Spectral, dyeing and antimicrobial properties of some monoazo naphthalimide dyes on polyamide

H Shaki1, K Gharanjig2,3,a & A Khosravi1

1Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran
2Department of Organic Colorants, Institute for Color Science and Technology, Tehran, Iran
3Center of Excellence for Color Science and Technology, Tehran, Iran

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A series of monoazo disperse dyes based on naphthalimide has been applied on to the nylon fabrics. The build-up values and dyeing properties of these dyes, such as leveling, and wash, light and rub fastnesses on nylon fabrics have been assessed. The dyes N-2-aminomethylpyridine-1,8-naphthalimide-azo-4″-N,N-diethyl meta toluidine (A) and N-2-aminomethylpyridine-1,8-naphthalimide-azo-2″- acetylamino-4″- N,N- diethyl aniline (B) show higher build-up values on polyamide fabrics as compared to the dyes N-2-aminomethylpyridine-1,8-naphthalimide-azo- 4″- N-hydroxy ethyl-N- ethyl aniline (C) and N-2-aminomethylpyridine-1,8-naphthalimide-azo- 4″- N-hydroxy ethyl-N- ethyl aniline quaternized with 1- bromobutane (D). All of the applied dyes exhibit excellent rub fastness, good wash fastness and moderate light fastness on nylon fabrics. In addition, the molar extinction coefficient, wavelengths of the maximum absorption and solvatochromism effects have also been studied using chloroform, toluene, and DMF as solvents. Positive solvatochromism occurs when toluene is replaced by DMF as solvent. The antimicrobial properties of dyed fabrics are evaluated against various bacteria; the dyed fabrics exhibit antimicrobial efficacy against both Gram-positive and Gram-negative bacteria.

Keywords: Antimicrobial activity, Monoazo dyes, Nylon fabric, Polyamide, Spectral property

1 Introduction

Textile polymers offer some sorts of exceptional media for microorganisms to grow and hence increase the cross-transmission of disease in hospitals, unhealthy indoor air quality in working areas which is stimulated by contaminated textiles1, 2. Besides, body odor and dermal interactions are created by these microorganisms. Pathogenic bacteria may result in many human diseases.

For preparing antimicrobial textile polymers, the substrates should be treated with antimicrobial agents like quaternary ammonium salts, phenolic compounds, polyamines and nanosilvers during finishing stage. Generally, in the case of textile fibres, antimicrobial finishing is carried out after dyeing. Combining dyeing and antimicrobial finishing stages reduce water and energy consumption, processing time and wastewater production3. Antimicrobial functional dyes should possess appropriate dyeing and antimicrobial finishing properties2, 4. For this purpose, the designing of chemical structures and synthesis of functional dyes are of great importance. From this point of view, many functional dyes have been introduced to prepare colored antimicrobial fabrics to date. These dyes as cited earlier are applied both as coloring matter and as antimicrobial agent on the textile fibres.

One group of dyes with significant antifungal activity is based on heterocyclic rings; these compounds were prepared by heating pyrazolylhydrazonomalononitriles with hydrazine monohydrate5. The synthesized dyes show positive solvatochromism effects with good antimicrobial properties in different solutions.

It is well known that some of azo disperse dyes based on sulfonamide derivatives have biological activities against Gram-positive, Gram-negative and fungi on wool and nylon fabrics6. These dyes show a range of very brilliant colors on wool and nylon with high light and wash fastness values. Also, disazo dyes containing urea and sulfonamide moieties were synthesized to impart antimicrobial property. These dyes show antifungal activity in vitro against Salmonella typhi, Shigella sonnei and Candida albicans7.

Azonaphthalimides containing thiosalicylic or salicylic acid functionalities were used as antibacterial acid dyes for dyeing polyamide fabrics2. These dyes

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Corresponding author.
E-mail: gharanjig@ icrc.ac.ir
exhibit antibacterial activity against both Gram-positive and Gram-negative bacteria and used successfully for dyeing polyamide fabrics with acceptable fastness properties.

