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GRAFT COPOLYMERIZATION OF 4-VINYLPYRIDINE ONTO MODIFIED CELLULOSIC FIBERS. THE CERIC ION CONCENTRATION EFFECT

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ABSTRACT

The graft copolymerization of 4-vinylpyridine was carried out on mercerized cellulose and partially carboxymethylated cellulose (PCMC) using ceric ammonium nitrate (CAN) as the initiator. The grafting parameters (grafting efficiency (*GE*), graft yield (*G*), and total conversion (C_t)) were studied as a function of CAN concentration. It was shown that by increasing the CAN concentration, *G* and C_t reached a maximum. The graft yields for PCMC were significantly higher than those for mercerized cellulose. The largest *GE* values appeared for PCMC and mercerized cellulose at low and high CAN concentrations, respectively. The Ce(IV) consumption during grafting increased with rising concentration of CAN, and it was greater in the case of PCMC than of mercerized cellulose. After acid hydrolysis of the polysaccharide backbone, the average molecular weight of grafts was determined viscometrically. Molecular weight decreased with initiator concentration. Graft frequency (*GF*), on the other hand, increased with CAN concentration. *GF* for PCMC was higher than that for mercerized cellulose. Ce(IV) consumption increased with CAN concentration and it was lower for mercerized cellulose than that consumed during grafting on PCMC. After that, the effect of CAN concentration on the graft copolymerization onto PCMC was examined while the total nitrate ion concentration was maintained constant at 1.59 *M* by addition of sodium nitrate. Maximum *G*, C_t, and Ce(IV) consumption were higher than in the previous case.

INTRODUCTION

Several synthetic polymers have been grafted onto cellulose by using various initiating systems with varying degrees of success to modify its properties: reviews are available [1, 2]. The successful grafting of vinyl monomers onto cellulose involves the generation of reactive sites on the backbone of cellulose by means of photoinitiation, low energy radiation in the presence and absence of sensitizers or chemical methods [1]. Metal ions in their higher valence states, e.g., Cr(VI) [3], V(V) [4], Ce(IV) [5], Co(III) [6], and Mn(IV) [7], have been used as initiators for polymerization of a number of vinyl monomers.

Of the various metal ions available, tetravalent cerium has been used in the present investigation because of its ability to cause higher yields of grafting. Ceric ions complex with cellulose hydroxyl groups and the decomposition of the complex results in the formation of free radicals on the backbone.

This paper presents the results of studies of the effect of ceric ammonium nitrate concentration on the graft copolymerization of 4-vinylpyridine (4-VP) onto partially carboxymethylated cotton and mercerized cotton.

EXPERIMENTAL

The experimental work was performed as previously indicated [8].

Cotton ($\overline{M}_v = 4.28 \times 10^5$) was purified [9] before use. 4-VP (Merck) was refluxed over potassium hydroxide and distilled under nitrogen prior to use. Ceric ammonium nitrate, reagent grade, was supplied by Fluka and was used without further purification.

Partially carboxymethylated cellulose (PCMC) was prepared by the Green method [10] by using sodium hydroxide and chloroacetic acid. The degree of substitution (*DS*), 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. [11]. A value of 0.24 was obtained.

For the mercerizing treatment, cotton was treated by refluxing in 20% aqueous sodium hydroxide for 18 h. After alkali treatment, the cotton was washed with distilled water at room temperature until the washing water was at neutral pH [9].

Graft polymerizations were carried out by mixing the cellulosic substrate (1 g) with a suitable amount of monomer (4-VP, 18.6 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. Hydroquinone was added at the end of the reaction to stop polymerization. The homopolymer poly-4-vinylpyridine, P(4-VP), was precipitated by the addition of aqueous NaOH, filtered, washed with water, and dried under phosphorous pentoxide. Homopolymer was completely removed from the crude by extraction with methanol in a Soxhlet extractor to constant weight.

The concentration of the ceric ion in the reaction mixture was determined volumetrically [12] with ferrous ammonium sulfate using ferrous *o*-phenanthroline as indicator.

The graft copolymers were immersed in 72% H_2SO_4 (22 mL) and stirred for 6 h at room temperature [13] to carry out the hydrolysis of the cellulosic copolymer backbone.

