

## Grafting of Formaldehyde-Crosslinked and Cyanoethylated Cotton Cellulose with Acrylate Monomers

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### Synopsis

Formaldehyde-crosslinked cotton and cyanoethylated cotton were grafted with methyl, ethyl, and *n*-butyl acrylates and methyl methacrylate using ceric ion as initiator. It was observed that the graft yields for formaldehyde-crosslinked cotton were significantly higher than those for native cotton. An increase in the bound formaldehyde resulted initially in a decrease in molecular weight of grafts; but later on, an increase was observed. In the case of cyanoethylated cottons, increasing the degree of substitution resulted in increase in graft yields. Molecular weights of the grafts increase up to a D.S. of 0.3, after which they decrease. These results are interpreted in terms of rates of initiation and termination being influenced by production of additional sites due to swelling of cellulose fibers.

### INTRODUCTION

The graft copolymerization of vinyl monomers onto natural cotton cellulose and modified cotton cellulose has been investigated by number of workers.<sup>1-4</sup> The grafting of acrylonitrile has been studied in some detail, while other vinyl monomers have been investigated only to a lesser extent; and the influence of chemical modification on grafting has not been systematically studied.

In the present work, the cotton cellulose was modified by (a) crosslinking with formaldehyde, (b) cyanoethylation. These chemically modified fibers were grafted with methyl, ethyl, and *n*-butyl acrylate and methyl methacrylate monomers. In case of cyanoethylated cotton, it is expected that chemical groups on modified cellulose could provide sites for better grafting; and for formaldehyde-treated cotton, the concerted effect of crosslinking and grafting could result in further desirable changes in physical properties.

### EXPERIMENTAL

#### Materials

Bleached California cotton yarns (5<sup>s</sup>, TPI = 3), extracted with methanol for 4 hr to remove grease and dirt, were used. BDH reagent-grade chemi-

cals were used. Monomers were freed from inhibitor and distilled before use.

### Crosslinking with Formaldehyde

Crosslinking was carried out by the method described by Kantouch et al.<sup>1</sup> The samples, 20–25 g were immersed in a bath containing 5% formaldehyde and 50% orthophosphoric acid. Fiber-to-liquor ratio was 1:30. After treating the samples for a desired interval of time in the reaction bath (for example, to achieve 0.42% bound formaldehyde, the samples were treated in the bath for 30 min), the samples were removed, squeezed to give a pickup of ca. 100%, and stored in a wet state in polythene sachets for 24 hr at room temperature. The samples were then neutralized with 2% sodium carbonate, thoroughly washed, and finally dried. The bound formaldehyde was estimated spectrophotometrically by the method described by Roff.<sup>5</sup>

### Cyanoethylation

Cotton yarns, 25 g, were immersed in a bath containing 6% NaOH (M:L = 1:40) overnight. They were squeezed to give a pickup of ca. 100% and then treated with acrylonitrile in a thermostat at 60°C for different intervals of time. Thus, 0.3% cyanoethylation was obtained by refluxing the sample in acrylonitrile for 30 min. After a predetermined interval of time, the samples were removed and washed in 5% acetic acid, water, methanol, and finally ether. They were dried in air at room temperature. The degree of substitution (D.S.) was computed from the nitrogen content determined by the Kjeldahl method.

### Graft Copolymerization

Cyanoethylated cotton with different degrees of substitution (0.12 to 0.7) and formaldehyde-crosslinked cotton with bound HCHO content ranging from 0.022% to 1.00% were graft copolymerized with methyl, ethyl, and *n*-butyl acrylate and methyl methacrylate as follows:

About 1 g of modified cotton was taken in a three-necked flask provided with a thistle funnel and an inlet and outlet for nitrogen. Ceric ammonium nitrate of 0.0075*N* concentration in 0.25*N* HNO<sub>3</sub> was used as initiator. Nitrogen was bubbled through the solution, and then 2.5 ml monomer was added. The polymerization was carried out for 4 hr at 30°C, and fiber-to-liquor ratio was 1:50. The flask was constantly shaken. At the end of the polymerization, the sample was removed, washed thoroughly with water, and then Soxhlet extracted with acetone till the homopolymer was completely removed. The concentrations of the reagents and the conditions used in this case are the optimum conditions for grafting obtained for grafting the acrylate monomers onto natural cellulose.<sup>6</sup>

