Photograft Copolymerization of Methyl Methacrylate on Silk Fiber Using Titanium(III) Chloride–Potassium Persulphate Redox Initiator in a Limited Aqueous System. I

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ABSTRACT: Graft copolymerization of methyl methacrylate (MMA) onto mulberry silk fibers has been investigated in a limited aqueous system employing titanium(III) chloride–$K_2S_2O_8$ as the redox initiator under a photoactive condition with visible light. Polymerization in the presence of light at $32 \pm 1°C$ has been found to be more pronounced than in the dark under identical conditions. The percentage of grafting, the percentage of total conversion, and the percentage of grafting efficiency have been studied by varying the reaction time, concentration of monomer, initiator concentration, solvent composition, and pH of the medium. A high percentage of grafting ($\sim 93\%$), high grafting efficiency ($\sim 97\%$), and the percentage of total conversion ($\sim 25\%$) have been obtained with little homopolymer formation. Characterization of the grafted fibers has been investigated by Fourier transform infrared spectroscopy and scanning electron microscopy. Finally, the reaction mechanism has been discussed by considering hydrogen bonding. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2187–2193, 1999

Key words: MMA; silk fiber; grafting

INTRODUCTION

Modification of silk fiber properties through graft copolymer formation has been the subject matter of many investigators in recent years.[1–3] Lenka[4] reviewed the various initiation methods employed for graft copolymerization of vinyl monomers onto silk fiber. Many workers[5–7] have reported the use of metal acetylacetonate for graft copolymerization of vinyl monomers on silk. The use of $K_2S_2O_8$–thiourea as a redox initiator[8] and the SO_2–isoquinoline charge transfer complex as a photoinitiator[9] have also been reported. However, only limited information regarding grafting of vinyl monomers onto silk under visible light is available. This article reports the results of graft copolymerization of methyl methacrylate (MMA) onto silk fiber using a combination of titanium(III) chloride and potassium persulphate as a redox initiator under visible light in a limited aqueous system.

EXPERIMENTAL

Materials

Mulberry silk fibers were collected from Gandhi Sangha Baswa, Birbhum, West Bengal. Raw silk fibers were purified by scouring in an aqueous solution containing 0.4% soap for 2 h, followed by washing with 0.05% sodium carbonate solution and, finally, by distilled water. Potassium persulphate and titanium(III) chloride (15% solution in 10% HCl) from E. Merck (Germany) were used directly. The MMA monomer was purified by

standard procedure.[10,11] Other reagents were of analytical grade and were used directly.

Grafting Procedure

A weighed amount of silk fiber was taken in a borosilicate glass ampule fitted with standard joint and was soaked with an aqueous solution of potassium persulphate of known volume and concentration. A known volume of MMA was then added, followed by soaking with a known volume and concentration of titanium(III) chloride solution under nitrogen atmosphere. The ampule was then tightly stoppered. A polymerization experiment was conducted by placing the ampules at the middle of the space in between two parallely placed illuminated fluorescent tube lamps (40 W, Philips India Ltd.; major spectral energy distribution range from 4000 to 7000 Å) apart by 10 cm for specified time periods.

After polymerization, the contents were washed, dried, weighed, and transferred into a Soxhlet unit. The free PMMA (homopolymer) was extracted from the cross product by using benzene as the solvent. The residue containing a mixture of silk fiber–poly(methyl methacrylate) (PMMA) graft copolymers and unreacted silk fibers were treated with petroleum ether–methanol mixture to collapse their swollen structure and were then dried in a vacuum drier at 40°C and weighed. The dried residue was termed "apparent graft copolymer." Percentage of grafting, the percentage of total conversion, and the grafting efficiency were calculated in the following way after the correction being made for the loss in weight on treatment without MMA solution.

% Grafting

$$= \frac{\text{PMMA in the apparent graft copolymer (g)}}{\text{Silk sample taken (g)}} \times 100$$

Total conversion (%)

$$= \frac{\text{Total PMMA formed (g)}}{\text{MMA taken (g)}} \times 100$$

Grafting efficiency (%)

$$= \frac{\text{PMMA in the apparent graft copolymer}}{\text{Total PMMA formed (g)}} \times 100$$

Measurements

The Fourier transform infrared (FTIR) spectra have been recorded on a Perkin–Elmer (model FTIR-1600) instrument.

