

Graft Copolymerization of Methyl Methacrylate on Silk Fiber Using Mohr's Salt—Potassium Persulfate as Redox Initiator Under Visible Light in a Limited Aqueous Medium

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SYNOPSIS

Graft copolymerization of methylmethacrylate onto mulberry silk fibers was studied under photoactive conditions with visible light using the Mohr's salt-potassium persulfate as the redox initiator in a limited aqueous medium. Polymerization in the presence of light at $40 \pm 1^\circ\text{C}$ was found to be more pronounced than that in the dark at $40 \pm 1^\circ\text{C}$. Percent grafting, percent total conversion, and grafting efficiency under different sets of conditions were studied, and the mechanisms of polymerization and graft copolymer formation were discussed. Characterization of the grafted fibers was done by Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, and thermogravimetry. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Silk possesses many outstanding properties such as moisture absorption, dyeability, and excellent fabric in striking contrast with the synthetic fibers. However, to make it more useful in its field of application, further improvement in its physicochemical properties is necessary. In recent years,¹⁻³ attention has been focused on the introduction of vinyl or other monomers into the silk network through grafting. Lenka⁴ has reviewed the various initiation methods for the graft copolymerization of vinyl monomers onto silk fibers. The use of various initiators for the graft copolymerization of vinyl monomers onto silk fibers has been reported by many workers.⁵⁻⁹ However, only limited information regarding the grafting of vinyl monomers onto silk fibers under visible light in limited aqueous media is available in the literature. This article reports the results of the graft copolymerization of methylmethacrylate (MMA) onto silk fiber using a combination of Mohr's salt and potassium persulfate as the redox initiator under visible light in limited aqueous medium.

EXPERIMENTAL

Materials

Mulberry silk fibers were collected by the courtesy of 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 with cold distilled water until it was alkali free. Mohr's salt from Glaxo laboratories and potassium persulfate from E. Merck were used directly. Monomer MMA was purified by a standard procedure.^{10,11} Other reagents used were of analytical grade.

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 persulfate of known volume and concentration. A known volume of MMA was then added, followed by soaking with a known volume and concentration of Mohr's salt solution under nitrogen atmosphere. The ampule was then tightly stoppered. The polymerization experiment was conducted by placing the ampules at the middle of the space between two par-

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Table I Polymerization of MMA on Silk (Initiator System: $K_2S_2O_8$ [10.80 mg], Mohr's Salt [15.80 mg], MMA [1 ml], Water [0.8 ml], pH [2.22])

Initiator System	Condition of Polymerization	Grafting (%)
Mohr's salt/ $K_2S_2O_8$	Dark, $40 \pm 1^\circ C$, 2 h	206.71
$K_2S_2O_8$	Dark, $40 \pm 1^\circ C$, 2 h	69.82
Mohr's salt	Dark, $40 \pm 1^\circ C$, 2 h	— ^a
Mohr's salt/ $K_2S_2O_8$	Photo, $40 \pm 1^\circ C$, 2 h	298.80
$K_2S_2O_8$	Photo, $40 \pm 1^\circ C$, 2 h	93.92
Mohr's salt	Photo, $40 \pm 1^\circ C$, 2 h	— ^a

^a Indicates no grafting.

allely placed and illuminated fluorescent tube lamps apart by 10 cm for specified time periods.

After polymerization, the contents were washed, dried, weighed, and transferred into a soxhlet unit. The free polymethylmethacrylate (PMMA) (homopolymer) was extracted from the gross product by using benzene as the solvent. The residue containing a mixture of silk fiber-PMMA graft copolymers and unreacted silk fibers was treated with petroleum ether-methanol mixture to collapse the swollen structure; it was then dried in a vacuum drier at $40^\circ C$ and weighed. The dried residue was termed "apparent graft copolymer." Percent grafting, percent total conversion, and grafting efficiency were calculated in the following way after correction was made for the loss in weight on treatment without MMA solution.

