Grafting Vinyl Monomers onto Silk Fibers. VIII. Graft Copolymerization of Methyl Methacrylate onto Silk using Tetravalent Manganese–Oxalic Acid Redox System

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Synopsis

The graft copolymerization of methyl methacrylate onto silk fibers was investigated in aqueous solution using the Mn(IV)–oxalic acid redox system. The copolymerization reaction was carried out under a variety of conditions such as different monomer, initiator, oxalic acid, acid concentrations, and temperatures. The graft yield increases with increasing initiator concentration up to $5 \times 10^{-3}M$, and with further increase of the initiator concentration it decreases. The graft yield also increases with increasing sulfuric acid concentration up to $15 \times 10^{-2}M$, and decreases thereafter. The rate of grafting also increases with increase in oxalic acid concentration up to $1.5 \times 10^{-2}M$ and $84.592 \times 10^{-2}M$, respectively, and thereafter the rate of grafting slows down. The effect of temperature, solvents, and salts on graft yield has also been investigated and a plausible rate expression has been derived.

INTRODUCTION

Permanganate ion is known to be a versatile oxidizing agent because of its ability to react with almost all types of functional groups.[1] This ion coupled with organic substrates acts as an efficient redox system for the initiation of vinyl polymerization. Palit and co-workers[2–4] and Mishra et al.[5–8] have already exploited this field of research using permanganate ion as an initiator. Nayak and co-workers[9–16] have reported the homopolymerization of some vinyl monomers involving several metal ions with a large number of organic substrates.

That permanganate ion could initiate graft copolymerization of vinyl monomers onto some natural and synthetic macromolecules has not been studied extensively. Hebeish et al.[17] have reported the graft copolymerization onto wool using permanganate ion as an initiator. Recently, Nayak and co-workers[18,20] have reported the graft copolymerization of methyl methacrylate onto wool and silk fibers using permanganate as an initiator. This paper presents the results of the graft copolymerization of methyl methacrylate onto silk using the permanganate–oxalic acid redox system as initiator.

EXPERIMENTAL

Mulberry silk fibroin was collected from the Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by a method mentioned in our previous communication.[21] Methyl methacrylate (MMA) was washed with 5%

sodium hydroxide solution, dried with anhydrous sodium sulfate, and distilled under nitrogen under reduced pressure before use.

Potassium permanganate (AR), H_2SO_4 (18M, 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 (0.1M in distilled water) and oxalic acid was used throughout the experiment. The concentration of permanganate in the experimental system was determined by cerimetry.

The reactions were carried out in Pyrex flasks equipped with gas inlet and outlet tubes. Dried and purified silk fibers were immersed in a solution of Mn^{4+} (4–10) $\times 10^{-3}M$, oxalic acid (0.5–3) $\times 10^{-2}M$, and H_2SO_4 (10.5–6) $\times 10^{-2}M$ at temperatures from 40 to 55°C. The required concentration of monomer was added to the reaction mixture. The reaction time was varied from 1 to 6 hr, and the material-to-liquor ratio was 1:100. After the desired reaction time, silk fibers were taken out and washed thoroughly with water and acetone. Finally, the fibers were Soxhlet extracted with benzene or acetone until the homopolymer was completely removed. They were then dried in an oven, cooled to room temperature, and weighed. The percentage of grafting was calculated according to the procedure described in our previous communication.[20]

RESULTS AND DISCUSSION

Effect of Monomer Concentration on Graft Yield

The graft copolymerization of methyl methacrylate onto silk was investigated by varying the monomer concentration (46.94–122.05) $\times 10^{-2}M$, keeping the concentration of all other reagents constant. A perusal of the result shows that the percentage of grafting increases initially with the increase of monomer concentration up to 84.59 $\times 10^{-2}M$ and thereafter it decreases with further increase of monomer concentration (Fig. 1).

The initial increase in the percentage of grafting with increase in the monomer concentration might be due to the following reasons: (1) complexation of silk with monomer enhances its reactivity (which is more pronounced at higher monomer concentration), thereby increasing graft percentage; (2) the monomer molecules might form some type of charge transfer complex with the oxidant which favors grafting; (3) the other reasons might be due to gel effect, i.e., increases in viscosity of medium, owing to solubility of poly(methyl methacrylate) in its own monomer, would be more pronounced at higher 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 silk backbone, thereby enhancing grafting.

