## Grafting Vinyl Monomers onto Silk Fibers. VI. Graft Copolymerization of Methyl Methacrylate onto Silk by Using Quinquevalent Vanadium-Thiourea Redox System

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## ABSTRACT

The graft copolymerization of methyl methacrylate onto silk fibers was investigated in aqueous solution using the $V^{5+}$-thiourea redox system. The rate of grafting was determined by varying monomer, thiourea, acidity of the medium, temperature, initiator concentration, and reaction medium. The percentage of graft yield increases significantly by increasing the initiator concentration up to 0.01 $\underline{M}$ and thereafter decreases with a further increase of initiator concentration. The graft yield increases with an increase of thiourea concentration up to $10.0 \times 10^{-4}$ $\underline{M}$ and then decreases with a further increase of thiourea concentration. The effect of increasing the monomer concentration brings about a significant enhancement in the graft yield. A suitable kinetic scheme has been proposed and the rate equation has been evaluated.

## INTRODUCTION

Modification of the properties of textile fibers in order to get a fiber of improved textile performance is the subject of study of

487

several groups of scientists and technologists [1-4]. Out of the several methods available, grafting promises to be a potentially effective means of altering the fiber properties through the added polymer formed in situ without destroying the basic properties of the parent fiber. A graft copolymer comprises a high molecular weight backbone to which a second polymer is attached at intervals of the chain by means of covalent bonds. This can be achieved by the creation of free radicals on the backbone of the fiber by several methods such as high energy radiation [5, 6], low energy radiation in the presence and the absence of sensitizers [7, 8], and redox systems [9-12]. The last method is of utmost importance since it minimizes the degradation of the base polymer.

The homopolymerization of vinyl monomers using thiourea as the reductant has been studied extensively by several groups of workers [13-15]. Nayak and co-workers have reported the polymerization of acrylonitrile using $V^{5+}$, $Cr^{6+}$, $Mn^{3+}$, bromate/HCl, and thiourea as the redox couple [16-20]. Hebeish and Bendak have used thiourea coupled with hydrogen peroxide [10], $Fe^{3+}$, and di-tert-butyl peroxide [11] for grafting vinyl monomers onto wool fibers. We have reported grafting methyl methacrylate onto silk fibers using several metal and nonmetal ions [21-25].

This paper presents the results of graft copolymerization onto silk using $V^{5+}$-thiourea as the redox couple.

## EXPERIMENTAL

Mulberry silk fibroin was collected from the Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by the method described in our earlier publication [21].

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

Ammonium metavanadate (AR), sulfuric acid (~18 M, AR, BDH), and thiourea (AR, BDH) were used. Water, distilled twice over alkaline permanganate and deionized by passing through a column of biodeminrolit resin (Permutit Co., United Kingdom) was used to prepare all solutions. A stock solution of $V^{5+}$ (≈0.4 N in ≈4 M $H_2SO_4$) was prepared by suspending ammonium metavanadate (4.7 g) in distilled water (25 mL) and adding 75 mL of 10 N $H_2SO_4$. The concentration of $V^{5+}$ in the experimental systems was determined by vanadometry. The reaction was carried out in Pyrex flasks equipped with gas inlet and outlet tubes. Dried and purified silk fibers were immersed in a solution of $V^{5+}$ (0.0025-0.025 M) in $H_2SO_4$ (0.45-1.245 M) and thiourea ($5 \times 10^{-4}$ to $17.5 \times 10^{-4}$ M) at temperatures from 35 to 50°C. The required concentration of monomer was added to the reaction mixture. The reaction time was varied from 1 to 6 h and the material to liquor ratio was 1:100. After the desired reaction
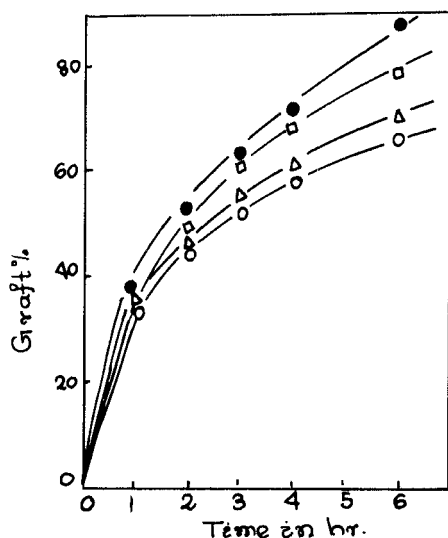
FIG. 1.   Effect of [monomer] on graft yield: $[V^{5+}]$ = 0.005 $\underline{M}$, [TU] = 0.001 M, $[H_2SO_4]$ = 0.9 $\underline{M}$, temperature = 50°C, M:L = 1:100, ( ○) [MMA] = 28.60 × 10$^{-2}$ M, (△) [MMA] = 65.70 × 10$^{-2}$ $\underline{M}$, ( □) [MMA] = 84.50 × 10$^{-2}$ $\underline{M}$, (●)[MMA] = 103.30 × 10$^{-2}$ $\underline{M}$.

