

# Preparation of DEAE Cotton-g-Poly(methacrylic acid) for Use as Ion Exchanger

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**ABSTRACT:** Diethylaminoethyl (DEAE) cottons having different % *N* were prepared by reacting cotton cellulose in the fabric form with diethylamine hydrochloride at different concentrations in the presence of sodium hydroxide. The modified samples so obtained were subjected to the graft polymerization reaction using methacrylic acid (MAA) as the vinyl monomer and potassium permanganate–citric acid system as the initiator. The percentage of grafting (PG) was found to increase by increasing the % *N*, indicating that the presence of the DEAE groups in the molecular structure of the cellulose enhances the susceptibility of the latter to grafting. DEAE groups seem to act as additional sites for grafting; and/or, by virtue of their basicity, they interact with the citric acid, thereby creating primary free radicals in the vicinity of the cellulose. As a result, grafting increases, increasing the initiator and monomer concentration, as well as the polymerization time and temperature functions in favor of the PG. It was also disclosed that DEAE cotton-g-poly (methacrylic acid) serves as cationic and anionic ion exchanger by virtue of the presence of both DEAE and carboxylic groups. This was evidenced by the results of a detailed investigation on the ability of the exchanger to adsorb direct and basic dyes as well as  $\text{Cu}^{2+}$  ions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 739–745, 1998

## INTRODUCTION

During the last 25 years, we have paid much attention to studying the graft polymerization reactions involving cellulose, vinyl monomer, and initiator. Grafting of various vinyl monomers onto different cellulosic materials using over 20 initiators have been extensively studied, and the subject has been reviewed.<sup>1,2</sup> Of particular interest are the results obtained with the chemically modified celluloses brought about by etherification, esterification, crosslinking, and oxidation.

Behavior of chemically modified celluloses towards grafting have been shown to depend upon the influence of newly or introduced groups on

properties of cellulose. Among these are (1) variation in the physical structure (perhaps the cellulose is held in an open state), (2) swelling of cellulose, (3) availability and accessibility of the cellulose hydroxyls to reaction, (4) reactivity of cellulose hydroxyls in the presence of newly created or introduced groups, (5) specific localization of the newly created or introduced groups on the anhydroglucose unit of cellulose, (6) the type of the reaction between the cellulose and initiator (whether specific or nonspecific), (7) reactivity of the introduced groups with the initiator, and (8) affinity of the monomer to modified cellulose.

In general, if the introduced groups increase the magnitude of (1), (2), (3), and (4), or if they act as additional sites for grafting (that is, *g*), grafting would be greatly enhanced. Among the modified cotton celluloses that constitute examples of this were partially carboxymethylated cot-

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ton,<sup>3</sup> cyanoethylated cotton,<sup>4</sup> carbamoylethylated cotton,<sup>5</sup> and cellulose carbamate.<sup>6,7</sup> Conversely, lower grafting would occur if the introduced groups adversely affect the reactivity of cellulose hydroxyls. The same situation would be encountered if the groups of the chemically modified cellulose take place at the same carbon atom in the anhydroglucose unit of cellulose, the hydroxyl groups of which are liable to react specifically with the initiator. These were exemplified by grafting on acetylated cellulose,<sup>8</sup> crosslinked cellulose,<sup>9</sup> as well as acrylamidomethylated cellulose, and its reaction product with mercaptoethanol or hydrogen sulphide.<sup>10</sup>

The present work is regarded as a continuity of the aforementioned previous efforts. It is concerned with synthesis of copolymeric products via grafting of diethylaminoethylated (DEAE) cotton with methacrylic acid (MAA) using potassium permanganate–citric acid system. Percentage of grafting (PG) is studied as a function of the parameters that influence grafting. Feasibility of the DEAE cotton-*g*-poly(MAA) to serve as ion exchanger is examined. This is done through monitoring of dye adsorption on the copolymeric products as a function of the nature and concentration of the dye as well as the temperature and duration of dyeing. Ability of the copolymers to remove metal ions from their solutions is also studied.