The decrease of the rate of grafting beyond 84.59 $\times 10^{-2}M$ of monomer concentration could be attributed to the following reasons. At higher monomer concentration, as the concentration of PMMA macroradicals increases, the rate of their combination and disproportionation is greater than their combination with silk molecules. On the other hand, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, which increases rapidly at high monomer concentration. Similar observations have been noted
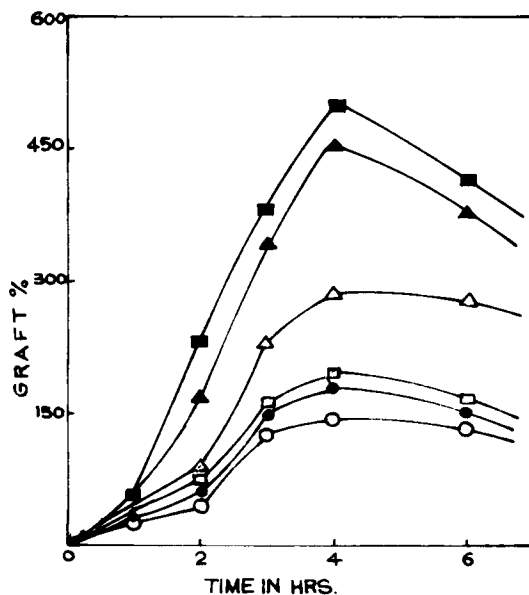
Fig. 1. Effect of [MMA] on graft yield: $[KMnO_4] = 5 \times 10^{-3}M$, $[H^+] = 15 \times 10^{-2}M$; [oxalic acid] $= 1 \times 10^{-2}M$; temp. $= 50°C$; $M:L = 1:100$; ($\bullet$) $[MMA] = 46.94 \times 10^{-2}M$; ($\triangle$) $[MMA] = 65.716 \times 10^{-2}M$; ($\bigcirc$) $[MMA] = 84.592 \times 10^{-2}M$; ($\square$) $[MMA] = 103.268 \times 10^{-2}M$; ($\blacktriangle$) $[MMA] = 122.044 \times 10^{-2}M$.

by Haworth and Holkar[22] in the case of grafting of acrylic acid onto nylon by ceric ion method.
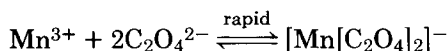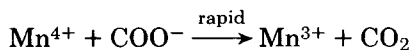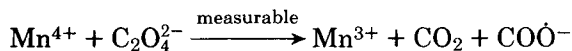
Effect of Initiator Concentration

The graft copolymerization was studied by varying the permanganate concentration $(4.0–10.00) \times 10^{-3}M$ (Fig. 2). The rate of grafting is found to increase progressively with increase of initiator concentration up to $5.00 \times 10^{-3}M$ and decrease thereafter.

In a system consisting of silk, permanganate ion, oxalic acid, sulfuric acid, and monomer, the free radicals might be forming in the following manner:

(1) The Mn(IV) ion might be attacking the groups present on the backbone of silk producing silk macroradicals:

$$SH + Mn(IV) \rightarrow S\cdot + Mn(III)$$
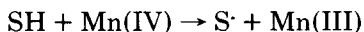
(2) The carboxyl free radicals ($C_2\dot{O}_4^-$ or $CO\dot{O}^-$) formed by the interaction of Mn(IV) with oxalic acid in the following mechanism[23] might be attacking the groups present on the silk backbone producing the silk macroradicals:
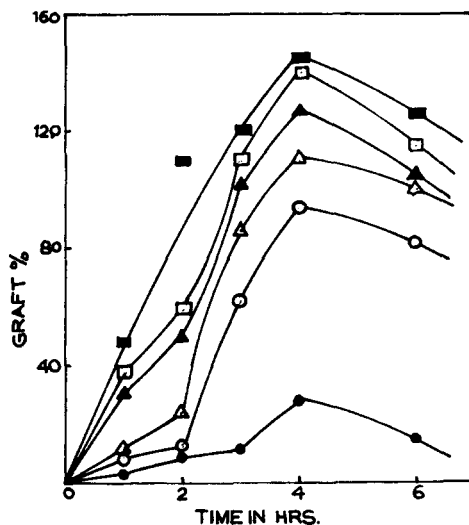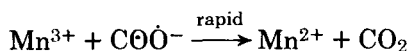
$$Mn^{4+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{3+} + CO_2 + CO\dot{O}^-$$

