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### Grafting Vinyl Monomers onto Wool Fibers. VI. Graft Copolymerization of Methyl Methacrylate onto Wool Using Tetravalent Manganese-Oxalic Acid Redox System

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## Grafting Vinyl Monomers onto Wool Fibers. VI. Graft Copolymerization of Methyl Methacrylate onto Wool Using Tetravalent Manganese-Oxalic Acid Redox System

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### ABSTRACT

Graft copolymerization of methyl methacrylate onto wool induced by the permanganate-oxalic acid redox system was investigated in aqueous medium. The rate of grafting was determined by varying the concentrations of monomer, oxalic acid, permanganate, acidity of the medium, temperature, and the reaction medium. The graft yield increases significantly with increasing oxalic acid concentration up to  $1.5 \times 10^{-2}$  M and thereafter it decreases. The graft yield also increases with an increase of the monomer concentration, initiator concentration, acid concentration, and temperature up to a certain range and then decreases. The effect of some inorganic salts and surfactants on the rate of grafting has also been investigated and a suitable reaction mechanism has been proposed.

### INTRODUCTION

The vigor of permanganate ion as an oxidizing agent is well known [1]. Its reactions are interesting because of the several oxidation

states to which it can be reduced. The fate of the manganese is largely determined by the reaction conditions, in particular the acidity of the medium.

Permanganate ion coupled with simple water-soluble organic substrates can produce free radicals which can initiate vinyl polymerization. Palit and co-workers [2-4] and Mishra et al. [5-8] have used a large number of redox initiators involving permanganate ion as the initiator. The reducing agents include oxalic acid, citric acid, and tartaric acid, and of all the redox systems permanganate-oxalic acid was proved to be one of the best initiating systems for the polymerization of vinyl monomers. Nayak and co-workers have reported the graft copolymerization of vinyl monomers onto wool and silk fibers using a multitude of metal and nonmetal ions as the redox initiators [9-16]. This communication presents the result of the graft copolymerization of methyl methacrylate onto wool using the permanganate-oxalic acid redox system as the initiator.

## EXPERIMENTAL

Indian Chokla wool fibers were purified by Soxhlet extraction with acetone for about 24 h followed by washing with cold distilled water and air drying.

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

Potassium permanganate (AR),  $H_2SO_4$  (~18 M, AR, BDH), and oxalic acid (AR) were used. Water, distilled twice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. A stock solution of permanganate (0.1 M in distilled water) was used throughout the experiment. The concentration of permanganate in the experimental system was determined by cerimetry.

The grafting reaction was carried out according to our previous communication [11].

## RESULTS AND DISCUSSION

### Effect of Oxalic Acid Concentration

The effect of oxalic acid concentration on graft yield was investigated by changing the oxalic acid concentration within the range of 0.5 to  $3 \times 10^{-2}$  M. The graft yield increases significantly with an increase of oxalic acid concentration up to  $1.5 \times 10^{-2}$  M, and further increase of the oxalic acid concentration causes a marked decrease in the extent of the graft yield (Fig. 1).

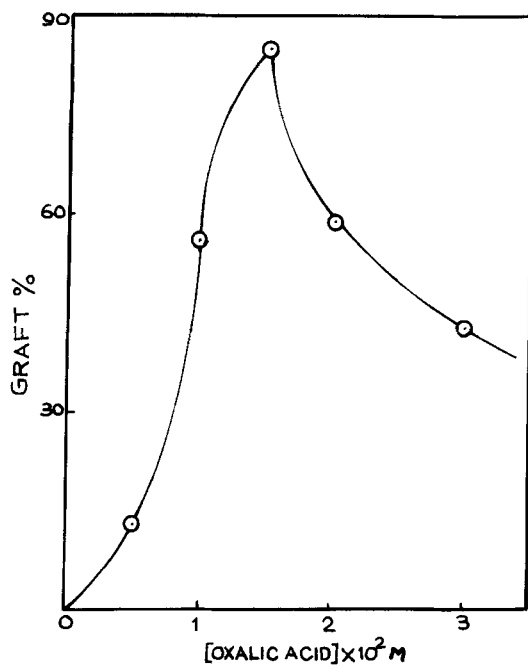
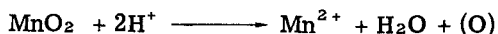


FIG. 1. Effect of [oxalic acid] on graft yield.  $[Mn^{4+}] = 5 \times 10^{-3} M$ ,  $[H^+] = 20.25 \times 10^{-2} M$ ,  $[MMA] = 5\% v/v$ , temperature =  $50^\circ C$ , time = 6 h, M:L = 1:100.

