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Grafting Vinyl Monomers onto Silk Fibers. V. Graft Copolymerization of Methyl Methacrylate onto Silk with Potassium Permanganate as Initiator

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ABSTRACT

The graft copolymerization of methyl methacrylate onto silk fibers in aqueous solution with the use of manganese (IV) ions as initiator was investigated. The rate of grafting was determined by varying monomer, acidity of the medium, temperature, nature of silk, and the reaction medium. The graft yield increases significantly with increase of manganese (IV) concentration up to 15 meq/liter; with further increase of manganese (IV) concentration, the graft yield decreases. The effect of the increase of monomer concentration brings about a significant enhancement in the graft yield up to 7%, and with further increase of monomer concentration the graft yield decreases. The graft yield is considerably influenced by chemical modification prior to grafting. The effect of some inorganic salts and anionic surfactants on the rate of grafting has been investigated.

INTRODUCTION

Grafting of vinyl monomers onto natural and synthetic macromolecules has attracted the attention of several groups of investigators in recent years [1-4]. It provides an effective means of improving the fiber properties with minimum degradation of the base polymer. A literature survey [5] reveals that grafting involves a radical mechanism. Hence, the primary step entails the creation of free-radical sites on the backbone of the fiber. This may be achieved by several methods such as high-energy radiation [6, 7], low-energy radiation in the presence or absence of sensitizers [8, 9], and redox systems [10-14]. The last method is of paramount importance, since it provides minimum degradation of the base polymer and minimizes the formation of homopolymer.

The homopolymerization of vinyl monomers initiated by potassium permanganate in acid medium has been studied rather extensively by several groups of investigators [15-20]. Nayak and co-workers [21-25] have reported the homopolymerization involving several other metal ions with a multitude of organic substrates. A few studies have shown the ability of potassium permanganate to induce graft copolymerization onto textile fibers [26-28].

Arai et al. [6] have reported the graft copolymerization onto silk using high-energy radiation. Nayak and co-workers have reported graft copolymerization of MMA onto wool [29-31] and silk [32-35] using several initiating systems, such as V(V), Cr(VI), Ce(IV), and $KBrO_3$/thiourea (TU) redox systems. This paper presents the results of graft copolymerization of MMA onto silk fibers by use of potassium permanganate as the 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 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 anhydrous sodium sulfate, and distilled under nitrogen under reduced pressure before use.

Potassium permanganate (AR) and H_2SO_4 ($\sim$ 18 $\underline{M}$, AR, BDH) were used. Water, distilled twice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co.), was used to prepare all solutions. A stock solution of permanganate (0.1 $\underline{M}$ in distilled water) was used throughout the experiments. The concentration of permanganate in the experimental system was determined by ceremetry.

The reactions were carried out in Pyrex flasks equipped with gas inlet and outlet tubes. Dried and purified silk fibers were immersed in a solution of Mn^{4+} (5-80 meq/liter) in H_2SO_4 (0.1-1 N) at temperatures from 40 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, washed thoroughly with water and acetone. Finally, the fibers were Soxhlet extracted with benzene or acetone 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 onto silk fiber was investigated by changing the monomer concentration and keeping the concentration of all other reagents constant. The graft yield increases with the increase of monomer concentration up to 7% and then decreases with further increase of monomer concentration (Fig. 1). A probable explanation for this is that as the concentration of PMMA macroradicals increases with the increase of monomer

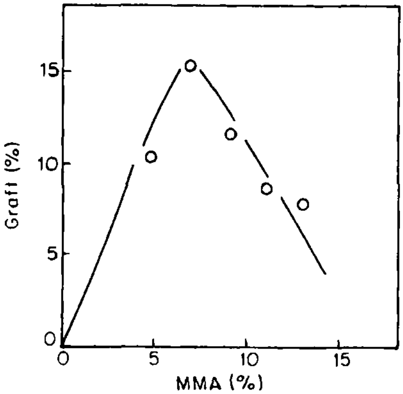

FIG. 1. Effect of [MMA] on graft yield. [$KMnO_4$] = 15 meq/liter; [H_2SO_4] = 0.4 N; methanol 20%; 6 hr; 50°C.

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 progressively affected by the polymer deposit formed which grows rapidly as the monomer concentration increases. Howrth and Holker [36] have reported similar observations in the case of grafting acrylic acid onto nylon with the use of tetravalent cerium as initiator.

Effect of Initiator Concentration

The effect of initiator concentration on graft yield was investigated by varying the permanganate concentration within the range of 5-80 meq/liter. The graft yield increases significantly with the increase of permanganate concentration up to 15 meq/liter, and further increase causes a decrease in the extent of graft yield (Fig. 2). A possible explanation for these observations might be as follows.