% Grafting

$$= \frac{\text{PMMA in the apparent graft copolymer (g)}}{\text{Silk sample taken (g)}} \times 100 \quad (1)$$

Total conversion (%)

$$= \frac{\text{Total PMMA formed (g)}}{\text{MMA taken (g)}} \times 100 \quad (2)$$

Grafting efficiency (%)

$$= \frac{\text{PMMA in the apparent graft copolymer (g)}}{\text{Total PMMA formed (g)}} \times 100 \quad (3)$$

Measurements

The Fourier transform infrared spectroscopy (FTIR) spectra have been recorded on a Perkin Elmer (Model FTIR-1600) instrument. The morphological structure has been investigated by a scanning electron microscope (Model Philips PSEM-500).

The differential scanning calorimetric (DSC) measurements have been performed at a heating rate of $20^\circ C/min$ on a DSC-7 instrument of Perkin Elmer under nitrogen atmosphere. The DSC range and sample weight of 5 mcal/s and 6 mg have been used in each case. Thermal decomposition has been studied using a delta series TGA-7 instrument of Perkin Elmer under nitrogen atmosphere at a heating rate of $20^\circ C/min$.

RESULTS AND DISCUSSION

Preliminary studies indicate (Table I) that the rate of polymerization in the dark at $40 \pm 1^\circ C$ is lower than that in the presence of light at $40 \pm 1^\circ C$. Therefore, all successive experiments have been carried out under photoactive conditions. The results showing the effect of the variation of time, monomer concentration, and initiator concentration are shown in Figures 1-4, and the effect of the variation of pH is given in Table II.

Effect of Variation of Time of Polymerization

Related results are shown in Figure 1. Both percent grafting and percent total conversion increase sharply up to 3 h of polymerization and then level off over the time period (1-5 h) studied. Grafting efficiency remains steady throughout the time period studied.

Effect of Variation of Monomer Concentration

The results of percent grafting, percent total conversion, and grafting efficiency over the range of monomer content (0.25-1.5 ml) are shown in Figure 2. For a given period of polymerization (2 h), both percent grafting and percent total conversion increase with increasing monomer concentration. Grafting efficiency remains steady throughout the

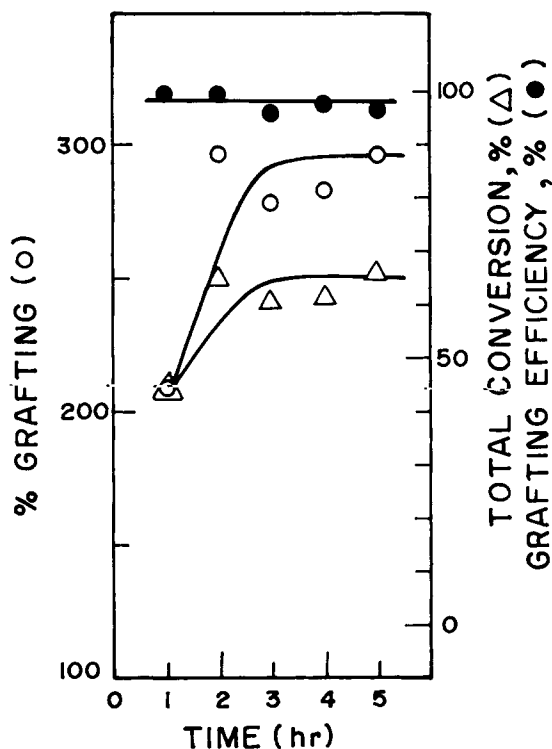


Figure 1 Effect of variation of time on photograft aqueous copolymerization of MMA on silk fiber. Temperature, $39 \pm 1^\circ\text{C}$; $\text{K}_2\text{S}_2\text{O}_8$ (aqueous), 10.8 mg; Mohr's salt (aqueous), 15.78 mg; water, 0.8 mL; MMA, 1 mL; silk fiber, 0.2 g; pH, 2.22.

range of monomer concentrations studied. The increasing trend may be due to the formation of complex between silk and monomer or gel effect.¹²

Effect of Variation of Mohr's Salt Content

The results are shown in Figure 3. Both percent grafting and percent total conversion increase rapidly initially and fall thereafter sharply. Grafting efficiency remains steady over the range of Mohr's salt concentration ($0.3 \times 10^{-1}\text{M}/0.30$ ml to $0.45 \times 10^{-1}\text{M}/0.45$ ml) studied. The decreasing trend at higher Mohr's salt concentration may be due to the consumption of sulfate ion radical ($\text{SO}_4^{\cdot-}$) by the ferrous ion present¹³ in the system, as shown by eq. (11). A similar observation was also reported by Bataille et al.¹⁴ for the emulsion polymerization of styrene initiated by the $\text{K}_2\text{S}_2\text{O}_8/\text{Fe}^{+2}$ redox system.