At higher concentrations of oxalic acid a considerable amount of  $MnO_2$  is used up in the side reaction:



where  $Mn^{4+}$  is reduced to  $Mn^{2+}$  in a single step and the intermediate reaction between  $Mn^{3+}$  and  $C_2O_4^{2-}$  producing carboxyl free radicals is suppressed. Thus the rate as well as the maximum conversion is found to decrease when the pH of the medium is reduced to a greater extent. The second reason for the decrease in the graft yield at higher concentrations of oxalic acid might be due to the constant production of inhibiting oxygen. Palit et al. [2-4] and Misra et al. [5-8] have made similar observations in the case of homopolymerization initiated by the permanganate-oxalic acid redox system.

#### Effect of Monomer Concentration

The effect of monomer concentration on grafting methylmethacrylate onto wool fiber was investigated by changing the monomer

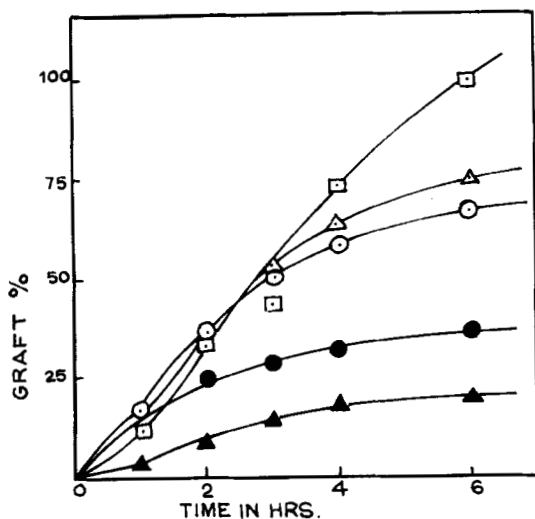


FIG. 2. Effect of  $[MMA]$  on graft yield.  $[Mn^{4+}] = 5 \times 10^{-3} M$ ,  $[oxalic\ acid] = 1.5 \times 10^{-2} M$ ,  $[H^+] = 20.25 \times 10^{-2} M$ , temperature =  $50^\circ C$ , M:L = 1:100. (○)  $[MMA] = 5\%$  v/v, (△)  $[MMA] = 7\%$  v/v, (□)  $[MMA] = 9\%$  v/v, (●)  $[MMA] = 11\%$  v/v, (▲)  $[MMA] = 13\%$  v/v.

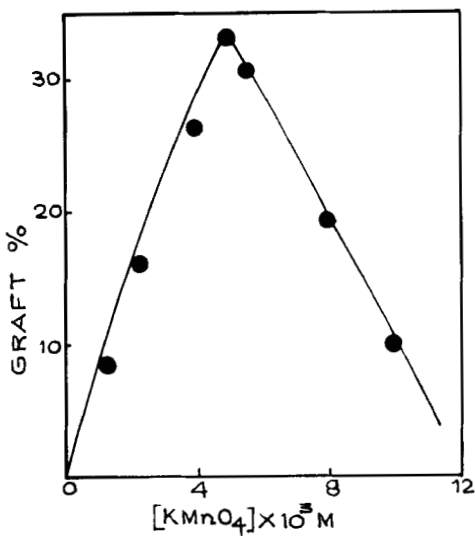


FIG. 3. Effect of  $[Mn^{4+}]$  on graft yield.  $[Oxalic\ acid] = 1 \times 10^{-2} M$ ,  $[H^+] = 20.25 M$ ,  $[MMA] = 5\%$  v/v, temperature =  $50^\circ C$ , time = 6 h, M:L = 1:100.

