

Grafting Vinyl Monomers onto Silk Fibers. XV. Graft Copolymerization of Methyl Methacrylate onto Silk Using Thallium (III) as Initiator

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Synopsis

The graft copolymerization of methyl methacrylate onto silk initiated by thallium (III) perchlorate was investigated in aqueous medium. The rate of grafting was evaluated varying the concentration of monomer, initiator, and acid, and the temperature. The graft yield was found to increase with increasing the monomer and initiator concentrations. The graft yield was found to decrease with increasing the acid concentration. The effect of inhibitors and various solvents on the graft yield was studied. From the Arrhenius plot the overall activation energy was found to be 4.2 kcal/mol. A suitable kinetic scheme has been proposed, and a rate equation has been derived.

INTRODUCTION

Grafting of vinyl monomers onto natural and synthetic polymers has been tested as an effective means of modifying the properties of a base polymer. This field of research has attracted attention in recent years, and several reviews are available on this subject.¹⁻⁶ Grafting provides a method of adding certain properties to a fiber without greatly disturbing the strength and other mechanical behavior of the fiber. Grafting of vinyl monomers onto wool,¹ cotton,⁷⁻⁹ starch,¹⁰⁻¹³ cellulose,¹⁴⁻²¹ etc., has been the subject of extensive investigations for the last several years. It is surprising that comparatively little attention has been paid towards grafting vinyl monomers on to silk fibers.^{22,23} Synthetic polymers are applied to silk to obtain improved textile performance and to overcome water straining, which seriously impedes the general use of silk fiber.

Graft copolymerization of vinyl monomers onto substrate polymers is generally considered to involve the generation of reactive sites on the polymer followed by the addition of monomer which propagates in a conventional manner. This can be achieved by several methods, such as high energy radiation,^{22,24} low energy radiation in the presence or absence of sensitizers,^{25,26} and chemical methods.²⁷⁻³⁰ The last method has attracted attention in recent years because it provides a direct experimental evidence of the existence of a transient radical intermediate generated by chemical reactions.

In the recent past, metal ions in their higher valency states have been extensively used for polymerization of a number of vinyl monomers in aqueous medium.³¹⁻³⁸ Mercuric acetate and thallium (III) acetate have been used as initi-

ators for homopolymerization of vinyl monomers,^{39,40} but no detailed study has been made using thallium (III) perchlorate as initiator for homopolymerization of vinyl monomers. Recently, we have carried out detailed studies using thallium (III) perchlorate as an initiator for homopolymerization of vinyl monomers. This communication presents the results of studies of grafting methyl methacrylate onto silk fibers using trivalent thallium ion as initiator.

EXPERIMENTAL

Mulberry silk fibroin was collected from the Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by scouring in an aqueous solution containing 0.4% soap for 2 h and washing with 0.05% sodium carbonate solution followed by boiling water. Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution, dried with anhydrous calcium chloride, and distilled under reduced pressure in nitrogen before use.

Thallium (III) perchlorate was prepared by dissolving thallium (III) oxide (from B. D. H., Analar.) in a minimum amount of perchloric acid (from E. Merck, Germany, 60%) at 75°C; thallium (III) perchlorate solution was prepared by dissolving a calculated amount of thallic perchlorate in a known volume of standard perchloric acid. Tl(III) concentration was estimated titrimetrically by an iodide-thiosulphate analytical procedure.⁴¹

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.

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 Tl(III) perchlorate in perchloric acid at temperatures from 40°C to 70°C. The required concentration of monomer was added to the reaction mixture. The reaction time was varied from 1 h to 6 h, 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 increase in weight over the original weight of the sample.

RESULTS AND DISCUSSION

The factors affecting the graft copolymerization of methyl methacrylate onto silk fibers initiated by thallium (III) perchlorate were investigated. Variables studied included monomer concentrations, thallium (III) concentrations, acid concentrations, temperature, and different solvents.

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentration and keeping the concentration of other reagents constant. The monomer concentration was varied from $28.16 \times 10^{-2}M$ to $103.26 \times 10^{-2}M$. The rate of grafting steadily increases with increase of monomer

concentration (Fig. 1). Since the copolymerization reaction was carried out at the same temperature and at a fixed concentration of Tl(III), 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 a variety of reasons. First, the silk might form some type of charge transfer complex with the monomer molecules, thus enhancing the activity of the monomer at higher monomer concentration. Secondly, gel effect, i.e., increase of viscosity of the medium due to the solubility of poly(methyl methacrylate) in its own monomer, becomes more pronounced at high monomer concentrations, as a result of which the bimolecular termination of growing polymer chains is hindered thus enhancing the graft yield. Besides, this gel effect also causes swelling of silk, thus facilitating diffusion of the monomer to growing chains and active sites on the silk matrix, thereby enhancing grafting at high monomer concentrations.

