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Antimicrobial cationic dyes. Part 3: simultaneous dyeing and antimicrobial finishing of acrylic fabrics

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Abstract

The antimicrobial cationic dyes were employed in dyeing acrylic fabrics. The effects of dyeing time, dyeing concentration and dyeing temperature were investigated, and the incorporated dye molecules on acrylics were analyzed. It was found that these functional dyes could be effectively introduced to acrylic fibers to achieve simultaneous coloration and functional finishing effects. All the treated fabrics exhibited antimicrobial efficacy against *Escherichia coli* and *Staphylococcus aureus*. The washing durability of antimicrobial functions on the treated fabrics was further studied.

Keywords: Simultaneous dyeing; Antimicrobial finishing; Acrylic fabrics

1. Introduction

Simultaneous dyeing and functional finishing of textiles offer economical and environmental advantages in textile manufacturing. Recently, many researches have explored in this field, such as the simultaneous dyeing and durable press finishing of cotton [1–3], the combination of dyeing and durable press finishing of silk [4,5], as well as the simultaneous dyeing and finishing of wool [6]. However, most of the studies are focusing on the treatment of natural fabrics, little study has been done in the area of synthetic fabrics. Furthermore, all of the reported studies are concerning about the dyeing and durable press finishing, the combination of dyeing and other functional finishing is less developed. In addition, most of the single-step studies are designed for some specific system. In these processes, the combination is usually based on the simple mixing of dyes, finishes and other auxiliaries, thus the compromise of dyeing and finishing conditions is usually required and the properties of the resultant fabrics are usually sacrificed. Therefore, further studies in the simultaneous dyeing and finishing are definitely needed.

Acrylic fabrics are widely used synthetic fabrics due to a combination of desirable properties, such as soft wool-like handle, good elasticity and mechanical properties, as well as the high resistance to outdoor exposure and many chemical compounds [7]. Extensive studies have been carried out in the cationic dyeing of acrylic fabrics [8,9], but less work has been done in the functional finishing of acrylic fabrics. Recently, some progress has been made to introduce antimicrobial functions into acrylic fabrics either by *N*-halamine moieties or by quaternary ammonium salts (QAS) [10,11]. Unfortunately, both the treatments may limit or affect the dyeing of the finished acrylics because chlorine bleach is needed in *N*-halamine treatments,

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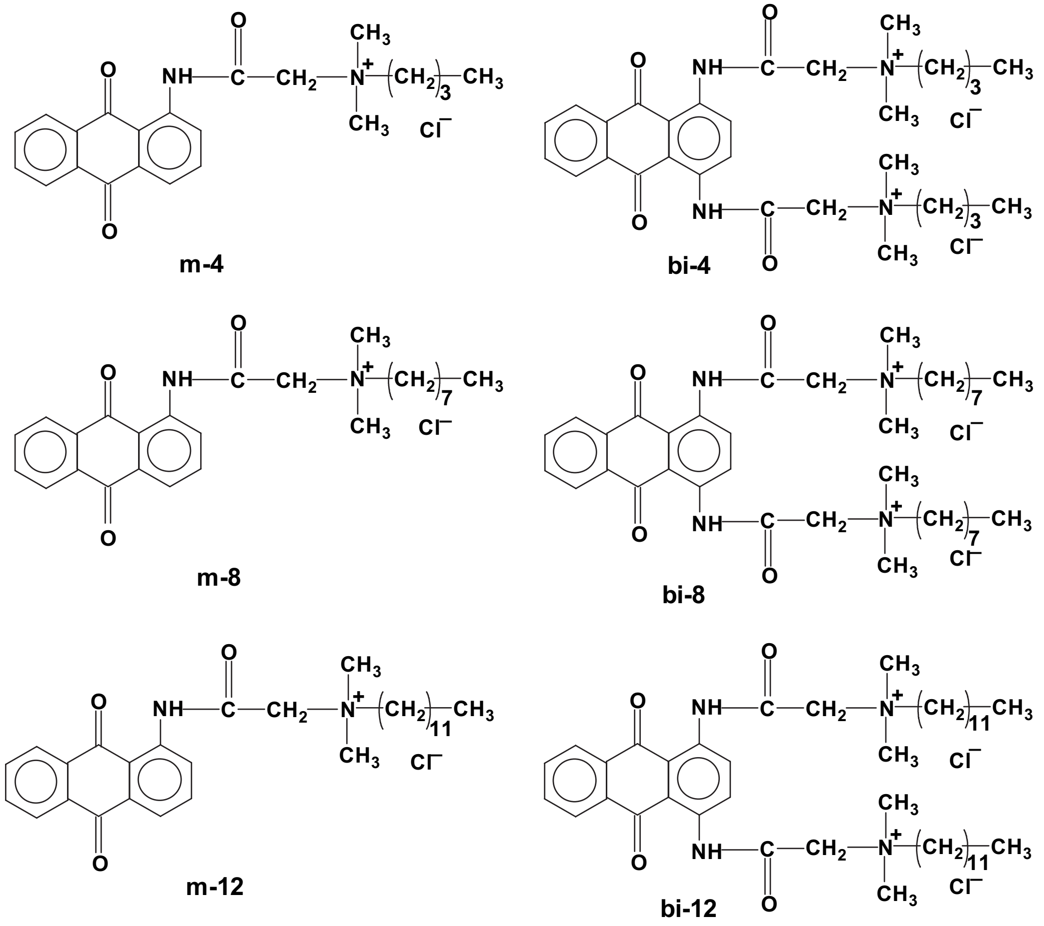

Fig. 1. Structures of the dyes.

while the use of QAS may occupy some available dye sites within the fabrics, thus to interfere the dyeing behaviors of the resultant fabrics.

