



**HAL**  
open science

## Electrochemical analysis of silicon nanoparticle lithiation – Effect of crystallinity and carbon coating quantity

Pierre Bernard, John Alper, Cédric Haon, Nathalie Herlin-Boime, Marion Chandesris

### ► To cite this version:

Pierre Bernard, John Alper, Cédric Haon, Nathalie Herlin-Boime, Marion Chandesris. Electrochemical analysis of silicon nanoparticle lithiation – Effect of crystallinity and carbon coating quantity. *Journal of Power Sources*, 2019, 435, pp.226769. 10.1016/j.jpowsour.2019.226769 . cea-02295163

**HAL Id: cea-02295163**

**<https://cea.hal.science/cea-02295163>**

Submitted on 21 Dec 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1  
2

3 **Note**

4 Declarations of interest: none

5 **Low-salt dyeing of cotton fabric grafted with pH-responsive**  
6 **cationic polymer of Polyelectrolyte**  
7 **2-(N,N-dimethylamino)ethyl methacrylate**

8 Weiwei Dong<sup>a</sup>, Man Zhou<sup>a</sup>, Yue Li<sup>a</sup>, Shixiong Zhai<sup>a</sup>, Kaili Jin<sup>a</sup>, Zhuizhui Fan<sup>a</sup>, Hong  
9 Zhao<sup>a</sup>, Weirong Zou<sup>a</sup>, Zaisheng Cai<sup>a\*</sup>

10 <sup>a</sup> *Key Lab of Science & Technology of Eco-textile, Ministry of Education, College of Chemistry,*  
11 *Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China*

12

13 **Abstract:** In this work, a pH-responsive polyelectrolyte 2-(N, N-dimethylamino)  
14 ethyl methacrylate (PDMAEMA) was grafted onto the cotton fabric by  
15 surface-initiated atom transfer radical polymerization by activator regenerated electron  
16 transfer (SI-ARGET ATRP). Then, the grafted cotton fabric was dyed by reactive dyes.  
17 SEM, XRD, FT-IR, TGA and whiteness test were investigated to characterize the  
18 PDMAEMA grafted cotton fabric. Meanwhile, the dyeing temperature, fixed  
19 temperature and pH value in the dye bath were carried out to explore the optimum  
20 dyeing process. Finally, the mechanism of salt-free dyeing of PDMAEMA grafted  
21 cotton fabric is proposed. The results showed that the cotton fabric was successfully  
22 grafted by PDMAEMA, which presents excellent dye up-take, fixation yield, K/S value  
23 and dyeing uniformity and color fastness under the dyeing temperature of 30 °C, the  
24 fixed temperature of 60 °C, and the pH value of 6. Moreover, the pH-responsive process  
25 not only realizes salt-free dyeing, but also increases the dye up-take, fixation yield and  
26 the dye levelness due to the migration dyeing process. This work provides a promising  
27 route to realize the salt-free dyeing of reactive dye on cotton fabric, which is beneficial  
28 to environment protection for the significant reduced content of dye and salt in waste  
29 water.

30

31 **Key words:** modified cotton fabric; cationization modification; salt-free dyeing;

32

33 **1. Introduction**

34 As the improvement of people's awareness for environment protection and  
35 increasingly stringent government regulations, the textile industry is seeking more

36 environmentally friendly processes to meet the needs of cleaner production.[1, 2]  
37 Cellulose fiber can meet the requirements of the use of cellulosic fibers as a renewable  
38 material possessing satisfying properties. For dyeing cellulose fiber, the reactive dyes  
39 are widely used due to the high wet rubbing fastness and bright colors.[3-5] During the  
40 dyeing process, Cellulose fiber surface was negatively charged in water bath. Then the  
41 electrostatic repulsion between the fibers with anionic reactive dyes makes the  
42 absorption of dye molecules on the fibers difficult.[6] Therefore, the traditional reactive  
43 dyeing needs to add a large amount of inorganic salts (such as NaCl, Na<sub>2</sub>SO<sub>4</sub>) to shield  
44 the negative surface of the fiber for dyeing easily.[7-11] However, the inorganic salts  
45 are almost all retained in the waste liquid after dyeing contains, which causes serious  
46 water pollution issue; moreover, the salt in the sewage penetrates into the soil, leading  
47 to the salinization problem of the land.[10, 12, 13] Therefore, the salt-free or low-salt  
48 dyeing technology of anionic dyes has attracted much attention, to replace traditional  
49 dyeing process with salt as dyeing accelerant.[14, 15]

50 Considering the shielding mechanism of the inorganic salt in the dyeing bath, the  
51 affinity between dyes and fibers is the key to realize the salt-free dyeing. At present,  
52 four main methods are studied: the development of substitute salt and salt-free dyeing  
53 auxiliaries;[16] the modification of molecular structure of the reactive dye;[17] using  
54 new machinery to improve the dyeing process to reduce the use of salt;[18] and the  
55 cationization of the fiber to achieve the purpose of salt-free dyeing.[19-21] One type of  
56 non-reactive cationic modification is the physical adsorption of the fiber to endow the  
57 fiber positively charged. However, due to the uncontrollable molecular weight, the  
58 dyeing fabric has low leveling property, poor color fastness and darkening of the color.  
59 Therefore, among these methods, the formation of cationic groups on the surface of  
60 cellulose fibers by chemical modification is the most promising for salt-free or low-salt  
61 dyeing.[22, 23] The cation modification is mainly through attaching a cationic  
62 chemical (mainly a nitrogen-containing compound) onto the surface of the cellulose  
63 fiber, which makes negative charges of the fiber hidden and limited by the  
64 addition/substitution of cations. [24-26] The modified cotton can be dyed with an  
65 anionic dye under neutral or weakly acidic electrolyte-free conditions.[27, 28]