### Determination of Molecular Weights of Grafts

The molecular weights of the grafts were determined viscometrically after separation of the cellulose base by the method of Thampy et al.<sup>7</sup> Solutions of different concentrations ranging from 0.5% to 1% were pre-

pared in acetone, and the intrinsic viscosities were determined. Molecular weight was then found using the equation

$$[\eta] = KM^\alpha$$

where  $K$  and  $\alpha$  are constants. The values of  $K$  and  $\alpha$  for the different polymers in acetone are as follows:

	$K \times 10^6$ , dl/g	$\alpha$	Temp., °C
Poly(methyl acrylate)	28.2	0.52	30
Poly(ethyl acrylate)	25.4	0.66	30
Poly( <i>n</i> -butyl acrylate)	6.85	0.75	25
Poly(methyl methacrylate)	7.7	0.70	30

## RESULTS AND DISCUSSION

### Grafting of Formaldehyde-Crosslinked Cotton

The results of grafting acrylate monomers onto formaldehyde-crosslinked cotton are presented in Figure 1. The striking feature is that cotton with a crosslinked formaldehyde content of 0.022% has also got the highest graft-on percentage or highest number of grafted moles with all the monomers, compared even with natural cellulose. With increase in the concentration of bound formaldehyde, there is a decrease in the percent graft-on, or number of moles grafted, in the case of all the monomers investigated upto 0.42% of bound formaldehyde, after which the decrease in the number of moles grafted is insignificant. The relative decrease in number of moles grafted is maximum in case of MMA, followed by butyl acrylate, methyl acrylate, and ethyl acrylate.

The sample of natural cotton grafted with these acrylate monomers has a slightly lower percent graft-on, or number of moles grafted, than cellulose crosslinked with 0.022% formaldehyde. This should be obvious, because the latter has a greater number of sites where grafting can take place as a result of swelling. The density of cotton cellulose falls sharply with the initial crosslinking but undergoes only a marginal decrease with further increase in crosslinking. This suggests that during the crosslinking reaction, considerable swelling must have taken place. With progressive increase in the percent bound formaldehyde, a decrease in the percent graft-on is observed. Since grafting can take place predominantly in the amorphous regions of cellulose which has approximately 40% amorphous region, any crosslink which can prevent the diffusion of monomer units into the reactive sites inside the core of the cellulose chain should have the result of decreasing the percent graft-on. Thus, increasing the number of crosslinks should decrease grafting within the core of the cellulose fibers and at the same time favor grafting at the sites on the surface of the fiber. If one compares the number of moles grafted of various monomers onto cotton cellulose with 0.022% to 0.42% bound formaldehyde, then the following trend is obvious (Fig. 1):