The molecular weights of the separated P(4-VP) grafts were calculated from intrinsic viscosities in absolute ethanol at 25°C [14] by employing an Ubbelohde viscometer.

The following grafting parameters were calculated as in a previous paper [8]. *G* is the ratio of grafted polymer to cellulose; *GE* is the ratio of grafted polymer to the total synthetic polymer; C_t is the monomer fraction that polymerizes; *GF* is the average number of grafted polymer chains per cellulose chain.

RESULTS AND DISCUSSION

With both substrates studied, it is observed from Fig. 1 that with an increase in the concentration of Ce(IV), the graft yield increases up to a certain limit, indicating that there exists a critical concentration of Ce(IV) which depends on the nature of the substrate, beyond which the graft yield decreases. Similar observations have also been reported with other monomers [5, 15, 16].

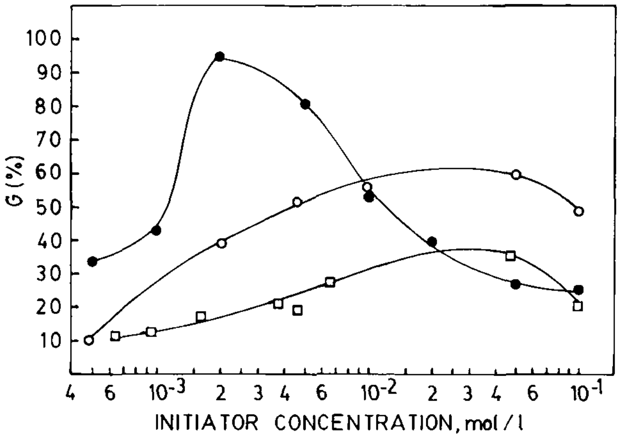

FIG. 1. Effect of initial CAN concentration on graft yield: (□) mercerized cotton; (○) PCMC, $[NO_3^-]_t \neq$ constant; (●) PCMC, $[NO_3^-]_t = 1.59$ *M*.

When 4-VP was grafted onto PCMC while the total nitrate ion concentration was kept constant (1.59 *M*) by sodium nitrate addition, the maximum graft yield (95%) is achieved at a CAN concentration of 2 mmol/L (Fig. 1). That value was higher than that obtained when the total nitrate ion concentration varies (59% at a CAN concentration of 50 mmol/L). At low CAN concentrations the graft yield values, when the total nitrate ion concentration is not constant, are lower than those at a total nitrate ion concentration of 1.59 *M*, but beyond a CAN concentration of about 10 mmol/L the curves intersect and the graft yield is higher than in the case where the total nitrate ion concentration is 1.5 *M*.

It is observed that the graft yields for PCMC are significantly higher than those for mercerized cotton.

In a previous paper we reported that changing the chemical structure of cellulose by carboxymethylation enhances the behavior of cellulose toward grafting [8]. This could be attributed to the combined influence of the following factors: (a) carboxymethyl groups increase the swellability of cellulose, thereby facilitating diffusion of monomer and initiator; and (b) the ionization of carboxyl groups along the cellulose chains introduces negative charges which attract ceric ions to the cellulose molecules, leading to formation on the cellulose backbone of more active sites abailable for the monomer, thus increasing the reactivityof cellulose.

The effect of ceric ion concentration on the average molecular weight of grafted side chains and on the graft frequency for both PCMC and mercerized cotton is shown in Figs. 2 and 3, respectively. Molecular weight decreases with initiator concentration. Graft frequency, on the other hand, increases with initiator con-

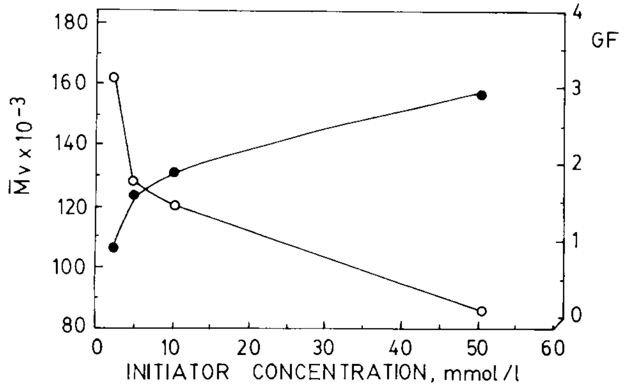

FIG. 2. Effect of initial CAN concentration on the molecular weight of the grafted polymer (○) and on the graft frequency of the graft copolymer (●). PCMC, $[NO_3^-]_t \neq$ constant.