66 Up to now, there are many types of modifiers reported for the cationization  
67 modification of cotton fabrics. Abkenar et al.[29, 30] grafted a large amount of primary  
68 and tertiary amino-modified PPI dendrimers by using a crosslinking agent. The  
69 modified cotton fabric obtained high dye utilization and color strength without salt.  
70 Wang et al. [31] synthesized a new amino-terminated hyperbranched polymer (at-HBP).  
71 The results showed that the K/S value of the modified ramie fabric was comparable to  
72 traditional salt dyeing without the electrolyte. The friction fastness of the modified  
73 ramie fabric was excellent. Tuba Toprak et al. [22] treated 4-vinylpyridine onto cotton  
74 fabric. The effects of the amount of polymer and the different treatment methods on the  
75 dyeing performance of the fabric were systematically investigated. Their method was  
76 confirmed can be used as an alternative to traditional dyeing. However, there are still  
77 some problems for with the reactive cationic modifier. Besides their low utilization rate,  
78 their relatively harsh reaction conditions (strong alkali, strong acid, high temperature,  
79 etc.) usually have a great influence on the fabric properties. In addition, due to the

80 positive electrical properties of the modified fabric, the dyeing rate is easy to cause  
81 uneven dyeing in the early stage of dyeing.

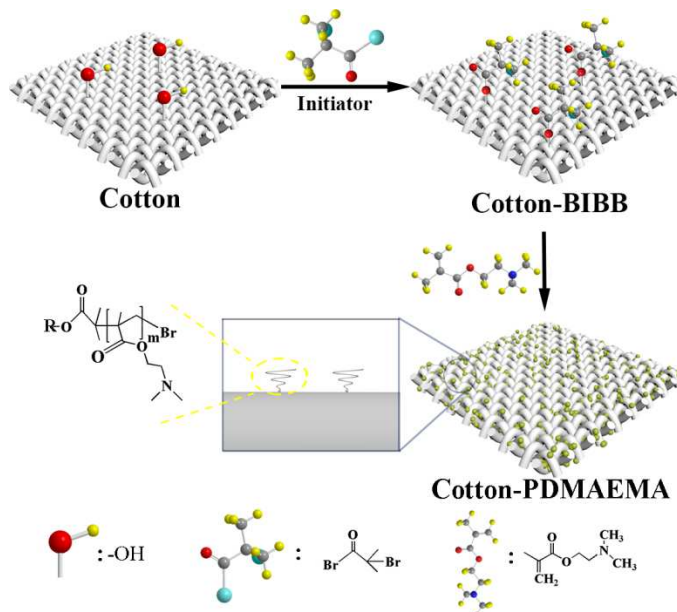
82 In the present work, a pH-responsive polymer PDMAEAM was grafted onto the  
83 surface of cotton fabric by SI-ARGET ATRP method. The effects of monomer dosage,  
84 synthesis time on fabric graft ratio and fabric whiteness were investigated. This  
85 responsive polymer mechanism of action was explored. During the dyeing stage, the  
86 graft polymer is protonated and positively charged by adjusting the dye bath to weak  
87 acidity. The positively charged polymer shields the negative charge on the cellulose  
88 fiber surface. Negatively charged anionic dyes are adsorbed onto positively charged  
89 fibers due to electrostatic attraction. In the following fixation stage, because the  $H^+$  in  
90 the dyeing bath are neutralized and then the dye bath turns to be alkaline, the graft  
91 polymer PDMAEMA is deprotonated with the increase of the temperature and the  
92 addition of alkaline  $Na_2CO_3$ . The negative charge shielding effect on the surface of the  
93 cotton fabric disappears and the surface of the fiber exhibits a negative charge. The dye  
94 adsorbed by the electrostatic attraction is returned to the dye bath, and secondary  
95 dyeing occurs, which increases the transfer dyeing and improves the dyeing levelness.  
96 Additionally, the dyeing process conditions were optimized: the effects of pH, dyeing  
97 and fixing temperature on fabric dyeing performance were investigated. Finally, the  
98 adsorption isotherms of fabric dyeing were explored. After our cationization  
99 modification with PDMAEMA on the cotton fabric, the leveling property and the K/S  
100 value of the dyed fabric are improved compared with the traditional dyed fabric.

101

## 102 2. Results and discussion

103 PDMAEMA is grafted onto the cotton fabric by SI-ARGET-ATRP method as  
104 shown in Fig.1, divided into two steps. The first one is the substitution reaction between  
105 the hydroxyl group on the cellulose fiber and the bromine group of the initiator. The  
106 initiator is grafted on to the cotton fabric firstly. Then, the monomer DMAEMA is  
107 polymerized under the participation of the reducing agent and the catalyst, which  
108 directly happens on the surface of the cotton fabric. Therefore, the cation-modified  
109 cotton fabric with PDMAEMA is obtained.