methyl acrylate > butyl acrylate > ethyl acrylate > methyl methacrylate

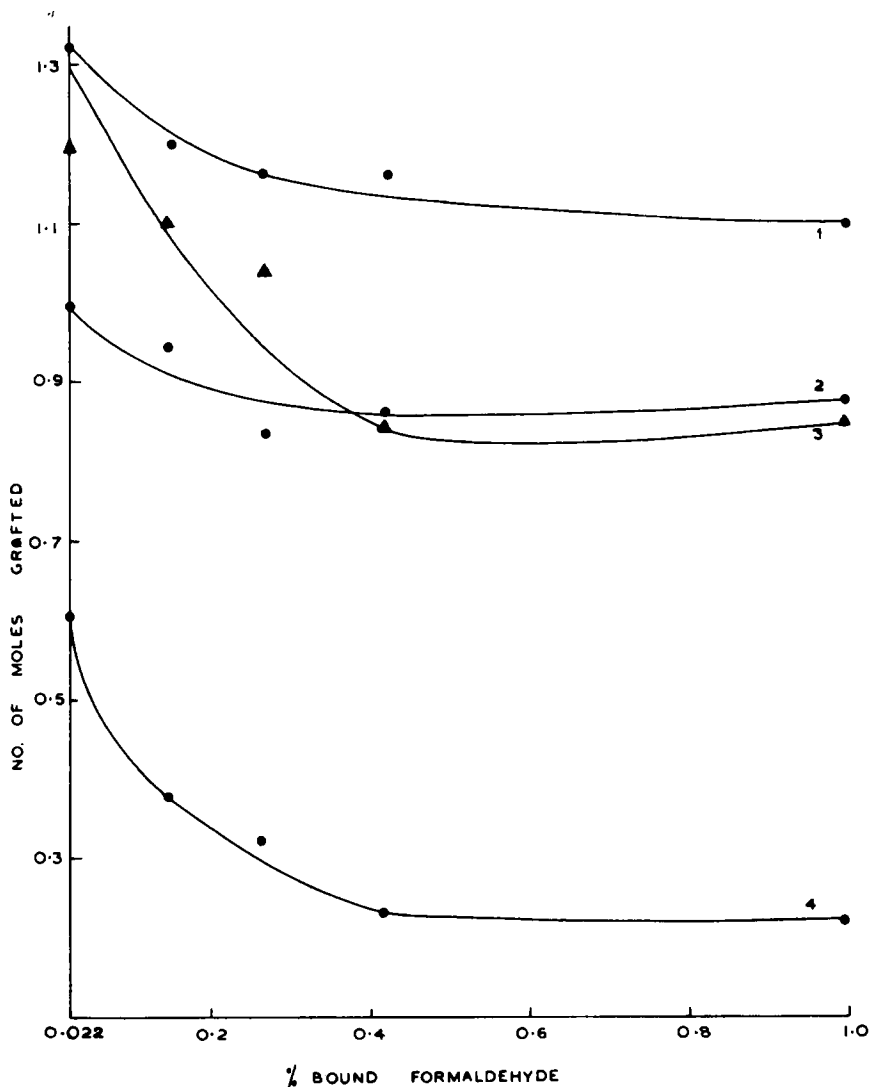
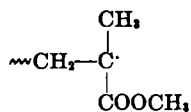
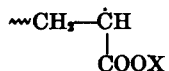


Fig. 1. Grafting of formaldehyde-crosslinked cotton cellulose: (1) methyl acrylate; (2) ethyl acrylate; (3) *n*-butyl acrylate; (4) methyl methacrylate.

At a bound formaldehyde percentage of 0.42 and above, the graft-on in butyl acrylate is approximately equal to that in ethyl acrylate. The low graft-on in case of methyl methacrylate may be due to the stability of the polymer radical which is tertiary in this case:



In case of the remaining monomers, the radical is secondary and therefore more reactive:



where X = —CH<sub>3</sub>, —C<sub>2</sub>H<sub>5</sub>, or —C<sub>4</sub>H<sub>9</sub>. The  $k_p$  for methyl methacrylate homopolymerization at 50°C is reported as 410 l./mole-sec, while for methyl acrylate it is 1000 l./mole-sec.<sup>8</sup> The tertiary radicals are more stable than secondary or primary ones due to stabilization by resonance.<sup>9</sup> The lower graft-on in ethyl acrylate as compared to butyl acrylate is difficult to explain.

With increase in the content of bound formaldehyde, the molecular weight of the grafted polymer decreased in all the cases up to a concentration of bound formaldehyde of 0.42%. At the highest degree of crosslinking, viz., 1%, the molecular weight showed an upward trend in the case of all the vinyl monomers that were used (Table I).

The degree of polymerization ( $\overline{\text{DP}}$ ) is related with rate of propagation, termination, and initiation by the following well-known relationship for free-radical polymerization:

$$\overline{\text{DP}} = \frac{k_p[\text{M}]}{k_{tr}[\text{SH}] + \left(\frac{k_{tc}}{2} + k_{td}\right) \left\{ \frac{I}{(k_{tc} + k_{td})} \right\}^{1/2}}$$

where  $k_p$ ,  $k_{tr}$ ,  $k_{tc}$ , and  $k_{td}$  are the specific rate constants for propagation, transfer, termination by combination, and termination by disproportionation, if any, respectively;  $I$  is the rate of initiation; and SH is the chain transfer agent, which may be the —OH group in cellulose. If the number of sites available for initiation is very large due to swelling, the rate of initiation will also be proportionately higher, thus reducing  $\overline{\text{DP}}$ . A growing polymer radical can be terminated either by combination or disproportionation with another radical or by abstracting a hydrogen atom from the OH group of cellulose. The variation in the  $\overline{\text{DP}}$  of the different grafted samples may be due to the variation in the rate of initiation and termination reactions.

