

Behavior of Chemically Modified Cellulose Towards Dyeing. IV. Dyeability of Poly(Methyl Vinyl Pyridine)-Cellulose Graft Copolymers Before and After Treatment with Epichlorohydrin

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Synopsis

Grafting of 2-methyl-5-vinyl pyridine (MVP) onto partially carboxymethylated cotton having 6 meq COOH/100 g cellulose (PCMC) was effected by a Fe^{2+} - H_2O_2 redox system. Different graft yields were obtained by varying MVP concentration from 10 to 100 wt % PCMC. In a subsequent step these graft copolymers were treated with epichlorohydrin. Dyeing of untreated cotton, PCMC, PCMC grafted with MVP, and epichlorohydrin-treated poly(MVP)-PCMC graft copolymers was carried out at room temperature (27 °C) for varying lengths of time (2.5–60 min) in the absence of alkali catalyst or any other additives. Three reactive dyes, Procion Red M-GS, Procion Orange Brown H-2GS, and Remazole Brilliant Blue; a direct dye, Orangé Solophényle 2RL; and an acid dye, Erio Blue Marine 2GR were used at a concentration of 2% by weight of material. It was found that none of the three reactive dyes or the acid dye interacts with untreated cotton or PCMC. In contrast, the direct dye did. PCMC grafted with MVP, on the other hand, showed a substantial extent of dye exhaustion regardless of the dye used. After-treatment of poly(MVP)-PCMC graft copolymers with epichlorohydrin significantly enhanced the extent of dye exhaustion. The latter reacted almost 100% with all the dye examined, irrespective of the graft yield, which varied from 1.6% to 63%. Dyeings for reactive dyes withstood soaping for 1 hr at boil and extraction with 50% dimethylformamide, whereas dyeings for the direct dye and the acid dye failed to do so. It is believed that the presence of pyridine moieties in the graft act as an internal, built-in catalyst for expediting the reaction of reactive dyes with cellulose hydroxyls and behave as a weak base capable of salt-linkage formation in case of the acid and direct dyes.

INTRODUCTION

Previous reports¹ have shown that chemical modification of cellulose prior to dyeing with reactive dyes brings about significant changes in cellulose dyeability. Partial acetylation up to 7% combined acetic acid caused an enhancement in dye fixation. Above this value, no perceptible shade could be obtained. A decrease in dye fixation was found with partially carboxymethylated cellulose and polyacrylonitrile-cellulose graft copolymers, particularly at higher degrees of modification. On the other hand, increasing the degree of modification in cyanoethylation or carbamoylethylation was accompanied by an increase in dye fixation. Similar studies have been carried out using some direct dyes.^{2,3} Moreover, recent work⁴ on dyeing of cellulose grafted with poly(methyl methacrylate) and polyacrylonitrile with some direct and reactive dyes has disclosed that the dyeability depends on the amount and nature of the grafted polymer, as well as on changes in the physical and/or chemical structure of cellulose brought about by grafting.

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This work was undertaken with a view of studying (1) the feasibility of poly(MVP)-cotton graft copolymers before and after treatment with epichlorohydrin in effecting reaction of reactive dyes with cellulose hydroxyls in the absence of external alkaline catalyst and (2) the affinity of such a substrate to acid and direct dyes.

EXPERIMENTAL

Purified Cotton. Egyptian Monofi cotton slivers were purified by a mild alkaline scouring (2% NaOH and 0.2% wetting agent by weight of material) for 5 hr at 110°C and 6–10 lb/in² using a liquor ratio of 10.

Partially carboxymethylated cotton (PCMC). PCMC was prepared as per a reported method^{5,6} using sodium chloroacetate (0.3*N*) and sodium hydroxide (12*N*).