time, the 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 graft yield was calculated as the percentage increase in weight over the original weight of the sample.

## Effect of Monomer Concentration

The effect of monomer concentration on grafting of methyl methacrylate onto silk is shown in Fig. 1.  The monomer concentration was varied from 28.60 × 10$^{-2}$ to 103.30 × 10$^{-2}$ $\underline{M}$, keeping all other reagents constant.  The percentage of graft yield increases with an increase of monomer concentration.  Since the copolymerization reaction was carried out at the same temperature and at a fixed concentration of $V^{5+}$, thiourea, and acidity, it is possible to assume that the concentration, nature, and efficiency of the free radicals and other species generated during the reaction would be the same.  Hence the higher rate of grafting observed upon increasing the monomer concentration could be attributed to the following reasons.  First, complexation of silk with
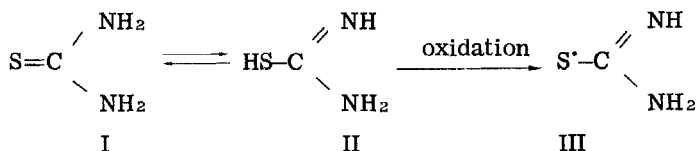
monomer which is required for enhancing monomer activity would be favored at higher monomer concentrations. The second reason might be due to gel effect, i.e., the solubility of poly(methyl methacrylate) in its own monomer; this could be more pronounced at higher monomer concentrations. This causes hindrance in termination, particularly by coupling of these growing chains. Besides, this gel effect also causes swelling of silk, thus facilitating diffusion of monomer to growing grafted chains and active sites on the silk backbone, thereby enhancing grafting. Third, some species which are either present or generated during the copolymerization reaction act as an efficient radical scavenger. Competition between this and the monomer in capturing the free silk radical would play the key role in the amount of graft formation. It is likely that the capturing of silk radicals by monomer predominates at higher monomer concentrations.

## Effect of Initiator Concentration

The effect of initiator concentration on grafting of MMA onto silk was studied by using different concentrations of $V^{5+}$ (0.0025 to 0.025 $M$), keeping the concentration of all other reagents constant. The graft yield increased progressively with an increase in the initiator concentration up to 0.01 $M$, and at higher concentrations of $V^{5+}$ it decreases (Fig. 2). A possible explanation for these observations might be as follows.

In a system consisting of $V^{5+}$ ion, sulfuric acid, MMA, thiourea, and silk, the free radical formation on the backbone of silk might be in two ways.

(a) In all the initiating systems containing thiourea (I), the redox component is isothiourea (II) [18], and a thiol (existing in a tautomeric equilibrium with thiourea in an aqueous solution) is the reductant. The generation of a free radical in this system takes place by the abstraction of the reactive hydrogen atom attached to the sulfur atom in isothiourea, generating the amidinosulfenyl free radical (III):

$$S=C \overset{\displaystyle /\, NH_2}{\underset{\displaystyle \backslash\, NH_2}{}} \quad \Longleftrightarrow \quad HS-C \overset{\displaystyle /\!/\, NH}{\underset{\displaystyle \backslash\, NH_2}{}} \quad \xrightarrow{\text{oxidation}} \quad S\cdot-C \overset{\displaystyle /\!/\, NH}{\underset{\displaystyle \backslash\, NH_2}{}}$$

$$\quad\quad I \quad\quad\quad\quad\quad\quad\quad\quad II \quad\quad\quad\quad\quad\quad III$$