Table I   Polymerization of MMA on Silk

Initiator System[a]	Condition of Polymerization	Grafting (%)
$K_2S_2O_8$–$TiCl_3$	Dark, 32 ± 1°C, 3 h	20.87
$K_2S_2O_8$	Dark, 32 ± 1°C, 3 h	—
$TiCl_3$	Dark, 32 ± 1°C, 3 h	—
$K_2S_2O_8$–$TiCl_3$	Photo, 32 ± 1°C, 3 h	44.07
$K_2S_2O_8$	Photo, 32 ± 1°C, 3 h	—
$TiCl_3$	Photo, 32 ± 1°C, 3 h	—

[a] Initiator system: $K_2S_2O_8$, 1.08 mg; [$TiCl_3$], $3 \times 10^{-3}M$; MMA, 1 mL; water, 0.7 mL; pH 0.95.

The morphological structure has been investigated by scanning electron microscopy (SEM; model Philips PSEM-500).

RESULTS AND DISCUSSION

Preliminary study indicates (Table I) that the rate of polymerization in the dark at 32 ± 1°C is lower than that in presence of light under identical conditions. Thus, all the experiments were carried out under photoactive conditions.

The results showing the effect of variation of time of polymerization, monomer concentration, and solvent composition are shown in Figures 1–3, and the effect of variation in initiator concentration and pH are given in Tables II and III.

Effect of Variation of the Time of Polymerization, Keeping Other Parameters Constant

Results are shown in Figure 1. The percentage grafting and the percentage of total conversion increases over the range of the time period (1–8 h) studied. Grafting efficiency sharply increases up to 2 h, and then a slow increasing trend is observed.

Effect of Variation of the Monomer Concentration, Keeping Other Parameters Constant

The results of the percentage of grafting, the percentage of total conversion, and the grafting efficiency over the range of monomer volume (0.5 to 3 mL) studied are shown in Figure 2. Both the percentage of grafting and the percentage of total conversion increase at first, and, thereafter, both of them fall sharply. The grafting efficiency first increases sharply, and, thereafter, it levels off
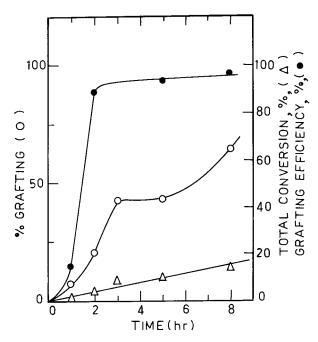
Figure 1   Effect of the variation of time on the photograft copolymerization of MMA on silk temperature, $32 \pm 1°C$; $K_2S_2O_8$ (aq), 1.08 mg; [$TiCl_3$], $3 \times 10^{-3}M$; total liquid volume, 1.7 mL; silk, 0.2 g; pH 0.95.

conversion, and the grafting efficiency are observed, whereas a decrease in trends are observed at the higher range of $TiCl_3$ content.

At higher a $TiCl_3$ concentration, the rate of termination probably prevails over initiation and propagation, and, therefore, the rate of polymerization decreases. A similar observation was reported by Bataille and Gonzalez[14] for the emulsion polymerization of styrene at a higher $TiCl_3$ concentration using the Ti^{+3}–S_2O_8'' redox system.

Effect of Variation of the Solvent Composition, Keeping Other Parameters Constant

The effects of solvent composition on the grafting of methyl methacrylate (MMA) on silk fiber are shown in Figure 3. In all cases, the percentage of grafting and the percentage of total conversion increases with a decrease in the solvent-to-water ratio to a maximum at a certain solvent-to-water composition, and, thereafter, both of them decrease. Among the different compositions studied, a solvent-to-water ratio of 43 : 57 for acetic acid, a ratio of 71.5 : 28.5 for ethanol, a ratio 57 : 43 for
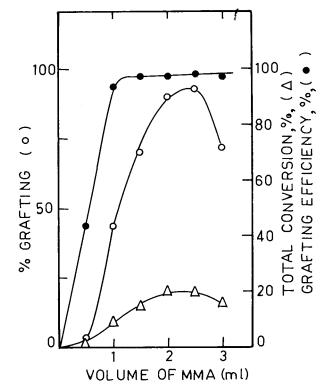
around 97%. The increasing trend is probably due to complexation of silk with the monomer and to the gel effect.[12] The decreasing trend at higher concentration range is probably due to the faster rate of combination and disproportionation of PMMA macroradical versus their combination with silk.[13]