$$Mn^{4+} + COO^- \xrightarrow{\text{rapid}} Mn^{3+} + CO_2$$

$$Mn^{3+} + 2C_2O_4^{2-} \underset{\text{rapid}}{\rightleftharpoons} [Mn[C_2O_4]_2]^-$$

$$Mn^{3+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{2+} + CO\dot{O}^- + CO_2$$
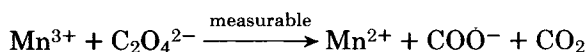
Fig. 2. Effect of [KMnO$_4$] on graft yield: [oxalic acid] = 1.5 × 10^{-2}M; [H$^+$] = 20.25 × 10^{-2}M; [MMA] = 46.94 × 10^{-2}M; temp. = 50°C; M:L = 1:100; (●) [KMnO$_4$] = 4.0 × 10^{-3}M; (○) [KMnO$_4$] = 5.0 × 10^{-3}M; (△) [KMnO$_4$] = 6.0 × 10^{-3}M; (▲) [KMnO$_4$] = 8.0 × 10^{-3}M.

$$Mn^{3+} + C\dot{O}O^- \xrightarrow{\text{rapid}} Mn^{2+} + CO_2$$

Weiss[24] has suggested that there is also the production of oxalic acid ion radicals (C$_2\dot{O}_4^-$) in such a system:

$$Mn^{3+} + C_2O_4{}^{2-} \longrightarrow C_2\dot{O}_4^- + Mn^{2+}$$
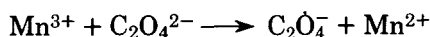
The free radicals (C$\dot{O}O^-$ or C$_2\dot{O}_4^-$) formed by the above mechanism might attack the silk, giving rise to silk macroradicals (S·) in the following way:
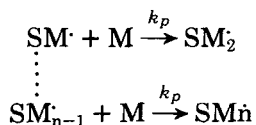
$$SH + R· \xrightarrow{k_d} S· + RH$$
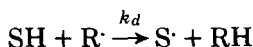
In such a system, since the formation and initiation of silk macroradicals carboxyl free radicals will be predominant, the following reaction scheme may be represented for graft copolymerization of MMA onto silk:
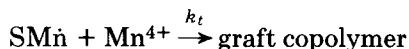
Initiation:

$$S· + M \xrightarrow{k_i} SM·$$
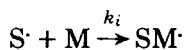
where S· = silk macroradical, M = monomer.

Propagation:

$$SM· + M \xrightarrow{k_p} SM_2^·$$
$$\vdots$$
$$SM_{n-1}^· + M \xrightarrow{k_p} SM\dot{n}$$

Termination:

$$\text{SM\.{n}} + \text{Mn}^{4+} \xrightarrow{k_t} \text{graft copolymer}$$

Oxidation:

$$\text{S}^{\cdot} + \text{Mn}^{4+} \xrightarrow{k_0} \text{oxidation products} + \text{Mn}^{3+}$$

Now,

$$\frac{d[\text{SM\.{n}}]}{dt} = k_i[\text{S}^{\cdot}][\text{M}] - [\text{SM\.{n}}][\text{Mn}^{4+}]k_t = 0$$

$$[\text{SM\.{n}}] = \frac{k_i[\text{S}^{\cdot}][\text{M}]}{[\text{Mn}^{4+}]k_t}$$

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

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

$$R_p = k_p[\text{SM\.{n}}][\text{M}] = \frac{k_p k_d k_i[\text{SH}][\text{M}]^2}{k_t[\text{Mn}^{4+}][k_i[\text{M}] + k_0[\text{Mn}^{4+}]}$$

