

Moisture Regain and Dyeability of Poly(acrylic Acid)- and Poly(styrene)-Carbamoylethylated Cotton Graft Copolymers Induced by Gamma Radiation

A. HEBEISH, *National Research Centre, Textile Research Division, Dokki, Cairo, Egypt*, A. H. ZAHRAN and A. M. K. EL-NAGGAR, *National Centre for Radiation Research and Technnology, Nasr City, Cairo, Egypt*, A. M. RABIE, *Ain Shams University, Faculty of Science, Chemistry Department, Cairo, Egypt*

Synopsis

Gamma radiation-induced graft copolymerization of either acrylic acid or styrene onto untreated cotton, alkali-treated cotton, and carbamoylethylated cottons having 0.392% N, 0.524% N, 0.725% N, 1.379% N, and 1.546% N was investigated under different conditions. Moisture regain and dyeability of these substrates before and after copolymerization were also examined. It was found that the graft yield increases by increasing monomer concentration and radiation dose irrespective of the monomer or substrate used. Using water-ethanol mixtures as polymerization media are advantageous for grafting of styrene. With both monomers, however, the graft yield for the modified cottons are substantially higher than untreated and alkali-treated cottons, indicating that the presence of carbamoylethyl in the molecular structure of cotton cellulose affords additional sites for graft copolymerization. Copolymers obtained using acrylic acid show much higher moisture regain than the ungrafted substrates, particularly when the carboxylic groups of the graft were in the sodium form. The opposite holds true for copolymers brought about by grafting with styrene. The color strength of all substrates dyed with a direct or a reactive dye decreases significantly after copolymerization with poly(acrylic acid) prior to dyeing. On the other hand, this copolymerization improves the affinity of the substrates for the basic dye and brings about perceptible shade. Copolymerization of the substrates in question with poly(styrene) improves the color strength of these substrates when dyed with direct, disperse, and basic dyes but decreases the color strength upon dyeing with a reactive dye.

INTRODUCTION

Vinyl graft polymerization onto cellulose and chemically modified celluloses using different physical as well as chemical means for initiation has been extensively studied and the subject reviewed elsewhere.¹ Studies dealing with graft polymerization of acrylonitrile onto carbamoylethylated cellulose using the ceric ion as initiator have disclosed that the graft yield obtained with this modified cellulose is substantially higher than that of the unmodified cellulose.²

The present work aims at studying (1) graft polymerization of acrylic acid and styrene onto carbamoylethylated cottons using gamma radiation and (2) moisture regain and dyeing properties of the cotton copolymers so obtained.

EXPERIMENTAL

Materials

Cotton Fabric

Mill-desized, scoured, bleached, and mercerized plain weave (31 picks and 36 ends/cm) supplied by El-Nasr Spinning, Weaving and Knitting Co. (Shourbagi) was used.

Carbamoylethylated Cotton

Carbamoylethylated cotton was prepared according to a method described by Frick et al.³ The fabric was treated with solution containing different concentrations of acrylamide and 5% sodium hydroxide as a catalyst. The treated fabrics, after being squeezed to a wet pickup of about 85%, was heated in an oven at 125°C for 6 min, then washed thoroughly with water and dried at ambient conditions.

Alkali-Treated Cotton

A control sample, namely, alkali-treated cotton, was prepared as described above but in the absence of acrylamide.

Dyestuffs

Four dyestuffs belonging to different classes were used. These dyes were a direct dye, Diamine Supra Turquoise Blue GL supplied by Cassela, Italy; a reactive dye, Remazol Brilliant Green CB (C.I. reactive green 14), supplied by Hoechst, West Germany; a basic dye, Sandocryl Orange B-3RLE (C.I. basic orange 39), supplied by Sandoz, Switzerland, and a disperse dye, Samaron Pink FRL (C.I. disperse 91), supplied by Hoechst, West Germany.

Graft Copolymerization Procedure

Copolymerization with Acrylic Acid

Samples of cotton and modified cottons were grafted with acrylic acid using the mutual irradiation technique; that is, the samples were immersed in the monomer solution and exposed to gamma radiation. Five concentrations of acrylic acid, 4, 8, 12, 16 and 20% in water, were prepared. The monomer solutions containing samples were irradiated to 0.5, 1.5, and 2 Mrad. Irradiation to the required radiation dose has been carried out in the cobalt-60 gamma source (3600 Ci) of the National Centre for Radiation Research and Technology. The untreated monomer was removed by washing with water. The samples were then extracted with boiling water to remove homopolymer followed by drying. Extraction and drying were repeated, until constant weight was achieved. The graft yield was expressed as milliequivalent -COOH groups per 100 g cellulose.

Copolymerization with Styrene

Samples of cotton and modified cottons were grafted with styrene under different conditions, including monomer concentration, radiation dose, and solvent composition. Three monomer concentrations, 5, 10, and 20% were used. Different methanol-water compositions (100% H₂O, 20:80 MeOH-H₂O, 60:40 MeOH-H₂O, and 100% MeOH) were employed. Samples immersed in the solvent-monomer mixtures were irradiated at 0.5 and 1.5 Mrad. The irradiated samples were first washed with water to remove the unreacted monomer, followed by air drying. The styrene homopolymer was removed by benzene extraction for 40 h. The graft yield was calculated as

$$\text{Graft yield\%} = \frac{\text{wt of grafted sample} - \text{wt of ungrafted sample}}{\text{wt of ungrafted sample}} \times 100$$

Dyeing Procedures*Dyeing with Basic Dye*

The dyeing process was carried out by pasting 4% of the dye with 1% acetic acid (based on the sample weight) and then dissolved in boiling water. The dissolved dye was added to the bath at 60°C, and the temperature was then raised slowly to the boil at the rate of 1°C per 3–4 min. The dyeing was continued for 60 min during which Glauber salt was added for complete exhaustion. The dye bath was cooled to 60°C, and then the samples were rinsed with cold water. The samples were then soaped with a solution containing 5 g/L Na₂CO₃ and 1 g/L detergent, washed with hot and cold water, and air dried.

