Trivalent Manganese Chelate-Initiated Graft Copolymerization of Methyl Methacrylate onto Silk Fibers

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Synopsis

The graft copolymerization of methyl methacrylate onto silk fibers was investigated in aqueous solution using Mn^{3+} acetyl acetonate [$Mn(acac)_3$] as initiator. The rate of grafting was determined by varying monomer, acidity of medium, temperature, and reaction medium. The graft yield increases significantly with increase of [$Mn(acac)_3$] concentration up to $0.01M$, and with further increase of [$Mn(acac)_3$] the graft yield decreases. The effect of the increase of monomer concentration brings about a significant enhancement in the graft yield, and with further increase the graft yield decreases. The rate of reaction is temperature dependent; with increasing temperature, the graft yield increases. Among the solvent composition studied, a water/solvent mixture containing 10% of the solvent seems to constitute the most favorable medium for grafting; and, with further increase of solvent composition, the graft yield decreases. The effect of some inorganic salts, organic solvents, and complexing agents has been investigated.

INTRODUCTION

Graft copolymerization onto silk fibers offers intriguing possibilities since grafting is usually considered to leave the backbone of the polymer essentially intact and provides additional properties through the added polymers.[1-4] It provides an effective means of improving the fiber properties with minimum degradation of the base polymer. The literature survey[5] reveals that grafting involves a radical mechanism. Hence, the primary step involves the creation of free-radical sites on the backbone of the fiber. In the recent past, much interest has been focused on vinyl graft copolymerization of silk through chemical initiation,[6-10] because it provides minimum degradation of the base polymer and minimizes the formation of homopolymer.

The homopolymerization of methyl methacrylate initiated by Mn^{3+}, coupled with a multitude of organic substrates as the redox components,[11-14] has been studied extensively. Otsu, Minamii, and Nishikawa[15] have reported Mn^{3+} acetyl acetonate to be the most excellent initiator in the homopolymerization of methyl methacrylate. Singh, Thampy, and Chipalkatti[16] and Namasivayam, Pattnaik, and Thampy[17] have reported that manganic sulfate in excess of sulfuric acid may form an effective redox system for grafting of poly(methyl methacrylate) onto cellulose and PVA. Nayudamma, et al.[18] reported Mn^{3+}-initiated graft copolymerization of vinyl monomers onto collagen. We have reported the graft

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copolymerization of acrylamide onto nylon 6 fibers[19] using Mn^{3+} as the initiator.

In this laboratory, there is a very ambitious research program to investigate the vinyl graft copolymerization onto silk using different metal chelate oxidants. This article reports the results of studies of the grafting of methyl methacrylate onto silk fibers using Mn^{3+} acetylacetonate 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 solution for 2 hr and washing with 0.05% sodium carbonate solution followed by boiling water. Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution, dried with sodium sulfate solution, and distilled with nitrogen under reduced pressure before use.

A reagent-grade sample of $Mn(acac)_3$ was used without further purification. 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 $0.1M$ $Mn(acac)_3$ was used throughout the experiment. Sulfuric acid used was B.D.H. AnalaR grade.

Graft copolymerization was carried out in well-stoppered vessels in nitrogen atmosphere. Silk fibers were immersed in a solution of Mn^{3+} acetylacetonate $(2 \times 10^{-3}M)$ in $0.03M$ H_2SO_4 at temperatures of from 35 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 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

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by changing the monomer concentration and keeping the concentrations of other reagents constant. From Table I it can be seen that as the monomer concentration

TABLE I
Variation of Percentage of Grafting at Different Monomer Concentrations[a]

Time, hr	Graft percentage				
	[M] = 0.027M	[M] = 0.045M	[M] = 0.063M	[M] = 0.081M	[M] = 0.099M
1	10.45	27.55	26.30	26.00	23.75
2	14.95	50.10	47.15	43.85	43.40
3	23.00	67.05	55.75	48.20	43.85
4	26.95	79.25	69.85	50.75	49.95
6	37.40	99.95	88.60	59.35	55.00

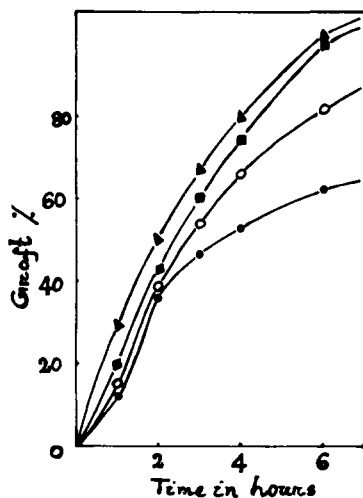[a] Recipe: $[Mn(acac)_3] = 2 \times 10^{-3}M$, $[H^+] = 0.03M$, temperature = 50°C.

