

## Graft Copolymerization of Vinyl Monomers on Modified Cottons. VI. Vinyl Graft Copolymerization Initiated by Manganese (IV)

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### Synopsis

The ability of potassium permanganate in the presence of different acids to induce grafting of methyl methacrylate and acrylonitrile onto sodium hydroxide-treated cotton, partially carboxymethylated cotton, partially cyanoethylated cotton, and partially acetylated cotton was investigated. The copolymerization reaction was carried out under a variety of conditions. The graft yields are greatly enhanced by increasing concentration of monomer, reaction time, and temperature. The opposite holds true for initiator at higher concentrations. The effectiveness of the acids was: nitric acid > sulfuric acid > perchloric acid > hydrochloric acid. The change in the physical and/or chemical structure of cellulose by its modification via etherification reaction or esterification reaction had a significant effect on the susceptibility of cellulose toward grafting. While partial carboxymethylation or partial cyanoethylation of cellulose prior to grafting increased the graft yield, partial acetylation caused a decrease.

### INTRODUCTION

Copolymerization initiated by free radicals formed on cellulose by chain transfer, high-energy irradiation in the presence of sensitizers, mechanical degradation, or redox systems have been recently reviewed.<sup>1</sup> The use of potassium permanganate in inducing homopolymerization has been studied by a number of investigators.<sup>2,3</sup> However, its employment as initiator for graft copolymerization of vinyl monomers on textile fibers has been limited.<sup>4-6</sup>

Recently, chemically modified celluloses have evoked a considerable interest in the grafting field. Indeed, grafting of synthetic polymer chains onto the modified celluloses has proved of value in getting a good understanding of the kinetics and mechanisms of grafting as well as in obtaining basic information needed for improvement to be made in the properties of the products.<sup>7-12</sup>

This paper presents the results of studies of graft copolymerization of methyl methacrylate and acrylonitrile onto modified cottons, viz., partially carboxymethylated cotton, partially cyanoethylated cotton, and partially acetylated cotton. Grafting of these monomers onto cotton treated with

sodium hydroxide was also studied. Potassium permanganate has been used as initiator for grafting.

### EXPERIMENTAL

Egyptian Monofi cotton slivers were purified by a mild alkaline scouring (2% NaOH and 0.2% wetting agent, on a weight of material) for 5 hr at 110°C and 6–10 lb/in.<sup>2</sup>, using a liquor ratio of 10.

Sodium hydroxide-treated cotton (NaOH-cotton) was prepared by treatment of the purified cotton slivers with aqueous sodium hydroxide (12*N*) at room temperature for 1 hr, followed by washing, neutralization with 1% HCl, washing again, and drying in air at room temperature.

Partial chemical modification of cotton via carboxymethylation, cyanoethylation, and acetylation was carried out as described earlier.<sup>7-9</sup> Potassium permanganate was A.R. grade.

Freshly distilled acrylonitrile (AN) was used. Methyl methacrylate (MMA) was shaken with 10% sodium hydroxide solution, washed with distilled water, and dried over calcium sulfate.

Unless otherwise stated, the graft copolymerization was carried out as follows: A 50-ml portion aqueous solution of potassium permanganate of known concentration containing 1 ml concentrated sulfuric acid per 100 ml solution was taken in a glass-stoppered Erlenmeyer flask. The latter was kept in a thermostat for 10–15 min at a specific temperature (30°, 40°, 50°, and 60°C). The cellulosic sample (0.5 g) was introduced in the flask and the required amount of monomer was immediately added. The flask was stoppered and the cellulose sample was kept well immersed in the reaction solution. After the desired reaction time, the sample was removed and washed well with water and given a light soaping to get rid of the loosely adhering homopolymer. The sample was then subjected to repeated Soxhlet extraction and drying until constant weight was obtained. For extraction, acetone and dimethylformamide were used as solvents for samples grafted with MMA and AN, respectively. Calculation of the percentage grafting was based on dry weight:

$$\text{per cent grafting} = \frac{\text{dry wt. of grafted product} - \text{dry wt. of cellulose}}{\text{dry wt. of cellulose}} \times 100$$

### RESULTS AND DISCUSSION

A study was made of the factors affecting grafting induced by manganese(IV). Variables studied include reaction time and temperature; concentration of initiator, acid, and monomer; kind of acid; as well as nature of the substrate. Figure 1 shows the results of graft yield obtained when MMA was grafted to partially carboxymethylated cotton (D.S. = 0.1) using potassium permanganate as initiator. It is clear that the grafting is characterized by an initial fast rate followed by a slower rate which levels off after a certain time. Leveling off of grafting with time could be attrib-