Dyeing with Reactive Dye

The reactive dye (shade concentration, 4%) was first dissolved using boiling water. Samples were introduced into the bath (1:20) containing the salts (80 g/L Glauber's salt and 5 g/L Na₂CO₃) at 25°C for 10 min. The dissolved dye was then added to the bath. After 15 min the temperature was raised to 60°C over a period of 30 min. The dyeing was continued for 30 min, and then the alkali sodium hydroxide (1 ml/L of 32.5%) was added. Again, the dyeing was continued for 30 min. Samples were rinsed with cold water and acidified with 1 ml/L acetic acid (60%) at 40°C. The samples were then soaped with an aqueous solution containing wetting agent (0.25 g/L) for 10–15 min. Finally, the samples were rinsed with hot and cold water and air dried.

Dyeing with Direct Dye

The direct dye was pasted with cold water by the aid of a nonionic wetting agent (Hostapal, Hoechst), and sufficient boiling water was added with constant stirring to bring it into solution. The dissolved dye was added to the bath (1:30). The salt (sodium chloride, 20%, based on sample weight)

was then added to the bath. At this end, sample was introduced into the bath at 40°C. The bath was raised to the boil over a period of 30–40 min, and dyeing was continued for 45–60 min. The sample was then soaped with a solution containing 5 g/L sodium carbonate and 1 g/L detergent, washed thoroughly, and dried at ambient conditions.

Dyeing with Disperse Dye

The dye bath was prepared by addition of the disperse dye (shade concentration, 4%) to hot water, and the pH of the bath was adjusted at 4.5–5 with acetic acid. Samples were introduced into the bath (1:20) at 60°C and held for 10 min. The temperature of the bath was raised to dye temperature 90–100°C over a period of 40 min. The dye bath was cooled to 60°C, and then samples were rinsed with hot water followed by cold water. The samples were soaped and washed as mentioned above for the basic dye.

Testing and Analysis

The carboxyl content was estimated according to a reported method.⁴ The nitrogen content was estimated according to the Kjeldahl method. Moisture regain was determined by the vacuum desiccator method with sodium nitrite to give 65% relative humidity (RH) at $21 \pm 1^\circ\text{C}$.

The color strength of the dyed samples was measured according to a reported method.⁵ In this method, the reflectance measurements of the dyed samples were done on an automatic filter spectrophotometer. The relative color strength (expressed as K/S values) was determined by applying the Kubelka-Munk equation⁶:

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_0)^2}{2R_0} = AC$$

where R is the decimal fraction of the reflectance of the coloured samples, R_0 is the decimal fraction of the reflectance of the uncoloured fabric, K is the absorption coefficient, S is the scattering coefficient, C is the dye concentration, and A is a proportionality factor.

RESULTS AND DISCUSSION

Gamma ray-induced graft polymerization of acrylic acid and styrene onto carbamoylethylated cottons having different carbamoylethyl contents, expressed, as %N, was studied with a view of clarifying the effect of the introduction of the carbamoylethyl groups in the molecular structure of cotton cellulose on the susceptibility of the latter toward grafting. To achieve the goal, unmodified cotton (substrate I), alkali-treated cotton (substrate II), and carbamoylethylated cottons having 0.392, 0.524, 0.725, 1.379, and 1.546% nitrogen (substrates III, IV, V, VI, and VII, respectively) were graft polymerized with either acrylic acid or styrene using different monomer concentrations and radiation doses.

Copolymerization with Acrylic Acid

Carbamoylethyl Content

Table I shows the effect of the carbamoylethyl content of the modified cotton on the graft yield. The graft yield was determined analytically and is expressed as milliequivalent-COOH groups per 100 g cellulose. It is seen that, for a given radiation dose and monomer concentration, the graft yield increases substantially by increasing the carbamoylethyl content within the range studied. It is also seen that the graft yields for carbamoylethylated cottons are much higher than the corresponding yields obtained with unmodified cotton and alkali-treated cotton. The graft yields follow the order

Carbamoylethylated cottons > alkali-treated cotton

> unmodified cotton

It is understandable that the higher graft yield obtained with alkali-treated cottons compared with the unmodified cotton is due to increased accessibility of cotton by the alkali treatment under the conditions used. On the other hand, the superiority of carbamoylethylated cottons suggests that the presence of carbamoylethyl groups in the molecular structure of cotton cellulose affords additional sites for graft polymerization. It is logical that that presence of $-\text{CONH}_2$ favors the abstraction of hydrogen from the carbon atom next to the $-\text{CONH}_2$ group, as detailed elsewhere using the ceric ion method.² In accordance with this are also the results of radiation-induced graft polymerization onto cotton cellulose bearing cyanoethyl groups.⁷ The $-\text{CN}$ group, by virtue of its negative induction effect, has been reported to facilitate hydrogen transfer, thereby affording additional sites for grafting.

