

Grafting of Vinyl Monomers onto Silk Fibers: Trivalent-Manganese-Initiated Graft Copolymerization of Acrylamide onto Silk Fibers

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Synopsis

Graft copolymerization of acrylamide (AM) onto silk fibers, using Mn(III)-sulphate as initiator, has been investigated, in aqueous sulphuric acid in the temperature range of 30–55°C. Grafting reaction has been studied by varying the concentration of monomer, Mn(III), sulphuric acid, temperature, and also with the modified silk. The graft yield increases significantly with increase of monomer concentrations to the extent of 0.85M, after which the rate falls. With increase in Mn(III) concentration and H⁺ ion concentration the graft yield increases, but after an optimum concentration a depression in the graft yield is noticed. The rate of the reaction is temperature-dependent; with increase of temperature the graft-on increases. Among the solvent composition studied a solvent/water mixture containing 10% of the solvent seems to constitute the most favorable medium for grafting, and a further increase of solvent composition decreases the graft yield. The effect of various additives such as transition metal salts, aromatic and heterocyclic amines on grafting reaction has been studied. A suitable mechanism for grafting has been proposed. Finally physical characterization such as thermal analysis (TGA) of the grafted samples has been carried out in order to ensure grafting and to study the change in the properties of the fibers.

INTRODUCTION

Modification of the properties of natural and synthetic fibers, such as wool, silk, nylon, etc., through graft copolymerization is attractive to chemists as a mean of chemical modification, since in general degradation can be minimized.¹ A variety of properties could be compared to the macromolecule without destroying the basic properties of the fiber. Some of the vital changes on properties which has been brought out by grafting are viscoelasticity, stereoregularities, hygroscopicity, water repellency, improved adhesion to a variety of substances, improve dyeability, soil resistance, and thermal stability.

Graft copolymerization onto silk fibers offers intriguing possibility, since grafting is usually considered to leave the backbone of the polymer essentially intact and provides addition properties through added polymers.^{2–5} The chemical method of initiation of grafting onto silk fibers has attracted attention in recent years.^{6–13} The use of Mn(III), either in the form of sulphate or pyrophosphate, as the initiator of graft copolymerization onto natural and synthetic fibers has been reported by various workers.^{14–17} Recently we have reported¹⁸ Mn(III)-acetylacetonate-initiated graft copolymerization of methyl methacrylate onto silk fibers. We now report the graft copolymerization of acrylamide onto

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silk fibers using Mn(III)-sulphate as initiator and propose the mechanism of grafting.

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% of soap solution for 6 h and washing with 0.05% sodium carbonate solution followed by boiling water. Acrylamide was recrystallized from methanol and then dried *in vacuo* over silica gel, melting point 84.5°C. Mn(III) stock solutions were prepared by electrolytic oxidation of appropriate Mn(II) salt solution (0.4–0.6M) in 3.5–6M sulphuric acid at a platinum anode^{19,20} and was analyzed for Mn(III) content by EDTA titration.

Water used for the preparation of solutions was obtained by redistilling distilled water over alkaline potassium permanganate in a glass quick-fit Pyrex setup, and passing through Bio-deminrolit (Permutit Co., U.K.) mixed-bed ion-exchange resin for removal of traces of ions.

All other reagents were of BDH quality and were used after usual purification.

Graft copolymerization was carried out in well-stoppered vessels under nitrogen atmosphere. Silk fibers immersed in a solution of Mn³⁺-sulphate solution ($3.5\text{--}8.75 \times 10^{-3}M$) at temperatures of 30–55°C. After the attainment of thermal equilibrium, the required concentration of monomer solution was added to the reaction vessel. The reaction time was varied from 1 to 8 hr and the material-to-liquor ratio was 1:100. After the required reaction time, the silk samples were removed and washed thoroughly with boiling water. The grafted samples were then subjected to repeated homopolymer extraction with boiling water and finally dried to constant weight. The graft yield was then calculated by the usual method.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentration, keeping the other reagent constant. The values of graft percentage for various monomer are recorded in Table I. It is seen that the graft percentage increases smoothly with increase in the concentration of monomer from 0.2M to 0.8M, after which a decrease trend is noticed. This might be due to the fact that at higher monomer concentrations a reaction such as combination and disproportionation probably takes place. When the concentration of polyacrylamide radical (PAAm) macroradical increases, the rate of their combination and disproportionation increases faster than the rate of their combination with silk molecules. On the other hand, the rate of monomer diffusion is bound to be progressively affected by polymer deposit formed which of course goes more rapidly when high concentration monomer used. Similar observations have been reported by Nayak et al.¹² in Cr(VI)-initiated graft copolymerization of vinyl monomers onto silk fibers, and by Haworth and Holker²¹ in the case of grafting of acrylic acid onto nylon by ceric ion method. We had also an identical