Uhlig and Teichmann [37] have reported that in a polymerization system initiated by potassium permanganate in the presence of an acid, the free radicals are formed through the reduction of manganese (IV) to manganese (III) and/or manganese (II). Thus, during the graft copolymerization onto silk with the use of potassium permanganate in the presence of sulfuric acid, the creation of free radicals in the system may be represented as in Eqs. (1)-(3).

$$Mn^{4+} + H_2SO_4 \longrightarrow Mn^{3+} + H^+ + HS\dot{O}_4 \qquad (1)$$

$$Mn^{4+} + H_2O \longrightarrow Mn^{3+} + H^+ + \dot{O}H \qquad (2)$$

$$HS\dot{O}_4 + H_2SO_4 \longrightarrow H_2SO_4 + \dot{O}H \qquad (3)$$

These free radicals ($HS\dot{O}_4$ or $\dot{O}H = R^{\cdot}$) might attack silk, giving rise to silk macroradicals [Eq. (4)].

$$\sim\!\sim SH + R^{\cdot} \xrightarrow{k_d} \sim\!\sim\!\sim S^{\cdot} + RH \qquad (4)$$

The other possibility is that in a system of Mn^{4+} ion, MMA and silk, an intermediate Mn^{4+}-silk complex might be formed which dissociates giving rise to free radicals on the backbone of the silk. The reaction scheme may be shown in Eqs. (5)-(12) represented for the graft copolymerization of MMA onto silk.

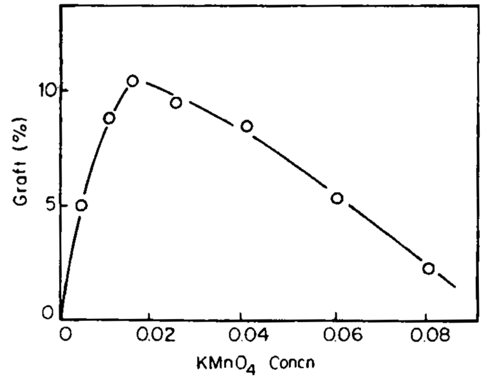

FIG. 2. Effect of $KMnO_4$] on graft yield. [H_2SO_4] = 0.4 N; [MMA] = 0.4694 M; 6 hr; 50°C.

$$\sim\!\sim SH + Mn^{4+} \xrightleftharpoons{K} \text{complex} \xrightarrow{k_d} S^{\bullet} + Mn^{3+} + H^{+} \qquad (5)$$

Initiation:

$$\sim\!\sim S^{\bullet} + M \xrightarrow{k_i} S - M^{\bullet} \qquad (6)$$

$$Mn^{4+} + M \xrightarrow{k_i'} M^{\bullet} + Mn^{3+} + H^{+} \qquad (7)$$

Propagation:

$$\sim\!\sim SM_n^{\bullet} + M \xrightarrow{k_p} SM_n^{\bullet} + 1 \qquad (8)$$

$$\vdots$$

$$\sim\!\sim M_m + M \xrightarrow{k_p} M_{m+1}^{\bullet} \qquad (9)$$

Termination:

$$\sim\!\sim SM_n^{\bullet} + Mn^{4+} \xrightarrow{k_t} \text{Grafted polymer} \qquad (10)$$

$$\sim\!\sim M_m^{\bullet} + Mn^{4+} \xrightarrow{k_t'} \text{Homopolymer} \qquad (11)$$

Oxidation:

$$\sim\!\sim S^{\bullet} + Mn^{4+} \xrightarrow{k_0} \text{Oxidation product} + Mn^{3+} + H^{+} \qquad (12)$$

At higher concentration of Mn^{4+}, 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^{4+} concentration, which results in a marked fall in the graft yield.

Secondly, at higher Mn^{4+} concentration, the metal ions might interact with the monomer to give rise to a higher amount of homopolymer thereby decreasing grafting.

Effect of Acid Concentration

The graft copolymerization has been carried out in the presence of sulfuric as well as perchloric acid. The concentration of acid was varied from 0.1 to 1 N. The result shows that the percentage of grafting increases with increase of the concentrations of both acids up to 0.4 N and then decreases with further increase of the acid concentration (Fig. 3). A higher percentage of grafting is observed with perchloric acid than with sulfuric acid.

The decrease in percentage of grafting at higher acid concentration might be due to the following reasons. Palit and co-workers [18] have reported that at lower pH, the coagulation of colloidal homopolymer in solution and within fibers increases during grafting. This retards the diffusion of both monomer and initiator into the silk fiber for grafting to occur. At higher acid concentration, MnO_2 might

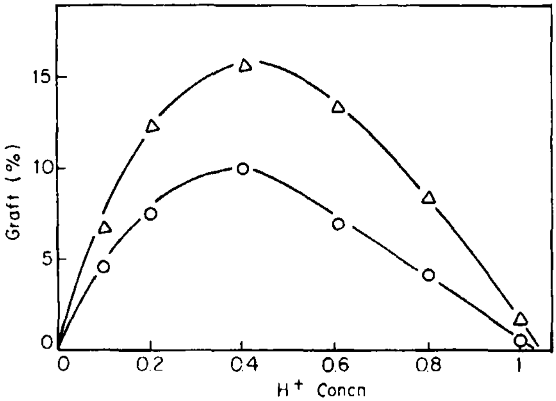

FIG. 3. Effect of [H_2SO_4] on graft yield. [$KMnO_4$] = 15 meq/liter; [MMA] = 0.4694 M; 6 hr, 50°C.