It is as well to note that irradiation of the seven substrates under investigation in the absence of acrylic acid causes enhancement in the carboxyl content (Table I). The carboxyl contents of carbamoylethylated cottons (substrates III through VII) are higher than those of alkali-treated cottons (substrate II) and untreated cotton (substrate I) when the original value of the carboxyl content of each substrate was subtracted from the corresponding value after irradiation. This is in accordance with previous reports,^{8,9} which ascribed the higher carboxyl content of alkali-treated cotton compared with the unmodified cotton to higher accessibility of the former and, therefore, higher susceptibility to radiation. In the case of the carbamoylethylated cottons, on the other hand, it is likely that, beside oxidation of the carbamoylethyl groups are converted to carboxyethyl groups under the influence of irradiation.⁸

Monomer Concentration

The effect of acrylic acid concentration on the graft yields obtained with unmodified, alkali-treated, and carbamoylethylated cottons is shown in Table I. It is obvious that, for a given radiation dose, increasing the monomer

TABLE I
Radiation-Induced Grafting of Acrylic Acid onto Unmodified Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Carbamylethylated Cottons (Substrates III-VII) Using Different Concentrations at Varying Radiation Doses*

Acrylic acid concentration (%)	Graft yield (milliequivalent — COOH per 100 g cellulose)																				
	Substrate I			Substrate II			Substrate III			Substrate IV			Substrate V			Substrate VI			Substrate VII		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
None	0.62	0.85	1.08	0.955	1.236	1.982	1.923	2.212	2.86	2.102	2.753	3.021	2.387	2.831	3.105	2.532	2.883	4.538	2.692	2.915	3.025
4	14.29	21.51	25.66	16.52	24.15	28.62	20.47	24.25	32.43	22.37	27.73	35.91	24.89	28.66	37.56	26.61	36.94	43.67	29.07	35.40	46.50
8	20.52	33.26	35.75	23.42	40.82	41.34	31.80	43.92	50.79	35.94	45.75	52.38	36.17	49.13	54.72	37.42	53.90	58.56	40.89	55.31	60.28
12	25.72	45.56	53.14	30.00	50.25	58.25	38.64	59.56	70.43	40.52	62.55	75.60	46.28	66.88	78.66	49.28	71.37	74.64	51.81	77.84	86.48
16	49.54	68.01	72.82	45.32	78.62	80.40	48.74	83.48	91.74	50.99	84.21	95.57	71.15	86.14	97.94	72.43	88.46	99.70	73.70	90.00	101.68
20	62.95	75.27	80.47	63.46	82.53	87.64	65.05	89.38	96.05	69.09	96.54	100.5	70.24	97.38	101.96	74.29	98.52	109.45	79.01	100.83	114.81

* substrate III, 0.392% N; Substrate IV, 0.524% N; substrate V, 0.725% N; substrate VI, 1.379% N; substrate VII, 1.546% N. (1) 0.5 Mrad, (2) 1.5 Mrad, and (3) 2 Mrad.

concentration is accompanied by a significant increase in the graft yield regardless of the substrate used. This may be interpreted in terms of the availability of monomer in excess to diffuse into the structure of the substrate and thus increase the chance to interact with the active sites on the substrate backbone.

Radiation Dosage

Table I shows the effect of radiation dose on the graft yields obtained with the seven substrates under investigation. As is evident, increasing the radiation dose from 0.5 to 2.0 Mrad brings about a substantial increment in the graft yield irrespective of the monomer concentration used. This could be associated with formation of larger number of active sites on the substrate backbone at higher radiation doses.

Based on the above, it is evident that the graft yields of unmodified cotton (substrate I), alkali-treated cotton (substrate II), and carbamoylethylated cottons (substrates III through VII) are dependent upon the acrylic acid concentration and radiation dose. However, carbamoylethylated cottons show higher graft yields than substrates I and II due to the presence of the carbamoylethyl groups, which seem to afford additional sites for grafting. Carbamoylethyl groups may also contribute in improving grafting of cotton through opening up the cellulose structure, thereby facilitating diffusion of the monomer inside the structure of cotton. This is substantiated by the finding that, although alkali treatment of cotton under conditions similar to those of carbamoylethylation enhances the susceptibility toward grafting through increased accessibility, the graft yields obtained with alkali-treated cotton (substrate II) are lower than their mates for carbamoylethylated cottons (substrates III through VII). Similar observations were reported for cyanoethylated cottons⁷ when used instead of carbamoylethylated cottons.

Moisture Regain and Dyeability of Poly(acrylic Acid)- Carbamoylethylated Cotton Graft Copolymers

Moisture Regain

Table II shows the moisture regain of unmodified cotton (substrate I), alkali-treated cotton (substrate II), and carbamoylethylated cottons having 0.392, 0.524, 0.725, 1.379, and 1.546% N (substrates III, IV, V, VI, and VII, respectively) before and after these substrates were copolymerized with poly(acrylic acid). It is observed that, before copolymerization, the moisture regain of the seven substrates varies substantially. Substrate II acquires higher moisture regain than substrate I by virtue of greater accessibility of the former than the latter. It is understandable that alkali treatment is accompanied by enhancement in the accessibility of cotton cellulose. A similar situation is encountered with carbamoylethylated cottons (substrates III through VII). Besides increasing accessibility of cotton under the influence of the alkaline environment of carbamoylethylation, introduction of carbamoylethyl groups in the molecular structure of cotton cellulose acts as spikes, preventing molecular association. As a result, the cellulose struc-

TABLE II
Moisture Regain of Graft Copolymers of Acrylic Acid and Unmodified Cotton (Substrate I, Alkali-Treated Cotton (Substrate II), and Carbamoylethylated Cottons (Substrates III-VII) at Different Graft Yields^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	MR	G	MR	G	MR	G	MR	G	MR	G	MR	G	MR
00.00	5.974 (7.51)	00.00	6.654 (7.831)	00.00	7.359 (9.399)	00.00	7.066 (10.580)	00.00	6.942 (7.931)	00.00	6.521 (10.61)	00.00	6.246 (9.029)
21.51	7.00 (7.51)	24.15	7.454 (7.831)	24.25	7.61 (9.399)	27.72	7.251 (10.580)	28.66	6.990 (7.931)	36.94	6.75 (10.61)	35.40	6.56 (9.029)
33.26	7.21 (7.941)	40.82	7.942 (8.845)	43.92	7.990 (9.421)	45.75	7.652 (9.521)	49.13	7.891 (9.730)	53.90	6.485 (10.051)	55.31	6.670 (10.13)
45.56	7.354 (8.763)	50.25	7.742 (9.231)	59.56	8.123 (9.531)	62.55	7.820 (9.237)	66.88	7.930 (9.995)	71.37	6.596 (11.559)	77.84	8.021 (11.266)
68.01	7.598 (8.887)	78.62	7.802 (9.321)	83.48	8.238 (9.732)	84.21	8.021 (10.231)	86.14	8.310 (11.341)	88.45	8.401 (12.423)	90.00	8.201 (12.266)
75.27	7.768 (9.033)	82.53	7.943 (9.301)	89.38	8.543 (10.141)	96.54	8.124 (12.434)	97.38	8.423 (10.487)	98.52	8.523 (13.488)	100.83	8.592 (11.750)