Effect of Variation of the $K_2S_2O_8$ Constant, Keeping Other Parameters Constant

Related results are shown in Table II. Increasing $K_2S_2O_8$ content shows an enhancement in the percentage of grafting and the percentage of total conversion. The grafting efficiency sharply increases initially and later remains more or less steady around 93%. The increasing trend may be due to the formation of more grafting sites on the silk backbone with an increase in the amount of $K_2S_2O_8$, as shown in eqs. (2), (3), and (4).

Effect of Variation of the Titanium(III) Chloride Content, Keeping Other Parameters Constant

The results are shown in Table II. At the lower range of $TiCl_3$ content, an increasing trend in the percentage of grafting, the percentage of total

Figure 2   Effect of the variation of the monomer content on the photograft copolymerization of MMA on silk temperature, $32 \pm 1°C$; $K_2S_2O_8$ (aq), 1.08 mg; [$TiCl_3$], $3 \times 10^{-3}M$; water, 0.7 mL; silk, 0.2 g; time, 3 h; pH 0.95.
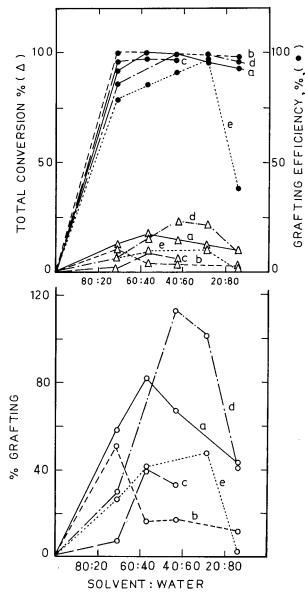
Figure 3 Effect of the variation of the solvent composition on the photograft copolymerization of MMA on silk temperature, $32 \pm 1°C$; $K_2S_2O_8$ (aq), 1.08 mg; [$TiCl_3$], $3 \times 10^{-3}M$; MMA, 1 mL; time, 3 h. Curves: (a) methanol, (b) ethanol, (c) formic acid, (d) acetic acid, and (e) dimethyl formamide.

methanol and formic acid, and a ratio of 28.5 : 71.5 for dimethyl–formamide forms the most suitable composition for grafting. The grafting efficiency in all cases more or less follows the same trend. With alcoholic solvents, the graft yield follows the order of MeOH > EtOH. With other solvents, the order is CH_3COOH > DMF > HCOOH. The variation in the amount of grafting in different solvent composition may be explained by considering the following factors:

1. Capability of swelling the fibers,
2. miscibility of the monomer,
3. formation of solvent radical/or hydrogen or hydroxyl radical from water by the primary radical species of the initiating systems, and
4. termination of the graft radical via chain transfer.

With increasing molecular weight of the alcohol, the hydrophilic character decreases, and the accessibility of monomer to the reactive sites on silk reduces. Therefore, the percentage of grafting decreases.

The organic acids, such as acetic acid and formic acid, are used as the solvents. In the case of acetic acid, the percentage of grafting is always better compared to that of formic acid. This is probably due to the fact that intermolecular hydrogen bonding is more pronounced in the case of formic acid, which protects the fiber from swelling. In the case of acetic acid, the swelling is better due to a lesser degree of hydrogen bonding. When DMF is used, it falls in between acetic acid and formic acid.

Effect of Variation of the pH of the System

Related results are shown in Table III. An enhancement in the percentage grafting, the percentage of total conversion, and the grafting efficiency are observed over the range of pH (0.3 to 0.95) studied. At higher pH, titanium(III) chloride hydrolyses, and the studies become difficult. This behavior may be due to the change in oxidation potential of $TiCl_3$ with change in acid concentration. With decreasing pH, the reducing ability of $TiCl_3$ gradually decreases and the radical generation process is retarded, which affects the percentage grafting. At lower pH, the fiber becomes brittle, and the study becomes impractical.

