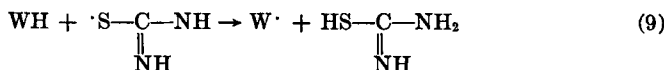
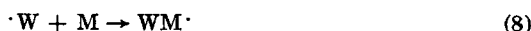
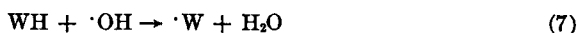


In order to accentuate the graft formation, thiourea was additionally incorporated into the wool–monomer–H₂O₂–water system. It might be considered that presence of a reducing agent such as thiourea in this system would accelerate the decomposition of H₂O₂ to produce free radicals owing to one electron transfer with concomitant cleavage of the O—O bond under the attack of this nucleophile. The reactions involved may be presented as follows:²⁰





From eq. (6) it is reasonable to assume that polymerization onto wool (WH) can be initiated either by the hydroxyl radical, eqs. (7) and (8), the isothiocarbamido radical, eqs. (9) and (10), or by both, eqs. (7)–(10):



In a complex system like this, the graft formation would be expected to depend mainly on (a) formation of reduced wool with higher susceptibility to grafting under the action of thiourea, (b) efficiency of the initiator free radicals in producing wool macroradicals, (c) solution of monomer and its diffusion from the solution phase to fiber phase, (d) adsorption of the monomer on fiber, (e) capturing of the wool macroradicals by monomer to initiate and propagate grafting, and (f) homopolymerization in solution. To check the validity of this, the following methods were implemented.

Method I. In this method, wool was immersed in thiourea solution for $\frac{1}{2}$ hr. The monomer and H_2O_2 were then added and the grafting reaction was conducted for different periods of time varying from zero to 120 min.

Method II. The wool was placed in a solution containing the thiourea and monomer for $\frac{1}{2}$ hr. At this point, H_2O_2 was added and the reaction was undertaken as described above.

Method III. The wool, thiourea, and H_2O_2 were present together and the reaction was allowed to proceed for different intervals of time as previously indicated.

In all cases, the concentrations of thiourea, monomer and peroxide were 4, 184, and 12 mmols/l., respectively. The reaction was carried out at 60°C using a material-to-liquor ratio of 1:50. The results obtained are shown in Figure 1.

Evidently, the graft yields obtained with method I are comparable with those of method II, while the graft yields of method III are considerably lower. This validates the above expectation since in methods I and II the thiourea was allowed to react with and physically adsorbed on the wool. Thus, decomposition of H_2O_2 under the catalytic influence of thiourea occurred in the proximity of wool, and partially reduced wool, molecules.

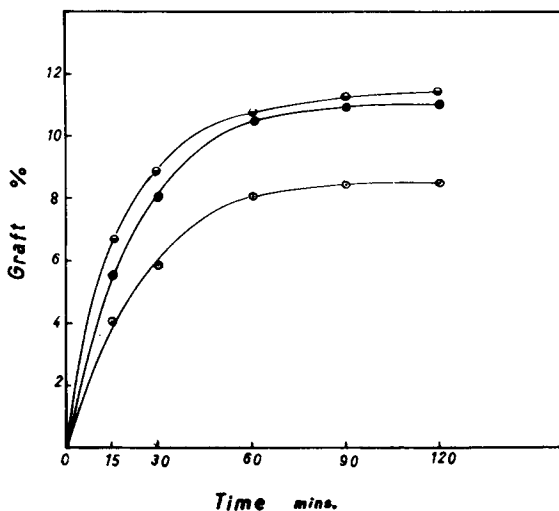


Fig. 1. Graft polymerization of methyl methacrylate onto wool with hydrogen peroxide-thiourea redox system by different methods (4 mmoles/l. thiourea; 184 mmoles/l. MMA; 12 mmoles/l. H_2O_2 , $60^\circ C$; liq. ratio 1:50): (—●—) method I; (—●—) method II; (—○—) method III.

This would certainly facilitate the interaction of the decomposition products, i.e., the hydroxyl radical as well as isothiocarbamido radical, with wool to produce wool radicals which are capable of initiating grafting of monomer in their vicinity. It is of importance to emphasize that reduced wool has been reported to be more amenable to grafting than unreduced wool.^{12,16,18}

Another approach was undertaken to induce graft polymerization of methyl methacrylate on wool fibers. This approach involves treatment of the wool sample with a solution containing thiourea (4 mmoles/l.) and H_2O_2 (12 mmoles/l.) at $60^\circ C$ for different periods of time (0–5 hr) using a liquor ratio of 50 before addition of the monomer. The time here will be referred to as time of activation. Figure 2 shows the graft yields obtained after a polymerization time of 2 hr using a monomer concentration of 184 mmoles/l.