110



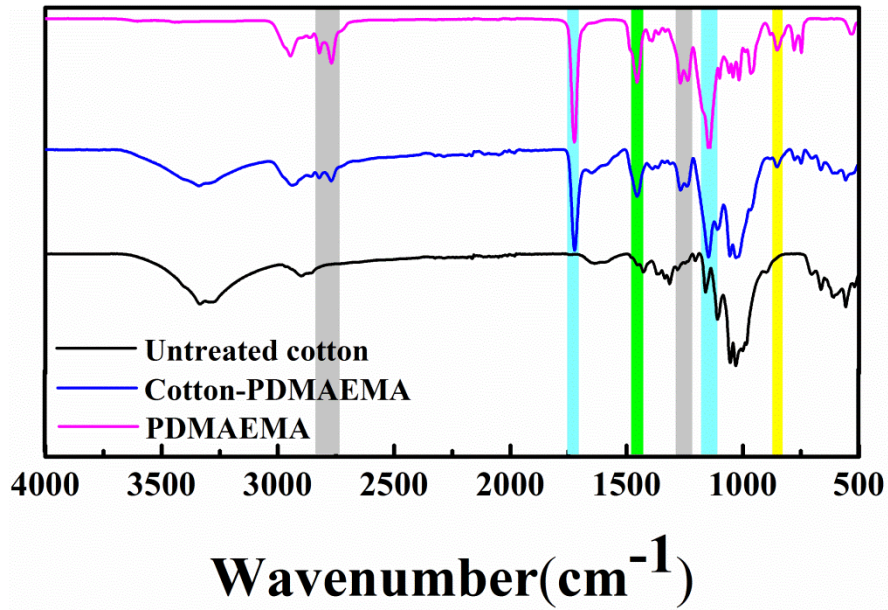
111  
112  
113  
114

Fig. 1 Schematic diagram of PDMAEMA grafted onto the cotton fabric by SI-ARGET-ATRP method.

## 115 2.1 Characterization of modified cotton fabric

### 116 2.1.1 FT-IR test

117 Fig.2 shows the FTIR spectras of PDMAEMA and cotton fabrics before and after  
118 grafting. The characteristic peaks of PDMAEMA are as follows: the peak at  $1724\text{ cm}^{-1}$   
119 is the stretching vibration of  $\gamma\text{ C=O}$ ; the peaks appeared at  $2827\text{ cm}^{-1}$  and  $2774\text{ cm}^{-1}$  are  
120 corresponding to the C-NH<sub>3</sub> vibration; the peak at  $1265\text{ cm}^{-1}$  and  $1449\text{ cm}^{-1}$  are the NH<sub>2</sub>  
121 vibration and symmetric bending vibration of CH<sub>2</sub>, respectively; the stretching  
122 vibration peak of  $\gamma\text{ C-N}$  appears at  $1265\text{ cm}^{-1}$ . Compared with the untreated cotton  
123 fabric, the additional characteristic peaks of PDMAEMA appeared on the FTIR spectra  
124 of cotton-PDMAEMA fabric. These results certify the PDMAEMA is successfully  
125 grafted onto the cotton fabric.

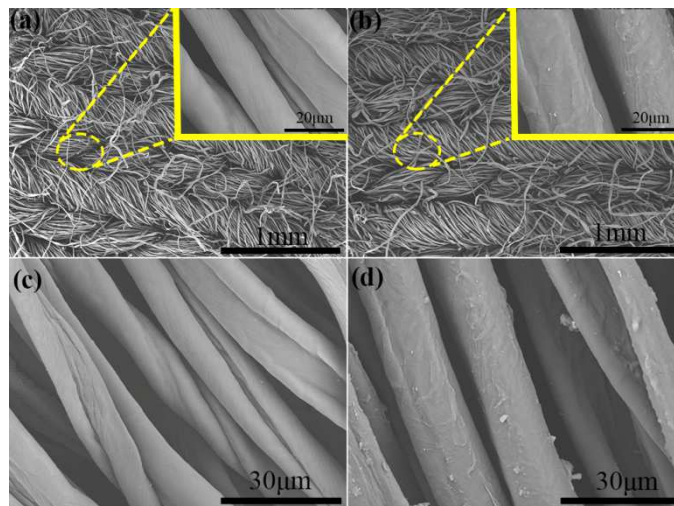


126

127 Fig. 2 FT-IR characterization of PDMAEMA 、 cotton fabric before and after grafting

128 2.1.2 SEM test

129 SEM images of the raw cotton fabric and the graft-modified cotton fabric are  
 130 shown in Fig.3a and 3b. It can be seen that the surface of the raw cotton fabric is  
 131 relatively smooth and the modified fabric has a film covering the surface of the  
 132 cellulose fiber. No obvious cracks can be observed indicating that PDMAEMA is  
 133 successfully grafted onto the cotton fabric.