In our previous study, antimicrobial cationic dyes have been successfully designed, synthesized and characterized (Fig. 1) [12]. In this paper, simultaneous dyeing and finishing of acrylic fabrics with these dyes will be investigated. It is expected that by simply following the traditional cationic dyeing process, these functional dyes will be incorporated into fabrics to provide color and antimicrobial functions simultaneously.

2. Experimental

2.1. Materials

Sulfonate-containing acrylic fabrics, spun *Orlon* 75 (#864), were purchased from Testfabrics Inc. (West Pittston, PA, USA). The fabrics were scoured in a solution of 5 g/L nonionic surfactant (Triton X-100, EM Science, USA) at 60 °C for 30 min, then rinsed thoroughly in tap water and dried in the open air. Sodium sulfate (EM Science, USA), sulfuric acid (EM Science, USA), sodium acetate (EM Science, USA) and acetic acid (99%, EM Science, USA) were used as received.

2.2. Methods

The dyeing of acrylic fabrics follows a traditional exhaustion dyeing procedure [9]. Dye solutions were prepared with the cationic dyes, sodium sulfate (2 g/L) and Triton X-100 (0.05%). The pH of the dyeing bath was adjusted to 3 by buffer solutions composed of sulfuric acid, sodium acetate and acetic acid. The bath ratio was kept at 1:50. The *Orlon* fabrics were immersed into the dyeing bath at initial dyeing temperatures for a certain period of time, and then fixed at 100 °C for another period of time to elevate the interactions between the fabrics and the dyes.

Hitachi U-2000 UV–vis spectrophotometer (Hitachi, Japan) was used to measure the UV–vis absorbance of the dye solutions before and after exhaustion. The concentration of dyes was calculated based on a previously established absorbance–concentration relationship at the λ_{max} of the dyes. Unfixed dye from the samples was extracted by hot water and also measured by the

UV–vis spectrophotometer. The amount of dyes fixed on the fabric (*F*, mMol/kg) was calculated by Eq. (1).

$$F = (N_0 - N_1 - N_2)/W \qquad (1)$$

where N_0 (μMol) is the initial dye quantity before exhaustion, N_1 (μMol) is the residual dye amount after exhaustion, N_2 (μMol) is the unfixed dye present in the extracted solution, and W (g) is the weight of untreated *Orlon* fabrics.

The antimicrobial activities of the treated *Orlon* were evaluated against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) according to American Association of Textile Chemist and Colorist (AATCC) test method 100-1999. Following this method, about 1 g of circular fabric swatches in disposable petri dishes was challenged with 1.0 ± 0.1 mL bacteria inoculum (containing 10^{5-6} colony forming unit of bacteria). After a certain period of contact time, the challenged fabric swatches were transferred to 250 mL containers filled with 100 mL of sterilized water, and the resultant supernatant was diluted to 10^1, 10^2, 10^3 and 10^4, respectively. Then 100 μL of each dilution were placed on a nutrient agar and incubated at 37 °C for 18 h. The same procedure was applied to an untreated *Orlon* fabric swatch as a control. Finally, viable bacteria colonies on the agar plate were counted, and the bacteria reduction was calculated using Eq. (2).

$$\text{Reduction percentage } (\%) = (A - B)/A \times 100\% \qquad (2)$$

where A represents the bacterial colonies in control, B represents the bacterial colonies in the dyed *Orlon* fabrics.

The surface resistivity of the treated fabrics was measured by a portable surface resistivity/resistance meter purchased from Monroe Electronics, Inc. (Model 272A). The visual color yields of the dyed fabrics were measured by GretagMacbeth™ Color-Eye® 7000A spectrophotometer (GretagMacbeth LLC, USA). The visual color yields of the fabrics were expressed by K/S values, which were derived from the reflectance measurement.

The treated fabric was also washed in a Launder-Ometer (Atlas, USA) according to AATCC Test Method 61-2001 to evaluate the wash durability of the treated fabrics. In this method, one cycle of a Launder-Ometer washing is considered equivalent to five machine washes in a home laundry.

3. Results and discussion

3.1. Effect of dyeing time

To investigate dyeing behavior of the dyes (Fig. 1), the effect of dyeing time was investigated, and the results are shown in Fig. 2. It can be seen that all the mono-substituted dyes showed higher fixation values than the corresponding bi-substituted ones. For example, the fixation of m-4 was higher than that of bi-4, and the fixation of m-8 was higher than that of bi-8. Also, for both mono-substituted and bi-substituted dyes, the fabrics exhibited increased fixation with the increase of alkyl chain length in the dyes.

