

## NOTES

### *Graft Polymerization of Methyl Methacrylate onto Silk Fibers with Ce(IV)-Sucrose Redox System*

#### INTRODUCTION

Chemical modification of natural polymers by grafting has received considerable attention in recent years.<sup>1-3</sup> With the wide variety of vinyl monomers available today grafting has been potentially a powerful method for producing substantial modification in the properties of natural fibers.

Vinyl graft copolymerization onto natural fibers is usually accomplished by free radical initiation mechanism. The primary step, therefore, involves formation of free radical sites on the backbone of fiber molecule<sup>4</sup> probably through abstraction of hydrogen. This can be achieved by several methods, i.e., high energy radiation<sup>5</sup> and use of redox systems.<sup>6-10</sup> Free radicals can also be produced by the use of powerful oxidizing agents such as ceric ions.<sup>11</sup>

In the recent years, the use of tetravalent cerium as an initiator of the graft polymerization of vinyl monomers on cellulosic and other textile materials has gained considerable importance on account of its high grafting efficiency<sup>12,13</sup> compared with the other known redox systems such as ferrous-hydrogen peroxide and thiosulphate-persulphate.<sup>14,15</sup> In this laboratory, there is a research program to investigate the vinyl graft polymerization onto various natural fibers using Ce(IV), permanganate, V(V), etc., as catalyst and carbohydrates, i.e., glucose, sucrose, etc., as cocatalyst with a view to achieving higher grafting efficiency. Use of sucrose, in particular, as the reducing component is of great industrial importance. This communication presents the results of studies of graft polymerization of methyl methacrylate onto silk fibers using Ce(IV)-sucrose redox system.

#### EXPERIMENTAL

Tushah silk fibers (obtained from Mayurbhanj, India) were purified by soxhlet extraction with acetone for about 24 h followed by cold distilled water washing and air drying. Commercial methyl methacrylate was washed with 5% NaOH solution and water. It was then dried with anhydrous calcium chloride.

Ceric ammonium sulphate (BDH), sucrose (AR,BDH), and sulphuric acid (AnalaR) were used as received without further purification.

The graft copolymerization was carried out in pyrex flasks with B<sub>24-29</sub> standard joints equipped with gas inlet and outlet tubes for nitrogen atmosphere. Appropriate quantities of reaction mixture containing silk fiber, monomer, sulphuric acid, and sucrose solution were taken in a reaction vessel. The mixture and the ceric solution were separately deaerated by passing purified nitrogen for 20 min. Homopolymerization and grafting started after addition of ceric solution to the mixture. After a specified time interval, the reaction was arrested by addition of a known excess of ferrous ammonium sulphate solution. The polymer along with the grafted silk fibers was filtered off, washed with water, and dried to constant weight. Finally, the fibers were extracted with acetone in a soxhlet apparatus for 12 h. Percentages of grafting were estimated using appropriate expression.

#### RESULTS AND DISCUSSION

The following factors effecting Ce(IV)-sucrose induced grafting of methyl methacrylate onto silk fibers were investigated. Variables studied include substrate, monomer, metal ion, acid, and temperature. Table I summarizes the results on grafting under different conditions.

##### Effect of Sucrose

The effect of sucrose concentration was studied by varying the concentration over a range of 0.005-0.04*M*. The percentage of graft yield increases with time and also with increase of sucrose concentration. However, beyond 0.01*M*, a considerable decrease in graft yield is observed. This may be due to the fact that, at higher sucrose concentration, sucrose acts as a free radical scavenger, thereby decreasing the graft yield.

TABLE I  
Grafting onto Silk Fibers (Time 2 h)

[Sucrose] (mL <sup>-1</sup> )	[Ce(IV)] (mL <sup>-1</sup> )	[MMA] (mL <sup>-1</sup> )	[H <sub>2</sub> SO <sub>4</sub> ] (mL <sup>-1</sup> )	Temp (°C)	Graft (%)
0.005	0.005	0.47	0.1	40	30.1
0.01	0.005	0.47	0.1	40	34.7
0.04	0.005	0.47	0.1	40	13.7
0.005	0.005	0.235	0.1	40	14.8
0.005	0.005	0.71	0.1	40	34.9
0.005	0.005	0.94	0.1	40	22.8
0.005	0.01	0.47	0.1	40	37.8
0.005	0.04	0.47	0.1	40	19.8
0.005	0.005	0.47	0.1	50	20.0

#### 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. As the monomer concentration increases, there is an increase in percentage of grafting in the lower concentration range; it reaches a maximum value and then significantly decreases with further increase of monomer concentration. At higher monomer concentration, reactions that are competitive to grafting probably take place in solution, i.e., combination and disproportionation of polymethyl methacrylate macroradicals.<sup>16</sup>

#### Effect of Temperature

The Graft copolymerization was carried out at two different temperatures (40°C and 50°C), keeping the concentrations of all other reagents constant. A perusal of the result indicates that the increasing temperature decreases the percent of grafting; this is probably due to the fact that at higher temperature chain transfer processes may occur, some of which may not favor grafting.

#### Effect of Metal Ion

The effect of the concentration of ceric sulphate on the grafting of methyl methacrylate to silk has been studied. Increasing the ceric sulphate concentration up to 0.01M increases the percentage of graft yield. Beyond this concentration, the graft yield decreases with the further increase of metal ion concentration. This is due to the termination of grafted radicals at higher concentration of ceric ions.

#### Infrared Spectra of Grafted Silk

The infrared spectra of the grafted silk gave additional evidence as to whether actual grafting had taken place. The spectrum shows absorption bands characteristic of both poly(methyl methacrylate) and silk.

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Received June 4, 1982  
Accepted December 13, 1982