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The Preparation and Properties of Acrylic and Methacrylic Acid Grafted Cellulose Prepared by Ceric Ion Initiation. Part I. Preparation of the Grafted Cellulose

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ABSTRACT

The ceric ion method has been used to graft acrylic acid directly onto cellulose with a minimum amount of homopolymer. The method utilizes the pretreatment of the cellulose with ceric ammonium nitrate followed by washing out any excess of the catalyst. Oxygen can be present with the pretreatment step, but must be excluded during the grafting reaction itself. The process, which is entirely aqueous in nature, would appear to be quite practical on a large scale. Wet strengthened papers which are essential for the use of the grafted products as ion-exchange media can also be grafted but with adequate but lower yields than with the untreated paper. Apart from ion exchange, the products are of considerable potential value as water sorbing agents. Methacrylic acid gave lower grafting yields than acrylic acid, but these were much improved at higher temperatures.

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INTRODUCTION

There is considerable industrial and academic interest in cellulose-g-poly(acrylic acid) and cellulose-g-poly(methacrylic acid) copolymers. The products are of value because of their ion-exchange properties and, in the form of their alkali metal salts, their high water absorbency. When prepared in a special way, the so-called super-water sorbents can be obtained. These can retain more than 30 times their weight in water and have potential applications for sanitary and medical uses, as soil conditioners, and many other applications. The usual method of preparation has been to graft, using chemical initiation, particularly ceric ion, monomers such as acrylonitrile and/or acrylate and methacrylate esters followed by alkaline hydrolysis. One of the main reasons for this two-step approach has been the large amounts of homopolymer formed when acrylic or methacrylic acids are grafted directly with chemical initiators. Excessive homopolymer can be avoided, however, by using high-energy radiation. The direct, mutual method requires the use of free radical inhibitors in the aqueous phase to reduce homopolymer to a minimum. The preirradiation technique essentially eliminates the problem [1]. Both methods are being pursued industrially to produce acrylic-acid-grafted polyethylene films for battery separators.

There is a growing interest and acceptance of high-energy radiation as a useful industrial initiator for polymerization grafting and crosslinking. In spite of this, many industries prefer the more familiar chemical appraoches. In the work previously reported using chemical initiation, the grafting yields were rather low and considerable homopolymer was formed [2-4]. More recently, Gangneux, Wattiez, and Marechal [5] have reported a method for grafting acrylic acid to cellulose powder, Solka Flóc, for use in textile wastewater treatments. The cellulose was pretreated with ceric ion in aqueous solutions, the excess removed by squeezing and the acrylic acid introduced in benzene solution. Since the hydrated ceric ions could not easily diffuse into the benzene solution of the monomer, comparatively little homopolymer was formed. Grafting yields of up to 70%, based on 100 parts of cellulose, were obtained but still with about 45% homopolymer. Quite recently McDowall, Gupta, and Stannett [6] have further refined the method with yields up to 60% and less than 5% homopolymer. However, this method still used organic solvents and for industrial use, particularly in the pulp and paper industry, all-aqueous systems are greatly preferred. The pretreatment of wood pulp with ceric ammonium nitrate followed by the addition of aqueous acrylic acid solution was found to give up to 18% grafting, together with an unknown amount of homopolymer, in an unpublished report by Ogiwara, Kubota, and Tanizaki [7]. This method has been further explored here in considerable detail and developed into a viable all-aqueous system. It should be pointed out that the use of acrylonitrile presents toxicity problems as it is a known carcinogen. In this respect, the direct grafting of acrylic acid offers a

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definite advantage in spite of the lower cost of acrylonitrile. This cost advantage is not found, however, when the nontoxic acrylic esters are used. The results of this work are reported in this paper.

EXPERIMENTAL

Materials

Filter paper prepared from bleached sulfite softwood pulp was the cellulose used throughout the investigation.

Ceric ammonium nitrate (CAN), reagent grade, was obtained from the Fisher Scientific Company and used without further purification.

