

# Dyeing and Fastness Properties of Polyamide Fabrics Using Some Acid-Based Monoazo Disperse Dyes

M. Sadeghi-Kiakhani,<sup>1</sup> K. Gharanjig,<sup>2</sup> M. Arami,<sup>1</sup> A. Khosravi<sup>3</sup>

<sup>1</sup>Faculty of Textile Engineering, Amirkabir University of Technology, Tehran, Iran

<sup>2</sup>Institute for Colorants, Paint, and Coatings, Department of Organic Colorants, Tehran, Iran

<sup>3</sup>Faculty of Polymer and Color Engineering, Amirkabir University of Technology, Tehran, Iran

Received 19 September 2010; accepted 23 February 2011

DOI 10.1002/app.34418

Published online 12 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A series of monoazo disperse dyes derived from naphthalimide containing butyric acid has been applied on polyamide fabrics. The build up and dyeing properties of these dyes such as leveling property, wash, light, perspiration for alkaline and acidic conditions, and rubbing fastnesses on polyamide fabrics have been investigated. The results showed that the applied dyes are capable of producing red to bluish red hues on polyamide fabrics. Because of the presence of both carboxylic acid and hydroxyl groups on the molecular structure of Dye 3, it showed desired and more strength in respect to other used dyes. Comparing the build up of these dyes

to commercial dyes such as disperse red 60 and disperse red 73 revealed that most of the used dyes have higher build up in comparison to the commercial ones. Measurement of fastness properties of dyed samples indicated that they have good wash (4–5), rubbing (4), perspiration (4–5), and heat fastnesses (4–5) and they possess less than moderate light fastness (3–4) on polyamide fabrics. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3390–3395, 2011

**Key words:** naphthalimide; polyamide fabrics; azo dyes; fastness properties; dyeing

## INTRODUCTION

Polyamide can be dyed with a variety of dye classes; due to the affinity of disperse dyes to nylon, they can be used to dye polyamides, while the presence of polar groups on the fiber allows the use of acid dyes.<sup>1,2</sup> Acid dyes are likely to be adsorbed through interaction with terminal amine ( $-\text{NH}_2$ ) groups in the polyamide chains and also through nonionic interactions with groups along the chains. However, the number of these amine groups in polyamide fiber is limited, thus polyamide fibers can be saturated with acid dyes at only moderate depths of shade. Since some of the acid dyes are relatively susceptible to chemical affinity variations therefore it can cause stripiness on nylon fibers.<sup>1</sup> As a result the disperse dyes which are nonionic can be utilized on the polyamide fibers to achieve good leveling properties.

Disperse dyes have very low solubility in water,<sup>3</sup> because of that these dyes are used as finely divided aqueous dispersions for dyeing of polyamide fibers. For this purpose, dispersing and wetting agents are used during dyeing of polyamide fibers. The nature of binding of disperse dyes to hydrophobic fibers

has been debated by various researchers, but solid solution mechanism is accepted by many of them. The solid solution mechanism proposes that the disperse dyes are simply dissolved by the hydrophobic fibers.<sup>4</sup>

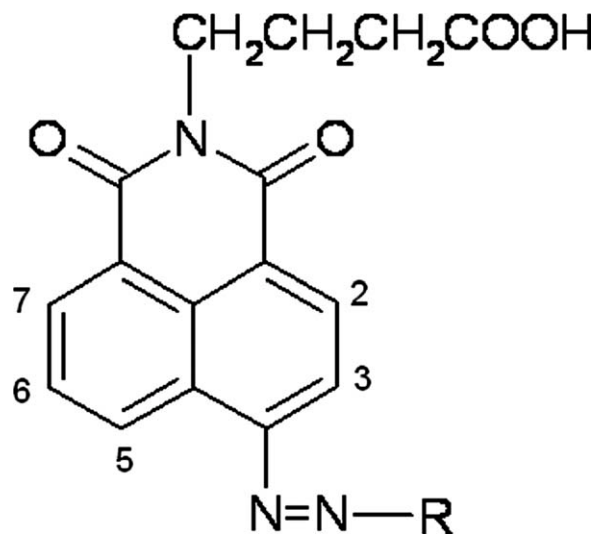
Until now, disperse dyes with different chemical structures have been utilized to dye polyamide fabrics, but a major percentage of them brought about various problems in dyeing process. Wash and rubbing fastnesses will decrease in high depth, due to the easy migration of disperse dye molecules into washing bath.<sup>2</sup>