In case of methyl acrylate, the crowding in monomer is less, and also the polymer radical is fairly reactive, thus increasing  $k_p$ , which results in a high  $\overline{\text{DP}}$ . Crosslinking with formaldehyde will reduce the diffusion of monomer in the vicinity of a growing polymer chain which may then be terminated by transfer reaction or by disproportionation, thus resulting in a decrease in  $\overline{\text{DP}}$ . Slight increase in  $\overline{\text{DP}}$  observed at 1% bound formaldehyde may be due to decrease in chain termination reaction because the concentration of free hydroxyl groups is reduced and also the diffusion of two polymer radicals in the vicinity of each other may be less. Similar arguments may be applied in the other monomers.

TABLE I  
Grafting of Acrylate Monomers on Formaldehyde-Crosslinked Cotton: Molecular Weights

% Formaldehyde crosslinked	Methyl acrylate			Ethyl acrylate			Butyl acrylate			Methyl methacrylate		
	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$
0	7.09	8.241	1.42	—	—	—	—	—	—	—	—	—
0.022	6.4	7.442	1.78	3.2	3.2	3.09	0.28	0.22	5.42	1.96	1.96	3.094
0.147	2.89	3.36	3.65	2.55	2.55	3.69	0.21	0.17	6.52	1.206	1.206	3.12
0.267	2.09	2.43	4.78	0.85	0.85	9.77	0.18	0.14	7.50	1.045	1.045	3.12
0.42	1.64	1.91	6.10	0.81	0.81	10.62	0.09	0.07	11.80	0.787	0.787	2.923
1.00	4.48	5.21	2.12	1.50	1.50	5.88	0.14	0.11	7.64	0.976	0.976	2.277

TABLE II  
Grafting of Cyanoethylated Cotton: Molecular Weights

Degree of substitution	Methyl acrylate			Ethyl acrylate			Butyl acrylate			Methyl methacrylate			
	Density, g/cc	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$	Mol. wt $\times 10^{-4}$	Degree of polymerization $\times 10^{-3}$	No. of grafted chains/unit cellulose $\times 10^4$
0.12	1.3	1.637	1.90	2.33	0.92	3.28	13.05	1.92	1.5	5.25	0.03	0.03	76.6
0.3	1.265	2.761	3.21	2.0	4.6	4.6	2.63	5.0	3.9	2.2	4.15	4.15	1.06
0.7	1.23	1.746	2.03	3.9	3.28	0.92	3.50	3.22	2.5	3.0	0.123	0.123	52.84

### Grafting of Cyanoethylated Cotton

The results of grafting acrylate monomers on cyanoethylated cotton are presented in Fig. 2. In agreement with the earlier results of grafting of acrylonitrile on cyanoethylated cotton,<sup>4</sup> we find a progressive increase in percent graft-on, or number of moles grafted, with the degree of substitution with reference to natural cotton. The behavior of methyl acrylate and methyl methacrylate is, however, different. Though increasing degree of substitution helps further grafting, the graft-on yield in general is less than that of natural cotton. Similar observations on grafting of methyl methacrylate on carboxymethylated cotton have been noticed by Kantouch et

