Graft Copolymerization of Vinyl Monomers with Modified Cotton.   II.   Grafting of Acrylonitrile and Methyl Methacrylate on Acetylated Cotton

A. HEBEISH, A. KANTOUCH, and M. H. EL-RAFIE, *National Research Centre, Textile Research Laboratory, Dokki, Cairo, U.A.R.*

Synopsis

Ce(IV)-induced polymerization of acrylonitrile and methyl methacrylate with acetylated cotton having different acetyl contents was investigated.   The extent of interaction between the cotton and monomer is dependent upon the acetyl content of the former as well as on the reaction conditions.   Increasing the acetyl content caused a significant decrease in the graft yield.   Increasing the acrylonitrile concentration was accompanied by a substantial increase in the graft yields.   The same effect was found with the initiator up to a certain concentration, but beyond it there was a reversal.   The rate of grafting increased by rising the temperature and follows the order $60° > 40° > 30°C$.   The Ce(IV) consumption during grafting is greater than that consumed during oxidation.   The consumption of Ce(IV) by the cellulosic materials was favorably influenced by the concentrations of monomer and initiator, time, and temperature.   Rates of grafting and Ce(IV) consumption during oxidation of acetylated cottons having different acetyl contents strongly support the postulated mechanism of grafting using the Ce(IV)–cellulose redox system.   Ce(IV) oxidation had practically no effect on the acetyl groups (expressed as per cent combined acetic acid) of the modified cotton.

INTRODUCTION

Various vinyl monomers such as acrylonitrile, acrylamide, and certain esters of acrylic and methacrylic acids have been successfully grafted on cellulosic materials using ceric ion type, Ce(IV), catalyst.[1-6]   This technique is based on the fact that when cellulose is oxidized by ceric salts such as ceric ammonium nitrate, free radicals capable of initiating vinyl polymerization are formed on the cellulose.[7,8]   Since the radicals produced are almost exclusively on the cellulose, grafting is favored much more than homopolymer formation as compared with other redox systems such as H_2O_2–Fe^{2+} and persulfate systems where the redox reaction generates radicals unattached to cellulose.[9]

It has been reported that Ce(IV) is a powerful oxidizing agent for alcohols containing a 1,2-glycol group.[10,11]   Thus grafting and oxidation of cellulose with Ce(IV) would proceed simultaneously.   Oxidation of cellulose with Ce(IV) is believed to occur mainly at the secondary hydroxyl groups of the anhydroglucose unit with cleavage of the C_2–C_3 bond, a reaction which

11

is similar to that of metaperiodate. Indeed, studies on the oxidation of alcohols such poly(vinyl alcohol)[10] and pinacol[11] and of model compounds such as 1,2-cyclohexanediol[6] with Ce(IV) as well as ESR studies[8] on Ce(IV) oxidized cellulose support this postulate. In addition to the glycol bond cleavage, oxidation of cellulose with Ce(IV) involves the hemiacetal group in the cellulose chain.[3,12,13]

In part I of this series,[14] we have shown that the change in the chemical structure of cellulose by partial carboxymethylation influences greatly the susceptibility of cellulose to grafting and oxidation with Ce(IV). However, only scanty information could be obtained with respect to the mode of oxidation of cellulose with Ce(IV).

The present work was undertaken with a view of elucidating (a) some of the important parameters which affect the grafting reaction of acetylated cotton with vinyl monomers, (b) the effect of the introduction of $COCH_3$ groups in the cellulose molecule on the grafting efficiency, and (c) the mechanism of grafting. For this purpose, acetylated cottons having different acetyl contents were treated with Ce(IV) and monomer, i.e., grafting, under various reaction conditions. Also treatments of the same substrates with Ce(IV), i.e., oxidation, were carried out under conditions identical with those of grafting except that the monomer was not added.

EXPERIMENTAL

Egyptian Monofi cotton was purified by a mild alkaline scouring (2% sodium hydroxide and 0.2% wetting agent, based on the weight of the material) for 5 hr at 110°C and 6–10 lb/in.[2] using a liquor ratio of 10.

Acetylated cottons having different acetyl contents were prepared by first activating the purified cotton slivers with glacial acetic acid for 1 hr. The activated cotton samples were then treated with a solution containing 1 ml of perchloric acid per 1 liter glacial acetic acid. At this point, the samples were treated with various concentrations of acetic anhydride in benzene for 24 hr using a liquor ratio of 20. The samples were then thoroughly washed and finally dried at room temperature.

