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Grafting Vinyl Monomers onto Tussah Silk Fiber. I. Graft Copolymerization of Methyl Methacrylate onto Nonmulberry Tussah Silk by Tetravalent Cerium Ion

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ABSTRACT

The graft copolymerization of methyl methacrylate onto nonmulberry natural tussah silk fibers was investigated in aqueous solution using tetravalent cerium as initiator. The rate of grafting was determined by varying the monomer concentration, the cerium(IV) concentration, the temperature, and the nature of the silk. With increasing monomer concentration the graft yield increased (up to 0.657 $\underline{M}$) and thereafter decreased. The graft yield also increased with increasing cerium(IV) concentration. The graft-on was influenced by chemical modification of the tussah silk prior to grafting. The effect of certain inorganic salts on the rate of grafting was investigated.

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INTRODUCTION

Modification of the properties of such natural macromolecules as wool, cotton, silk, cellulose, and collagen by graft copolymerization has attracted attention in recent years. Tussah fiber, an excellent nonmulberry natural silk, has been extensively used in the textile industry. Synthetic polymers were grafted onto tussah silk by the authors to obtain improved textile performance. This paper presents the results of studies of grafting methyl methacrylate onto tussah silk fibers using tetravalent cerium ion. Tetravalent cerium ions in aqueous solution have been used extensively in redox studies of organic as well as inorganic substrates [1, 2]. Initiation of polymerization of vinyl monomers by ceric ions has been reported by Bacon [3]. Saldick [4] quantitatively studied the initiating capacities of ceric ions in different acid media. Mino, Kaizerman, and Rasmussen [5] reported the kinetics of vinyl polymerization using the redox system. Katai et al. [6] investigated the kinetics of polymerization of vinyl monomers by the ceric sulfate-ethylene glycol system. Santappa et al. [7-9], Machida et al. [10-13], and Mohanty and co-workers [14-16] have also extensively studied the aqueous polymerization of various vinyl monomers initiated by the ceric ion/organic substrate redox system. On account of its high initiating efficiency compared to other known redox systems, it has gained considerable importance in grafting vinyl monomers onto cotton cellulose [17-27], wool [28, 29], collagen [30-32], and nylon [33-35]. The redox graft copolymerization of vinyl monomers onto mulberry silk has been reported by Nayak et al. [36]. This communication presents the results of studies of grafting methyl methacrylate onto nonmulberry tussah silk fibers using tetravalent cerium ion. An investigation regarding changes in desirable physical properties of the grafted fiber is underway.

EXPERIMENTAL

Materials

Tussah silk fibers were collected from Orissa Co-op Handicrafts Corporation Ltd., Bhubaneswar, India. The raw fibers were purified by scouring for 2 h in an aqueous solution containing 0.4% soap and then washed with 0.05% Na_2CO_3 solution followed by boiling water and lastly by soxhleting in acetone for 12 h. The methyl methacrylate (MMA) used was freed from stabilizer by washing with 5% NaOH solution and then dried with anhydrous Na_2SO_4 and distilled under N_2 with reduced pressure. Water, twice distilled over alkaline permanganate, was used, and the other reagents, such as ceric ammonium sulfate, ferrous ammonium sulfate, and sulfuric acid, were BDH AnalaR products. Ceric ion concentration in stock ceric solution was estimated by titrating against standard ferrous sulfate solution.

Procedure

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 Ce(IV) (0.005-0.05 M) in H_2SO_4 (0.5 M) at temperatures from 30 to 50°C. The required concentration of monomer was added to the reaction mixture. The reaction time was varied from 1 to 8 h, and the material-to-liquor ratio of 1:100 was maintained. After the desired reaction time, silk fibers were taken out and washed thoroughly with water 3 or 4 times. Finally, the grafted fibers were Soxhlet extracted with benzene or acetone until the homopolymers were completely removed. They were then dried in an oven at 60°C, cooled to room temperature, and weighed. The graft yield was calculated as the percentage increase in weight over the original weight of the sample.

The acetylated fiber was prepared according to the method of Janowski and Speakman [37]. The trinitrophenylated fiber was prepared according to the method of Middlebrook [38].

