Chemical Modification of Cotton Fabrics by a Bifunctional Cationic Polymer for Salt-Free Reactive Dyeing

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ABSTRACT: Cotton modification exhibited great potential in the fabric dyeing industry. A bifunctional cationic polymer with a moderate cationic degree and low molecular weight was achieved via free radical polymerization between dimethyl diallyl ammonium chloride and allyl glycidyl ether. Then, it was further utilized for the modification of cotton fabrics. The formation of the cationic polymer was identified using Fourier transform infrared and nuclear magnetic resonance spectroscopies. The structure and properties of both treated and untreated cotton were analyzed by X-ray photoelectron spectroscopy and scanning electron microscopy. The modified cotton fabrics could be salt-free dyed with reactive dyes at low temperatures. While obtaining satisfactory color fastness and leveling properties, the dyeability of the modified cotton was improved significantly compared with the conventional dyeing of native cotton. Besides, the prepared cationic polymer has good flocculating properties to avoid secondary pollution, suggesting high potential for achieving an economical and eco-friendly dyeing process.

1. INTRODUCTION

Cotton fabric is the most widely used cellulosic raw material.  

It is pretty popular due to its excellent properties such as high breathability, good softness, and moisture absorption.  

Nowadays, reactive dyes have been most widely used for dyeing cotton fabrics because of their outstanding performance such as a wide range of hue, brilliance, and good wet fastness.  

More than 400 000 tons of reactive dyes were used in the textile industry every year.  

The cotton dyeing with the reactive dyes requires usually adding a lot of inorganic salts like Na₂SO₄ or NaCl to increase the dye exhaustion rate. However, salt-based dyeing reveals some disadvantages. For instance, the dye utilization of about 50−70% is attained and the inorganic salts can be neither destroyed nor exhausted after dyeing.  

As a result, the residual dyes and salts have led to high production costs and serious environmental pollution. Therefore, finding a way to improve dye utilization and meanwhile avoid the use of inorganic salts are important issues in the field of cotton coloration.

To achieve the aim, a potential strategy is to enhance the affinity of reactive dyes toward the cotton fabrics. Previous studies indicated that a few methods such as the use of cationic reactive dyes, the development of the dyeing process, and the modification of cotton fabrics were applicable and effective. Among these efforts, the chemical modification of cotton fabrics was one of the most promising methods to reduce the consumption of inorganic salts in the reactive dyeing process. It was achieved by introducing amino or cationic groups into/onto cotton fibers through covalent bonding. It was found that the amino groups are more reactive than the primary hydroxyl groups to react with the reactive dyes. The cationic groups can change the surface potential of cotton fibers from negative to positive, thereby increasing the substantivity and reactivity of fibers toward reactive dyes. The chemical modifiers of cotton fabrics are usually classified into two categories according to their molecular weight. The first one is low molecular weight chemicals such as (3-chloro-2-hydroxypropyl)trimethylammonium chloride, and glycine betaine. However, this modification method is limited by some shortcomings, for example, toxicity, unpleasant odor, potential pollution, and high production cost. The other type of modifier is polymers.
with multiple amino or cationic groups such as the amine-terminated hyperbranched polymer, \(^27\) poly-2-methacryloyloxy ethyl trimethylammonium chloride, \(^28\) polyethyleneimine, \(^29\) the poly-4-vinyl pyridine quaternary ammonium compound, \(^30\) and poly amino carboxylic acid. \(^31\) A major limitation of treating cotton with cationic polymers is that the effective modification mostly occurred on the fiber surface while rarely on the inside, which resulted in undesirable effects on the dyeing levelness. \(^22,32\) One possible reason is that the molecular weight of the used cationic polymers is too high to mediate permeation of polymers into the internal dense structure of natural cotton. \(^33\)