The acetyl content, expressed as combined acetic acid % yield, was determined according to a method described by Hawiett and Martin.[15]

A control was prepared by treatment of the cotton slivers with glacial acetic acid for 1 hr.

Ceric ammonium nitrate (CAN) and ceric ammonium sulfate (CAS), B.D.H. reagent grade, were used after standardization with ferrous sulfate.[11]

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.

The graft polymerization of AN and MMA was conducted according to a method described elsewhere.[14] The procedure was carried out as follows:

Ceric salt solution of known concentration, 30 ml, containing concentrated HNO_3 or H_2SO_4 (1% for CAN and CAS, respectively) in a 50-ml

stoppered Erlenmeyer flask was kept in a thermostat for 10–15 min. The required amount of monomer was added, and 1 g of the cellulosic sample was immediately introduced into the flask. The flask was well stoppered and the contents stirred occasionally during polymerization. After the desired reaction time, the samples were washed well by extraction with several portions of water, with a little soap to remove the loosely adhering polymer, washed, and dried. For grafting with AN, it was observed that further extraction of grafted samples with dimethylformamide caused negligible loss in weight. Removal of homopolymer from the fiber was therefore carried out with thorough soaping and washing; solvent extraction was not considered necessary. In case of MMA, the grafted samples were extracted repeatedly with dry acetone to constant weight; calculation of the per cent grafting was based on dry weight:

$$\% \text{ grating} = \frac{\text{dry wt. of grafted product} - \text{dry wt. of cellulose}}{\text{dry wt. of cellulose}} \times 100.$$

Oxidation of cellulosic samples with CAN and CAS was carried out under conditions identical with those described above, except that the monomer was omitted.

RESULTS AND DISCUSSION

The effect of introducing acetyl groups in the cellulose molecule on its behavior toward grafting with AN and MMA was investigated under various reaction conditions. Variables studied were concentration of ceric salt and monomer, reaction time, and temperature.

Grafting with Acrylonitrile

Figure 1 shows data for the graft yield obtained with acetylated cotton having 39.5% combined acetic acid. For comparison, data for graft yield obtained with cotton treated with glacial acetic acid (control) are also illustrated in the figure. It is clear that with acetylated cotton, the grafting proceeds very slowly in the early stages of the reaction, and the graft formation is only considerable after 30 min reaction time. Thereafter, increasing the reaction time causes a substantial increment in the graft yield within the range studied. This is so probably because the introduction of —COCH$_3$ groups along the cellulosic chains reduces greatly its swellability. Diffusion of the monomer as well as the initiator inside the fiber would therefore be very difficult, specially in the early stages of the reaction. As a result, a small amount of graft copolymer is formed. Sufficient time enhances swelling of the fiber, and diffusion of both monomer and initiator thereby gives rise to a substantial amount of graft formation. With respect to the control, the grafting reaction shows an initial fast rate followed by a slower rate. Besides substrate accessibility consideration, this could be due also to a fall in the concentration of the monomer and the

initiator as well as to a decrease in the available sites for grafting on the cellulose molecule.

The graft yield obtained with acetylated cotton is significantly lower than that obtained with the control.   The presence of bulky groups such as —COCH$_3$ in the cellulose causes two effects: (a) reducing the swelling capacity of cellulose thereby decreasing diffusion and adsorption of both monomer and initiator, and (b) blocking some of the hydroxyl groups along the cellulose chains.   The two effects lead to lower grafting.

Initiator Concentration

The effect of the concentration of CAS on the graft yield of acetylated cotton having 39.5% combined acetic acid and that of the control may be realized from Figure 1.   With both substrates, increasing the CAS concentration from 0.005M to 0.05M has practically no effect on the graft yield in the early stages of the reaction.   As grafting proceeds, the effect of initiator concentration is pronounced and the yield increases by increasing the CAS concentration up to 0.05M.   Further increase brings about lower yields.   This is in agreement with previous results[11] where this phenomenon was ascribed to fast termination of the growing polymer chains owing to the presence of excess ceric ions.
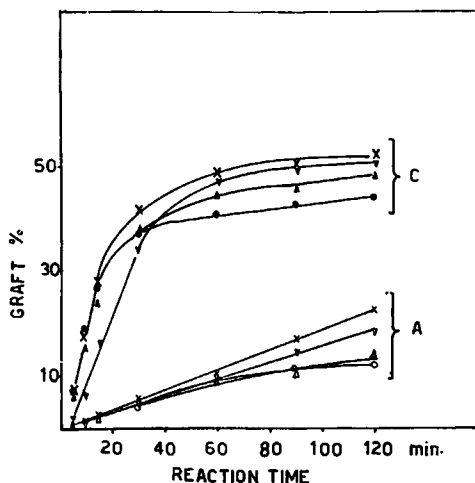