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated by gradually varying it while keeping the concentration of other reagents constant. The variation of percentage of grafting with monomer concentration is shown in Fig. 1. It is seen that as the monomer concentration increases, there is an increase in percentage of grafting (up to 0.657 M) and thereafter it decreases with any further increase of monomer concentration. This is explained by assuming that at higher monomer concentration the concentration of PMMA macroradicals increases and the rate of their combination and disproportionation are faster than the rate of their combination with silk molecules. Another reason may be that the rate of monomer diffusion is progressively affected by the polymer deposit formed on the fiber which grows most rapidly when increasing concentrations of monomer are used. Similar observations have been noted by Haworth and Holker [39] in the case of grafting acrylic acid onto nylon by the ceric ion method.

Effect of Initiator Concentration

The effect of ceric ion concentration on the graft copolymerization of MMA onto silk is shown in Fig. 2. The percentage of grafting increases with increasing initiator concentration up to 0.03 mol/L and thereafter the percentage of grafting decreases. A possible explanation may be that in the system of ceric ion, MMA, and silk, an inter-

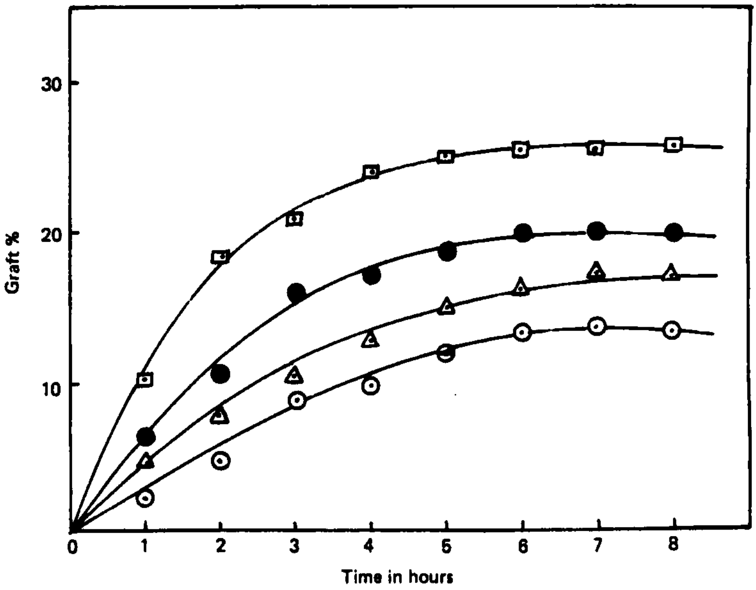

FIG. 1. Effect of monomer concentration on graft yield: [Ce(IV) = 0.03 mol/L; [H_2SO_4] = 0.5 mol/L; 50°C; (⊙) [MMA] = 2.80 × 10^{-1} mol/L; (△) [MMA] = 4.69 × 10^{-1} mol/L; (⊡) [MMA] = 6.57 × 10^{-1} mol/L; (●) [MMA] = 8.45 × 10^{-1} mol/L.