The copolymer of dimethyl diallyl ammonium chloride with allyl glycidyl ether (P[DMDAAC−AGE]) has been used for cotton antibacterial research. \(^34−37\) In this work, it was prepared and used for modifying the cotton fabrics. Different from the macromolecular polymer in the conventional modification process, the prepared P[DMDAAC−AGE] with a moderate cation degree and a low molecular weight was obtained by optimizing the reaction conditions including the monomer ratio, initiator content, reaction time, and temperature. In this way, the dyeability of the modified cotton could be greatly improved. Meanwhile, the good levelness of the dyed fabrics could be obtained. Since the prepared cationic polymer is relatively stable, eco-friendly, and has good flocculation properties, a feasible modifying process is proposed so that salt-free dyeing of cotton fabrics can be achieved.

2. RESULTS AND DISCUSSION

2.1. Optimum Conditions for the Preparation of P[DMDAAC−AGE]. P[DMDAAC−AGE] was prepared using DMDAAC and AGE as reaction monomers and potassium persulfate (KPS) as an initiator. A series of cationic polymers were synthesized under different conditions by adjusting the initiator content, monomer ratio, reaction time, and temperature. The effects of these conditions on the synthesis of P[DMDAAC−AGE] were evaluated with the T% (C.I. Reactive Black 5) of the modified cotton fabrics in maintaining good levelness, and the results are displayed in Figure 1.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c01530)

**Figure 1.** Effects of different synthetic (a) time, (b) temperature, (c) monomer ratio, and (d) initiator content on the T% of polymer-modified cotton fabrics.

Figure 1a shows that polymerization is complete within 4 h. After 4 h of polymerization, T% reaches a plateau with a value of about 90%. In other control experiments, it is found that the T% of cationic cotton was improved with an increase of the synthetic temperature and mass ratio of DMDAAC, as shown in Figure 1b,c. In addition, the effect of the content of the initiator on T% was investigated, and it could be found that the initiator content of 1% was the optimal initiator content (Figure 1d). Based on the above control experiments, the optimal conditions for the synthesis of P[DMDAAC−AGE] could be around the parameters with a DMDAAC-to-AGE mass ratio of 7:5:1, 1% KPS, a polymerization temperature of 80 °C, and a reaction period of 4 h.

2.2. Characterization of P[DMDAAC−AGE]. The prepared cationic polymer was first characterized by Fourier transform infrared (FT-IR) and \(^1^H\) nuclear magnetic resonance (NMR) spectra. Figure 2a shows the FT-IR spectrum of P[DMDAAC−AGE], in which the absorption peaks 1665 and 620 cm\(^{-1}\) are assigned to the C−N group and the peak at 1224 cm\(^{-1}\) is ascribed to the stretching vibration of the C−O−C group. In addition, the peaks appearing at 956 and 850 cm\(^{-1}\) are attributed to the C−O−C bond in the epoxy group. It should be noted that no peak of C≡C appears at 1640 cm\(^{-1}\), which indicates that the monomers have been completely converted into the copolymer. \(^38\)

The typical \(^1^H\) NMR spectrum of P[DMDAAC−AGE] is presented in Figure 2c. The proton peak of N−CH\(_3\) is observed at 3.03 ppm. \(^39\) The O−CH\(_2\) proton peak appears at 3.27 ppm. The peaks of −CH\(_2\) and −CH that belong to the epoxy group are seen at 2.83 and 3.16 ppm, respectively. \(^40\) The N−CH\(_2\) linkage is at 3.92 ppm, which agrees well with previous reports. \(^41,42\) Notably, the peaks of C≡C are not present in Figure 2c. This indicates that DMDAAC and AGE have been completely polymerized to form P[DMDAAC−AGE].

It can be seen from Figure 2b that the weight-average molar mass is determined to be 2315 g/mol. Approximately 90% of the mass is no more than 4500 g/mol. The molar mass distribution of the prepared cationic polymer is relatively narrow.
On the basis of the above analysis, it can be concluded that the designed cationic polymer has been obtained successfully and the yield of the cationic polymer was 84.19% by calculation.

