

Grafting Vinyl Monomers onto Silk Fibers. X. Graft Copolymerization of Methyl Methacrylate onto Silk Using Hydrogen Peroxide–Thiourea Redox System

GADADHAR PANDA, NRUSINGHA C. PATI, and PADMA L. NAYAK,
*Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw
College, Cuttack-753003, Orissa, India*

Synopsis

The graft copolymerization of methyl methacrylate onto silk fibers initiated by a hydrogen peroxide–thiourea redox system was investigated under various conditions. The effects of monomer, initiator, temperature, acidity of the medium, and solvent on the rate of grafting were studied. The graft yield increases with the increase of monomer and initiator concentration. The graft yield also increases with the increase of acid concentration upto $22.50 \times 10^{-2}M$ and thereafter it decreases. The effect of some inorganic salts on the rate of grafting has also been investigated, and a suitable mechanism has been suggested.

INTRODUCTION

Graft copolymerization of vinyl monomers onto some natural fibers like wool, silk, and cellulose and their characterization has received considerable attention in recent years.¹⁻⁸ It is difficult to distinguish between the ungrafted polymer and grafted polymer formed within the fiber, since ungrafted polymer entangled within the fiber matrix is not removed easily by the usual solvent extraction techniques. Grafting of polymer to the fiber involves only a limited number of grafting sites and analysis of possible sites of attachment is difficult because of the complexity of the fiber molecule.

During the last few years, Nayak and co-workers have used thiourea coupled with a large number of metal and nonmetal ions for the initiation of aqueous vinyl polymerization.⁹⁻¹³ Thiourea has also been used as a reductant for the graft copolymerization¹⁴⁻¹⁷ of wool, silk, cellulose, and nylon. This communication presents the result of graft copolymerization of methyl methacrylate onto silk using a hydrogen peroxide–thiourea redox system as the cocatalyst.

EXPERIMENTAL

Mulberry silk fibroin was collected from Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by a method mentioned in our previous paper.¹⁴ Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution, dried with sodium sulfate (anhydrous), and distilled under nitrogen and reduced pressure before use.

Hydrogen peroxide (30% w/v S.D.S.), thiourea (BDH), and H_2SO_4 (18M, AR, BDH) were used. Water, distilled twice over alkaline permanganate and deionized by passing through a Biodeminrolit resin (Permutit Co., U.K.) was

used to prepare all solutions. A stock solution of hydrogen peroxide ($0.08M$ in distilled water) was used throughout the experiment. The concentration of hydrogen peroxide in the experimental system was determined by titration with permanganate.

The reactions were carried out in Pyrex flasks equipped with glass inlet and outlet tubes. Dried and purified silk fibers were immersed in a solution of thiourea [$(0.5-7.5) \times 10^{-3}M$], monomer ($28.16-122.0M$), sulfuric acid [$(7.5-75.00) \times 10^{-2}M$] at temperatures from 40 to $55^\circ C$. The required concentration of H_2O_2 [$(2.00-27.70) \times 10^{-3}M$] 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 graft yield was calculated as the percentage in weight over the original weight of the sample.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The graft copolymerization of methyl methacrylate onto silk was investigated by varying the monomer concentration from $28.16 \times 10^{-2}M$ to $122.0 \times 10^{-2}M$, keeping the concentration of all other reagents constant. The results show that with increasing monomer concentration the rate of grafting increases significantly (Fig. 1). The higher rates of grafting observed by increasing the monomer concentration could be ascribed to the following reasons: (1) complexation of

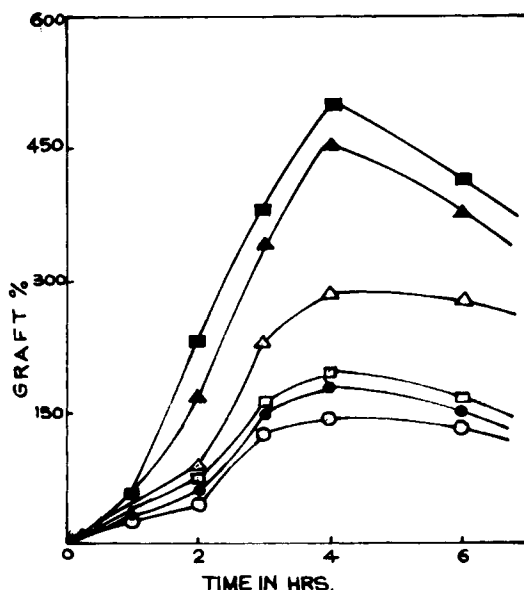


Fig. 1. Effect of [MMA] on graft yields: $[H_2O_2] = 27.70 \times 10^{-3}$ mole/liter; $[TU] = 2.5 \times 10^{-3}$ mole/liter; $[H^+] = 22.5 \times 10^{-2}$ mole/liter; temperature: $50^\circ C$; $M:L = 1:100$; [MMA] (mole/liter) = (○) 28.16×10^{-2} ; (●) 46.94×10^{-2} ; (□) 65.72×10^{-2} ; (△) 84.60×10^{-2} ; (▲) 103.27×10^{-2} ; (■) 122.0×10^{-2} .