In our previous work, we reported synthesis and characterization of four novel monoazo dyes based on N-pyridine-1,8-naphthalimide. In addition, we studied antimicrobial properties of the synthesized dyes in solutions. In this paper, we report application of these dyes on nylon 6 fabrics and study on the antimicrobial activities of the dyed fabrics. The dyeing properties of these dyes such as build-up, leveling and color fastness have also been investigated.

2 Materials and Methods

2.1 Materials and Apparatus

All compounds used in this study were of analytical grade unless otherwise stated. The UV-Visible spectra of dyes were measured with a Cecil 9200 double beam spectrophotometer. The parameters \( \lambda_{\text{max}} \), \( \epsilon \), \( \Delta \lambda_{1/2} \) and solvatochromic effects of dyes have been determined. Nylon 6 fabrics (Alyaf Co., Iran) were utilized in the study. The colorimetric data were obtained by a Gretag Macbeth 7000A spectrophotometer (D65 illumination, 10 \(^\circ\) observer). The light, wash and rub fastness values of all the samples were measured according to BS 1006-1990 UK-TN, ISO105-A02:1993 and ISO 105-X12:1993(E) standards respectively.

To study the antibacterial effects, the Gram-positive bacteria \textit{Staphylococcus aureus} (ATCC25923) and the Gram-negative bacteria \textit{Escherichia coli} (ATCC25922) were provided by The Culture Collection Centre, Shahid Beheshti University, Tehran, Iran.

2.2 Preparation of Dyes

The monoazo Dyes A-C were synthesized by reacting 4-amino-N-2-aminomethylpyridine-1,8-naphthalimide as the diazo component with N,N-diethyl-meta-toluidine, 3-(N,N-diethylamino) acetonilide and N-hydroxyethyl-N-ethyl aniline respectively as the coupling components. The Dyes A-C were prepared by the following general procedure. Sodium nitrite (2 mmol) was added to 1 mL of sulphuric acid (98\%) at temperature \( T < 10 \, ^\circ \text{C} \). The temperature of the reaction was increased to 65 \(^\circ\)C till all the sodium nitrite was dissolved. The solution was then cooled down to \( T < 10 \, ^\circ \text{C} \), then 2 mmol 4-amino-N-2-aminomethylpyridine-1,8-naphthalimide was added and the reaction mixture was stirred for 3 h below 10 \(^\circ\)C. The diazonium salt was added gradually within 30 min to a solution of the coupling components (2 mmol) dissolved in 1 mL of acetic acid and stirred for 1 h below 10 \(^\circ\)C. The pH was maintained in the range of 4-5 by adding saturated sodium acetate solution. The mixture was stirred for 3 h, filtered to get precipitate, washed with hot water and dried. Dye D was prepared by mixing a solution of Dye C (0.47 mmol) and 6.4 mmol 1-bromobutane in 5 mL dry acetonitrile. The mixture was heated to 90 \(^\circ\)C for 72 h. The final product (Dye D) was obtained by precipitation from THF solvent. The chemical names and structures of four synthesized dyes are illustrated in Fig. 1.

2.3 Determination of Spectral Properties of Dyes A-D

Solutions of all the four Dyes A-D in the concentration of \( 1 \times 10^{-4} \text{ mol L}^{-1} \) were prepared in various solvents such as chloroform, toluene and N,N-dimethyl formamide (DMF), and the visible absorbance values (optical densities) were measured at the wavelength of maximum absorption with a Cecil 9200 double beam spectrophotometer. The half-band widths (\( \Delta \lambda_{1/2} \)), the molar extinction coefficients (\( \epsilon \)) and the wavelengths of maximum absorption (\( \lambda_{\text{max}} \)) of the dyes were determined.

2.4 Preparation of Dye Dispersion

Four dispersions containing dye (0.5 g), dispersing agent (Lyoprint EV, Ciba, 1g) and water (2 mL) were milled for 60 min in a mortar. The resulting mixture was diluted with 20 mL of water, transferred to a ball mill and milled again for another 20 h. The volume of the dispersion was adjusted to 100 mL and filtered through a 5 \( \mu \)m Micro-Prazisions Sieb Fritsch.

