

## Synthesis of Red Disperse Dyes with Various Diazo Components and Coloration of Unmodified Pure Polypropylene Fibers

Taekyeong Kim<sup>†</sup>, Kyungjin Jang and Seonhee Jeon

Department of Textile System Engineering, College of Engineering, Kyungpook National University, Daegu 702-701, Korea

(Received: February 9, 2010/Revised: March 17, 2010/Accepted: March 19, 2010)

**Abstract**— The five new red disperse dyes for unmodified pure polypropylene fibers were synthesized. As a coupling component, a di-*n*-hexyl substituent was used in common, while various substituents were used for the diazo component. The dye having electron donating group at diazo component showed hypsochromic shift compared to the unsubstituted dye, while the dyes having electron withdrawing groups showed bathochromic shift. Owing to their extreme hydrophobicity caused by the di-*n*-hexyl substituent, all dyes exhibited very high affinity toward pure polypropylene fibers. Fastness to washing was very good for all dyes and fastness to light was good except two purplish red dyes.

**Keywords:** polypropylene, disperse dyes, hydrophobicity, alkyl substitution, dyeing

### 1. Introduction

Polypropylene fiber has the strength of 4.5~9.0g/d and the elasticity of 25~60%, which are comparable to those of polyester and nylon fibers in terms of their application to apparel and industrial aspects. In addition, the fiber has excellent chemical resistance as well. They are also known as a floating fiber since the density is 0.90~0.92<sup>1-3)</sup>, the lowest of all kinds of fibers, and expected for the usage for light weight sportswear<sup>4)</sup>. Polypropylene fiber can be used in the fields of fast drying and heat insulation materials as moisture regain and thermal conductivity are as low as 0.05% and 0.12W/mK respectively<sup>2,5)</sup>. However, it has been generally considered that the polypropylene fiber was impossible to dye at any dyeing systems because of the extreme hydrophobicity of the fiber<sup>6,8)</sup>.

In order to dye this polypropylene fiber, two kinds of coloration methods are being considered. One is adding pigment at the stage of fiber formation, and the other is the blending with dyeable polymer or the chemical modification of the polypropylene fiber. The first method is possible to dye polypropylene fibers but the

application is relatively restricted since the color is determined at the stage of fiber formation. The second method is also possible to dye the fiber but there are disadvantages such as the loss of the typical properties of polypropylene fibers by chemical modification<sup>6,8)</sup> and low color fastnesses. For dyes to have affinity toward the extremely hydrophobic fibers like polypropylene, they also need to have extreme hydrophobicity.

The previous studies show that the dyeing of polypropylene fibers without any physical and chemical modifications is possible at the established process by super hydrophobic dyes having long alkyl substituents which impart extreme hydrophobicity to the dyes<sup>9,12)</sup>. Anthraquinoid blue dyes were selected and investigated at first<sup>9,10)</sup>. And then disazo and monoaz yellow dyes were synthesized and examined<sup>11,12)</sup>. Apart from that, in order for new series of dyes to be utilized for textiles, it is necessary to acquire at least three dyes of primary colors, such as blue, yellow, and red.

Therefore, in this subsequent study, the new red dyes having long alkyl substituents were synthesized by combination with various diazo components. The color values and fastnesses of the dyeing were examined on unmodified pure polypropylene fiber.

<sup>†</sup>Corresponding author. Tel.: +82-53-950-5639; Fax.: +82-53-950-6617; e-mail: taekyeong@knu.ac.kr

## 2. Experimental

### 2.1 Materials

Unmodified pure polypropylene fabrics (plain weave, 120g/m<sup>2</sup>) were used for dyeing experiments after scouring with acetone. All the chemicals for synthesis of dyes were reagent grades of minimum 98% purity except for 37% aqueous hydrochloric acid and used without further purification. The surfactant used for dispersion of dyes was didodecyldimethylammonium bromide (DDDMAB).

### 2.2 Synthesis of dyes

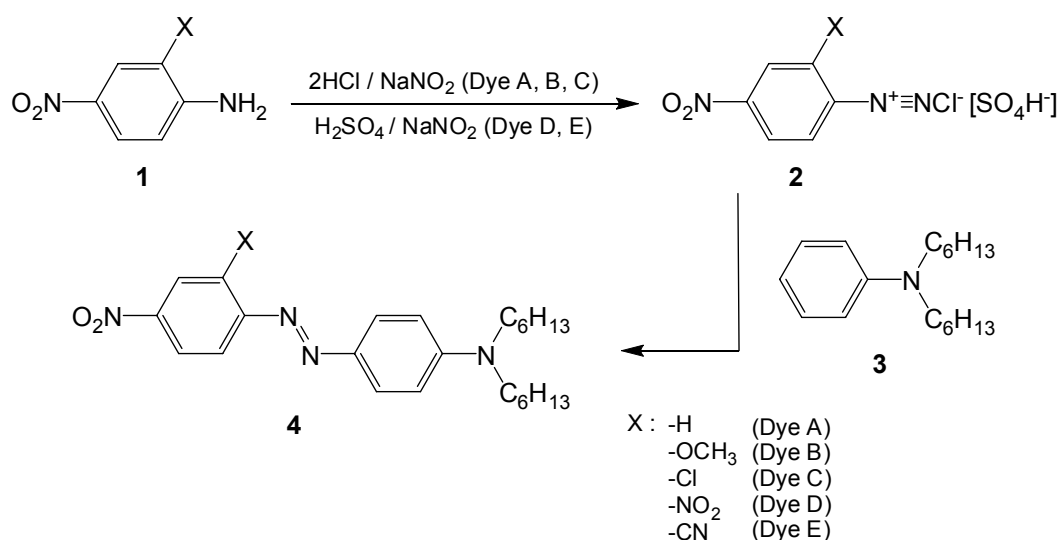
Synthesis procedure is shown in Scheme 1. Dye A, B and C were synthesized by the general diazotization method which used sodium nitrite and hydrochloric acid. Diazo components (**1**, 0.01mole) were dissolved in the 1:1 volume mixture of water and acetone (50ml) and the solution (solution 1) was maintained at 0~5°C in an ice bath. Sodium nitrite (0.01mole) and hydrochloric acid (0.021mole) dissolved in the 1:1 volume mixture of water and acetone (30ml) were then added to the solution 1 in order to change the structure **1** to diazonium salt (**2**) and stirred for 30 minutes maintaining at 0~5°C. N,N-di-n-hexylaniline (**3**, 0.01mole) was dissolved in acetone (50ml) (solution 2).