Fig. 1. Effect of ceric ammonium and sulfate concentration on grafting of acrylonitrile (AN) on acetylated cotton having 39.5% combined acetic acid (A) and cotton treated with acetic acid (C): (O), (●) 0.005M CAS; (△) (▲) 0.01M CAS; (X)(X) 0.05M CAS; (▽) (▼) 0.1M CAS; 1 g AN; 40°C.

Monomer Concentration

The effect of acrylonitrile concentration on the graft yields obtained with acetylated cotton having 39.5 combined acetic acid is shown in Figure 2.   Increasing the monomer concentration is accompanied by a significant
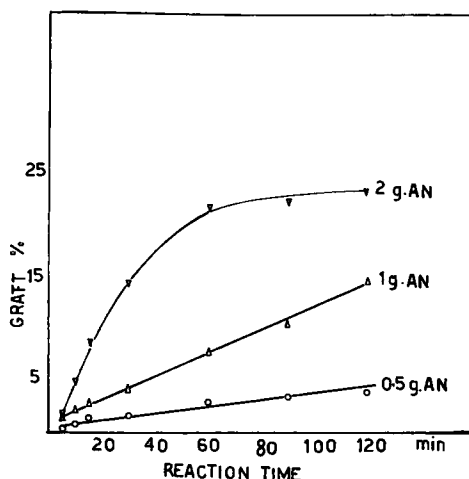
Fig. 2. Influence of concentration of acrylonitrile (AN) on rate of grafting of acetylated cotton having 39.5% combined acetic acid; 0.01M CAS; 40°C.

increase in the rate of grafting. However, at lower monomer concentration, i.e., 0.5 g and 1 g AN, grafting continues to increase with increasing reaction time up to 2 hr. On the other hand, with higher monomer concentration, i.e., 2 g AN, though the grafting proceeds at a rate which is higher than those of lower monomer concentration, yet the rate of grafting does slow down and then levels off to give a maximum yield. Levelling off of grafting in this case could be attributed to the substantial amount of polymer grafted onto the substrate backbone which impedes diffusion of Ce (IV) as well as monomer into the cellulose for further grafting.

Temperature

The effect of temperature on grafting of AN on to acetylated cotton having 39.5% combined acetic acid as well as of the control was studied for a series of polymerization at 30°, 40°, and 60°C. The results are shown in Figure 3. It is apparent that the rate of grafting increases by raising the temperature from 30° to 60°C and follows the order of 60° > 40° > 30°C, which is in full agreement with previous results.[4,14] This is observed with both substrates. However, the maximum graft yields obtained with acetylated cotton at 40° and 60°C are comparable despite the significant difference in the yields during the early stages of the reaction. Grafting to acetylated cotton appears to occur at the point of maximum swelling in the Ce(IV)–AN–water system. Beyond this, the grafted polyacrylonitrile probably forms a diffusion barrier and inhibits the diffusion of acrylonitrile monomer. It is well known that introduction of —COCH$_3$ groups reduces swelling of the cellulose considerably. Thus, lack of swelling and rapid slowing down of diffusion of initiator and monomer as grafting proceeds would account for the comparable maximum yield obtained at 40° and 60°C.
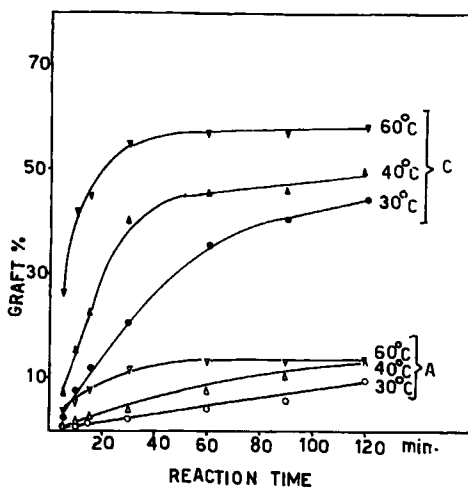
Fig. 3. Effect of temperature on rates of grafting of acetylated cotton having 39.5% combined acetic acid (A) and cotton treated with acetic acid (C); 1 g AN; 0.01M CAS.