^a Substrate III, 0.392% N; substrate IV, 0.524% N; substrate V, 0.725% N; substrate VI, 1.379% N; substrate VII, 1.546% N; G, Graft yield milliequivalent -COOH per 100 g cellulose; MR, moisture regain%.

ture is held open and thus permits more moisture accommodation. It should be noted, however, that increasing carbamoylethyl groups tends to decrease the moisture regain by virtue of its hydrophobic nature. The moisture regain of carbamoylethylated cotton having the highest nitrogen content (substrate VII) is not only lower than substrate III with the lowest nitrogen content but also lower than alkali-treated cotton (substrate II).

Table II shows that the moisture regain values of substrates I through VII exhibit substantial improvement after copolymerization with poly(acrylic acid). Nevertheless, the magnitude of moisture regain depends upon the percentage of graft and its form, as well as the original nature of the substrate. The moisture regain increases by increasing the level of grafting within the range studied. Also, the sodium salt of the graft induces much higher moisture regain compared with its hydrogen form. This is observed irrespective of the substrate used. However, both effects, that is, the level of grafting and the form of the graft, are more pronounced with the carbamoylethylated cottons (substrates III through VII) than the unmodified and alkali-treated cottons (substrates I and II). Furthermore, the moisture regain is higher the higher the carbamoylethyl content of the modified cotton.

Enhancement in moisture regain by introducing poly(acrylic acid) in the molecular structure of cotton cellulose is a direct consequence of the hydrophilic environment created in the cellulose structure by the graft, particularly when the latter is in the sodium form. Attachment of the graft to the carbamoylethyl groups in case of the carbamoylethylated cottons (substrates III through VII) perhaps reduces the hydrophobic nature of these groups and helps establish more favorable resting places for water molecules. Indeed, at a roughly equal grafting level, the moisture regain tends to be higher the higher the carbamoylethyl content of the modified cotton.

Dyeing with Basic Dye

It is well known that cotton cellulose has no affinity for basic dyes because it contains no acidic groups required for reaction with the cationic groups of the basic dye. Table III shows the color strength, expressed as K/S , of the seven substrates in question before and after graft copolymerization with poly(acrylic acid) when these substrates were dyed under identical conditions with a basic dye, namely, Sandocryl Orange B-3RLE.

It is observed (Table III) that before graft copolymerization all the said substrates show no significant perceptible shade since the color strength is quite poor. Nevertheless, mention should be made of the higher color strength obtained with carbamoylethylated cottons (substrates III through VII) as compared with the ungrafted and alkali-treated cottons (substrates I and II). This could be ascribed to the presence of carboxyethyl groups formed via partial hydrolysis of the carbamoylethyl groups during preparation of the carbamoylethylated cottons. It is also likely that the latter acquire high affinity for the dye since the color strength is higher the higher the carbamoylethyl content of the modified cotton.

Graft copolymerization of substrates I through VII with poly(acrylic acid) not only improves their affinity for the dye in question but also brings about significant perceptible shade. As is evident (Table III), the magnitude of

TABLE III
 Behavior of Cotton and Carbamoylethylated Cottons Copolymerized with Poly(acrylic Acid) Toward Dyeing with Basic Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	0.125	00.00	0.175	00.00	0.328	00.00	0.403	00.00	0.502	00.00	0.527	00.00	0.552
14.29	1.195	16.52	1.250	20.47	1.443	22.37	1.465	24.89	1.883	26.61	2.210	29.07	2.25
20.52	1.582	23.42	2.000	31.80	2.67	35.95	2.80	36.16	2.62	37.42	2.83	40.89	3.16
25.72	2.123	30.00	2.55	30.64	3.13	40.52	3.25	46.28	3.421	49.28	3.640	51.81	3.56
44.54	3.44	45.32	3.38	48.74	3.44	50.99	3.56	71.15	3.770	72.40	4.00	73.70	4.31
62.95	3.50	63.46	3.52	65.05	3.64	69.09	3.91	70.24	3.91	74.29	4.15	79.07	4.36

^aSubstrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cotton having 0.392, 0.524, 0.725, 1.379, and 1.546% N, respectively. G, graft yield (milliequivalent -COOH group/100 g cellulose. Basic dye, sandocryl Orange B-3RLE; dye concentration, 4%; dyeing temperature, boiling; duration of dyeing, 60 min; liquor ratio, 1:30.

color strength is quite substantial regardless of the substrate used. Furthermore, the magnitude of grafting seems to be the essential factor that determines the value of color strength. This is expected, since the presence of the graft containing carboxylic groups in the structure of cotton cellulose would permit the latter to react with the dye via an ionic bond. Carbamoylethylatin of cotton prior to its copolymerization with poly(acrylic acid) seems to have a slight favorable effect on dyeing of the copolymers with the basic dye.