Acrylic acid (AA) and methacrylic acid (MAA) were obtained from the Rohm and Haas Co. and purified by distilling twice under vacuum in the presence of copper powder to prevent polymerization. Other monomers were obtained from the Fisher Scientific Company and distilled at atmospheric pressure before use.

Nitrogen gas containing less than 1 ppm of oxygen was obtained from Air Products Inc.

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Grafting Procedure

After considerable experimentation, the following procedure was adopted. A 500-mL glass kettle fitted with an electric stirrer and nitrogen inlet and outlet parts was used. The nitrogen inlet had a fritted glass end. The temperature was controlled at 25°C by use of a thermostatted water bath. The filter paper was separated from the stirrer by a spacer consisting of two glass rings connected by vertical rods.

The actual procedure consisted of the following steps: 1) pretreatment of the paper with catalyst solution, 2) washing out excess catalyst, 3) reaction with the monomer solution, 4) washing out any homopolymer formed. The details of each step were as follows:

1. In all experiments, a 6 in. × 4 in. filter paper (machine direction × cross direction) was used. Fresh catalyst solution was prepared by dissolving a known amount of ceric ammonium nitrate in 0.1 N nitric acid and mixing with deionized water to obtain the required concentration. Typically, 300 mL of the catalyst solution containing 105 mL of 0.1 N nitric acid was used in the pretreatment step. The catalyst solution in the glass vessel was maintained at a constant temperature by immersing it in a constant temperature water bath. The solution was bubbled through a sintered glass with a continuous stream of nitrogen gas. Cellulosic filter paper was placed in the catalyst solution for the required amount of time. The typical pretreatment time

was 2 h. The cerium content of the paper was determined when needed by neutron activation analysis.

2. After pretreatment, the paper was removed from the catalyst solution and rinsed thoroughly with deionized water twice. At least 200 mL of deionized water was used each time. Then the filter paper was passed through rubber press rolls to squeeze out excess water. Thorough washing of the filter paper was found to be necessary in order to prevent homopolymer formation in the reaction stage.

3. The reaction medium in the reaction kettle, consisting of deionized water and nitric acid, was first degassed by passing nitrogen through the solution for at least 30 min. The catalyst-treated cellulosic filter paper was then placed in the reaction kettle to which was added 30 mg of copper powder, to inhibit homopolymer formation, and the monomer(s). Nitrogen gas continued to be bubbled through the medium during the whole reaction period. After the reaction time was completed, the grafted paper was removed from the solution and was washed thoroughly to remove the soluble contents. The typical pretreatment and grafting conditions used are summarized in Table 1.

4. Finally, the grafted paper was extracted with the solvent appropriate for the homopolymer, viz., methanol for polyacrylic acid, benzene for polymethyl acrylate, and N,N-dimethylformamide, at 80°C, for polyacrylonitrile. The methanol and benzene extractions were

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TABLE 1. Typical Reaction Conditions

A. Pretreatment conditions:	
Total volume	300 mL
CAN concentration	200 mmol/L
Nitric acid concentration	0.035 N
Time	2.0 h
Temperature	25°C
B. Grafting conditions:	
Total volume	600 mL
Monomer concentration	5% by volume
Nitric acid concentration	0.27 N
Copper powder	30 mg
Time	5.0 h
Temperature	25°C

carried out in a Soxhlet apparatus for 24 h. The percent graft was calculated by weighing after drying at 40°C under vacuum and based on the original dry weight of the cellulose. This value represents the unextractable polymer in the cellulose substrate. Twenty-four hours was found to lead to constant weights.