134

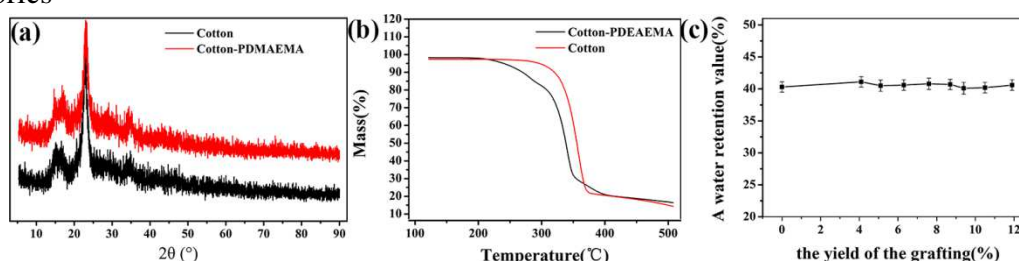
135 Fig. 3 SEM images of the raw cotton fabric (a) (c) and the modified cotton fabric (b) (d)  
 136 under various magnifications,

137 2.1.2 XRD and TG test

138 Fig. 4a shows the XRD spectra of the fabrics before and after the cation  
 139 modification. The characteristic diffraction peaks of two fabrics have no obvious  
 140 difference, showing the surface modification does not affect the crystal form of the



141 cotton fabric. The crystallinity is relative to the molecular arrangement and tightness. In  
 142 detail, loose molecular arrangement of the fiber leads to small crystallinity, then easy  
 143 swelled in the dyeing bath. Therefore, the effect of the modification on swelling  
 144 property of the cellulose fiber is negligible. Fig. 4b is thermogravimetric analysis (TGA)  
 145 curves before and after the modification. The modified cotton fabric shows two thermal  
 146 decomposition peaks at 210°C (sublimation of PDMAEMA polymers) and 290°C  
 147 (sublimation of cotton), respectively, while the thermal decomposition temperature of  
 148 the raw cotton fabric is at about 290°C. Therefore, compared to pure cotton, the  
 149 appearance of additional peak at 210°C in modified cotton fabric proves the  
 150 combination of cotton and PDMAEMA modifier. Fig 4c shows the effect of the yield of  
 151 the grafting on the water retention value of cotton fabrics, indicating that the yield of  
 152 the grafting of the fabric has a small effect on the water retention performance of cotton  
 153 fabrics



154 Fig. 4 XRD characterization (a), TGA curves (b) and A water retention value test (c) of  
 155 the raw cotton fabric and the modified cotton fabric.  
 156  
 157

## 158 2.2 Dyeing performance

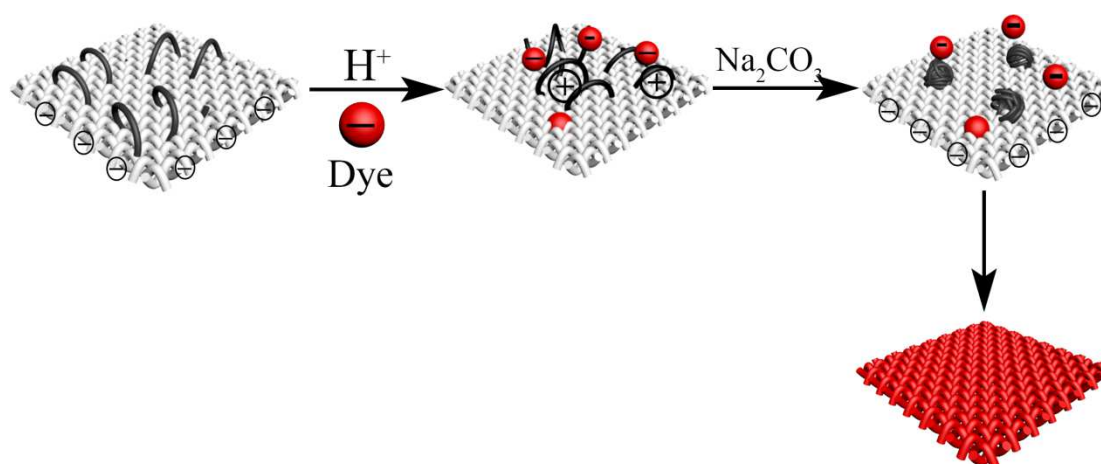
159 Further, the effect of grafting rate, dyeing bath pH, dyeing temperature and  
 160 fixation temperature on dyeing performance of modified cotton fabrics were  
 161 investigated. Moreover, the dyeing thermodynamics and kinetics of the modified cotton  
 162 fabrics were discussed to illustrate the dyeing mechanism.  
 163

### 164 2.2.1 Dyeing process

165 The schematic diagram of the dyeing procedure of the modified cotton fabric with  
 166 reactive dyes is shown in Fig. 5. It can be seen that at the beginning of the dyeing  
 167 process, the addition of acetic acid at a lower temperature makes the dye bath weakly  
 168 acidic. The polymer PDMAEMA is positively charged and protonated to achieve a  
 169 shielding function to the negative charge on the surface of the cotton fiber. After the  
 170 anionic reactive dye is added, they are directly attracted to the positively charged cotton  
 171 fabric. The dye molecules were adsorbed by modified cotton fabric through coulomb  
 172 attraction. Then, they diffuse into internal of the fiber and complete the combination  
 173 of dye molecules and modified cotton fabric. The entire dyeing process were achieved  
 174 by Langmuir adsorption. After  $\text{Na}_2\text{CO}_3$  added to the dye bath at fixation stage,  $\text{H}^+$  is  
 175 neutralized in the alkaline environment, which leads to the deprotonation of the  
 176 polymer PDMAEMA. Therefore, the shielding effect disappears and the fiber surface

177 expose the negative charges. Then, the dyes adsorbed on PDMAEMA bonded by  
 178 electrostatic attraction during the dyeing stage are off from PDMAEMA and into the  
 179 dye bath, which happen to the secondary dyeing(The positive surface of the fiber is  
 180 higher in higher grafting rate of fiber surfaces, leading to a higher amount of dye  
 181 molecules absorbed by the fiber and the polyelectrolyte. Therefore, polyelectrolyte is  
 182 deprotonated and more dye molecules removed from the higher grafting rate fiber  
 183 surfaces. And the dye molecules transfer to lower grafting rate fiber surfaces). This  
 184 process improves the migration dyeing process and benefits significantly the dyeing  
 185 levelness.