2.3. Optimum Conditions for the Chemical Modification of Cotton Fabrics. Different modification conditions were explored to obtain higher dye utilization. Besides, to achieve the levelness dyeing, the modification was performed slowly at low temperatures so that the cationic charge would be evenly distributed on the cotton fiber.

Based on Figure 3, the optimized modification conditions are suggested by adjusting the pH, the reaction time, and the concentration of the cationic polymer to 13, 6 h, and 0.7 g/L, respectively.

2.4. Characterization of Modified and Unmodified Cotton Fabrics. The chemical composition of the cotton before and after modification was analyzed by the X-ray photoelectron spectroscopy (XPS) technique. The wide-scan spectra of cotton samples are given in Figure 4a,b, and the high-resolution spectra are given in Figure 4c,d. It can be seen from Figure 4a that the main elements in the unmodified cotton are carbon and oxygen. The trace of nitrogen observed at around 400 eV is attributed to the glycoproteins in the cotton cell wall. Figure 4b shows that the area of the nitrogen peak was increased from 0.26 to 0.7% after the modification. Comparing Figure 4c with Figure 4d, it can be found that the N 1s spectrum of unmodified cotton exhibited two peaks at 399.6 and 401.4 eV, which are ascribed to the C−N−C and N−H bands, respectively. Moreover, the modified sample spectrum caused a new peak at 402.2 eV, corresponding to the binding energy of the N+(CH3)3 group. The XPS results demonstrate that the cationic polymer has chemically bonded to the cotton fiber.

The ζ-potential values of the cationic and native cotton were measured to be +22.1 and −24.6 mV, respectively. The result further confirms that cationic sites have been introduced onto cotton fibers, and therefore, more negative-charged reactive dyes could be absorbed onto the cationic polymer-modified cotton fabric than the unmodified one.

Based on the obtained XPS and ζ-potential analysis, cotton fabrics had been chemically modified by P[DMDAAC−AGE].

2.5. Reactive Dyeing of Polymer-Modified Cotton Fabrics. Five different vinyl-sulfone reactive dyes were used to evaluate the dyeing properties of both modified and unmodified cotton fabrics. The cationic cotton fabrics were dyed without adding any salt at 35 °C, while the native cotton fabrics were dyed with a conventional method. No retarding agents were added in both dyeing methods.

Table 1 shows that the T% and the color yield were all greatly enhanced by cationic modification of cotton fabrics. The levelness in the dyed fabric was evaluated with RUI. According to a previous report, when the RUI was smaller than 0.2, it could be evaluated as “excellent levelness”. The RUI values shown in Table 1 suggest that the levelness dyeing has been achieved in both unmodified and modified cotton fabrics. The color fastness properties of different reactive dyes on the treated and untreated fabrics are determined and summarized in Table 2. It is found that the modified cotton fabrics in salt-free dyeing showed satisfactory fastness properties. This indicates that the chemical modification did not affect the color fastness of the cotton fabrics and that it could meet the application standard and requirements of dyed fabrics.
Chromatography analysis showed that the mass ratio of fabrics increased from 0.64 to 1.202 mg/g, and the DS of found that after modi

The DS was determined by two different methods. It could be calculated to be 0.69%, which was extremely close to the process was 1.403/100 (Figure 6). Then, the DS was calculated to be 0.65%. Ion chromatography data of N+ with different concentrations and (b) the standard curve for the N+ solution with

