Studies in the Graft Copolymerization of Vinyl Monomers on Cellulosic Materials

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Synopsis

Graft copolymerization of acrylonitrile, methyl methacrylate, and vinyl acetate on bleached holocellulose initiated by ceric ions in aqueous medium was studied at 29°C. The extent of graft copolymer formation was poly(methyl methacrylate) > polyacrylonitrile > poly(vinyl acetate), indicating the influence of polarity of monomer on graft copolymerization. It was found that, although the molecular weights of the grafted polyacrylonitrile copolymer were lower than the values obtained for poly(methyl methacrylate), the latter was less frequently incorporated on the cellulosic backbone polymer than the polyacrylonitrile grafts. The marked reductions in graft level associated with thiolation of the cellulosic material suggest that hydrogen abstraction reactions from carbon atom carrying hydroxyl groups may not be important in graft copolymer formation.

INTRODUCTION

The use of ceric ions to initiate graft copolymerization of vinyl monomers on cellulosic materials has been reported by several workers.[1-20] Initiation of graft copolymerization is generally considered to result from propagation by radicals formed on the cellulosic backbone polymer by oxidation reactions of ceric ions with cellulose chain ends containing hemiacetal linkages,[1] glycol linkages leading to C—C bond cleavage (at between C_2 and C_3),[6] and/or with carbonyl groups in the cellulosic substrate.[7] Besides, hydrogen abstraction from a carbon-atom-carrying hydroxyl group was considered important in the initiation of graft polymer formation.[9] However, the relatively high levels of homopolymer formation associated with grafting is inconsistent with the idea of graft polymer formation resulting mainly from radicals formed on the cellulosic substrate. Consequently, Gaylord and Anand[10] proposed a nonradical mechanism in which the formation of graft polymer is considered to result from a donor–acceptor type of interaction between cellulose–water–monomer–ceric ion complex and uncomplexed monomer rather than from radicals generated on the cellulosic substrate. Thus, although the use of ceric ions to initiate graft copolymerization of vinyl monomers on cellulose has been extensively reported, a gap exists in the present knowledge of the mechanism of graft polymer formation. For instance, could graft polymer chain result from the interactin of radicals formed on the substrate with growing homopolymer chains formed in the aqueous phase? This communication reports on the grafting characteristics of acrylonitrile, methyl methacrylate, and vinyl acetate on unmodified and modified (thiolated and oxidized) bleached holocellulose from Gosweilerodenron balsamiferum, a tropical hardwood.

MATERIALS AND METHODS

Acrylonitrile, methyl methacrylate, and vinyl acetate monomers from Hopkin and Williams Ltd. were extracted with aqueous sodium hydroxide/sodium chloride solution to remove the hydroquinone stabilizer. The hydroquinone-free monomers were distilled through vigreaux columns, and the middle fractions were collected as pure monomer samples. Ceric ammonium nitrate from BDH Ltd. was used without further purification. Aliquots of a $0.5M$ solution of the salt in $0.01M$ nitric acid were used to initiate polymerization. Bleached holocellulose from the tropical hardwood meal was prepared as described previously.[12]

Oxidation of the Bleached Holocellulose

A portion of the bleached holocellulose was steeped in acidic dichromate solution ($0.1M$ $K_2Cr_2O_7$ in $1M$ H_2SO_4) for 10 min. The oxidized holocellulose was washed several times with deionized water and air-dried.

