

Behavior of Cellulose Grafted with Poly(methyl Methacrylate) and Polyacrylonitrile Toward Some Direct and Reactive Dyes

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Synopsis

Viscose rayon fibers modified with polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA) were dyed with some direct and reactive dyes. Exhaustion rate of the dye onto fibers was governed by the amount and nature of the polymer grafted. In general, the dye affinity for cellulose and dye exhaustion onto fibers decreased as the graft yield increased. Dye affinity for the PAN-cellulose graft copolymers was greater than that found with PMMA-cellulose graft copolymers. Except in a few cases, the tendency of cellulose graft copolymers of ca. 13% graft to accept direct dyes was more than that of the untreated cellulose, whereas the affinity of reactive dyes for cellulose graft copolymers of up to ca. 43% polymer was more than that of untreated cellulose. The dye fixation, based on the weight of cellulose component, increased as the graft yield increased. The dyeability of cellulose oxidized with ceric ammonium nitrate was also examined. Oxidation of cellulose prior to dyeing reduced the affinity of the dye for cellulose.

INTRODUCTION

Vinyl graft copolymerization onto cellulose has been studied extensively using a variety of methods, e.g., chain transfer, high energy radiation, low energy radiation in the presence of sensitizer, and redox system to initiate free-radical formation.¹ The modification of textile properties of cellulose has also been reported. Changes in fibrous morphology and in physical and chemical properties of cellulose have been observed after copolymerization with vinyl monomers. Cellulose-polyvinyl copolymers exhibit some of the properties of cellulose and the grafted polymer.²⁻⁶ However, very few studies have dealt with the behavior of cellulose graft copolymers to different dyes.^{7,8}

This work was undertaken with a view of studying (a) the affinity of different direct and reactive dyes to cellulose graft copolymers, (b) the influence of the amount and nature of the grafted polymer on dyeability of cellulose, and (c) the effect of the changes in the physical and/or chemical structure of cellulose brought about by grafting on the dye fixation in case of reactive dyes.

EXPERIMENTAL

Materials

Viscose staple fibers (1.5 den) were purified by boiling in 0.5 g/l. soap solution for 2 hr, washed well, and air dried. The fibers acquire a copper number of 0.39 and carboxyl group of 2.2 meq/100 g cellulose. Determination of copper number and carboxyl groups was carried out according to reported methods.^{9,10}

A number of direct and reactive dyes were selected for this study. The direct dyes were Solophenyl Scarlet BNL, Solophenyl Yellow FFL, Solophenyl Red 6BL, and Diphenylbrown MIN 200%. Reactive dyes based on monochloro- and trichloropyrimidines were Cibacron Blue 3 GA, Cibacron Brilliant Yellow 3 G-E, Cibacron Orange T3G-E, and Cibacron Rubine R-E. A reactive dye based on sulfatoethylsulfone, namely, Remazole Golden Yellow G, was also used. All the dyes were purified before use.

Ceric ammonium nitrate, Merk reagent grade, was 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.

Graft Copolymerization Procedure

Graft polymerization of AN and MMA onto the cellulosic material was carried out at 40°C using ceric ammonium nitrate (0.05*M*) in 0.3*M* perchloric acid. A material-to-liquor ratio of 1:25 was used. The experimental technique adopted was as follows.¹² The ceric solution in a stoppered Erlenmeyer flask was kept in a thermostat for 10–15 min. The required amount of monomer was added, and the cellulosic sample was immediately introduced into the flask. The flask was well stoppered and the contents stirred occasionally during polymerization. After 2 hr, the sample was washed well by extraction with several portions of water, with a little soap to remove the loosely adhering polymer, and dried. The sample was then extracted repeatedly with organic solvents (acetone for PMMA and dimethylformamide for PAN) to constant weight. Calculation of the per cent grafting was based on dry weight of cellulose:

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

Different graft yields were obtained by changing the concentration of monomer as shown in Table I.