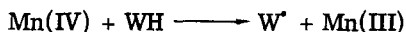
concentration and keeping the concentration of all other reagents constant. The graft yield increases with increasing monomer concentration up to 9% and then decreases with further increases of monomer concentration (Fig. 2). A probable explanation for this is that as the concentration of PMMA macroradicals increases with the increase of monomer concentration, the rate of their combination and disproportionation increases faster than the rate of their combination with wool molecules. Further, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, which increases rapidly as the monomer concentration increases. Similar observations were reported by Haworth and Holker [17].

### Effect of Initiator Concentration

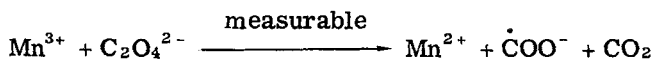
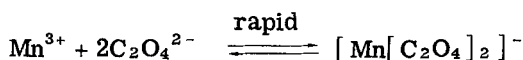
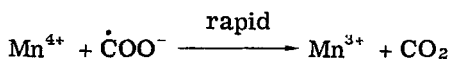
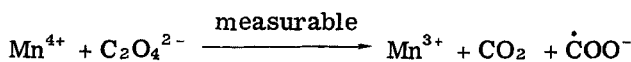
Figure 3 shows the effect of initiator concentration on graft yield. The concentration of the permanganate was varied from 0.5 to  $10 \times 10^{-3}$  M, keeping the concentration of all other reagents constant. The result shows that the percentage of graft yield first increases with the increase of the permanganate concentration up to  $5 \times 10^{-3}$  M and then decreases with a further increase of the permanganate concentration.

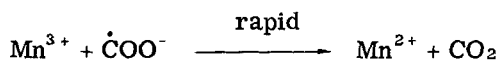
In a system consisting of wool, permanganate, oxalic acid, sulfuric acid, and monomer, the free radical formation might take place in the following ways.

(a) First, the Mn(IV) ion might attack directly the wool matrix, resulting in the formation of a wool macroradical.

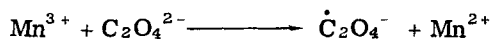


(b) Second, Palit and co-workers [2-3] have suggested that carboxyl radicals ( $\dot{\text{C}}_2\text{O}_4^-$  or  $\text{COO}^{\cdot}$ ) are actually the initiators in such a system. The mechanism for the generation of carboxyl radicals is possibly that given by Launer and Yost [18]:

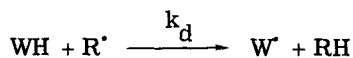




Weiss [19] has suggested that the continuous production of the active oxalic acid ion radical ( $\overset{\cdot}{\text{C}}_2\text{O}_4^-$ ) in this system is governed by the reaction

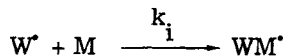


The free radicals ( $\overset{\cdot}{\text{C}}\text{OO}^-$  or  $\overset{\cdot}{\text{C}}_2\text{O}_4^- = \text{R}^*$ ) formed by the above mechanism might attack wool, giving rise to wool macroradicals ( $\text{W}^*$ ):



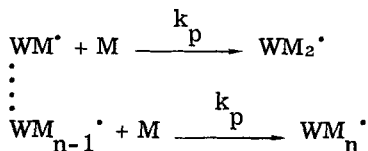
Since oxalic acid acts as a better reductant than wool, taking into account the second possibility, the following reaction scheme may represent graft copolymerization of MMA onto wool.

(i) Initiation:

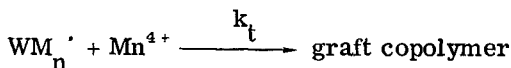


where  $\text{W}$  = wool and  $\text{M}$  = monomer.