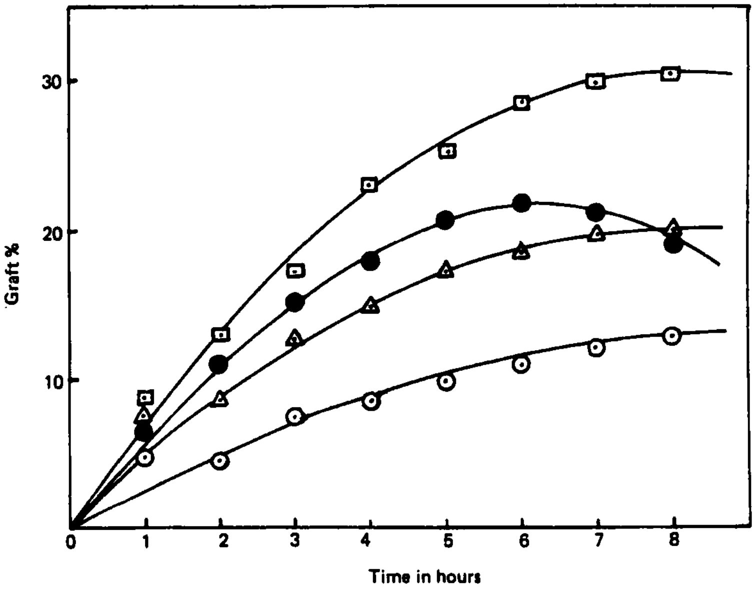

FIG. 2. Effect of cerium(IV) concentration on graft yield: [MMA] = 0.469 mol/L; [H_2SO_4] = 0.5 mol/L; 40°C; (⊙) [Ce(IV)] = 0.005 mol/L; (▲) [Ce(IV)] = 0.0075 mol/L; (●) [Ce(IV)] = 0.03 mol/L; (⊡) [Ce(IV)] = 0.05 mol/L.

mediate complex of ceric-silk might be formed which dissociates, giving rise to free radicals on the backbone of the silk material.

The following reaction scheme to explain the experimental finding has been proposed for the graft copolymerization of tussah silk.

Initiation:

$$\sim\text{SH} + \text{Ce}^{4+} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k_d} \text{S}^\bullet + \text{Ce}^{3+} + \text{H}^+ \qquad (1)$$

(S = silk and M = monomer)

$$\text{S}^\bullet + \text{M} \xrightarrow{k_i} \text{S–M}^\bullet \qquad (2)$$

$$\text{Ce}^{4+} + \text{M} \xrightarrow{k_i'} \text{M}^\bullet + \text{Ce}^{3+} + \text{H}^+ \qquad (3)$$

Propagation:

$$\text{SM}_n^\bullet + \text{M} \xrightarrow{k_p} \text{S–M}_{n+1}^\bullet \qquad (4)$$

$$\text{M}_m^\bullet + \text{M} \xrightarrow{k_p'} \text{M}_{m+1} \qquad (4')$$

Termination:

$$\text{SM}_n^\bullet + \text{Ce}^{4+} \xrightarrow{k_t} \text{SM}_n + \text{Ce}^{3+} + \text{H}^+ \qquad (5)$$

$$\text{M}_m^\bullet + \text{Ce}^{4+} \xrightarrow{k_t'} \text{M}_m + \text{Ce}^{3+} + \text{H}^+ \qquad (5')$$

Oxidation:

$$\text{S}^\bullet + \text{Ce}^{4+} \xrightarrow{k_0} \text{oxidation product} + \text{H}^+ \qquad (6)$$

Here ~ S–H denotes a reactive group in silk, M denotes monomer, K is the equilibrium constant, and k_i, k_i', k_p, k_p', k_t, k_t', and k_0 are rate constants.

Equilibriums (4') and (5') are propagation and termination reactions for homopolymers, and Eq. (6) represents the oxidation of silk macroradical by ceric ion. It is assumed that the homopolymer and graft copolymer show the same rate constant; that is, $k_p = k_p'$ and $k_t = k_t'$. By applying steady-state conditions to the concentrations [S] and [S–M] in Reactions (1)-(6), the overall rate of polymerization can be derived as follows:

$$R_p = k_p[S\text{–}M_n^{\bullet}][M]$$

Now

$$k_i[S][M] = k_t[S\text{–}M_n^{\bullet}][Ce^{4+}]$$

$$[S\text{–}M_n^{\bullet}] = \frac{k_i}{k_t}\,\frac{[M][S^{\bullet}]}{[Ce^{4+}]}$$

Further,

$$k_d[S\text{–}H][Ce^{4+}] = k_{-d}[S^{\bullet}][Ce^{3+}][H^{+}] + k_0[Ce^{4+}][S^{\bullet}] + k_i[S^{\bullet}][M]$$

$$[S^{\bullet}] = \frac{k_d[S\text{–}H][Ce^{4+}]}{k_{-d}[Ce^{3+}][H^{+}] + k_0[Ce^{4+}] + k_i[M]}$$