Homopolymerization

Poly(methyl methacrylate) (PMMA) and polyacrylonitrile (PAN) were obtained by polymerization of MMA and AN independently under conditions identical to those of grafting, except that the cellulose was absent. Films of

both polymers were made by first dissolving PAN in dimethylformamide and PMMA in benzene, then spreading the viscous solutions on glass plates by means of special film-making instrument (Erichsen, West Germany) so as to give a thickness of 0.04 cm. The films were allowed to dry at ambient conditions.

Oxidation

Oxidation of the cellulosic sample with ceric solution was carried out under conditions identical with those described above for grafting, except that the monomer was omitted. The oxidized cellulose has a copper number of 4.9 and a carboxyl content of 3.1 meq/100 g cellulose.

Dyeing Procedures

Direct Dyes

Dye solutions were prepared containing 1% dye (on wt of fibers) and 0.5% sodium sulfate. The dyeing bath was allowed to attain a temperature of 70°C and kept constant at this temperature. The cellulosic material was then introduced into the dye bath, and dyeing was performed with continuous stirring for different intervals of time (5–90 min). A material-to-liquor ratio of 1:30 was used. Small aliquots were withdrawn from the dyeing bath after different times for determination of the dye exhaustion.

Reactive Dyes

Cibacron Dyes. Dye solutions were prepared containing 1% dye (on wt of fibers), 2% sodium carbonate, and 6% common salt. The temperature of the dye bath was raised to 90°C, then lowered to 70°C and kept constant at this temperature. The material was then placed in the dye solution, and dyeing was allowed to proceed while stirring for different lengths of time (5–105 min). A material-to-liquor ratio of 1:20 was used. After 105 min, the sample

TABLE I
Graft Copolymerization of Acrylonitrile and Methyl Methacrylate Onto Cellulose^a

Monomer	Monomer concentration, %	Graft yield, %
Acrylonitrile	1	13.5
	2	43.7
	3	51.5
Methyl methacrylate	4	73.2
	2	14.0
	4	43.5
	6	66.8
	8	93.2

^a Ceric ammonium nitrate concentration, 0.1M in 0.3M perchloric acid; temperature, 40°C; reaction time, 2 hr; material/liquor ratio, 1:25.

was removed from the dye solution, thoroughly rinsed with distilled water, washed in a solution containing Ulthan HD (1 g/l.) for 15 min at the boil, rinsed with distilled water, extracted with 50% dimethylformamide for 15 min at the boil, and finally dried at ambient conditions.

Remazole Dye. Dye solutions were prepared containing 2% dye (on wt of fibers) 0.1% Calgon T, 0.5% sodium sulfate, and 0.1% trisodium phosphate. The dye solution was heated for 20 min at 60°C before commencing dyeing. The cellulosic material was then introduced, and dyeing was carried out while stirring for different durations (50–60 min). After 60 min, the dyed material was dipped in dilute acetic acid solution. Following this, the sample was placed in distilled water at 70°C for 10 min, followed by washing in a solution containing Hostpal CV (1 g/l.) for 10 min. At this end, the material was extracted with dimethylformamide as described above.

Dye exhaustion and dye fixation were estimated spectrophotometrically according to a reported method.¹³ Calculations were done as follows:

$$\% \text{ exhaustion} = \frac{\text{wt of dye in original dye solution} - \text{wt of dye in the dye solution after certain time of dyeing}}{\text{wt of dye in original dye solution}} \times 100$$

$$\text{dye reacted with cellulose (\%)} = \frac{\text{wt of reacted dye}}{\text{dry wt of dyed sample}} \times 100.$$

RESULTS AND DISCUSSION

Dyeing with Direct Dyes

Figure 1 shows the rates of dye exhaustion with time for untreated cellulose and PAN–cellulose graft copolymers. Dyeing of these substrates was carried out under similar conditions using Solophenyl Red 6BL as described above. It is clear that, regardless of the substrate used, the exhaustion curve is characterized by an initial fast rate followed by a slower one, then leveling off to give maximum exhaustion. Nevertheless, the magnitude of the initial and maximum exhaustions relies on the nature of the substrate.