Fig. 1. Variation of % grafting: effect of oxidant concentration. $[H^+] = 0.03M$, $[MMA] = 0.045M$, temp. 50°C. Plots of graft % vs. time in hr. ●, $[Mn(acac)_3] = 0.005M$; ▲, $[Mn(acac)_3] = 0.01M$; ■, $[Mn(acac)_3] = 0.015M$; ○, $[Mn(acac)_3] = 0.02M$.

[MMA] increases from 0.027 to 0.045M, there is an increase in the percentage of grafting until it reaches a maximum and then decreases with further increase in monomer concentration. A probable explanation for this is that as the concentration of poly(methyl methacrylate) macroradicals increases with the increase in monomer concentration, the rate of their combination and disproportionation increases faster than the rate of their combination with silk molecules. Further, the rate of monomer diffusion is bound to be affected progressively by the polymer deposit formed which grows rapidly as the monomer concentration increases. Similar observations have been reported by Nayak, Nayak and Samal[19] for grafting vinyl monomers onto nylon fibers using Mn^{3+}, and by Haworth and Holker[20] for grafting acrylic acid onto nylon by the ceric ion method.

Effect of Initiator Concentration

The effect of $[Mn(acac)_3]$ concentration on the graft copolymerization of MMA onto silk is shown in Figure 1. The percentage of grafting increases with the increasing initiator concentration up to 0.01M, and thereafter the percentage of grafting decreases. This might be explained by considering the following reaction scheme.

As has been pointed out by Arnett and Mendelsohn,[21] the initiation mechanism by $Mn(acac)_3$ is considered to occur through homolysis of the metal—oxygen bonds in the reaction medium:
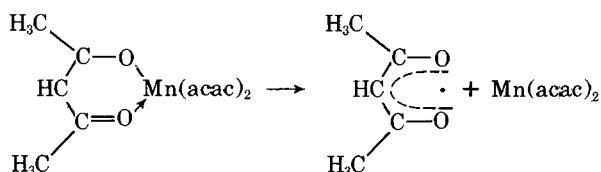
This mechanism has been supported by Bamford and Lind[22] from the observed rate equation, i.e.,
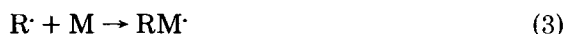
$$R_p = K'[\text{MMA}]$$

Hence, the acetyl acetonate radical must be produced as an initiating radical, and at the same time the valence of the central metal ion of Mn(acac)_3 must be reduced.
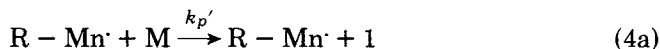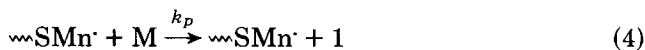
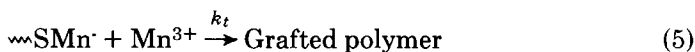The initiating acetyl acetonate free radical $(R\cdot)$ might attack silk giving rise to silk macroradicals.

$$\text{\footnotesize www}\text{SH} + \text{R}\cdot \xrightarrow{k_d} \text{\footnotesize www}\text{S}\cdot + \text{RH} \tag{1}$$

Initiation:

$$\text{\footnotesize www}\text{S}\cdot + \text{M} \xrightarrow{k_i} \text{\footnotesize www}\text{S} - \text{M}\cdot \tag{2}$$

$$\text{R}\cdot + \text{M} \rightarrow \text{RM}\cdot \tag{3}$$

Propagation:

$$\text{\footnotesize www}\text{SMn}\cdot + \text{M} \xrightarrow{k_p} \text{\footnotesize www}\text{SMn}\cdot + 1 \tag{4}$$

$$\text{R} - \text{Mn}\cdot + \text{M} \xrightarrow{k_p'} \text{R} - \text{Mn}\cdot + 1 \tag{4a}$$

Termination:

$$\text{\footnotesize www}\text{SMn}\cdot + \text{Mn}^{3+} \xrightarrow{k_t} \text{Grafted polymer} \tag{5}$$

$$\text{R} - \text{Mn}\cdot + \text{Mn}^{3+} \xrightarrow{k_t'\cdot} \text{Homopolymer} \tag{5a}$$

Oxidation:

$$\text{\footnotesize www}\text{S}\cdot + \text{Mn}^{3+} \xrightarrow{k_o} \text{Oxidation product} + \text{Mn}^{2+} + \text{H}^+ \tag{6}$$

At higher concentration of Mn(acac)_3, the free radicals produced on the backbone of the silk fiber might be oxidized to give rise to oxidation products or the termination of most of the formed reactive sites by the exceedingly formed free radicals at higher Mn (III) concentration, which results in a marked fall in the graft yield (Fig. 1).