FTIR Spectra

The FTIR spectra of the ungrafted silk fiber and grafted silk fiber are shown in Figure 4. The absorption bands at 1654 cm^{-1} and in the range of 3292–3308, 1543–1559, 1231–1241, and 668–682 cm^{-1}, which appear in the spectra of ungrafted and grafted silk fiber are due to amide-I, N—H $\cdots$ O amide-II, amide-III, and amide-V, respectively. The absorbance at 1734 cm^{-1}, which is due to the ester group of PMMA present in the grafted silk fiber, indicates the evidence of grafting.

Table II   Effect of Variation of K₂S₂O₈ and TiCl₃ Content on Photograft Copolymerization of MMA on Silk Under Visible Light

$K_2S_2O_8$ (mg)	$TiCl_3 \times 10^{-3} M$	Grafting (%)	Total Conversion (%)	Grafting Efficiency (%)
0.674	3.0 (fixed)	16.0	4.0	86.0
0.943	3.0 (fixed)	39.0	9.0	93.0
1.078	3.0 (fixed)	44.0	10.0	94.0
0.782 (fixed)	2.5	23.0	6.0	91.0
0.782 (fixed)	3.5	18.0	5.0	83.0
0.782 (fixed)	4.0	6.0	2.0	73.0

Silk, 0.2 g; MMA, 1 mL; Time, 3 h; pH 0.95; Temperature, 32 ± 1°C.

Morphological Structure

The morphological structure of the ungrafted and grafted silk fibers are shown in Figure 5. The surface of the ungrafted silk fiber is smooth. The presence of granules and lumps on the surface of the grafted fibers are due to chemically bonded MMA homopolymer.

MECHANISM

Arai et al.[15] and Enomoto and Suzuki[16] showed that the glycine residue was the site of grafting on silk. Valiev et al.[17] also showed the rupture of intermolecular hydrogen bonding while studying the grafting of vinyl fluoride on silk. Now, from our FTIR spectroscopic study, as shown in Figure 6, it is observed that the characteristic absorption band of N—H · · · O (N—H stretching vibration due to hydrogen bonding) at 3292.1 cm⁻¹ for ungrafted silk gradually shifts to 3307.9 cm⁻¹ as the percentage of grafting increases. This may be due

Table III   Effect of Variation of pH on Photograft Copolymerization of MMA on Silk at 34.5 ± 0.5°C in a Limited Aqueous System Using a Ti⁺³–S₂O₈ Redox System

pH of the Medium	Grafting (%)	Total Conversion (%)	Grafting Efficiency (%)
0.30	1.70	0.80	45.33
0.54	25.71	6.16	88.94
0.75	35.52	7.88	96.22
0.95	64.42	13.80	99.61

Initiator system: $K_2S_2O_8$, 1.08 mg; [$TiCl_3$], $3 \times 10^{-3} M$; MMA, 1 mL; Water, 0.7 mL; Time, 3 h.

to weakening of hydrogen bonding[18] between adjacent silk chains. Hence, on the basis of the observations of the above-mentioned workers, together with ours, it may be predicted that the glycine part of the silk is the most accessible sites for grafting.

Again, the end group analysis[19] of the free homopolymer (PMMA) from the gross products gave a positive response for sulphate and hydroxyl end groups, which confirms the presence of sulphate ion radical ($SO_4^{-\bullet}$) and hydroxyl radicals ($^\bullet OH$) as primary radicals in this system. Taking all of the above into consideration, the probable mechanism may be described as follows.