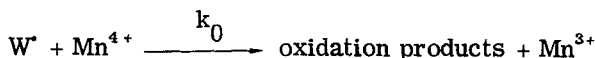
(ii) Propagation:



(iii) Termination:



(iv) Oxidation:



Now,

$$\frac{d[\text{WM}_n^*]}{dt} = k_i[\text{W}^*][\text{M}] - [\text{WM}_n^*][\text{Mn}^{4+}]k_t = 0$$

Therefore

$$[WM_n^{\cdot}] = \frac{k_i [W^{\cdot}] [M]}{[Mn^{4+}] k_t}$$

$$\frac{d[W^{\cdot}]}{dt} = k_d [WH] [R^{\cdot}] - k_i [W^{\cdot}] [M] - k_0 [W^{\cdot}] [Mn^{4+}] = 0$$

Therefore

$$[W^{\cdot}] = \frac{k_d [WH] [R^{\cdot}]}{(k_i [M] + k_0 [Mn^{4+}])}$$

Therefore

$$R_p = \frac{k_p k_d k_i [M]^2 [WH]}{k_t [Mn^{4+}] [k_i [M] + k_0 [Mn^{4+}]]}$$

$$= \frac{k_p k_i}{k_t} \frac{k_d [WH] [M]^2}{[Mn^{4+}] (k_i [M] + k_0 [Mn^{4+}])}$$

At higher concentration of  $Mn^{4+}$ , the free radicals produced on the backbone of the wool fiber might be oxidized to give rise to oxidation products. As a result, the rate of grafting decreases, as is evident from the above equation.

Second, at higher concentration of  $Mn^{4+}$ , the metal ions might interact with oxalic acid, giving a higher amount of carboxyl free radicals which results in the production of more homopolymer, thereby reducing the percentage of grafting.

### Effect of Acid Concentration

The effect of acid concentration on graft copolymerization of MMA onto wool was studied by varying the concentration of sulfuric acid in the range  $10.5$  to  $60 \times 10^{-2}$  M, keeping the concentration of all other reagents constant. The graft yield increased initially with the increase of the acid concentration up to  $15 \times 10^{-2}$  M and thereafter it decreased with a further increase of acid concentration (Fig. 4). A probable explanation for these observations might be as follows.



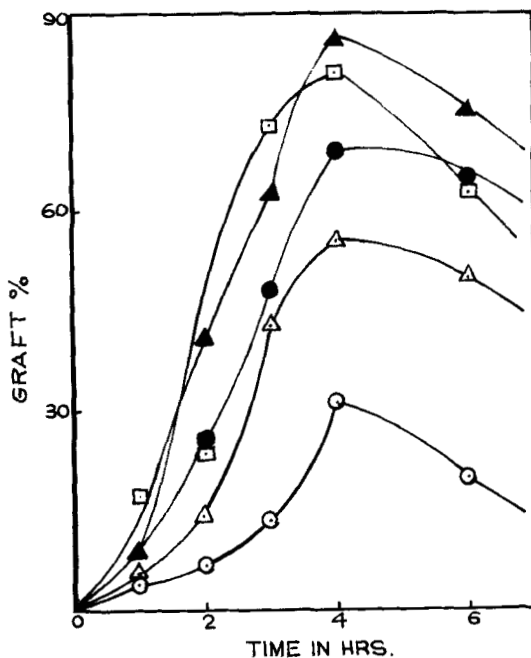


FIG. 4. Effect of  $[\text{H}_2\text{SO}_4]$  on graft yield.  $[\text{Mn}^{4+}] = 5 \times 10^{-3} \text{ M}$ ,  $[\text{oxalic acid}] = 1.5 \times 10^{-2} \text{ M}$ ,  $[\text{MMA}] = 5\% \text{ v/v}$ , temperature =  $50^\circ\text{C}$ , M:L = 1:100. (●)  $[\text{H}_2\text{SO}_4] = 10.5 \times 10^{-2} \text{ M}$ , (▲)  $[\text{H}_2\text{SO}_4] = 15.0 \times 10^{-2} \text{ M}$ , (□)  $[\text{H}_2\text{SO}_4] = 20.10 \times 10^{-2} \text{ M}$ , (△)  $[\text{H}_2\text{SO}_4] = 30.0 \times 10^{-2} \text{ M}$ , (○)  $[\text{H}_2\text{SO}_4] = 60.0 \times 10^{-2} \text{ M}$ .

(a) Palit and co-workers [3] have reported that at lower pH the coagulation of colloidal homopolymer in solution and within fibers increases during grafting. This retards the diffusion of both monomer and initiator into the wool fiber for grafting to occur.

(b) At higher acid concentration,  $\text{MnO}_2$  might react with acid-producing oxygen, which might inhibit the grafting process.