It is clear that the graft yield shows an initial rapid decrease followed by a slower one on increasing the time of activation. The following tentative explanation is offered. In the early stages of activation, the wool free radicals are largely localized on the wool surface and/or nearby; thus, they will be more amenable to termination before commencing polymerization. In later stages of activation, on the other hand, it may be presumed that grafting is brought about mainly by free radicals formed in the interior of the wool structure. These free radicals seems to persist for longer periods of time compared with those generated at the wool surface because their termination is greatly inhibited by the wool matrix.

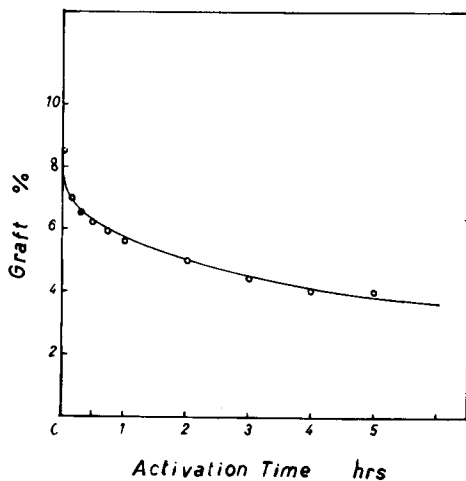


Fig. 2. Effect of time of activation on graft yield. Wool samples were treated with a solution containing 4 mmoles/l. thiourea, 12 mmoles/l. H_2O_2 for different activation times before addition of monomer. Grafting was then carried out using 184 mmoles/l. MMA for 2 hr. Both activation and grafting were performed at $60^\circ C$ using a material-to-liquor ratio of 1:50.

Effect of Reaction Time

The effect of reaction time on grafting of wool with methyl methacrylate using the H_2O_2 -thiourea system may be realized from Figure 1. The polymerization reaction showed no induction period regardless of the method employed. It started rapidly, slowed down, then leveled off after a period of about 1 hr. The decrement in the grafting efficiency at prolonged duration could be interpreted in terms of the depletion of monomer and initiator concentration, particularly owing to homopolymer formation. Indeed, a tremendous amount of the latter was observed at longer reaction times.

Effect of Hydrogen Peroxide Concentration

The effect of hydrogen peroxide concentration on the graft yield may be realized from Table I. Experiments were carried out by immersing the

TABLE I
Effect of Hydrogen Peroxide and Thiourea Concentrations on Grafting Yield of Methyl Methacrylate Onto Wool

Hydrogen peroxide concn., moles/l.	Thiourea concn., mmoles/l.	Graft yield, %
4.0	4.0	6.3
8.0	4.0	10.2
12.0	4.0	11.0
12.0	6.0	11.4
12.0	8.0	12.0
12.0	12.0	12.8
12.0	16.0	13.2

wool (1 g) in the thiourea solution (50 ml, 4–12 mmoles/l.) at 60°C for 1/2 hr. Monomer (184 mmoles/l.) was then introduced, followed immediately by addition of the requisite amount of hydrogen peroxide (4–12 mmoles/l.). At this point the grafting reaction was allowed to proceed for different periods of time (15–120 min).

Table I shows that increasing the concentration of the peroxide from 4 to 12 mmoles/l. caused a significant enhancement in the graft yield. Further increment in the peroxide concentration has practically no effect on the graft formation. The initial increase could be explained on the basis of an increase in the speed of initiating the graft polymerization with increasing concentration of the peroxide, owing to which, within the time studied, the growing polymer chains have more time for growth.

From eqs. (7) and (8), the hydroxyl radicals can initiate grafting onto wool. In addition, the hydroxyl radicals can either recombine among themselves or with some other created radicals; they can result in homopolymerization or can stop transfer or propagation of growing chains. The observation that peroxide concentration has no effect on the graft yield suggests that besides inducing grafting, the hydroxyl radicals seem to largely participate in terminating the growing chain radicals as well as initiating homopolymerization. As a matter of fact, homopolymerization was observed to be greatly accelerated at high peroxide concentration.

Effect of Thiourea Concentration

In order to study the effect of thiourea concentration on graft yield, experiments in which the thiourea concentration varied from 4 to 16 mmole/l. were carried out. In each experiment, wool was first immersed in the thiourea solution at 60°C for 1/2 hr, and the grafting reaction was performed at the same temperature for 2 hr using 368 mmoles/l. MMA and 12 mmoles/l. H₂O₂ at a liquor ratio of 50. Results of these experiments are given in Table I. As is evident from Table I, the graft yield is independent of the thiourea over the concentration range of 4 to 16 mmoles/l. The independence of the graft yield on the thiourea concentration suggests that at higher concentration some species must have been generated that is acting as an efficient radical scavenger.