Thiolation of the Bleached Holocellulose

Portions of about 100 g of the bleached holocellulose were treated with aqueous thioglycollic acid solution ($0.3–3.0M$) for between 1 and 24 h at 29°C in a well-ventilated hood. The thiolated holocellulose was washed thoroughly, first with water, followed with methanol, and finally with water and air-dried. The thiol content of the reduced cellulosic material was determined as reported previously.[13] In a typical experiment, a 0.5 g sample of the thiolated material was reacted with 20 mL of $0.1M$ aqueous iodine solution at neutral pH. The unreacted iodine was estimated by titration with standard thiosulphate solution. The average of triplicate titrations was used to estimate the thiol content of the holocellulose.[13]

Graft Polymerization

Graft copolymerization of acrylonitrile, methyl methacrylate, and vinyl acetate on the unmodified and modified holocellulose was carried out using various amounts of the monomers and ceric ions and a constant amount of cellulosic substrate (1.0 g) dispersed in 100 mL of distilled water at 29°C. The polymerization procedure was based on the method described by Lepoutre and Hui.[8] Polymerization was allowed to proceed for 1 h and the reaction was stopped by the addition of 1 mL of 1% (w/v) quinol solution to the reaction mixture. The mixture was filtered and the residue air-dried.

Extraction of Homopolymers

The ungrafted polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAC) homopolymers were Soxhlet-extracted with dimethyl formamide tetrahydrofuran, and methyl ethyl ketone, respectively. The grafted cellulosic materials were air-dried and reweighed. The weight of grafted polymer (W_g) expressed as a percentage of the weight of the cellulosic substrate was reported as percentage graft level (P_g).

Isolation and Molecular Weight Determination of Grafted Chains

The grafted polymers were isolated from the holocellulosic substrate with 72% sulfuric acid.[7] The mixture was filtered, the residue was extracted twice with a suitable solvent, and the grafted polymer was precipitated in a large excess of a nonsolvent. The isolated PAN, PMMA, and PVAC copolymers were purified by solution in dimethyl formamide, tetrahydrofuran, and methyl ethyl ketone, respectively, and precipitation in ethanol, methanol, and chilled heptane, respectively. The molecular weights of the copolymers were determined from viscosity measurements: PAN in dimethyl formamide solution at 30°C using the relationship[21]

$$\log_{10}[\eta] = \log_{10} 2.09 \times 10^{-4} + 0.75 \log \bar{M}_v \tag{1}$$

PMMA in acetonitrile at 30°C using the relationship[21]

$$\log_{10}[\eta] = \log_{10} 3.93 \times 10^{-6} + 0.50 \log \bar{M}_v \tag{2}$$

and PVAC in methyl ethyl ketone at 30° using the relationship[21]

$$\log_{10}[\eta] = \log_{10} 1.07 \times 10^{-4} + 0.71 \log \bar{M}_v \tag{3}$$

Frequency of Grafting

The weight of polymer grafted divided by the average molecular weight of the grafted chains ($\bar{M}$) gives the number of grafted chains (N_g). The number of grafted chains divided by the molecular weight of the repeat unit of the cellulosic substrate ($M_0 = 162$) represents the degree of substitution of the substrate by the copolymer grafts. The reciprocal of the degree of substitution gives a measure of the frequency of grafting (F_g)

$$F_g = M_0/N_g \tag{4}$$

The higher the value of F_g, the smaller the frequency of grafting.[22]