Recently, azonaphthalimide derivatives are known as disperse dyes for dyeing synthetic fibers. Most of these derivatives have been prepared as disperse dyes to dye polyester fabrics. Monoazo disperse dyes containing naphthalimide residue have been found to have acceptable dyeing and fastness properties.<sup>5–8</sup> They displayed excellent thermal stabilities and good dyeing fastness properties.<sup>9,10</sup>

A group of disperse dyes based on *N*-alkyl, *N*-alkylglycinates, and *N*-butyric acid-1,8-naphthalimide were synthesized and their dyeing and fastness properties on polyester fibers were investigated. They showed good build up and good fastness properties.<sup>11–13</sup>

In this study, a group of disperse dyes based on naphthalimides including butyric acid group were applied on polyamide fabrics. The chemical structures of these dyes are shown in Figure 1. The

Correspondence to: K. Gharanjig (gharanjig@icrc.ac.ir).



**Figure 1** The chemical structure of the utilized dyes.

dyeing and fastness properties of the utilized dyes such as washing, light, heat, perspiration, and rubbing fastnesses were also evaluated on polyamide fabrics.

## EXPERIMENTAL

### Materials and apparatus

The synthesis of noted dyes and the preparation of their dispersions have been reported previously.<sup>13,14</sup> Polyamide knitted fabric ( $101 \text{ g m}^{-2}$ ) was used in this study. Nonionic detergents (Lotensol, Hansa) were utilized for scouring the fabrics. The dyeing of the fabrics was fulfilled in acidic media (glacial acetic acid, Merck) by using laboratory HT dyeing machine.

UV-visible absorption spectra were measured on a Cecil 9200 double beam spectrophotometer. The reflectance characteristics of the dyed samples were measured on a Grating Macbeth 7000 A, color eye reflection spectrophotometer (D65 illumination,  $10^\circ$  observer).

### Preparation of the polyamide fabrics

Polyamide fabrics (1 g) were treated with  $5 \text{ g L}^{-1}$  nonionic detergent at  $60^\circ\text{C}$  for 20 min in a liquor ratio (L.R) of 50 : 1 after which, the substrate was rinsed and dried.

### Dyeing of polyamide fabrics

Dyeing of polyamide fabrics was carried out in a liquor ratio of 50 : 1 at  $30^\circ\text{C}$  and pH 5–5.5. The temperature of dyebath was augmented to  $100^\circ\text{C}$  in 45 min. Then, the dyeing was done for 60 min in  $100^\circ\text{C}$  (Fig. 2); the dyed samples were then cooled down to

room temperature and washed with an aqueous solution of a nonionic detergent ( $5 \text{ g L}^{-1}$ ) at  $50^\circ\text{C}$  for 20 min.

The color strength of dyed fabrics expressed as  $K/S$  was measured according to a previously reported method by the light reflectance technique, and the relative color strength was calculated by applying the Kubelka-Munk eq. (1):

$$\text{Color strength } (K/S) = \frac{(1 - R)^2 / 2R}{(1 - R_A^\circ)^2 / 2R_A^\circ} \quad (1)$$

where  $R$  and  $R_A^\circ$  are the decimal fraction of the reflectance of the colored and uncolored fabrics, respectively.  $K$  is the absorption coefficient and  $S$  is the scattering coefficient.

The dye bath exhaustions of dyes on fabrics (up-take) were calculated using eq. (2).

$$E (\%) = (A_1 - A_2) / A_1 \times 100 \quad (2)$$

where  $E$  is exhaustion (%) and  $A_1$  and  $A_2$  are absorbance of solutions before and after dyeing, respectively.

### Fastness properties

#### Wash fastness measurement

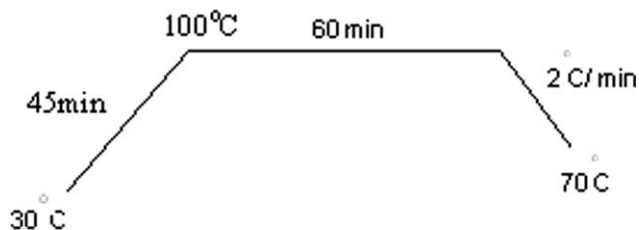
Wash fastness was assessed by the standard ISO 105 C06 C2S:1994 (E) method. The washing was conducted at  $60^\circ\text{C}$  for 30 min, rinsed with cold water, air dried, and analyzed.