Acetyl Groups

It was shown above that the change in the chemical structure of cellulose by introducing —$COCH_3$ groups in the cellulose molecules causes a significant change in its behavior toward grafting. It was, therefore, of interest to study the effect of —$COCH_3$ content of acetylated cotton on the grafting reaction. Figure 4 shows the graft yields obtained at 60°C for samples of acetylated cotton having different acetyl contents, expressed as per cent combined acetic acid. Similar trends were also obtained at 30° and 40°C.
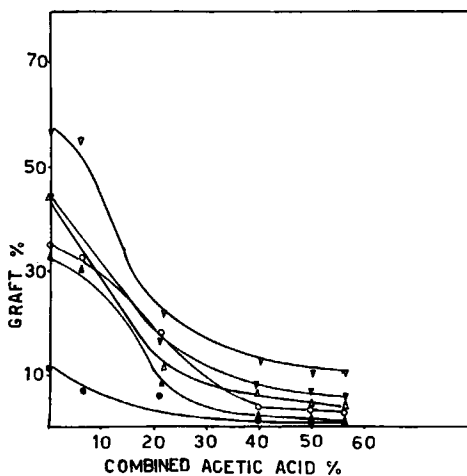

Fig. 4. Acetyl content (expressed as % combined acetic acid) vs. % graft yield using acrylonitrile as a monomer; (●) 30°C, (▲) 40° C, (▼) 60°C at 15 min; (O) 30°C, (△) 40°C, (▽) 60°C at 60 min; 1g AN; 0.01 M CAS.

It is clear that increasing the —COCH$_3$ groups along the cellulosic chains is accompanied by a significant decrease in the graft yields, probably because of the lack of swelling and blocking of the cellulose hydroxyls; both are favorably influenced by the presence of —COCH$_3$ groups. This will be discussed later in detail (see below).

Ceric Consumption During Grafting and Oxidation

Ce(IV) consumption by the cellulosic materials at 60°C in the absence of monomer, i.e., oxidation, and consumption during grafting using CAS as initiator are shown in Figure 5. Consumption is expressed as mmole/100 g cellulose. Similar trends were also obtained at 40° and 30°C. It is obvious that the Ce(IV) consumed during grafting and that consumed during oxidation decrease as the —COCH$_3$ content of acetylated cotton increases. Our analogous trend has been observed with graft yield (Fig. 4). As previously pointed out, introduction of —COCH$_3$ groups into the cellulose molecule decreases the susceptibility of cellulose to Ce(IV) attack (by lowering swelling) and at the same time decreases the number of the cellulose hydroxyls. Another point of additional interest is that with all the acetylated cottons, Ce(IV) consumed during grafting is higher than that consumed during oxidation. Hebeish and Mehta[4] noticed the same with various cellulosic substrates and ascribed this phenomenon to homopolymer formation.

The effect of concentration of initiator and monomer, temperature, and reaction time on the Ce(IV) consumption during grafting and oxidation of acetylated cotton was also studied. The results agree in general with the expected behavior of the polymerization and oxidation processes. Some
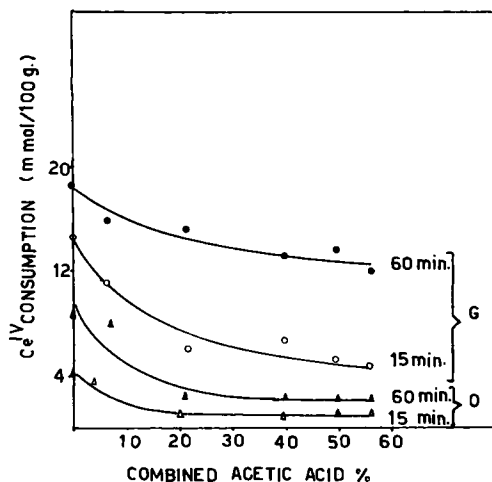

Fig. 5. Acetyl content (expressed as % combined acetic acid) vs. consumption of ceric during grafting (G) and oxidation (O); 1 g AN; 0.01M CAS; 60°C.

of these results are given in Figure 5, from which it may be seen that Ce (IV) consumption increases by increasing these variables.