TABLE I
Variation of Percentage of Grafting at Different Monomer Concentrations^a

Time (h)	Graft %						[AM]
	[AM] = 0.2M	[AM] = 0.4M	[AM] = 0.6M	[AM] = 0.8M	[AM] = 1.0M	[AM] = 1.2M	
1	2.015	5.156	9.816	12.56	10.112	8.012	
2	3.968	8.202	12.332	16.956	13.565	10.263	
3	5.015	13.691	21.560	26.882	20.198	15.018	
4	6.915	18.562	29.120	32.511	29.220	20.141	
6	8.005	26.960	35.122	40.232	36.122	29.362	
7	9.876	32.152	41.320	47.198	40.175	35.162	
8	10.567	41.732	45.790	49.158	42.996	38.191	

^a Receipt: $[Mn^{3+}] = 7 \times 10^{-3}M$; $[H^+] = 0.85M$; $\mu = 1.0M$; temperature = $50^\circ C$.

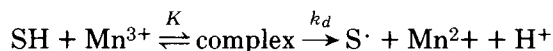
observation in the case of grafting of acrylamide onto nylon 6 initiated by man- ganic ion.¹⁷

Effect of Initiator Concentration

The effect of Mn^{3+} ion concentration on the graft copolymerization of acryl- amide onto silk fibers is shown in Figure 1. The graft percentage increases with increasing the initiator concentration up to $7 \times 10^{-3}M$, and thereafter the graft value decreases. The most probable explanation for this type of behavior can be obtained by considering the following reaction scheme.

In a system such as Mn(III) ion, acrylamide, sulphuric acid, and silk fibers, an intermediate complex of Mn(III)-silk might be formed which dissociates, yielding free radicals on the backbone of the silk molecules.

Initiation:



(where SH = silk) (1)

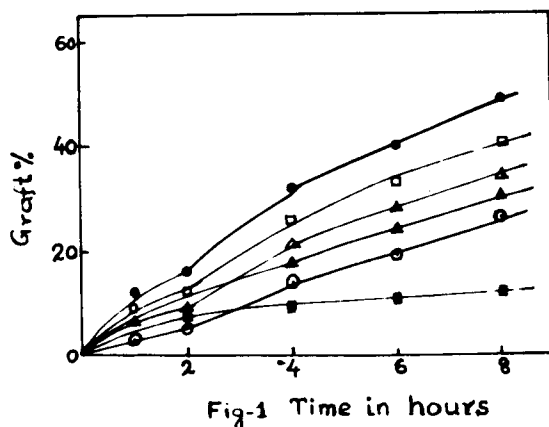
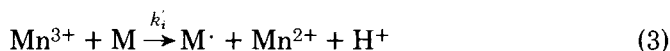
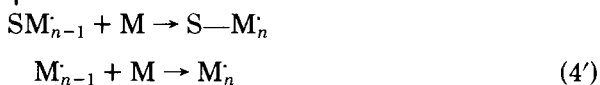


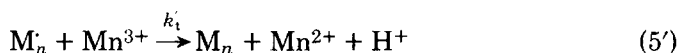
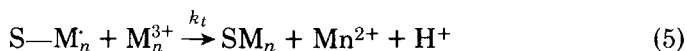
Fig. 1. Variation of graft % vs. time; effect of catalyst concentration: $[H^+] = 0.85M$; $\mu = 1M$; $[AM] = 0.8M$; temp = $50^\circ C$. $[Mn^{3+}]$: (O) $2.05 \times 10^{-3}M$; (Δ) $3.5 \times 10^{-3}M$; (\square) $5.2 \times 10^{-3}M$; (\bullet) $7 \times 10^{-3}M$; (\blacktriangle) $8.25 \times 10^{-3}M$; (\blacksquare) $10.05 \times 10^{-3}M$.



