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Grafting Vinyl Monomers onto Silk Fibers. XI. Graft Copolymerization of Methyl Methacrylate onto Silk Using Fe^{3+}-Thiourea Redox System

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ABSTRACT

The graft copolymerization of methyl methacrylate onto silk fibers initiated by the ferric chloride-thiourea redox system has been investigated in aqueous medium. The rate of grafting was calculated by varying the concentrations of monomer, initiator, and thiourea, the acidity of the medium, and the temperature. The rate of grafting increases significantly with an increase of [$FeCl_3$] up to 1.25×10^{-3} M and thereafter it slows down. The rate of grafting also increases with an increase of [thiourea] and [$HClO_4$] up to 2.5×10^{-3} and 23.325×10^{-1} M, respectively, and thereafter it decreases. The graft percentage increases with an increase of the monomer concentration. The effect of some inorganic salts, solvents, and surfactants on the rate of grafting has also been investigated.

INTRODUCTION

In recent years, grafting has proved to be a potentially effective means of modifying fiber properties without destroying the basic properties of the fiber, and hence it has been the subject of study by several groups of workers [1-6]. Nayak and co-workers [7-15] have reported graft copolymerization of vinyl monomers onto wool, silk, cellulose, and nylon using several metal and nonmetal ions as initiators. Bendak and Hebeish et al. [16-20] have also reported grafting onto wool and cellulose using a number of redox systems as initiators.

This paper presents the results of graft copolymerization of methyl methacrylate onto silk using the ferric chloride-thiourea redox system.

EXPERIMENTAL

Mulberry silk fibroin was collected from the Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by the method mentioned in our earlier communication [10]. Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution, dried with anhydrous sodium sulfate, and distilled under nitrogen under reduced pressure before use.

Ferric chloride (Anhydrous Analar), thiourea (BDH), and $HClO_4$ (60% GR) were used. Water distilled twice over alkaline permanganate and deionized by passing through a Biodeminrolit resin (Permutit Co., United Kingdom) was used to prepare all solutions. A stock solution of ferric chloride (0.1 M in distilled water) was used throughout the experiment. The concentration of ferric(III) in the experimental system was determined by iodometry [21].

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

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The effect of monomer concentration on graft copolymerization of methyl methacrylate onto silk fibers using Fe^{3+} as initiator was studied by varying the monomer concentration from 27.56×10^{-2} to 122.044×10^{-2} M, keeping the concentrations of the other reagents constant. A perusal of the results shows that the graft yield increases steadily with an increase of the monomer concentration (Fig. 1). This might be due to (1) complexation of silk with a monomer which enhances monomer activity at high monomer concentration, or (2) the gel effect which increases due to the solubility of polymethyl methacrylate in its own monomer which would be more pronounced at a high monomer concentration. This causes hindrance in termination, particularly by coupling of growing polymer chains. The gel effect also causes swelling of silk, thus facilitating diffusion of monomer to growing chains and active sites on the silk backbone, thereby enhancing grafting.