### Effect of Temperature

The graft copolymerization of MMA onto wool was studied at four different temperatures ranging from  $40$  to  $55^\circ\text{C}$ , keeping the concentration of all other reagents constant (Fig. 5). The percentage of graft yield increases initially with the rise of temperature up to  $50^\circ\text{C}$ ,

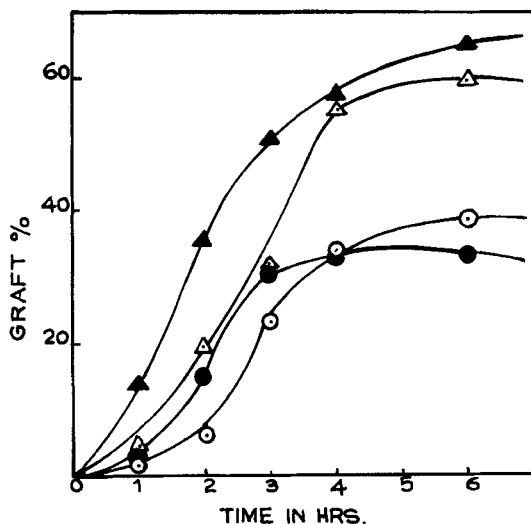


FIG. 5. Effect of temperature on graft yield.  $[Mn^{4+}] = 5 \times 10^{-3} M$ ,  $[oxalic\ acid] = 1.5 \times 10^{-2} M$ ,  $[H^+] = 20.25 \times 10^{-2} M$ ,  $[MMA] = 5\% v/v$ , M:L = 1:100. (●) 40°C, (△) 45°C, (▲) 50°C, (○) 55°C.

and then falls with a further increase of temperature. The dependence of the rate of grafting on temperature between 40 and 50°C could be ascribed to the greater activation energy. The swellability of silk, the solubility of monomer, and its diffusion rates are enhanced by increasing the temperature. Beyond 50°C the decrease in percentage of grafting is probably due to the greater possibility of combination rates of radicals at higher temperature. Again, at high temperatures side reactions such as  $C_2O_4^{2-} + Mn^{3+} \rightarrow 2CO_2 + Mn^{2+}$  might set in, thereby increasing the possibility of the destruction of the initiating species, as a result of which the graft-on decreases.

From the Arrhenius plot of  $\log R_p$  versus  $1/T$  (Fig. 6), the overall activation energy was found to be 15.20 kcal/mol. Using the value of  $(E_p - \frac{1}{2}E_t) = 4-5$  kcal/mol given by Tobolsky [20], where  $E_p$  and  $E_t$  are the energies of propagation and termination, respectively, the activation energy of initiation ( $E_d$ ) was calculated from these values as follows:

$$E_d = 2E_a - (2E_p - E_t)$$

where  $E_a$  is the overall activation energy and  $E_d = 21.40$  kcal/mol for

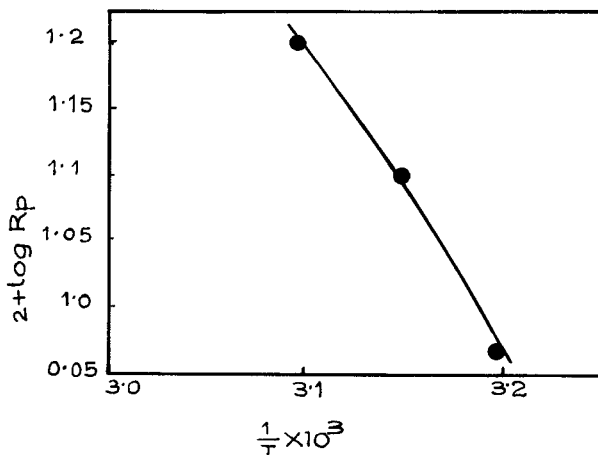


FIG. 6. Arrhenius plot for graft copolymerization of MMA onto wool initiated by  $Mn^{4+}$ -oxalic acid redox system.