Propagation:



Termination:



Oxidation:



Applying the steady state conditions, we obtained the overall rate of polymerization as

$$R_p = \frac{k_p k_i [M]^2}{k_t [Mn^{3+}]} \left[\frac{k_d [Mn(III)][SH]}{K_{-d} [Mn(III)][H^+] + k_i [M] + k_0 [Mn^{3+}]} \right] \quad (7)$$

At low manganic ion concentrations,

$$R_p = k_p k_i [M]^2 \left[\frac{k_d [Mn^{3+}][SH]}{K_{-d} [Mn^{3+}][H^+] + k_i [M]} \right] \quad (8)$$

which shows that, with increase in manganic ion concentration, the rate of polymerization should increase, which is found to be true.

But at higher concentration of Mn^{3+} and when $k_t \gg k_p$ and k_i

$$R_p = \frac{k_p k_i [M]^2}{k_t [Mn^{3+}]} \left[\frac{k_d [Mn^{3+}][SH]}{K_{-d} [Mn^{3+}][H^+] + k_i [M] + k_0 [Mn^{3+}]} \right] \quad (9)$$

Equation (9) requires that increase in Mn^{3+} ion concentration increases the magnitude of the denominator, which results in decreasing the value of R_p . A maximum value of the graft percentage is obtained in an optimum concentration of Mn^{3+} ion beyond which the percentage graft decreases. We had an identical observation in the case of grafting acrylamide onto nylon 6.¹⁷

Effect of Acid Concentration on Grafting

The effect of acid concentration on grafting of acrylamide onto silk was studied at variable concentrations of sulphuric acid (0.4–0.7M). The graft percentage increases, on increasing the concentration of H_2SO_4 up to 0.6M, after which the

rate decreases. This type of behavior might be due to the change in oxidation potential of Mn^{3+} with change in H_2SO_4 concentration.²² At higher concentration of H_2SO_4 , the oxidizing ability of Mn^{3+} is higher, which might favor the termination of the growing polymer chains, thereby decreasing the graft percentage. The termination of vinyl polymerization by higher valency transition metal ions is well recognized.²³

Effect of Temperature on Grafting

The grafting reaction was carried out at five different temperatures, between 35–55°C; and the results are shown in Figure 2. The graft percentage increases with increasing temperature up to 50°C, above which the rate falls. The enhancement in the rate between 35°C and 50°C may be ascribed to greater activation energy. The swellability of the fibers and the diffusion rate of the monomer into the fibers are greatly enhanced with increasing temperature. The decrease in the rate above 50°C may be attributed to (i) the increase in the rate of termination of polymer chains and (ii) thermal polymerization of acrylamide.

Effect of Solvent Composition

The effect of solvent composition on the grafting of acrylamide onto silk fibers is computed in Figure 3. An increase in the solvent/water mixture tends to decrease grafting, of these, a mixture of solvent/water at a ratio 10:90 constitutes the most favorable medium, for acetic acid, methanol, formic acid, and a ratio of 20:80 for dioxan and DMF constitutes the most favorable medium for grafting. Variation in grafting using different proportions of solvent and water could be explained by considering the following factors: (i) miscibility of the monomer, (ii) capability of the swelling of the fibers, (iii) formation of solvent radical and/or hydrogen or hydroxyl radicals from water under the influence of primary radical species of the initiating systems, (iv) contribution of these solvents, hydrogen, and/or hydroxyl radicals in activation of the silk, and (v) termination of the graft

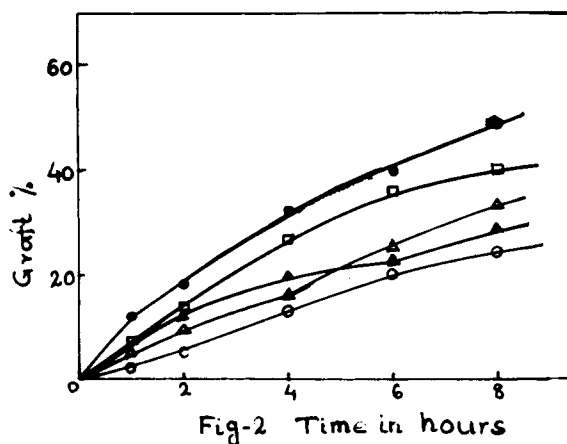


Fig. 2. Variation of graft % with time; effect of temperature on grafting: $[Mn^{3+}] = 7 \times 10^{-3}M$; $[H^+] = 0.85M$; $\mu = 1M$; $[AM] = 0.8M$. Temp (°C) (○) 35; (△) 40; (■) 45; (●) 50; (▲) 55.