Effect of Monomer Concentration

The effect of monomer concentration on grafting of MMA on wool was evaluated in a series of polymerizations in which five concentrations of the monomer were used. In each case, the wool was first immersed in the thiourea solution (4 mmoles/l.) for 1/2 hr at 60°C, the requisite amount of monomer was then introduced followed by addition of the peroxide (12 mmoles/l.), and the grafting reaction was conducted for 2 hr at 60°C using a liquor ratio of 50. As can be seen from Figure 3, the proportion of monomer converted to grafted polymer increased significantly by increasing the monomer concentration.

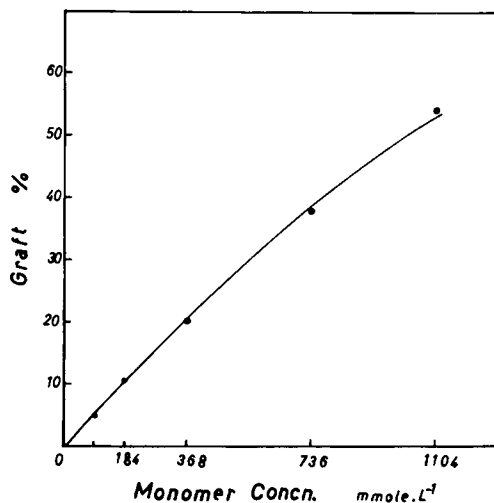


Fig. 3. Variation of graft yield with monomer concentration (4 mmoles/l. thiourea; 12 mmoles/l. H_2O_2 ; 60°C, 120 min; liq. ratio 1:50).

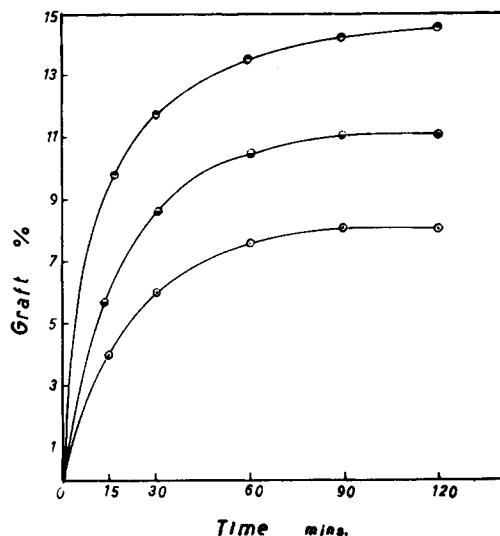


Fig. 4. Effect of temperature on grafting of methyl methacrylate onto wool under the catalytic influence of hydrogen peroxide-thiourea redox system (4 mmoles/l. thiourea; 184 mmoles/l. MMA; 12 mmoles/l. H_2O_2 ; liq. ratio 1:50): (—○—) 40°C; (—●—) 60°C; (—●—) 80°C.

The increased graft formation at high monomer concentration could be interpreted in terms of gel effect, i.e., increase in viscosity of the medium. At high monomer concentration the viscosity of the medium would be high because of the solubility of the poly(methyl methacrylate) in its own residual monomer. Hence, at higher viscosities, termination by coupling of the growing polymer chains is hindered, whereas the other steps in the graft polymerization process, namely, initiation, propagation, and radical chain

processes, are not affected to the same degree by increasing viscosity because the mobility of the polymer chains is restricted by the wool structure. It is rather possible that complexation of wool with methyl methacrylate is more pronounced at higher concentration of the latter. This results in activation of the monomer due to the formation of a donor-acceptor complex (see below).