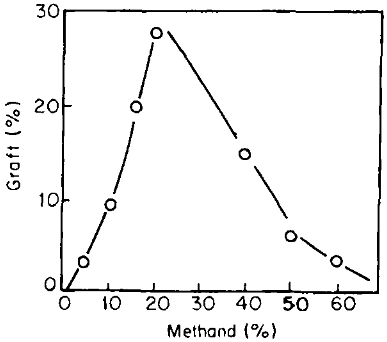

FIG. 4. Effect of methanol on graft yield. [$KMnO_4$] = 15 meq/liter; [H_2SO_4] = 0.4 N; [MMA] = 0.4694 M; 6 hr; 50°C.

react with acid producing oxygen, which might inhibit the grafting process.

$$MnO_2 + 2H^+ \longrightarrow Mn^{2+} + H_2O + O \qquad (13)$$

Effect of Methanol Concentration

The graft copolymerization was also studied with varying methanol concentrations from 5 to 50%. The percentage of grafting significantly increases with increase of the concentration of methanol up to 20% and thereafter it decreases (Fig. 4). This decrease may be attributed to the exhaustion of most of the formed free radicals in oxidation of methanol and/or to termination of the growing polymer chains, grafted onto the substrate, via chain transfer giving rise to free methanol radicals.

Effect of Temperature on Grafting

The graft copolymerization was studied at four different temperatures ranging from 40 to 55°C, keeping the concentration of all other reagents constant (Fig. 5). The results show that with increase of temperature up to 50°C the percentage of grafting increases and thereafter there is a fall in the percentage of grafting. The dependence of the 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

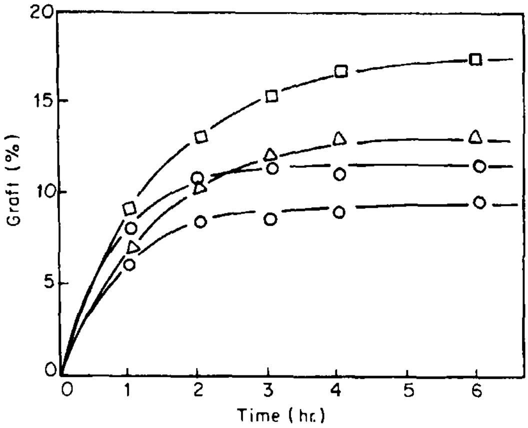

FIG. 5. Effect of temperature on graft yield: (○) 40°C; (△) 45°C; (□) 50°C; (●) 55°C. [$KMnO_4$] = meq/liter; [H_2SO_4] = 0.4 N; methanol = 20%; [MMA] = 0.4694 M.

by increasing temperature. However, beyond 50°C, the decrease in percentage of grafting is probably due to the greater possibility of combination rates of monomer at higher temperature. Hebeish and Mehta [38] have noted similar observations during grafting acrylonitrile onto cellulose by ceric ion method.

Effect of Reaction Medium

The reaction medium plays an important role in grafting vinyl monomers onto silk fibers (Fig. 6). The graft yield follows the order: acetic acid > dimethyl formamide > ethanol.

The dependence of the rate of grafting on the nature of the solvents suggests that the solvents examined differ considerably in their capability of swelling of silk, miscibility with monomer, formation of solvent radical from the primary radical species of the initiating system, contribution of the solvent radical in activation of silk, and termination of the graft radical and silk macroradical via chain transfer. While the first four factors favor grafting by simplying access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft. The lower graft yields could be ascribed to its adverse effect on the swelling of silk by water.

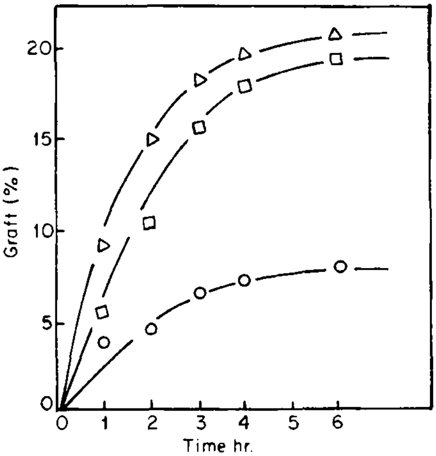

FIG. 6. Effect of solvent on graft yield: (○) C_2H_5OH; (□) DMF; (△) CH_3COOH. $[KMnO_4]$ = 15 meq/liter; $[H_2SO_4]$ = 0.4 N; [MMA] = 0.4694 M; solvent = 10%; 50°C.