The reaction of thiourea with $V^{5+}$ is therefore likely to be analogous to that between $V^{5+}$ and mercaptans [26]. It is likely that $V^{5+}$ first forms a complex with the isothiourea moiety and the complex breaks down, giving rise to the amidinosulfenyl free radical as shown below. Similar complexes have been shown to occur in the oxidation of alpha-mercapto acids by $V^{5+}$ [26].
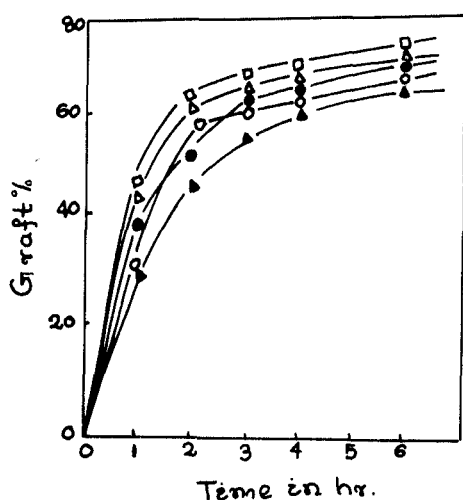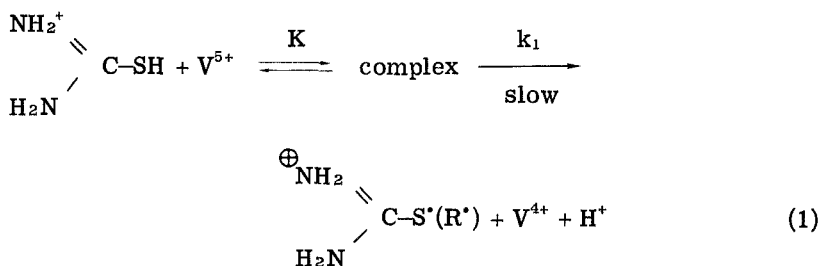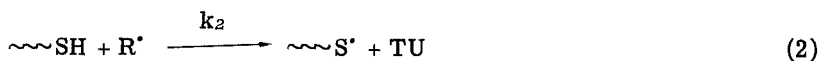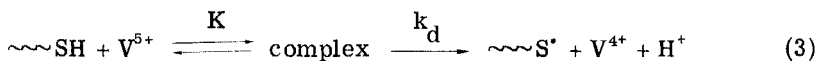
FIG. 2.  Effect of $[V^{5+}]$ on graft yield: $[TU] = 0.001$ M, $[H_2SO_4]$ = 0.9 M, $[MMA] = 0.4694$ M, temperature = $50°$C, M:L = 1:100, ( ○ ) $[\overline{V^{5+}}] = 2.5 \times 10^{-3}$ M, ( ● ) $[V^{5+}] = 5.0 \times 10^{-3}$ M, ( □ ) $[V^{5+}] = 10.0 \times 10^{-3}$ M, ( △ ) $[V^{5+}] = 15.0 \times 10^{-3}$ M, ( ▲ ) $[V^{5+}] = 25.0 \times 10^{-3}$ M.

$$\begin{array}{c} NH_2^+ \\ \diagdown \\ \diagup \\ H_2N \end{array} C\text{--}SH + V^{5+} \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow[\text{slow}]{k_1}$$

$$\begin{array}{c} \overset{\oplus}{NH_2} \\ \diagdown \\ \diagup \\ H_2N \end{array} C\text{--}S^{\bullet}(R^{\bullet}) + V^{4+} + H^+ \qquad (1)$$

The isothiocarbamido radicals abstract hydrogen from the amino or hydroxyl groups in silk to yield silk macroradicals ($S^{\bullet}$):

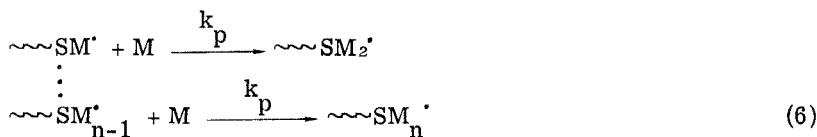$$\sim\sim SH + R^{\bullet} \xrightarrow{k_2} \sim\sim S^{\bullet} + TU \qquad (2)$$