2.5 Dyeing Procedure

Heat setting of fabrics was carried out before dyeing of fabrics in a stenter. The setting time and temperature were 190 \(^\circ\)C and 20 s and 190\(^\circ\)C respectively. The polyamide fabric samples (1 g) were dyed in a dye bath consisting of dispersions, wetting agent (Irgasol DAM, Ciba Co.), and acetic acid (pH 4-5) with an L:G ratio of 50:1 according to the dyeing profile (Fig. 2). When the dyeing cycle completed, the polyamide fabric samples were removed from the dye bath, washed off with water thoroughly and dried at room temperature.

2.6 Antimicrobial Assessment of Fabrics

The antimicrobial activities of dyed polyamide fabrics were tested according to AATCC test method 100-1999. In this method, about 1 g of circular fabric,
swatched in disposable petri dishes, were exposed to 1.0 ± 1.0 mL of bacteria inoculums (containing $10^5$-$10^6$ 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 mL of each dilution was placed on a nutrient agar and incubated at 37°C for 18 h. The same procedure was applied to an untreated polyamide fabric swatch as a control sample. Finally, viable bacteria colonies on the agar plate were counted. The reduction of bacteria was calculated using the following equation:

$$R(\%) = [(A-B)/A] \times 100\% \quad \ldots (1)$$

where $A$ is the number of bacterial colonies in control; $B$, the number of bacterial colonies in the dyed fabric; and $R$, display the reduction percentage of bacterial colonies.

3 Results and Discussion

3.1 Spectral Properties

Relationship between color and constitution is a highly interesting aspect of dye development and commercialization. In this context, the wavelengths of maximum absorption, molar extinction coefficients and half-band widths ($\Delta\lambda_{1/2}$) are important parameters for dyes. A higher extinction coefficient and a broader half-band width are attributed to a stronger chromophore which make the final product more cost effective. The UV-Visible absorption data for Dyes A-D were determined in toluene, chloroform and DMF as solvent (Table 1).

The molar extinction coefficients of the dyes in DMF vary from $1.0031 \times 10^4$ to $3.4277 \times 10^4$ l mol$^{-1}$ cm$^{-1}$. The molar absorption coefficient of dyes increases as maximum wavelength of absorption is increased. This finding is founded according to Thumb rule.
For the synthesized dyes molar absorption coefficient values tend to rise with increasing electron withdrawing capacity in the acceptor ring and increasing electron donating group in coupler component. In this respect, the presence of electron acceptor group (naphthalimide ring) in diazonium component and electron donating group on coupler can increase molar absorption coefficient considerably. Dye B shows the highest value of extinction coefficient while Dye D shows the lowest. This can be explained by the existence of NHCOCH₃ electron donating group on the coupling component structure at ortho position of the azo linkage. Generally, red dyes are based on the acylamino derivatives; which have brighter in hue and higher tinctorial strength than un-substituent azo dyes. Recent evidence suggests that intramolecular hydrogen-bonding is responsible for these effects. In this work, CH₃ (Dye A) and NHCOCH₃ (Dye B) groups are electron donor groups located in the ortho position of the azo linkage. However, NHCOCH₃ (Dye B) group is a stronger electron donor group, therefore it has the highest molar absorption coefficient. Results show that the Dyes A-C according to their molar extinction coefficient (ε) values are in the order of Dye C< Dye A< Dye B. The lower extinction coefficients of Dye C and D are ascribed to the lower electron donating ability of N-ethyl-N-hydroxyethyl group in comparison with amine groups. The molar extinction coefficient of Dye C is higher than Dye D because of a quaternary ammonium alkyl group present in the structure of Dye D; quaternary ammonium alkyl groups decrease color intensity of dyes.

The λ_max values show the position of the most intense absorption band, which depends on the possibility of dye existing in the azo or the hydrazone form. The λ_max of the Dyes A-D in DMF are between 530 nm and 562 nm. Comparison of λ_max values of the dyes shows that they follow the order of Dye B > Dye A > Dye C > Dye D whereas in a less polar solvent (toluene) they lie somewhere between 510 nm and 530 nm (Table 1).