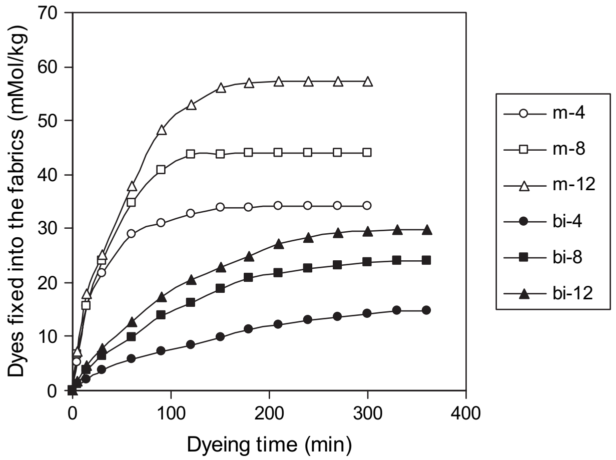

Fig. 2. Effect of dyeing time on acrylic dyeing (dye concentrations: 1 mMol/L; pH: 3; bath ratio: 1:50; dyeing temperature: 100 °C).

We believe that these results may be explained by the thermodynamic characteristics of the dyeing process. It is well established that dyeing of most fibers is a thermodynamically reversible process. Therefore, it is permissible to apply thermodynamic functions to the dye–fiber systems [8]. In a dye–fiber system, dyes are distributed in both the fiber and the dyebath. If A_f represents the activity of the dye in the fiber and A_d is the activity of the dye in the dyebath, then the chemical potential of the dye in the fibers (μ_f) and in the dyebath (μ_d) can be expressed as the following, respectively:

$$\mu_f = \mu_f^o + RT \ln A_f \quad \mu_d = \mu_d^o + RT \ln A_d$$

where $\mu_f{}^o$ and $\mu_d{}^o$ are the chemical potentials when the activity is unity, i.e. when the substance is in its standard state.

At equilibrium, μ_f equals to μ_d, therefore,

$$\mu_f^o + RT \ln A_f = \mu_d^o + RT \ln A_d$$

$$\text{and} \quad -\Delta\mu^o = -\left(\mu_f^o - \mu_d^o\right) = RT \ln \left(A_f/A_d\right) \qquad (3)$$

On dyeing, $-\Delta\mu^o$ is termed as the standard affinity and is a measure of the tendency of the dye to move from its standard state in the dyebath onto the fiber. If Van der Waals interactions between dyes and fabrics are stronger, then the value A_f is bigger, so is the value of $-\Delta\mu^o$. That is to say, with the increase of Van der Waals interactions between dyes and fabrics, more dyes may tend to move from the dyebath to the fiber, leading to higher fixation or dyeing results.

In our study, the bi-substituted dyes contain two positively charged nitrogen atoms in each structure. So compared to the mono-substituted ones, they are more favorable to stay in the dyebath. That is to say, $-\Delta\mu^{o}$ is lower for the bi-substituted dyes, so is the fixation. For both series, with the increase of alkyl chain length, the hydrophobicity of the dyes increases, suggesting that the dyes may become less favorable to stay in the dyebath. On the other hand, with the increase of alkyl chain length, the Van der Waals interactions between the fabrics and the dyes increase. So the total effect of longer alkyl chains is the increased $-\Delta\mu^{o}$, and thus higher fixation is observed in both mono-substituted and bi-substituted dyes with the increase of alkyl chain length.

Fig. 2 also showed that the mono-substituted dyes approached equilibrium after 120 min, while the bi-substituted ones needed as long as 300 min to level off. Again, we believe that this may be related to the thermodynamic characteristics of the dyeing process. Compared to the bi-substituted dyes, the mono-substituted ones are less favorable to stay in the dyebath. That is to say, they are more favorable to the fiber than the bi-substituted dyes in the dyeing, A_f and $-\Delta\mu^{o}$ may be higher, so more dyes may be driven to the fiber to occupy the dye sites, and the equilibrium is achieved faster.

It is worthy of mentioning that the fiber saturation value of *Orlon* 75 is 2.5% [9], which means 1 g of *Orlon* can bind 2.5% of a pure basic dyestuff called malachite green crystals ($M_W = 400$ g/Mol) if all the dye sites are occupied by the dye. Based on this definition, we can calculate that 1 g *Orlon* can bind 0.025 g malachite green crystals. That is to say, theoretically, 1 g *Orlon* can bind 0.0000625 Mol of the dye, or 1 kg of *Orlon* contains 62.5 mMol anionic dye sites.

Based on the results, the fixation of m-12 on the *Orlon* is around 60 mMol/kg, very close to the theoretical result; and that of bi-12 is around 30 mMol/kg, half of the calculated value. This difference might be caused by the fact that each mono-substituted dye occupies one dye site within the fabric during the fixation, while each bi-substituted dye may occupy two dye sites. However, the dyes with shorter alkyl chain, such as m-4, m-8, bi-4 and bi-8 showed lower fixation compared to the calculated results. Such a result may be caused by the weaker Van der Waals interactions present between the dyes and the fabrics, which makes A_f smaller and $-\Delta\mu^{o}$ lower (see Eq. 3). Therefore, compared to m-12 or bi-12, these dyes are more favorable to stay in the dyebath, so that they cannot fully occupy all the dye sites.