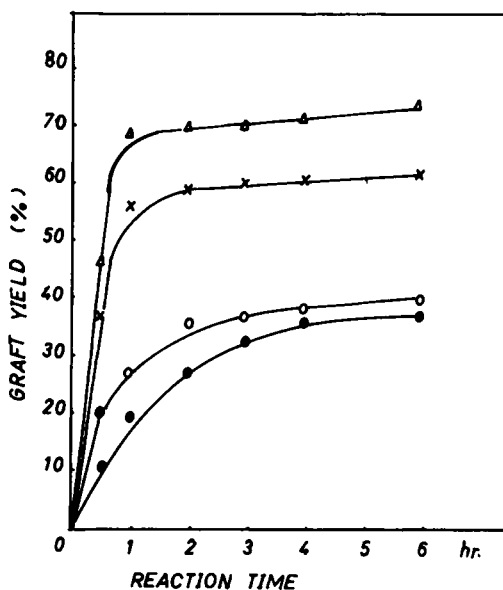


Fig. 1. Variation of grafting onto partially carboxymethylated cotton (D.S. = 0.1) with reaction time and temperature:  $\text{KMnO}_4$  concentration, 50 meq/l.; MMA, 2%; (●) 30°C; (○) 40°C; (×) 50°C; (Δ) 60°.

uted to a decrease in concentration for both initiator and monomer as well as to a reduction in the number of sites on the cellulose backbone accessible for grafting as the reaction proceeds.

The effect of raising the temperature of the polymerization system is to bring about a significant enhancement in the rate of grafting (Fig. 1). This is expected since increasing the temperature would favorably influence the swellability of cellulose, solubility of monomer, diffusion of both monomer and initiator rate of permanganate decomposition and initiation and propagation of the graft. The net effect of all these parameters leads to high grafting.

#### Initiator Concentration

Figure 2 shows the effect of potassium permanganate concentration on the extent of grafting obtained with MMA and AN on partially carboxymethylated cotton. Obviously increasing the initiator concentration up to 20 meq/l. causes a rapid increment in the graft yield. Further increases in the permanganate concentration causes a decrease in the amount of graft formation, particularly when the polymerization system was allowed to proceed for a prolonged time. This is observed with both monomers i.e. MMA and AN.

It has been reported<sup>8</sup> that radical formation in a polymerization system initiated by potassium permanganate in the presence of an acid seems likely to occur through reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{2+}$ . Thus, during

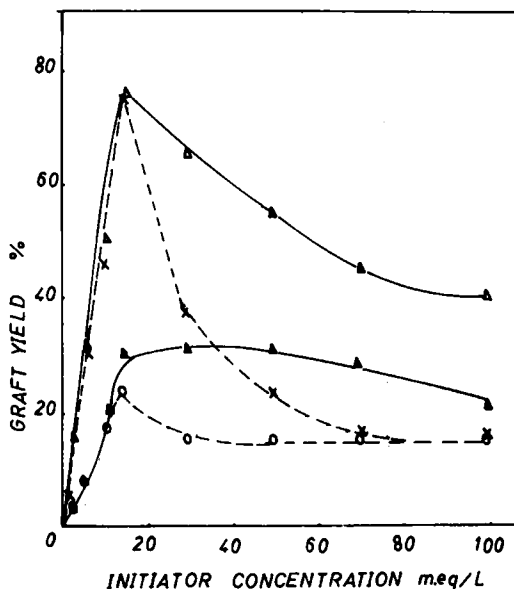
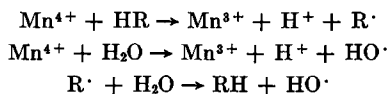
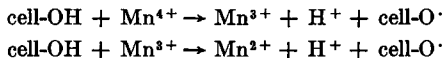


Fig. 2. Effect of initiator concentration on graft yield obtained with partially carboxymethylated cotton of D.S. = 0.1: monomer concentration, 2%; temperature, 30°C: (▲) AN (1 hr); (△) AN (6 hr); (○) MMA (1 hr); (×) MMA (6 hr).

vinyl copolymerization on cellulose (cell-OH) under the catalytic influence of potassium permanganate in the presence of an acid (HR), creation of free radicals in the system may be represented as follows:



The acid radical or hydroxyl radical attacks cellulose, the result being a cellulose macroradical. The latter may also be formed according to the following reactions:



The graft yield would be greatly enhanced if the free radicals formed on the cellulose are capable of capturing the monomer. On the other hand, the yield would be reduced if the active sites on cellulose are combined with other agents rather than the monomer. Also, formation of homopolymer certainly competes with grafting since it does lower the initiator as well as monomer concentrations. The data suggest that at higher potassium permanganate concentration and under the conditions studied, homopolymerization and termination of the graft-initiating species prevails over the grafting reaction. Indeed, extensive homopolymerization was observed at high permanganate concentration.

It is interesting to note that the graft yield obtained using AN is much higher than that of MMA (Fig. 2). This is in agreement with previous

results<sup>7</sup> which ascribed the lower reactivity of MMA, compared with AN, to its lower solubility in the reaction medium as well as the effect of the two methyl groups in MMA making growth of the polymer chain sterically more difficult.

### Acid Concentration

The reaction scheme given above makes it evident that presence of an acid in the graft copolymerization system initiated by permanganate is essential. It is, therefore, of interest to study the effect of acid concentration on the graft yield. Figure 3 shows this effect when perchloric, nitric, sulfuric, and hydrochloric acids were used.

Regardless of the kind of the acid employed, the graft yield increases with increasing concentration of the acid, attains a maximum, and then falls at higher concentration. The fall in the graft yield at higher concentration of acid could be attributed to the following reasons:

1. The coagulation of the colloidal homopolymer in solution and within fibers during grafting reaction increases at lower pH.<sup>2</sup> This retards diffusion of both monomer and initiator into the cellulose fiber for grafting to occur.

2. The side reactions such as



increases at higher acid concentration. Thus, besides consuming some  $\text{MnO}_2$  (required for production of initiating species), this leads to constant production of inhibiting oxygen.<sup>2</sup>

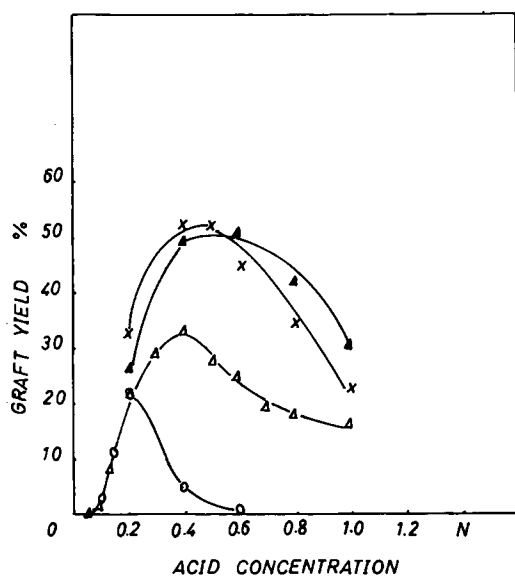


Fig. 3. Effect of concentration and kind of acid on graft yield obtained with partially carboxymethylated cotton of D.S. = 0.1:  $\text{KMnO}_4$  concentration, 50 meq/l.; 2% AN; temperature, 30°C; (O) hydrochloric acid; (Δ) perchloric acid; (▲) sulfuric acid; (X) nitric acid.

3. The initiating species may be destroyed by side reactions, for instance, reaction of the acid radicals with  $Mn^{3+}$ .

### Kind of Acid

Results of the kind of acid are shown in Figure 3. Obviously, the effectiveness of the acids follows the order nitric acid > sulfuric acid > perchloric acid > hydrochloric acid. The following possibilities may be looked upon in explaining this phenomenon:

1. The side reactions already pointed out may be less pronounced and follow an opposite order, i.e., the side reactions are much greater in case of hydrochloric acid compared with nitric, sulfuric, and perchloric acids.

2. The affinity of the acid species for cellulose seems to have the same order as their efficiency in inducing grafting.

3. Perhaps the half-life of the free radicals formed in case of hydrochloric acid is exceedingly short compared to that of free radicals formed with nitric, sulfuric, and perchloric acids. The reason for this is that chlorine radicals can be easily combined to give inactive initiating species, i.e., chlorine atoms.