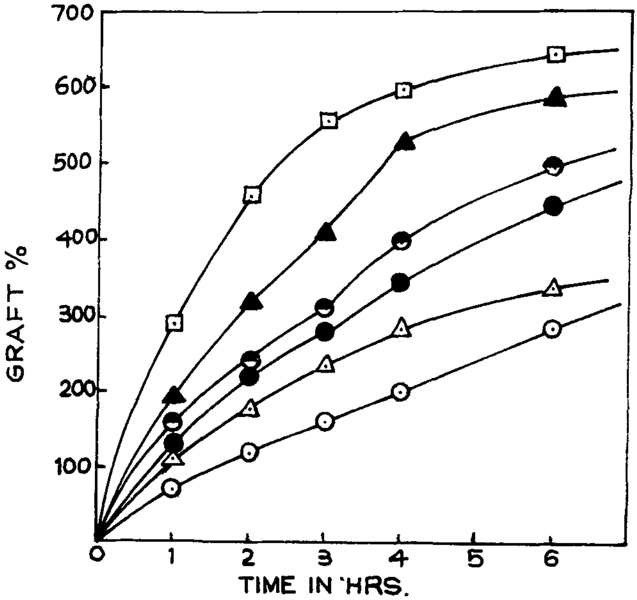


FIG. 1. Effect of [MMA] on graft yield. [$FeCl_3$] = 5.0 × 10^{-3} mol/L. [TU] = 5.0 × 10^{-3} mol/L. [$HClO_4$] = 2.33 × 10^{-1} mol/L. Temperature = 50°C. (⊙): [MMA] = 27.56 × 10^{-2} mol/L. (◬): [MMA] = 46.94 × 10^{-2} mol/L. (●): [MMA] = 65.71 × 10^{-2} mol/L. (◒): [MMA] = 84.592 × 10^{-2} mol/L. (▲): [MMA] = 103.268 × 10^{-2} mol/L. (▣): [MMA] = 122.044 × 10^{-2} mol/L.

Effect of Initiator Concentration

The effect of initiator concentration on graft yield was studied by varying the concentration of Fe^{3+} within the range of 0.5 × 10^{-3} to 35 × 10^{-3} M. The data indicate that the graft yield increases initially with an increase of initiator concentration up to 1.25 × 10^{-3} M and thereafter the rate falls with a further increase of the initiator concentration (Fig. 2). The rate of grafting also slows down as the reaction time is prolonged. A probable explanation for the above observations might be as follows.

In an initiating system containing thiourea (I), the redox component is isothiourea (II). In the presence of an initiator like $FeCl_3$ and acid ($HClO_4$), the isothiourea moiety first complexes with Fe^{3+} which breaks down, giving rise to the amidinosulfenyl free radical (III) as shown below [22].

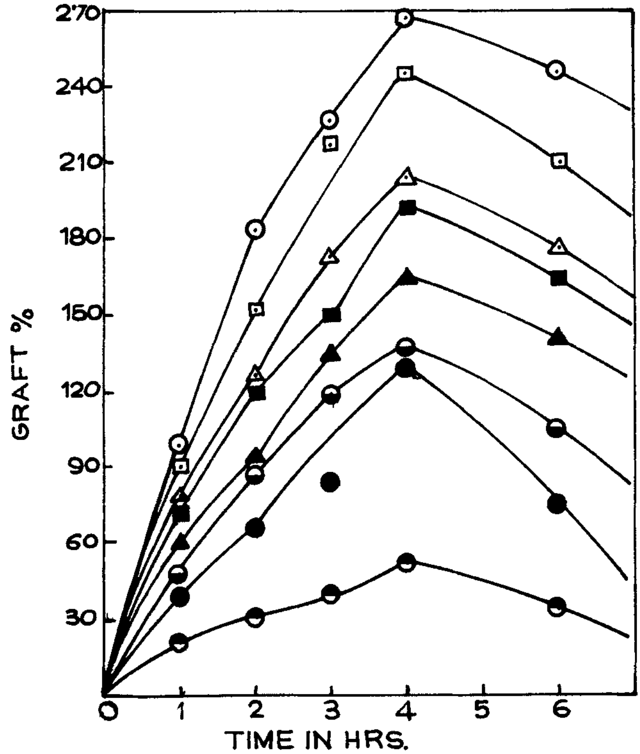
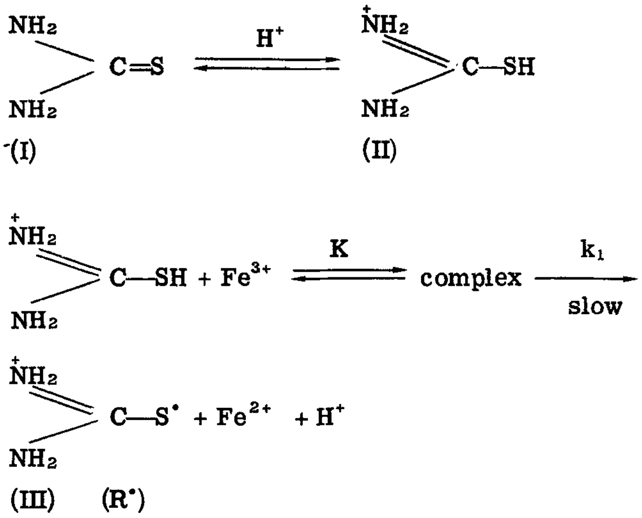