186 When dyeing the modified fabric, the dyeing conditions have a great influence on  
 187 the dyeing performance of the fabric, so the effect of the dyeing temperature, dyeing  
 188 bath pH and polymer graft ratio was investigated.  
 189



190  
 191

Fig. 5 Dyeing procedure of the modified cotton fabric with reactive dyes.

### 192 2.2.2 Effect of the yield of the grafting of PDMAEMA on dyeing performance

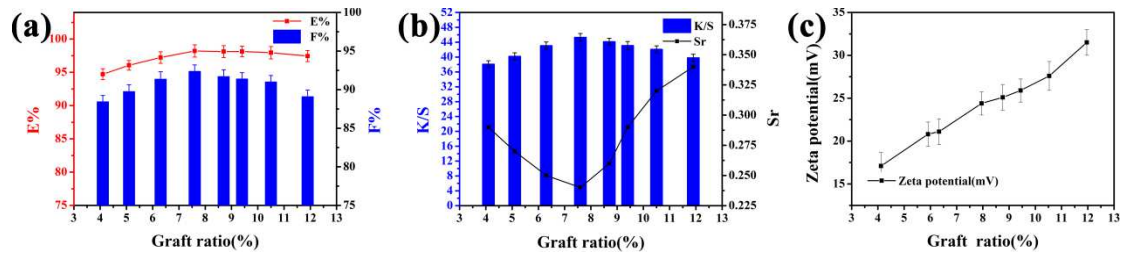
193 Cotton fabrics with different the yield of the grafting of 4.1%, 5.1%, 6.3%, 7.6%,  
 194 8.7%, 9.4%, 10.5% and 11.9% were prepared (the detail is shown in Supporting  
 195 Information). The modified cotton fabrics with different grafting rates were dyed under  
 196 the same conditions.

197 As shown in Fig. 6a, when the graft ratio is less than 7.6, the dye up-take, reaction  
 198 rate and fixation yield increases with the increase of the graft ratio. When the graft ratio  
 199 is more than 7.6, they are slowly reduced. The change tendency of K/S value is related  
 200 to the color strength which is consistent with the dye up-take, reaction rate and fixation  
 201 yield, as the bar chart shown in Fig. 6b. On the other hand, the curve in Fig. 6b is the  
 202 relative unevenness of the fabric with different graft ratios.

203 Fig. 6c shows the surface zeta potential of cotton fabrics with different graft ratios  
 204 under weakly acidic condition at pH = 6. It can be seen that the zeta potential enhances  
 205 with the increase of graft ratio. For the dyeing process, cotton fabrics with more  
 206 positive zeta potential can adsorb the dyes more strongly, so the dye up-take is higher  
 207 and higher with the increase of graft ratio, when it is less than 7.6. The leveling property  
 208 of the fabric also becomes better. That might be ascribe to the different densities of the  
 209 graft modifier on the surface. At low grafting rate, the fabric did not reach its optimum



210 grafting rate, and the molecular distribution of the graft polymer was sparse, so that the  
 211 dye absorption capacity of different parts of the fabric was different, resulting in a  
 212 decrease in the levelness of the fabric. However, after the graft ratio exceeds 7.6  
 213 (dyeing rate exceeds 98%), with the grafting rate increasing, the amount of dye  
 214 molecules absorbed by the grafting polymer increasing, and the amount of dye  
 215 molecules absorbed by the fiber decreasing. At the same time, due to the van der Waals  
 216 force, the polymer also adsorbs dye molecules, which increases floating color on the  
 217 fiber surfaces. Therefore, the reaction rate decreases and the evenness becomes worse.  
 218 In addition, during the fixation stage, the dye molecules off from PDMAEMA are much  
 219 more than ones fixed on the fiber by covalent bond, which further leads to the decrease  
 220 of the dye up-take, reaction rate and fixation yield.  
 221



222  
 223 Fig.6 PDMAEMA graft ratio versus (a) reactive dye uptake (E%) and fixation yield  
 224 (F%), (b) dyed fabric surface color depth (K/S) and the relative unevenness (Sr) and (c)  
 225 effects of Zeta potential.

### 226 2.2.3 Effect of starting dyeing pH on dyeing performance

227 The modified cotton fabric with graft ratio of 7.6 typically was dyed by in the dye  
 228 bath under various starting dyeing pH in the range of 3-7.