## EXPERIMENTAL

### Materials

Mill desized, scoured, and bleached cotton fabric (poplin) was supplied by Misr Company for Spinning and Weaving, Mehalla El Kubra, Egypt. The fabric was purified in the laboratory by scouring at 100°C for 60 min using solution containing Na<sub>2</sub>CO<sub>3</sub> (2 g L). It was then thoroughly washed with water and dried at ambient conditions.

### Chemicals

B-Chloroethyldiethylamine hydrochloride, sodium hydroxide, methacrylic acid potassium permanganate, citric acid, and copper sulphate were of laboratory-grade chemicals.

Dyes used included direct dye, Solophenyl Orange TGL, and basic dye, Maxilon Blue TL. These dyes were kindly supplied by Ciba Giegy, Switzerland.

### Preparation of DEAE Cotton

Diethylaminoethyl (DEAE) cotton was prepared according to reported modification of Hartman Process.<sup>11</sup> The fabric was padded twice to approximately 100% wet pick-up with aqueous solution of B-chloroethyldiethylamine hydrochloride and dried at 60°C for 10 min. The fabric was then immersed in 8% sodium hydroxide solution for 10 min at 95°C, washed in dilute acetic acid, and then washed under tap water, followed by drying at ambient conditions.

### Preparation of Alkali-Treated Cotton

The fabric is immersed in 8% aqueous sodium hydroxide at 95°C for 10 min. The excess alkali is removed by washing the fabric with dilute acetic acid and then under tap water, followed by drying as above.

### Grafting Process

#### *Treatment with Potassium Permanganate*

Unless otherwise indicated, grafting of cotton, alkali-treated cotton, and DEAE cotton was carried out as per the following procedure. The sample was treated with a solution containing KMnO<sub>4</sub> (0.08%) at 50°C for 30 min using a material-to-liquor ratio of 1 : 50 with continuous shaking to avoid the heterogeneity of MnO<sub>2</sub> deposition on the fabric surface. After this treatment, the fabric was thoroughly washed with water and squeezed between two filter papers, then immersed in the polymerization solution.

#### *Graft Polymerization*

The so-obtained KMnO<sub>4</sub>-treated sample was introduced in 100-mL stoppered conical flask containing an aqueous solution of MAA at a concentration of 100%, based on fabric weight, and 0.5 mmol L<sup>-1</sup> citric acid. Polymerization was allowed to proceed at 70°C for 60 min. At the end of the reaction, the sample was removed, thoroughly washed several times with cold and boiled water, and dried at 105°C for 180 min.<sup>12</sup>

## TESTING AND ANALYSIS

1. The nitrogen content of treated cotton samples was determined according to Kjeldahl method.<sup>13</sup>

**Table I** Dependence of the Percentage of Grafting (PG) on the Nature of the Cotton Substrate<sup>a</sup>

Sample	<i>N</i> (%)	PG	Moisture Regain (%)
Untreated fabric	—	5.41	4.12
Alkali-treated	—	14.63	5.92
DEAE cotton	0.109	23.72	6.06
DEAE cotton	0.211	25.61	6.21
DEAE cotton	0.430	29.81	6.12

<sup>a</sup> Conditions of grafting are as follows. [KMnO<sub>4</sub>]: 0.08%; [citric acid], 0.5 mmol/L<sup>-1</sup>. [MAA]: 200% based on weight of substrate. Material-to-liquor ratio, 1 : 50; temp, 50°C; time, 30 min.

- The percentage of grafting (PG) was calculated as follows:

$$PG = \frac{W_1 - W_0}{W_0} \times 100$$

where  $W_1$  is the dry weight of the grafted sample, and  $W_0$  is dry weight of the ungrafted sample.