Quite a lot of properties of chemical structures of dyes depend on the nature of their solvents. The solvents change the absorbance spectra characteristics of the dissolved molecules. In some cases, this phenomenon is revealed by solvent-induced differences that has caused in electronic spectra. This property is called solvatochromism. Many factors influence the spectral behavior of dissolved dyes, especially polarity of solvents, temperature and hydrogen bonding donating or accepting capacity. Strong solvatochromic properties are examined for dipolar molecules demonstrating large variations in their dipole moment during electronic transitions. These variations can stabilize the ground and/or the excited state in polar and non-polar solvents. The solvatochromic effect is negative if hypsochromic shifts are observed with increasing solvent polarity. Positive solvatochromism occurs when bathochromic shifts are observed under the same circumstances. In all the dyes, λ_max increases with increasing the solvent polarity. By changing the solvent from toluene to DMF, positive solvatochromism (Δλ_max, 20-32 nm) is observed. The highest and lowest bathochromic shifts are observed in Dyes B and D respectively.

The half band width (Δλ₁/₂) can be taken as an acceptable parameter for the elucidation of the dyes brightness. The dyes with lower values of Δλ₁/₂ show brighter hues in comparison to those with higher Δλ₁/₂, which provides dull hues. Table 1 shows the brightness of the Dyes A-D according to their Δλ₁/₂ values in the order of Dye C< Dye B< Dye A< Dye D (Table 1). The lowest Δλ₁/₂ belongs to Dye B in which 3-(N,N-Diethy lamino) acetanilide is used as coupling component. The higher brightness of Dye B might be ascribed to the intramolecular hydrogen bonding between azo linkage and acetylamino groups. The presence of -NHCOCH₃ group at ortho position of the azo linkage in Dye B causes a decline in its Δλ₁/₂. Therefore, the brightness of Dye B is higher than other dyes, while the highest Δλ₁/₂ value belonged to Dye C (4-amino-N-2-

<table>
<thead>
<tr>
<th>Dye</th>
<th>Toluene λ_max, nm</th>
<th>Cloroform λ_max, nm</th>
<th>DMF λ_max, nm</th>
<th>DMF ε, 1 mol⁻¹ cm⁻¹</th>
<th>Toluene-DMF Δλ_max, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>519</td>
<td>533</td>
<td>548</td>
<td>2.319±10⁶</td>
<td>118</td>
</tr>
<tr>
<td>B</td>
<td>530</td>
<td>544</td>
<td>562</td>
<td>3.427±10⁶</td>
<td>108</td>
</tr>
<tr>
<td>C</td>
<td>512</td>
<td>522</td>
<td>536</td>
<td>1.645±10⁶</td>
<td>123</td>
</tr>
<tr>
<td>D</td>
<td>510</td>
<td>519</td>
<td>530</td>
<td>1.003±10⁶</td>
<td>119</td>
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aminomethylpyridine-1,8-naphthalimide as a diazo component and N-hydroxyethyl-N-ethylaniline as a coupling component).

3.2 Dyeing Properties

All the prepared dyes have been applied on polyamide fabrics as explained in experimental section. Figure 3 illustrates the build-up curves of Dyes A-D. It is apparent that they generally attain saturation at dye concentrations of about 2% owf. The results reveal that Dye B has the highest build up value on the polyamide fabric samples (K/S >20, where K and S are absorption coefficient and scattering coefficient of dyed sample respectively), whereas Dye D has a poor build-up value (K/S<15). In these series, Dyes A-C are disperse dyes and Dye D is a cationic dye. Therefore, the mechanism of their adsorption on polyamide fabrics is different. Dye D as a cationic dye is adsorbed onto the anionic sites of polyamide fabrics. Since these sites on polyamide fibres are limited, the build-up value of the applied cationic dye is lower than the others. However, the synthesized disperse dyes may have some advantages to conventional acid dyes for dyeing of polyamide fibres. Disperse dyes have good migration and levelness on polyamide fibres. They generally cover stripiness on polyamide fibres. In addition, these dyes give both the color and antimicrobial properties to substrate. Simultaneous dyeing and functional finishing of textiles offer economical and environmental advantages in textile manufacturing. In addition, it might be used for dyeing of modified nylon.