RESULTS AND DISCUSSION

Effect of the Processing Variables on Acrylic Acid Grafting

The Pretreatment Step

The cerium content of the filter paper was determined, using neutron activation analysis, after various times of immersion in the CAN solution containing nitric acid. Typical results are shown in Fig. 1 together with the conditions used. Although nitrogen was used, it was found subsequently that air was also suitable for this step of the process (see also Ref. 6). The amount of ceric ion sorbed rose steadily to a maximum at 2 h and then decreased somewhat. The decrease, although reproducible, was somewhat unexpected. It was presumably due to some concurrent decomposition and solution of the ceric-cellulose complex. A detailed study of the sorption of CAN by cellulose together with a discussion of the various reactions and mechanisms has been presented by Ogiwara, Ogiwara, and Kubota [8]. A pretreatment time of 2 h, giving the maximum cerium concentration, was selected for all the experiments reported in this study.

The Grafting Process

Typical grafting-time curves at two monomer concentrations are shown in Fig. 2. The rate increased somewhat with time, perhaps because of oxygen exhaustion or monomer diffusion effects. Good yields were obtained in 2-5 h.

The effect of monomer concentration is presented in Fig. 3. As is normal, except at high concentrations where swelling effects may be involved, the yield steadily increases; at 8% monomer solutions, more than 200% grafting was obtained.

Varying the concentration of CAN in the pretreatment step also affects the yield and the homopolymer formation as shown in Fig. 4. The falling off of yield at higher concentrations is a well-known phenomena [9] and ascribed to the increasing participation of the ceric ion in the termination process. Since this is particularly marked in the homopolymer yield, presumably noncomplexed ceric ions are present, some of which can escape into the supernatant monomer solution. At 15 mmol/L of CAN, there is nearly 45% grafting with essentially no homopolymer. At 20 mmol/L, grafting has increased to 128% but together with 22% of homopolymers.

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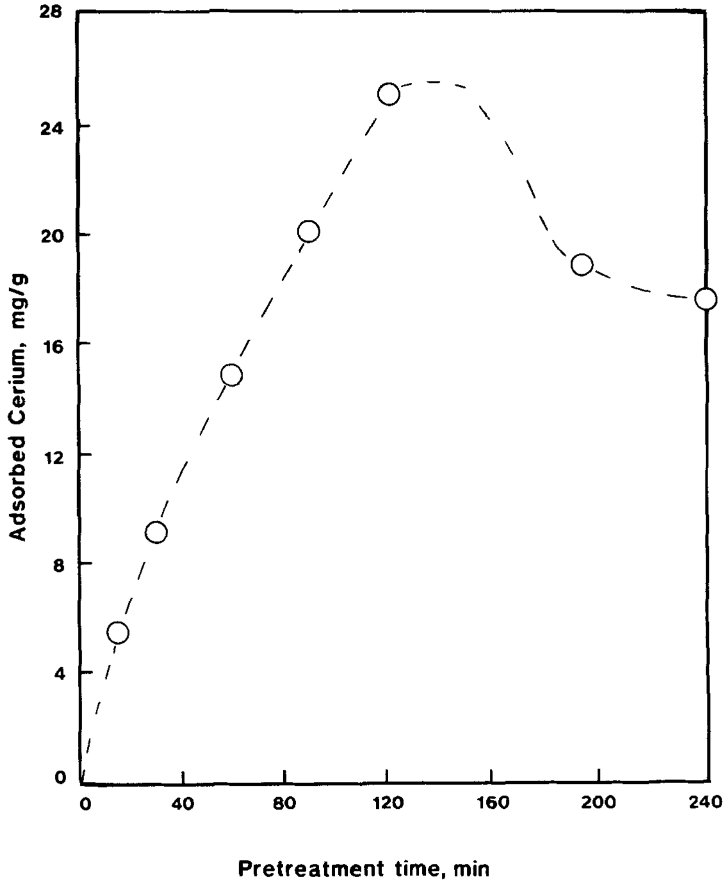

FIG. 1. The rate of adsorption of cerium by cellulose at 25°C from 20 mmol CAN/L in 0.035 N nitric acid solution.

The effect of pH is quite dramatic both with acrylic acid and acrylonitrile as can be seen in Fig. 5. These effects have been noted also by Teraski and Matsuki [10], by Ogiwara et al. [7], and by Katai et al. [11] in the direct polymerization of acrylonitrile. It is believed that the dissociation constants of the cellulose, or other, ceric ion complexes sharply decrease at higher pH values.

