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GRAFT COPOLYMERIZATION OF 4-VINYLPYRIDINE ONTO PARTIALLY CARBOXYMETHYLATED CELLULOSE. THE DEGREE OF SUBSTITUTION EFFECT

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ABSTRACT

The graft copolymerization of 4-vinylpyridine (4-VP) onto partially carboxymethylated cotton (PCMC), having different carboxymethyl contents, was investigated. Under similar reaction conditions, both the graft yield and ceric ion consumption increased by increasing the degree of substitution of carboxymethyl groups of PCMC up to a value of 0.11, beyond which grafting and Ce(IV) consumption decreased. Proof for grafting onto PCMC was provided through IR analysis. The ceric salt-initiated polymerization of 4-VP in the absence of PCMC was also studied. Three series of homopolymerization reactions of 4-VP directly initiated by ceric ammonium nitrate were carried out with varying reaction times. Each series was run at a different nitric acid concentration. Both conversion and ceric ion consumption, as well as molecular weight, increased with reaction time. Increasing the nitric acid concentration increased both conversion and ceric ion consumption while the molecular weight decreased.

INTRODUCTION

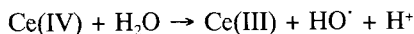
Grafting of vinyl monomers onto cellulose has been studied extensively with a variety of methods, e.g., chain transfer, high energy radiation, low energy

radiation in the presence of sensitizer, and redox systems, to initiate free radical formation. Detailed mechanisms of the reactions involved in grafting have been reviewed [1]. On account of its high efficiency compared to other known redox systems, the tetravalent cerium redox system has gained considerable importance in grafting vinyl monomers onto wool [2], silk [3], and collagen [4]. A large number of papers are available on the graft copolymerization of vinyl monomers onto cellulose [5] using Ce(IV) as initiator. This technique is based on the fact that when cellulose is oxidized by ceric salts such as ceric ammonium nitrate or ceric ammonium sulfate, free radicals capable of initiating vinyl polymerization are formed on the cellulose [6]. Since the radicals produced are extensively formed on the cellulose, grafting is usually more favored than homopolymer formation.

Studies [7–9] dealing with grafting of various vinyl monomers, such as acrylonitrile, methyl methacrylate, and acrylamide, onto partially carboxymethylated, acetylated, and cyanoethylated cellulose, using tetravalent cerium as initiator, have appeared. According to these reports, the substitution of cellulose hydroxyls by carboxymethyl [7], acetyl [8], or cyanoethyl [9] groups greatly affects the graft yield.

It was shown that the presence of $-\text{CH}_2\text{COOH}$ groups in the cellulose molecules substantially increases the amount of grafting [10].

Ceric ions form an effective redox pair with various reducing agents like alcohols (ethylene glycol [11], primary alcohols [12]), aldehydes (formaldehyde [13]), acids (glycolic [14] and malonic [15] acids), thiols (propanethiol [16]), and amines [17] for the polymerization of vinyl monomers. However, studies on polymerization by ceric ions alone, in the absence of a reducing agent, have been scanty [18–23]. Ananthanarayanan and Santappa [18] carried out a systematic kinetic study of the thermal polymerization of methyl methacrylate, methyl acrylate, and acrylonitrile. They pointed out that under the experimental conditions used, there was practically no oxidation of water by ceric ion and hence production of hydroxyl radicals by this means was negligible. They concluded that initiation took place by a direct reaction between monomer and ceric ion, involving an electron transfer from the former to the latter and producing a radical ion of the type $^+\text{CH}_2-\dot{\text{C}}\text{HX}$. Takahasi et al. [19] studied the effect of reaction time on ceric salt-initiated polymerization of acrylamide. Ghosh et al. [20] reported the aqueous polymerization of methyl methacrylate initiated by ceric sulfate in a dilute H_2SO_4 medium. An average of about 2 hydroxyl end groups per polymer chain was obtained by the application of the dye interaction technique. From this they proposed that initiation of polymerization by Ce(IV) was due to OH radicals formed by the reaction



In this paper the capacity of ceric ion to initiate the polymerization of 4-VP in the absence of a reducing agent, as well as the effect of the degree of substitution

(*DS*) of PCMC on the graft copolymerization of 4-VP onto PCMC, have been studied.