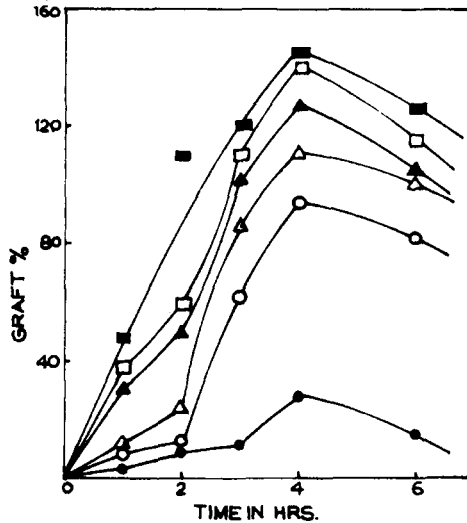
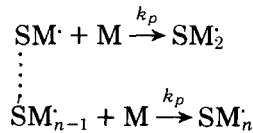
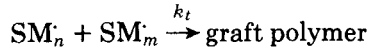


Fig. 2. Effect of $[\text{H}_2\text{O}_2]$ on graft yield (mole/liter): $[\text{TU}] = 2.5 \times 10^{-3}$; $[\text{MMA}] = 46.94 \times 10^{-2}$; $[\text{H}^+] = 15.00 \times 10^{-2}$; temperature = 50°C ; $M:L = 1:100$; $[\text{H}_2\text{O}_2]$ (mole/liter) = (●) 1.97×10^{-3} ; (○) 3.90×10^{-3} ; (Δ) 7.90×10^{-3} ; (▲) 11.90×10^{-3} ; (□) 19.80×10^{-3} ; (■) 27.70×10^{-3} .

Propagation:



Termination:



Now

$$\begin{aligned} \frac{d[\text{R}\cdot]}{dt} &= Kk_1 [\text{TU}][\text{H}_2\text{O}_2] - k_d [\text{SH}][\text{R}\cdot] = 0 \\ [\text{R}\cdot] &= Kk_1 [\text{TU}][\text{H}_2\text{O}_2]/k_d [\text{SH}] \end{aligned} \quad (3)$$

where TU = thiourea.

$$\begin{aligned} \frac{d[\text{SM}_n]}{dt} &= k_i [\text{S}\cdot][\text{M}] - [\text{SM}_n]^2 k_t = 0 \\ [\text{SM}_n] &= (k_i [\text{S}\cdot][\text{M}]/k_t)^{1/2} \end{aligned} \quad (4)$$

Again

$$\begin{aligned} \frac{d[\text{S}\cdot]}{dt} &= k_d [\text{SH}][\text{R}\cdot] - k_i [\text{S}\cdot][\text{M}] = 0 \\ [\text{S}\cdot] &= k_d [\text{SH}][\text{R}\cdot]/k_i [\text{M}] \end{aligned} \quad (5)$$

Substituting the value of $[\text{R}\cdot]$ in eq. (5), we get

$$[\text{S}\cdot] = Kk_1 [\text{TU}][\text{H}_2\text{O}_2]/k_i [\text{M}]$$

Substituting the value of $[\text{S}\cdot]$ in eq. (4), we get

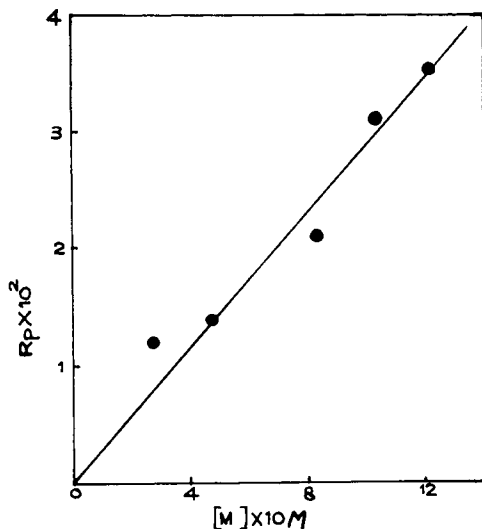


Fig. 3. Plot of R_p vs. $[M]$ for grafting MMA onto silk using H_2O_2 -TU redox system.