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

As the concentration of permanganate increases, a large number of silk macroradicals are formed by the interaction of carboxyl free radicals with the groups present in the silk backbone which initiate grafting, thereby increasing the graft yield. When permanganate ion concentration increased beyond $5.0 \times 10^{-3}M$, there is a fall in graft yield which is attributed to the following reasons: (1) There will be abundance of free radicals in the solution because of the increase of the concentration of the oxidant which might terminate the growing chain. (2) At higher concentration of oxidant, the free radicals produced on the backbone of the silk fiber might be oxidized to give rise to oxidation products, thereby decreasing the percentage of grafting which is evident from the rate expression. (3) raft formation and homopolymerization in such a system depend upon the direct attack of carboxyl free radicals bn silk and monomer. At higher permanganate ion concentration, 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 Oxalic Acid Concentration

The effect of oxalic acid concentration on the graft copolymerization of MMA onto silk is shown in Figure 3. The percentage of grafting increases with the increase of oxalic acid concentration up to $1.5 \times 10^{-2}M$ and then decreases with further increase in oxalic acid concentration. A possible explanation of this observation follows.

At higher concentration of oxalic acid, a considerable amount of MnO_2 is used up in the side reaction:
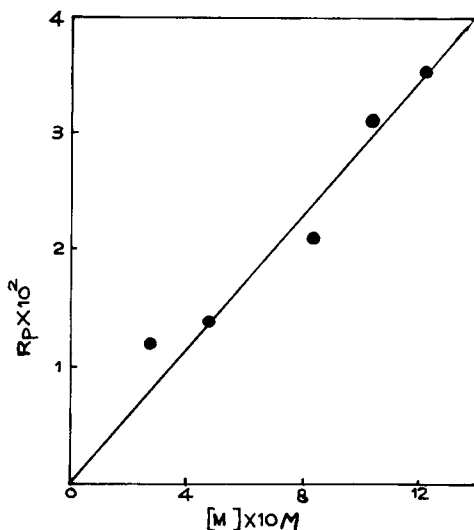
$$\text{MnO}_2 + 2\,\text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + (\text{O})$$

Fig. 3. Effect of [oxalic acid] on graft yield: $[KMnO_4]$ = 5.0 × $10^{-3}M$; $[H^+]$ = 15.0 × $10^{-2}M$; [MMA] = 46.94 × $10^{-2}M$; temp. = 50°C; $M:L$ = 1:100; (O) [oxalic acid] = 0.5 × $10^{-2}M$; (●) [oxalic acid] = 1.0 × $10^{-2}M$; (△) [oxalic acid] = 1.5 × $10^{-2}M$; (▲) [oxalic acid] = 2.0 × $10^{-2}M$; (□) [oxalic acid] = 3.0 × $10^{-2}M$.

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 of grafting is decreased.

The second reason might be that at higher oxalic acid concentration there will be a constant production of inhibiting oxygen, and as a result the percentage of grafting might be decreasing. Similar observations have been found by Palit et al.[2,3] and Mishra et al.[5,6] in the homopolymerization of certain vinyl monomers.

Effect of Acid Concentration

Since the effectiveness of permanganate ion is largely determined by the acid concentration, it is essential to study the effect of $[H_2SO_4]$ on the graft copolymerization of MMA onto silk initiated by the permanganate ion–oxalic acid redox system. The concentration of the sulfuric acid was varied from 10.5 to 60.0 (× $10^{-2}M$), keeping the concentration of all other reagents constant. The result shows that the percentage of grafting increases with increase in acid concentration up to 15.00 × $10^{-2}M$ and decreases thereafter (Fig. 4).

The initial increase in the graft yield might be due to the fact that the acid enhances the oxidizing power of permanganate ion up to 15.00 × $10^{-2}M$ and beyond that it reduces.