### Monomer Concentration

The effect of monomer concentration on grafting of MMA on partially carboxymethylated cotton (D.S. = 0.1) was evaluated in a series of polymerization in which four concentrations of the monomer were used. As can be seen from Figure 4, increasing the monomer concentration is accom-

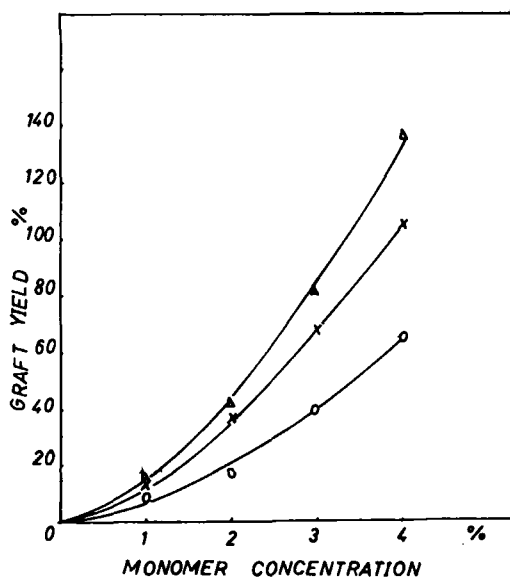


Fig. 4. Relationship between MMA concentration and graft yield: substrate, partially carboxymethylated cotton of D.S. = 0.1;  $KMnO_4$  concentration, 50 meq./l.; temperature, 30°C; (O) 1 hr; (X) 3 hr; (Δ) 4 hr.

panied by a significant increase in the graft yield. Moreover, the proportion of monomer converted to grafted polymer is substantially greater at high monomer concentration.

The accelerated grafting at high monomer concentration could be associated with the gel effect, i.e., an increase in viscosity of the medium. Since poly(methyl methacrylate) is soluble in its own monomer, the viscosity of the medium would be high at higher monomer concentration. Hence, at higher viscosities, bimolecular termination of the growing chains is hindered, whereas the other steps in the graft polymerization process, namely, initiation, propagation, and radical chain processes, are not affected to the same degree by increasing viscosity because the mobility of the polymer chains is restricted by the cellulose structure. In addition, the gel effect causes swelling of cellulose and thus assists diffusion of monomer to the growing chains and active sites on the cellulose, thereby enhancing grafting.

### Substrate Structure

The behavior of chemically modified cellulose toward grafting would be expected to depend on the influence of the newly introduced groups on the properties of cellulose. Among these are (a) variation in the fiber structure (perhaps the cellulose is held in an open state); (b) swellability of the cellulose; (c) availability and accessibility of the cellulose hydroxyls to reaction; (d) reactivity of the cellulose hydroxyls in the presence of the

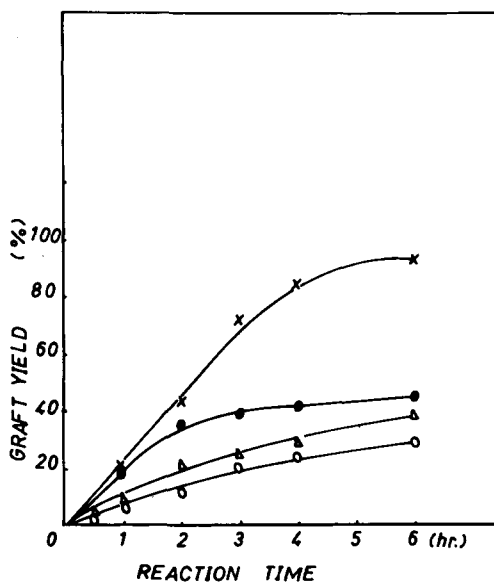


Fig. 5. Effect of introducing increasing amounts of carboxymethyl groups in the cellulose molecule on grafting:  $\text{KMnO}_4$  concentration, 50 meq/l.; AN, 2%; temperature, 30°C; (○) NaOH-treated cotton (control); (Δ) (●) (×) partially carboxymethylated cotton of 12, 32, and 62 meq COOH groups/100 g cellulose.