$$[SM_n] = \{(K k_1/k_t)[TU][H_2O_2]\}^{1/2}$$

$$R_p = k_p [SM_n][M]$$

Thus,

$$R_p = \frac{k_p K^{1/2} k_1^{1/2}}{k_t^{1/2}} [TU]^{1/2} [H_2O_2]^{1/2} [M] \quad (6)$$

Thus the linear plot of R_p vs. $[M]$ and $[H_2O_2]^{1/2}$ favors the above reaction scheme (Figs. 3 and 4).

Effect of Acid Concentration

Figure 5 shows the effect of acid concentration on graft yield. The grafting reaction was carried out by varying the acid concentration from $7.5 \times 10^{-2}M$ to $75.0 \times 10^{-2}M$ keeping the concentration of all other reagents constant. It is

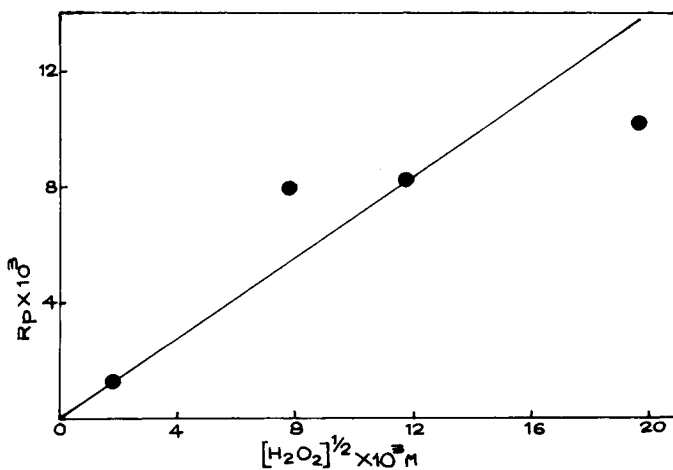


Fig. 4. Plot of R_p vs. $[H_2O_2]^{1/2}$ for grafting MMA onto silk using H_2O_2 -TU redox system.

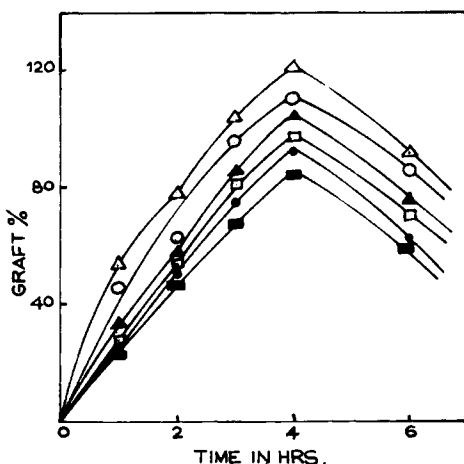


Fig. 5. Effect of $[\text{H}_2\text{SO}_4]$ on graft yield (mole/liter): $[\text{H}_2\text{O}_2] = 27.70 \times 10^{-3}$; $[\text{TU}] = 2.5 \times 10^{-3}$; $[\text{MMA}] = 46.94 \times 10^{-2}$; temperature = 50°C ; $[\text{H}_2\text{SO}_4]$ (mole/liter) = (●) 7.5×10^{-2} ; (○) 15.00×10^{-2} ; (Δ) 22.5×10^{-2} ; (▲) 30.00×10^{-2} ; (◻) 45.00×10^{-2} ; (■) 75.00×10^{-2} .

observed that the graft yield increased by increasing the acid concentration up to $22.5 \times 10^{-2}M$, and thereafter it slowed down as the acid concentration was increased. This observation may be explained basing on the following points.

The initial increase in graft yield may be due to the fact that the decomposition of the complex formed between the peroxide and thiourea [eq. (2)] proceeds much faster at higher acid concentration since the reducing properties of thiourea is higher at higher acid concentration,²¹ and eq. (1) is more shifted to the right-hand side at higher acid concentration, thereby enhancing the formation of more isothio-carbamido radicals that initiates grafting.

The fall in graft yield beyond $22.5 \times 10^{-2}M$ might be due to the coagulation of colloidal homopolymer in solution and within fibers which increases during grafting. This retards the diffusion of both monomer and initiator into the silk matrix for grafting to occur.