Effect of Variation of $\text{K}_2\text{S}_2\text{O}_8$ Content

Results showing the variation of $\text{K}_2\text{S}_2\text{O}_8$ content ($0.30 \times 10^{-1}\text{M}/0.30$ ml– $0.45 \times 10^{-1}\text{M}/0.45$ ml) (Figure 4) indicate that percent grafting and percent

total conversion follow an increasing trend with increasing $\text{K}_2\text{S}_2\text{O}_8$ content, whereas grafting efficiency remains steady. The increasing trend may be due to the formation of more grafting sites on the silk backbone with the increase in the amount of $\text{K}_2\text{S}_2\text{O}_8$, as shown by eqs. (5), (6), and (7).

Effect of Variation of pH of the System

Related results are shown in Table II. An enhancement in grafting (%) is observed over the range of pH (1.78–2.22) studied. With decreasing pH, the reducing ability of ferrous ion gradually decreases¹⁵ and the radical generation process is retarded, which affects the grafting reaction.

FTIR Spectra

The FTIR spectra of ungrafted silk and MMA-grafted silk fiber are shown in Figure 5. It is ob-

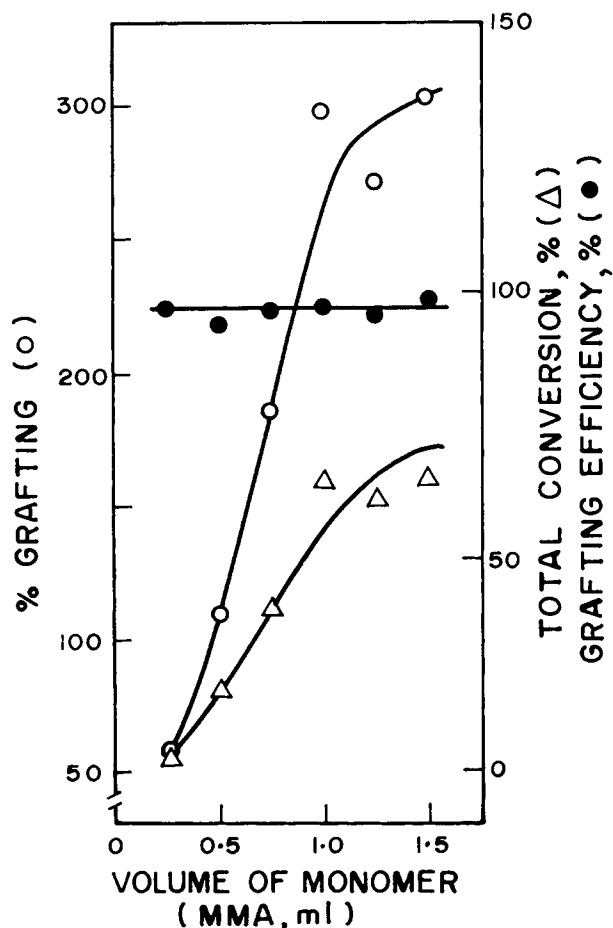


Figure 2 Effect of variation of monomer content on photograft copolymerization of MMA on silk fiber. Temperature, $39 \pm 1^\circ\text{C}$; $\text{K}_2\text{S}_2\text{O}_8$ (aqueous), 10.8 mg; Mohr's salt (aqueous), 15.78 mg; water, 0.8 mL; silk fiber, 0.2 g; time, 2 h; pH, 2.22.