RESULTS AND DISCUSSION

The effect of thiolation on the levels of incorporation of polyacrylonitrile and PMMA graft polymers is shown in Figure 1. It would be seen that the levels of grafting on the thiolated holocellulose are markedly lower than on the unmodified holocellulose, with maximum graft levels of 26 and 62% for PAN and PMMA, respectively. If initiation of graft copolymerization by ceric ions occurred by hydrogen abstraction from carbon atoms carrying hydroxyl groups, the replacement of some of the OH groups on the cellulose with SH groups would be expected to accentuate the hydrogen abstraction reaction and should lead to improved levels of grafting. The marked reductions in graft level accompanying thiolation of the holocellulose indicates that hydrogen abstraction reaction may not be the predominant mode of initiation graft copolymerization by ceric ions.[13]
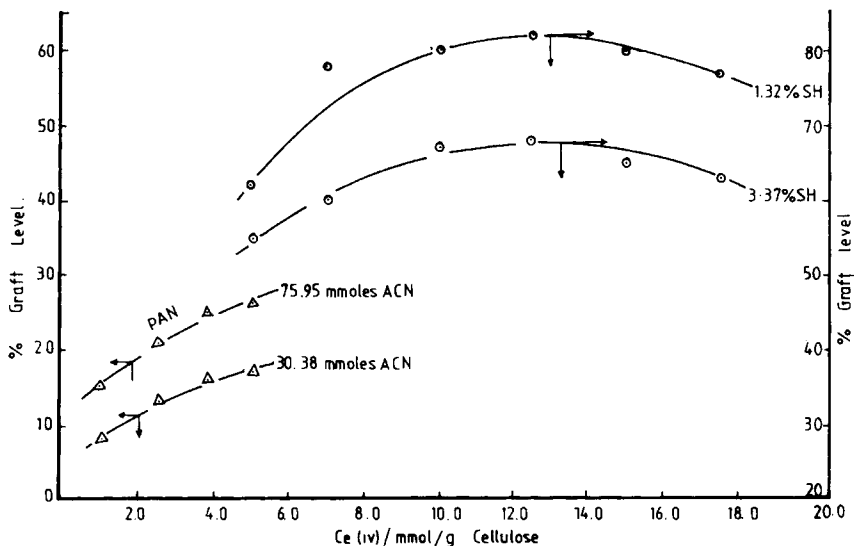
Fig. 1. Grafting acrylonitrile (ACN) (▲) on thiolated holocellulose (1.32% SH) and of methyl methacrylate (⊙) (28.20 mmol) on thiolated holocellulose at 29°C.

The molecular weight data of PAN and PMMA are shown in Tables I and II, respectively. It would be seen from Table I that the molecular weights of grafted PAN chains are lower than the molecular weights of the ungrafted homopolymer and that the molecular weights of grafted chains on the thiolated holocellulose are about the same order of magnitude as the values obtained for PAN grafts on the unmodified holocellulose. These results show that the incorporated thiol groups do not interact with growing graft polymer chains. The frequency of grafting acrylonitrile on the holocellulosic material is small and is of the order of PAN graft per 10^6 cellulose repeat units. Table II shows the molecular weight of PMMA grafts on both the unmodified and thiolated holocellulose. It can be seen that the molecular weights of the grafted PMMA chains are higher than those of the grafted PAN chains. However, the PMMA grafts are less frequently incorporated in the holocellulose than PAN grafts, with graft frequencies of the order of PMMA graft per 10^7 cellulose repeat units.

Figure 2 shows the effect of oxidation on the P_g of vinyl acetate on bleached holocellulose. It can be seen that the levels of incorporation of PVAC grafts on

TABLE I
Molecular Weight ($\overline{M}_v$) of Grafted Polyacrylonitrile
Polymer and Homopolymer

Amt. of ceric ion (mmol/g cellulose)	Amt. of monomer (mmol/g cellulose)	Average molecular weight ($\overline{M}_v$)			
		Grafted copolymer		Homopolymer	
		Bleached holocellulose	1.32% SH– holocellulose	Bleached holocellulose	1.32% SH– holocellulose
5.0	30.4	4.91×10^3	—	—	—
5.0	76.0	6.83×10^3	—	1.90×10^5	—
5.0	106.3	9.62×10^3	9.75×10^3	4.01×10^5	4.02×10^5

TABLE II

Molecular Weight ($\overline{M}_v$) and Number of Grafted Poly(methyl Methacrylate) Chains on Unmodified and Thiolated Holocellulose Using 28.17 mmol Monomer

