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NOTE

GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ON THIOLATED HOLOCELLULOSE

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The use of ceric ions for initiating graft copolymerization of vinyl monomers on cellulosic materials has been reported by several workers [1-10]. Initiation of graft copolymerization is often thought to be by radicals generated on the cellulose by the abstraction of a hydrogen atom from a carbon atom carrying hydroxyl groups [1], oxidation of glycol linkages leading to C—C bond scission [2], oxidation of cellulose chain ends containing hemiacetal linkages [3], or interaction of ceric ions with carbonyl groups on cellulose [5]. Besides, Gaylord and Anand [6] suggested that grafting on cellulose can result from donor-acceptor interaction between monomer-cellulose-water-ceric ion complexes and uncomplexed monomer. Thus, the mechanism of the initiation process is not completely understood.

MATERIALS AND METHODS

Commercial methyl methacrylate monomer was extracted with dilute NaOH solution to remove the hydroquinone stabilizer, dried over calcium chloride, and distilled under reduced pressure. Ceric ammonium nitrate was used without further purification. Holocellulose from *Gosweilerodenron balsamiferum* was obtained as described previously [7]. The holocellulose was steeped in sodium hypochlorite solution for 45 min at 29°C and then rinsed in a large volume of distilled water and air-dried. About 25 g portions of the bleached holocellulose were soaked in thioglycolic acid solutions (between 0.3 and 3.0 *M*) for various periods of time at 29°C and then washed thoroughly with dis-

tiled water, followed by methanol, and finally with distilled water again and then air-dried. The thiol contents were determined by reaction of 0.5 g portions with excess iodine at neutral pH, followed by back-titration of the unreacted iodine with thiosulfate [8].

Grafting of methyl methacrylate on the unmodified and thiolated holocellulose was carried out by using various amounts of ceric ions and a constant amount of the substrate (1.0 g) and monomer (18.8 mmol) dispersed in 50 mL of distilled water. The polymerization procedure was based on the method described by Lepoutre and Hui [4]. 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, followed by filtration, air drying, and weighing.

The ungrafted poly(methyl methacrylate) homopolymer was removed by Soxhlet extraction with tetrahydrofuran. The grafted material was then air dried and reweighed. The measured weight increase divided by the weight of the substrate and then multiplied by 100 was reported as the percent graft level.

The grafted polymer was isolated from the holocellulosic substrate by the method of Ogiwara et al. [9] and purified by solution in tetrahydrofuran and precipitation with methanol. The molecular weight of the isolated polymer was determined by measuring the intrinsic viscosity in acetonitrile at 30°C, using the relationship

$$[\eta] = 3.93 \times 10^{-6} \times \bar{M}_v^{1/2}.$$

RESULTS AND DISCUSSION

The results in Table 1 show that the incorporation of poly(methyl methacrylate) in the thiolated materials are lower than in the unmodified holocellulose. During the initial stages, ceric ions are consumed in the following reactions: 1) production of radicals on cellulose (initiation of graft polymerization); 2) abstraction of hydrogen from monomer in the continuous aqueous phase (initiation of homopolymer formation); and 3) sorption of ceric ions on the cellulosic substrate (inactivation of ceric ions). The relative extents of these reactions are believed to determine the level of grafting and the number of grafted copolymer chains. If initiation occurred by hydrogen abstraction from carbon atoms carrying hydroxyl groups, the replacement of some of the OH groups with SH groups would be expected to accentuate hydrogen abstraction and should lead to increased levels of grafting. The marked reductions in grafting in the presence of thiol groups indicates that hydrogen ab-

TABLE 1. Grafting Characteristics of Methyl Methacrylate on Holocellulosic Material

Grafting concentration, g/50 mL	Graft level, %				Average molecular weight, $\bar{M}_v \times 10^{-4}$				
	Bleached holocellulose	SH-Holocellulose		Bleached holocellulose	SH-Holocellulose		Bleached holocellulose	SH-Holocellulose	
		0.33%	1.32%		0.33%	1.32%		0.33%	1.32%
54	—	—	—	—	—	—	—	—	—
80	53	42	22	—	—	6.2	6.1	—	—
85	70	58	38	5.0	—	4.7	4.9	3.3	—
71	72	60	39	—	—	3.5	3.6	2.2	—
69	78	62	50	3.6	—	3.2	3.2	2.2	—
—	75	60	—	—	—	2.9	2.9	—	—
—	70	57	—	—	—	2.8	2.8	—	—

straction from the cellulosic material may not be the predominant mode of initiation.

Table 1 also shows that, as expected, the MW of the grafted copolymer decreases with increasing concentration of ceric ions. The MW of the PMMA grafted on thiolated holocellulose is of about the same order of magnitude as, but somewhat lower than, the MW of the PMMA grafted on unmodified holocellulose. Thus, although the presence of thiol groups is associated with marked reductions in the levels of grafting, its influence on the MW of the grafted copolymer is less significant.

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