#### Light fastness measurement

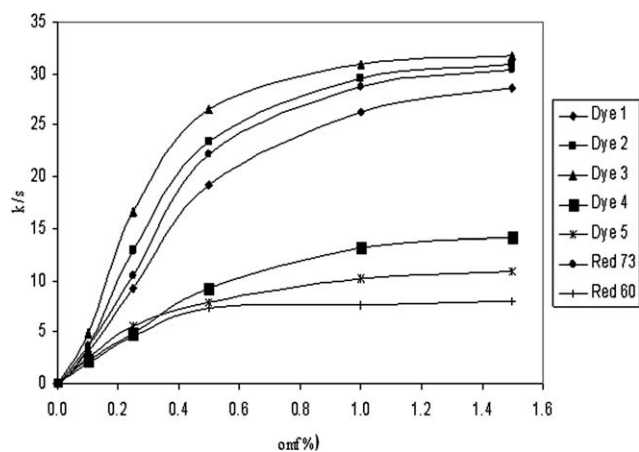
Light fastness test ISO 105 B02:1988 (E) was carried out with the xenon arc lamp using blue reference samples.

#### Color fastness to dry heat

Color fastness to dry heat (excluding pressing) of the dyes was determined according to ISO 105 P01:1993 (E) method using a composite sample sandwiched from each side by the undyed polyester at  $150^\circ\text{C}$  for 30 s.



**Figure 2** Dyeing profile of the utilized dyes on polyamide fabrics.



**Figure 3** The build up curves of Dyes 1–5 and their comparison with disperse red 60 and 73 on polyamide fabrics.

#### Color fastness against rubbing

The rubbing fastness test was carried out using a crockmeter in accordance with ISO105-X12:1993 (E).

#### Color fastness to perspiration

The perspiration fastness was conducted in acid and alkali conditions by the standard ISO 105 - E04:1994 (E) method.

## RESULTS AND DISCUSSION

### Dyeing

All the utilized dyes were applied to polyamide fabrics at boiling temperature as elucidated in dyeing section. Figure 3 demonstrates the build up curves of Dyes 1–5 on polyamide fabrics. It is found that most of the dyes generally have remarkable build ups on the polyamide fabrics and the dyes reach saturation at concentrations of 0.5–1% omf. The build up of the Dyes 1–5 on the polyamide is in the order of  $3 > 2 > 1 > 4 > 5$ . The results revealed that Dyes 3 and 5 have the highest and lowest build ups, respectively. These findings are the outcomes of the distinction of chemical structures of these dyes. There are hydrophobic and hydrophilic sections in the polyamide fibers which could be dyed with disperse and acid dyes. Whereof there are hydrophobic and hydrophilic sections in the polyamide fibers which it can be dyed with disperse and acid dyes. All used dyes due to possessing carboxylic acid group in their chemical structure have weak solubilities in water. Dyes 1, 2, and 4 are more hydrophobic while, Dye 3 due to having additional hydroxyl groups is more hydrophilic than the other dyes. Although Dye 5 contains a hydroxyl group, it shows more hydrophobic characteristics as a result of intramolecular hydrogen bonding between hydroxyl group of 1-naphthol ring and azo groups. As it is

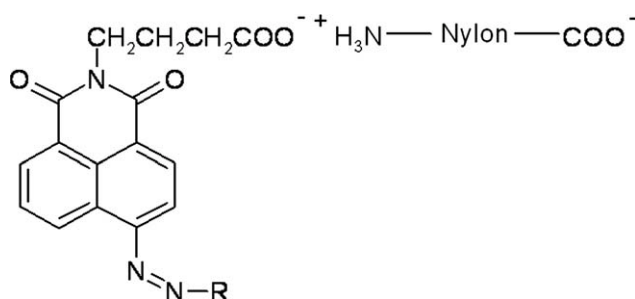
known the mechanism of dyeing polyamide fibers with disperse dyes is based on solid solution mechanism, while in this process the dyes were occluded within the fiber. Though, the presence of physical forces and hydrogen bonding are effective in this mechanism too. While the mechanism of polyamide fibers with acid dyes is based on electrostatic attractions, hydrogen bonding, and physical forces. The chemical linkage of all dyes on polyamide fabrics are shown in Figure 4, which emphasizes on the formation of electrostatic bonds between the dye molecule and polyamide fiber. In addition to that intermolecular hydrogen bonding between suitable groups in the fiber, especially the amide group and the azo group in chemical structure of the dyes are also formed.