In addition, dye sizes may also play an important role in the acrylic dyeing. Smaller dyes may diffuse faster into the fabric, while the larger ones may diffuse slower. However, our calculation of the dye sizes indicates that all the dyes have maximum diameters within 1–2.5 nm, as shown in Table 1. Since all the dyes are small and the size difference is not significant, the above difference in fixation rates was not caused by the difference in diffusion of the dyes due to size difference.

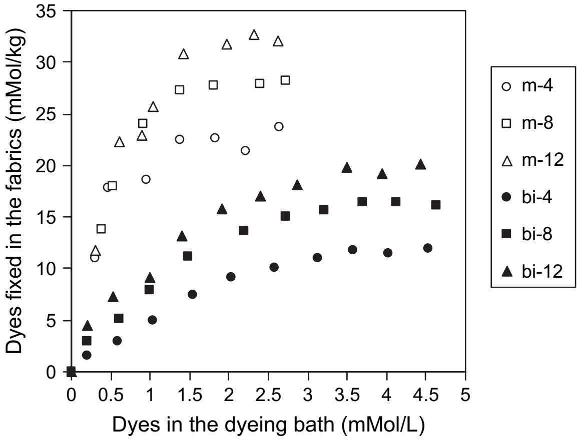

Fig. 3. Effect of dye concentrations on the acrylic dyeing (pH: 3; bath ratio: 1:50; initial dyeing temperature: 95 °C for 50 min; fixation: 100 °C for 10 min).

3.2. Effect of dye concentrations

The effect of dye concentrations was also studied in the acrylic dyeing, and the results are shown in Fig. 3. It can be seen that the overall trends observed in Fig. 3 were very similar to those in Fig. 2. For example, all the mono-substituted dyes showed higher fixation values than the corresponding bi-substituted ones, and for both series, the fabrics exhibited increased fixation with the increase of alkyl chain length in the dyes.

However, the fixed dye amount of each dye was lower in Fig. 3 than that in Fig. 2, which may be caused by the shorter dyeing and fixation period. Fig. 2 shows that to achieve saturation, the mono-substituted dyes need about 120 min, and the bi-substituted ones need 300 min. So if the total dyeing and fixation is only 60 min, it is not surprising to observe lower fixation values.

It should also be mentioned that the number of cations present in the dyes may also contribute to the different dye fixation values. As stated earlier, the bi-substituted dyes may occupy twice the amounts of dye sites within the fabrics compared to the mono-substituted ones. Therefore, theoretically one fixed bi-substituted dye should be equivalent to two mono-substituted dyes interacting with

Table 1
Molecular sizes of the dyes calculated by "HyperChem" software (edition 7.0) using semi-empirical, AM1 and geometry optimization

Dyes	m-4	m-8	m-12	bi-4	bi-8	bi-12
Maximum diameter (nm)	1.19	1.25	1.35	1.80	2.16	2.20

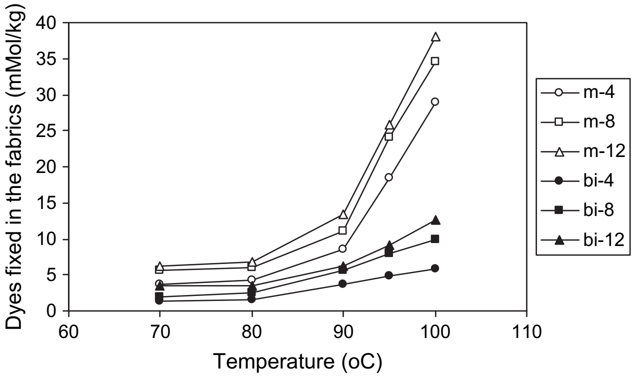

Fig. 4. Effect of initial dyeing temperatures on acrylic dyeing (dye concentrations: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 50 min; fixation: 100 °C for 10 min).

Orlon polymers if the dye sites are constant and fully occupied. However, if the dye sites are far from being fully occupied the number of cations present in the dyes may not become a major factor in determining the amount of fixed dyes shown in Fig. 3.

3.3. Effect of dyeing temperature

The effect of temperature on the acrylic dyeing was also investigated, and the results are shown in Fig. 4. It can be seen that below 80 °C, only a little amount of dyes were fixed into the *Orlon*. When the temperature changed from 80 °C to 90 °C, an increase around two folds of fixed dyes was observed for all dyes. When the temperature was increased from 90 °C to 100 °C, the amounts of fixed dyes increased about three folds in the mono-substituted dyes, and two folds in the bi-substituted ones.

Apparently, these observations are related to the glass transition temperature (T_g) of the fabrics. It was reported that in acrylic dyeing, only few dye molecules can enter the polymers below T_g due to the highly compact structure [7,9]. T_g denotes the temperature at which polymers change from a glassy state to a rubbery one. At a temperature above the T_g of the fiber, the movement of the polymer segments begins. With the further increase of the temperature, segment mobility becomes intensive, and the free volume may be increased exponentially within the polymers, then more dyes will be able to enter the polymers.