Grafting of cellulose with PAN affected both the rate of exhaustion onto the modified cellulose and the affinity of the dye for cellulose during the 90-min dyeing periods (Fig. 1). Cellulose graft copolymer containing ca. 13% PAN increased the affinity of the dye for cellulose, particularly in the initial stages of dyeing. On the other hand, the dye affinity of PAN–cellulose graft copolymer having ca. 43% PAN or more was much less than the untreated cellulose.

Figure 2 illustrates the exhaustion curves of Solophenyl Red 6 BL obtained with PMMA–cellulose graft copolymers having different graft yields. The corresponding curve for the untreated cellulose is included in the same figure for comparison. The latter indicates that copolymers containing ca. 13% and 43% PMMA showed higher initial dye exhaustion than the untreated cellulose. The opposite holds true for maximum exhaustion. However, both the initial and maximum dye exhaustions depend upon the graft yield, being de-

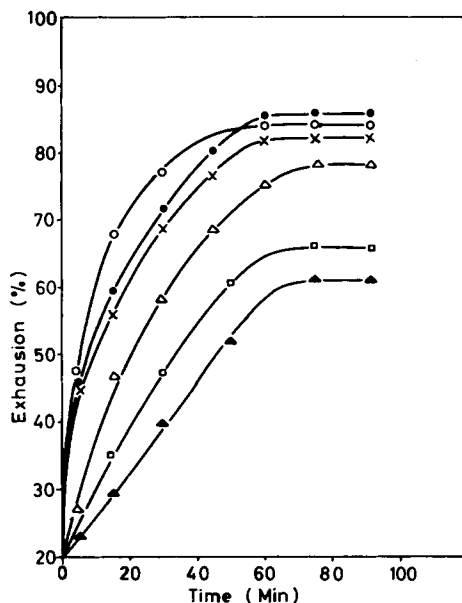


Fig. 1. Effect of grafting of cellulose with PAN on dyeing with Solophenyl Red 6 BL at 70°C: (●) untreated cellulose; (X) oxidized cellulose; (○) 13.5% PAN; (△) 43.7% PAN; (□) 51.5% PAN; (▲) 73.2% PAN.

creased as the graft yield increased. In accordance with this, exhaustion for copolymers of cellulose containing ca. 66% and 93% PMMA was significantly lower than that of the untreated cellulose, specially in the later stages of dyeing.

Grafting occurs exclusively in the accessible amorphous regions of cellulose.^{14,15} Dye adsorption is also confined to these regions since dyeing was carried out in aqueous medium. The physical and/or chemical changes in the structure of cellulose brought about by grafting are reflected in the affinity of the dye for cellulose. For a given dye, this affinity would essentially rely on sites prevalent for dye adsorption, i.e., the cellulose hydroxyls. A decrease in the latter hinders dye adsorption. It appears that at lower grafting, although the grafted polymer chains open up the structure of the cellulose, yet the pendent chains are efficiently packed. At higher grafting, however, the packing of the polymer and cellulose chains become progressively less efficient. Hence, the high dye affinity observed with substrates containing low polymer content could be interpreted in terms of opening up the cellulose structure while keeping most of the cellulose hydroxyls intact. At higher grafting, on the other hand, the presence of a great amount of hydrophobic polymer with little acceptability for the dye adversely affects the sites for dye adsorption and offsets the advantages gained by opening up the cellulose structure which might be in full swing at higher grafting.