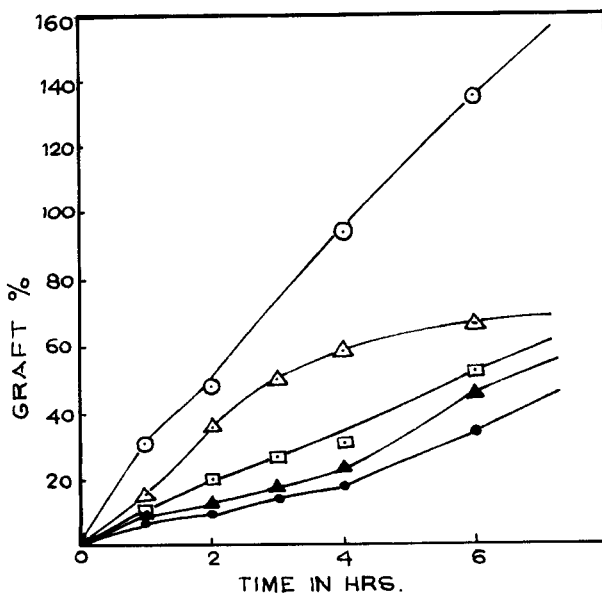


FIG. 7. Effect of solvents on graft yield.  $[Mn^{4+}] = 5 \times 10^{-3} M$ ,  $[oxalic\ acid] = 1.5 \times 10^{-2} M$ ,  $[H^+] = 20.25 \times 10^{-2} M$ ,  $[MMA] = 5\%$  v/v, M:L = 1:100,  $[solvents] = 10\%$  v/v, temperature =  $50^\circ C$ . (○) dioxane, (□) formic acid, (▲) acetic acid, (●) methanol, (△) control.

the total conversion reaction of MMA to PMMA. This calculated value is very small compared to that seen in the usual redox polymerization system.

### Effect of Reaction Medium

The reaction medium plays a vital role in graft copolymerization reactions. For the solvents studied, the graft yield follows the order dioxane > formic acid > acetic acid > methanol.

The data show (Fig. 7) that, except for dioxane, the other solvents depress the rate of grafting. Similar observations have been reported by Palit and co-workers [2, 3] in the case of aqueous polymerization initiated by permanganate. The dependence of the rate of grafting on the nature of the solvents suggests that the solvents examined differ considerably in their (1) capability of swelling of the wool fiber, (2) miscibility with monomer, (3) formation of solvent radical from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of wool, and (5) termination of the graft radical and wool macroradical via chain transfer. While the first four factors favor grafting by simplifying the access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft. The lower graft yields could be ascribed to its adverse effect on the swelling of wool by water.

### Effect of Inorganic Salts and Surfactants

The addition of neutral salts such as KCl, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, and LiNO<sub>3</sub> depresses the rate of grafting whereas complexing agents such as NaF increase the rate of grafting (Fig. 8). The order of their effect on graft yield is NaF > Na<sub>2</sub>SO<sub>4</sub> > MgSO<sub>4</sub> > LiNO<sub>3</sub> > KCl. A probable explanation for the depression of their graft yield is the ionic dissociation of the added electrolyte which interferes with the usual polymerization reaction, resulting in the premature termination of the growing chains. The increase in graft yield with NaF might be due to the complexation of fluoride ions with Mn<sup>3+</sup> ions, and this complex acts essentially as a slower but steadier source of free radicals, as a result of which the initial rate falls but subsequently increases.

The effect of CuSO<sub>4</sub> concentration on grafting is quite interesting. It is observed that with increasing CuSO<sub>4</sub> concentration the graft yield increases up to 0.005 M and then decreases (Fig. 9). The initial increase in graft yield might be due to the fact that the presence of Cu<sup>2+</sup> ions in the vicinity of wool matrix certainly favors grafting since the involvement of Cu<sup>2+</sup> ion in a wool-monomer complex would be easier. Furthermore, the creation of free radical species under the influence of Cu<sup>2+</sup> ions would be in the proximity of wool, thus assisting the formation of wool macroradicals. The drop in the graft yield with