The study showed that unmodified polyacrylonitrile fibers had a very high T_g due to its highly compact structure, but the copolymerization of acrylonitrile with other co-monomers brought about a decrease in T_g [9]. Depending on the type of co-monomer used and the amount of co-monomer added, T_g of the acrylic fibers might vary from 60 °C to 80 °C [9]. Thus, at higher temperatures, the free volumes of acrylics may increase dramatically, and the accessibility of anionic dye sites and the rate of dye diffusion may also increase correspondingly. Therefore, in our study, the dye fixation began to increase around 80 °C, and the further increase of temperature lead to a dramatic increase in the dye fixation.

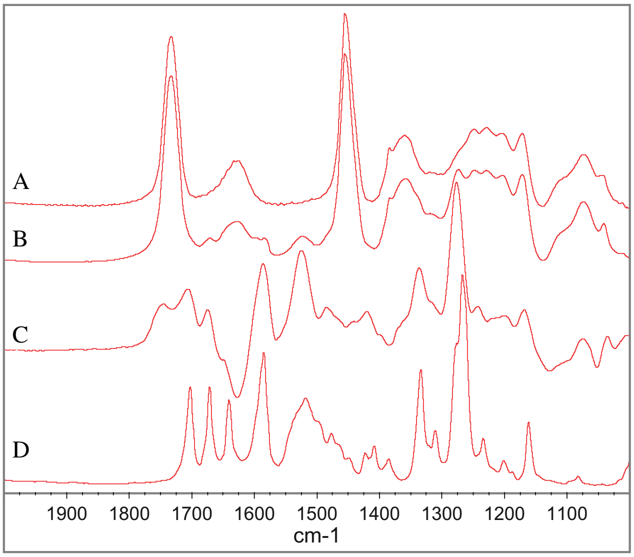

Fig. 5. FT-IR spectra of (A) untreated *Orlon*, (B) *Orlon* dyed with m-4 (dye concentrations: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 100 °C for 50 min; fixation: 100 °C for 10 min), (C) difference spectrum of B and A (subtracting A from B), and (D) pure m-4.

3.4. FT-IR analysis

Fig. 5 shows a typical example of FT-IR spectra in the range of 1000–2000 $\mathrm{cm^{-1}}$. In the spectrum of untreated *Orlon* (spectrum A), a strong adsorption band centered at 1732 $\mathrm{cm^{-1}}$ can be observed, which attributes to the carbonyl groups of the acrylate co-monomers. The weak peak at 1630 $\mathrm{cm^{-1}}$ is most likely caused by the impurities of the fibers [13]. In the spectrum of m-4 treated fabric (spectrum B), although several shoulders appear, they overlap with the 1630 $\mathrm{cm^{-1}}$ band; and the assignment of the new peaks is proven to be difficult. However, after subtracting spectrum A from spectrum B, their difference spectrum can be obtained (spectrum C), which represents the sum of the m-4 contributions to the dyed fabrics as well as any changes due to the interactions between the dye and the fabrics. It can be seen clearly in spectrum C that the 1630 $\mathrm{cm^{-1}}$ band disappears, and two new peaks centered at 1706 $\mathrm{cm^{-1}}$ and 1673 $\mathrm{cm^{-1}}$ appear. The peak at 1706 $\mathrm{cm^{-1}}$ can be attributed to the amide carbonyl group in the dyes, and the band around 1673 $\mathrm{cm^{-1}}$ may be caused by the carbonyl group present in the anthraquinone ring. These assumptions are further confirmed by the spectrum of pure m-4, as shown in spectrum D.

Different from the spectrum of *Orlon* treated by m-4, the *Orlon* treated with the bi-substituted dyes exhibits

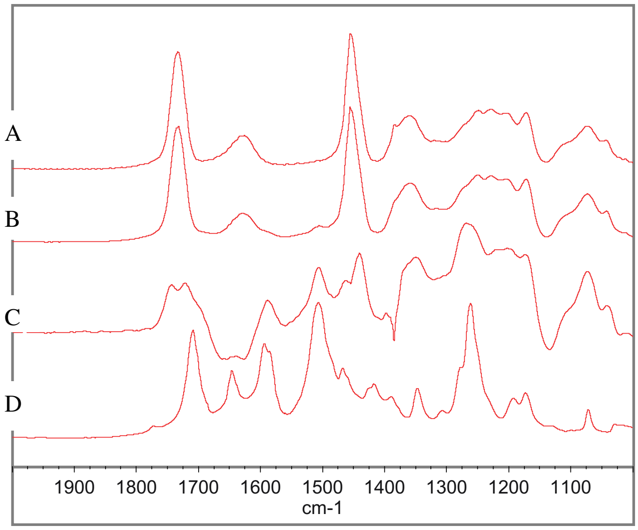

Fig. 6. FT-IR spectra of (A) untreated *Orlon*, (B) *Orlon* treated with bi-12 (dye concentrations: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 100 °C for 50 min; fixation: 100 °C for 10 min), (C) difference spectrum of B and A (subtracting A from B), and (D) pure bi-12.

a slightly different FT-IR spectrum pattern. As a typical example, in Fig. 6, spectrum B shows the spectrum of bi-12 treated *Orlon*. It can be seen that around 1630 cm^{-1}, the shoulders become less obvious. However, after subtracting spectrum A from spectrum B, their difference spectrum C also exhibits a new peak at 1718 cm^{-1}, corresponding to the amide carbonyl groups in the dyes.