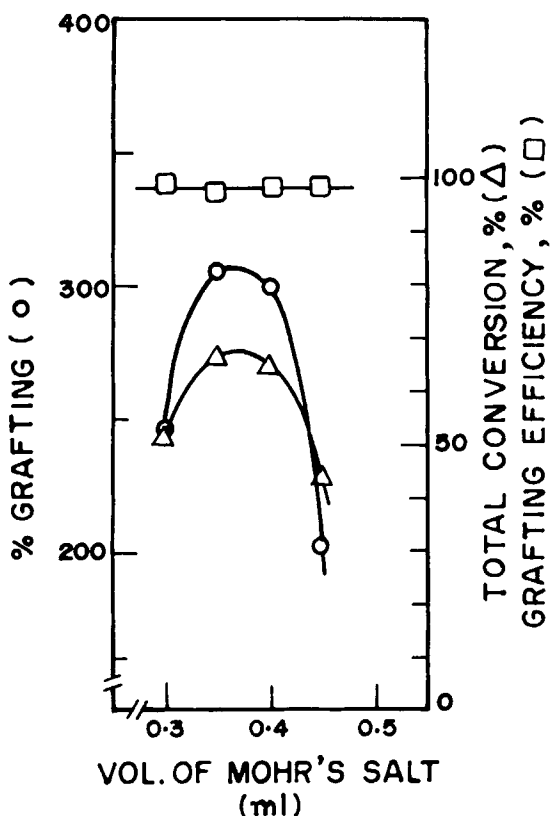


Figure 3 Effect of variation of Mohr's salt content on photograft copolymerization of MMA on silk. Temperature, $39 \pm 1^\circ\text{C}$; $\text{K}_2\text{S}_2\text{O}_8$ (aqueous), 10.8 mg; Mohr's salt (aqueous), 11.83–17.75; silk fiber, 0.2 g; time, 2 h; pH, 2.22.

served that both ungrafted and grafted silk show the characteristic absorption band of NH - - O, amide I, amide II, amide III, and amide V at 3,292–3,312.2, 1,654, 1,522–1,543, 1,231–1,242, and 668–682 cm^{-1} , respectively. The absorbance at 1,734 cm^{-1} in the grafted silk fiber and also in the homopolymer (PMMA) confirms the presence of an ester group.

Morphological Structure

The morphological structures of the ungrafted and MMA-grafted silk fibers of varying percent grafting are shown in Figure 6. The surface of the ungrafted silk fiber is smooth. The presence of granules or lumps on the surface of the grafted fibers is due to the chemically bonded PMMA on the fiber.

DSC Studies

Figure 7 shows the DSC thermograms of controlled silk (ungrafted), MMA-grafted silk fiber, and PMMA (homopolymer). Ungrafted silk fiber [Fig. 7(d)] shows a single endothermic peak at 330.8°C ,

which is attributed to the thermal decomposition of silk fibroin.¹⁶ PMMA [Fig. 7(e)] exhibits a sharp endothermic peak at around 375.7°C . The thermogram of a physical mixture of silk and PMMA (2 : 1) is shown in the Figure 7(c). Figure 7(a) shows the thermograms of MMA-grafted silk fiber of 56.01% grafting, and it exhibits two endothermic peaks at 333.8 and 387°C (in the shoulder form). Figure 7(b) shows the thermogram of 298.80% grafted fiber. The position of one endothermic peak which is due to the decomposition of silk fibroin remains almost unchanged, regardless of MMA grafting. The other peak, which is due to MMA polymer, shifts to a higher temperature as percent grafting increases. A similar shifting in trend to a higher temperature was reported by Tsukada and Yamaguchi.¹⁷ These DSC results indicate that the grafted silk fibers show a low compatibility in thermal properties in the relationship between silk fiber and grafted chains of PMMA.