Poly (MVP)-PCMC Graft Copolymers. These copolymers were prepared by graft polymerization of MVP onto PCMC as follows: The PCMC samples were treated in 0.25% ferrous sulfate solution for 15 min at room temperature, squeezed, thoroughly washed with distilled water, and dried. The samples were then introduced into stoppered Erlenmeyer flasks containing emulsions of MVP (10, 20, 50, and 100 wt-% PCMC) and H₂O₂ (20 meq/l.). Emalfour (0.05%) was used as emulsifier. The flasks were kept in a thermostat at 80°C for 2 hr. The reaction products were then thoroughly washed with distilled water, dried, and repeatedly extracted with methanol until a constant weight achieved. The graft yield was based on the dry weight of PCMC.⁷

Treatment of Poly(MVP)-PCMC Graft Copolymer with Epichlorohydrin. The poly(MVP)-PCMC graft copolymers were immersed in a solution containing epichlorohydrin that was slightly in excess of the equivalent amount required for complete quaternization at 90°C for 2 hr. The samples were then thoroughly washed with methanol and distilled water prior to drying.

Dyeing. Three reactive dyes, Procion Red M-GS, Procion Orange Brown H-2Gs, and Remazol Brilliant Blue; an acid dye, Erio Blue Marine 2GR; and a direct dye, Direct Orangé Solophényle 2RL were employed. All dyes were used as received without further purification. Dye solution was prepared with 2% dye (based on the weight of material) without any other additions. The dyeing was carried out at the ambient temperature. The material was then placed in the dye solution, and dyeing was allowed to proceed while stirring for different lengths of time (2.5–60 min). A material to liquor ratio of 1:400 was used. Small aliquots were withdrawn from the dyeing bath after different times for determination of dye exhaustion.⁴

RESULTS AND DISCUSSION

The Fe²⁺-H₂O₂ forms an effective redox system to induce vinyl graft copolymerization onto cotton cellulose.^{8,9} Previous reports^{10–12} have also disclosed that the grafting reaction depends to a large extent on the conditions of the experiment. The best technique appears to be to first subject the cellulose to a solution of ferrous salt. The ferrous ions are absorbed by the cellulose, and the

subsequent reaction with H_2O_2 in the presence of monomer will therefore take place in close proximity to the cellulose molecules at a large concentration of these molecules.

Hence in order to ensure homopolymer depression and in order to pursue grafting, the cation binding capacity of cotton cellulose was accentuated by the introduction of a small amount of carboxyl groups (6 meq/100 g cellulose) via partial carboxymethylation. The partially carboxymethylated cotton (PCMC) so obtained was grafted with MVP so as to give different grafting levels, as described in the Experimental section. Further modification of cotton was effected by treating the PCMC-poly(MVP) graft copolymers with epichlorohydrin. These graft copolymers were dyed before and after modification with some reactive, direct, and acid dyes to see, in particular, the effect of such modifications on the behavior of cotton towards dyeing. The results obtained are presented below along with appropriate discussion.

Dyeing with Reactive Dyes

It is well established that reactive dyes containing cyanuryl halide groups or sulfonic sulfatoethyl groups react with cellulose in alkaline medium via formation of covalent bonds between the dye and cellulose.¹³⁻¹⁸ It is also known that some dye molecules are hydrolyzed in the course of the process depending on the structure of the dye.^{19,20}

Current work reveals that neither cotton nor PCMC reacts with any of the reactive dyes used in the absence of alkali as a catalyst (external catalyst), reflecting the well-known fact that an external alkaline catalyst is a must. Nevertheless, built-in nucleophilic branches, as present in poly(MVP)-PCMC graft copolymers, catalyze the reaction of the reactive dyes with cotton. The catalytic influence of the internal (built-in) graft significantly increases if the copolymers are treated with epichlorohydrin prior to dyeing. This may be seen in Figures 1-3.

Figures 1-3 show the dyeing rate curves for Procion Orange Brown H-2GS, Procion Red M-GS, and Remazol Brilliant Blue, respectively, on poly(MVP)-PCMC graft copolymers having different graft yields before and after the copolymers were treated with epichlorohydrin. As is evident, the figures reveal some common features: (1) dyeing does occur in absence of external alkaline catalyst, (2) the favorable effect of the graft yield on the extent and rate of dyeing is not very significant, and (3) treatment of the copolymers in question with epichlorohydrin causes an outstanding enhancement in the extent and rate of dyeing.