| reactive dye | fabric   | wash fastness | shade change | staining | rub fastness |
|--------------|----------|---------------|--------------|----------|--------------|
|              |          | E (%) | T (%) | K/S | RUI | E (%) | T (%) | K/S | RUI |
| C.I. Reactive Black 5 | modified  | 97.86 | 90.98 | 22.82 | 0.10 | 72.42 | 61.45 | 14.48 | 0.11 |
| C.I. Reactive Blue 19 | modified  | 91.58 | 85.18 | 17.63 | 0.09 | 70.69 | 54.53 | 10.86 | 0.16 |
| C.I. Reactive Blue 21 | modified  | 92.33 | 85.71 | 22.40 | 0.07 | 63.15 | 46.08 | 16.18 | 0.15 |
| C.I. Reactive Red 195 | modified  | 90.05 | 83.73 | 22.14 | 0.05 | 60.36 | 51.99 | 11.71 | 0.09 |
| C.I. Reactive Yellow 176 | modified  | 89.72 | 85.41 | 20.13 | 0.10 | 68.82 | 55.76 | 10.35 | 0.09 |

The realization of uniform dyeing of the modified cotton fabrics was calculated to be 0.65%. Ion chromatography data of N+ with different concentrations and (b) the standard curve for the N+ solution with

The calculation results, the DS of cationic cotton is much lower than reported. Finally, the low-temperature process also improved the levelness properties, according to a previous report. Based on the above three factors, uniform dyeing of the modified cotton fabric was achieved.

2.7. Reusability and Flocculation Properties of P-[DMDAAC–AGE]. It is interesting that the solution of P[DMDAAC–AGE] is relatively steady and can be used for sustainable production. In this section, 10-times reuse of 100 mL solutions of P[DMDAAC–AGE] was made for successively modifying 10 pieces of 1.0 g of cotton fabrics. Certain amounts of P[DMDAAC–AGE] and NaOH solution were supplemented to maintain a constant concentration of 0.7 g/L and a pH of 13. The value of 7% for each reuse was found to locate between 88.48 and 92.46% (Figure 7a), demonstrating that the cationic polymer could be reused multiple times to realize the continuous modifying of cotton fabrics for economizing water consumption.

The result of the flocculation experiment is shown in Figure 7b. The dyeing wastewater consisting of 0.1 g/L reactive dyes and 0.1 g/L the nonionic surfactant could be decolorized by flocculating with the cationic polymer. The concentration of P[DMDAAC–AGE] was the most important factor affecting the flocculation effect, and almost 90% efficiency was achieved at 0.1 g/L dosage.

Based on the above result, the washing liquid of modified cotton fabrics could be used to flocculate the dye wastewater because it contained a small amount of cationic polymer. It is beneficial for easier treatment of modified and dyeing wastewater. Furthermore, the flocculated dye may be recycled as a pigment and a filler after treatment.

3. CONCLUSIONS

In summary, based on the FT-IR and 1H NMR spectra, the successful synthesis of a bifunctional cationic polymer with a moderate cationic degree and a low weight-average molecular weight was confirmed. The optimum preparation process conditions and modification process conditions were determined. The per cent of the reactive dyes on the modified cotton fabrics was improved greatly upon comparison with the unmodified fabrics, and the modified cotton fabrics showed the calculation results, the DS of cationic cotton is much lower than reported. Finally, the low-temperature process also improved the levelness properties, according to a previous report. Based on the above three factors, uniform dyeing of the modified cotton fabric was achieved.

The realization of uniform dyeing of the modified cotton fabrics may be attributed to the following three main factors. First, the prepared cationic polymer has a low molecular weight with a narrow distribution. The cationic degree of the cationic polymer was calculated to be 3.034 mmol/g. The Mw of 2315 g/mol was much lower than the reported value of tens to hundreds of thousands. Second, the low degree of substitution (DS) of quaternary ammonium groups on cationic cotton was another factor to obtain good dyeing uniformity. The DS was determined by two different methods. It could be found that after modification, the nitrogen content of cotton fabrics increased from 0.64 to 1.202 mg/g, and the DS of modified cotton fabrics was calculated to be 0.65%. Ion chromatography analysis showed that the mass ratio of P[DMDAAC–AGE] to cotton fabrics in the modification process was 1.403/100 (Figure 6). Then, the DS was calculated to be 0.69%, which was extremely close to the calculation result based on the nitrogen content. According to
satisfactory color fastness and levelness properties. Besides, the cationic polymer revealed good flocculation properties so that the modifier residue could be used for the treatment of dyeing wastewater. This work provided an economic and promising way for salt-free dyeing of reactive dyes on cotton fabrics.