Effect of Tl(III) Concentration

The effect of thallium (III) concentration on graft copolymerization of methyl methacrylate onto silk fibers is shown in Figure 2. The rate of grafting has been investigated by changing the Tl(III) concentration within the range 4.08×10^{-3} – $20.40 \times 10^{-3}M$. The data indicate that increase of Tl(III) concentration is accompanied by a significant increase in graft yield. A possible explanation for these observations might be as follows: As the concentration of the initiator goes on increasing, more and more free radicals are formed as a result of the interaction of thallium (III) ions with the groups present in the silk backbone, thus increasing the graft yield.

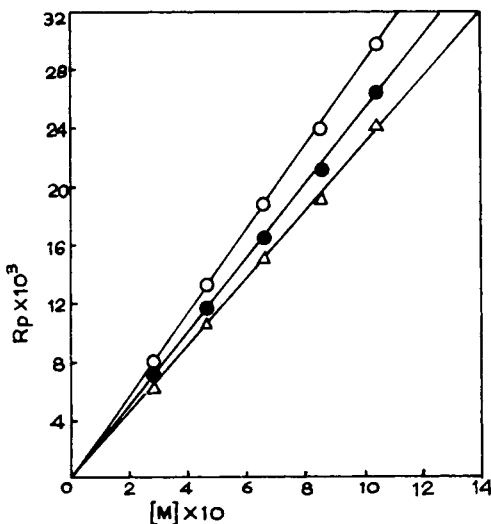


Fig. 1. Effect of monomer concentration on rate of grafting $[HClO_4] = 4.75 \times 10^{-1}$ m/L; ether concentration = 2.5% v/v; time = 6 h; temp = $70^\circ C$; M:L = 1:100. (Δ) $[Tl^{3+}] = 4.08 \times 10^{-3}$ m/L; (\bullet) $[Tl^{3+}] = 8.16 \times 10^{-3}$ m/L; (\circ) $[Tl^{3+}] = 12.24 \times 10^{-3}$ m/L.

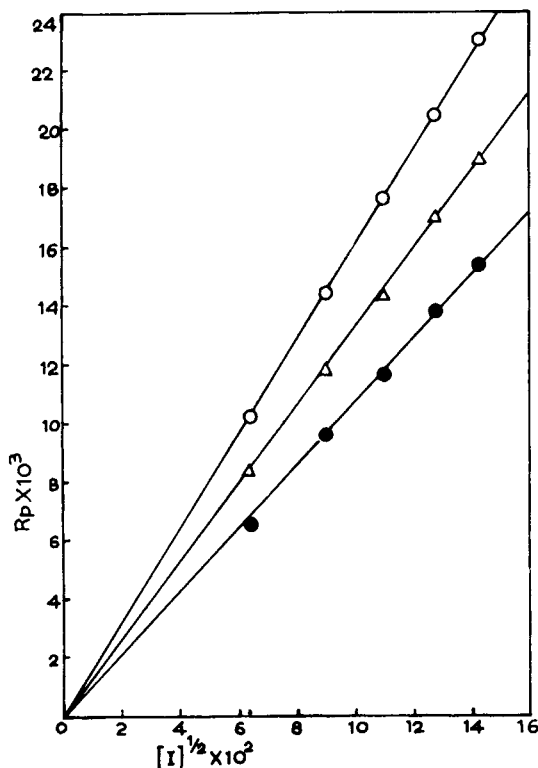


Fig. 2. Effect of Tl(III) concentration on rate of grafting: $[\text{HClO}_4] = 1.2 \text{ m/L}$; other concentration = 2.5% v/v; time = 6 h; temp = 70°C ; M:L = 1:100. (●) $[\text{MMA}] = 4.694 \times 10^{-1} \text{ m/L}$; (Δ) $[\text{MMA}] = 7.041 \times 10^{-1} \text{ m/L}$; (○) $[\text{MMA}] = 9.388 \times 10^{-1} \text{ m/L}$.