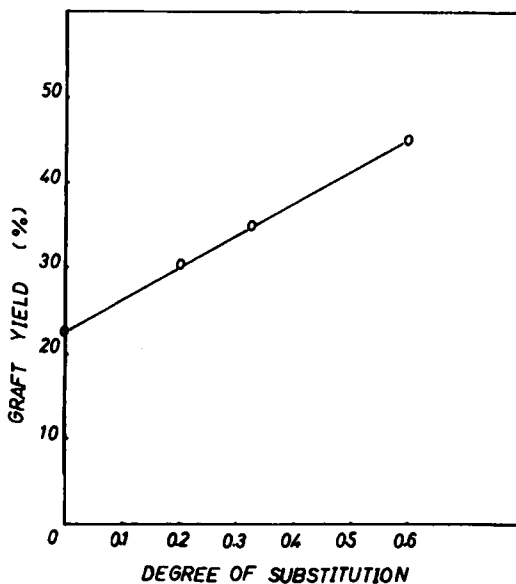


Fig. 6. Effect of degree of substitution (D.S.) of cyanoethylated cotton on grafting:  $\text{KMnO}_4$  concentration, 50 meq./l.; AN, 2%; temperature, 33°C; reaction time, 4 hr.

newly introduced groups; (e) specific localization of the newly introduced groups on the anhydroglucose unit of cellulose; (f) the type of reaction between the cellulose and initiator (whether specific or nonspecific); and (g) reactivity of the introduced group with the initiator.

In general, if the introduced groups increase the magnitude of (a), (b), (c), and (d) or if they act as additional sites for grafting, i.e., (g), grafting would be greatly enhanced. Conversely, lower grafting would occur if the introduced groups adversely affect the reactivity of cellulose hydroxyls. The same situation would be encountered if the groups of the chemically modified cellulose take place at the same carbon atom in the anhydroglucose unit of cellulose, the hydroxyl groups of which are liable to react specifically with the initiator.

Thus, in the range studied, the enhanced rate of grafting (Fig. 5) obtained by introducing increasing amounts of carboxymethyl groups in the cellulose molecule, as compared with sodium hydroxide-treated cotton, could be anticipated in view of the greater swellability of the modified cotton. The presence of  $-\text{CH}_2\text{COOH}$  groups in the cellulose may open up the structure, thus increasing the diffusion of the initiator and monomer.<sup>7</sup> There is no significant effect on the availability of the cellulose hydroxyls nor on their reactivity by the  $-\text{CH}_2\text{COOH}$  groups. On the contrary, the accessibility of remaining hydroxyl groups of partially carboxymethylated cotton to grafting is greater, since higher graft yields are obtained with the latter.

Figure 6 shows the results of studies of grafting AN onto partially cyanoethylated cotton. It is clear that the extent of graft yields increases



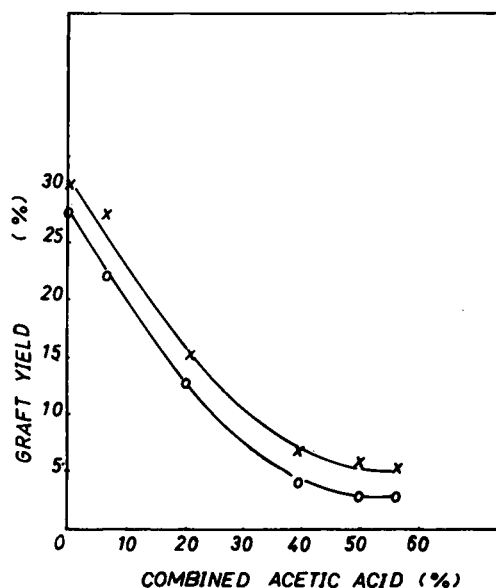


Fig. 7. Grafting of acrylonitrile onto cotton having different acetyl contents:  $\text{KMnO}_4$  concentration, 50 meq/l.; temperature,  $50^\circ\text{C}$ ; (O) reaction time, 1 hr; (X) reaction time, 3 hr.

by increasing the D.S. of cyanoethylated cotton. Besides, by opening up the cellulose structure, the cyanoethyl groups afford additional sites for grafting thereby enhancing graft formation. This confirms previous results.<sup>9</sup>

The effect of introducing acetyl groups in the cellulose is to cause a significant decrease in its susceptibility toward grafting. This may be realized from Figure 7, where the rate of grafting obtained with cellulose having a high acetyl content (ca. 56% combined acetic acid yield) is much lower than that of cellulose having smaller amounts of acetyl groups and of the control. This is due to lack of swellability and blocking of the cellulose hydroxyls; both are favorably influenced by the presence of acetyl groups. In addition, the free hydroxyl groups in highly acetylated cotton appears to be inaccessible for grafting, perhaps because of steric hindrance.<sup>8</sup>

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