4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. Bleached woven cotton fabric (120 g/m²) was supplied by the Hongli Dyeing Corporation (Shandong, China). Dimethyl diallyl ammonium chloride (DMDAAC, 60% purity) was acquired from the Adamas Reagent Co., Ltd. (Shanghai, China). Allyl glycidyl ether (AGE), potassium persulfate (KPS), sodium hydroxide, sodium carbonate, and sodium sulfate anhydrous were all of reagent grade purchased from the Sinopharm Chemical Regent Co., Ltd. (Beijing, China). Five reactive dyes were used in this work, in which the C.I. Reactive Blue 21 and C.I. Reactive Black 5 were supplied by the Zhejiang Jinhua Group Co., Ltd. (Zhejiang, China), and C.I. Reactive Blue 19, C.I. Reactive Red 195, and the C.I. Reactive Yellow 176 were supplied by the Jiangsu Jinji Industrial Co., Ltd. (Jiangsu, China). The molecular structures of the reactive dyes are shown in Figure 8.

![Molecular structures of the reactive dyes used in this work.](image)

Figure 8. Molecular structures of the reactive dyes used in this work.

4.2. Preparation of P[DMDAAC–AGE]. The synthesis of P[DMDAAC–AGE] is based on the route shown in Figure 9a. Under continuous stirring at 300 rpm, the mixture was transferred into a reactor equipped with a reflux condenser at a specific temperature. KPS was dissolved in a small amount of deionized water and added to the reactants as an initiator. After stirring for a period of time, the mixture was transferred into a small beaker and cooled to 25 °C. The copolymer was precipitated with acetone and dried under vacuum at 50 °C, and then its yield was calculated.

4.3. Modification of Cotton Fabrics with the Prepared Cationic Polymer. The chemical modification of cotton fabrics with the cationic polymer is presented in Figure 9b. The synthesized cationic polymer P[DMDAAC–AGE] was formulated into a solution of a certain concentration. Then, the pH of this solution was adjusted to a certain value with 1 mol/L NaOH solution, and the cotton fabrics were immersed into the solution and stirred for a certain period of time at 25 °C. The modified cotton fabrics were thoroughly washed with deionized water to remove the physically attached cations and then dried in air for subsequent use.

4.4. Characterization Techniques. The cationic degree of the fabricated polymer was determined by the method reported in the literature. Fourier transform infrared (FT-IR) spectroscopy measurement was carried out on a Nicolet IS 10 FT-IR spectrometer (Nicoret), and 1H nuclear magnetic resonance (NMR) was performed in D2O using a Bruker AV-500 spectrometer (Bruker Biospin, Switzerland). The weight-average molecular weight (Mw) and the molar mass distribution of the synthesized cationic polymer were determined by gel permeation chromatography (GPC) (Wyatt Heleos System), X-ray photoelectron spectroscopy (XPS) analyses were carried out with an EscaLab 250Xi spectrometer (Thermo Fisher Scientific) to investigate the surface chemical changes of the cotton fibers before and after cationic modification. All binding energies values were corrected according to 284.8 eV of C 1s. Surface structures of both cationized and original cotton fibers were imaged by a scanning electron microscope (SEM) (Hitachi S-4800, Japan). ζ-Potential was measured using a Zetasizer Nano S90 (Malvern Panalytical, England). The cotton fabrics were modified with a solution containing 0.7 g/L cationic polymer for 4 h. The pH value of the solution was 13. Then, the modified cotton fabrics were cut into small pieces of 1 mm and treated with ultrasonic for 10 min in 0.001 mol/L KCl at pH of 7 before measurement. Each sample was measured five times to ensure reproducibility.