Secondly, at higher Mn (III) concentration, the metal ions might interact with the monomer to give rise to higher amount of homopolymer, thereby decreasing grafting.

Effect of Acid Concentration on Grafting

The effect of acid concentration on grafting methyl methacrylate was studied by varying the concentrations of sulfuric acid between 0.02 and 0.3M. The percentage of grafting increases by increasing H_2SO_4 concentration up to 0.03M, and then a decreasing trend was noticed (Fig. 2). Similar observations have been
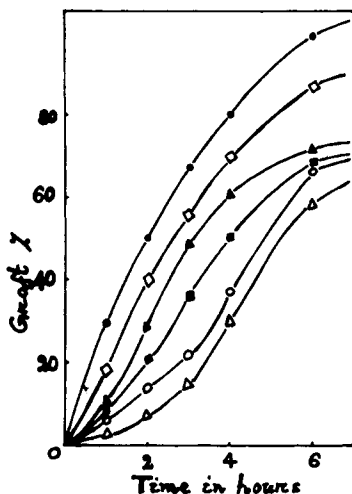
Fig. 2. Variation of % grafting: effect of acid concentration. [Mn(acac)$_3$] = 2 × 10^{-3}M, [MMA] = 0.045M, temp. = 50°C. (□), [H$^+$] = 0.02M; ●, [H$^+$] = 0.03M; ▲, [H$^+$] = 0.075M; ■ [H$^+$] = 0.15M; ○, [H$^+$] = 0.225M; △, [H$^+$] = 0.3M.

reported by Ranga Rao and Kapur[23] in the case of grafting acrylonitrile onto cotton using the ceric ion method.

In the reaction scheme previously described, if all the reactions are irreversible, then pH should not influence the rate of polymerization: this was not found to be true. This leads to the conclusion that the reactions (1) and (3) should be reversible, and if this is so, the increase in H$^+$ concentration should suppress the generation of radicals. This means that with increase in H$^+$ concentration, the graft-on should be reduced, which was found, in our case, after certain value of acid concentration.

The second reason might be due to the fact that the oxidation potential of Mn^{3+} changes with change of sulfuric acid concentration.[24] At higher concentration of acid, the oxidizing ability of Mn (III) is higher, which might favor the termination of growing polymer radical, thereby increasing the percentage of grafting.

Effect of Temperature on Grafting

The graft copolymerization was carried out at four different temperatures in the range of 40–55°C, keeping the concentrations of all other reagents constant (Fig. 3). The percentage of graft-on increases with increasing temperature up to 50°C, above which there is a decreasing trend. The dependence of rate of grafting on temperature between 40 and 50°C could be ascribed to the greater activation energy. The swellability of silk, solubility of monomer, and its diffusion rates are enhanced by increasing the temperature. Beyond 50°C, the decrease in percentage of grafting is probably due to the greater possibility of combination rates of the monomer at higher temperature.
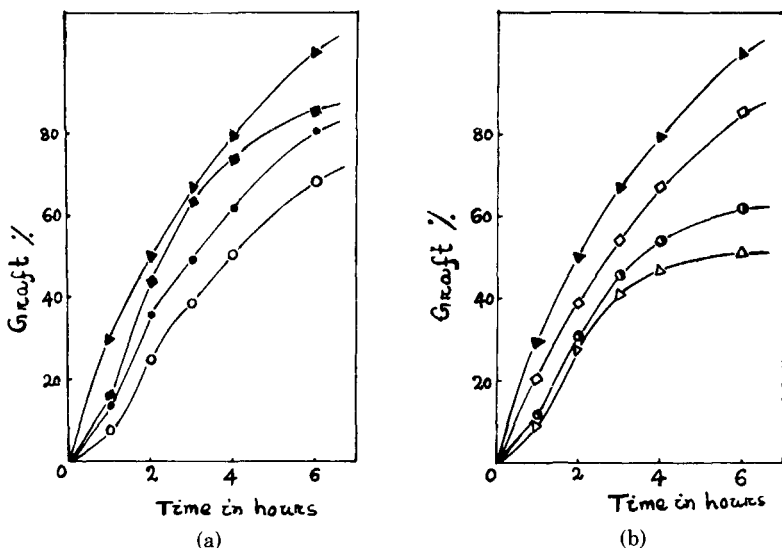
Fig. 3. Variation of % grafting: effect of temperature and some complexing agents. [Mn(acac)₃] = $2 \times 10^{-3}M$, [H⁺] = 0.03M, [MMA] = 0.045M. (a) Plots of graft % vs. hr at different temp.: O, temp. = 40°C; ●, temp. = 45°C; ▲, temp. = 50°C, ■, temp. = 55°C. (b) Plots of graft % vs. time in hr, in presence of complexing agents. ▲, control; △, [NaF] = 0.02M; □, [succinic acid] = 0.02M; ◐, [lutidine] = 0.02M.