A comparison between the dye affinity for PAN-cellulose graft copolymers (Fig. 1) and that for PMMA-cellulose graft copolymers (Fig. 2) revealed a common feature: the dye affinity decreased as the polymer content increased. However, the magnitude of dye affinity for the two copolymers differed appreciably, being much greater for PAN-cellulose graft copolymers

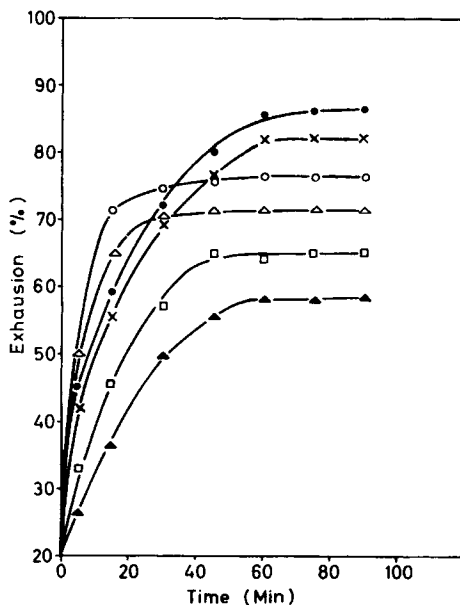


Fig. 2. Effect of grafting of cellulose with PMMA on dyeing with Solophenyl Red 6 BL at 70°C: (●) untreated cellulose; (X) oxidized cellulose; (○) 14% PMMA; (△) 43.5% PMMA; (□) 66.8% PMMA; (▲) 93.2% PMMA.

than for PMMA-cellulose graft copolymers. This difference could be associated with differences in the electronic nature of the substituents on the grafted polymer, molecular weight, and molecular weight distribution of the graft as well as frequency of the grafted chains.

Indeed, the rate of dye exhaustion obtained with a film made of PMMA homopolymer was much less than that for a film made of PAN homopolymer (Fig. 3). It may be argued that the homopolymers of PMMA and PAN are not identical with the corresponding grafted polymer chains, which are perhaps admixed molecularly throughout the cellulose matrix, but the data of Figure 3 clearly illustrate the difference. No stress was applied during grafting, and the grafted polymer most probably exists in an amorphous state, similar to that of the homopolymer.

Dye exhaustion curves for untreated cellulose and PAN-cellulose graft copolymer having a graft yield of ca. 73% are given in Figure 4. Dyeing was performed with three direct dyes, viz., Solophenyl Yellow FFL, Solophenyl Scarlet BNL, and Diphenylbrown MIN 200%. Here, too, the affinity of the dye for PAN-cellulose graft copolymer was much lower than that for untreated cellulose. Presence of grafted polymer decreased the dye affinity and exhaustion of the direct dyes, the decrease being very significant with dyes having relatively lower affinity for the untreated cellulose. Differences in dye affinity are probably associated with differences in steric configuration and molecular size of the dye.

Dyeing with Reactive Dyes

Dyeings of untreated cellulose and PAN-cellulose graft copolymers with two reactive dyes, viz., Remazole Golden Yellow G and Cibacron Blue 3 GA,

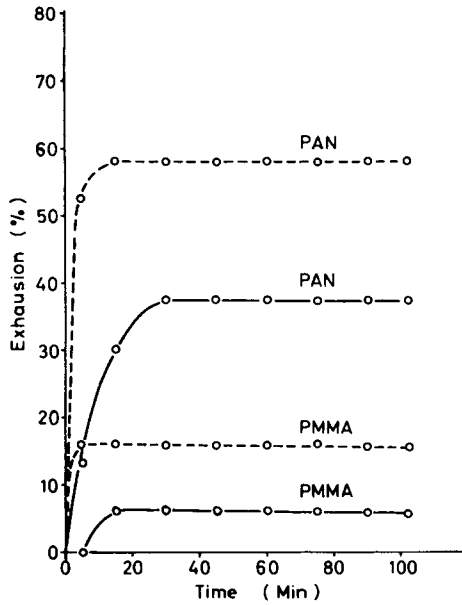


Fig. 3. Behavior of films made of PAN and PMMA homopolymers toward direct and reactive dyes: (—) Cibacron Blue 3 GA; (---) Solophenyl Red 6 BL.