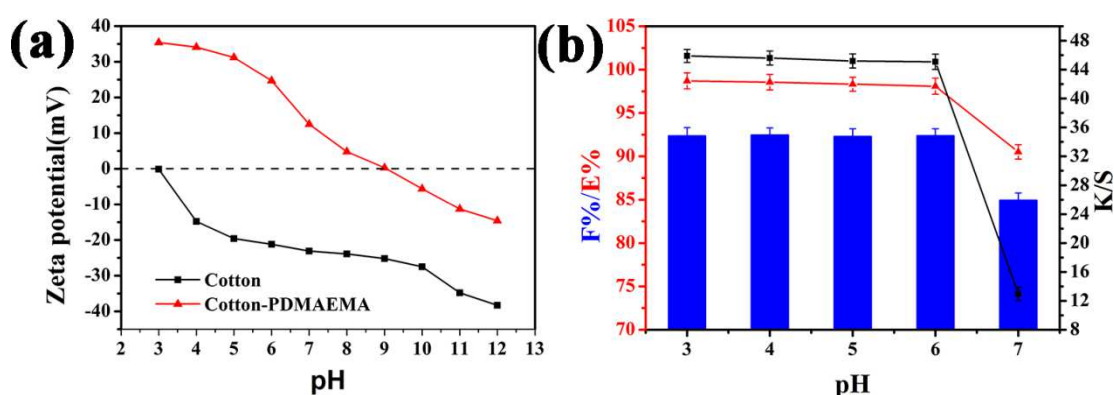
229 The molecular structure of PDMAEMA polymer consists of a tertiary amine  
 230 group which can undergo a “protonation-deprotonation” transition, exhibiting different  
 231 states as pH of the solution change. This endows them with different  
 232 hydrophilic-hydrophobic balance values, exhibiting pH sensitivity. Fig. 7a shows the  
 233 surface zeta potential of the raw cotton and the modified cotton fabric under different  
 234 pH. The zeta potential of the raw cotton fabric is negative under different pH condition,  
 235 while the PDMAEMA-grafted modified cotton fabric is positively charged under acidic  
 236 conditions. Under strong acidic condition (pH in the range of 3~5), the zeta potential of  
 237 the modified cotton fabric has little change with the increase of pH. After the pH  
 238 increased to 6, the surface zeta potential of the fabric decreases rapidly with the  
 239 increase of the dyeing bath pH. When pH reaches to ~9, the zeta potential decreases to  
 240 the negative value. The zeta potential is closely relative to the degree of protonation of  
 241 the cotton fabric. The degree of protonation of the the modified cotton fabric can be  
 242 calculated by Henderson-Hasselbalch as shown in Formula (1). Accordingly, the  
 243 degree of protonation is 99.8% at pH=5、 98.04% at pH=6 and 0.99% at pH=9.

$$244 \quad pH = pK_a - \log \frac{\beta}{1-\beta} \quad (1)$$

245 where  $pK_a = 7.7$ , which is the apparent dissociation constant of the polymer in water,  
 246 and  $\beta$  is the degree of protonation of the polymer at a certain pH. Therefore, if the

247 starting pH of dyeing bath is in the range of 3~7, the zeta potential of the modified  
 248 cotton fabric can make sure to keep a relatively highly positive, which is beneficial to  
 249 dyes absorption at the beginning of dyeing process.

250 Fig. 7b reflects the various starting dyeing pH from 3 to 7 effect on the dye  
 251 up-take and fixation yield. The pH of the dye solution was adjusted by adding glacial  
 252 acetic acid at the beginning of the dyeing. It can be seen that at the starting dyeing pH  $\leq$   
 253 6, the dye up-take and fixation yield changes unobvious. They decrease with the  
 254 increase of the starting dyeing pH. Because when the starting dyeing pH is  $\sim$ 7, the zeta  
 255 potential of the fabric surface is low as shown in Fig. 7a, the degree of protonation of  
 256 the graft polymer is relatively reduced. So ionic bond between cationic cotton and  
 257 anionic reaction dyes is weak, resulted in a low dyes absorption at the beginning of  
 258 dyeing process, then a low dye up-take and fixation yield.  
 259



260

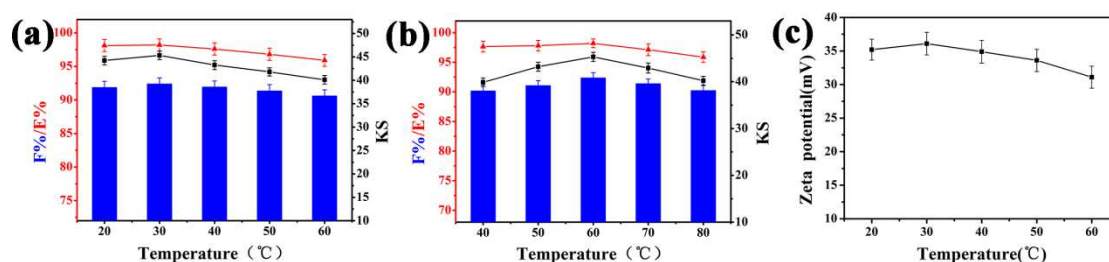
261 Fig. 7 (a) Surface zeta potential of the raw cotton fabric and the modified cotton fabric  
 262 at different pH; pH value versus (b) reactive dye uptake (E%), fixation yield (F%) and  
 263 dyed fabric surface color depth (K/S).