(b) The second possibility is that an intermediate complex of $V^{5+}$-silk might be formed which dissociates, giving rise to free radicals on the backbone of the silk which facilitates grafting.  The following reaction scheme may be represented for the graft copolymerization of MMA onto silk:
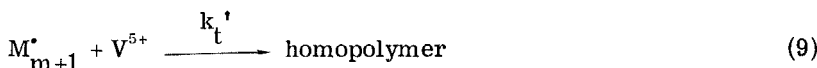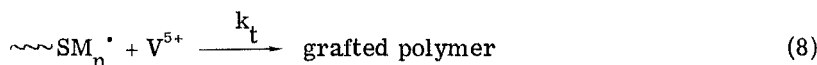
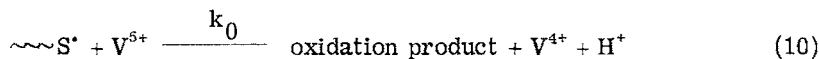$$\sim\sim SH + V^{5+} \underset{K}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k_d} \sim\sim S^{\bullet} + V^{4+} + H^{+} \tag{3}$$

(i) Initiation:

$$\sim\sim S^{\bullet} + M \xrightarrow{k_i} \sim\sim SM^{\bullet} \tag{4}$$

$$R^{\bullet} + M \xrightarrow{k_i'} RM^{\bullet} \tag{5}$$

(ii) Propagation:

$$\sim\sim SM^{\bullet} + M \xrightarrow{k_p} \sim\sim SM_2{}^{\bullet}$$
$$\vdots$$
$$\sim\sim SM^{\bullet}_{n-1} + M \xrightarrow{k_p} \sim\sim SM_n{}^{\bullet} \tag{6}$$

$$M^{\bullet}_m + M \xrightarrow{k_p'} M^{\bullet}_{m+1} \tag{7}$$

(iii) Termination:

$$\sim\sim SM_n{}^{\bullet} + V^{5+} \xrightarrow{k_t} \text{grafted polymer} \tag{8}$$

$$M^{\bullet}_{m+1} + V^{5+} \xrightarrow{k_t'} \text{homopolymer} \tag{9}$$

(iv) Oxidation:

$$\sim\sim S^{\bullet} + V^{5+} \xrightarrow{k_0} \text{oxidation product} + V^{4+} + H^{+} \tag{10}$$

Since thiourea acts as a better reductant than silk, taking into account Eqs. (1), (2), (4), (6), and (8) and applying the steady-state assumption to both $[R^{\bullet}]$ and $[SM^{\bullet}]$, separately, the following expressions have been derived:

$$\frac{d[R^{\bullet}]}{dt} = k_1 K[TU][V^{5+}] - k_2[SH][R^{\bullet}] = 0 \tag{11}$$

$$\frac{d[\,SM^{\bullet}\,]}{dt} = k_i[\,S^{\bullet}\,][\,M\,] - k_t[\,SM^{\bullet}\,][\,V^{5+}\,] = 0$$

$$[\,S^{\bullet}\,] = k_2[\,SH\,][\,R^{\bullet}\,]/k_i[\,M\,]$$

$$[\,SM^{\bullet}\,] = k_1 K[\,TU\,]/k_t$$

$$R_p = k_p[\,SM^{\bullet}\,][\,M\,] = (k_i K k_p/k_t)[\,TU\,][\,M\,] \qquad (12)$$

The dependence of $R_p$ on $[\,M\,]$ and $[\,TU\,]$, which was experimentally observed, favored the above scheme.

At higher concentrations of $V^{5+}$ the free radicals produced on the backbone of the silk fibers might be oxidized to give rise to the oxidation products. Hence the expression for the derivation of $R_p$ will include Eq. (10) and could be represented as follows:

$$R_p = \frac{k_i k_p k_1 K[\,M\,]^2[\,TU\,]}{k_i[\,M\,] + k_0[\,V^{5+}\,]}$$

Hence at the higher concentrations of $V^{5+}$, the rate of grafting would decrease.