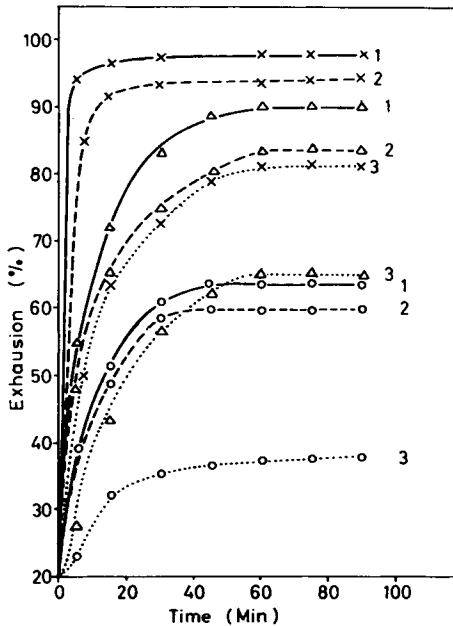


Fig. 4. Dyeing of PAN-cellulose graft copolymer with various direct dyes at 70°C: (1) untreated cellulose; (2) oxidized cellulose; (3) PAN-cellulose graft copolymer (73.2% PAN); (X) Solophenyl Yellow FFL; (Δ) Solophenyl Scarlet BNL; (O) Diphenylbrown MIN 200%.

were carried out under the conditions given for each in the experimental section (Fig. 5). Obviously, regardless of the graft yield, PAN-cellulose graft copolymers showed increased affinity for Cibacron Blue 3 GA in comparison with the untreated cellulose, although the increase became less as the graft yield increased (Fig. 5). A similar trend was observed with Remazole Golden

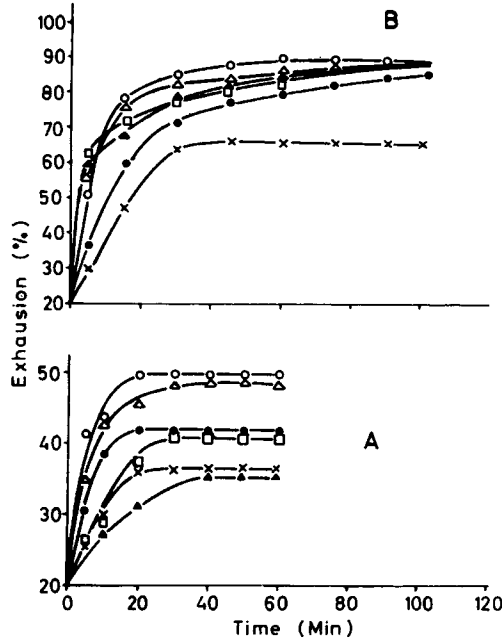


Fig. 5. Effect of grafting of cellulose with PAN on dyeing with reactive dyes: (A) Remazole Golden Yellow G; (b) Cibacron Blue 3 GA; (●) untreated cellulose; (X) oxidized cellulose; (○) 13.5% PAN; (△) 43.7% PAN; (□) 51.5% PAN; (▲) 73.2% PAN.