That dyeing of poly(MVP)-PCMC graft copolymers with reactive dyes occurs in the absence of alkaline catalyst is rather interesting. The presence of the poly(MVP) graft in the cotton cellulose molecules seems to alter the anion-exchange properties of the cellulose. Reaction of the dye at the cellulose hydroxyls is most probably catalyzed by Lewis base tertiary amines (pyridine moieties) of the graft or the anion associated with these moieties. That is, poly(MVP) graft forms a built-in nucleophilic catalyst in PCMC which is capable of catalyzing the reaction of the reactive dye with cellulose hydroxyls, since the

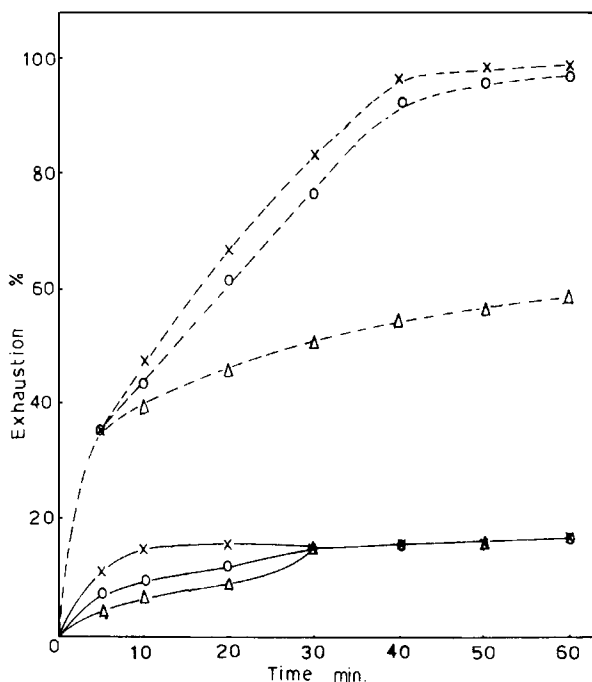


Fig. 1. Dyeing rate curves for Procion Orange Brown H-2GS on PCMC grafted with MVP before (—) and after (---) treatment with epichlorohydrin for the following percent grafts: 11.2 (Δ), 22 (O), and 63 (X). Dye concentration, 2% by weight of material; dyeing temperature, 25°C.

latter does not react with the former in the absence of external alkaline catalyst.

It may be argued that the attachment of the dye to cotton cellulose takes place via salt formation, but subjecting the dyed cotton samples to soaping for 1 hr at boil or to extraction with DMF (50%) or both failed to completely remove the dye. Indeed, with Procion Red M-GS and Orange Brown H-2GS, no color could be detected in either the aqueous soap solution or in the DMF extract. With Remazol Brilliant Blue, on the other hand, slight coloration could be observed, indicating partial removal of the dye.

After-treatment of poly(MVP)-PCMC graft copolymers with epichlorohydrin markedly enhances the extent and rate of dyeing with reactive dyes irrespective of the dye used within the range studied. As is evident from Figures 1–3, an exhaustion of 100% is achieved in almost all cases, regardless of the graft yield of the copolymer. Moreover, these dyeings withstand soaping at the boil and DMF extraction in a manner similar to those observed with copolymers before treatment with epichlorohydrin.

These findings suggest that the copolymer in question is quaternized with epichlorohydrin, thereby increasing the magnitude of the anion-exchange properties of cotton. That is, the effectiveness of the built-in nucleophilic catalyst is accentuated by quaternization of the pyridine moieties. It is also likely that the reaction of epichlorohydrin with PCMC occurs through abnormal ring opening, similar to 1-chloro-2,3-epithiopropene,²¹ as shown by the mechanism