EXPERIMENTAL

The experimental work was performed as previously indicated [10].

Cotton ($\overline{M}_v = 4.28 \times 10^5$) was purified before use [24]. 4-VP (Merck) was refluxed over potassium hydroxide and distilled under nitrogen prior to use. Ceric ammonium nitrate (CAN), reagent grade, was supplied by Fluka and was used without further purification. The water used in all the experiments was prepared by the redistillation of distilled water containing a small amount of alkaline KMnO_4 .

PCMC preparation was based on the Green method [25], using sodium hydroxide and chloroacetic acid. PCMCs of various degrees of substitution were obtained by using different concentrations of chloroacetic acid. The degree of substitution, i.e., the average number of carboxymethyl groups introduced per anhydroglucose unit in the cellulose, was determined by the acid-wash method reported by Eyler et al. [26].

Graft polymerizations were carried out by mixing the cellulosic substrate (1 g) with a suitable amount of monomer (18.6 mmol) and CAN (2×10^{-4} mmol) in a nitric acid aqueous medium to get a total volume of 42 mL, under nitrogen atmosphere and continuous stirring (110 rpm) at 30°C for 4 h. Polymerizations were terminated by the addition of a small amount of hydroquinone. The homopolymer poly-4-vinylpyridine, precipitated by the addition of aqueous NaOH, was filtered, washed with water, and dried under phosphorous pentoxide. Homopolymer was removed from the crude by extraction with methanol in a Soxhlet extractor to constant weight.

Homopolymerization reactions were carried out at different intervals in the same way as the graft copolymerizations but in the absence of cellulose.

The concentration of the ceric ion in the reaction mixture was determined volumetrically [27] with ferrous ammonium sulfate using ferrous *o*-phenanthroline as indicator.

The molecular weights of poly(4-vinylpyridine) were calculated from intrinsic viscosities in absolute ethanol at 25°C [28] by employing an Ubbelohde viscometer.

The following grafting parameters were calculated as in a previous paper [10]. Graft yield, *G*, is the ratio of grafted polymer to cellulose; grafting efficiency, *GE*, is the ratio of grafted polymer to the total synthetic polymer; total conversion, *C_t*, is the monomer fraction that polymerizes; graft conversion, *C_g*, is the monomer

fraction that gives place to grafted polymer; and homopolymer conversion, C_h , is the monomer fraction that gives place to homopolymer.

Infrared spectra of samples were obtained by means of a Beckman 4250 spectrophotometer by use of the potassium bromide pellet technique.

RESULTS AND DISCUSSION

Effect of the Degree of Substitution of Carboxymethyl Groups

Figure 1 shows the graft yields for samples of PCMC of different DS . It is clear that increasing the DS up to 0.11 is accompanied by an increase in the graft yield of 4-VP, but beyond that point, DS does not cause a significant change of the maximum graft yield; the graft yield obtained with DS 0.38 is lower than that with DS 0.11 or 0.24.

It appears [7] that the introduction of $-\text{CH}_2\text{COOH}$ on the cellulose molecules causes two opposing effects: (a) opening up the cellulose structure, thereby enhancing diffusion and adsorption of both monomer and initiator; (b) blocking some of the hydroxyl groups present along the cellulose chains. Effect (a) leads to an increase in the graft yields whereas Effect (b) gives rise to a decrease. The predominating effect is the main controlling factor of graft yields. This, in turn, depends on changes in the substrate composition and in the reagents participating in the process as the grafting proceeds. It is likely that, for 4-VP, Effect (a) predominates up to a DS of 0.11, after which Effect (b) becomes much more pronounced.