It might be concluded that, the presence of polar carboxylic acid group on the dyes potentially increases the adsorption of the dyes on polyamide fibers. The ionization of polar groups generates the negative charges on dye molecules which would facilitate the dye adsorption on the positive locations of polyamide fibers (Fig. 4).

The presence of hydroxyl group in chemical structure of Dye 3 causes an increasing of hydrogen bonding between dye molecule and polyamide fiber. In addition, the presence of hydroxyl group in dye molecule causes increment of dye solubility in water. Consequently, the degree of exhaustion of the dye on polyamide fiber is increased.

Despite the fact that the presence of the hydroxyl group should increase the degree of exhaustion, Dye 5 indicates a relatively low exhaustion rate in comparison to Dye 3 on polyamide fiber. This finding for Dye 5 is due to the intramolecular hydrogen bonding between OH and the azo groups of the dye (Fig. 5).<sup>15,16</sup> The formation of the intramolecular hydrogen bond in this molecule decreases the hydrophilicity and solubility of the dye in water.<sup>17</sup> However, the most applied dyes showed relatively good build ups comparing to the conventional disperse dyes on polyamide fibers (Fig. 3).

Up-take data of dyes are given in Table I by polyamide fabrics to the following order:  $3 > 2 > 1 > 4$



**Figure 4** Schematic of dyes adsorption on polyamide fibers.

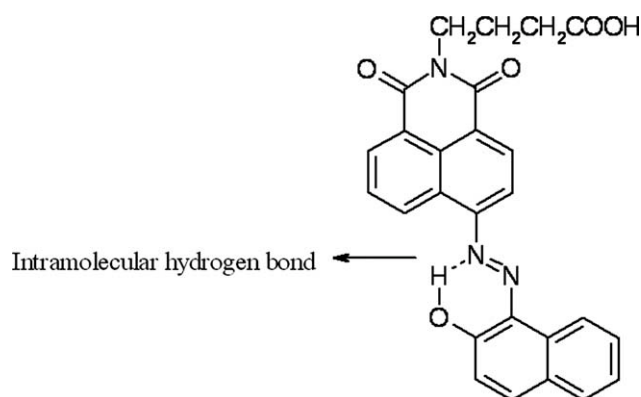


Figure 5 Intramolecular hydrogen bond in Dye 5.

> 5. The results represent that Dye 3 has the highest up-take and Dye 5 has the lowest. The high up-take rate of Dye 3 can be attributed to the presence of both chemical (electrostatic and hydrogen bonding) and physical forces (Vanderwaals and London) between dye molecules and polyamide fibers. Therefore, the used dyes can dye fibers better than commercial disperse dyes (Disperse Red 73 and Disperse Red 60). Intramolecular hydrogen bonding of Dye 5 caused the decrease in the up-take on the polyamide fibers. As a consequence of the formation of the physical and chemical bonds between dye and polyamide fiber, the other dyes have reasonably acceptable up-take on the polyamide fabrics.

### Color characteristics of the dyed fabrics

The colorimetric properties of the dyed fabrics were obtained, using a reflectance spectrophotometer. The absorption maxima of dyed fabrics showed that the highest  $\lambda_{\max}$  values belonged to Dye 2 (Table II). The increasing absorption maxima of the dyed samples are as follow:  $2 > 1 = 3 = 4 = 5$ .

The hues of the dyed polyamide fabrics represented a good correlation with the maximum wavelengths of the dyes in solutions, especially in acetone. A comparison of the colorimetric data of all dyes is indicated in Table II. The dyed fabrics of Dye 2 were bluish red, while other samples were red. The  $b^*$  values and hue angle of all dyes were about zero and in the range of  $0.06^\circ$ – $6.36^\circ$ , except for Dye 2.