Second, at higher concentrations of $V^{5+}$ the metal ions might interact with thiourea, giving higher amounts of amidinosulfenyl free radicals $(R^{\bullet})$ which results in producing more homopolymer, thereby reducing the percentage of grafting.

## Effect of Acid Concentration

Graft copolymerization has been carried out in the presence of sulfuric acid. The concentration of the acid was varied from 0.45 to 1.245 M. A perusal of the results (Fig. 3) indicates that the percentage of grafting increases with an increase of the acid concentration up to 0.9 M and then decreases with a further increase of the acid concentration. In the initial stages, with the increase of acid concentration, the following species of $V^{5+}$ are formed, which might interact with silk to produce more free radicals on the backbone of the silk and hence increase the percentage of graft:

$$VO_2^+ + H_3O^+ \overset{K}{\rightleftharpoons} V(OH)_3{}^{2+}$$
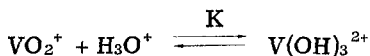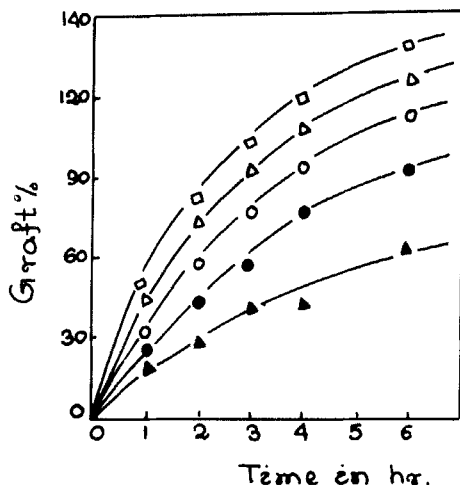
With a further increase of acid concentration (beyond 0.9 M), the

FIG. 3. Effect of $[H_2SO_4]$ on graft yield: $[V^{5+}]$ = 0.005 M, $[TU]$ = 0.001 M, $[MMA]$ = 0.4694 M, temperature = 50°C, M:L = 1:$\overline{100}$, ( ○ ) $[H_2SO_4]$ = 0.45 M, ( △ ) $[H_2\overline{SO_4}]$ = 0.75 M, ( □ ) $[H_2SO_4]$ = 0.90 M, ( ● ) $[H_2SO_4]$ = $\overline{0.99}$ M, ( ▲ ) $[H_2SO_4]$ = $\overline{1.245}$ M.

less reactive species of $V^{5+}$ [ such as $V(OH)(HSO_4)$, $VO.OH^{2+}$, and $VO_2SO_4^{3-}$ ] might have formed, thereby reducing the oxidizing capacity of $V^{5+}$. A similar explanation has been advanced by Nayak and co-workers in the case of the polymerization of acrylonitrile initiated by the $V^{5+}$/thiourea redox system [17].

## Effect of Thiourea Concentration

The effect of thiourea concentration was studied by varying the thiourea concentration over the range $5 \times 10^{-4}$ M to $17.5 \times 10^{-4}$ M. The percentage of graft yield increased with an increase of the concentration of thiourea up to $10.00 \times 10^{-4}$ M and thereafter it decreased with a further increase of thiourea concentration (Fig. 4). This might be due to the following reasons: (a) the increased amount of free-radical inhibitor in thiourea, which is always present (the relatively pure product may contain inhibitors up to 0.48 mol% [26]); (b) fixed amounts of thiourea being converted to isothiourea which actually participates in producing initiating species; and (c) at a higher concentration of thiourea some species might be generated that might act as radical scavengers.
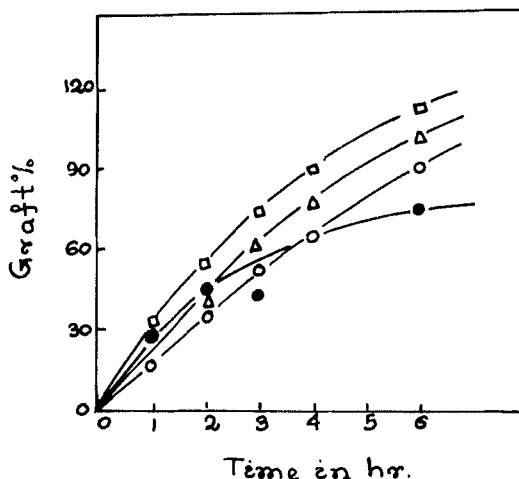
FIG. 4. Effect of $[TU]$ on graft yield: $[V^{5+}]$ = 0.005 M, $[H_2SO_4]$ = 0.9 M, $[MMA]$ = 0.4694 M, temperature = 50°C, M:L = 1:100, ( o ) $[\overline{TU}]$ = $0.5 \times 10^{-3}$ M, ( △ ) $[TU]$ = $0.75 \times 10^{-3}$ M, ( □ ) $[TU]$ = $1.00 \times 10^{-3}$ M, ( • ) $[\overline{TU}]$ = $1.75 \times 10^{-3}$ M.