Effect of Reaction Time

The effect of reaction time on the graft yield may be realized from Figures 1, 2, and 5. Initially the graft yield increases with increase of time, and at a later stage it decreases. This could be due to depletion in monomer and initiator concentrations as well as reduction in the available active centres on the substrate backbone as the reaction proceeds. Similar observations have been noted by others.²²⁻²⁵

Effect of Temperature

The graft copolymerization of MMA onto silk using H_2O_2 -thiourea cocatalyst was also investigated at four different temperatures ranging from 40 to 55°C . It is observed that the graft yield increases significantly with the increase of temperature up to 50°C , beyond which it decreases (Fig. 6). The increase of the

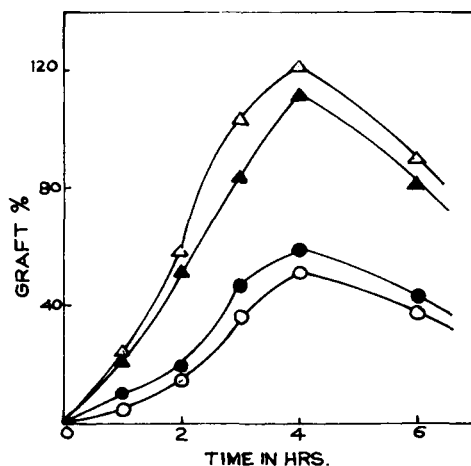


Fig. 6. Effect of temperature on graft yield (mole/liter): $[\text{H}_2\text{O}_2] = 27.70 \times 10^{-3}$; $[\text{TU}] = 2.5 \times 10^{-3}$; $[\text{H}^+] = 22.5 \times 10^{-2}$; $[\text{MMA}] = 46.94 \times 10^{-2}$; $M:L = 1:100$; temperature ($^\circ\text{C}$) = (O) 40; (●) 45; (Δ) 50; (▲) 55.

percentage of grafting with temperature upto 50°C could be ascribed to a greater activation energy.

As the temperature increases the solubility of monomer in the reaction medium, its diffusion from the solution phase to the fiber phase and swellability of the fiber are greatly enhanced. Hence the complexation of monomer with silk matrix and its activity are increased, resulting in the graft on increase. However, beyond 50°C the decrease in graft yield might be due to the greater possibility of combination rates of radicals at higher temperature.

From the Arrhenius plot of $\log R_p$ vs. $1/T$, the overall activation energy was found to be 12.00 kcal/mole (Fig. 7). Using the values of $E_p - \frac{1}{2}E_t = 4-5$ kcal/mole given by Tobolsky²⁶ et al., where E_p and E_t are energies of propagation and termination, respectively, the activation energy of initiation E_d can be calculated from the following values:

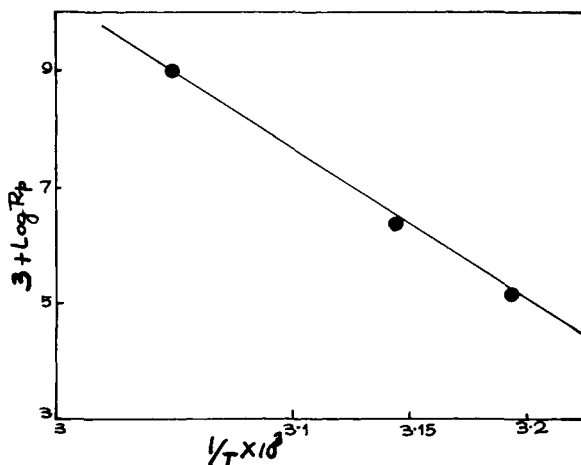


Fig. 7. Arrhenius plot of $1/T$ vs. $\log R_p$ for grafting MMA onto silk using H_2O_2 -TU redox system.

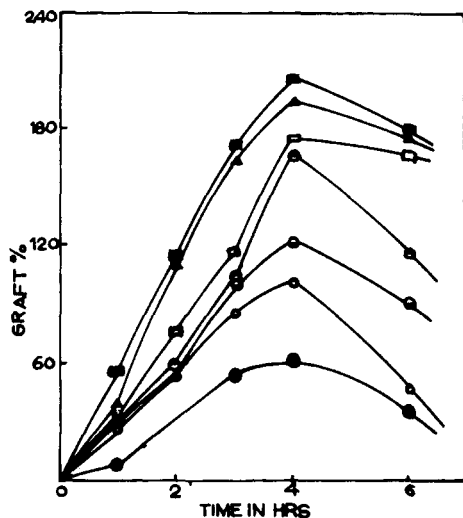


Fig. 8. Effect of solvents on graft yield (mole/liter): $[H_2O_2] = 27.70 \times 10^{-3}$; $[TU] = 2.5 \times 10^{-3}$; $[H^+] = 22.5 \times 10^{-2}$; temperature = $50^\circ C$; $[MMA] = 46.94 \times 10^{-2}$ mole/liter; [solvent] = 10%; $M:L = 1:100$; (●) methyl alcohol, (○) ethyl alcohol, (▲) propanol, (□) butanol, (■) formic acid, (⊙) acetic acid, (⊖) nil.