- Determination of moisture regain was done as follows. The samples were conditioned at 65% relative humidity, at 30°C, and weighed. They were oven-dried at 105°C for 4 h and weighed again, in which

Moisture Regain %

$$= \frac{\text{Weight of conditioned sample} - \text{Weight of dry sample}}{\text{Weight of dry sample}} \times 100$$

- Evaluation of ion exchange as a dye absorbant was carried out using photoelectric colorimeter model 528.
- Cu<sup>2+</sup> was determined using the Perkin-Elmer 1100 B atomic adsorption spectrophotometer.<sup>14</sup>

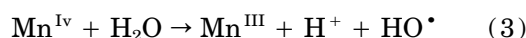
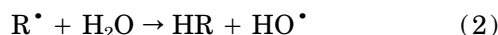
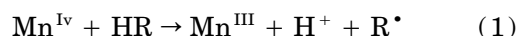
## RESULTS AND DISCUSSION

### Tentative Mechanism

Untreated cotton fabric, alkali-treated cotton, and DEAE cotton having different degrees of aminization, expressed as % *N*, were graft-polymerized with MAA, as described in the Experimental Sec-

tion. Results of the percentage of grafting obtained with these five substrates are set out in Table I. It is seen that the PG exhibits almost a threefold increase by treating the cotton fabric with alkali prior to grafting. A sixfold increase in PG is observed with DEAE cotton having 0.43% *N*. Lower than the latter value renders the modified cotton samples less susceptible to grafting. It is certain, however, that DEAE cottons acquire higher PG values than the untreated and alkali-treated cotton, irrespective of the % *N* of DEAE cotton.

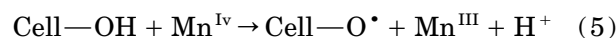
According to previous report,<sup>15</sup> creation of primary free radicals in the permanganate–citric acid (HR) system occurs presumably as follows:



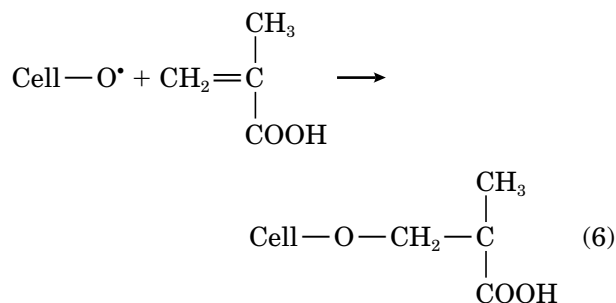
These free radical species attack the cellulose molecule (Cell—OH) and results in cellulose macroradical via abstraction of hydrogen atom, as exemplified by the reaction suggested by eq. (4), as follows:



The cellulose macroradical may also be formed via direct attack of Mn<sup>IV</sup>, as shown by eq. (5), as follows:

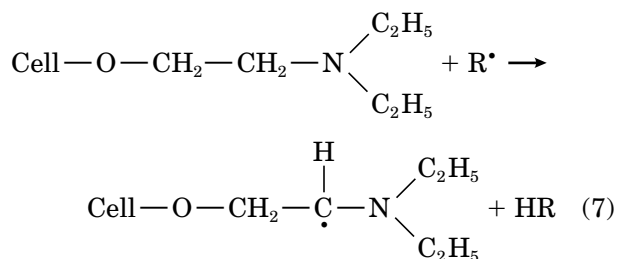


Addition of the cellulose radical to the double bond of MAA initiates grafting through the formation of a chemical bond between the cellulose and MAA molecule with creation of free radical on the latter as, suggested by eq. (6), as follows:



This is followed by the subsequent addition of MAA molecules, thereby propagating the grafted chain, which will be terminated by combination, disproportionation, or other means.

The threefold increase in the PG by treatment of cotton with alkali prior to grafting suggests that cotton undergoes physical changes that act in favor of grafting. Most probably, cotton is rendered more accessible; and therefore, more cellulose hydroxyls will be available for the reaction. Enhanced accessibility facilitates diffusion and adsorption of monomer and initiator, thereby providing a better environment for grafting to proceed. The same holds true for modified cotton with the additional effect of the DEAE groups. Introduction of these groups in the molecular structure of cotton cellulose in the presence of alkali holds the structure open, as evidenced by the higher moisture regain. This, in combination with increased accessibility, would make the DEAE cotton a better candidate for grafting but cannot account for the as high as sixfold increase in the PG observed with DEAE cotton. Grafting seems to be affected by the presence of DEAE groups as a chemical moiety. It is likely that these groups act as additional sites for grafting as shown by eq. (7), as follows:



It is also possible that the citric acid molecule is attached to the DEAE groups by virtue of basicity of the latter; and, in so doing, favors formation of free radicals in the proximity of the cellulose, thereby promoting grafting over homopolymerization.