The effect of DS on ceric consumption is shown in Fig. 2. It can be appreciated that the Ce(IV) consumed during the graft reaction increases as the DS grows up to 0.11. Any further increase in DS decreases Ce(IV) consumption. A similar trend is observed for the graft yield (Fig. 1). As mentioned previously, the introduction of carboxymethyl groups on the cellulose molecule increases the susceptibility of cellulose to Ce(IV) attack (by attracting Ce(IV) ions from the reaction medium), and at the same time decreases the number of hydroxyl groups. It is likely that increasing the DS of PCMC up to 0.11 favors the Ce(IV) attraction, while further increases operate adversely because of the reduction of free hydroxyl groups in cellulose. It is likely that this DS (0.11) constitutes a critical point at which maximum graft yield and maximum Ce(IV) consumption can be obtained. Kantouch et al. [7] observed the same behavior when grafting acrylonitrile onto PCMC of DS 0.0647 to 0.152. The maximum Ce(IV) consumption and maximum graft yield were obtained at a DS of 0.124.

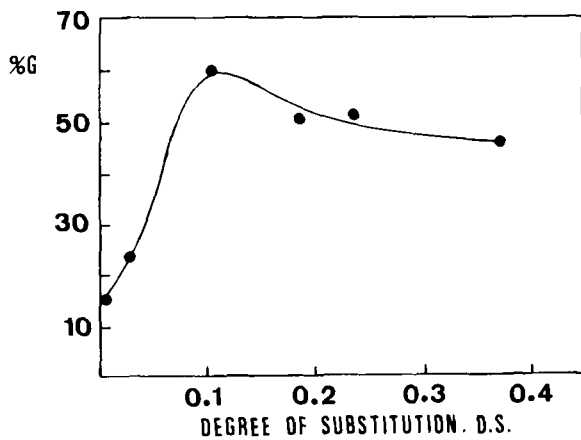
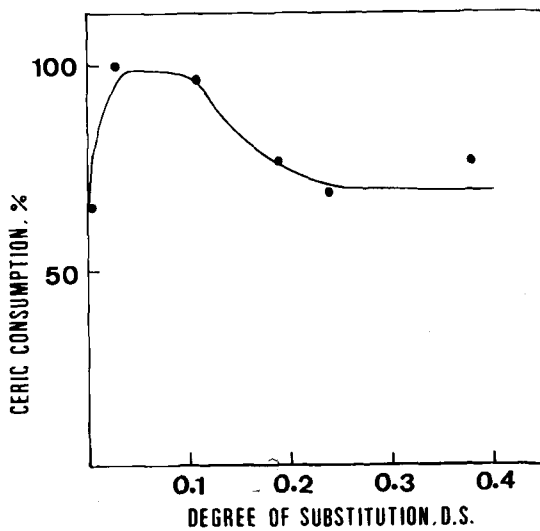


FIG. 1. Effect of degree of substitution on graft yield.

FIG. 2. Effect of degree of substitution on Ce^{IV} consumption.

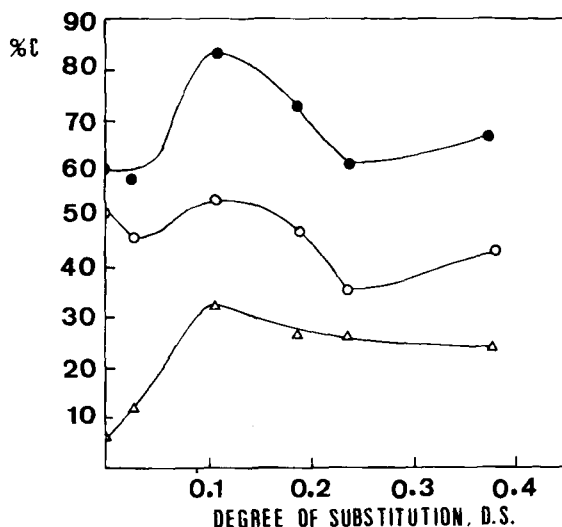


FIG. 3. Effect of degree of substitution on graft (Δ), homopolymer (\circ), and total conversion (\bullet).

The effect of the degree of substitution of partially carboxymethylated cotton on graft, homopolymer, and total conversion is shown in Fig. 3. Homopolymer conversion shows a trend similar to that of grafting. This parallelism appears to be due to a similar action of the captured ceric ion on cellulose, affecting both graft copolymerization and homopolymerization. Figure 4 shows that increasing the *DS* is accompanied by an increase in grafting efficiency.