Effect of Inorganic Salts and Surfactants

The addition of neutral salts such as Na_2SO_4, KCl, and $ZnSO_4$ increases the graft yield (Fig. 7). The order of their effect on graft yield: $ZnSO_4 > KCl > Na_2SO_4$. The higher percentage of grafting when $ZnSO_4$ is added as an electrolyte may be due to that it might be catalyzing the propagation step where as the lower percentage of grafting with KCl and Na_2SO_4 is 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 effect of $CuSO_4$ concentration on grafting in the presence of methanol has been investigated. The percentage of grafting increases with the increase of $CuSO_4$ concentration (Fig. 8). A probable explanation for this is that the presence of Cu^{2+} ions in the vicinity of silk certainly favors grafting, since the involvement of Cu^{2+} ion in the silk-monomer complex would be easier. Further, the creation of free radical species under the influence of Cu^{2+} ions would be in the proximity of silk, thus assisting formation of macroradicals. The percentage of grafting has also been calculated in the presence of an anionic surfactant, sodium lauryl sulfate, at the critical micelle concentration (CMC). At CMC, micelles are formed which are

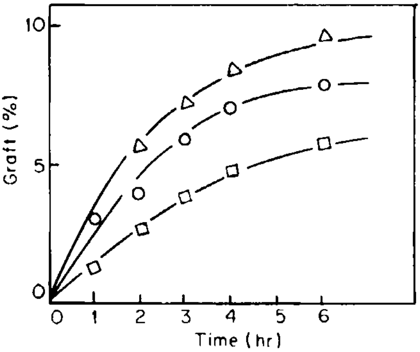

FIG. 7. Effect of [salt] on graft yield: (○) KCl; (△) $ZnSO_4$; (□) Na_2SO_4. [$KMnO_4$] = 15 meq/liter; [H_2SO_4] = 0.4 N; [MMA] = 0.4694 M; [salt] = 0.01 N; 50°C.

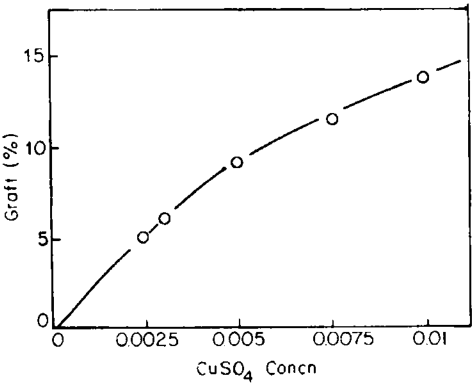

FIG. 8. Effect of [$CuSO_4$] on graft yield. [$KMnO_4$] = 15 meq/liter; [H_2SO_4] = 0.4 N; methanol = 20%; [MMA] = 0.4694 M; 6 hr; 50°C.

roughly spherical in size with the sulfate ions forming the Gouy-Chapman double layer [39, 40]. The enhancement of graft yield by NaLS at the CMC can be explained on the assumption that the micelles become entangled with the silk fiber as a result of which the Mn(IV) ion is electrostatically attracted towards the silk matrix. The concentration of Mn(IV) ions will be more near the vicinity of the fiber, and free radical formation on the silk backbone will be facilitated as a result of which the graft yield increases.

Effect of Amount of Silk on Grafting

The percentage of grafting increases with increasing the amount of silk from 0.1 to 0.6 g. The grafting efficiency increases as the amount of silk in the polymerization medium increases. This suggests that graft copolymerization of MMA onto silk fiber initiated by Mn^{4+} ion takes place preferentially on the silk matrix with abundance of silk in the medium, hence the integrated surface area of the fibers affects greatly the diffusion of the monomer and the free radical species as well as increase the possibility of free radical formation on the silk backbone.

Nature of the Substrate

The effect of the changes in the physical or chemical structure of silk brought about by esterification or trinitrophenylation on its behavior towards grafting has been investigated. The order is as follows: unmodified silk > esterified silk > trinitrophenylated silk. Acetylation and trinitrophenylation of silk reduces significantly its ability towards grafting. When silk fiber is subjected to acetylation or trinitrophenylation, the amino and the carboxyl groups will be blocked. Free radicals cannot be created at the silk backbone by the interaction of the metal ions as a result of which the graft yield decreases. The other reasons for the low graft yield might be lowering of the swellability of the fiber or hindrance of adsorption of MMA owing to low fiber swellability and repulsion of MMA molecule by the negatively charged substituted nitro groups in the case of TNP - silk. The net effect of all these factors is the decrease of grafting.

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