Fig. 7 summarizes the FT-IR spectra of *Orlon* fabrics treated by both mono-substituted and bi-substituted dyes. It can be seen that all the fabrics treated with the mono-substituted dyes show very similar results, so do the fabrics treated by the bi-substituted ones. Therefore, it can be concluded that all the synthesized antimicrobial cationic dyes can be incorporated into *Orlon* fabrics by following the traditional cationic dyeing process.

3.5. The antimicrobial results

The antimicrobial efficacy of the treated *Orlon* fabrics was studied. Table 2 shows the effect of bacteria concentrations and contact time. It can be seen that with the increase of bacteria concentrations, the antimicrobial activities of fabrics decrease at each contact time. When *E. coli* concentration is lower than 10^7 CFU/mL, the treated fabrics show the highest antimicrobial efficacy after 6 h of contact. With the further increase or decrease of the contact time, the antimicrobial activities decrease. However, when the bacteria concentration is higher than 10^7 CFU/mL, the fabric can only show 86.7% of inactivation at 3 h of contact. Longer contact time leads to no kill at all.

It is believed that these phenomena may be explained by the antimicrobial mechanism of the dyes. It has been reported that quaternary ammonium salts (QAS), the active antimicrobial component of the dyes, kill microorganisms by disturbing their cytoplasmic

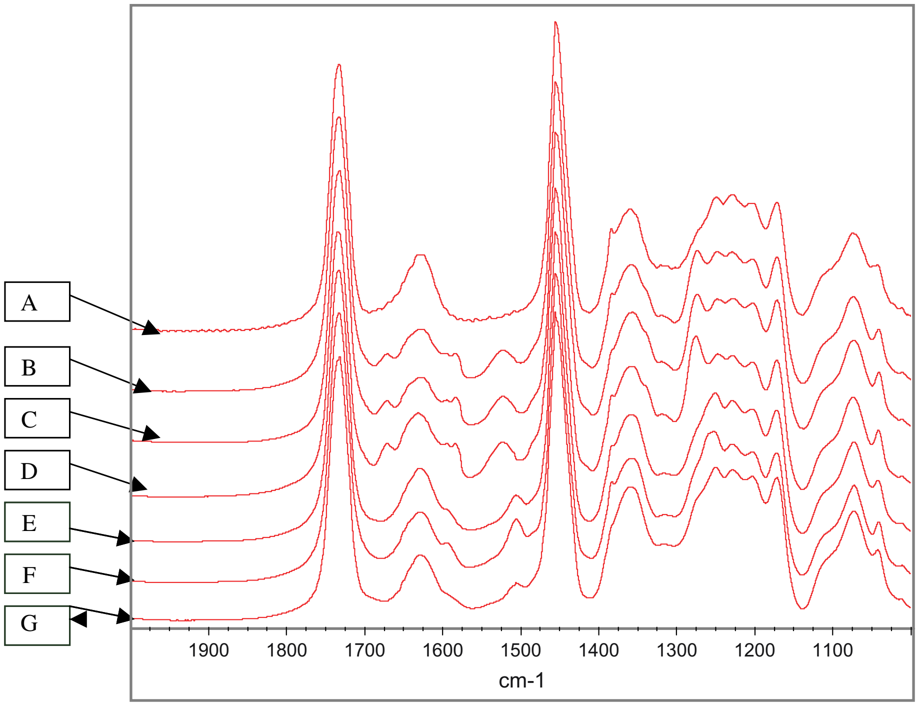

Fig. 7. FT-IR spectra of (A) untreated *Orlon*, (B) *Orlon* treated with m-4, (C) *Orlon* treated with m-8, (D) *Orlon* treated with m-12, (E) *Orlon* treated with bi-4, (F) *Orlon* treated with bi-8, and (G) *Orlon* treated with bi-12 (dye concentrations: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 100 °C for 50 min; fixation: 100 °C for 10 min).

Table 2
Effect of bacteria concentrations and contact time on antimicrobial efficacy

E. coli concentration (CFU/mL)	Contact time (h)			
	3	6	9	12
10^5–10^6	93.3%	99.9%	93.3%	66.7%
10^6–10^7	92.5%	95.8%	83.3%	50%
10^7–10^8	86.7%	0%	0%	0%

All fabrics were treated by 1 mMol/L bi-12 at pH 3. Dyeing: 100 °C for 50 min; fixation: 100 °C for 10 min. Bath ratio: 1:50.

membranes [14]. During this process, a competition may exist between the death and the growth of bacteria. When *E. coli* concentration is lower than 10^7 CFU/mL, in the beginning of the contact, the dyes may be able to kill the bacteria efficiently. When the contact time increases to 6 h, the antimicrobial efficacy also increases due to more efficient contact. However, further increase of contact time may use up all the available QAS, thus the growth of bacteria may become favorable, and decreased antimicrobial efficacy is observed. When the bacterial concentration is higher than 10^7 CFU/mL, the QAS concentration is relatively low compared to that of the bacteria, so even in the beginning, low antimicrobial efficacy is observed. It seems that all the available QAS may be used up quickly in this case, therefore, with the further increase of contact time, no bacterial reduction is observed.