Effect of Acid Concentration

The graft copolymerization reaction was carried out in aqueous perchloric acid medium. The acid concentration was varied from 0.19M to 0.59M. The graft yield was found to decrease with increasing acid concentration (Fig. 3). The decrease in the percentage of grafting at high acid concentration might be due to the recombination and disproportionation of the graft macroradicals and also might be due to the decrease in the initiating efficiency of thallium (III) perchlorate at high acid concentrations.

Effect of Temperature

The graft copolymerization was carried out at four different temperatures ranging from 40°C to 70°C , keeping the concentrations of all other reagents constant. The graft yield was found to increase progressively with the rise in temperature (Fig. 4). This might be due to various reasons. First, this might be due to the increase in the activity of thallium (III) with increase in temperature. Secondly, this may be due to the increase in activation energy at high temperatures. As a result of increase in the activation energy, the swellability of the fiber, the solubility of the monomer, and its diffusion rate from the solution phase to the fiber phase increases. Besides, the rate of initiation and propagation also increases thus increasing the graft yield.

From the Arrhenius plot of $\log R_p$ vs. $1/T$ (Fig. 5) the overall activation energy was found out to be 4.2 kcal/mol.

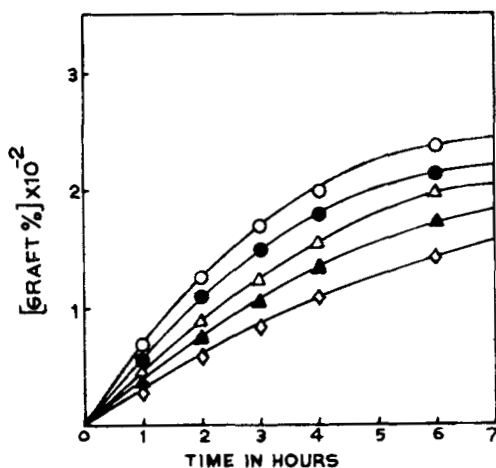


Fig. 3. Effect of acid concentration on graft yield: $[MMA] = 4.694 \times 10^{-1}$ m/L; $[Tl^{3+}] = 3.26 \times 10^{-3}$ m/L; $[\text{ether}] = 2.5\%$ v/v; $\text{temp} = 70^\circ\text{C}$; $M:L = 1:100$. (○) $[\text{HClO}_4] = 1.90 \times 10^{-1}$ m/L; (●) $[\text{HClO}_4] = 2.90 \times 10^{-1}$ m/L; (△) $[\text{HClO}_4] = 3.90 \times 10^{-1}$ m/L; (▲) $[\text{HClO}_4] = 4.90 \times 10^{-1}$ m/L; (◇) $[\text{HClO}_4] = 5.90 \times 10^{-1}$ m/L.

Effect of Polymerization Medium

The reaction medium plays an important role in grafting vinyl monomers onto silk fibers. Different solvents were added to the reaction medium, and their effect on graft yield was studied. The order of solvents as far as percentage of grafting is concerned, follows the following sequence (Fig. 6):

dimethyl formamide > dioxan > acetone > methanol > propanol >
carbon tetrachloride > chloroform

The solvents might affect the swellability of the silk fiber. Any change in silk swellability would be reflected on its behavior towards grafting since the diffusion of monomer and initiator, availability of functional groups, propagation and termination of the graft macromolecules, etc., would depend to a considerable

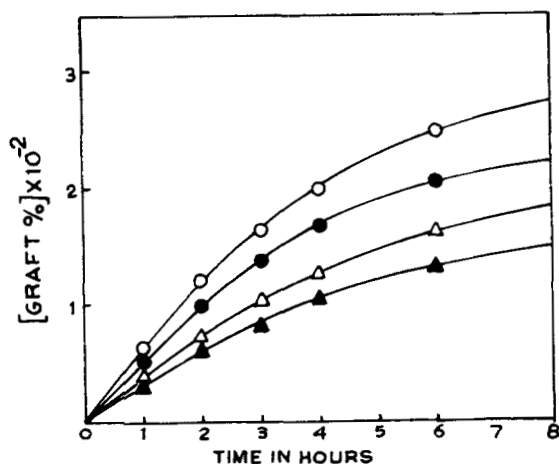


Fig. 4. Effect of temperature on graft yield: $[MMA] = 4.694 \times 10^{-1}$ m/L; $[Tl^{3+}] = 8.16 \times 10^{-3}$ m/L; $[\text{HClO}_4] = 4.75 \times 10^{-1}$ m/L; $[\text{ether}] = 2.5\%$ v/v; $M:L = 1:100$. $\text{Temp} (^\circ\text{C})$: (▲) 40; (●) 60; (△) 50; (○) 70.