The well-known inhibiting effect of oxygen was also operative in this work. For example, the grafting yield dropped from 125% under nitrogen to only 2% under similar experimental conditions but in air.

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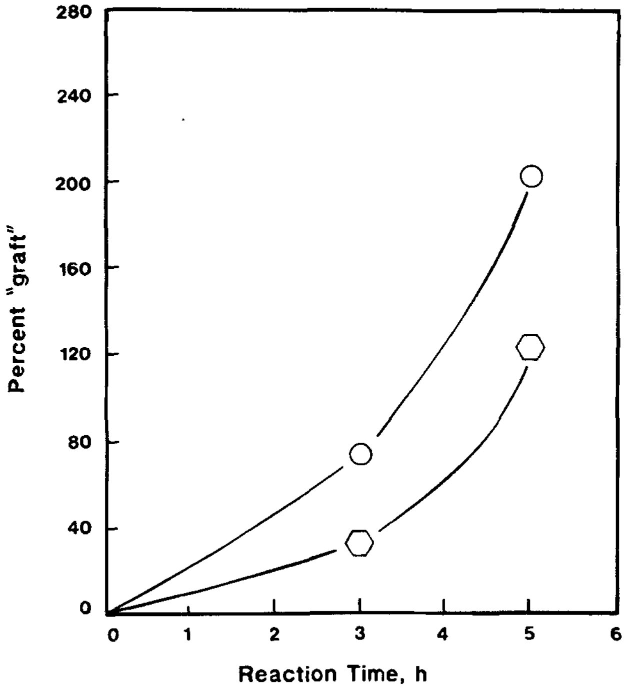

FIG. 2. The rate of grafting of acrylic acid to filter paper at 25°C. Pretreated with 20 mmol/L in 0.035 N nitric acid solution for 2 h. Reaction in 0.27 N nitric acid at 8% (○) and 5% (⬡) aqueous monomer concentrations by volume.

The Grafting of Methacrylic Acid

Methacrylic acid was graft copolymerized onto cellulose under various conditions; the results are presented in Table 2. When graft copolymerization was carried out at a temperature of 25°C, poor graft yields (less than 16% "graft") were obtained even under different concentrations of the catalyst in the pretreatment step, whereas under identical conditions, much higher graft yields (higher than 120% graft) were achieved with acrylic acid (see Fig. 4). Therefore attempts were made to graft methacrylic acid at a higher temperature, i.e., 50°C. It is apparent from the results presented in Table 2 that good graft yields are achievable at a higher temperature. Similarly, in the graft copolymerization of methacrylic acid by the conventional

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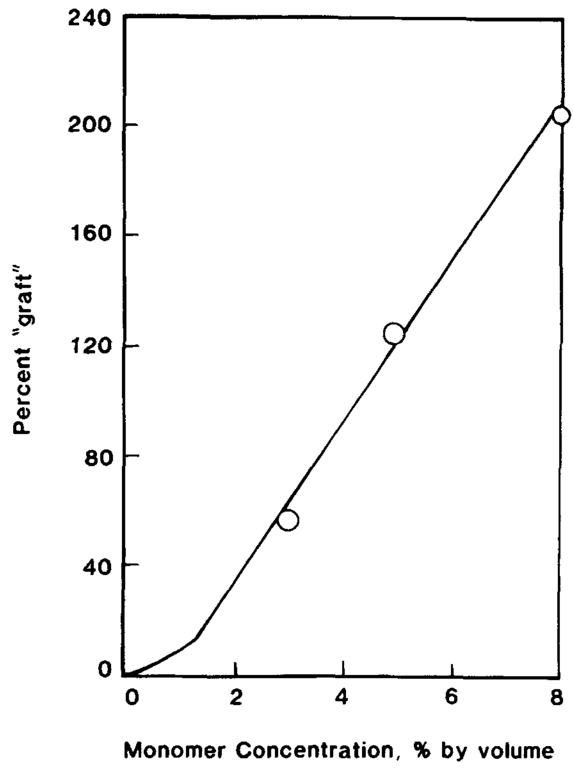

FIG. 3. Effect of monomer concentration on percent grafting at 25°C for 5 h in 0.27 N nitric acid solution. Pretreated as in Fig. 2.