FIG. 2. Effect of [Initiation] on graft yield. [TU] = 5.0 × 10^{-3} mol/L. [$HClO_4$] = 9.33 × 10^{-1} mol/L. [MMA] = 46.94 × 10^{-2} mol/L. Temperature = 50°C. (⊡): [$FeCl_3$] = 0.5 × 10^{-3} mol/L. (⊙): [$FeCl_3$] = 1.25 × 10^{-3} mol/L. (△): [$FeCl_3$] = 2.5 × 10^{-3} mol/L. (■): [$FeCl_3$] = 5.0 × 10^{-3} mol/L. (▲): [$FeCl_3$] = 10.0 × 10^{-3} mol/L. (⊖): [$FeCl_3$] = 15.0 × 10^{-3} mol/L. (●): [$FeCl_3$] = 25.0 × 10^{-3} mol/L. (⊖): [$FeCl_3$] = 35.0 × 10^{-3} mol/L.



(1)

The isothiocarbamido radicals abstract hydrogen from the amino or hydroxyl groups in silk to yield silk macroradicals (S•) which interacts with the monomer to initiate grafting:

$$\sim\!\sim S + R^{\bullet} \xrightarrow{k_2} \sim\!\sim S^{\bullet} + TU \qquad (2)$$

Initiation:

$$\sim\!\sim S^{\bullet} + M \xrightarrow{k_i} \sim\!\sim SM^{\bullet} \qquad (3)$$

Propagation:

$$\begin{gathered} \sim\!\sim SM^{\bullet} + M \xrightarrow{k_p} \sim\!\sim SM_2^{\bullet} \\ \vdots \\ \sim\!\sim SM^{\bullet}_{n-1} + M \xrightarrow{k_p} \sim\!\sim SM_n^{\bullet} \end{gathered} \qquad (4)$$

Termination:

$$\sim\!\sim SM_n^{\bullet} + Fe^{3+} \xrightarrow{k_t} \text{grafted polymer} \qquad (5)$$

Oxidation:

$$\sim\!\sim S^{\bullet} + Fe^{3+} \xrightarrow{k_o} \text{oxidation product} + Fe^{2+} + H^{+} \qquad (6)$$

Applying the steady-state assumptions to both $[R^\bullet]$ and $[SM^\bullet]$ separately, the following expressions may be derived:

$$\frac{d[R^\bullet]}{dt} = k_1K[TU][Fe^{3+}] - k_2[S][R^\bullet] = 0$$

$$[R^\bullet] = \frac{k_1K[TU][Fe^{3+}]}{k_2[S]}$$

$$\frac{d[S^\bullet]}{dt} = k_2[S][R^\bullet] - k_i[S^\bullet][M] - k_0[S^\bullet][Fe^{3+}] = 0$$

$$[S^\bullet] = \frac{k_2[S][R^\bullet]}{k_i[M] + k_0[Fe^{3+}]}$$

$$\frac{d[SM^\bullet]}{dt} = k_i[S^\bullet][M] - k_t[SM^\bullet][Fe^{3+}]$$

$$[SM^\bullet] = \frac{k_i[S^\bullet][M]}{k_t[Fe^{3+}]} = \frac{k_ik_1K[TU][M]}{k_t[k_i[M] + k_0[Fe^{3+}]]}$$

$$R_p = k_p[SM^\bullet][M^\bullet]$$

$$= \frac{k_pk_ik_1K[TU][M]^2}{k_t\{k_i[M] + k_0[Fe^{3+}]\}}$$

$$= \frac{k_pk_1K[TU][M]^2}{k_t[[M] + k_0/k_i[Fe^{3+}]]}$$

Hence the rate of grafting would decrease with increasing Fe^{3+} concentration.