## Effect of Temperature on Grafting

Graft copolymerization was carried out at three different tem-
peratures ranging from 35-50°C, keeping the concentration of the
reagents constant (Fig. 5). The data indicate that with increasing
temperature the percentage graft-on increases. The dependence of
the rate of grafting with an increase in temperature could be ascribed
to greater activation energy. The swellability of silk, solubility of
monomer, and its diffusion rates are enhanced by increasing the re-
action temperature. From the Arrhenius plot of log $R_p$ versus $1/T$
(Fig. 6), the overall activation energy was found to be 6.00 kcal/mol.
This rather small value, however, approximates those obtained in
other polymerization systems in the presence of a macromolecule.
Using the value of $E_p - \frac{1}{2}E_t$ = 4 ~5 kcal/mol, given by Tobolsky et al.
[28], where $E_p$ and $E_t$ are energies of propagation and termination,
respectively, the activation energy of initiation $E_d$ was calculated as
follows:

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

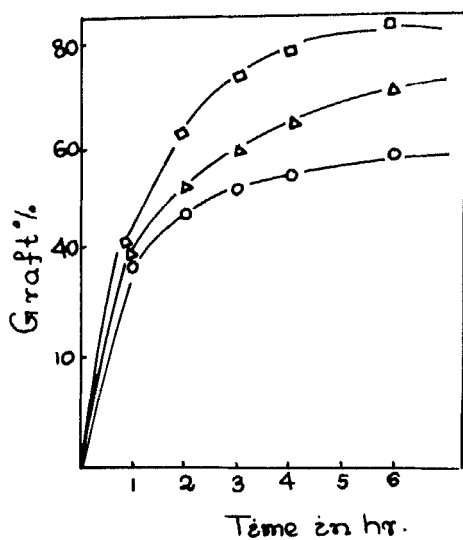where $E_a$ is the overall activation energy and $E_d$ = 3.00 kcal/mol for

FIG. 5.  Effect of temperature on graft yield:  $[V^{5+}]$ = 0.005 M,
$[H_2SO_4]$ = 0.9 M, $[TU]$ = 0.001 M, $[MMA]$ = 0.4694 M, M:L = 1:100,
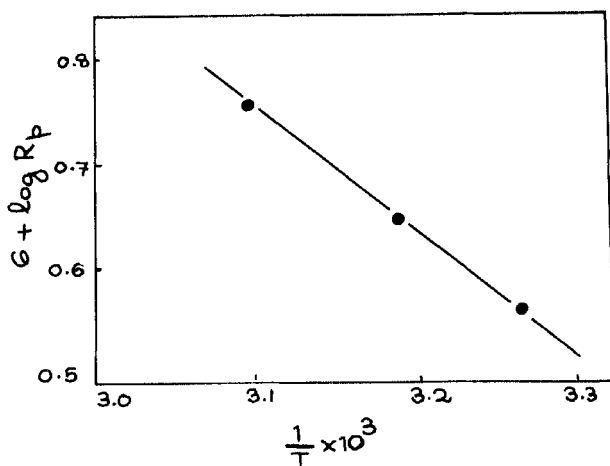( ○ ) temperature = 35°C, ( △ ) temperature = 40°C, ( ▫ ) temperature
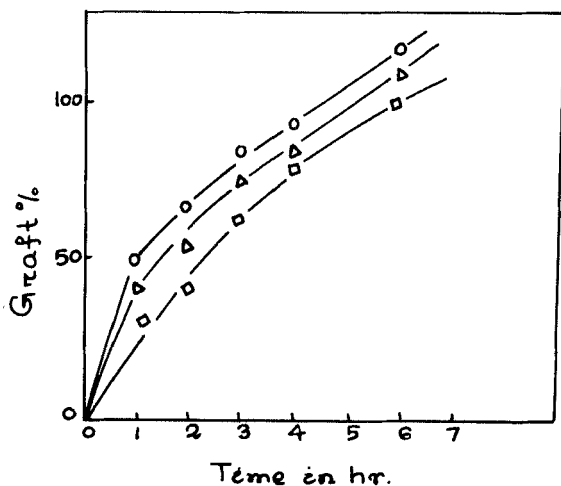= 50°C.