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ceric ion process, Ogiwara et al. [7] also obtained very poor graft yields at low temperature (0°C) but higher grafting at 45 and 60°C. Zahran et al. [1] found higher grafting yields both to rayon and cotton using the preirradiation technique but at 70°C. It is clear that considerable further work is needed with the two monomers before a reasonable explanation can be presented.

Grafting of Acrylic Acid to Wet Strength Resin Treated Papers

The polyacrylic acid grafted papers possessing ion-exchange properties show potential applications in the treatment of aqueous streams such as the filtration of fruit juices and beverages, where

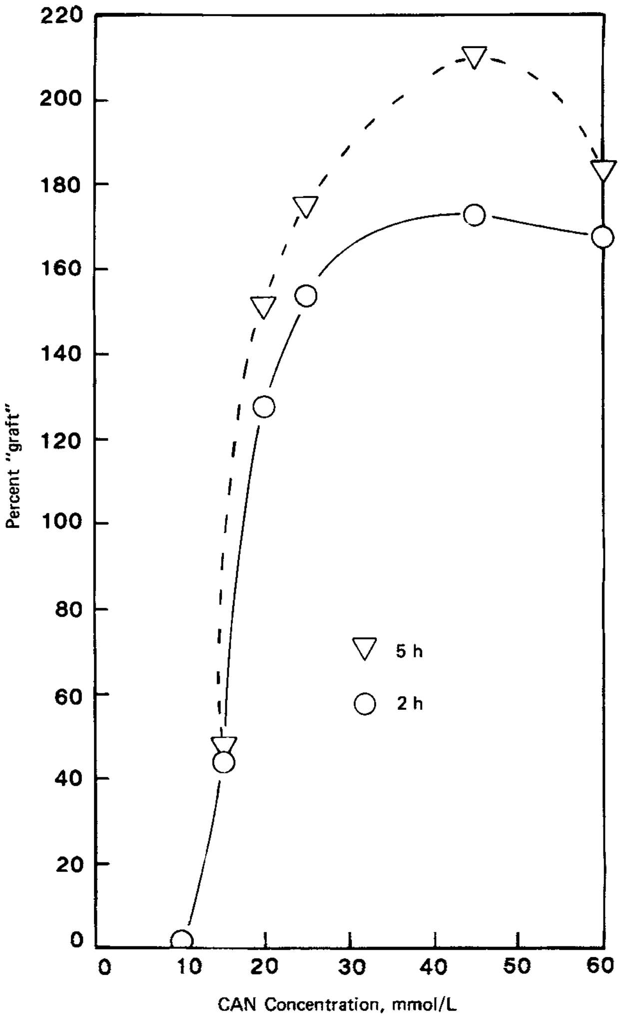

FIG. 4. Effect of CAN concentration in the pretreatment step on the percent grafting at 25°C. Pretreatment for 2 h in 0.035 N nitric acid solution at 25°C (○). Five hours reaction time in 0.27 N nitric acid (▽).