### Initiator Concentration

Table II shows the effect of concentration of  $\text{KMnO}_4$  on the PG, keeping the citric acid concentration constant. DEAE cotton having 0.43% *N* was used as the substrate. It is evident that the PG increases significantly by increasing the  $\text{KMnO}_4$  concentration up to 0.08%. Above this concentration, no practical increase in PG is ob-

**Table II** Effect of Concentration of Potassium Permanganate-Citric Acid on the Percentage of Grafting of DEAE Cotton Having 0.43% *N*

( $\text{KMnO}_4$ ) (%)	PG	(Citric acid) $\text{mmol L}^{-1}$	PG
0.02	11.20	0.1	11.8
0.04	18.35	0.3	21.0
0.06	21.32	0.6	30.1
0.08	38.00	1.0	38.1
0.10	38.10	1.3	43.9
0.12	37.02	1.6	39.0

[Citric acid]: 1  $\text{mmol L}^{-1}$ . [ $\text{KMnO}_4$ ]: 0.08%. Temp: 50°C. Time: 30 min. Conditions for grafting are as follows. [MAA]: 200% based on the weight of the sample. Material-to-liquor ratio: 1 : 50. Temp: 70°C. Time: 60 min.

served. The favorable effect of the  $\text{KMnO}_4$  concentration on PG is a manifestation of the  $\text{Mn}^{\text{IV}}$  contribution in the reaction suggested by eqs. (1), (3), and (5). This contribution is expected to be higher at a higher  $\text{KMnO}_4$  concentration. Nevertheless, the observation that the PG almost levels off after a certain  $\text{KMnO}_4$  concentration, within the range studied, calls for the participation of  $\text{Mn}^{\text{IV}}$  and/or the free radicals created thereof in the termination process.

Table II shows the dependence of PG for DEAE cotton having 0.43% *N* on the citric acid concentration when the  $\text{KMnO}_4$  concentration was kept constant. It is seen that the PG exhibits higher values at higher citric acid concentrations up to 1.3 m mol; that is, PG increases significantly by increasing citric acid concentration to attain a value of 43.9% at a concentration of 1.3%  $\text{mmol L}^{-1}$ . Thereafter, the PG decreases, as evidenced by PG of 39% at a citric acid concentration of 1.6%. This is almost the trend observed with  $\text{KMnO}_4$  concentration and could be explained on a similar basis. Contribution of citric acid in graft initiation seems to prevail over its contribution in the termination process up to a certain concentration, beyond which the reverse is the case. However, the possibility of enhanced contribution of the  $\text{KMnO}_4$ -citric acid system upon using higher concentration of either or both components in producing higher amounts of homopolymer formation cannot be ruled out. It is understandable that grafting and homopolymerization are two competitive reactions that occur simultaneously.

### Monomer Concentration

The effect of the MAA concentration on the PG of DEAE cotton having 0.43% is shown in Table III.

**Table III Dependence of the Percentage of Grafting (PG) on MAA Concentration**

[MAA] Based on Weight of Sample	50	100	150	200	250	300
PG	18.2	27.3	30.4	38.0	50.6	58.8

[KMnO<sub>4</sub>]: 0.08%. [Citric acid]: 1 mmol L<sup>-1</sup>. Material-to-liquor ratio, 1 : 50. Temp, 70°C. Time, 60 min.

It is clear that increasing the MAA concentration is accompanied by a significant enhancement in the PG within the range studied. Greater availability of MAA molecules in the vicinity of the DEAE cotton substrate at higher monomer concentrations would account for this. The substrate macroradicals are immobile, and their reaction with MAA molecules would rely on the presence of the latter in their proximity. It is also possible to interpret this enhancement in PG in terms of gel effect. The latter creates a viscous environment through dissolution of poly(MAA) in its own monomer and, in so doing, impedes termination of the graft. As a result, the molecular weight of the graft and, therefore, the PG, increases.