Hence,

$$[S\text{–}M_n^{\bullet}] = \frac{k_i[M]}{k_t[Ce^{4+}]}\;\frac{k_d[S\text{–}H][Ce^{4+}]}{k_{-d}[Ce^{3+}][H^{+}] + k_0[Ce^{4+}] + k_i[M]}$$

$$R_p = \frac{k_p k_i[M]^2}{k_t[Ce^{4+}]}\left[\frac{k_d[S\text{–}H][Ce^{4+}]}{k_{-d}[Ce^{3+}][H^{+}] + k_i[M] + k_0[Ce^{4+}]}\right] \qquad (7)$$

At low ceric ion concentration,

$$R_p = k_p k_i[M]^2\left[\frac{k_d[Ce^{4+}][S\text{–}H]}{k_{-d}[Ce^{3+}][H^{+}] + k_i[M]}\right] \qquad (8)$$

Equation (8) shows that, with an increase in ceric ion concentration, the rate of polymerization should increase. This is found to be true.

But at higher concentration of Ce^{4+} and when $k_t \gg k_p$ and k_i,

$$R_p = \frac{k_p k_i[M]^2}{k_t[Ce^{4+}]}\left[\frac{k_d[Ce^{4+}][S\text{–}H]}{k_{-d}[Ce^{3+}][H^{+}] + k_i[M] + k_0[Ce^{4+}]}\right] \qquad (9)$$

Katai et al. [6], using ceric ion as the indicator, estimated that $k_0/k_i = 50$. Therefore, an increase in Ce^{4+} concentration increases the magnitude of the denominator in Eq. (9). Hence, R_p should decrease with an increase in Ce^{4+} ion concentration. Experimentally, this study is realized because a maximum percentage of grafting is obtained at a particular optimum concentration of Ce^{4+}, beyond which the percentage of grafting decreases progressively. A similar explanation has been advanced by Ogiwara and co-workers [24] for the grafting of MMA onto cellulose initiated by ceric ion method.

Effect of Temperature on Grafting

The effect of temperature (30 to 50°C) on graft copolymerization is shown in Fig. 3. It shows that the percentage of graft-on increases with increasing temperature.

From the Arrhenious plot of log R_p versus 1/T, the overall activation energy was found to be 10.9 kcal/mol (Fig. 4). Using the value of $E_p - \frac{1}{2}E_t$ = 4-5 kcal/mol given by Tobolsky [40] (when E_p and E_t are the energies of propagation and termination, respectively), the activation energy of initiation, E_d, can be calculated as follows:

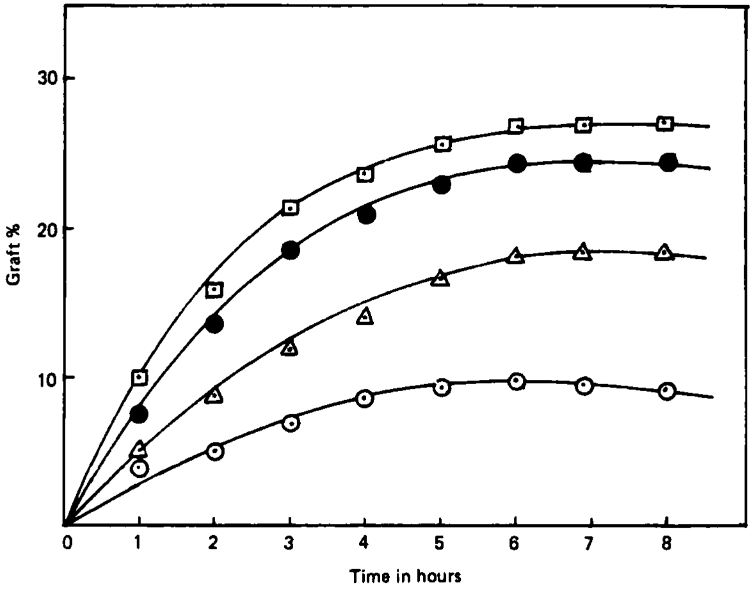

FIG. 3. Effect of temperature on graft yield: [Ce(IV)] = 0.03 mol/L;[MMA] = 0.469 mol/L; [H_2SO_4] = 0.5 mol/L; (⊙) 30°C; (▲) 40°C; (●) 45°C; (▣) 50°C.