The DS of modified cotton was calculated by two methods. One of which was to measure the increase in the nitrogen content of cotton after cationic modification by a Multi EA3100 Trace 5/N cube (Analytik Jena AG, Germany). Another method for calculating the DS was to determine the amount of change in cation concentration in the solution before and after modification using CIC-D120 ion chromatography (Shenghan, China) with an SH IC-C18 pretreatment column.

4.5. Dyeing Procedure for Modified and Unmodified Cotton Fabrics. The dyeing procedure for modified cotton fabrics was carried out at a liquor ratio of 1:30 without adding salts. The modified cotton fabrics were immersed in a dye bath (3% on-weight-fabric, owf) at 25 °C and dyed for 30 min. Then, the temperature of the dyebath was slowly increased to 35 °C. After that, 15 g/L of Na2SO4 was added to the dyebath under stirring. The dye-fixing process was carried out at 35 °C for 4 h. Then, the dyed fabrics were soaped at 95 °C for 10 min in a solution of 1 g/L nonionic surfactant and rinsed thoroughly with tap water.

The unmodified cotton fabrics were dyed by a conventional process. The dyeing and washing processes were the same as that of the modified cotton except that 50 g/L Na2SO4 was...
added to the dyebath and the dye fixation was carried out at 60 °C.

4.6. Determination of Dye Utilization. The dyebath absorbance was measured at $\lambda_{\text{max}}$ of the dye using a 760CRT UV–vis spectrophotometer. The total dye utilization (T%) of the reactive dye is calculated using eqs 1–3, where E% and F% are the dye exhaustion and fixation and $A_0$ and $A_1$ are the absorbances of the dyebath before and after dyeing, respectively.

\[
E = \frac{(A_0 - A_1)}{A_0} \times 100\%
\]

(1)

\[
F = \frac{(A_0 - A_1 - A_2)}{(A_0 - A_1)} \times 100\%
\]

(2)

\[
T = E \times F
\]

(3)

4.7. Color Yields and Levelness Analysis. The color strength ($K/S$ value) was determined using eq 4, where $R$ is the reflectance at $\lambda_{\text{max}}$. Five discrete points on each dyed sample were measured using a Ci6X Spectrophotometer (X-Rite Pantone). The levelness properties of the dyed fabrics were estimated by a relative unlevelness index (RUI) value calculated using eqs 5 and 6. Smaller RUI values reflected the better dyeing levelness of the fabrics.

\[
K/S = \frac{(1 - R)^2}{2R}
\]

(4)

\[
S_i = \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{n - 1}}
\]

(5)

\[
\text{RUI} = \frac{\sum_{\lambda=400}^{700} (S_i/R)V_i}{700}
\]

(6)

$S_i$ represents the standard deviation of reflectance values measured at a specific wavelength, $R_i$ is the reflectance value for the $i$th measurement at each wavelength, and $\bar{R}$ is the average of the reflectance value of $n$ measurements for each wavelength, $V_i$ is the photopic relative luminous efficiency function.

4.8. Flocculation of the Reactive Dyes. The flocculation experiments for the residual dyeing liquor were carried using C.I. Reactive Black 5. The dyeing solution was mixed with P[DMDAAC–AGE] and then stirred rapidly at 500 rpm for 10 min, followed by stirring slowly at 50 rpm for 30 min and sedimentation for 60 min. The absorbance of the initial mixed solution was measured to be $A_0$, and after flocculation, it was measured as $A_1$. The flocculation decolorization rate ($D\%$) is determined using eq 7.

\[
D = \frac{(A_3 - A_4)}{A_4} \times 100\%
\]

(7)

**Figure 9.** (a) Synthesis of P[DMDAAC–AGE]; (b) reaction between P[DMDAAC–AGE] and cellulose.

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**Notes**

The authors declare no competing financial interest.

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