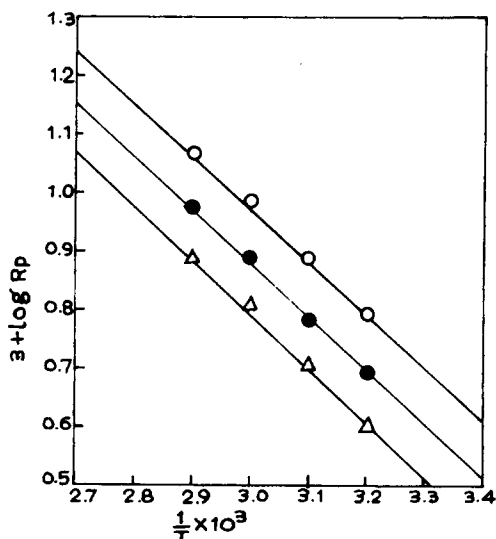


Fig. 5. Arrhenius plot of $\log R_p$ vs. $1/T$: (Δ) 3 h; (\bullet) 4 h; (\circ) 6 h.

extent on the swelling properties of silk. The above variation of graft percentage with the use of different solvents could be due to the difference in either of the following factors: (i) capability of swelling of silk, (ii) miscibility with monomer, (iii) formation of solvent radical from the primary radical species of the initiating system, (iv) contribution of the solvent radical in activation of silk, and (v) termination of the graft chain radicals and silk macroradical via chain transfer. Out of the above factors, the first four favor grafting, while the last factor adversely affects grafting by lowering the molecular size of the graft macromolecules.

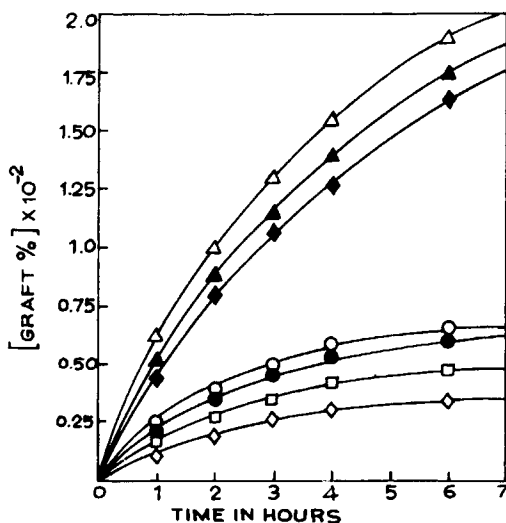


Fig. 6. Effect of polymerization medium on graft yield: $[\text{MMA}] = 4.694 \times 10^{-1}$ m/L; $[\text{Ti}^{3+}] = 8.16 \times 10^{-3}$ m/L; $[\text{HClO}_4] = 1.2$ m/L; [ether] = 2.5% v/v; [solvent] = 25% v/v; temp = 70°C; M:L = 1:100. (Δ) dimethyl formamide; (\blacktriangle) dioxan; (\blacklozenge) acetone; (\circ) methanol; (\bullet) propanol; (\square) carbon tetrachloride; (\diamond) chloroform.

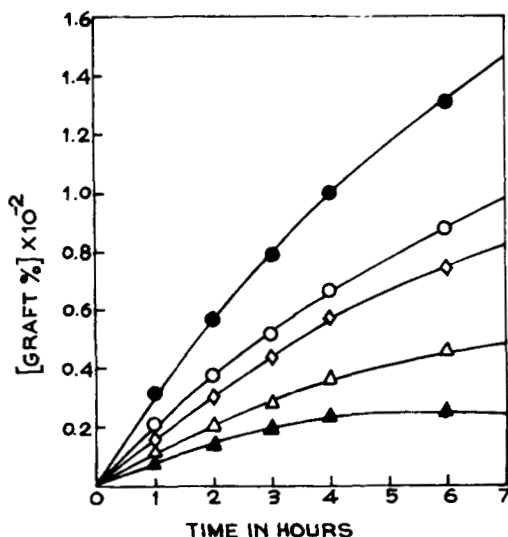


Fig. 7. Effect of inhibitors on graft yield: $[\text{MMA}] = 4.694 \times 10^{-1}$ m/L; $[\text{Tl}^{3+}] = 3.26 \times 10^{-3}$ m/L; $[\text{HClO}_4] = 1.9 \times 10^{-1}$ m/L; [ether] = 2.5 % v/v; temp = 70°C ; M:L = 1:100. (●) [Picrylchloride] = 5×10^{-5} m/L; (○) [picrylchloride] = 10×10^{-5} m/L; (◇) [picrylchloride] = 15×10^{-5} m/L; (△) [picrylchloride] = 20×10^{-5} m/L; (▲) [picrylchloride] = 25×10^{-5} m/L.

