

# Graft Copolymerization of Methyl Methacrylate on Holocellulose

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## Synopsis

Graft copolymerization of methyl methacrylate initiated by ceric ion in aqueous medium on bleached holocellulose was studied at 29°C. It was found that an increase in the concentration of ceric ion and oxidation of the holocellulose with aqueous potassium dichromate solution resulted in increased levels of incorporation of poly(methyl methacrylate) graft copolymer, but were associated with reductions in the efficiency of grafting. Thiol groups were introduced on the holocellulose by treatment with dilute thioglycolic acid solutions at 29°C. The influence on the level of grafting and on the molecular weight of the grafted polymer by the incorporated thiol groups on the substrate was examined.

## INTRODUCTION

The use of ceric ion for initiating graft copolymerization of vinyl monomer on cellulosic materials has been reported by several workers.<sup>1-15</sup> It is generally believed that initiation of free radicals on cellulose involves abstraction of hydrogen atom from a carbon carrying hydroxyl group,<sup>1</sup> oxidation of glycol linkages leading to C—C bond cleavage (at C<sub>2</sub> and C<sub>3</sub> carbons),<sup>2</sup> or oxidation of cellulose chain ends containing hemiacetol linkages.<sup>6</sup> Besides, the consumption of ceric ion by cellulosic materials has been shown to depend on the carbonyl and carboxyl content of cellulose,<sup>9-11</sup> suggesting the importance of these functional groups in the initiation of graft copolymerization. It was thought that by converting the carbonyl groups on cellulose to carboxyl groups, and by replacing some of the OH groups on cellulose with SH groups, further information on the initiation site of graft copolymerization by ceric ion would be obtained. This communication reports on the grafting characteristics of methyl methacrylate on holocellulosic material from *Gosweilerodenron balsamiferum*, a tropical hard wood.

## MATERIALS AND METHODS

Commercial methyl methacrylate monomer was extracted with dilute NaOH solution to remove the hydroquinone stabilizer. The monomer was then distilled under reduced pressure. Ceric ammonium nitrate was used without further purification. Holocellulose from *Gosweilerodenron balsamiferum* was obtained as described previously.<sup>16</sup> The holocellulose was steeped in sodium hypochlorite solution for 45 min at 29°C. The bleached holocellulose was then rinsed in a large volume of distilled water and then air-dried. A portion of the

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bleached holocellulose was oxidized with acidic dichromate solution (0.1M  $K_2Cr_2O_7$  in 1.0M  $H_2SO_4$ ). The oxidized material was washed thoroughly with deionized water and then air-dried. The bleached holocellulose was treated with various concentrations of thioglycolic acid at 29°C for 24 h. The thiol contents of the reduced holocellulose were determined by reaction with excess iodine at neutral pH followed by back titration of the unreacted iodine with thiosulphate solution.

Graft copolymerization of methyl methacrylate on (a) unbleached, (b) bleached, (c) bleached and oxidized, and (d) bleached and reduced holocellulose was carried out at 29°C using various amounts of ceric ion and a constant amount of the substrate (0.5 g) dispersed in 50 mL of distilled water. The polymerization procedure was based on the method described by Lepoutre and Hui.<sup>7</sup> Polymerization was allowed to proceed for 60 min and the reaction was stopped by the addition of 2 mL of 0.1% (w/v) hydroquinone solution.

The ungrafted poly(methyl methacrylate) homopolymer was Soxhlet-extracted with tetrahydrofuran. The grafted cellulosic material was then dried and reweighed. The measure weight increase divided by the weight of the substrate multiplied by 100 was reported as the percent graft level. The percent efficiency of grafting was taken as the weight of the polymer grafted divided by the weight of polymer grafted plus the weight of the homopolymer, multiplied by 100.

The grafted polymer was isolated from the holocellulose using the method described by Ogiwara et al.<sup>17</sup> and purified by solution in tetrahydrofuran and precipitation with methanol. The average molecular weight of the isolated polymer was determined by viscosity measurements in acetonitrile solution. The number of grafted chains was reported as the ratio of the percent graft level to the average molecular weight of the grafted chains.