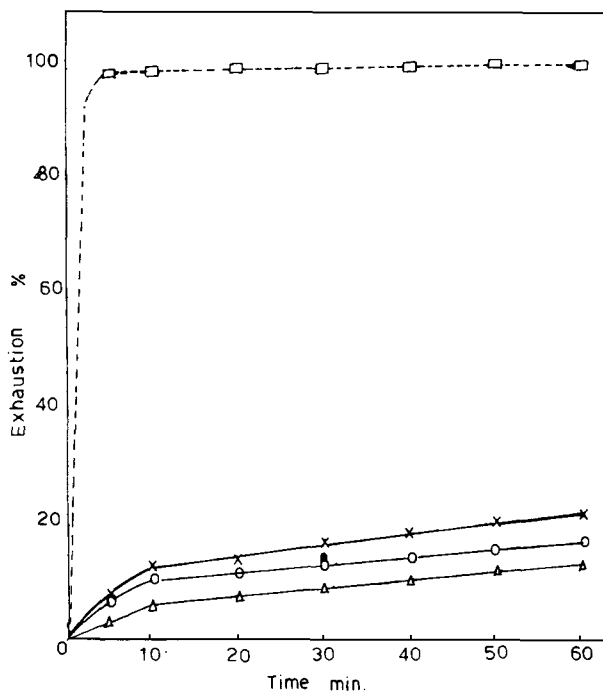
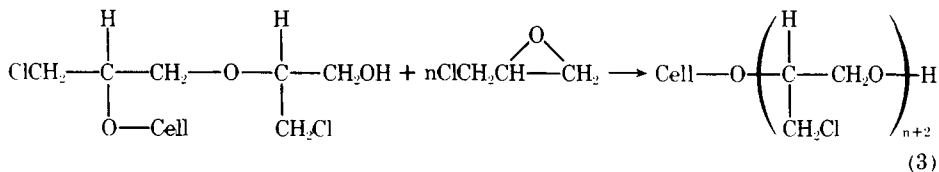
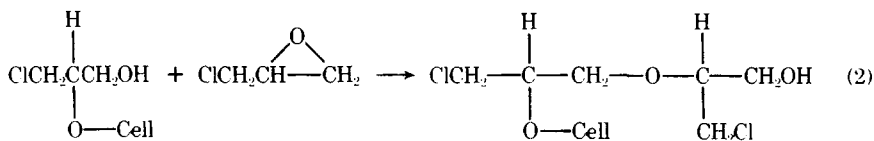
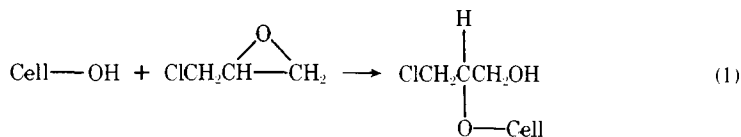
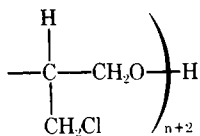


Fig. 2. Dyeing rate curves for Procion Red M-GS on PCMC grafted with MVP before (—) and after (---) treatment with epichlorohydrin for the following percent grafts: 11.2 (Δ), 22 (\circ), and 63 (\times). Open squares represent values for all three grafts. Dye concentration and dyeing temperature same as in Fig. 1.

suggested by eq. 1–3:



Obviously, the ultimate product, eq. (3) contains, besides the poly(MVP) graft, a side chain



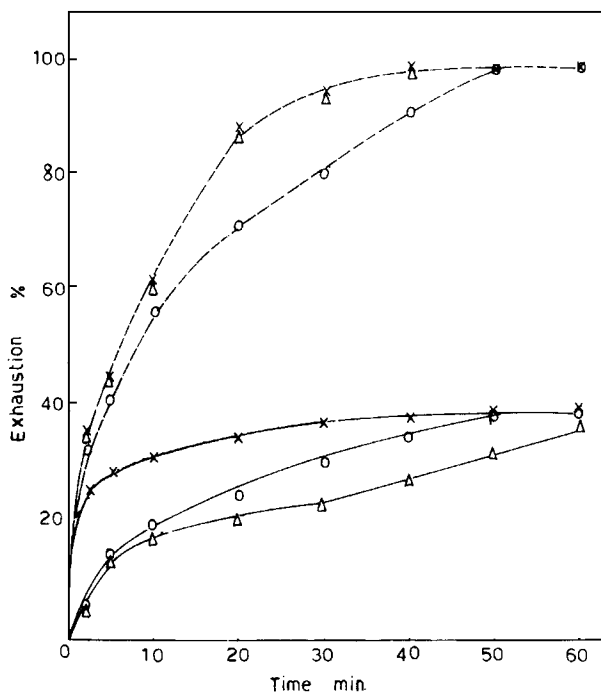


Fig. 3. Dyeing rate curves of Remazole Brilliant Blue on PCMC grafted with MVP before (—) and after (---) treatment with epichlorohydrin for the following percent grafts: 11.2 (Δ), 22 (\circ), and 63 (\times). Dye concentration and dyeing temperature same as in Fig. 1.