#### Time of Polymerization

Table IV shows the effect of polymerization time on the extent and rate of grafting of DEAE cotton having 0.43% *N* with MAA. Obviously, grafting proceeds initially fast then almost levels off after 60 min. The PG exhibits a value of 38% after 60 min. This is against a value of 41.1% after 120 min, a point which calls for depletion in monomer and initiator concentration as the reaction pro-

**Table IV Effect of Time and Temperature of the Copolymerization on the Percentage of Grafting (PG) of DEAE Cotton**

Time <sup>a</sup> (min)	PG	Temp <sup>b</sup> (°C)	PG
15	12.53	40	25.32
30	22.44	50	28.51
60	38.08	60	28.74
90	40.93	70	41.02
120	41.15	80	41.91

<sup>a</sup> Temperature: 70°C.

<sup>b</sup> Time: 60 min.

Other parameters of grafting are as follows. [MAA]: 200% based on the weight of the sample. [KMnO<sub>4</sub>]: 0.08%. [Citric acid], 1 mmol L<sup>-1</sup>. Material-to-liquor ratio, 1 : 50.

ceeds. In combination with this are the shortage of grafting sites on the DEAE cotton backbone, giving more opportunity for homopolymerization.

#### Effect of Polymerization Temperature

The effect of temperature of polymerization on the PG of DEAE cotton (0.43% *N*) is shown in Table IV. The results indicate that the enhancement in PG upon raising the polymerization temperature from 40 to 60°C is not that striking. On the other hand, considerable increase in PG could be achieved by raising the temperature further to 80°C. This state of affairs could be associated with the effect of temperature on factors that function in favor of grafting such as swellability of DEAE cotton, diffusion of monomer and initiator, formation of primary free radicals and substrate macroradical, initiation and propagation of the graft, etc.

#### Ionic Exchange Properties of DEAE Cotton-g-Poly(MAA)

The presence of DEAE groups along with the poly(MAA) graft in the modified cotton under investi-

**Table V Variation of Direct Dye Adsorption on DEAE Cotton-g-Poly(MAA) with Time and Temperature of the Dye Treatment**

PG	Direct Dye Adsorption (mg per L gS)			
	1 h	2 h	3 h	4 h
Control	—	0.12	0.15	(0.10)
10	92	98.00	103.00	(94.00)
20	95	107.00	110.00	(99.00)
30	99	110.00	114.00	(103.00)
40	108	113.00	115.00	(110.00)
50	111	116.00	120.00	(113.00)
60	114	121.00	123.00	(118.00)

Conditions used are as follows: [Dyes], 200 mg L; Temp, 90°C; pH, 4. Values in parentheses were obtained when the dye adsorption was allowed to proceed at room temperature (ca. 25°C). gS = weight of ion exchanger in grams.

**Table VI Dependence of Basic Dye Adsorption on Time and Temperature of Dye Treatment Using DEAE-Cotton-g-Poly(MAA) as the Adsorbant**

PG	Basic Dye Adsorption (mg per L gS)			
	1 h	2 h	3 h	4 h
Control	0.3	0.9	1.01	(1.03)
10	79	101	110	(98)
20	88	104	118	(105)
30	90	107	120	(112)
40	91	109	121	(117)
50	96	112	124	(129)
60	98	124	131	(131)

Conditions used are as follows: Dye concentration, 200 mg L; Temp, 90°C; pH, 3 gS Weight of ion exchanger in grams. Values in parentheses were obtained when the adsorption of the dye was allowed to proceed at room temperature (ca. 25°C).

gation is expected to impart to it ionic exchange properties. While the DEAE groups are capable of binding the anions, the carboxyl groups bind the cations. That is, this modified cotton is characterized by anionic as well as cationic properties. To check the validity of this, DEAE cotton-g-poly(MAA) samples having different PG ranging from 10 to 60% were examined for dye adsorption using 0.2 g of each sample and 150 mL dye solution. Dye adsorption was studied under a variety of conditions. The ability of these substrates to adsorb  $\text{Cu}^{2+}$  ions was also studied.