## RESULTS AND DISCUSSION

The variation of the level of incorporation of poly(methyl methacrylate) graft on the holocellulosic material with ceric ion concentration using 18.8 mmol of the monomer is shown in Figure 1. It can be seen that the graft level varies linearly with the ceric ion concentration within the whole range of initiator concentration. Although an increase in ceric ion concentration is accompanied by an increase in the level of incorporation of the graft copolymer, the efficiency of grafting methyl methacrylate on the holocellulosic material, with the exception of the holocellulose-containing SH groups, is significantly reduced (by up to 60%) as the amount of ceric ion in the polymerizing system was increased from 2.5 to 7.8 mmol (Table I).

During polymerization, ceric ions are consumed in the initiation process and by adsorption on the cellulosic material.<sup>9,10</sup> Any unreacted or unadsorbed ceric ion in the polymerizing system could initiate homopolymerization by transfer to monomer. The observed decrease in efficiency of grafting suggests that a relatively large proportion of the ceric ions are present in the continuous aqueous medium rather than at the substrate/aqueous medium interface. The presence of SH groups on the holocellulose would be expected to accentuate adsorption of the initiating ceric ions. This would lead to a reduction in the amount of ceric ion available in the continuous phase to initiate homopolymer

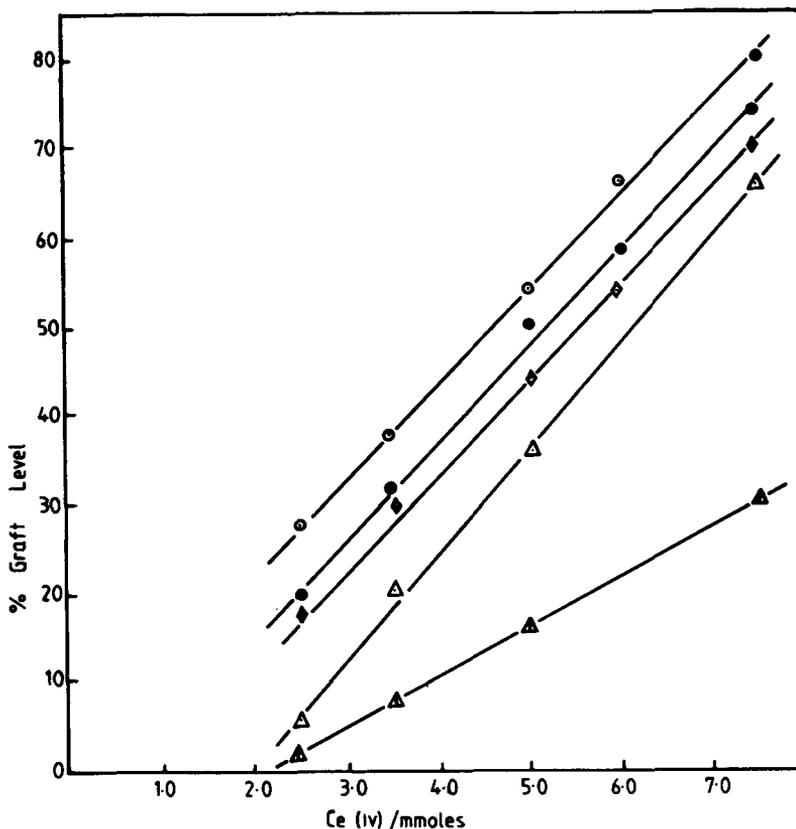


Fig. 1. Grafting methyl methacrylate on unbleached ( $\Delta$ ), bleached ( $\diamond$ ), bleached and oxidized for 10 min ( $\bullet$ ), and for 30 min ( $\circ$ ) and reduced 3.3% SH groups ( $\Delta$ ) holocellulose at 29°C using 18.8 mmol of the monomer.

formation and should result in improved efficiency of grafting. For instance, it is estimated that about 30% of ceric ions is bound from 10 mmol/L solution by dissolving pulp and semichemical pulp.<sup>9</sup> The fraction of ceric ion inactivated by adsorption would be expected to increase with the incorporation of thiol groups on the substrate.