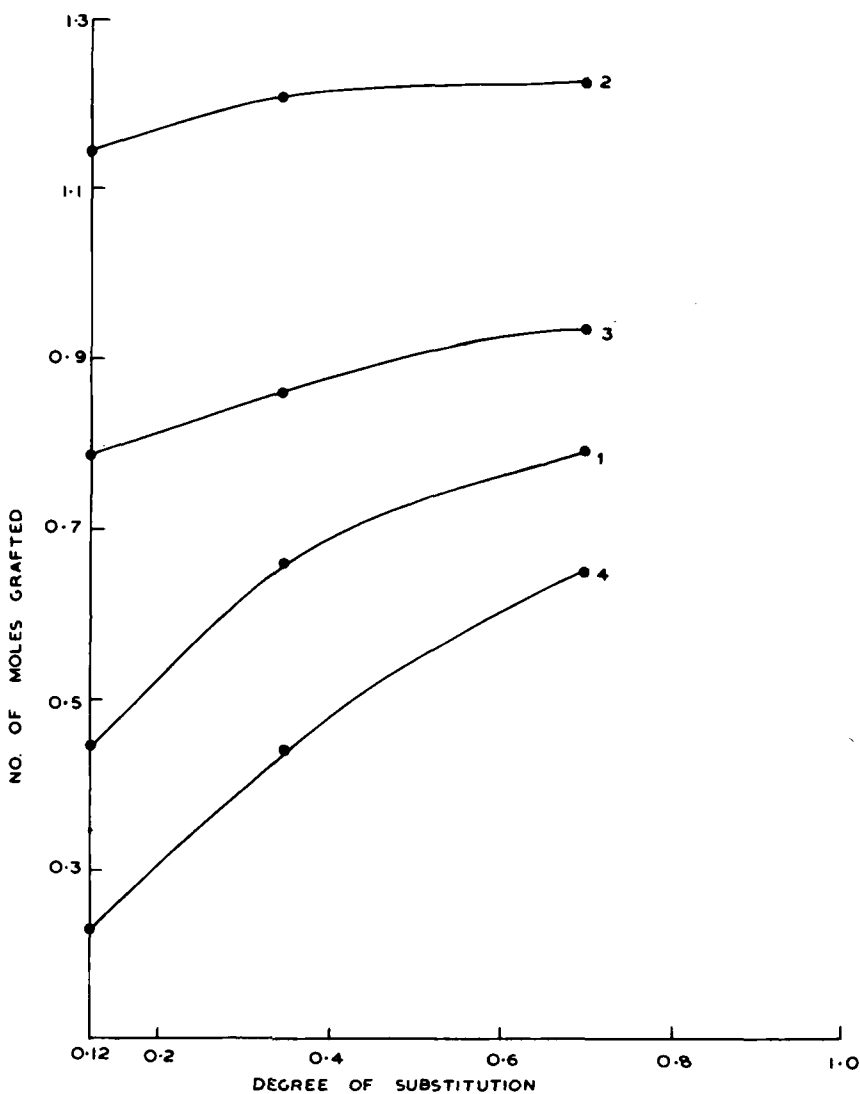


Fig. 2. Grafting of cyanoethylated cotton cellulose: (1) methyl acrylate; (2) ethyl acrylate; (3) *n*-butyl acrylate; (4) methyl methacrylate.

al.<sup>10</sup> But cyanoethylated cotton gives a higher yield with methyl methacrylate in another of their investigation. Our observations on the grafting of methyl methacrylate onto cyanoethylated cotton are different from the literature value.<sup>4</sup>

The densities of the cyanoethylated samples decrease appreciably with increasing degree of substitution, suggesting a high degree of swelling at higher degree of substitution. The molecular weights of the grafts show a marked fall from a high value in the natural cotton to an appreciably low value at a degree of substitution of 0.12. This is followed by an increase in the molecular weight and a subsequent fall with all the monomers employed. The highest molecular weight is obtained at a degree of substitution of 0.3 (Table II).

Reaction of acrylonitrile with cotton is largely limited to the surfaces of the fibers.<sup>11</sup> Cyanoethylation, therefore, takes place at the surface hydroxyls, leaving the core hydroxyls unaffected. Grafting of the monomers can take place on all the hydroxyl sites and also on the newly created cyanoethyl sites which are formed by removal of labile hydrogen of OH group. With increase in the degree of substitution two types of sites are available for grafting of which cyanoethyl groups may be more reactive. Higher rate of initiation effectively decreases the  $\overline{DP}$  with a consequent fall in the molecular weight up to a D.S. of 0.12. With increase in D.S., more free OH groups are cyanoethylated. The free OH groups may be acting as good chain transfer agents; and by their removal such reactions will decrease and so the  $\overline{DP}$  will increase as is observed at D.S. 0.3. Swelling increases considerably with further D.S., as is obvious by a remarkable fall in density. The core hydroxyls are now thrown open to attack by the monomer. Hence, there is a decrease in  $\overline{DP}$ . The lower graft-on values in the case of methyl methacrylate may be attributed to the same factors as discussed with formaldehyde-bound cellulose.

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