#### 264 2.2.4 Effect of temperature on dyeing performance

265 The effect of dyeing temperature and fixing temperature are discussed on dyeing  
 266 performance by the dye up-take, fixation yield, K/S value and relative unevenness of  
 267 the fabric. As shown in Fig. 8a, the dyeing temperature has an important effect on the  
 268 dye up-take and fixation yield of the modified cotton fabric. They increase first and  
 269 then decrease with the increase of the dyeing temperature, which is consistent with the  
 270 K/S value tendency. Fig. 8c reflects the zeta potential of the modified fabric surface  
 271 under various temperature. On one hand, during the dyeing stage, the polymer is  
 272 protonated. The macromolecular chain stretches the macromolecular segment due to  
 273 the repulsive force between the positive charges. On the other hand, at lower  
 274 temperature, the molecules chains also elongate and the protonation sites is increased.  
 275 And the degree of protonation increases correspondingly during the dyeing process, as  
 276 shown in Fig. 8c, the zeta potential is relatively high, which causes the higher attraction  
 277 force to dyes. When the temperature increases, the polymer molecular chain shrinks,  
 278 the contact area between PDMAEMA and  $H^+$  decreases, which leads to the decrease  
 279 of the cotton protonation degree and dye up-take, fixation yield and K/S value. It's  
 280 noteworthy that the K/S value in our work can be up to  $\sim$ 40, while the traditional salt

281 dyeing K/S value is only ~15, which can achieve the requirement of dyeing dark color  
 282 at low concentration, significantly saving cost and reducing pollution. Herein, the  
 283 optimum dyeing temperature is 30 °C.

284 Fig. 8b shows the effect of fixing temperature on the dye up-take, fixation yield,  
 285 K/S value and leveling property of the modified cotton fabric. As the fixation  
 286 temperature increasing, both the internal molecular motion of the fiber and the  
 287 reactivity of dye molecules increases, which is beneficial to the diffusion of the dye into  
 288 the fiber. Thus, the dye up-take, fixation yield, K/S value are gradually increased  
 289 when the fixation temperature  $\leq 60$  °C. However, when the the fixation temperature  
 290 continues to increase, the greater amount of dye hydrolysis leads to the low dye up-take,  
 291 fixation yield, K/S value. Therefore, the optimum fixing temperature is 60 °C.  
 292



293

294 Fig. 8 The effect of dyeing temperature (a) and fixing temperature versus (b) on dye  
 295 up-take (E%), fixation yield (F%) and dyed fabric surface color depth (K/S), (c)  
 296 temperature on zeta potential of modified cotton fabric.

### 297 2.2.5 Effect of pH-responsiveness on leveling property

298 As shown in Table 1, the dyeing unevenness of the modified cotton fabric in our  
 299 work keeps substantially below 0.3 under various conditions, which is superior to  
 300 conventional salt dyeing.

301

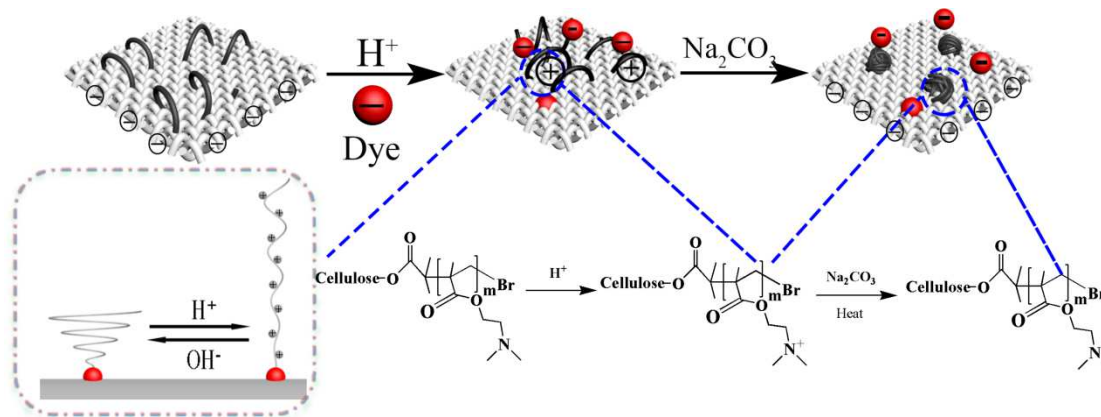
302 Table 1 leveling properties of raw cotton fabric and the modified cotton fabric

Sample	Unmodified	modified
Reactive blue KN-R	0.369	0.231
Active golden K-2RA	0.336	0.221
Reactive brilliant red M-8B	0.318	0.205

303

304 The fixation stage is key for the leveling property of the modified cotton fabric. As  
 305 well known, if cotton was modified by non-responsive cationic, the cationic cotton and  
 306 reactive dye molecules will be combined by ionic bonds after dyeing process. The  
 307 uneven treatment of the cationic modifier will directly cause the uneven dyeing. In this  
 308 study, the cotton was treated by responsive cationic, which has a better leveling than  
 309 traditional non-responsive cationic. As shown in Fig 9, H<sup>+</sup> will be neutralized after  
 310 adding Na<sub>2</sub>CO<sub>3</sub> (alkaline environment), leading to the deprotonation of the polymer  
 311 PDMAEMA. Therefore, the shielding effect disappears and the fiber surface expose the  
 312 negative charges. Then, the dyes adsorbed on PDMAEMA bonded by electrostatic

313 attraction during the dyeing stage are off from PDMAEMA and into the dye bath, dyes  
 314 transfer from high concentration to low concentration and happen to the secondary  
 315 dyeing ( The positive surface of the fiber is higher in higher grafting rate of fiber  
 316 surfaces, leading to a higher amount of dye molecules absorbed by the fiber and the  
 317 polyelectrolyte. Therefore, polyelectrolyte is deprotonated and more dye molecules  
 318 removed from the higher grafting rate fiber surfaces. And the dye molecules transfer to  
 319 lower grafting rate fiber surfaces). This process improves the migration dyeing process  
 320 and benefits significantly the dyeing levelness.  
 321