Dyeing with Reactive Dye

Table IV shows the color strength for a reactive dye, Remazol Brilliant Green CB, on unmodified cotton (substrate I), alkali-treated cotton (substrate II), and carbamoylethylated cottons (substrates III through VII) before and after these substrates were graft copolymerized with poly(acrylic acid). It is clear that all the substrates in question exhibit substantial color strength by virtue of the good affinity and reactivity of the dye for cotton.¹⁰ However, the color strengths of the seven substrates differ substantially. Based on the color strength obtained, the susceptibility of the seven substrates toward dyeing with the said dye follows the order

Substrate VII > substrate VI > substrate V >
substrate IV > substrate III > substrate II >
substrate I

The order implies that (1) the susceptibility of cotton toward the dye is enhanced by alkaline treatment, (2) this susceptibility is enhanced also by carbamoylethylation, and (3) the susceptibility is higher the higher the carbamoylethyl content of the modified cotton. Enhancement in color strength brought about by alkali treatment of cotton prior to dyeing could be interpreted in terms of greater accessibility of the alkali-treated cotton (substrate II) than the unmodified cotton (substrate I). On the other hand, the increment in color strength brought about by carbamoylethylatin could be associated with (1) opening up the cellulose structure by the presence of the carbamoylethyl groups, thus facilitating diffusion and adsorption of the dye, (2) increased accessibility of cotton cellulose under the influence of the alkaline carbamoylethylation medium during preparation of carbamoylethylated cotton, and (3) formation of $-\text{CONH}_2$ groups — with greater reactivity with the dye — in carbamoylethylated cotton via partial hydrolysis during its preparation and/or dyeing.¹¹

Table IV shows that when the seven substrates were copolymerized with poly(acrylic acid), their color strength decreases significantly but still persists in the above order. This could be attributed to ionization of the carboxylic groups of the graft during dyeing. Ionization results in substrates with negative surfaces that repel the similarly charged dye ions. However, this phenomenon is much less pronounced in the case of poly(acrylic acid)-carbamoylethylated cotton graft copolymers, particularly those having high carbamoylethyl contents.

TABLE IV
 Behavior of Cotton and Carbamoylethylated Cottons Copolymerized with Poly(acrylic Acid) Toward Dyeing with Reactive Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	1.298	00.00	2.120	00.00	2.30	00.00	2.24	00.00	2.56	00.00	2.85	00.00	3.19
25.66	1.344	28.62	1.58	32.43	1.781	35.91	1.767	37.56	1.929	43.67	2.509	46.50	2.10
53.14	0.759	58.25	0.954	70.43	1.046	75.60	1.060	78.66	1.220	74.63	1.960	86.48	1.600
80.47	0.664	87.64	0.756	96.05	0.880	100.50	1.046	101.96	1.000	109.45	1.588	114.81	1.129

^aSubstrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cotton having 0.992, 0.524, 0.725, 1.379, and 1.546% N, respectively. G, Graft yield, (milliequivalent - COOH groups per 100 g cellulose). Reactive dye, Remazol Brilliant Green CB; dye concentration, 4%; dyeing temperature, 60°C; duration of dyeing, 90 min; liquor ratio, 1:20.

Dyeing with Direct Dye

Table V shows the color strength of a direct dye, Diamine Supra Turquoise Blue GL obtained with unmodified cotton (substrate I), alkali-treated cotton (substrate II), and carbamoylethylated cottons (substrates III through VII) before and after copolymerization with poly(acrylic acid). It is evident that the color strength of the seven substrates before copolymerization varies considerably. The color strength for the unmodified cotton is much higher than that for the carbamoylethyl contents. Alkali-treated cotton, on the other hand, acquires a color strength very close to the strength of the unmodified cotton, indicating that increased accessibility of cotton by alkali treatment has practically no effect on dyeing with this particular dye.

Since the binding forces in dyeing with direct dyes are purely physical, with the certainty that the cellulose hydroxyls play a significant part,¹⁰ current data (Table V) suggests that the presence of carbamoylethyl groups along the cellulose chain molecules reduces the affinity of cellulose for the dye. Carbamoylethyl groups seem to reduce the physical forces holding the dye and the cellulose and impede intimate association of dye molecules with the fiber by virtue of the hydrophobic nature of these groups, thereby giving rise to lower color strength. In combination with this is the presence of carboxyethyl groups along with the carbamoylethyl groups, which are most probably formed via hydrolysis of the latter during preparation of carbamoylethylated cottons, as reported earlier.⁸ Ionization of these carboxyethyl groups brings about a negatively charged fiber surface that repels the similarly charged dye anion. It is the same reason that accounts for the significant decrement in color strength when the seven substrates were graft copolymerized with poly(acrylic acid). As is evident, the color strength decreases drastically by introducing a graft containing ionizable carboxylic groups in the molecular structure of cotton and modified cottons. As expected, the color strength decreases as the graft yield increases, although most of the decrement in color strength is caused by merely producing a relatively small amount of the graft in the molecular structure of the seven substrates in question.

Copolymerization with Styrene*Carbamoylethyl Content*

Table VI shows variations of the graft yield with the carbamoylethyl content of the modified cotton (substrates III through VII) when the latter were graft copolymerized with styrene. It is observed that, for a favorable set of polymerization conditions, for example, 20% styrene in methanol-water mixture at a ratio of 60:40 and a radiation dose of 1.5 Mrad, the graft yield increases by increasing the carbamoylethyl content within the range examined. The graft yields, for carbamoylethylated cottons are also higher than the corresponding yields obtained with unmodified and alkali-treated cotton. This is in accordance with the results obtained with graft copolymerization of acrylic acid discussed above and could be explained on a similar basis.