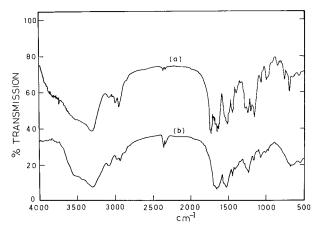$$^-O_3S—O—O—SO_3^- + Ti^{+3} \rightarrow$$

$$Ti^{+4} + SO_4^{-\bullet} + SO_4^= \quad (1)$$

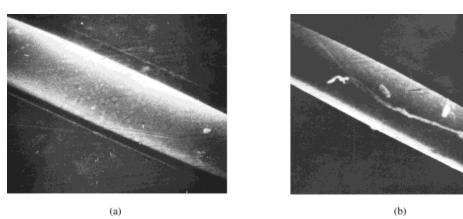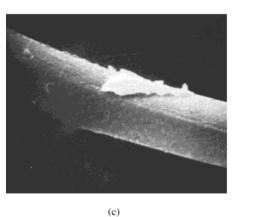**Figure 4**   FTIR spectra of (a) grafted silk fiber and (b) upgrafted silk fiber.
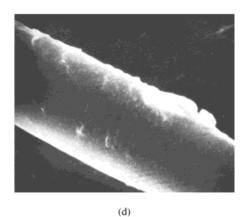
(a)   (b)

(c)   (d)

Figure 5   Scanning electron micrographs of MMA-grafted silk fibers (3200×). Graft yield (%): (a) 0, (b) 21.20, (c) 93.30, and (d) 113.20.

$$SO_4^{-} + H_2O \rightarrow HSO_4^{-} + HO^{\bullet} \qquad (2)$$

$$S_2O_8^{=} \rightarrow 2\,SO_4^{-} \qquad (3)$$

Equations (1), (2), and (3) are faster in the presence of light compared to those in dark (Table I). Now, the formation of free radicals on the silk backbone and the initiation step may be represented by eqs. (4) and (5).

$$\rangle NH + SO_4^{-\bullet}/HO^{\bullet} \xrightarrow{k_i} \rangle N^{\bullet} + HSO_4^{-}/H_2O \qquad (4)$$

$$\rangle N^{\bullet} + M \xrightarrow{k_i} \rangle NM^{\bullet} \qquad (5)$$

where $\rangle NH$ comes from the glycine part of silk, $\rangle N^{\bullet}$ is the corresponding radical, M is the monomer, k_i and k_i are the respective rate constants.

Propagation and termination steps are shown by eqs. (6) and (7).

$$\rangle NM^{\bullet}_{n-1} + M \xrightarrow{k_p} \rangle NM^{\bullet}_{n} \qquad (6)$$

$$\rangle NM^{\bullet}_{n} + \rangle NM^{\bullet}_{n} \xrightarrow{k_t} \text{dead polymer} \qquad (7)$$

where k_p and k_t are rate constants for propagation and termination.

Furthermore, it may be assumed that the decrease in grafting (%) (as shown in Table II) with an increase in the $TiCl_3$ content is due to the consumption of SO_4^{-} by Ti^{+3} ion,[14] as shown by the following equation:

$$Ti^{+3} + SO_4^{-} \rightarrow Ti^{+4} + SO_4^{=}$$

effective in the presence of visible light compared to that of the dark (Table I) for the graft copolymerization of MMA on silk. The formation of a little homopolymer is also an added advantage to this system. Characterization of the grafted products by FTIR and SEM indicate the direct evidence of grafting on the silk fiber backbone.
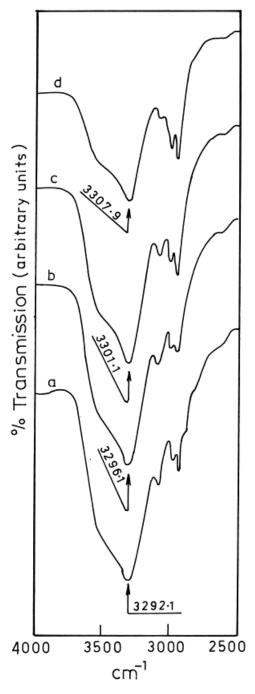
Figure 6 FTIR spectra of MMA-grafted silk fibers in the region of 4000–2500 cm^{-1}. Graft yield (%): (a) 0, (b) 21.20, (c) 44.07, and (d) 93.30.

CONCLUSION

From experimental results, it is clear that the present initiator system (Ti^{+3}–S$_2$O$_8''$) is very much

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