Effect of Reaction Medium

The reaction medium plays an important role in grafting vinyl monomers onto silk fibers (Fig. 4). Addition of 10% (v/v) different water-soluble organic solvents decreases the graft yield. The graft yield follows the order acetone>acetic acid>dimethyl formamide>formic acid.

Further, the graft yield obtained with silk in different solvent/water mixtures is studied thoroughly (Fig. 5). It is clear that regardless of the solvents used,
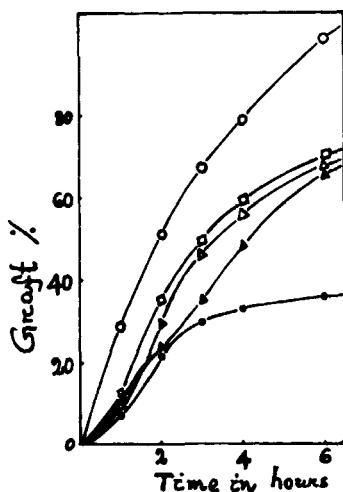

Fig. 4. Variation of % grafting: effect of 10% water miscible organic solvents. [Mn(acac)₃] = $2 \times 10^{-3}M$, [H⁺] = 0.03M, [MMA] = 0.045M, temp. = 50°C. Plots of graft % vs. time in hr: O, control; △, [CH₃COOH] = 10% (v/v); □, [CH₃COCH₃] = 10% (v/v); ●, [HCOOH] = 10% (v/v); ▲, [DMF] = 10% (v/v).
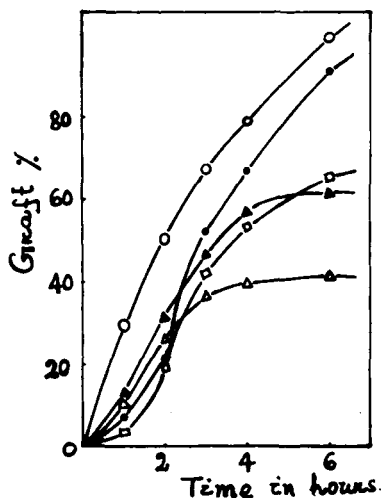
Fig. 5. Variation of % grafting: effect of solvent composition. [Mn(acac)$_3$] = 2 × 10^{-3}M, [H$^+$] = 0.03M, [MMA] = 0.045M, temp. = 50°C, time = 4 hr.   Plots: % graft vs. solvent composition: ●, dioxane; ▲, CH$_3$COOH; ■, HCOOH; ○, CH$_3$COCH$_3$.

an increase in the amount of solvent in the solvent/water mixture tends to decrease grafting.   Of these, a mixture of solvent/water at a ratio of 20:80 constitutes the most favorable medium for acetic acid, acetone, and DMF, while for dioxane and formic acid a 10:90 ratio constitutes the most favorable medium for grafting. Variation in grafting using different proportions of solvent and water could be explained by considering several factors such as: (1) miscibility of the monomer, (2) capability of swelling of the fiber, (3) formation of the solvent radical and/or the hydrogen and hydroxyl radicals from water under the influence of the primary radical species of the initiating system, (4) contribution of these solvents, hydrogen, and/or hydroxyl radicals in activation of silk, and (5) termination of the graft chain radical and silk macroradical via chain transfer.   While the first four
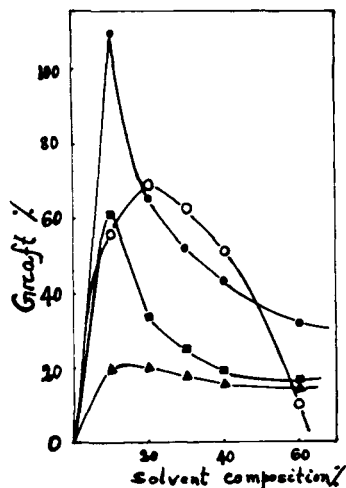