Further, at a higher concentration of ferric chloride, the free radicals produced on the backbone of the silk fiber might be oxidized

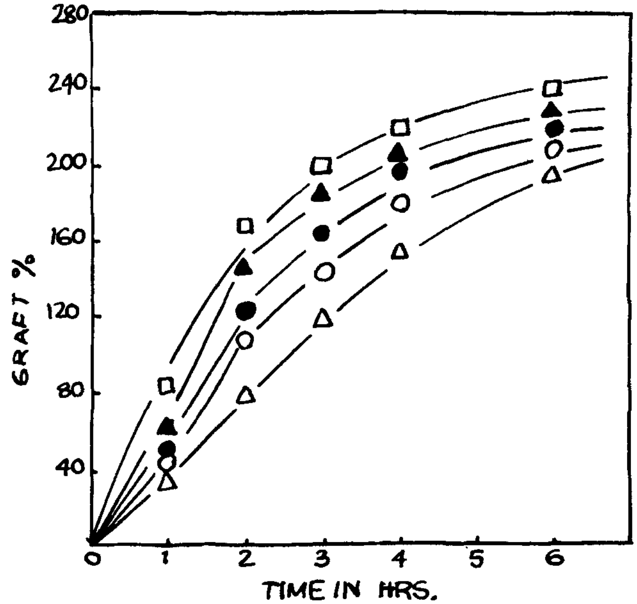


FIG. 3. Effect of [$HClO_4$] on graft yield. [Fe^{3+}] = 5.0×10^{-3} mol/L. [TU] = 5.0×10^{-3} mol/L. [MMA] = 46.94×10^{-2} mol/L. Temperature = 50°C. (Δ): [$HClO_4$] = 9.33×10^{-1} mol/L. (●): [$HClO_4$] = 13.99×10^{-1} mol/L. (▣): [$HClO_4$] = 23.325×10^{-1} mol/L. (▲): [$HClO_4$] = 37.315×10^{-1} mol/L. (◎): [$HClO_4$] = 46.65×10^{-1} mol/L.

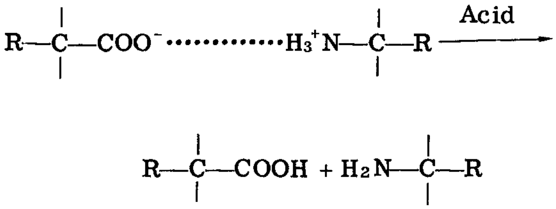
to give rise to oxidation products, thereby decreasing grafting. Hence the rate of grating would decrease with increasing Fe^{3+} concentration.

Second, at higher initiator concentrations, a larger amount of homopolymers might be formed as a result of which the rate of grafting decreases. The decrease in graft yield as the reaction time is prolonged might also be due to the production of a larger amount of homopolymer. A similar explanation has been advanced by Hebeish et al. [16] in graft copolymerization onto wool induced by the Fe^{3+}-thiourea redox system.

Effect of Acid Concentration

The effect of perchloric acid concentration on the rate of grafting of methyl methacrylate onto silk is shown in Fig. 3. The concentration of the acid was varied from 9.33×10^{-1} to 46.65×10^{-1} M, keeping the concentration of all other reagents constant. A perusal of the result indicates that the graft yield increases with the increase of the perchloric acid concentration up to 23.325 × 10^{-1} $\underline{M}$ and thereafter it decreases. These observations could be explained as follows.