Grafting with Methyl Methacrylate

Factors affecting grafting, viz., nature of the substrate, type of initiator, reaction time, and temperature, were studied for methyl methacrylate (MMA). The results are summarized in Table I (cf. Fig. 7). It is

TABLE I

Grafting of Methyl Methacrylate on Partially Acetylated Cotton (Combined Acetic Acid Yield = 21.6%) and Cotton Treated with Glacial Acetic Acid (Control)[a]

Reaction time, min	CAS, graft %			CAN, graft %		
	30°C	40°C	60°C	30°C	40°C	60°C
Cotton Treated with Glacial Acetic Acid						
5	1.0	1.0	3.0	3.2	3.2	18.8
10	1.5	1.6	4.0	4.4	4.8	35.0
15	1.7	1.8	6.0	4.8	7.2	37.4
30	3.6	3.8	9.8	7.0	16.8	39.7
60	4.0	4.6	16.8	12.3	22.0	38.9
90	4.2	8.2	17.5	15.2	26.0	41.0
120	5.4	10.0	18.6	18.2	30.0	41.0
Acetylated Cotton Having 21.6% Combined Acetic Acid						
5	0.0	0.0	0.2	1.4	3.4	5.2
10	0.7	0.9	0.8	1.6	3.4	9.2
15	0.9	1.0	1.9	2.0	4.0	13.3
30	1.6	1.4	3.6	4.0	6.8	14.0
60	2.0	4.0	7.0	6.0	7.8	14.7
90	4.0	4.8	9.0	9.8	12.6	16.0
120	4.0	4.8	9.5	10.5	12.5	16.6

[a] Ce(IV) concentration = $0.01M$; monomer = 1 g; cellulose, 1 g; liquor ratio = 30.

apparent that with CAS, increasing the reaction time favorably influences the graft yield; this effect being increased by raising the temperature in the following order: 60° > 40° > 30°C. Grafting levels off after a certain time when the reaction is conducted only at 60°C in case of the control, whereas it does level off in case of acetylated cotton regardless of the temperature in the range studied. The same holds true for CAN. However, the graft yields obtained with CAN are much higher than those of CAS. This is in accordance with the previous results.[14]

The graft yields obtained with acetylated cotton (Table I) are much lower than those of the control. Furthermore, increasing the —COCH$_3$ groups of the modified cotton causes a significant decrease in the graft yield (Fig. 7). Similar observations were found in case of CAN. The explanation given previously for this would apply here also. However, with all substrates studied, the graft yields obtained with AN (cf. Fig. 4) are markedly higher

than those of MMA. This is again, in full agreement with previous results.[14]

Data for Ce(IV) consumption during grafting and oxidation of acetylated cotton and the control with CAS and CAN at 30°, 40°, and 60°C are given in Table II. The consumption is expressed as mmole Ce(IV)/100 g

TABLE II
Ce(IV) Consumption During Grafting and Oxidation of Partially Acetylated Cotton
(Combined Acetic Acid Yield = 21.6%) and Cotton Treated with Glacial Acetic
Acid (Control)[a]

Reaction time, min	Ce(IV) consumption, mmoles/100 g cellulose					
	CAS			CAN		
	30°C	40°C	60°C	30°C	40°C	60°C
During Oxidation of the Control						
5	1.2	1.5	2.1	3.9	4.8	15.3
10	1.8	2.1	3.0	4.2	8.4	18.3
15	1.8	2.4	4.2	5.1	9.0	23.1
30	2.1	2.4	5.1	9.0	12.0	26.7
60	2.4	3.3	7.2	10.2	15.5	27.9
90	3.3	3.9	8.1	10.8	22.8	27.9
120	3.9	4.8	11.7	15.0	27	27.9
During Grafting of the Control						
5	2.7	2.4	3.6	6.0	7.2	12.3
10	3.0	3.3	5.7	6.6	8.4	17.7
15	3.0	4.2	6.9	7.2	9.0	20.1
30	3.9	5.1	12.6	9.6	15.9	21.3
60	5.4	6.3	20.4	13.2	25.8	23.1
90	5.4	9.3	26.4	16.5	29.4	24.9
120	6.6	13.2	29.4	21.6	30.0	24.6
During Oxidation of Acetylated Cotton						
5	0.6	1.2	1.2	1.8	3.3	9.0
10	0.9	1.8	1.7	2.7	5.7	10.2
15	0.9	1.9	1.8	3.6	6.9	10.4
30	1.2	1.9	1.8	4.8	9.0	10.8
60	1.5	2.4	2.4	4.8	11.9	11.8
90	1.5	3.1	3.6	8.1	15.9	12.6
120	2.7	3.7	3.8	12.6	16.5	13.2
During Grafting of Acetylated Cotton						
5	1.5	1.9	3.0	3.0	8.7	7.2
10	2.1	2.2	4.5	5.1	9.0	12.0
15	2.1	2.7	6.6	6.6	9.3	15.0
30	3.0	3.9	11.1	9.6	20.1	23.4
60	4.8	5.7	19.8	15.0	28.5	24.0
90	6.6	8.1	29.4	20.1	28.5	24.9
120	12.0	11.1	29.7	22.8	29.1	24.6