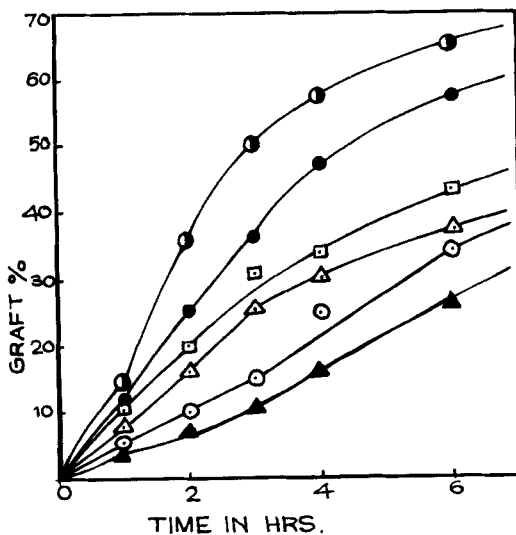


FIG. 8. Effect of salts on graft yield.  $[\text{Mn}^{4+}] = 5 \times 10^{-3} \text{ M}$ ,  $[\text{oxalic acid}] = 1.5 \times 10^{-2} \text{ M}$ ,  $[\text{MMA}] = 5\% \text{ v/v}$ ,  $[\text{H}^+] = 20.25 \times 10^{-2} \text{ M}$ ,  $[\text{salts}] = 0.01 \text{ M}$ , temperature =  $50^\circ\text{C}$ , M:L = 1:100. (○) Control, (●) NaF, (□)  $\text{Na}_2\text{SO}_4$ , (○)  $\text{LiNO}_3$ , (△)  $\text{MgSO}_4$ , (▲) KCl.

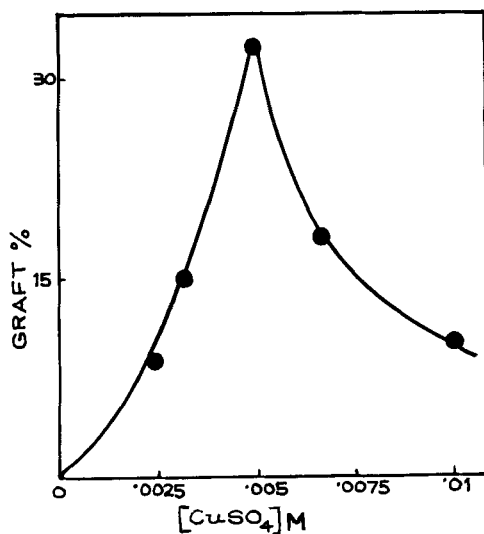


FIG. 9. Effect of  $[\text{CuSO}_4]$  on graft yield.  $[\text{Mn}^{4+}] = 5 \times 10^{-3} \text{ M}$ ,  $[\text{oxalic acid}] = 1.5 \times 10^{-2} \text{ M}$ ,  $[\text{H}^+] = 20.25 \times 10^{-2} \text{ M}$ ,  $[\text{MMA}] = 5\% \text{ v/v}$ , time = 6 h, temperature =  $50^\circ\text{C}$ , M:L = 1:100.

a higher concentration of cupric sulfate solution is attributed to a variety of reasons. First, with the termination of free radicals in solution, on polymer, and/or on wool, the  $\text{Cu}^{2+}$  ions seem to act as radical traps. Second, a particular concentration of  $\text{Cu}^{2+}$  ions favors complexation of monomer with wool, and beyond this concentration they perturb such complexations.

The percentage of grafting has also been calculated in the presence of the anionic surfactant sodium lauryl sulfate (NaLS) as well as of the cationic surfactant cetyl trimethyl ammonium bromide (CTABr) at their critical micelle concentrations (CMC). It is observed that the anionic surfactant enhances the rate of grafting whereas the cationic surfactant depresses the rate. At CMC, micelles are formed which are roughly spherical in size, with the sulfate ions forming a Gouy-Chapman double layer [21, 22]. The enhancement of graft yield by NaLS at CMC can be explained on the assumption that the micelles become entangled with the wool fiber as a result of which the  $\text{Mn}^{4+}$  ion is electrostatically attracted toward the wool matrix. The concentration of  $\text{Mn}^{4+}$  ions will be higher in the vicinity of the fiber, so the free radical formation on the wool backbone will be facilitated. As a result, graft yield increases.

#### ACKNOWLEDGMENTS

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