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 silk fiber, and as a result the graft yield decreases. Secondly, at higher acid concentration, MnO_2 might react with acid producing oxygen which might inhibit the grafting process:
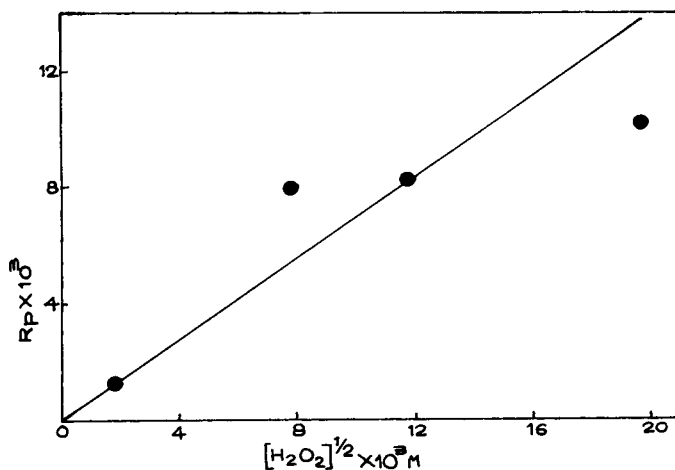
$$MnO_2 + 2H^+ = Mn^{2+} + H_2O + (O)$$

Fig. 4. Effect of [H$_2$SO$_4$] on graft yield: [KMnO$_4$] = 5.0 × 10^{-2}M; [oxalic acid] = 1.5 × 10^{-2}M, [MMA] = 46.94 × 10^{-2}M; temp. = 50°C; M:L = 1:100; (O) [H$_2$SO$_4$] = 10.5 × 10^{-2}M; (●) [H$_2$SO$_4$] = 15.0 × 10^{-2}M; (△) [H$_2$SO$_4$] = 20.25 × 10^{-2}M; (◀) [H$_2$SO$_4$] = 30.0 × 10^{-2}M; (□) [H$_2$SO$_4$] = 60.0 × 10^{-2}M.

Effect of Temperature

The graft copolymerization was carried out at four different temperatures ranging from 40 to 55°C (Fig. 5). The percentage of grafting increases with increase in temperature up to 50°C, and beyond this it decreases. The increase of the percentage of grafting with temperature up to 50°C could be ascribed to a greater activation energy.

As the temperature increases the solubility of monomer in the reaction medium, the diffusion of the monomer from the solution phase to the fiber phase and the swellability of the fiber are greatly enhanced. Hence, the complexation of monomer with the silk matrix and its activity are increased, and as a result the graft-on increases. But beyond 50°C the decrease in graft yield might be due to greater combination rates of radicals. Again at higher temperatures side reactions such as

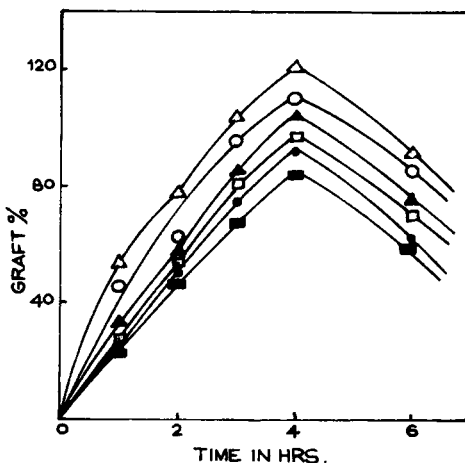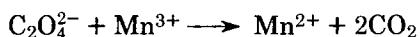Fig. 5. Effect of temperature on graft yield: [KMnO$_4$] = 5.0 × 10^{-3}M; [oxalic acid] = 1.0 × 10^{-2}M, [H$^+$] = 15.0 × 10^{-2}M; [MMA] = 46.94 × 10^{-2}M; M:L = 1:100; (□) 40°C; (●) 45°C; (O) 50°C; (△) 55°C.

$$C_2O_4^{2-} + Mn^{3+} \longrightarrow Mn^{2+} + 2CO_2$$

might set in,[3] thereby increasing the possibility of the destruction of initiating species, and as a result graft-on decreases.

From the Arrhenius plot of log R_p vs. $1/T$, the overall activation energy was found to be 16.60 kcal/mol (Fig. 6). Using the value of $E_p - 1/2E_t$ = 4–5 kcal/mol given by Tobolsky,[24] where E_p and E_t are energies of propagation and termination, respectively, the activation energy of initiation, E_d, can be 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 = 24.10 kcal/mol for total conversion reaction of MMA to PMMA.