[a] Ce(IV) concentration = 0.01M; monomer = 1 g; cellulose = 1 g; liquor ratio = 30.

cellulose. As in case of AN, the Ce(IV) consumption during grafting of MMA increases with increasing reaction time at the three temperatures studied. The same is true for the consumption during oxidation. This is observed with both initiator and holds true for acetylated cotton as well as the control. However, the consumption is much higher with the latter than with the former, probably because of lack of swelling and blocking of some of the cellulose hydroxyls in case of acetylated cotton. Also, the Ce (IV) consumption during grafting is greater than that consumed during oxidation, perhaps due to homopolymer formed during grafting.[4] Further-more, the consumption obtained with CAN is much higher than that of CAS owing to the higher stability of the latter.[4]

It is noteworthy that in case of the control, the Ce(IV) consumption during grafting and oxidation increases by raising the temperature and follows the order $60° > 40° > 30°C$ when CAS was used. The same trend was observed with CAN for the oxidation only. The Ce(IV) consumption during grafting, on the other hand, is lower at $60°C$ than at $40°C$ in the later stages of the reaction. The relatively greater graft formation on the cellulose backbone (which impedes Ce(IV) diffusion) as well as the rela-tively higher Ce(IV) consumption in the early stages of the reaction (which decreases the Ce(IV) concentration in the reaction medium) at $60°C$ may account for the lower consumption at $60°C$ than at $40°C$ during grafting.

With respect to acetylated cotton, the Ce(IV) consumption during graft-ing and oxidation increases with raising the temperature and also follows the order $60° > 40° > 30°C$ when CAS was used. With CAN, on the other hand, the Ce(IV) consumption during grafting and oxidation was higher at $40°C$ than at $60°C$. The diffusion barrier brought about by the graft (which is greater at $60°C$) may explain this observation during grafting. Oxidation of acetylated cotton with Ce(IV) is expected to differ consider-ably from that of the control. It is likely that the oxidation products of acetylated cotton are less susceptible for further Ce(IV) attack. This and the fact that Ce(IV) concentration decreases considerably in the early stages of the reaction at $60°C$ as compared with that at $40°C$ would account for the lower Ce(IV) consumption at $60°C$ than at $40°C$ in the latter stages of the reaction during oxidation.

Mechanism of Grafting

Mino and co-workers[11] have shown that in the case of glycols e.g., pinacol, the 1,2-glycol group is cleaved during oxidation reaction with Ce (IV). Thus, during grafting onto cellulose, cleavage of the C_2-C_3 glycol bond is also expected in this system of graft initiation. Terasaki and Matsuki,[12] Cumberbirch and Holker,[6] and Arthur and co-workers[8] have also postulated glycol bond cleavage in cellulose during grafting initiated by Ce(IV). Kulkarni and Mehta[13] have studied the oxidation of cellulose by Ce(IV) and have shown that, in the initial stage of oxidation, the reac-tion proceeds very rapidly owing to formation of a Ce(IV)–cellulose com-plex and oxidation of the hemiacetal groups of cellulose. Thereafter, oxi-
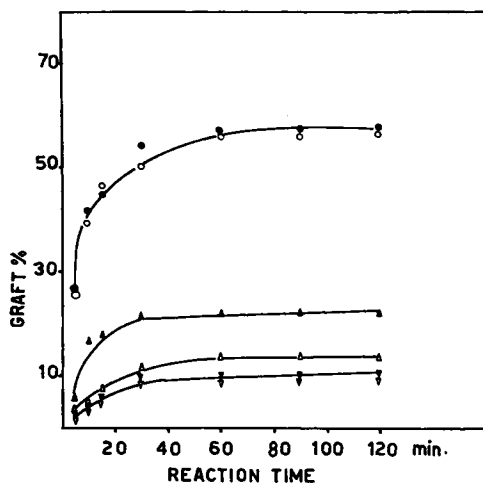
Fig. 6. Rates of grafting of cotton treated with acetic acid and acetylated cottons having different acetyl content (expressed as % combined acetic acid %): (●) 0%; (○) 6.48%; (▲) 21.6%; (△) 39.5%; (▼) 49.65%; (▽) 56.2%; 1 g AN; 0.01M CAS; 60°C.