Fig. 6. Variation of % grafting: effect of neutral electrolytes. [Mn(acac)$_3$] = 2 × 10^{-3}M, [H$^+$] = 0.03M, [MMA] = 0.045M, temp. = 50°C.   Plots: % grafting vs. time in hr: ○, control; △, [KCl] = 0.02M; □, [MnSO$_4$] = 0.02M; ●, [CuSO$_4$] = 0.02 M; ▲, [Na$_2$SO$_4$] = 0.02M.

factors enhance grafting by simplifying access and diffusion of the monomer, the last factor adversely effects grafting by lowering the molecular size of the graft.

Effect of Inorganic Salts and Complexing Agents

The addition of neutral salts such as KCl, $MnSO_4$, $CuSO_4$, and Na_2SO_4 (0.02M) lowers the percentage of grafting (Fig. 6). This might be attributed to the ionic dissociation of the added electrolyte, which interferes with the usual polymerization reaction resulting in the premature termination of the growing chains. The addition of some complexing agents like NaF, succinic acid, and lutidine decreases the graft yield to a considerable extent (Fig. 3).

References

1. I. C. Watt, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C5**, 176 (1970).
2. K. Arai, *Block Graft Copolym.*, **1**, 193 (1973).
3. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.*, **14**, 193 (1976).
4. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.*, to appear.
5. W. L. Wasley, *Block Graft Copolym.*, **1**, 311 (1973).
6. K. Arai, S. Komino, and M. Negishi, *J. Polym. Sci. Part A-1*, **8**, 917 (1970).
7. K. Arai, M. Negishi, and T. Okaba, *J. Polym. Sci.*, **9**, 3456 (1965).
8. A. Hebeish and A. Bendak, *J. Polym. Sci.*, **18**, 1305 (1974).
9. A. Hebeish, S. H. Abdel-Fattah, and A. Bendak, *Angew. Makromol. Chem.*, **37**, 11 (1974).
10. A. Bendak, S. H. Abdel-Fattah, and A. Hebeish, *Angew. Makromol. Chem.*, **43**, 11 (1975).
11. M. C. Nayak, P. L. Nayak, and R. K. Samal, *J. Polym. Sci.*, **17**, 1 (1979).
12. M. C. Nayak, P. L. Nayak, and R. K. Samal, *Polymer*, to appear.
13. R. K. Samal, G. V. Suryanarayana, G. Panda, D. P. Das, and M. C. Nayak, *J. Appl. Polym. Sci.*, **26**, 41 (1981).
14. R. K. Samal, M. C. Nayak, P. C. Dash, A. K. Dhal, and D. P. Das, *J. Polym. Sci.*, submitted for publication.
15. T. Otsu, N. Minamii, and Y. Nishikawa, *J. Macromol. Sci. Chem.*, **2**(5), 905 (1968).
16. H. Singh, R. T. Thampy, and V. B. Chipalkatti, *J. Polym. Sci. Part A-3*, 1247 (1965).
17. D. Namasivayam, B. K. Pattnaik, and R. T. Thampy, *Makromol. Chem.*, **105**, 144 (1967).
18. K. Satish Babu, K. Panduranga Rao, K. T. Joseph, M. Santappa, and Y. Nayudamma, *Leather Sci.*, **21**, 261 (1974).
19. M. C. Nayak, P. L. Nayak, and R. K. Samal, *Angew Makromol. Chem.*, **80**, 95 (1979).
20. S. Haworth and J. R. Holker, *J. Soc. Dyer Colour.*, **82**, 257 (1966).
21. E. M. Arnett and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 3824 (1962).
22. C. H. Bamford and D. J. Lind, *Chem. Ind. (London)*, 1627 (1965).
23. S. Ranga Rao and S. L. Kapur, *J. Appl. Polym. Sci.*, **13**, 2646 (1969).
24. K. B. Wiberg, *Oxidation in Organic Chemistry*, Academic, New York, 1964.