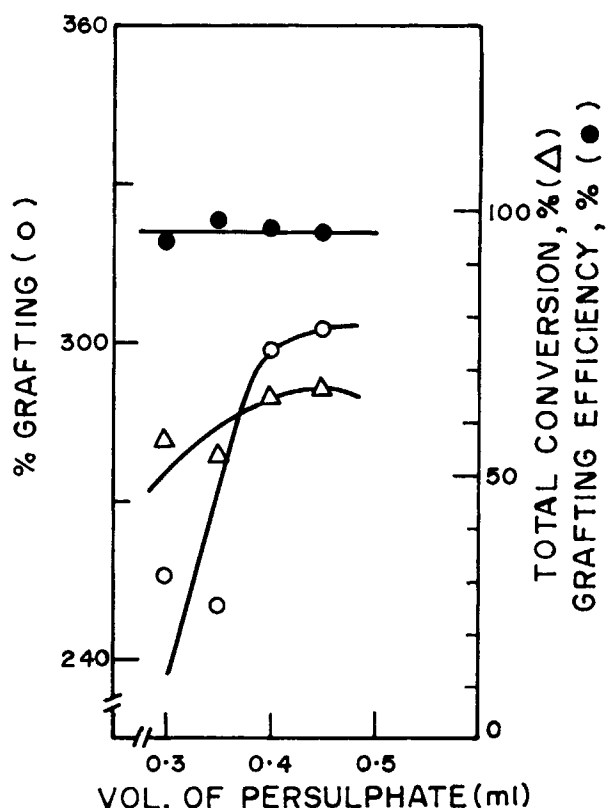


Figure 4 Effect of variation of potassium persulfate content on photograft copolymerization of MMA on silk fiber. Temperature, $39 \pm 1^\circ\text{C}$; Mohr's salt (aqueous), 15.78 mg; $\text{K}_2\text{S}_2\text{O}_8$ (aqueous), 8.1–12.15 mg; silk fiber, 0.12 g; time, 2 h; pH, 2.22.

Table II Effect of Variation of pH on Photograft Copolymerization of MMA on Silk at $36 \pm 1^\circ\text{C}$ in Limited Aqueous System Using Mohr's Salt/ $\text{K}_2\text{S}_2\text{O}_8$ Redox Initiator System (Initiator System: $\text{K}_2\text{S}_2\text{O}_8$ [10.80 mg], Mohr's Salt [15.80 mg], MMA [1 ml], Water [0.8 ml], Time [2 h])

Medium pH	% Grafting	Total Conversion (%)	Grafting Efficiency (%)
1.78	236.76	52.48	96.23
2.22	269.18	57.44	99.50
2.31	297.65	65.19	97.14

Thermogravimetric Analysis

Table III shows the initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), and residual weight (RW) for controlled silk, MMA-grafted silk fiber, MMA polymer, and the physical mixture of silk and PMMA. With an increase in percent grafting, an enhancement in decomposition temperature (T_D) values is observed. T_m values for both stages of pyrolysis are higher than that of controlled silk. RW follows a decreasing trend with an increase in percent grafting. The only exception is in the case of MMA-grafted silk fiber, with a graft yield of 56.01%.

Table IV shows the T_D at different weight losses for different samples. It is observed that the T_D values are higher than that of controlled silk up to 50% decomposition; beyond that, the values are lower than that of ungrafted silk. Again, with an increase in percent grafting, a falling trend in T_D values is observed. From Table IV, it can be said that the

effect of grafting on the thermal stability of the silk depends on the amount of PMMA incorporated into the fiber.

The increasing trend is probably due to the elimination of small molecules like H_2O , NH_3 , CO_2 , etc., from the grafted fibers; with the formation of cross-linking, which acts as an infusible support and provides some thermal resistance to the fiber.¹⁸ The decreasing trend may be due to the earlier decomposition of PMMA chains than the chains of the silk fiber.

Mechanism

From the FTIR spectroscopic study (Figure 8), it is observed that the characteristic absorption band of $\text{NH} \cdots \text{O}$ (N—H stretching vibration due to hydrogen bonding) at $3,292.1 \text{ cm}^{-1}$ for ungrafted silk fiber shifts to $3,310.9 \text{ cm}^{-1}$ for 56.01% fiber. This