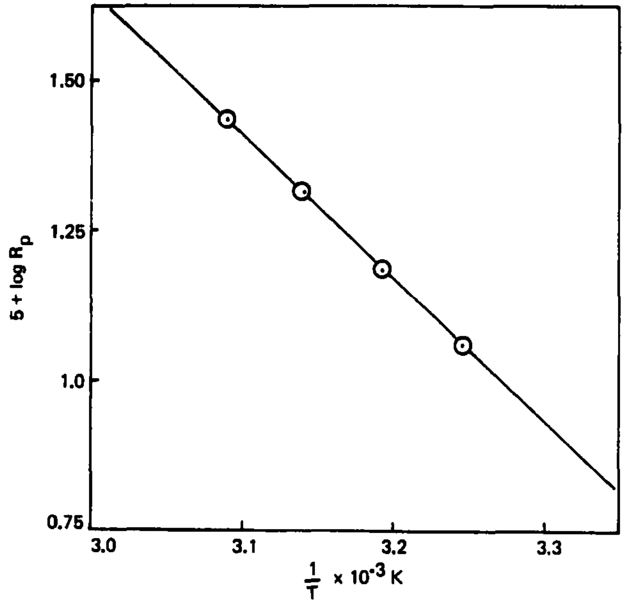

FIG. 4. Arrhenious plot for graft copolymerization of MMA onto silk by cerium(IV) ion.

$$E_d = 2E_a - (2E_p - E_t)$$

where E_a is the overall activation energy. The value of E_d was calculated to be 11.8 kcal/mol.

Nature of the Substrate

The effect of chemical modification of the fiber brought about by esterification or trinitrophenylation on its behavior toward grafting has been investigated. The order of graft yield is as follows: unmodified tussah silk > esterified tussah silk > trinitrophenylated tussah silk.

Acetylation and trinitrophenylation of tussah silk significantly reduces its ability toward grafting. When silk fibers are subjected to acetylation or trinitriphenylation, the amino, imino, and carboxyl groups are blocked. Hence free radicals formation on the silk backbone by the interaction of metal ions decreases, and the graft yield decreases as a result.

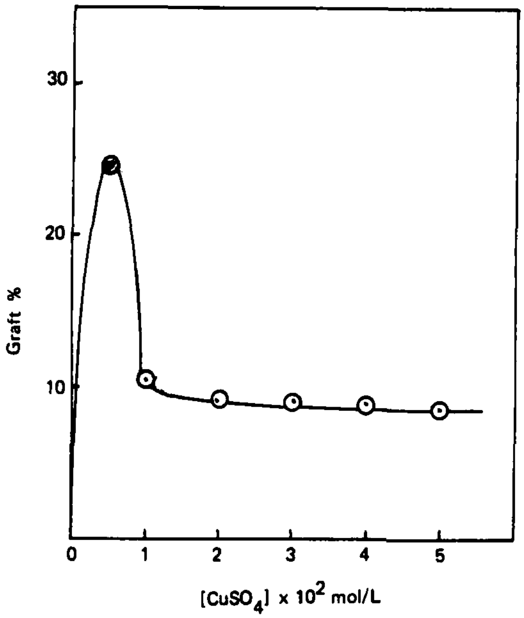

FIG. 5. *Effect of copper sulfate concentration on graft yield:* [Ce(IV)] = 0.03 mol/L; [H_2SO_4] = 0.5 mol/L; [MMA] = 0.4690 mol/L; 50°C.

Effect of Copper Sulfate

It is observed that the graft yield first increases and then decreases with increasing copper sulfate concentration, (Fig. 5). The initial increase in graft yield might be due to easier formation of a silk-monomer complex with copper ion than with cerium ion when the former are in the vicinity of silk backbone. The drop in graft yield with a higher concentration of copper sulfate may be attributed to a variety of reasons. First, the higher concentration of copper ions may be responsible for the termination of free radicals on the homopolymer and/or on silk by acting as a radical trap. Second, a particular concentration of cupric ion may favor complexation of monomer with silk, but higher concentrations of cupric ions might perturb such a complexation.

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