TABLE V
Behavior of Cotton and Carbamoylethylated Cottons Copolymerized with Poly(acrylic Acid) Toward Dyeing with Direct Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	1.305	00.00	1.120	00.00	0.956	00.00	0.920	00.00	0.782	00.00	0.664	00.00	0.500
21.51	0.932	24.15	0.921	24.25	0.705	27.73	0.684	28.66	0.555	36.94	0.332	35.40	0.317
33.26	0.710	40.82	0.752	43.92	0.540	45.75	0.486	49.13	0.422	53.90	0.275	55.31	0.264
45.56	0.633	50.25	0.673	59.56	0.465	62.55	0.445	66.88	0.380	71.37	0.283	77.84	0.259
68.01	0.550	78.62	0.512	83.48	0.401	84.21	0.378	86.14	0.334	88.46	0.258	90.00	0.247
75.27	0.461	82.53	0.500	89.38	0.391	96.54	0.336	97.38	0.328	98.52	0.240	100.83	0.237

^a Substrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cottons having 0.392, 0.524, 0.725, 1.379, and 1.546% N, respectively. G, Graft yield (milliequivalent -COOH groups per 100 g cellulose). Direct dye, Diamine Supra Turquoise Blue GL; dyeing temperature, boiling; dye concentration, 4%; duration of dyeing, 100 min; liquor ratio, 1:30.

TABLE VI
 Radiation-Induced Grafting of Styrene onto Unmodified Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Carbamoylethylated Cottons (Substrates III-VII) at Different Doses^a

Solvent composition (%)	Styrene concentration (%)	Graft yield (%)													
		Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
		1	2	1	2	1	2	1	2	1	2	1	2	1	2
100 (H ₂ O)	5	5.09	6.91	6.059	7.15	6.15	8.82	6.71	9.92	6.77	9.90	6.87	10.00	6.78	10.90
	10	7.72	8.79	9.32	10.54	10.52	13.42	10.86	14.98	10.94	18.35	11.32	20.62	11.46	21.58
20:80 (MeOH:H ₂ O)	5	7.11	7.65	8.29	9.38	9.35	11.34	9.63	12.28	9.74	12.83	9.63	12.92	9.47	13.13
	10	12.35	13.57	15.76	18.42	16.76	27.29	16.87	27.63	17.88	27.85	17.39	28.22	18.31	28.88
60:40 (MeOH:H ₂ O)	5	17.72	18.40	18.80	35.54	20.98	40.52	21.84	47.74	21.88	49.52	21.82	51.21	21.75	52.49
	10	18.15	19.02	21.68	24.11	26.67	37.33	27.74	40.07	28.52	41.59	30.27	43.26	30.34	45.87
100 (MeOH)	5	26.84	30.85	28.39	41.50	30.92	47.92	33.98	58.19	35.82	58.95	40.74	60.64	39.99	63.23
	10	0.35	2.06	0.54	2.98	0.92	37.0	1.23	5.20	1.33	6.52	1.59	9.81	2.34	10.92
	10	10.54	19.00	13.04	22.53	14.84	25.81	17.31	21.60	20.12	29.53	24.62	34.72	26.47	26.47
	20	32.68	43.79	43.13	54.95	45.68	58.32	46.26	51.86	48.95	51.08	50.45	63.29	51.55	64.37

^a Substrate III, 0.392% N; substrate IV, 0.524% N; substrate V, 0.725% N; substrate VI, 1.379% N; substrate VII, 1.546% N; (1) 0.5 Mrad; (2) 1.5 Mrad.

Monomer Concentration

Table VI depicts the effect of styrene concentration on the graft yield. As is evident, increasing the styrene concentration is accompanied by a significant enhancement in the graft yield irrespective of the substrate, polymerization medium, and radiation dose used. However, the nature of the substrate does affect the magnitude of grafting, as indicated above, and so also do the polymerization medium and radiation dose, as shown below.

The enhancement in graft yield by increasing styrene concentration could be interpreted in terms of gel effect brought about by the solubility of styrene in its own monomer as the styrene concentration increases.¹² The consequence of the gel effect is to hinder termination of the growing grafted chain radicals by coupling, thereby giving rise to increased grafting.

Radiation Dosage

Table VI shows the graft yield obtained when styrene was grafted onto substrates I through VII at two radiation doses 0.5 and 1.5 Mrad. It is clear that the graft yields at 1.5 Mrad are higher than those at 0.5 Mrad. This is observed regardless of the other factors studied that affect grafting, such as the polymerization medium, monomer concentration, and the nature of the substrate. However, such factors determine the magnitude of the graft yield at the two radiation doses examined by virtue of their influence on (1) introduction of free radicals in the structure backbone, (2) swellability of the substrate, (3) mixability of styrene in and its diffusion from the polymerization medium to fiber phase, (4) adsorption of styrene onto the substrate matrix-containing free radicals and/or available to their formation, (5) ability to promote the phenomenon of gel effect, and (6) rate of grafting vis-à-vis the rate of homopolymerization. This seems to account for the significant differences between the graft yields obtained upon using the two radiation doses in some cases and the smaller differences in other cases.

Polymerization Medium

Previous reports¹³ have dealt with the role of solvents in mutual irradiation grafting of vinyl monomers onto cellulose. It has been disclosed that the presence of solvent results in a substantial enhancement in the graft yield when compared with irradiation of cellulose and monomer alone.

Table VI shows the graft yields obtained with the seven substrates under investigation when they were grafted with styrene in water, methanol, or water-methanol mixtures. It is seen that, for a given radiation dose and monomer concentration, the graft yield obtained with a water-methanol mixture at a ratio of 80:20 is much higher than that obtained in the aqueous polymerization medium irrespective of the substrate used. Further improvement in the graft yield could be achieved upon using a water-methanol mixture at a ratio of 40:60. Using only methanol as the polymerization medium causes more significant enhancement in the graft yield provided that styrene is employed at a concentration of 20%. Below this concentra-

tion, the graft yields are lower than their corresponding yields for water/methanol mixtures.