Amt. of initiator [Ce(IV)/mmol]	Average molecular weight (10^{-5} $\overline{M}_v$)		No. of grafted polymer chains (mmol/100 g Cellulose)	
	Bleached holocellulose	1.32% SH– holocellulose	Bleached holocellulose	1.32% SH– holocellulose
2.5	6.7	—	8.1×10^{-5}	—
5.0	—	6.1	—	6.8×10^{-5}
7.5	5.0	4.9	17.0×10^{-5}	11.9×10^{-5}
10.0	—	3.6	—	16.4×10^{-5}
12.5	3.6	3.2	21.9×10^{-5}	19.3×10^{-5}
15.0	—	2.9	—	20.8×10^{-5}
17.5	—	2.8	—	20.5×10^{-5}

the oxidized holocellulose are about 10% higher than the levels on the unmodified holocellulose. Oxidation of cellulose with acidic dichromate solution is associated with the conversion of carbonyl groups to carboxyl groups and with partial degradation of cellulose. Although the change in both the carbonyl and carboxyl content of the holocellulose was not estimated, the improved graft levels associated with oxidation of the holocellulose may be due to the formation of more cellulose chain ends following the partial degradation of cellulose, which are capable of interaction with ceric ions to produce grafting sites.

Table III shows the molecular weight data of PVAC grafts on oxidized holocellulose. The low levels of P_g (lower than 20%) obtained on the unmodified holocellulose precluded isolation and molecular weight determination of the grafted chains. The molecular weight and frequency of grafting of PVAC
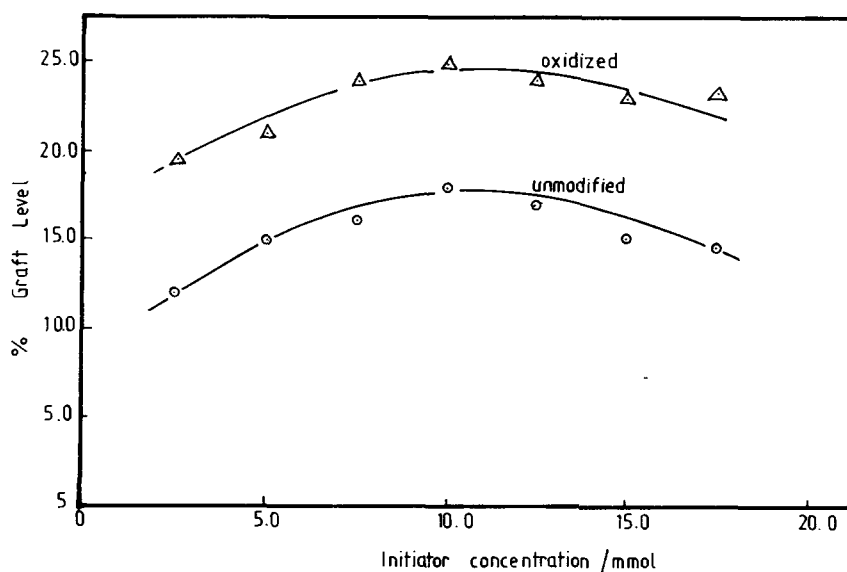

Fig. 2.   Grafting vinyl acetate monomer on (⊙) unmodified and (▲) oxidized holocellulose using 50.1 mmol monomer.

TABLE III
Molecular Weight Data of Poly(vinyl Acetate) Grafts
on Oxidized Holocellulose

Amt. of ceric ion (mmol/g cellulose)	Amt. of monomer (mmol/g cellulose)	Average molecular weight of grafted copolymer ($10^{-4}\ \overline{M}_v$)	No. of grafted copolymer chains (mmol/100 g cellulose)	Frequency of grafting
5.0	54.07	3.47	7.49×10^{-4}	2.16×10^7
5.0	86.51	4.37	5.49×10^{-4}	2.95×10^7
12.5	54.07	2.86	8.39×10^{-4}	1.89×10^7
17.5	54.07	1.88	1.28×10^{-3}	1.27×10^8

on the oxidized holocellulose are intermediate of the values reported for PMMA and PAN grafts.

It would seem from these results that the extent of graft polymer formation depends on the polarity of the monomer, with the more polar monomers showing little tendency towards grafting. The observed low frequency grafting indicates that only a small portion of the radicals formed on the cellulose backbone (probably those resulting from the interaction of ceric ion with cellulose chain ends) may be reactive towards graft polymer formation.

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