All the treated *Orlon* fabrics were further challenged against *E. coli* and *S. aureus*. As shown in Tables 3 and 4, before washing, all the treated fabrics can provide efficient antimicrobial activities, but to different degrees depending on the dyes used. Generally speaking, for both mono-substituted and bi-substituted dyes, with the increase of alkyl chain length, the treated fabrics show higher antimicrobial efficacy. For example, the fabric treated by m-4 can kill 95.7% of *E. coli*, and the *Orlon* treated by m-12 can kill 99.9% in the same contact time. In most cases, the fabrics treated by the bi-substituted dyes exhibited higher antimicrobial efficacy compared to the ones treated by the corresponding mono-substituted dyes. For example, the fabric treated by bi-8 can kill 93.9% of *S. aureus*, and the fabric treated by m-8 can kill 92.4%. Also, all the treated fabrics show higher antimicrobial efficacy to *E. coli* than to *S. aureus*.

Table 4
K/S measurements of dyed *Orlon* fabrics after washing

Wash times		*Orlon* treated by					
		m-4	m-8	m-12	bi-4	bi-8	bi-12
0 wash	*K/S*	4.80	6.96	6.00	1.52	2.32	1.60
	λ_{max} (nm)	390	390	390	450	450	450
5 washes	*K/S*	4.72	6.88	5.80	1.52	2.20	1.52
	λ_{max} (nm)	390	390	390	450	450	450
10 washes	*K/S*	4.72	6.44	5.80	1.44	2.20	1.52
	λ_{max} (nm)	390	390	390	450	450	450
20 washes	*K/S*	4.72	6.32	5.78	1.44	2.20	1.52
	λ_{max} (nm)	390	390	390	450	450	450

As mentioned earlier, the active antimicrobial component of the dyes, QAS, kill bacteria by disturbing their cytoplasmic membranes. It has been reported that if the alkyl chain of QAS contained less than eight carbons, they could only show weak antimicrobial activities [15,16]. These results agree well with our findings in the antimicrobial testing. It is believed that the higher antimicrobial activities of the fabrics treated by the bi-substituted dyes are caused by the higher QAS contents in the dyes, and the higher antimicrobial efficacy to *E. coli* may also be related to the fact that *E. coli* shows less resistance to mechanical rupture compared to *S. aureus* [17].

However, Table 3 shows that the washing durability of the treated fabrics was low. For example, after five washes, the fabric treated by m-12 can only kill 81.3% of *E. coli*, after 10 washes, the antimicrobial activities disappear totally. The fabrics treated by bi-12 are a little better. After five washes, the fabric can still kill 99.3% of *E. coli*, after 10 washes, the antimicrobial efficiency drops to 60%. However, after 20 washes, the antimicrobial efficacy is also totally vanished.

Table 3
Antimicrobial efficacy of the dyed *Orlon* fabrics

Wash times	Bacteria	*Orlon* treated by					
		m-4	m-8	m-12	bi-4	bi-8	bi-12
0 wash	*E. coli*	95.7%	98.6%	99.9%	97.1%	98.6%	99.9%
	S. aureus	86.4%	92.4%	99.9%	87.5%	93.9%	99.9%
5 washes	*E. coli*	44.0%	44.0%	81.3%	37.5%	50.0%	99.3%
	S. aureus	50.0%	37.5%	75.0%	36.4%	50.0%	81.8%
10 washes	*E. coli*	0%	0%	0%	0%	46.7%	60.0%
	S. aureus	0%	0%	0%	0%	37.5%	45.5%
20 washes	*E. coli*	0%	0%	0%	0%	0%	0%
	S. aureus	0%	0%	0%	0%	0%	0%

All fabrics were treated by 1 mMol/L of the dye at pH 3. Dyeing: 100 °C for 50 min; fixation: 100 °C for 10 min. Bath ratio: 1:50. *E. coli* or *S. aureus* concentration: 10^5–10^6 CFU/mL; contact time: 6 h.

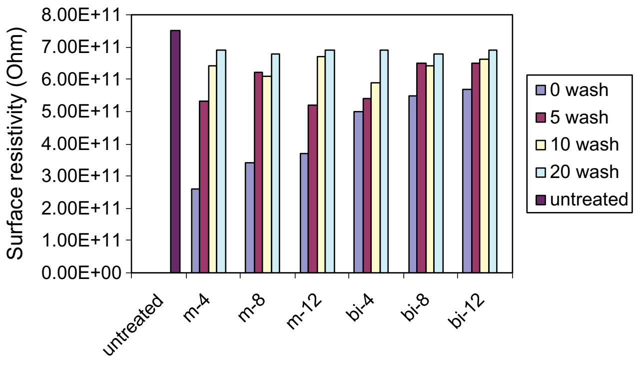

Fig. 8. Surface resistivity of the treated *Orlon* fabrics.

It is believed that the low washing durability of the treated *Orlon* may be caused by the loss of dyes during washing. To confirm this assumption, the surface resistivity of the same fabrics was measured and the results are shown in Fig. 8. It can be seen that all the dyed fabrics showed lower resistivity than the untreated *Orlon*, indicating that the electric conductivity of the dyed fabrics are higher due to the incorporation of the cationic dyes. However, with the increase of washing times, the surface resistivity increases, indicating a decrease in the conductivity of the fabrics. We believe that this decrease must be caused by the loss of some dyes, which agrees well with our antimicrobial results.