The cation binding capacity of silk is high in acidic medium. This is due to the fact that besides the carboxyl groups at the end of the polypeptide chains of silk, free carboxyl groups are created in the presence of acid as a result of the breakage of the salt linkages:



$$R-\overset{|}{\underset{|}{C}}-COO^{-}\cdots\cdots H_3^{+}N-\overset{|}{\underset{|}{C}}-R \xrightarrow{\text{Acid}} R-\overset{|}{\underset{|}{C}}-COOH + H_2N-\overset{|}{\underset{|}{C}}-R$$

Hence more free carboxyl and amino groups are formed as the concentration of the acid is increased, and they are the active centers for the production of silk macroradicals.

The initiating efficiency of the system is increased due to the formation of more isothiocarbamido radicals (Eq. 1) as the concentration of the acid is increased.

The decrease of the rate of grafting beyond 23.325 × 10^{-1} $\underline{M}$ might be due to the fact that thiourea probably loses its reducing properties at higher acid concentrations.

Effect of Thiourea Concentration

The effect of thiourea concentration on the rate of grafting was studied by varying the thiourea concentration over a range of 0.5 × 10^{-3} to 10 × 10^{-3} $\underline{M}$. The rate of grafting first increases with an increase of the thiourea concentration up to 2.5 × 10^{-3} $\underline{M}$ and thereafter it falls (Fig. 4). A probable explanation of these observations might be as follows.

From Eq. (1) it is evident that as the thiourea concentration is increased, more isothiocarbamido radicals are produced which are the initiating species. Hence the graft yield increases with an increase of thiourea concentration.

The decrease of graft yield beyond 2.5 × 10^{-3} $\underline{M}$ might be due to (1) the increased amount of free radical inhibitor in thiourea (the relatively pure product might contain inhibitors up to 0.48 mol% [23]) or (2) the generation of some species which act as radical scavengers.

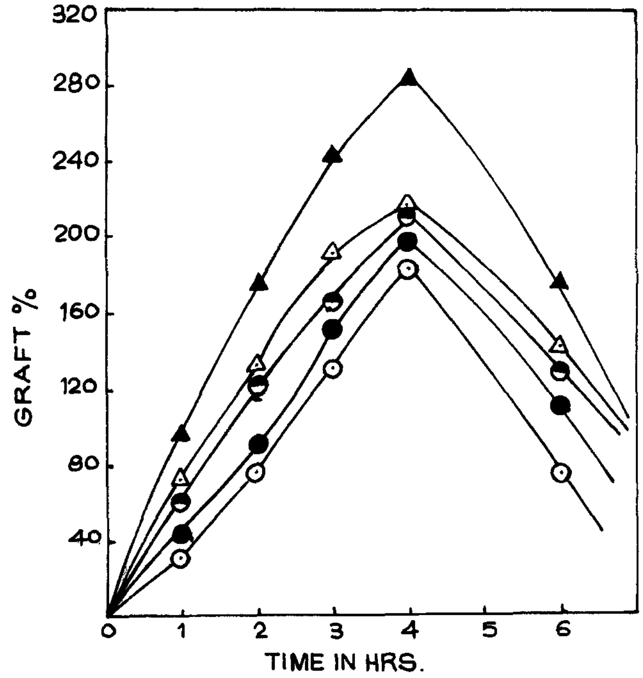


FIG. 4. Effect of [TU] on graft yield. [Fe^{3+}] = 5.0 × 10^{-3} mol/L. [$HClO_4$] = 2.33 × 10^{-1} mol/L. [MMA] = 46.94 × 10^{-2} mol/L. Temperature = 50°C. (⊙): [TU] = 0.5 × 10^{-3} mol/L. (◬): [TU] = 1.25 × 10^{-3} mol/L. (▲): [TU] = 2.5 × 10^{-3} mol/L. (◓): [TU] = 7.5 × 10^{-3} mol/L. (●): [TU] = 10.0 × 10^{-3} mol/L.

Effect of Temperature on Graft Yield

Graft copolymerization was also carried out at temperatures ranging from 40 to 60°C. The data indicate that the graft yield increases with an increase of temperature up to 50°C and then falls (Fig. 5). The dependence of the rate of grafting on temperature up to 50°C could be ascribed to the greater activation energy. The swellability of silk, the solubility of monomer, and the diffusion rates are enhanced by increasing the temperature, as a result of which the graft yield increases. The decrease in graft yield beyond 50°C might be due to the greater possibility of combination rates of radicals at higher temperatures.