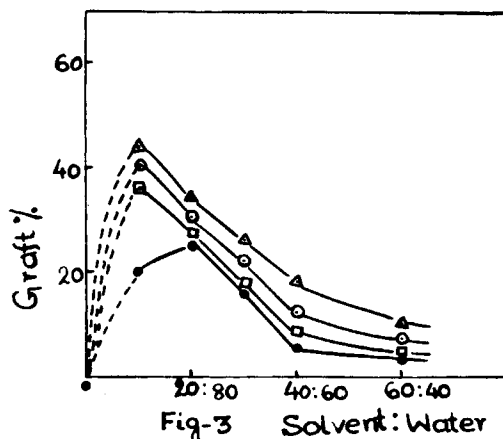


Fig. 3. Variation of percentage graft; effect of solvent composition: $[Mn^{3+}] = 7 \times 10^{-3}M$; $[H^+] = 0.85M$; $\mu = 1M$; $[AM] = 0.8M$; temp = $50^\circ C$; time = 8 hr. Plots: (O) acetic acid; (Δ) methanol; (\square) formic acid; (\bullet) dioxan.

chain radicals and silk radical via chain transfer. While the first four factors enhance grafting, the last factor adversely effects grafting by lowering the molecular size of the graft.

Effect of Transition Metal Salts

Addition of $0.02M$ $CuSO_4$ and $FeCl_3$ solutions to the grafting reaction decreases the graft yield to a considerable extent [Fig. 4(a)]. This might be due to the interaction of the Cu^{2+} and Fe^{3+} ion with the growing polyacrylamide chain rad-

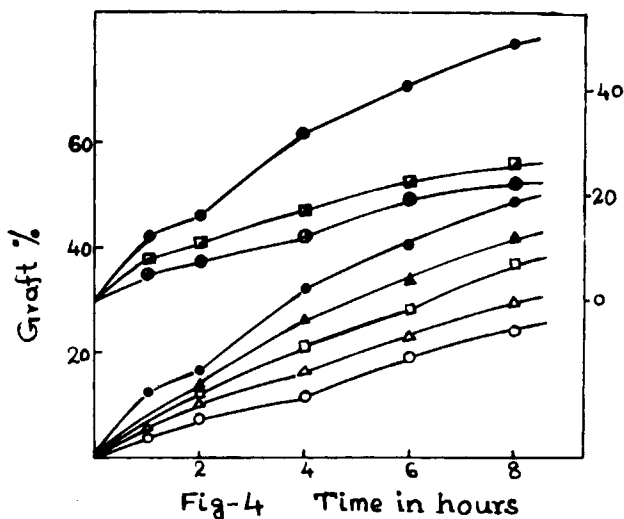
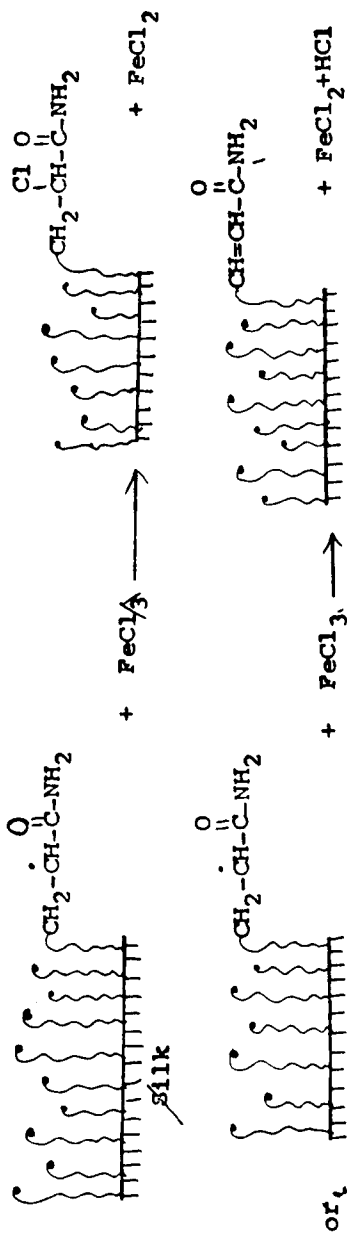