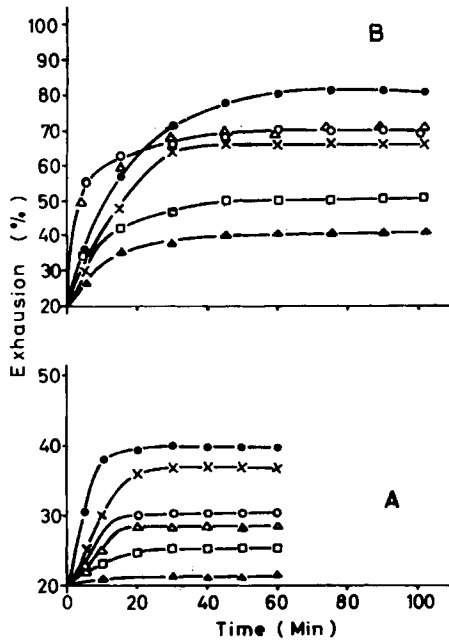


Fig. 6. Effect of grafting of cellulose with PMMA on dyeing with reactive dyes: (A) Remazole Golden Yellow G; (B) Cibacron Blue 3 GA; (●) untreated cellulose; (X) oxidized cellulose; (○) 14% PMMA; (△) 43.5% PMMA; (□) 66.8% PMMA; (▲) 93.2% PMMA.

Yellow G, but the exhaustion of this dye onto fibers containing relatively high polymer contents (ca. 51% and 73% PAN) was slower than that found with the untreated cellulose.

Figure 6 shows the exhaustion curves for cellulose modified with PMMA when these substrates were dyed with Cibacron Blue 3 GA and Remazole Golden Yellow G. Unlike PAN-cellulose graft copolymers, cellulose modified

TABLE II
Effect of Nature of Substrate on Dye Affinity of Some Reactive Dyes for Cellulose

Substrate	Dye ^a	Exhaustion after different time periods, %				
		5 min	15 min	30 min	40 min	105 min
Untreated cellulose	Cibacron brilliant Yellow 3 G-E	52.38	62.86	69.52	78.10	78.10
Ceric-oxidized cellulose		17.40	23.81	23.81	23.81	23.81
PAN-cellulose graft copolymer (13.5% graft)		22.52	36.40	42.70	49.74	49.76
PAN-cellulose graft copolymer (73.2% graft)		15.24	26.00	37.48	45.95	45.95
PAN-cellulose graft copolymer (66.8% graft)		25.08	35.29	40.59	40.76	40.76
Untreated cellulose	Cibacron Orange T3G-E	88.79	90.52	90.52	90.52	90.52
Ceric-oxidized cellulose		73.28	81.90	81.90	81.90	81.90
PAN-cellulose graft copolymer (13.5% graft)		79.24	83.76	90.70	90.70	90.70
PAN-cellulose graft copolymer (73.2% graft)		77.54	87.07	87.07	87.07	87.07
PAN-cellulose graft copolymer (66.8% graft)		75.59	79.31	79.31	79.31	79.31
Untreated cellulose	Cibacron Rubine R-E	92.38	96.19	96.19	96.19	96.19
Ceric-oxidized cellulose		83.03	88.39	91.07	91.07	91.07
PAN-cellulose graft copolymer (13.5% graft)		74.29	79.05	86.67	89.95	89.95
PAN-cellulose graft copolymer (73.2% graft)		60.85	75.07	76.07	77.78	77.78
PAN-cellulose graft copolymer (66.8% graft)		62.20	74.50	77.93	77.93	77.93

^a Dye concentration, 1% (on weight of fibers); temperature of dyeing, 70° C.

with PMMA had a lower tendency to accept both dyes in comparison with the untreated cellulose.

Table II lists the affinity of the three reactive dyes, viz., Cibacron Brilliant Yellow 3 G-E, Cibacron Orange T3G-E, and Cibacron Rubine R-E, for different substrates. It is evident that the maximum exhaustion of Cibacron Brilliant Yellow 3 G-E and Cibacron Orange T3G-E onto fibers was higher for PAN-cellulose graft copolymers than that of cellulose modified with PMMA. Comparable dye exhaustion was found when dyeing was performed with Cibacron Rubine R-E. This reflects the effect of the nature of the dye.