From the Arrhenius plot of log R_p versus 1/T, the overall activation energy was found to be 12.80 kcal/mol (Fig. 6). Using the value of

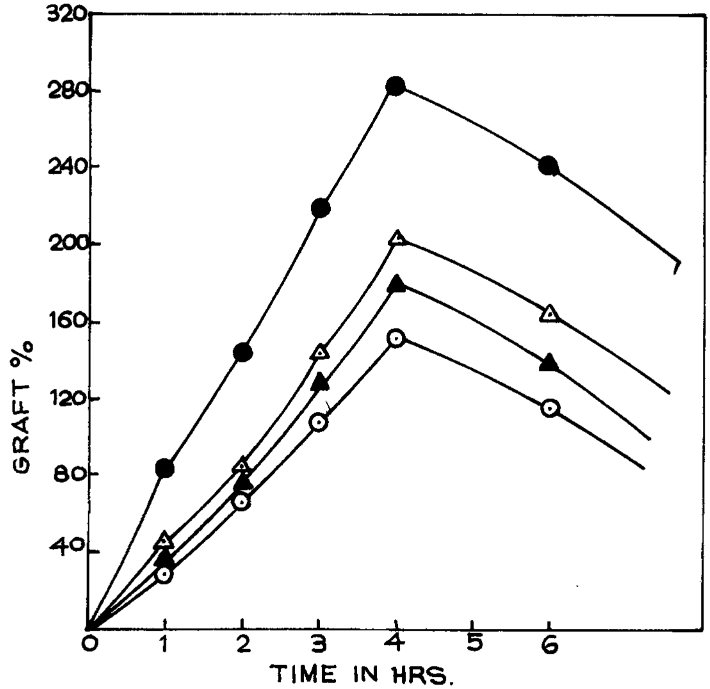


FIG. 5. Effect of temperature on graft yield. [Fe^{3+}] = 5.0 × 10^{-3} mol/L. [TU] = 5.0 × 10^{-3} mol/L. [MMA] = 46.94 × 10^{-2} mol/L. [$HClO_4$] = 2.33 × 10^{-1} mol/L. (⊙): Temperature = 40°C. (△): Temperature = 45°C. (●): Temperature = 50°C. (▲): Temperature = 55°C.

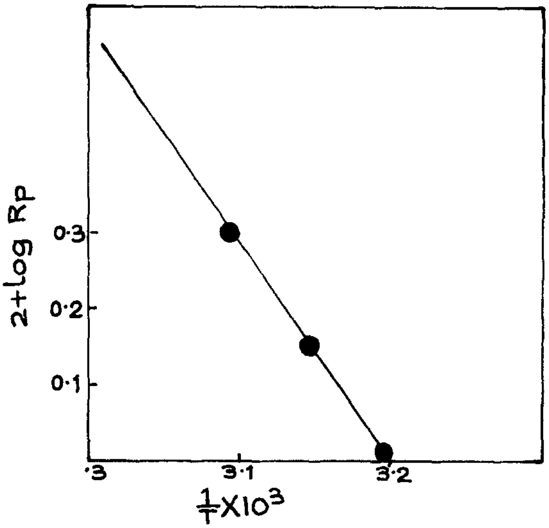


FIG. 6. Arrhenius plot of log R_p versus 1/T for grafting MMA onto silk using Fe^{3+}-TU redox system.

$E_p - \frac{1}{2}E_t$ = 4-5 kcal/mol given by Tobolsky et al. [24], where E_p and E_t are the energies of propagation and termination, respectively, the activation energy of initiation, E_d, can be calculated from these values by

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

where E_a is the overall activation energy, and E_d = 14.70 kcal/mol for the total conversion reaction of MMA to PMMA.