Tables V and VI show the variation of adsorp-

tion of direct and basic dyes on DEAE cotton-g-poly(MAA) with time and temperature of the dye treatment, whereas Table VII shows the dependence of dye adsorption on dye concentration. The result signify (1) that the dye adsorption increases by increasing the PG of DEAE cotton; (2) that for a given PG, the dye adsorption increases by prolonging the time of dye treatment; (3) that the dye adsorption is higher at 90°C than at room temperature; (4) that the dye adsorption increases significantly by increasing dye concentration during the dye treatment; and (5) that for given set of conditions, the dye adsorption of the basic dye is much higher than the direct dye.

The above makes it evident that the modified cotton in question, i.e., DEAE cotton-g-poly(MAA), is much superior with respect to dye uptake in comparison, if any, with the control. Furthermore, the dye uptake is determined by the PG of the modified cotton, and the nature and concentration of the dye, as well as the time and temperature of the dye treatment. These findings imply that this modified cotton may serve as an ion exchanger. In the latter, the DEAE groups are essentially responsible for the dye uptake in the case of the direct dye. With the basic dye, on the other hand, the two functional groups in the exchanger play this role. That is, the dye uptake in the case of the basic dye occurs through its interaction with the DEAE cotton-g-poly(MAA) through the DEAE groups and the carboxyl groups of the graft. This, indeed, explains why the amounts of dye adsorption observed with the basic dye is higher than those of the direct dye (Table VII).

**Table VII Effect of Basic and Direct Concentration on Their Adsorption on DEAE Cotton-g-poly(MAA) Having Different PG**

PG	Dye Adsorption (mg per L gS) Using Dye Concentration of					
	50		100		200	
	Direct Dye	Basic Dye	Direct Dye	Basic Dye	Direct Dye	Basic Dye
Control	0.12	0.15	0.18	1	0.3	1.2
10	69	78	81	88	109	112
20	79	91	89	95	113	120
30	81	97	94	102	116	126
40	85	99	105	109	119	132
50	87	101	109	112	121	136
60	98	103	114	116	124	139

Conditions used are as follows. [Dye], mg 1 gS; Time, 4 h; temp, 90°C; pH, 4. gS = the weight of the sample of the ion exchanger in grams.

**Table VIII Dependence of Copper Adsorption on the PG of DEAE Cotton-g-poly(MAA) and Duration of the Treatment**

PG	Cu Adsorption mg per 1 gS			
	1 h	2 h	3 h	Overnight
Control	0	0	0	0.10
10	4.93	6.98	8.22	10.01
20	5.83	7.99	9.65	11.08
30	6.57	8.34	9.84	11.78
40	7.25	8.87	10.01	12.12
50	7.82	9.98	10.93	12.81
60	8.89	10.20	11.50	13.25

Conditions used are as follows.  $\text{CuSO}_4$  concentration, 200 mg L; temp, room temp (ca. 25°C); pH, 5. gS = weight of the ion exchanger in grams.

The favorable effect of dye concentration and temperature and time of the dye treatment, as well as the PG of the ion exchanger under investigation, is a manifestation of (1) increased swelling of the exchanger (modified cotton) at higher temperature and longer time with subsequent better diffusion and adsorption of the dye, (2) greater availability of dye molecules, which are immobile, at a high dye concentration in the proximity of the functional groups of the exchanger; and (3) provision of more active sites for dye interaction at higher PGs.

Table VIII shows the dependence of the extent and rate of copper adsorption on the PG of DEAE cotton-g-poly(MAA) ion exchanger. It is obvious that the amount of copper adsorbed on the exchanger increases by increasing the PG within the range studied. This is rather expected since higher PG means more active sites (carboxyl groups) and, therefore, more interaction with the  $\text{Cu}^{2+}$  ions. It is also seen that prolonging the duration of contact between the exchanger and copper sulphate solution promotes copper adsorption.

With the above in mind, it may be concluded that the DEAE cotton-g-poly(MAA) can serve as an ion exchanger. The latter may be used in the removal of dyes and metal ions from aqueous solution. Hence, DEAE cotton-g-poly(MAA) deserves additional research to signify its feasibility in the treatment of wastewater effluent of the textile chemical industry.

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