TABLE I  
Dyeing Properties

Dye (owf)	Dye uptake % (polyamide fabrics)		
	0.1%	0.5%	1%
1	94	90	83
2	95	92	84
3	97	96	86
4	90	85	75
5	87	77	69

TABLE II  
Colorimetric Data of Dyed Polyamide with Dyes at 1/1 Standard Depth ( $C_{\text{dye}} = 0.5\%$ )

Dye	$L^*$	$a^*$	$b^*$	$C^*$	$h^\circ$	$\lambda_{\max}$ (nm)
1	37.911	41.120	-1.187	41.137	358.34	550
2	33.880	37.537	-17.982	37.55	334.40	560
3	40.530	44.327	1.922	44.36	2.48	540
4	41.729	45.489	5.074	45.771	6.36	540
5	60.329	34.970	0.036	34.970	0.058	540

The bathochromic shift of Dye 2 compared to Dye 1 can be attributed to the presence of the methyl group in 3 position of *N,N*-diethyl-*m*-toluidine in comparison to *N,N*-diethylaniline (10–20 nm). However, the introduction of an electron donating group at suitable positions in the coupling components affects the absorption characteristics of the dyed samples. The bathochromic shift can be obtained by enhancing electron donating properties of the couplers.<sup>8,9</sup> In Dye 3 the presence of ethoxyamino group in benzene ring caused hypsochromic shift compared to Dyes 1, 2, and 4. In general, all used dyes on polyamide fibers in comparison to polyester showed greater bathochromic shift.<sup>13,14</sup>

Table II displays the color properties of the dyed polyamide fabrics at 0.5% (omf). The leveling properties of the dyes were excellent for all the dyed fabrics. The dyed fabrics by Dye 2 have bright violet (bluish red) hues. The dyed fabrics using the Dyes 1, 3, 4, and 5 have bright red hues.

### Fastness properties

#### Washing fastness of dyed fabrics

Washing fastness measurement of the treated dyed fabrics was carried out according to the standard ISO 105 C06 C2S. After washing process in these series, Dye 3 showed the highest improvement in wash fastness properties, which can be attributed to the presence of both carboxylic acid and hydroxyl groups in the dye molecules. The presence of these groups in the dye molecule (Dye 3) caused the easy hydrolysis of the adsorbed dyes on fibers and then being converted into water solublized dye. The water solublized dyes on polyamide surface can be removed easily by the wash-off treatment. Therefore, the dye remaining on the surface of the fabric can be eliminated. This property in this group of dyes improves the wash fastness of the dyeing processes and also its brightness.<sup>15,18,19</sup> In comparison to used commercial dyes, the synthesized dyes had good washing fastness properties on polyamide fabrics. The color change of dyed fabrics with disperse red 60 and 73 against to washing was 2–3 and 3–4, respectively, while the synthesized dyes had excellent wash fastness (5).

**TABLE III**  
Color Fastness of Dyed Polyamide Fibers with Dyes at 1/1 Standard Depth ( $C_{\text{dye}} = 0.5\%$ )

Dye	Fastnesses												
	Washing				Perspiration						Rubbing		
	C <sup>S</sup>	N <sup>S</sup>	Ch	Light	Acid			Alkali			Heat (150°C)	Dry	Wet
					C <sup>S</sup>	N <sup>S</sup>	Ch	C <sup>S</sup>	N <sup>S</sup>	Ch			
1	4	4-5	5	3	4	4-5	4-5	4-5	4-5	4-5	5	4	3-4
2	4	4-5	5	3-4	4-5	3-4	5	4	4	4-5	5	4	3
3	4	4-5	5	4	4	4	4-5	4	4	4	5	4-5	4
4	4-5	5	5	3-4	4-5	4	4-5	4-5	4-5	4-5	5	4-5	4-5
5	5	4-5	5	3	4	4-5	4-5	4-5	4	5	5	4-5	4-5
DR60	5	3	2-3	4	4	4-5	4-5	5	4	5	3-4	5	5
DR73	5	3	3-4	3	4-5	4	4-5	5	3	5	3-4	5	5

#### Heat fastness of dyed fabrics

Heat fastness at 150°C was excellent (5). All synthesized dyes showed high sublimation fastness properties on polyamide relative to dyed fabrics with disperse red 60 and 73 (Table III). Increasing heat fastness properties of the synthesized dyes on polyamide relative to dyed fabrics with commercial dyes can be attributed to chemical structure of these dyes. The presence of carboxylic acid group which is a polar group and naphthalimide system in dye molecule caused the increase in the heat fastness property.<sup>13</sup>

#### Rubbing fastness of dyed fabrics

All dyed samples showed similarly high rubbing fastness values (Table III). These results indicated that the used dyes had moderate to good rubbing fastness values, which can be related to the polar groups in dye's molecular structure like the washing fastness. The dyed fabrics with commercial dyes had relatively better rubbing fastness than the dyed fabrics with synthesized dyes.