EFFECT OF REACTION MEDIUM

The effect of certain water-soluble organic solvents and dioxane on the graft copolymerization reaction has been studied (Fig. 7). The solvents studied follow the order: dioxane > methanol > ethanol > propanol > butanol > formic acid > acetic acid.

The dependence of the rate of grafting on the nature of the solvents examined differs considerably in their (1) capability of swelling of silk, (2) miscibility with monomer, (3) formation of solvent radicals

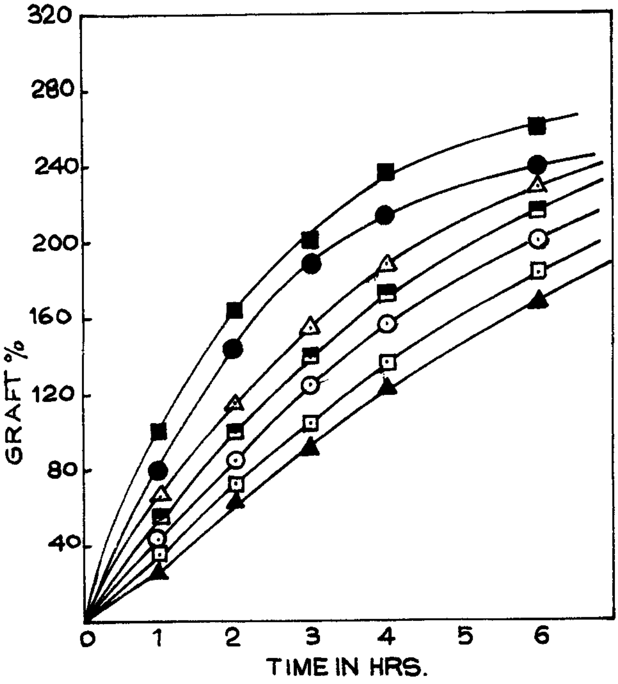


FIG. 7. Effect of solvents on graft yield. [Fe^{3+}] = 5.0 × 10^{-3} mol/L. [TU] = 5.0 × 10^{-3} mol/L. [HClO$_4$] = 2.33 × 10^{-1} mol/L. [MMA] = 46.94 × 10^{-2} mol/L. Solvent = 10% v/v. Temperature = 50°C. (●): Methanol. (⊟): Propanol. (⊡): Formic acid. (■): Dioxane. (◬): Ethanol. (⊙): Butanol. (▲): Acetic acid.

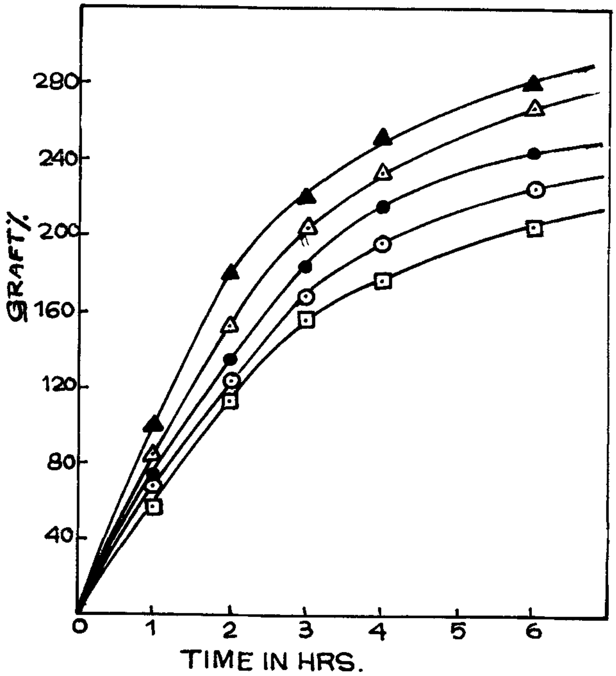


FIG. 8. Effect of salts on graft yield. [Fe^{3+}] = 5.0 × 10^{-3} mol/L. [TU] = 5.0 × 10^{-3} mol/L. [$HClO_4$] = 2.33 × 10^{-1} mol/L. [MMA] = 46.94 × 10^{-2} mol/L. [Salt] = 0.01 mol/L. Temperature = 50°C. (⊙): NaF. (▲): $MnSO_4$. (⊡): KCl. (△): Na_2SO_4. (●): $MgSO_4$.