Effect of Reaction Medium

The reaction medium plays an important role in the graft copolymerization reaction. Water-soluble organic solvents might affect the swelling properties of silk. Any change in silk swellability would be reflected in the behavior of silk toward grafting, since diffusion of monomer and initiation, availability of functional groups (sites of grafting), and propagation and termination of the graft, etc. would depend to a considerable extent on the swelling properties of silk. The results of various solvents affecting the percentage of grafting follow the order (Fig. 7)

dioxan > formic acid > propanol > acetic acid > ethanol > methanol

Effect of Neutral Salts and Surfactants

The effect of the addition of certain neutral inorganic salts on the graft copolymerization reaction was studied. The result shows that the addition of KCl, Na_2SO_4, $MgSO_4$, and $LiNO_3$ depresses the rate of grafting, whereas the complexing agent NaF increases the rate of grafting (Fig. 8). The order of their effect on the graft yield is
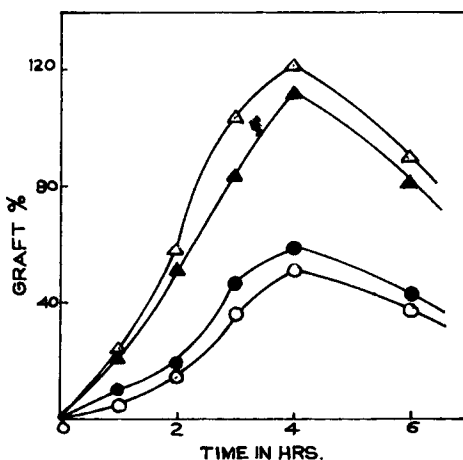

Fig. 6. Arrhenius plot of $1/T$ vs. log R_p for grafting MMA onto silk using $KMnO_4$–oxalic acid redox system.
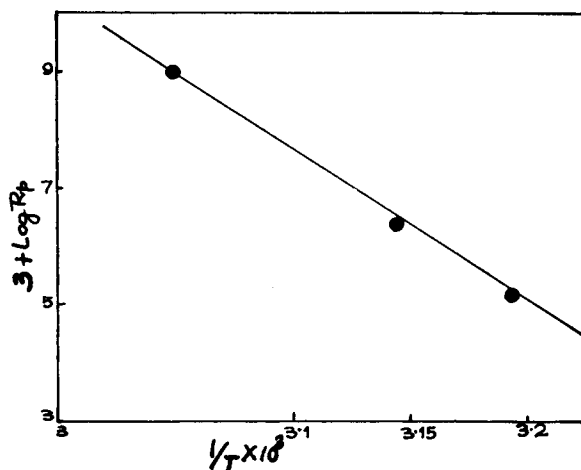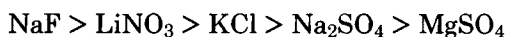
Fig. 7. Effect of solvents on graft yield: $[KMnO_4]$ = 5.0 × $10^{-3}M$; [oxalic acid] = 1.0 × $10^{-2}M$; $[H^+]$ = 15.0 × $10^{-2}M$; [MMA] = 46.94 × $10^{-2}M$; [solvent] = 10%; temp. = 50°C; $M:L$ = 1:100; (●) formic acid; (△) acetic acid; (□) methanol; (○) dioxan; (▲) ethanol; (■) propanol.

$$NaF > LiNO_3 > KCl > Na_2SO_4 > MgSO_4$$

A probable explanation for the depression of 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^{3+} ions, and this complex acts essentially as a slower but steadier source of free radicals, and as a result the initial rate falls but subsequently increases.

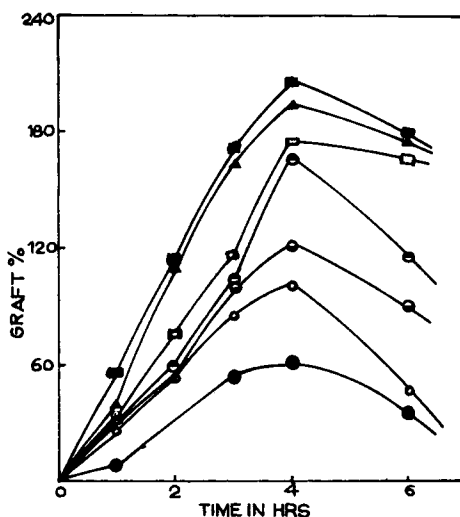The effect of $CuSO_4$ concentration on graft yield was also studied. Upon in-

Fig. 8. Effect of salts on graft yield: $[KMnO_4]$ = 5.0 × $10^{-3}M$; [oxalic acid] = 1.0 × $10^{-2}M$; $[H^+]$ = 15.0 × $10^{-2}M$; [MMA] = 46.94 × $10^{-2}M$; [salt] = 0.01M; temp. = 50°C; $M:L$ = 1:100; (○) NaF; (●) $LiNO_3$; (□) $MgSO_4$; (▲) KCl; (△) Na_2SO_4.