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

where E_a is the overall activation energy and $E_d = 15.00$ kcal/mole for total conversion reaction of MMA to PMMA.

Effect of Reaction Medium

The reaction medium plays an important role in graft copolymerization reaction. The reaction medium might affect the swelling properties of silk. Any change in silk swellability would be reflected on the behavior of silk toward grafting, since diffusion of monomer and initiation, availability of functional

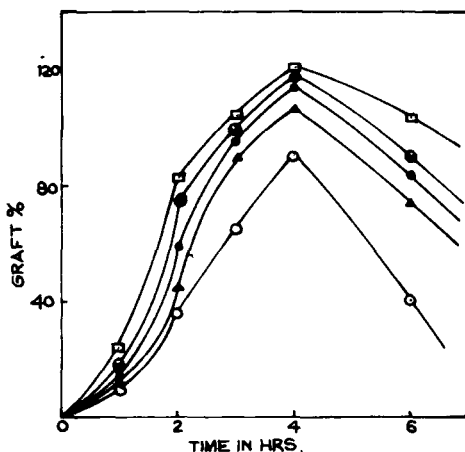


Fig. 9. Effect of salts on graft yield (mole/liter): $[H_2O_2] = 27.90 \times 10^{-3}$; $[TU] = 2.5 \times 10^{-3}$; $[H^+] = 22.5 \times 10^{-2}$; temperature = $50^\circ C$; $[MMA] = 46.94 \times 10^{-2}$ mole/liter; [salt] = 0.01 mole/liter; $M:L = 1:100$; (●) Na_2SO_4 , (▲) $MgSO_4$, (○) $MnSO_4$, (⊙) KCl , (□) nil.

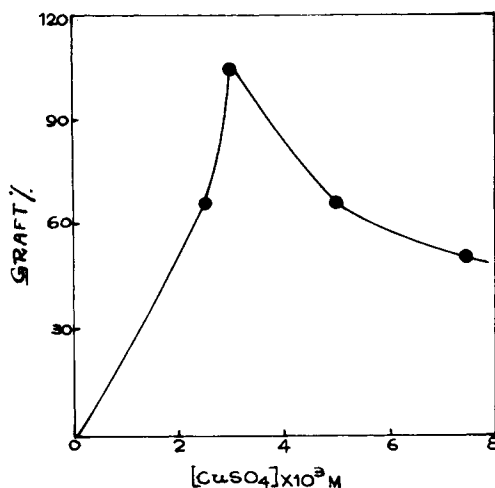


Fig. 10. Effect of $[\text{CuSO}_4]$ on graft yield (mole/liter): $[\text{H}_2\text{O}_2] = 27.70 \times 10^{-3}$; $[\text{TU}] = 2.5 \times 10^{-3}$; $[\text{H}^+] = 22.5 \times 10^{-2}$; temperature = 50°C ; $[\text{MMA}] = 46.94 \times 10^{-2}$ mole/liter; Time = 6 hr; $M:L = 1:100$.

groups (sites of grafting), propagation and termination of 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. 8): formic acid > propanol > butanol > acetic acid > ethyl alcohol > methyl alcohol.

Effect of Neutral Salts

The effect of the addition of certain neutral inorganic salts on the graft copolymerization reaction has been studied. The result shows that the addition of KCl, Na_2SO_4 , and MgSO_4 depresses the rate of grafting than without any neutral salts (Fig. 9). The order of their effect on graft yield is Nil > KCl > Na_2SO_4 > MgSO_4 > MnSO_4 .

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 effect of CuSO_4 concentration on graft yield has also been studied. Upon increasing the CuSO_4 concentration up to $3 \times 10^{-3}M$, the graft yield increases, but thereafter it decreases with the further increase of the CuSO_4 concentration (Fig. 10). 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 $3.0 \times 10^{-3}M$ 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, and (2) a particular concentration of Cu^{2+} ions favors complexation of monomer with silk and beyond this concentration of Cu^{2+} ions perturb such complexation.

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