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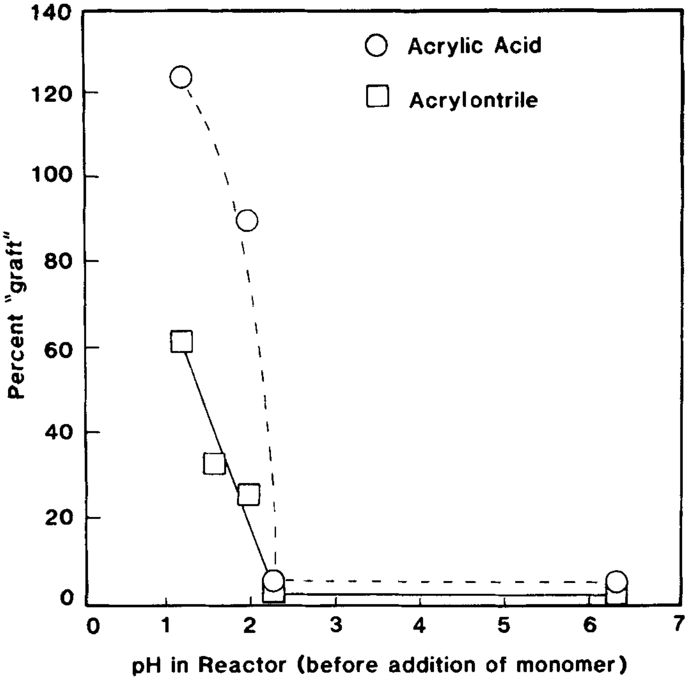

FIG. 5. Effect of pH, before addition of monomer, on the percent grafting at 25°C. Pretreatment as in Fig. 2. Nitric acid concentration varied.

TABLE 2. Grafting of Methacrylic Acid to Paper[a]

CAN concentration, mmol/L	Reaction temperature, °C	Reaction time, h	% "Graft"
20	25	5.0	16
25	25	5.0	14
40	25	5.0	10
20	50	4.0	73
20	50	5.5	99
20	50	7.5	124

[a] Pretreatment conditions: Time = 2 h, temperature = 25°C, nitric acid = 0.035 N. Reaction conditions: Monomer concentration = 5% by volume, nitric acid = 0.27 N.

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both ion exchange and filtration can be carried out in one operation. The filter paper has a very low wet tensile strength (15% of the dry tensile strength), and thus improvements in the wet strength are sought for these products for higher operational service life. There are two approaches to solving this problem: 1) wet strength resin-treated paper can be used as a substrate in the graft copolymerization process, and 2) paper can be graft copolymerized with acrylic acid first and then cured with wet strength resin later. The above two approaches have been studied, and the results on the strength improvements will be presented in another paper. The results of the grafting of acrylic acid to a wet strength resin-treated filter paper is described here. Papers were treated with melamine-formaldehyde resin and different levels of weight increase were obtained as described in the experimental section. These papers were graft copolymerized with acrylic acid by the adsorbed ceric ion process, and the results on the effect of melamine resin in the paper on the grafting process are presented in Table 3. It is apparent from Table 3 that the graft yield drops sharply from 150 to 9% "graft" upon treating the filter paper with melamine resin to a content of 0.69%. Richards and White [2] have also observed very poor graft yields in the case of grafting methyl acrylate to urea-formaldehyde resin-treated paper by the conventional ceric ion process. However, it is also apparent from Table 3 that the graft yield increases with an increase in the melamine resin content of the paper.

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TABLE 3. Effect of Melamine Resin in Paper on the Graft Copolymerization of Acrylic Acid[a]

Melamine resin in paper, % based on dry paper	Reaction time, h	Monomer concentration, % by volume	% "Graft"
0.00	5	5	150
0.69	5	5	9
2.04	5	5	20
4.38	5	5	78

[a] Pretreatment conditions: CAN concentration = 25 mmol/L, temperature = 25°C, nitric acid = 0.035 N. Reaction conditions: Nitric acid = 0.27 N, temperature = 25°C.

CONCLUSIONS

A viable all-aqueous system for the direct grafting of acrylic acid onto paper and wood pulp has been developed. The process is capable of being exploited industrially. A pretreatment of the cellulose with the ceric salt followed by washing off the excess was used. Methacrylic acid grafts to much lower yields than acrylic acid under the room temperature conditions used.

Paper prepared with melamine resin to confer wet strength properties, essential for ion-exchange use, have also been successfully grafted but with lower yields.

The water sorbing, ion-exchange, and mechanical properties of papers grafted with the technique presented above will be described in Parts II and III of this series.

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