322

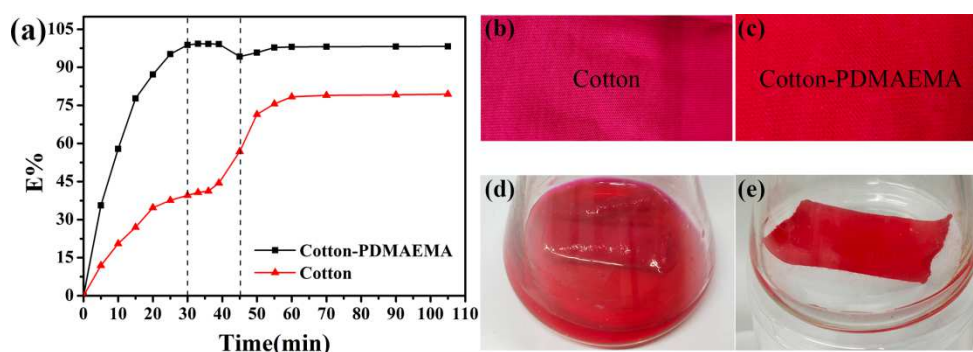
323

Fig. 9 Schematic diagram of polymer response process

### 324 2.2.6 Dyeing rate curve

325 The traditional salt dyeing and salt-free dyeing in this work were carried out under  
 326 the same condition. Fig. 10a shows the dyeing rate curves of salt-dyed and modified  
 327 cotton fabrics with salt-free dyeing. The modified cotton fabrics have a fast dyeing  
 328 speed in early stage. The dyeing rate reach to maximum after 30 minutes, then  
 329 gradually decreases with the time extending. With the dye bath heated to fixation stage,  
 330 dye molecules separate from the fabric for secondary dyeing, and the dye uptake rate  
 331 decreases slightly before fixing.

332 Fig. 10b and 10c show the dyed fabrics images through traditional reactive dyeing  
 333 process with salt and the salt-free reactive dyeing of modified cotton fabric with  
 334 PDMAEMA. It can be seen that the dyeing color of modified fabric is much deeper and  
 335 brighter than traditional dyeing with salt. As for the pictures of the waste liquid after  
 336 dyeing of traditional salt dyeing process (Fig. 10d), the dye bath of the salt-free dyeing  
 337 of modified cotton fabric with PDMAEMA (Fig. 10e) becomes clear and transparent,  
 338 illustrating the higher dye up-take, while the waste liquid of traditional reactive dyeing  
 339 with salt retains a amount of dye and salt. This is a crucial improvement for the reactive  
 340 dyeing, which produce the dyeing waste liquid with no dyes and salt, avoid  
 341 environmental pollution and reduce the cost of dyeing waste liquid and sewage  
 342 treatment.



343

344 Fig. 10 The dyeing rate curves (a) and the dyed fabrics images through traditional salt  
 345 dyeing process (b) and the salt-free dyeing of modified cotton fabric with PDMAEMA  
 346 (c), the pictures of the waste liquid after dyeing of traditional salt dyeing process (d)  
 347 and the salt-free dyeing of modified cotton fabric with PDMAEMA (e).

348

349 To better understand the color difference of reactive dyes on modified and  
 350 unmodified cotton fabrics. We performed some dyeing performance tests shown in  
 351 Tables 2 (E%, F%, L\*, a\*, b\*, c\*, K/S and Sr). It can be seen that  
 352 Cotton-PDMAEMA's dye up-take (E%) and fixation yield (F%) are much higher than  
 353 those of unmodified cotton fabric, showing a better dyeing effect. Because the K/S  
 354 value of dyed fabric is higher than that of conventional salt dyeing, therefore, the  
 355 brightness is slightly lower than that of salt dyeing (the dyeing depth is inversely  
 356 proportional to the brightness). In addition, Cotton-PDMAEMA has a higher a\* value.  
 357 This is because the dyeing K / S value of the modified cotton fabric is higher than the  
 358 conventional salt dyeing, so the chroma is higher.

359 Table 2 Comparison of dyeing performance of reactive dyes on untreated and treated  
 360 cotton

Sample	E%	F%	L*	a*	b*	K/S	Sr
Cotton	82.1	68.3	30.28	49.32	4.86	10.8	0.26
Cotton-PDMAEMA	98.8	92.4	38.78	46.21	5.14	45.2	0.24

361

362

### 363 2.2.7 Dye sorption isotherms

364 Fig. 11 shows the relationship between the equilibrium dye concentration ( $C_s$ ) of  
 365 the three reactive dyes and the equilibrium adsorbed dye amount ( $C_f$ ). By comparing  
 366 the correlation coefficient values ( $R_2$ ) obtained from the Langmuir and Freundlich  
 367 isotherm models (in Table 3) and fitting the model to the experimental data, it can be  
 368 concluded that a good agreement with Langmuir equation.  $R_L > R_F (> 0.99)$  reflects the  
 369 adsorption process between three reactive dyes and the modified cotton fabrics. This  
 370 suggests that Langmuir model can be used to fit experimental data better than the  
 371 Freundlich model. According to the Langmuir adsorption model, the adsorption of  
 372 anionic dyes could be related to Coulomb attraction until the surface functional site  
 373 ( $-NH_3^+$ ) is completely occupied, and then the dye diffuses into the fiber cavity.