Fig. 4. (a) Variation of graft percentage with times; effect of transition metal salts: $[Mn^{3+}] = 7 \times 10^{-3}M$; $[H^+] = 0.85M$; $\mu = 1M$; $[AM] = 0.8M$; temp = $50^\circ C$. Plots: (O) control; (\oplus) $[CuSO_4] = 0.02M$; (\square) $[FeCl_3] = 0.02M$. (b) Variation of graft percentage with time; effect of organic nitrogen compounds: $[Mn^{3+}] = 7 \times 10^{-3}M$; $[H^+] = 0.85M$; $\mu = 1M$; $[AM] = 0.8M$; [nitrogen compounds] = $0.02M$; temp = $50^\circ C$. Plots: (\bullet) control; (O) piperidine; (Δ) pyridine; (\square) quinaldine; (\blacktriangle) - picoline.



Scheme I.

icals, which results in a premature termination of the radical ends of the growing chains. A similar observation was noticed by us, in the grafting of methyl methacrylate (MMA) onto silk fibers initiated by Mn(III)-acetyl acetonates,¹⁸ in the presence of CuSO₄. Premature termination of polymer chains was also noticed by Bamford et al.²⁴ in the AIBN-initiated polymerization of acrylonitrile in the presence of FeCl₃ and by Bengouch and Fsirservice²⁵ in the AIBN-initiated polymerization of methyl methacrylate in the presence of CuCl₂. The reaction shown in Scheme I probably takes in the presence of the salts.

Effect of Organic Nitrogen Compounds

Organic nitrogen compounds such as aromatic amines and nitrogen heterocycles have been found to exhibit both retardation and inhibition effect on the polymerization reactions. The addition of 0.02*M* solution of aniline, *N,N*-diethylaniline, α -picoline, quinaldine lutidine, etc. to the reaction mixture depresses the graft yield [Fig. 4(b)]. The retardation in grafting in case of α -picoline, quinaldine, and lutidine might be due to the retarding effect of *N*-oxides, produced by oxidation of the heterocycles by Mn(III)-sulfate *N*-oxides, well known to be ideal retarders of radical polymerization.²⁶ With aniline and *N,N*-diethylaniline, negligible or even no grafting took place; rather the reaction mixture became raddish which persisted. The behavior of aniline and diethylaniline might be due to their oxidation to quinones.²⁷ Similar observation was noticed by Saha and Chaudhuri²⁸ in the Ce(IV)-initiated polymerization of acrylonitrile in the presence of *N,N*-dimethyl aniline.

Dependence of Graft Yield on the Nature of the Substrate

Changes in the physical and chemical structure of silk fibers adversely affects grafting. It is noticed that acetylation and trinitrophenylation of silk, significantly, reduce its ability towards grafting. The order follows:

unmodified silk > esterified silk > trinitrophenylated silk

The most probable explanation for this phenomenon is that when silk fiber is subjected to acetylation and trinitrophenylation, the amino and the carboxyl groups obtained by the cleavage of amide linkages will be blocked. Free radicals cannot be created at the silk backbone by interaction of the Mn³⁺ ion, as a result of which the graft yield decreases. The other reasons for low grafting in the case of the modified silk fibers might be due to: (i) lowering of the swellability of the fiber; (ii) hindrance to adsorption of acrylamide AM molecules, due to repulsion caused by the ester group and the negatively charged nitro groups on phenyl rings. This observation is identical to that noticed by Nayak et al.,²⁹ in case of ceric-ion-initiated graft copolymerization of methyl methacrylate onto silk fibers.

The authors are grateful to Professor Y. Ikada, Center for Bio-Medical Research, Kyoto University, Japan, for inspiration and valuable suggestions.

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Received September 29, 1982

Accepted October 25, 1982