dation of the secondary hydroxyl group at C_2 occurs without the C_2–C_3 bond cleavage. The glycol bond cleavage occurs at high Ce(IV) concentration, e.g., 0.5 M, and on prolonged oxidation of cellulose, e.g., 18–24 hr.

Figure 6 shows the rates of grafting for acetylated cottons having different acetyl content; the latter is expressed as per cent combined acetic acid. Rate of grafting of cotton treated with glacial acetic acid, as a control, is also given in the figure. Similar trends were also obtained for Ce(IV) consumption during oxidation (cf. Fig. 7).

It is clear that the rate of grafting of acetylated cotton having the lowest combined acetic acid, i.e., 6.48%, is very rapid at first but subsequently decreases, and a maximum grafting level is reached. An identical rate is also brought about by the control. This indicates that the presence of —COCH₃ in a small amount, such as the one in question, along the cellulose molecule does not alter the cellulose susceptibility to grafting. Increasing the combined acetic acid to 21.6% considerably lowers the maximum grafting level. However, the grafting shows an initial fast rate followed by a slower rate. This suggests that acetylation might have taken place exclusively at the primary hydroxyl group, i.e., at C_6 of the anhydroglycose unit in the cellulose, without attacking the secondary hydroxyl at C_2 and C_3. It is known, from esterification studies, that the C_6 group is esterified ten times as fast as the other groups.[16] Thus, the hydroxyls at C_2 and C_3 may be responsible for the initial fast rate; an assumption which is in agreement with previous postulations.[6,8,12,13] Lowering of the maximum grafting level is presumably caused by a lack of swelling of the acetylated cotton.

Allowing the acetylation reaction to proceed so as to give acetylated cottons having more than 21% combined acetic acid would certainly in-

volve the hydroxyls at either C_2, C_3, or both.   If these two hydroxyls are, the only groups which account for the rapid initial rate, as postulated above, one would expect that their partial or complete blocking would appreciably influence the rate of grafting.   Indeed, increasing the combined acetic acid to 39.5% slows down considerably the initial rate as well as the maximum
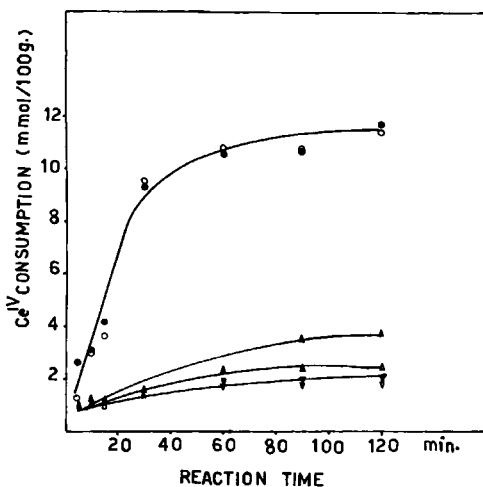

Fig. 7. Ceric consumption during oxidation of cotton treated with acetic acid and acetylated cottons having different acetyl contact (expressed as % combined acetic acid): (●) 0%; (○) 6.48%; (▲) 21.5%; (△) 39.5%; (▼) 49.65%; (▽) 56.2%; $0.01M$ CAS; 60°C.
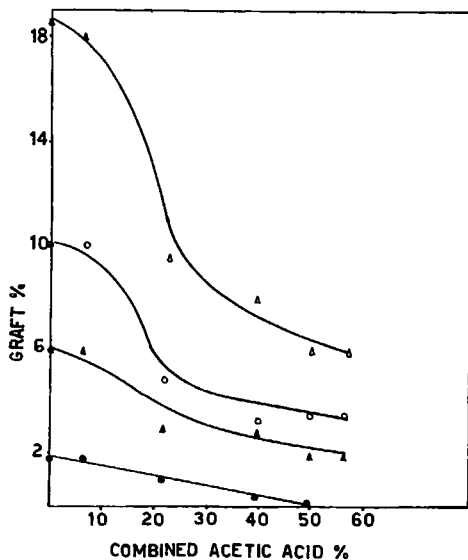