The favorable effect of methanol on the graft yield has been explained earlier.^{7,13} Methanol seems to interact with both styrene and the activated cellulose, and as a result, the accessibility of activated sites to styrene increases. In other words, more free radicals are produced in methanol than in styrene, and the interaction of activated methanol with styrene may have increased the effectiveness of styrene. This situation seems to be valid at all styrene concentrations in water-methanol mixtures and only at the highest styrene concentration (20%) in 100% methanol. Using the latter along with lower concentrations of styrene seems to offset the effectiveness of styrene through abundance of methanol free radicals, which may participate in termination processes rather than activation processes.

Moisture Regain and Dyeability of Poly(Styrene)-Carbamoylethylated Cotton Graft Copolymers

Moisture Regain

Table VII shows variation of the moisture regain of substrates I through VII with the graft yields. It is seen that moisture regain decreases as the graft yield increases irrespective of the substrate used. However, at roughly equal graft yield of about 13% there is a tendency that the decrement in moisture regain by increasing the graft yield is less pronounced in the case of carbamoylethylated cottons than unmodified and alkali-treated cottons. This tendency could be associated with differences in nature among the substrates under investigation. Such differences would be reflected in molecular weight and molecular weight distribution of the graft, as well as frequency of grafting, which in turn affect the accessibility of cotton cellulose. At any event, however, the observed lower moisture regain could be associated with the hydrophobic environment brought by the presence of polystyrene graft in the structure of cotton cellulose.

Dyeing with Basic Dye

Table VIII shows the color strength, expressed as K/S , of substrates I through VII before and after copolymerization with poly(styrene) when they were dyed with a basic dye, Sandocryl Orange B-3RLE. Obviously, copolymerization with poly(styrene) makes the seven substrates amenable to dyeing with the basic dye since the copolymers exhibit substantial color strength. It is also seen that the color strength increases as the graft yield increases. This is observed regardless of the substrate used. The nature of the substrate seems to play no significant role because at roughly equal graft yield the color strength values of cotton (substrate I), alkali-treated cotton (substrate II), and carbamoylethylated cottons (substrates III through VII) after subtracting the corresponding color strength values before copolymerization are very comparable. Hence, the ability to dyeing is solely due to the presence of the poly(styrene) graft.

TABLE VII
Moisture Regain of Graft Copolymers of Styrene and Unmodified Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Carbamoylethylated Cottons (Substrates III-VII) at Different Graft Yields^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	MR	G	MR	G	MR	G	MR	G	MR	G	MR	G	MR
00.00	5.975	00.00	6.245	00.00	7.359	00.00	7.066	00.00	6.942	00.00	6.521	00.00	6.246
7.65	5.033	9.38	5.627	11.34	6.090	12.28	6.283	12.83	6.313	12.92	5.908	13.13	6.017
13.57	4.435	18.42	5.134	27.29	4.738	27.63	4.916	27.85	4.800	28.22	4.866	28.88	5.202
18.40	4.408	35.54	4.549	40.52	3.825	47.74	3.937	49.52	3.827	51.21	3.739	52.49	3.788

^aSubstrate III, 0.392% N; substrate IV, 0.524% N; substrate V, 0.725% N; substrate VI, 1.379% N; substrate VII, 1.546% N. G, Graft yield (%), MR, % moisture regain.

TABLE VIII
Behavior of Cotton and Carbamoylethylated Cottons Copolymerized with Poly(styrene) Towards Dyeing with Basic Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	0.125	00.00	0.205	00.00	0.518	00.00	0.543	00.00	0.618	00.00	0.763	00.00	0.799
8.51	2.22	12.71	2.35	15.20	2.67	15.76	2.77	17.23	3.13	19.34	3.190	20.93	3.210
18.15	2.59	21.68	2.65	26.67	3.37	27.74	2.72	28.52	3.30	30.27	3.300	30.34	3.464
26.84	3.44	28.39	3.49	30.92	3.56	33.98	3.56	35.82	3.77	40.74	3.81	39.99	3.990

^a Substrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cotton having 0.392% N, 0.524% N, 0.725% N, 1.379% N, and 1.546% N, respectively. G, % Graft yield. Basic dye, Sandocryl Orange B-3RLE; dye concentration, 4%; dyeing temperature, boiling; duration of dyeing, 60 min; liquor ratio, 1:30.

TABLE IX
Behavior of Cotton and Carbamoylethylated Cottons Copolymerized with Poly(styrene) Toward Dyeing with Disperse Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	0.380	00.00	0.392	00.00	0.389	00.00	0.342	00.00	0.373	00.00	0.391	00.00	0.399
8.51	1.713	12.71	1.754	15.20	1.802	15.76	1.838	17.23	2.01	19.34	2.13	20.93	2.22
18.15	1.750	21.68	1.832	26.67	1.929	27.74	2.04	28.52	2.17	30.27	2.26	30.34	2.35
26.84	2.34	28.39	2.39	30.92	2.38	33.98	2.39	35.82	2.39	40.74	2.40	39.99	2.43

^aSubstrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cotton having 0.392% N, 0.524% N, 0.725% N, 1.379% N, and 1.546% N, respectively. G, % Graft yield. Disperse dye, Samaron Pink FRL; dye concentration, 4%; dyeing temperature, 90-100°C; duration of dyeing, 90 min; liquor ratio, 1:20.

TABLE X
Behavior of Cotton and Carbamoylethylated Cotton Copolymerized with Poly(styrene) Toward Dyeing with Reactive Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	1.298	00.00	2.132	00.00	2.64	00.00	2.64	00.00	2.56	00.00	2.85	00.00	3.23
7.11	1.112	8.29	1.900	9.35	1.913	9.63	1.929	9.74	2.04	9.63	2.54	9.47	2.86
12.35	1.100	15.76	1.751	16.76	1.809	16.87	1.781	17.88	1.55	17.39	2.39	18.31	2.66
17.72	1.074	18.80	1.521	20.98	1.624	21.84	1.809	21.88	1.565	21.82	1.883	21.75	2.59

^aSubstrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cottons having 0.392% N, 0.524% N, 0.725% N, 1.379% N, and 1.546% N, respectively. G, % Graft yield. Reactive dye, Remazol Brilliant Green CB, dye concentration, 4%; dyeing temperature, 60°C; duration of dyeing, 90 min; liquor ratio, 1:20.