The color characteristics of the dyed polyamide fabric samples were measured at 1/1 standard depth according to ISO 105-A06 (Table 2). Results show that the value of a* and b* are positive and negative respectively. This means that the dyed fabrics have a bluish red hue. The visual observations of dyed samples show that the used dyes have good leveling properties on polyamide fabrics.

The light, wash and rub fastness values are presented in Table 3. The wash fastness and rub fastness of all dyes are good to excellent (4 - 5), while their light fastness varies from poor to moderate (3-4) (Table 3). Influencing factors on light fastness property of dyes based on aminoazobenzene are intricate. However, it has been identified that many dyes fade much faster in the presence of oxygen. Oxidative reaction of azo dyes has been joining together with cleavage azo linkage. Generally, dyes with acceptor group in the diazo component and electron donating group on the coupler have high light fastness property. These factors result in lowering of electron density at the nitrogen atoms in both diazo and couplers components. Accordingly, Dyes B and C contain electron donor on coupler and hence have relatively better light fastness than Dye C. Dye D has a cationic charge in the diazo component. Therefore, it reduces electron density of nitrogen atom of azo group. This phenomenon may cause increment of light fastness of dyed fabrics.

3.3 Antimicrobial Property

Antimicrobial property of the treated nylon fabrics has been evaluated against *E. coli* and *S. aureus*. Table 4 illustrates the effects of antimicrobial efficacy of the dyed nylon fabrics in various dye concentrations. It can be observed that with increasing
the dye concentrations, the antimicrobial activities of fabrics also increase at contact time. The results show that Dye D shows the best antimicrobial properties than other dyes. It is believed that this phenomenon may be explained by the antimicrobial mechanism under which Dye D features. It has been reported that quaternary ammonium salts (QAS), the active antimicrobial component of the dyes, kill microorganisms by penetrating their cytoplasmic membranes.  

<table>
<thead>
<tr>
<th>Dye</th>
<th>Bacteria</th>
<th>Dyes concentration</th>
<th>A</th>
<th>B</th>
<th>R²</th>
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<tbody>
<tr>
<td>A</td>
<td>E. coli</td>
<td>2</td>
<td>200000</td>
<td>157000</td>
<td>21.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
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<td>144400</td>
<td>27.80</td>
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<tr>
<td></td>
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<td>361500</td>
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<tr>
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<tr>
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<td>155200</td>
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</tr>
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<td></td>
<td></td>
<td>4</td>
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<td>141600</td>
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<td></td>
<td></td>
<td>4</td>
<td>544400</td>
<td>238200</td>
<td>56.25</td>
</tr>
</tbody>
</table>

R=(A-B)/A x 100. E. coli and S. aureus concentrations: 10⁻⁵⁻¹⁰⁶ CFU/mL, Contact time: 1 h.

4 Conclusion

It is observed that the dyed polyamide fabric samples produced bluish-red shades with generally good build-up values. The color of dyed fabrics and the color of the dyes in solution are showed in good correlation. The spectrophotometric properties of the monoazo disperse dyes in various solvents are also examined. The visible absorption data for the dyed samples show that the color of the dye is influenced by the introduction of additional donor groups into the coupling component structure. The wavelengths of maximum absorption are in the order of Dye B > Dye A > Dye C > Dye D and the molar extinction coefficients of the dyes in DMF vary within the range from 1.0031 x 10⁴ to 3.4277 x 10⁴ l mol⁻¹ cm⁻¹. Dyeing properties and light, wash and rub fastness values of dyed polyamide fabrics are also evaluated. All the dyes offer excellent rub fastness, good wash fastness and weak to moderate light fastness on polyamide fabrics. All dyed fabrics also exhibit antimicrobial efficacy against E. coli and S. aureus bacteria.

References