#### Light fastness of dyed fabrics

The measurement of light fastness property of the all dyes on polyamide fabrics demonstrated that all dyes had light fastness less than moderate (3-4).

#### Perspiration fastness on dyed fabrics

Measurement of color fastness to perspiration has been carried out with the dyed fabrics in contact with adjacent fabrics (i.e., cotton and nylon) in alkaline and acidic solutions containing histidine. The dyed fabrics are subsequently drained and placed under constant pressure. The specimens are then placed in an incubator for 4 h at 37°C. After drying, change in color of the dyed fabrics and staining of

the adjacent fabrics is evaluated with Gray Scales. Results show that the synthesized and commercial dyes had good perspiration fastness values on polyamide fabrics in both different solutions containing alkaline and acidic media (Table III).

### CONCLUSIONS

A series of monoazo disperse dyes derived from *N*-carboxylic acid-1,8-naphthalimide were applied on polyamide fabrics. Polyamide fabrics cause the build-up and gave reddish-blue to red hues. The presence of the naphthalimide system also leads to the production of a deep and intense color. The dyed fabrics with the used dyes showed that the color of the dye is influenced by the introduction of additional donor groups into the coupling component. The electrostatic and physical forces between the used dyes and polyamide fibers lead to the build up and give good wet fastness properties significantly better than conventional disperse dyes where only physical forces were involved. By comprising the build up the dyed polyamide fabrics with utilized and conventional disperse dyes proved that the used dyes have acceptable dyeing and fastness properties. Based on the finding of this research it could be concluded that, the naphthalimides (containing carboxylic acid) and analogous compounds are suitable monoazo disperse dyes and give good wet fastness properties on polyamide fabrics.

### References

1. Nunn, D. M. *The Dyeing of Synthetic-Polymer and Acetate Fibres*; SDC: Bradford, 1979.
2. Giles, C. H. *Giles's Laboratory Course in Dyeing*, 4th ed.; SDC: Bradford, 1989.
3. Hunger, K. *Industrial Dyes Chemistry, Properties, Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2003.
4. Perkins, W. S. *Textile Coloration and Finishing*; Durham, North Carolina: Carolina Academic Press, 1996.

5. Peters, A. T.; Bide, M. J. *Dyes Pigments* 1986, 7, 237.
6. Wojciechowski, K.; Szadowski, J. *Dyes Pigments* 1991, 16, 35.
7. Wojciechowski, K. *Dyes Pigments* 1988, 9, 401.
8. Szadowski, J.; Wojciechowski, K.; Malinowski, W. *JSDC* 1985, 101, 105.
9. Wojciechowski, K. *Dyes Pigments* 1993, 22, 239.
10. Wojciechowski, K. *Dyes Pigments* 1997, 33, 149.
11. Khosravi, A.; Moradian, S.; Gharanjig, K.; Afshar Taromi, F. *Dyes Pigments* 2006, 69, 79.
12. Gharanjig, K.; Arami, M.; Bahrami, H.; Movassagh, B.; Mahmoodi, N. M.; Rouhani, S. *Dyes Pigments* 2008, 76, 684.
13. Sadeghi-Kiakhani, M.; Gharanjig, K.; Arami, M.; Mokhtari, J.; Mahmoodi, N. M. *J Chin Chem Soc* 2008, 55, 1300.
14. Sadeghi-Kiakhani, M.; Gharanjig, K.; Arami, M.; Mokhtari, J.; Mahmoodi, N. M.; *Fibers Polym* 2009, 10, 446.
15. Chao, Y. C.; Lin, S. M. *Dyes Pigments* 2000, 44, 209.
16. Chao, Y. C.; Lin, S. M. *Dyes Pigments* 1998, 37, 357.
17. Gordon, P. F.; Gregory, P. *The Organic Chemistry in Color*; Berlin, Germany: Springer-Verlag Publication, 1987.
18. Koh, J.; Greaves, A. J.; Kim, J. P. *Dyes Pigments* 2003, 56, 69.
19. Sing, K.; Sing, S.; Taylor, J. A. *Color Technol* 2003, 119, 158.