Ceric Salt-Initiated Homopolymerization of 4-Vinylpyridine

Three series of direct homopolymerization reactions of 4-VP with ceric ion while varying the reaction time were carried out (Table 1). Each series of reactions was performed at a different nitric acid concentration. For HNO_3 concentrations of 0.53 and 0.5 *N*, an increase in conversion (*C*) with time is observed, reaching a constant value after 3 h. It should be noted that complete ceric ion consumption is reached, leading to constant *C*. On the other hand, for a HNO_3 concentration 0.49 *N*, a continuous increase of conversion throughout the time interval studied is observed.

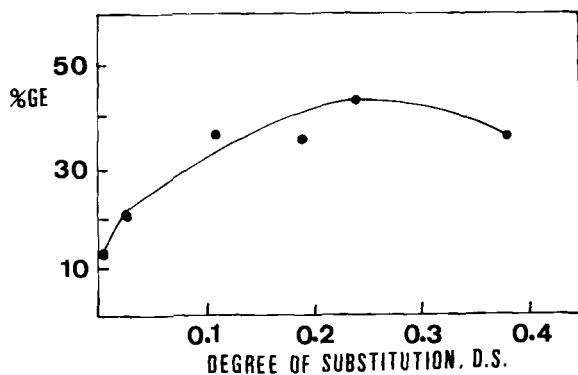


FIG. 4. Effect of degree of substitution on grafting efficiency.

As can be seen in Table 2, the molecular weight increases with time until it reaches a constant value after 3 h of reaction. The reaction conversion is higher when polymerization is carried out at a HNO_3 concentration of 0.53 N than for 0.5 N HNO_3 , but the \bar{M}_v resulted in the opposite manner, so it is deduced that the number of polymer chains is higher in the former case.

The ceric ion consumption, $(\text{Ce}^{\text{IV}})_c$, increases with both time and nitric acid concentration (Table 1). The higher ceric ion consumption in most acidic media

TABLE 1. Effect of Reaction Time on Homopolymerization of 4-VP by CAN Initiation

t (min)	[HNO_3] = 0.49 N		[HNO_3] = 0.5 N		[HNO_3] = 0.53 N	
	C (%)	$(\text{Ce}^{\text{IV}})_c$ (%)	C (%)	$(\text{Ce}^{\text{IV}})_c$ (%)	C (%)	$(\text{Ce}^{\text{IV}})_c$ (%)
15	14	10	20	22	24	68
30	20	25	23	50	32	87
60	22	35	29	48	36	—
120	22	32	39	51	45	—
180	38	32	63	80	73	100
240	47	64	62	100	74	100
300	60	61	61	100	72	100

TABLE 2. Effect of Reaction Time on Molecular Weight of P(4-VP) Homopolymerized by CAN

t (min)	$\bar{M}_v \times 10^{-3}$	
	[HNO ₃] = 0.5 <i>N</i>	[HNO ₃] = 0.53 <i>N</i>
15	112	115
30	155	165
60	188	172
120	214	—
180	269	208
240	—	204
300	267	218

may be due to an increase in the oxidation power of the latter ion with increasing nitric acid concentration, having as a consequence a higher participation of this ion in the initiation and termination reactions, which explains why the molecular weights obtained at an HNO₃ concentration of 0.53 *N* are lower than at 0.5 *N*.

The following mechanism was proposed [5]:

Initiation:



Propagation:



Termination by combination:



Termination by disproportionation:



Transfer to monomer:



Termination by electron transfer:



The transfer constant to 4-VP is very small, 7×10^{-5} [29], and therefore Reaction (6) is unimportant.

The amount of poly(4-vinylpyridine) obtained in homopolymerization reactions is lower than what is obtained as a by-product in graft reactions at the same reaction conditions [30].

Ceric ion consumption is lower in direct homopolymerization reactions. This higher ceric ion consumption in graft reactions occurs because the ceric ion, in addition to attacking the monomer, participates in cellulosic radicals generation. In such reactions the amount of poly(4-vinylpyridine) involved is higher than in the direct homopolymerization reaction. It seems that there could be an electron transfer from the cellulosic radicals to the monomer molecules, resulting in homopolymerization.