Based on the above findings (Figs. 5 and 6 and Table II), it is probably correct to say that the affinity of the reactive dyes for cellulose graft copolymers relies mainly on (a) the nature of the dye, (b) the extent of disruption in the microstructure of cellulose by grafting, being dependent upon the nature and amount of grafted polymer, and (c) the affinity of the dye for the grafted polymer. For a given dye, increasing the magnitude of functions (b) and (c) would lead to increased dye exhaustion onto fibers. However, the general trend is that increasing the amount of grafting causes substantial reduction in dye exhaustion onto fibers, particularly with dyes of relatively low affinity for cellulose. The large disruption in cellulose microstructure at high polymer

TABLE III
Fixation of Reactive Dyes on Different Substrates

Substrate	Cibacron Brilliant Yellow 3 GE ^a ; dye reacted with cellulose, %		Remazol Golden Yellow ^b dye reacted with cellulose, %	
	Based on wt of copolymer	Based on wt of cellulose only	Based on wt of copolymer	Based on wt of cellulose only
Untreated	---	0.86	---	0.48
Ceric-oxidized cellulose	---	0.78	---	0.39
PAN-cellulose graft copolymer (13.5% graft)	0.94	1.04	0.57	0.63
PAN-cellulose graft copolymer (43.7% graft)	1.04	1.72	0.52	0.86
PAN-cellulose graft copolymer (51.5% graft)	1.17	2.34	0.51	1.02
PAN-cellulose graft copolymer (73.2% graft)	0.76	2.78	0.31	1.11
PMMA-cellulose graft copolymer (14.0% graft)	1.04	1.16	0.47	0.52
PMMA-cellulose graft copolymer (66.8% graft)	0.42	1.47	0.31	0.88

^a Dye concentration, 1% (on wt of fibers); temperature of dyeing, 70°C; duration of dyeing, 105 min.

^b Dye concentration, 2% (on wt of fibers); temperature of dyeing, 60°C; duration of dyeing, 60 min.

contents seems to be outweighed by the low affinity of the dye for the grafted polymer. The dye acquires little affinity for PMMA, in contrast to PAN, for which the dye has considerable affinity (cf. Fig. 3). This would also explain the higher exhaustion onto cellulose modified with PAN than that found with cellulose modified with PMMA. In this regard, however, differences in molecular weight, molecular weight distribution, and grafting frequency between the two copolymers cannot be ruled out.

Dye fixation on untreated cellulose, PAN-cellulose graft copolymers, and PMMA-cellulose graft copolymers is shown in Table III. It is obvious that the dye fixation obtained with PAN-cellulose graft copolymers having up to 51% PAN was higher than that found with the untreated cellulose. The reverse is the case with a copolymer of ca. 73% PAN. However, when the dye fixation was calculated on the weight of cellulose component only, the fixation increased significantly as the graft yield increased. The same situation was encountered when the dye fixation on PMMA-cellulose graft copolymers was determined (Table III). This leads to the conclusion that the grafted chains disrupt the microstructure of cellulose and increase the accessibility of the cellulose hydroxyls to react with the dye molecules. For a given dye, the magnitude of this effect seems to rely on the amount and nature of the polymer grafted.

Dyeability of Oxidized Cellulose

Oxidation of cellulose with ceric ions prior to dyeing with direct or reactive dyes has a considerable effect on both the rate of exhaustion onto the oxidized cellulose and the affinity of the dye for cellulose during the duration of dyeing (Figs. 1, 2, 4, 5, and 6). Regardless of the type of the dye, ceric-oxidized cellulose showed lower affinity for the dye than the untreated cellulose, being dependent upon the nature of the dye. This implies that conversion of some cellulose hydroxyls to aldehydic and/or carboxyl groups brings about a reduction in adsorption of the dye on cellulose. Furthermore, these groups are known to be nonreactive with fiber-reactive dyes, and the extra carboxyl groups, though very little, lower the affinity of the dye for cellulose by enhancing the negative surface potential of cellulose. That is, the carboxyl groups ionize and repel the similarly charged dye anions.¹⁶⁻¹⁸ Indeed, with reactive dyes, the per cent dye fixation on oxidized cellulose was found to be lower than the untreated cellulose (Table III).

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