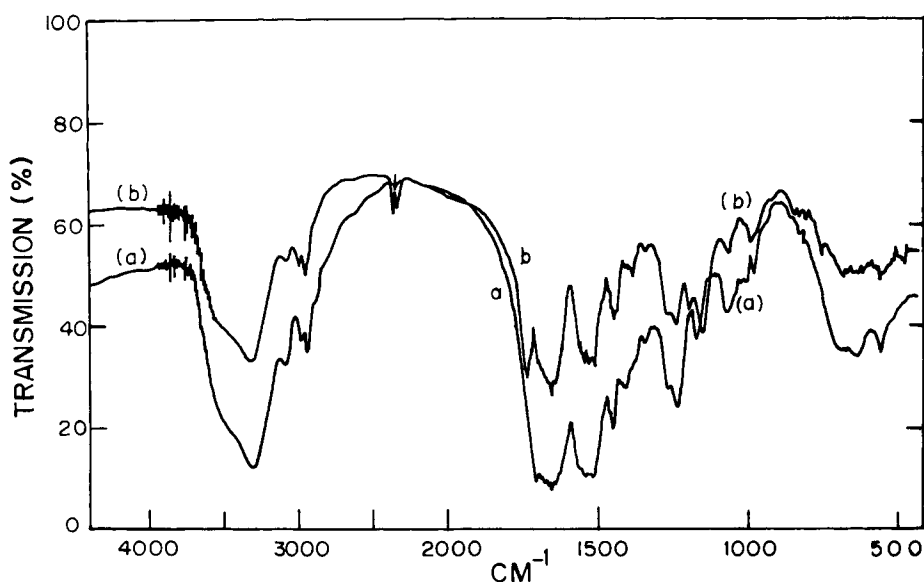


Figure 5 FTIR spectra of (a) ungrafted and (b) grafted silk fiber.