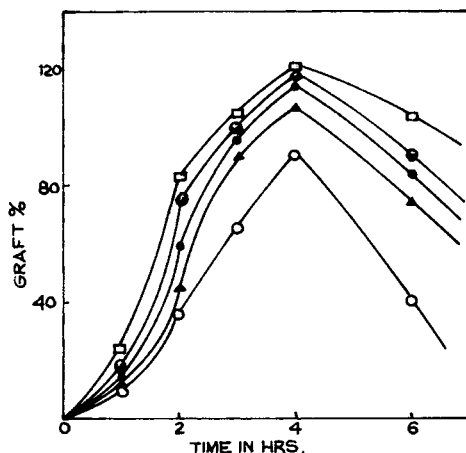Fig. 9. Effect of [CuSO₄] on graft yield: [KMnO₄] = 5.0 × 10⁻³M; [oxalic acid] = 1.0 × 10⁻²M; [H⁺] = 15.0 × 10⁻²M; [MMA] = 46.94 × 10⁻²M; temp. = 50°C; time = 6 hr; M:L = 1:100.

creasing the $CuSO_4$ concentration up to $5.0 \times 10^{-3}M$ the graft yield increases, but it decreases with further increase in the $CuSO_4$ concentration (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 proximity of silk, thus assisting the formation of silk macroradicals. The drop of graft yield beyond $5.0 \times 10^{-3}M$ of copper sulfate concentration is due to (1) the termination of free radicals in solution; on polymer, and/or on silk, the Cu^{2+} ions seem to act as radical trap; (2) a particular concentration of Cu^{2+} ions favors complexation of
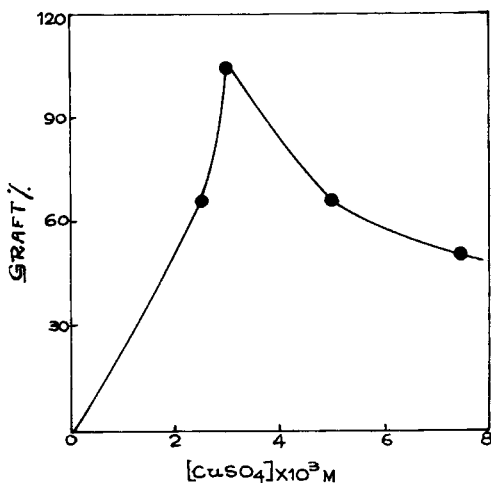

Fig. 10. Effect of surfactants on graft yield: [KMnO₄] = 5.0 × 10⁻³M; [oxalic acid] = 1.0 × 10⁻²M; [H⁺] = 15.0 × 10⁻²M; [MMA] = 46.94 × 10⁻²M, temp. = 50°C; [surfactant] = CMC; M:L = 1:100; (O) surfactant = CTABr; (△): surfactant = NaLS.

monomer with silk, and beyond this concentration the ions perturb such complexation.

The graft copolymerization was also carried out in the presence of the anionic surfactant sodium lauryl sulfate (NaLS) as well as the cationic surfactant cetyl trimethylammonium bromide (CTABr) at their critical micelle concentrations (CMC). The anionic surfactants enhances the rate, whereas the cationic surfactants depress the rate (Fig. 10). At CMC, micelles are formed which are roughly spherical in size, with the sulfate ions forming a Gouy–Chapman double layer.[26,27] The enhancement of graft yield by NaLS at CMC can be explained on the assumption that the micelles become entangled with the silk fiber, and as a result the Mn^{4+} ion is electrostatically attracted toward the silk matrix. The concentration of Mn^{4+} ion will be higher near the vicinity of the fiber and free-radical formation on the backbone of the silk fiber will be facilitated, and as a result the graft yield decreases.

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