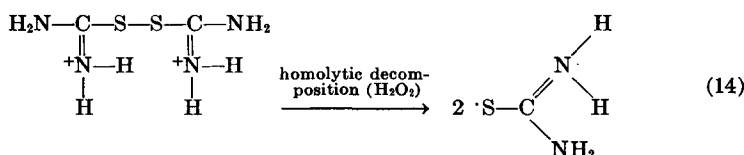
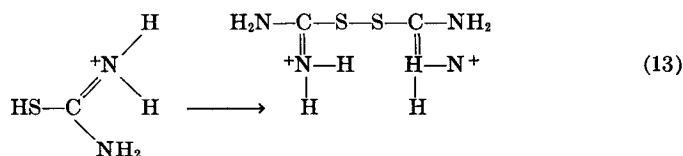
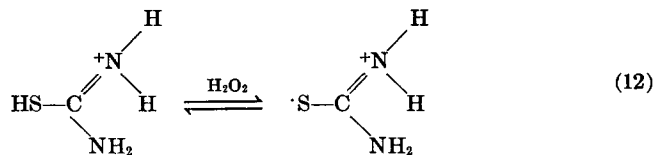
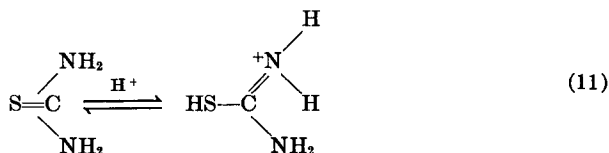
Effect of Temperature

Figure 4 shows the effect of temperature on grafting of MMA on wool using H_2O_2 and thiourea as a cocatalyst. The grafting operation was carried out by first impregnating the wool in thiourea solution for $1/2$ hr, and the monomer and peroxide were then added. It is clear that the graft yield increased considerably by raising the temperature of polymerization from 40° to $80^\circ C$; it follows the order $80^\circ > 60^\circ > 40^\circ C$. The reason for this is that increasing the temperature would advantageously influence certain parameters (which affect grafting) such as the swellability of wool, solubility of monomer and its diffusion, decomposition of H_2O_2 under the catalytic influence of thiourea, and initiation and propagation of the graft.

Effect of pH

As shown in Figure 5; the rate of grafting is dependent on the pH value over the range 2 to 8; the rate of grafting decreases as the pH increases. This observation may be associated with the following:

1. Equation (5) is more shifted to the right-hand side at low pH values. It is rather possible that the sequence of reactions shown below takes place:²¹



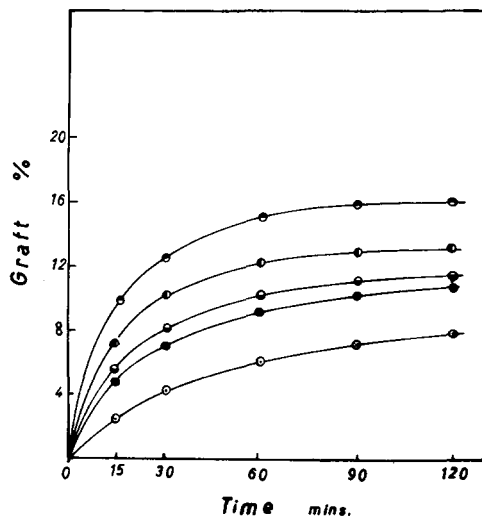


Fig. 5. Influence of pH of grafting medium on the rate of grafting (4 mmoles/l. thiourea; 184 mmoles/l. MMA; 12 mmoles/l. H_2O_2 ; $60^\circ C$; liq. ratio 1:50): (—○—) pH 2; (—●—) pH 4; (—◐—) pH 5.6 (no buffer); (—●—) pH 6; (—○—) pH 8.

Thus, besides the participation of the hydroxyl and isothiocarbamido radicals in producing wool radicals, free radicals formed according to eqs. (12) and (13) seem to contribute in such an interaction.

2. Decomposition of the complex formed between the peroxide and thiourea, eq. (6), proceeds much faster on the acidic side than on the alkaline side. The reason for this is that the reducing properties of thiourea is higher at low pH values.²¹

3. The reaction of wool with both the hydroxyl and the isothiocarbamido radicals to produce wool radicals, eqs. (7) and (9), is favored on the acidic side. Similar observation was reported when Fe^{3+} -thiourea cocatalyst was used as the initiation system.²⁴

4. The effect of thiourea on wool to bring about reduced wool with higher susceptibility to grafting is enhanced at low pH values because thiourea probably loses its reducing properties as the pH increases.²¹

The net effect of all these functions leads to a higher rate of grafting.

Effect of Cupric Ions

The presence of traces of copper sulfate in a cellulose-acrylonitrile-per-sulfate-sodium thiosulfate-water system has been reported to yield higher polymer content of the cellulose as well as to reduce the induction period of the grafting reaction.²⁶ Similarly, addition of cupric ion to a mixture of methyl methacrylate and purified cotton in the presence of water increases the polymer yield.²⁷ Recently, it has been suggested that cupric ions participate in complexes formed between cellulose and monomer, thus promoting the development of high concentration of donor-acceptor com-