Fig. 8. Acetyl content (expressed as % combined acetic acid) vs. % graft yield using methyl methacrylate (MMA) as monomer; (●) 40°C; (▲) 60°C at 15 min.; (○) 40°C; (△) 60°C at 120 min; 1 g MMA; $0.01M$ CAS.

grafting level. Further decrease in the initial rate of grafting and the maximum level are achieved with acetylated cotton having 49.65% combined acetic acid, indicating that partial blocking of the glycol groups does affect the rate of grafting. Acetylated cotton having 56.2% combined acetic acid shows a rate of grafting which is identical with that obtained with acetylated cotton having 49.65% combined acetic acid, despite the fact that nearly all the cellulose hydroxyls are blocked in case of the former. This implies that introduction of —COCH₃ groups up to a certain limit, i.e., ca. 50% combined acetic acid, in the cellulose adversely affects the rate of grafting. Beyond this value, the influence of —COCH₃ groups on the rate of grafting is not marked. It appears that the free hydroxyl groups in highly acetylated cottons are not accessible for grafting, perhaps because of steric hindrance and/or stabilization of the glycol bond with resulting resistance to Ce(IV) attack. However, great lack of swellability in these cases as compared with other acetylated cottons, in the range studied, cannot be ruled out.

At any event, an initial fast rate of grafting is observed even when nearly all the cellulose hydroxyls are blocked. This reveals that the hemiacetal groups (corresponding to C_1 linkage in the end unit of the cellulose molecules) do contribute to the initial fast rate of grafting, a conclusion which is in agreement with previous postulations[12,13] Thus Ce(IV)-induced polymerization of vinyl monomer in the presence of cellulose yields a mixture of graft copolymer (by Ce(IV) attack at C_2 or C_3) and block copolymer (by Ce(IV) attack at the hemiacetal group) as well as homopolymer (monomer attack by Ce(IV)). It is interesting to note that Iwakura and co-workers[3] have reported that the Ce(IV)-induced vinyl copolymerization into cellulose produces a mixture of graft and block copolymers.

Finally, it is noteworthy that measurements of the acetyl content (expressed as per cent combined acetic acid yield) of the Ce(IV)-oxidized samples indicate that Ce(IV) oxidation leaves the acetyl groups unaltered. This may lead to the conclusion that grafting reaction has practically no effect on the acetyl groups of the acetylated cotton.

References

1. S. Kaizerman, G. Mino, and L. F. Mienhold, *Text. Res. J.*, **32**, 136 (1962).
2. F. K. Guthrie, *Tappi*, **46**, 656 (1963).
3. Y. Iwakura, T. Kurosaki, and Y. Imai, *J. Polym. Sci. A*, **3**, 1185 (1965).
4. A. Hebeish and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1625 (1968).
5. A. Hebeish and P. C. Mehta, *Text. Res. J.*, **39**, 99 (1969).
6. R. J. E. Cumberbirch and J. R. Holker, *J. Soc. Dyers Colour*, **82**, 59 (1966).
7. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958).
8. J. C. Arthor, Jr., P. J. Baugh, and O. Hinojosa, *J. Appl. Polym. Sci.*, **10**, 1591 (1966).
9. E. H. Immergut, in *Encyclopedia of Polymer Science and Technology*, Vol. 3, H. F. Mark, N. G. Gayland, and N. M. Bakler, Eds., Interscience, New York, 1965, p. 242.

10. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **39**, 523 (1959).

11. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Amer. Chem. Soc.*, **81**, 1494 (1959).

12. I. Terasaki and M. Matsuki, *J. Soc. Text. Cellul. Ind. Japan*, **18**, 147 (1962).

13. A. Y. Kulkarni and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1321 (1968).

14. A. Kantouck, A. Hebeish, and M. H. El-Rafie, *Eur. J. Polym.*, in press.

15. F. Hawiett and E. Martin, *J. Text. Inst.*, **35**, T1 (1944).

16. A. I. Skrigan, M. A. Shishko, and R. G. Zhbanov, *Vestsi Akad. Nauk Belarus.* SSR, Ser. Fiz-Tekh. Nauk, **61**(4), (1962); *Abstr. Bull. Inst. Paper Chem.*, **33**(10), 8492 (1963).