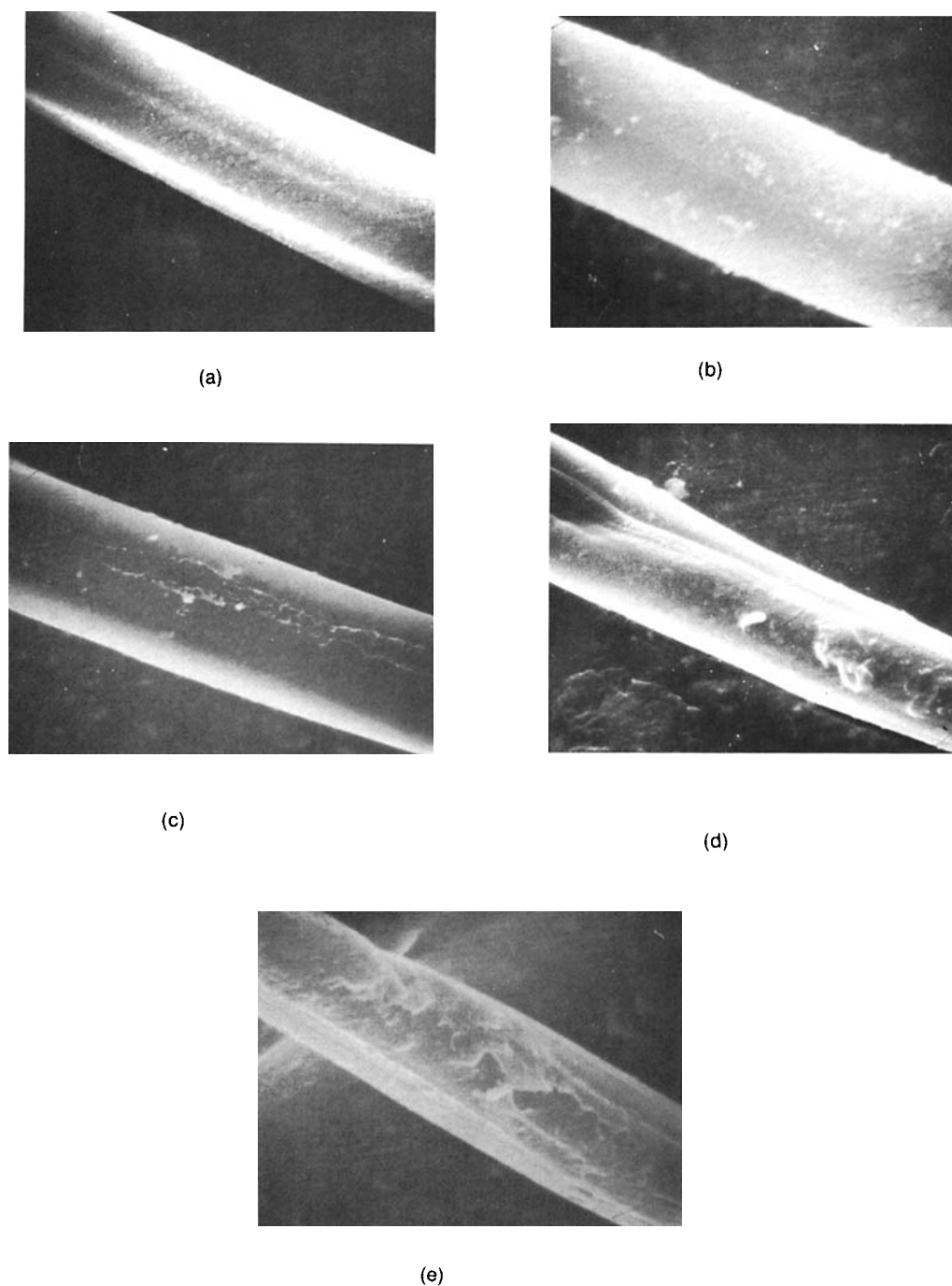


Figure 6 Scanning electron micrographs of MMA-grafted silk fibers (3,200 \times). Graft yield (%): (a) 0, (b) 56.01, (c) 110.11, (d) 208.65, (e) 306.46.

value remains practically steady with a further increase in percent grafting.

This shift in absorption to a higher-wave number may be ascribed to the weakening of hydrogen bonding¹⁹ between adjacent silk chains. Valeiv et

al.²⁰ observed the rupture of intermolecular hydrogen bonding while studying the grafting of vinyl fluoride on silk. Arai et al.²¹ and Enomoto and Suzuki²² showed that the glycine residue was the site of grafting on silk. Hence, on the basis of the observations

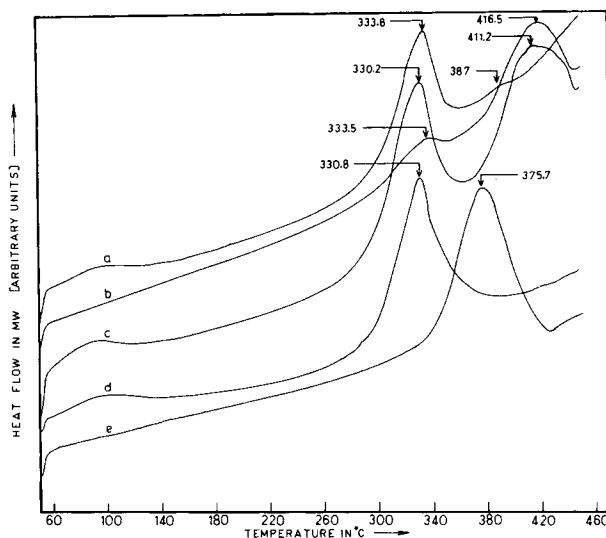
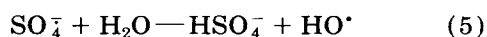
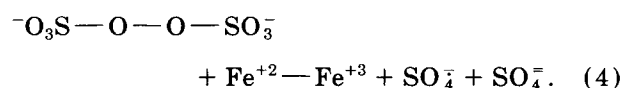


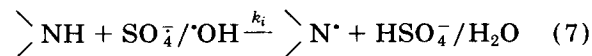
Figure 7 DSC thermograms of MMA polymer (e) and MMA-grafted silk fibers. Graft yield (%): (a) 56.01, (b) 298.80, (c) mixture of silk and PMMA (2 : 1), (d) 0.

of the above-mentioned workers together with ours, it may be predicted that the NH part of glycine is the most accessible site for grafting initially.