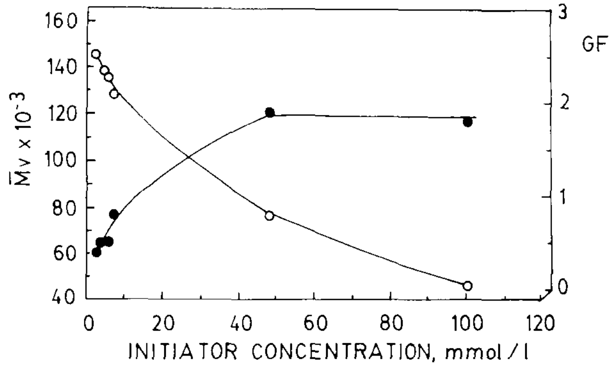

FIG. 3. Effect of initial CAN concentration on the molecular weight of the grafted polymer (○) and on the graft frequency of the graft copolymer (●). Mercerized cotton.

centration. This is in accordance with previous studies carried out by Kubota and Ogiwara [17], Lepoutre and Hui [18], Huang and Chandramouli [19], and Ogiwara et al. [20]. It should also be noticed that the values for graft frequency are higher for PCMC than those for mercerized cotton. The $\overline{M}_v$ do not differ appreciably.

The parameter's behavior may be interpreted as reflecting the action of ceric ions on the generation of active sites on the cellulose macromolecules and the oxidative termination of the growing chains, i.e., the increasing concentration of ceric ions results in (a) an increase in the total number of the complex cellulose–ceric ions which decompose to give more active sites (graft frequency increases) and, on the other hand, (b) an increase in the concentration of free ceric ions which quench, by oxidative termination, the growth of the grafted chains; this may explain the decrease in molecular weight observed for the poly(4-vinylpyridine) grafts. It is likely that effect (a) predominates up to a critical concentration of Ce(IV) (graft yield increases) beyond which effect (b) becomes much more pronounced (graft yield decreases).

The effect of CAN concentration on total conversion has been also studied (Fig. 4). Total conversion with both mercerized cotton and PCMC increases as the CAN concentration increases, attain maxima, and then fall at higher concentrations. But maximum total conversion for mercerized cotton is achieved at lower CAN concentration than that for maximum graft yield. Since total conversion is the sum of monomer converted to grafted polymer as well as to homopolymer, this finding implies that grafting is more favored than homopolymerization at low CAN

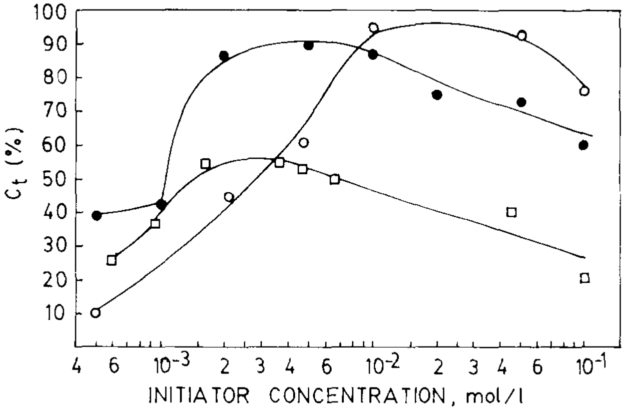

FIG. 4. Effect of initial CAN concentration on total conversion: (□) mercerized cotton; (○) PCMC, $[NO_3^-]_t \neq$ constant; (●) PCMC, $[NO_3^-]_t = 1.59$ *M*.

concentrations. In the case of PCMC, when the total nitrate ion concentration is not constant, maxima in graft yield and conversion to homopolymer appear at the same range of CAN concentration. But at a constant total nitrate ion concentration of 1.59 *M*, maximum grafting is achieved upon using a CAN concentration of 2 mmol/L, in contrast to 10 mmol/L for the maximum homopolymer conversion. The total monomer conversions at low CAN concentrations are lower for the 1.59 *M* total nitrate ion concentration case.