The above findings indicated show the large capacity of the ceric ion to initiate direct polymerization of 4-VP, which explains the fact that for graft copolymerization reactions the grafting efficiency values achieved are lower than 50%, because homopolymerization is more favored than grafting.

Direct homopolymerization of 4-VP of metal ions has been reported [21–23]. Wang [21] proposed that the initiation of polymerization of 4-VP by metal ions (Fe^{3+} , Cu^{2+} , Ce^{4+}) took place by a one-electron transfer process. The cation radicals from 4-VP may undergo rearrangement to form the corresponding carbon radicals, which then initiate polymerization.

Tazuke et al. [22, 23] studied the polymerization of 4-VP initiated by cupric acetate. Polymerization was found to be inhibited in the presence of air, which supported a radical mechanism. The results indicated that polymerization occurred by the spontaneous (unimolecular) decomposition of the 4-vinylpyridine–cupric acetate complex, which involves reduction of the cupric species to the cuprous species. The presence of a coordination bond between cupric ion and nitrogen of the pyridine group seems to be absolutely necessary because the addition of acetylacetone to the system inhibited polymerization. It seemed that the more stable copper(II) acetylacetonate was formed and prevented the cupric ion from coordinating with 4-VP.

IR Spectra of Graft Copolymer and Homopolymer

Figure 5 shows the infrared spectra of poly(4-vinylpyridine) which was isolated after being hydrolyzed from the cellulose backbone. It shows bands at 1600 ($\nu_{\text{C}=\text{C}}$, $\nu_{\text{C}=\text{N}}$), 1492 ($\nu_{\text{C}=\text{C}}$), 992 ($\delta_{\text{CH in-plane}}$) and 882 ($\delta_{\text{CH out-of-plane}}$) cm^{-1} [31]. In Fig. 6 the infrared spectra of PCMC ($DS = 0.24$) is compared with the spectrum of PCMC-*g*-poly(4-vinylpyridine) ($G = 40\%$). PCMC (Fig. 6, A) exhibits a broad band centered at 1700 cm^{-1} , which is assigned to the C=O group [32], and the characteristic broad band of hydroxyl groups around 3300 cm^{-1} . The spectrum of grafted PCMC (Fig. 6, B) shows an absorption band at 1740 cm^{-1} of cellulosic substrate and an additional peak at 1600 cm^{-1} , typical of poly(4-vinylpyridine).

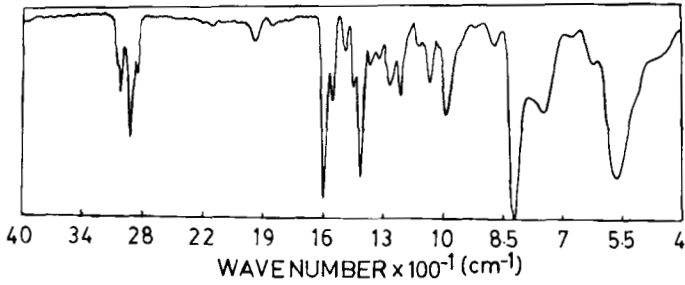


FIG. 5. Infrared spectra of poly(4-vinylpyridine) obtained after hydrolysis of PCMC-*g*-poly(4-vinylpyridine).

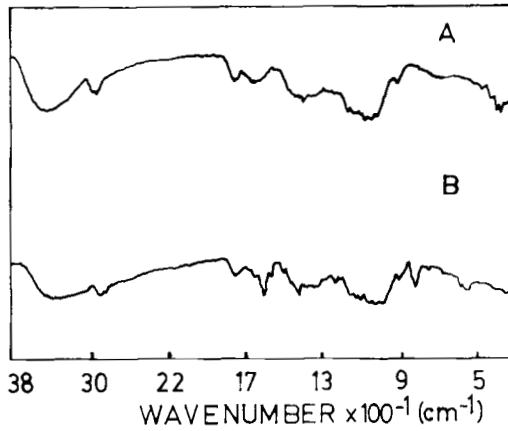


FIG. 6. Infrared spectra of (A) PCMC and (B) PCMC-*g*-poly(4-vinylpyridine).

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