If created, the hydroxyl end group of this chain may afford an additional site for the dye reaction. Furthermore, the side chain would be expected to cause an opening up of the cellulose structure. As a result, diffusion of the dye inside the cotton fibers is favored. Both functions of the side chain lead certainly to a higher extent and rate of dyeing.

In short, it may be correct to say that after-treatment of PCMC-poly(MVP) graft copolymer with epichlorohydrin converts cotton to a polyelectrolyte capable of a self-catalyzing reaction with reactive dyes. A dye exhaustion of up to 100% could be achieved irrespective of the graft yield. It was also observed that the amount of dye removed by soaping at boil and/or extraction with DMF (50%) was nil with the Procion dyes and negligible with the Remazole dye. Elimination of dye hydrolysis by omitting the alkaline catalyst from the dyeing system accounts for this.

Dyeing with Acid Dyes

Figure 4 shows rate curves for the acid dye (Erio Blue Marine 2GR) on PCMC grafted with MVP before and after treating the grafted PCMC with epichlorohydrin. As can be seen, substantial dye exhaustion is achieved with the grafted PCMC regardless of the graft yield. However, the magnitude of dye exhaustion depends on the graft yield. For instance, exhaustion of 40 and 28% in 1 hr of dyeing could be obtained with substrates having 63% and 22% graft, respectively.

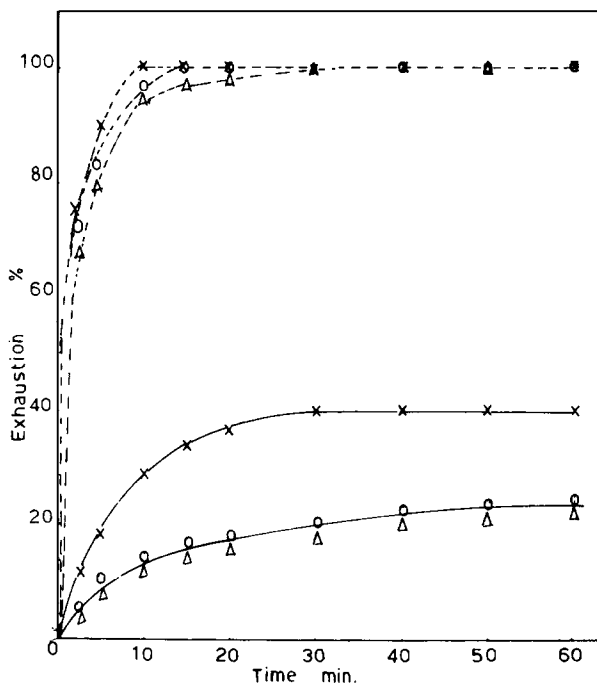


Fig. 4. Dyeing rate curves of acid dye Erio Blue Marine 2GR on PCMC grafted with MVP before (—) and after (---) treatment with epichlorohydrin for the following percent grafts: 11.2 (Δ), 22 (O), and 63 (X). Dye concentration and dyeing temperature same as in Fig. 1.

Treatment of grafted PCMC with epichlorohydrin significantly enhances the extent and rate of dyeing and eliminates the difference caused by the degree of grafting, i.e., graft yield. For example, a 100% dye exhaustion is obtained after 30 min irrespective of the graft yield.

The acceptability of PCMC-poly(MVP) graft copolymers to the acid dye is in full agreement with previous reports,²²⁻²⁵ which ascribed this to the formation of linkages between the pyridine moieties and the acidic groups of the dye. After-treatment of the copolymers with epichlorohydrin prior to dyeing seems to considerably accentuate this interaction.