As a result of all of these factors, grafting efficiency (Fig. 5) is affected by the

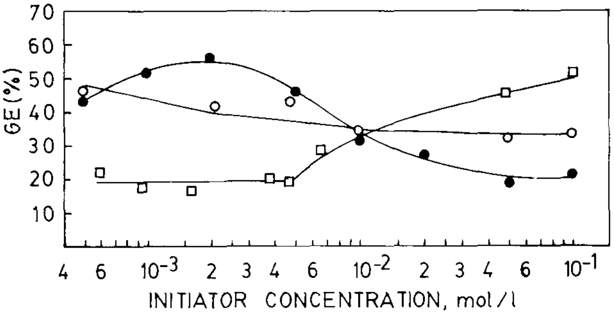

FIG. 5. Effect of initial CAN concentration on grafting efficiency: (□) mercerized cotton; (○) PCMC, $[NO_3^-]_t \neq$ constant; (●) PCMC, $[NO_3^-]_t = 1.59$ *M*.

ceric ion concentration according to laws noticeably different depending on the nature of the cellulosic substrate. The grafting efficiency for mercerized cotton remains constant with the CAN concentration in the 0.6–4.7 mmol/L range and starts increasing at higher concentrations, achieving a *GE* value of 51% at the higher CAN concentration used: 100 mmol/L. For PCMC the grafting efficiency for the constant total nitrate ion concentration case shows a maximum at low CAN concentrations and then decreases with increasing initiator concentration. In the variable total nitrate ion concentration case the grafting efficiency decreases slowly over all the CAN concentrations studied, and its values at CAN concentrations up to 10 mmol/L are lower than those for the 1.59 *M* total nitrate ion concentration case.

Under the same reaction conditions, higher grafting efficiency values are shown by PCMC at low CAN concentrations, while higher values for mercerized cotton at high CAN concentrations are obtained.

The consumptions of Ce(IV) during grafting onto mercerized cotton and PCMC are illustrated in Fig. 6. It is clear that with the two substrates, although the values differ, the Ce(IV) consumption increases with CAN concentration. It is also of interest to note that Ce(IV) consumption is complete at low CAN concentration (2 mmol/L). Ce(IV) consumption during grafting on mercerized cotton is significantly lower than that consumed during grafting on PCMC; with this substrate the

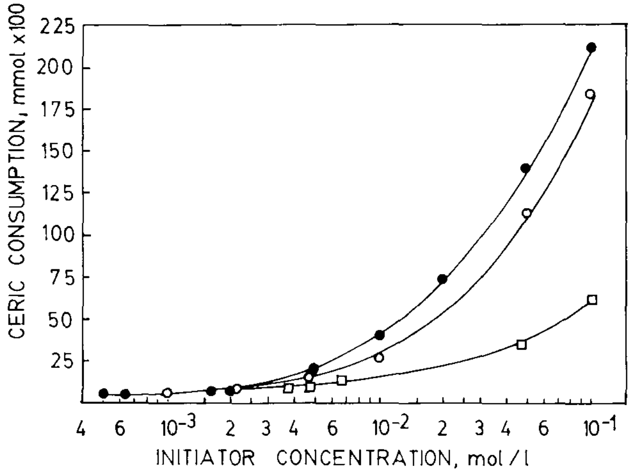

FIG. 6. Effect of initial CAN concentration on ceric ion consumption: (□) mercerized cotton; (○) PCMC, $[NO_3^-]_t \neq$ constant; (●) PCMC, $[NO_3^-]_t = 1.59$ *M*.

ceric ion consumption is higher when the total nitrate ion concentration is constant.

Tetravalent cerium in nitric acid solution is known to be coordinated with nitrate ions, hydroxyl ions, and water molecules [21–24]. The relative concentration of each species is not known. In addition, these complexes vary with the nitrate ion and hydrogen ion concentrations in the solution. In the present study the ceric ion consumption increased when $NaNO_3$ was added to the reaction medium; it is probable that the ceric complexes present are stronger oxidizing agents, promoting both the oxidation of cellulose and the initiation and termination of the radicals present.

Although it is generally accepted that the grafted, synthetic polymer is bonded at carbon C_2 and C_3 along the cellulose chain, there are indications [25–29] that allow us to suggest that a portion of the synthetic polymer may be linked at the hemiacetal group at the end of the cellulose chain, which would actually constitute a block copolymer.

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