Effect of Inhibitors

The effect of different inhibitors such as hydroquinone and picryl chloride on the graft yield was studied at a fixed concentration of all other reagents (Figs. 7 and 8). From the results it was observed that the graft percentage was greatly suppressed in presence of either inhibitor. It was observed that the inhibiting efficiency of picryl chloride was more than hydroquinone. The data also indicate

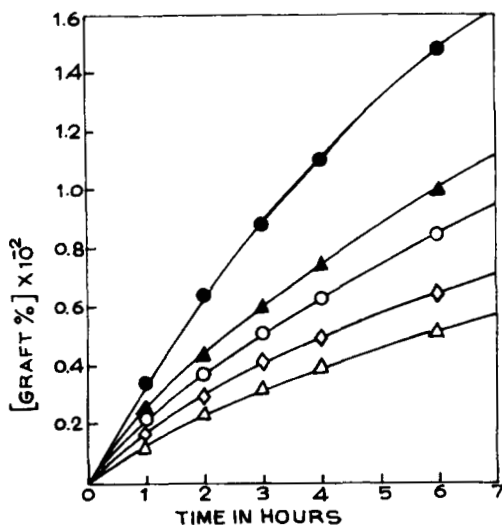


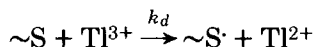
Fig. 8. Effect of inhibitors on graft yield: $[\text{MMA}] = 4.694 \times 10^{-1}$ m/L; $[\text{Tl}^{3+}] = 3.2 \times 10^{-3}$ m/L; $[\text{HClO}_4] = 1.9 \times 10^{-1}$ m/L; [ether] = 2.5 % v/v; temp = 70°C ; M:L = 1:100. (●) [Hydroquinone] = 5×10^{-5} m/L; (▲) [hydroquinone] = 10×10^{-5} m/L; (○) [hydroquinone] = 15×10^{-5} m/L; (◇) [hydroquinone] = 20×10^{-5} m/L; (△) [hydroquinone] = 25×10^{-5} m/L.

that the extent of inhibition increases with increase in the concentration of the inhibitor. As the concentration of the inhibitor increases, it traps more and more free radicals, thereby reducing the molecular size of the graft and hence decreasing the graft yield.

MECHANISM

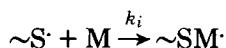
The following mechanism has been suggested for the graft copolymerization of methyl methacrylate onto silk fibers using thallic ion as the initiator.

(i) Production of free radical on silk backbone:



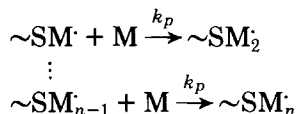
(where S = silk)

(ii) Initiation:

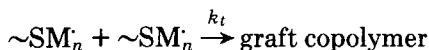


(where M = monomer and S· = silk macroradical)

(iii) Propagation:



(iv) Termination:



Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows

$$-\frac{d[\text{S}\cdot]}{dt} = k_d[\text{TI}^{3+}][\text{S}] - k_i[\text{S}\cdot][\text{M}] = 0$$

$$[\text{S}\cdot] = \frac{k_d[\text{TI}^{3+}][\text{S}]}{k_i[\text{M}]}$$

$$-\frac{d[\text{SM}_n]}{dt} = k_i[\text{S}\cdot][\text{M}] - k_t[\text{SM}_n]^2 = 0$$

$$[\text{SM}_n] = \left\{ \frac{k_i[\text{S}\cdot][\text{M}]}{k_t} \right\}^{1/2}$$

Substituting the value of [S·] in the above equation,

$$[\text{SM}_n] = \left\{ \frac{k_d[\text{TI}^{3+}][\text{S}]}{k_t} \right\}^{1/2}$$

Then

$$R_p = k_p[\text{M}][\text{SM}_n]$$

or

$$R_p = k_p(k_d/k_t)^{1/2} [S]^{1/2} [TI^{3+}] [M]$$

The plots of R_p vs. $[M]$ (Fig. 1) and R_p vs. $[\text{initiator}]^{1/2}$ (Fig. 2) are linear, passing through the origin, which confirms the validity of the above reaction scheme.

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