It is worth emphasizing that subjecting the acid dyeings to soaping at boil for 1 hr caused complete removal of the dye, in contrast to reactive dyes. This clearly reflects the difference in the mode of interaction of the two dyes with the copolymers in question. Reactive dyes react with the copolymer via strong covalent bonds between the reactive functional group in the reactive dye and cellulose hydroxyls, whereas the acid dye attaches to cellulose via salt linkages between the acidic groups of the dye and the pyridine moieties of the graft.

Dyeing with Direct Dyes

Figure 5 shows the dyeing rate curves for the direct dye, Orangé Solophényle 2RL, on untreated cotton, PCMC, PCMC grafted with MVP, and PCMC-poly(MVP) graft copolymers treated with epichlorohydrin. It is obvious that the dyeing rate curves of untreated cotton and PCMC nearly coincide, indicating that partial carboxymethylation within the range studied has no effect on dyeing

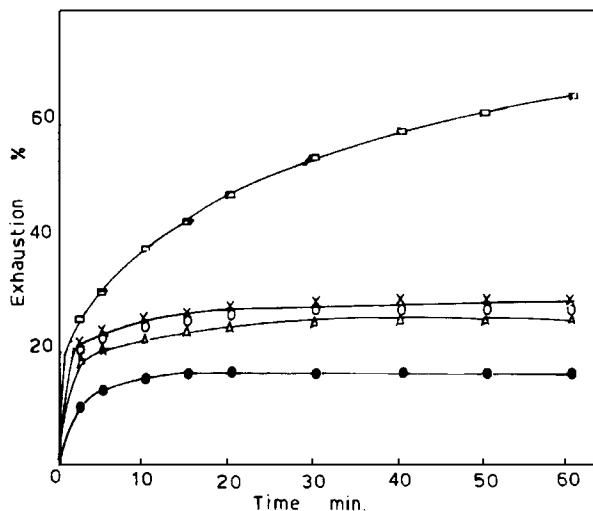


Fig. 5. Dyeing rate curves of direct dye Orangé Solophényle 2RL on purified cotton and PCMC (●); PCMC grafted with MVP before treatment with epichlorohydrin at the following percent grafts: 11.2 (▲), 22 (○), and 63 (×); and grafted PCMC after treatment with epichlorohydrin for the same grafts, all represented by the open square. Dye concentration and dyeing temperature same as in Fig. 1.

with this direct dye. Grafting PCMC with MVP prior to dyeing substantially enhances the extent and rate of dyeing irrespective of the degree of grafting, since the extent and rate of dyeing for graft copolymers having 11.2, 22, and 63% graft are nearly equal.

After-treatment of PCMC-poly(MVP) graft copolymer with epichlorohydrin prior to dyeing brings about a significant increase in the extent and rate of dyeing with Orangé Solophényl 2RL (Fig. 5). Here too, the magnitude of the graft yield has no effect on the extent and rate of dyeing.

The enhancement in the extent and rate of dyeing with the direct dye by grafting of MVP onto PCMC and the further enhancement on treating the graft copolymer with epichlorohydrin could be associated with: (1) opening up the cellulose structure, thus facilitating diffusion of the dye from the aqueous phase into the fiber phase; (2) producing a favorable environment in the cellulose matrix, thereby increasing the rate of dye adsorption; and (3) the basicity imparted by the pyridine moieties of the graft would lead to salt linkages between the acidic solubilizing group of the dye and these pyridine moieties.

As with the acid dye, dyeings for the direct dye could not withstand soaping at boil. The dye was removed almost completely on boiling in an aqueous solution containing 5 g soap and 2 g sodium carbonate per liter for 30 min.

Based on the findings discussed above for the reactive, acid, and direct dyes, it is obvious that the magnitude of grafting does not play a substantial role in the extent and rate of dyeing, particularly when the graft copolymer is treated with epichlorohydrin prior to dyeing. For practical significance, dyeing with these dyes was therefore independently carried out on epichlorohydrin-treated PCMC-poly(MVP) graft copolymers having 1.6 and 5% graft.

It was observed that the extent and rate of dyeing were nearly equal to those obtained with these dyes on a copolymer having as much as 63% graft. This

implies that it is the polyelectrolyte behavior of the epichlorohydrin-treated graft copolymer that plays the key role in dyeing and reflects the potential value of this modification in the dyeing field.

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