The results (Fig. 1) clearly show the effects of oxidation and incorporation of SH groups on the level of incorporation of poly(methyl methacrylate) graft copolymer on bleached holocellulose. It can be seen that the graft levels are highest for the substrate treated with the oxidizing dichromate solution and lowest for the bleached holocellulose treated with thioglycolic acid solution. Oxidation of cellulosic material with acidic dichromate solution is associated with the conversion of carbonyl groups in cellulose to carboxyl groups.<sup>17</sup> Although a quantitative estimate of the carbonyl and carboxyl contents of the holocellulose was not carried out, the enhanced level of incorporation of poly(methyl methacrylate) grafts on the oxidized holocellulose leads to the suggestion that ceric ion interacts more readily with carboxyl groups than with the carbonyl groups in the initiation of the copolymer grafts. Besides, the treatment of the bleached holocellulose with acidic dichromate solution would

TABLE I  
Efficiency of Grafting Methyl Methacrylate on Holocellulose at 29°C Using 18.8 mmol of Monomer and 0.5 g of the Substrate Dispersed in 50 mL of H<sub>2</sub>O

Amount of ceric ions (mmol)	% Efficiency of grafting on holocellulose		
	Bleached holocellulose	Bleach and oxidized with dichromate solution for 10 min	Bleached and reduced holocellulose (3.3% SH)
2.5	90.0	83.3; 63.6 <sup>a</sup>	50.0
3.5	88.2	82.3; 61.3 <sup>a</sup>	66.7
5.0	31.3	62.5; 58.7 <sup>a</sup>	68.7
6.0	30.7	34.5; 44.0 <sup>a</sup>	—
7.5	28.2	28.0; 31.5 <sup>a</sup>	75.0

<sup>a</sup>Efficiency of grafting on bleached holocellulose oxidized with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for 30 min.

TABLE II  
Effect of Ceric Ion Concentration on the Number of Grafted Polymer Chains and Molecular Weight of Grafted Copolymer in the Graft Polymerization of Methyl Methacrylate on Holocellulose at 29°C

Amount of ceric ion (mmol)	Average molecular weight ( $\bar{M}$ )		Number of grafted polymer chains (mmol/100 g cellulose)	
	Bleached holocellulose	Bleached and reduced holocellulose (4.6% SH)	Bleached holocellulose	Bleached and reduced holocellulose (4.6% SH)
2.5	$6.7 \times 10^5$	—	$8.1 \times 10^{-5}$	—
5.0	$6.0 \times 10^5$	—	$1.5 \times 10^{-5}$	—
7.5	$5.0 \times 10^5$	$3.2 \times 10^5$	$1.7 \times 10^{-4}$	$1.2 \times 10^{-4}$
10.0	$4.1 \times 10^5$	$3.0 \times 10^5$	$1.8 \times 10^{-4}$	$1.2 \times 10^{-4}$
12.5	$3.6 \times 10^5$	$2.9 \times 10^5$	$2.2 \times 10^{-4}$	$1.2 \times 10^{-4}$

lead to further delignification of the holocellulose and hence to enhanced levels of grafting.<sup>9</sup>

Table II shows the variation of the molecular weight and the number of grafted poly(methyl methacrylate) chains with the amount of ceric ions in the polymerization mixture. It can be seen that the molecular weight of the grafted polymer and the number of the grafted chains decrease with increase in the concentration of ceric ion. The results show that the molecular weight of the grafted polymer and the number of grafted chains on the holocellulose-containing SH groups are about the same order of magnitude but are somewhat lower than the values obtained for grafting on the bleached holocellulose. If initiation of graft polymerization by ceric ion occurred by hydrogen abstraction from carbon atoms carrying hydroxyl groups, the replacement of some of the hydroxyl groups with SH groups would be expected to enhance the level of incorporation of the poly(methyl methacrylate) grafts. A reduction in both the number of grafted chains and in the molecular weight of the grafted polymer indicates that hydrogen abstraction reactions are not the predominant mode of initiation of graft polymerization by ceric ion on holocellulose.

The results from this study confirm the relative importance of hydroxyl, carbonyl, and carboxyl groups in the initiation of graft polymerization initiated by ceric ion on holocellulosic material. The marked reduction in the graft level of poly(methyl methacrylate) caused by the presence of SH groups on the holocellulose is surprising. If it is due to increased ceric ion inactivation through adsorption, the introduction of SH groups on holocellulose would provide modified materials that may be useful in recovery and/or removal of metals from aqueous effluents.

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