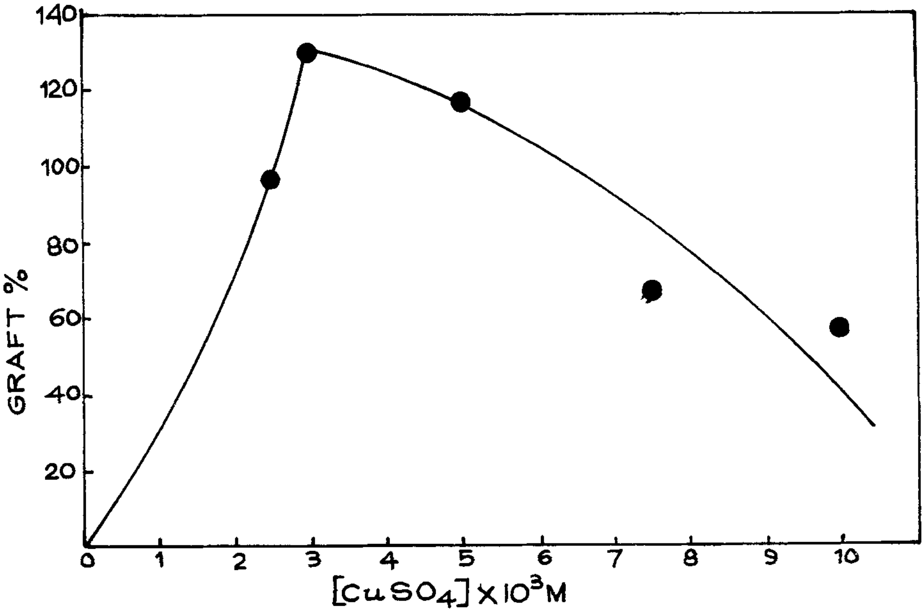


FIG. 9. Effect of $[CuSO_4]$ on graft yield. $[Fe^{3+}] = 5.0 \times 10^{-3}$ mol/L. $[TU] = 5.0 \times 10^{-3}$ mol/L. $[HClO_4] = 2.33 \times 10^{-1}$ mol/L. $[MMA] = 46.94 \times 10^{-2}$ mol/L. Temperature = 50°C. Time = 6 h.

from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of silk, and (5) termination of the graft radical and silk macroradical via chain transfer. Out of these factors, the first four favor grafting by simplifying the access and diffusion of monomer, whereas the last factor adversely affects grafting.

Effect of Salts

Figure 8 shows the effect of certain neutral inorganic salts on graft yield. The result indicates that the graft yield of the salts studied follows the order: $MnSO_4 > Na_2SO_4 > MgSO_4 > NaF > KCl$.

A probable explanation for their variation on graft yield might be the ionic dissociation of the added electrolytes which interferes with the usual polymerization reaction, resulting in the premature termination of the growing chains.

The effect of $CuSO_4$ concentration on graft yield has also been studied. Upon increasing the $CuSO_4$ concentration up to 5×10^{-3} M, the graft yield increases but thereafter it decreases (Fig. 9). The initial increase in graft yield might be due to the creation of free-radical species under the influence of Cu^{2+} ions which would be in the area of silk, thus assisting in the formation of silk macroradicals. The drop of graft yield beyond 5.0×10^{-3} M of copper sulfate concentration is due to (1) the termination of free radicals in solution and on silk (the Cu^{2+} ions seem to act as a radical trap) and (2) a particular concentration of Cu^{2+} ions favor complexation of monomer with silk, and beyond this concentration the Cu^{2+} ions perturb such a complexation.

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