FIG. 6.  Arrhenius plot of log $R_p$ vs 1/T.

FIG. 7. Effect of solvents on graft yield: $[V^{5+}]$ = 0.005 M,
$[H_2SO_4]$ = 0.9 M, $[MMA]$ = 0.4694 M, $[TU]$ = 0.001 M, Solvent =
10% v/v, temperature = 50°C, M:L = 1:100, ( △ ) solvent = $CH_3COOH$,
( ○ ) solvent = $CH_3OH$, ( □ ) solvent = DMF.

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

Effect of Reaction Medium

The reaction medium plays an important role in grafting vinyl
monomers onto silk fibers. For the solvents studied (Fig. 7), the
graft yield follows the order: acetic acid > methyl alcohol >
dimethylformamide.
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 silk, (2) miscibility with monomer, (3) forma-
tion of solvent radical from the primary radical species of the initiat-
ing 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. While the first four factors favor grafting by
simplifying 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 the adverse effect of the
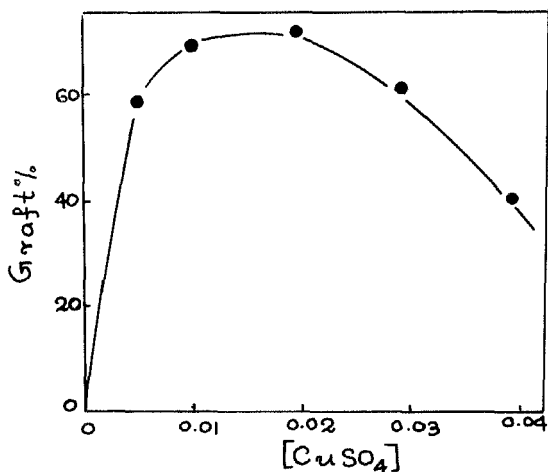swelling of silk by water.

FIG. 8. Effect of [CuSO$_4$] on graft yield: [V$^{5+}$] = 0.005 M, [H$_2$SO$_4$] = 0.9 M, [MMA] = 0.4694 M, [TU] = 0.001 M, temperature = 50°C, time = 6 h, M:L = 1:100.


## Effect of Copper Sulfate Concentration

The effect of CuSO$_4$ concentration on grafting has been studied by keeping the concentration of all other reagents constant. It is observed that with increasing CuSO$_4$ concentration, the graft yield increases up to 0.02 M and then decreases (Fig. 8). The initial increase in graft yield might be due to the fact that the presence of Cu$^{2+}$ ions in the vicinity of silk certainly favors grafting since the involvement of Cu$^{2+}$ ions in a silk-monomer complex would be easier. Furthermore, the creation of free radical species under the influence of Cu$^{2+}$ ions would be in the proximity of silk, thus assisting formation of silk macroradicals. The drop in the graft yield at higher concentrations of cupric sulfate solution is attributed to a variety of reasons. First is the termination of free radicals in solution, for on homopolymer and/or on silk the Cu$^{2+}$ ions seem to act as a radical trap. Second might be that a particular concentration of Cu$^{2+}$ favors complexation of monomer with silk, and beyond this concentration it perturbs such a complexation.


## ACKNOWLEDGMENTS

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