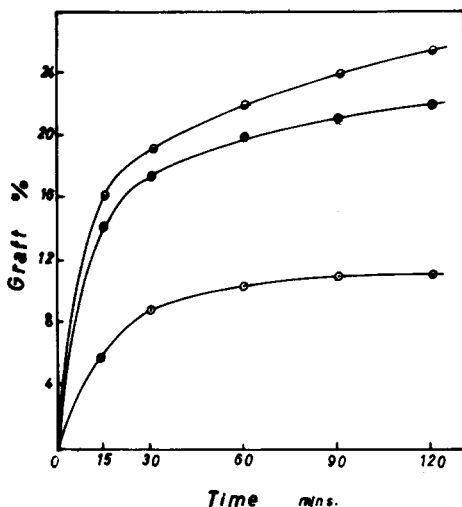


Fig. 6. Effect of traces of cupric ions on rate of grafting (4 mmoles/l. thiourea; 184 mmoles/l.; MMA; 12 mmoles/l. H_2O_2 ; $60^\circ C$; liq. ratio 1:50); (—○—) no copper; (—●—) 0.4 mmoles/l. $CuSO_4$; (—◐—) 0.8 mmoles/l. $CuSO_4$.

plexes which undergo initiation by radicals formed on cellulose as a result of radical-producing initiator.²⁸

In Figure 6 are shown the rates of grafting with and without addition of cupric ions. Obviously, the addition of cupric ions to a mixture of methyl methacrylate and wool in the presence of thiourea, H_2O_2 , and water greatly increases the rate of grafting. This implies that cupric ion plays an important role in polymerizing methyl methacrylate onto wool by the H_2O_2 -thiourea redox system. Hence, it may be assumed that polymerization of methyl methacrylate in the presence of wool involves a formation of complex between the wool hydroxyls, amides, water, and monomer. The complexation of an acceptor monomer such as MMA entails interaction with its carbonyl group, enhancing its electron-accepting capability and promoting the formation of donor-acceptor complex. Presence of cupric ion seems to enhance such complexation probably via participation in its formation. That is, the acceleration of polymerization onto wool in the presence of cupric ion is the result of enhanced reactivity of MMA owing to formation of a donor-acceptor complex in which the uncomplexed MMA, though normally an electron acceptor, behaves as a donor relative to the complexed MMA (i.e., wool-MMA-Cu(II)- H_2O_2 complex) which has been converted to a stronger acceptor. Enhanced monomer reactivity is also apparently due to association of complexed monomer into organized array since wool acts as a matrix for such alignment.

Solubility Properties

Figure 7 shows the variation of the solubility of wool with polymer content. In one case, the polymer content represents the graft yield ob-

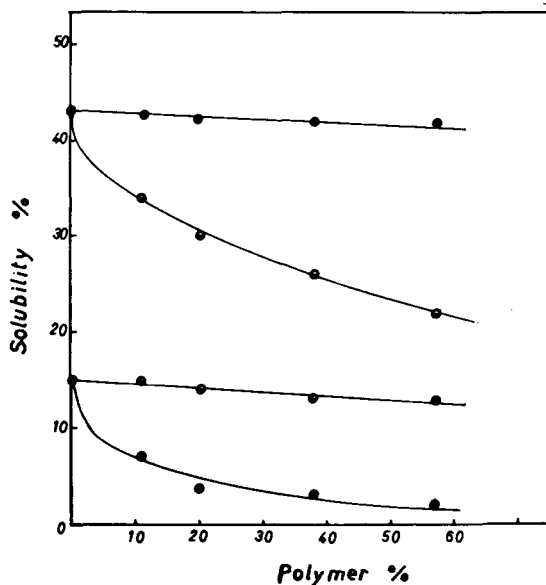


Fig. 7. Variation of solubility properties of wool with its polymer content. Alk. solubility: (—○—) physical mixture; (—●—) grafted wool. Urea bisulfite solubility: (—○—) physical mixture; (—●—) grafted wool.

tained by polymerizing methyl methacrylate with wool; while in the other case it represents the same amount of homopoly(methyl methacrylate) which was physically mixed with the untreated wool. The solubility was performed either in aqueous sodium hydroxide²⁹ or urea bisulfite³⁰ solutions.

It is clear (Fig. 7) that the alkali solubility of wool decrease by increasing the polymer content of wool. The same holds true for urea bisulfite solubility. Nevertheless, the decrease in solubility of grafted wool is very significant, while it is very minor in case of the physical mixture. This is indicative of grafting of wool with methyl methacrylate in the presence of H_2O_2 -thiourea redox system. The polypeptide chains, salt linkages, and disulfide linkage in wool are protected by the grafted polymer which is acting as diffusion barrier for the solubilizing agents to penetrate into the fibers.

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