Again, the end-group analysis²³ of the free PMMA separated from grafted fiber indicates the presence of a sulfate ion radical (SO_4^-) and a hydroxyl radical ($\cdot\text{OH}$) as the primary radicals in the system. Taking all these into consideration, the probable mechanism may be described as

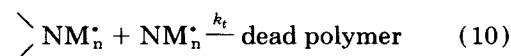
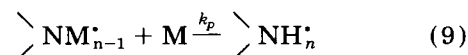


Equations (4), (5), and (6) are faster in the presence of light compared with dark, as revealed by the experiment. Now the formation of free radical on silk backbone and the initiation step may be represented by eqs. (7) and (8):



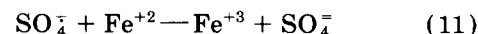
where >NH comes from the glycine part of silk, $\text{>N}\cdot$ is the corresponding radical, M is the monomer, and k_i and k_i' are the respective rate constants.

The propagation and termination steps are represented by eqs. (9) and (10).



Where k_p and k_t are the rate constants for propagation and termination, respectively.

Furthermore, the decrease in percent grafting with the increase in Mohr's salt content may be explained by the following equation



CONCLUSION

From the experimental results, it is seen that the initiator system ($\text{Fe}^{+2}/\text{S}_2\text{O}_8^{2-}$) is much more effective

Table III Thermal Analytical Data for Controlled Silk, MMA Grafted Silk, MMA Polymer, and Physical Mixture of Silk and MMA Polymer

Sample	% Grafting	T_i	T_{m1}^a	T_{m2}^b	RW (%)
Controlled silk (ungrafted)	—	241	347	—	38.75
Silk grafted with MMA	56.01	258	394	—	47.97
	110.11	274	390	456	28.33
	298.89	280	—	460	14.86
MMA polymer	—	270	—	420	Negligible
Physical mixture of silk and MMA polymer (64 : 36)	—	278	388	423	34.73

^a T_m value for first step.

^b T_m value for second step.

Table IV Temperature of Decomposition (T_D) of Different Weight Losses of Controlled Silk, MMA Grafted Silk, MMA Polymer, and Physical Mixture of Silk and MMA Polymer

Sample	% Grafting	Temperature of Decomposition (T_D) in °C at Weight Loss (%)				
		20	30	40	50	60
Controlled silk (ungrafted)	—	329	349	369	420	493
Silk grafted	56.01	379	403	433	489	—
	110.11	378	390	424	447	467
	298.80	380	402	423	438	455
MMA polymer	—	382	393	400	407	412
Physical mixture of silk and MMA polymer (64 : 36)	—	385	402	416	426	440

in the presence of visible light compared with dark (Table I). The characterization of the grafted products by FTIR, DSC, scanning electron microscopy, and thermogravimetry indicates the direct evidence of grafting on the silk fiber backbone.

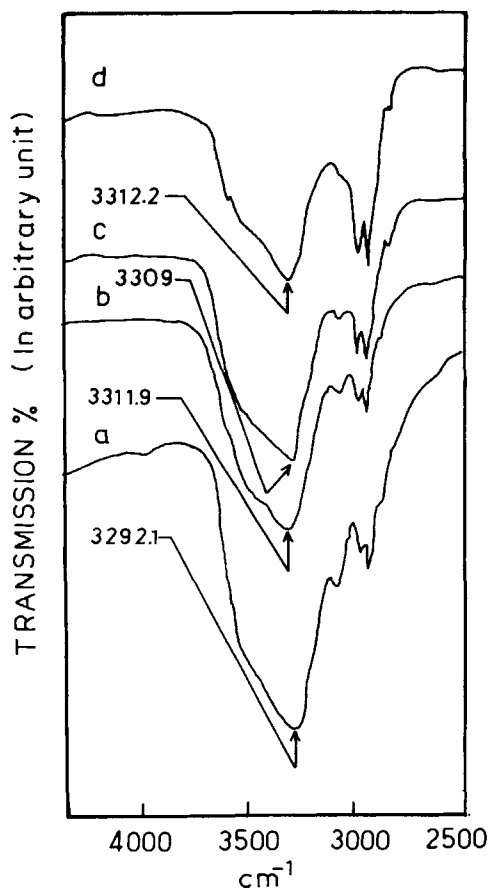


Figure 8 FTIR spectra of MMA-grafted silk fibers in the region 2,500–4,000 cm^{-1} . Graft yield (%): (a) 0, (b) 56.01, (c) 110.11, (d) 298.80.

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