TABLE XI
Behavior of Cotton and Carbamoylethylated Cotton Copolymerized with Poly(styrene) Toward Dyeing with Direct Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI		Substrate VII	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
00.00	1.305	00.00	1.138	00.00	1.262	00.00	1.187	00.00	1.001	00.00	0.944	00.00	0.848
7.11	1.929	8.29	1.792	9.35	2.37	9.63	2.22	9.74	1.945	9.63	2.39	9.47	2.34
12.35	1.913	15.76	1.990	16.76	2.28	16.87	2.28	17.88	2.80	17.39	2.50	18.31	2.640
17.72	1.600	18.80	1.80	20.98	2.11	21.84	2.11	21.88	2.44	21.82	2.47	21.75	2.62

^a Substrate I, unmodified cotton; substrate II, alkali-treated cotton; substrates III-VII, carbamoylethylated cottons having 0.392% N, 0.524% N, 0.725% N, 1.379% N, and 1.546% N, respectively. G, % Graft yield. Direct dye, Diamine Supra Turquoise Blue GL; dye concentration, 4%; dyeing temperature, boiling; duration of dyeing, 100 min; liquor ratio, 1:30.

Dyeing with Disperse Dye

Table IX shows the color strength obtained with unmodified cotton, alkali-treated cotton, and carbamoylethylated cottons before and after copolymerization with poly(styrene) when these substrates were dyed with a disperse dye, Samaron Pink FRL. It is observed that, before graft copolymerization with poly(styrene), none of the substrates used acquires practically acceptable color strength. This is rather expected since cotton has no affinity for disperse dyes. On the other hand, all the substrates show substantial color strength after graft copolymerization with poly(styrene). Furthermore, the color strength is higher the higher the graft yield. An indication of this is that the presence of the poly(styrene) graft in the molecular structure of cotton and carbamoylethylated cottons induces certain affinity for the disperse dye.

Dyeing with Reactive Dye

Table X shows the color strengths obtained with unmodified cotton, alkali-treated cotton, and carbamoylethylated cottons when they were dyed with a reactive dye, Remazol Brilliant Green CB. As is evident, copolymerization of unmodified and alkali-treated cottons with poly(styrene) is accompanied by a decrement in color strength. The same holds true for carbamoylethylated cottons. Nevertheless, the decrement in color strength brought about by the copolymerization of the carbamoylethylated cottons is more significant than that of unmodified and alkali-treated cottons, reflecting the effect of original nature of the substrate in determining the characteristics of its copolymer. At any event, however, the decrement in color strength brought about by introducing poly(styrene) in the molecular structure of the substrate is a direct consequence of blocking some of the cellulose hydroxyls (reactive centers for the dye), as well as the creation of a hydrophobic environment unfavorable for dye affinity.

Dyeing with Direct Dye

Table XI shows the effect of the introduction of poly(styrene) in the molecular structure of the seven substrates in question on their dyeability with a direct dye, Diamine Supra Turquoise Blue GL. Data of the color strength signify that the latter increases by increasing the graft yield up to a certain limit, then tends to decrease by further increasing the magnitude of grafting. Nevertheless, within the range studied, the graft copolymers acquire higher color strengths than their corresponding substrates before copolymerization, indicating that the presence of poly(styrene) in the molecular structures of the substrates under investigation enhances their dyeability with the direct dye. Enhancement in dyeability could be interpreted in terms of molecular disruption by the graft since there is no reason to believe that these copolymers possess a higher affinity for the dye. Once

this disruption occurred, more resting places for dye molecules and/or aggregates could be created in the interior of the fiber.

References

1. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, (1981).
2. Kantouch, A. Hebeish, and M. H. El-Rafie, *J. Appl. Polym. Sci.*, **15**, 1924 (1971).
3. J. W. Frick, W. A. Reeves, and J. D. Guthrie, *Text. Res. J.*, **27**, 294 (1957).
4. O. Samuelson and A. Wennerblalu, *Sevensh. Paepperstidn.*, **58**, 713 (1955).
5. D. B. Judd and G. Wyszecski, *Colour in Business, Science and Industry*, 3rd Ed., John Wiley & Sons, New York, (1975).
6. P. Kubelka and F. Munk, *Z. Technol. Phys.*, **12**, 593 (1931).
7. A. Hebeish, A. H. Zahran, A. M. Rabie, and A. M. K. El-Nagggar, *Angew. Makromol. Chem.*, (accepted for publication)
8. A. Hebeish, A. H. Zahran, and A. M. K. El-Nagggar, *Angew. Makromol. Chem.*, (sent for publication).
9. A. Hebeish, A. H. Zahran, and A. M. K. El-Nagggar, *J. Appl. Polym. Sci.*, (accepted for publication).
10. E. R. Trotman, *Dyeing and Chemical Technology of Textile Fibres*, Charles Griffin & Company, London, 1975, p. 489.
11. M. Kamel, A. Hebeish, and A. Z. Moursi, *J. Soc. Dyers Col.*, **90**, 352 (1974).
12. J. T. Guthrie, M. B. Huglin, and G. O. Phillips, *J. Appl. Polym. Sci.*, **16**, 1017 (1972).
13. S. Dilli, J. L. Garnett, E. C. Mortin, and D. H. Phuoc, *J. Polym. Sci., C*, **37**, 57 (1972).

Received May 6, 1985

Accepted July 6, 1985