To further confirm the dye loss during washing, the K/S values of the same samples were also measured, and the results are listed in Table 4. It can be seen that the K/S values also show a slight decrease after washing, however, the change is not significant, indicating that the visual effects are not influenced significantly.

Due to the hydrophobic nature of *Orlon* fabrics, there may not be sufficient contact between the fabrics and the bacterial or detergent solutions during the experiments. It is believed that the fixed dyes may be divided into water accessible and water inaccessible parts when the temperature is below the T_g of the fabrics. The water accessible dyes mainly locate on the surface of the fabrics. In the antimicrobial testing, it is the water accessible dyes that contribute to the antimicrobial efficacy of the treated *Orlon* since only they can come into contact with the bacteria and thus kill the bacteria. During washing, it is also these water accessible dyes that may be washed away since they can come into contact with the detergent solutions, the water inaccessible dyes may not be affected much by washing. So after washing, the antimicrobial activities of the treated fabrics dropped significantly, possibly due to the loss of water accessible dyes. Meanwhile, the surface resistivity indicates the amount of dyes bound to the surface of the fabrics. It is believed that most of these surface dyes are water accessible and will be lost during washing. Therefore, after washing, the surface resistivity of the fabrics also exhibited big difference compared to that of the unwashed ones. However, K/S measures the shade depth of the fabrics [18], which indicate the total visual effect to the human's eye. Both the water accessible dyes and the water inaccessible dyes inside the fabrics may contribute to the shade depth. Therefore, the total visual effect may not be affected significantly by the loss of the water accessible dyes.

It is also worth mentioning that after dyeing, all the dyes showed a different λ_{max} in the fabrics compared to that in aqueous solutions [12]. For example, the *Orlon* fabric treated by m-4 exhibited a λ_{max} at 390 nm, while the aqueous solution of m-4 had a λ_{max} at 379 nm. As mentioned earlier, K/S measures the shade depth of the fabrics [18]; it is influenced by the dye concentration, the physical states of the dyes, as well as the surface structures of the fabrics. Apparently, the physical states of the dyes in the fabrics are different from those in the aqueous solutions, thus a bathochromic shift of the dyes is observed in the *Orlon* fabrics. Table 4 also showed that all the treated fabrics did not change the λ_{max} during washing, indicating that all the fixed dyes were stable, no decomposition or other structural change occurred during washing.

4. Conclusions

Orlon fabrics were dyed by the antimicrobial cationic dyes, and the dyed fabrics were challenged with bacteria cultures. As expected, both the mono-substituted and the bi-substituted dyes could be introduced into orlon by following traditional cationic dyeing procedures. All the mono-substituted dyes showed higher fixation than the corresponding bi-substituted dyes. For both series, the fixation increased with the increase of alkyl chain length in the dyes. All the treated fabrics exhibited antimicrobial efficacy against *E. coli* and *S. aureus*. However, the washing durability of the treated fabrics was low, possibly caused by the loss of dyes on fiber surfaces during washing. The measurement of surface resistivity and K/S values of the same fabrics further confirmed that wash might cause dye loss.

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References

[1] Dong YC, Wang JJ, Liu PF. Coloration Tech 2001;117(5):262.
[2] Raheel M, Guo C. Text Res J 1998;68(8):571.

[3] Choi HM, Srinivasan M, Morris NM. J Appl Polym Sci 1994; 54(13):2107.

[4] Sharma P, Gahlot M. Man-made Text India 2002;45:257.

[5] Shyu JP, Cheng CC. Am Dyestuff Rep 1992;81:60.

[6] Nasr HI, Abdel-Fattah SH, El Kharadly EA. Radiat Phys Chem 1980;16:491.

[7] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. Glasgow: Blackie Academic & Professional, Chapman & Hall; 1995.

[8] Bird CL, Boston WS. The theory of coloration of textiles. London: Dyers Company Publications Trust; 1975.

[9] Munn DM. The dyeing of synthetic-polymer and acetate fibres. England: Dyers Company Publications Trust; 1979.

[10] Sun YY, Sun G. J Appl Polym Sci 2002;84:1592.

[11] Kim YH, Sun G. Text Res J 2002;72(12):1052.

[12] Ma M, Sun Y, Sun G. Dyes Pigments 2003;58:27.

[13] Sun YY, Shao ZZ, Ma MH, Hu P, Liu YS, Yu TY. J Appl Polym Sci 1997;65:959.

[14] Latlief MA, Goldsmith MT, Friedl JL, Stuart LS. J Pediatr 1951; 39:730.

[15] Pavlikova-Moricka M, Lacko I, Devinsky F, Masarova L, Mlynarcik D. Folia Microbiol 1994;39(3):176.

[16] Devinsky F, Kopecka-leitmanova A, Sersen F, Balgavy P. J Pharm Pharmcol 1990;42:790.

[17] Hugo WB. J Appl Bacteriol 1967;30(1):17.

[18] Yang YQ, Li SQ, Stewart N. AATCC Rev 2003;3:29.