The solution 2 was added to the solution 1

prepared previously. The solution 1 was then stirred continuously for 1 hour maintaining at 0~5°C to produce the final products (**4**). After the reaction, the solution was heated under reduced pressure to remove acetone. And then benzene (300ml) was added in order to separate the final products from the aqueous reaction solution. The benzene was evaporated to obtain the synthesized dyes.

Dye D and E were synthesized by nitrosylsulfuric acid method which used sodium nitrite and sulfuric acid instead of hydrochloric acid. Diazo components (**1**, 0.01mole) were dissolved in the 7:1 volume mixture of acetic acid and water (80ml) and the solution (solution 3) was maintained at 0~5°C in an ice bath. Sodium nitrite (0.01mole) was dissolved in sulfuric acid (5ml) to produce nitrosylsulfuric acid, which was added to the solution 3 in order to change the structure **1** to diazonium salt (**2**) and stirred for 30 minutes maintaining at 0~5°C. N,N-di-n-hexylaniline (**3**, 0.01mole) was dissolved in acetic acid (10ml) (solution 4). The solution 4 was added to the solution 3 prepared previously.

The solution 3 was then stirred continuously for 1 hour maintaining at 0~5°C to produce the final products (**4**). After the reaction, the solution was neutralized with dilute sodium hydroxide aqueous solution and heated under reduced pressure to remove acetone. And then benzene (300ml) was added in order to separate the final products from



Scheme 1. Synthesis of the dyes.

the aqueous reaction solution. The benzene was evaporated to obtain the synthesized dyes.

### 2.3 Analysis of dyes

In order to analyze the structure of dyes, a mass spectrometer (*JMS700, JEOL*), a proton NMR spectrometer (*400MHz, Avance Digital 400, Bruker*) and an elemental analyzer (*EA1110, Fisons Instrument*) were used. For the proton NMR analysis, the synthesized dyes were dissolved in deuteriochloroform ( $\text{CDCl}_3$ ) containing 0.03% of tetramethylsilane.

To investigate the absorption spectra of visible light by the dyes, a UV-Vis. spectrophotometer (*Nicolet evolution 300, Thermo Electron Corporation*) was used as well and the spectra were obtained in *N,N*-dimethylformamide.

### 2.4 Preparation of dye dispersions

A certain amount of dyes was dissolved in 50ml tetrahydrofuran and mixed with the solution of DDDMAB (2 molar ratio to dye amount) dissolved in 50ml tetrahydrofuran. The mixture was heated under reduced pressure and then dried under vacuum for 24 hours to remove the tetrahydrofuran entirely. In this procedure, the uniform mixture of dyes and dispersant (DDDMAB) was prepared. The 1 hour exposure in an ultrasonic apparatus after the addition of water to this mixture makes uniform and stable dye solution by the dispersion activity of DDDMAB<sup>9-15</sup>. This solution was finally used for dyeing. If necessary, an additional amount of water was added to adjust the liquor ratio needed.

### 2.5 Dyeing

The unmodified pure polypropylene fibers (1.0g) were dyed with basically 5% owf dyes at a liquor ratio of 50:1. The temperature of dye bath was elevated to 130°C at a rate of 2°C/min and maintained at this temperature for 60 minutes. The dyed materials were reduction-cleared in an aqueous bath comprising sodium hydroxide (2g/l), sodium hydrosulfite (2g/l), and nonionic surfactant (5g/l) at 70°C for 10 minutes.

### 2.6 Measurement of color and color strength

The color strength of dyed fabrics was measured by a color measurement instrument (*Spectrophotometer CM-3600d, Konica Minolta*) and expressed by  $f_k$  value which was the sum of the weighted  $K/S$  values in the visible region of the spectrum; it was calculated using Eq. (1)<sup>16</sup>. Meanwhile, the  $K/S$  is the color strength at single wavelength which is calculated using Eq. (2) from the reflectance ( $R$ ) of the single wavelength obtained at every 10nm in the range of 400~700nm<sup>17,18</sup>. The measurement was carried out with 10° standard observer under standard light D<sub>65</sub>.

$$f_k = \sum_{\lambda=400}^{700} (K/S)_{\lambda} (\bar{x}_{10,\lambda} + \bar{y}_{10,\lambda} + \bar{z}_{10,\lambda}) \quad (1)$$

$$K/S = (1 - R)^2 / 2R \quad (2)$$

where,  $\bar{x}_{10,\lambda}$ ,  $\bar{y}_{10,\lambda}$ , and  $\bar{z}_{10,\lambda}$  are color matching functions for the 10° standard observer at each wavelength.

The color values of dyed fabrics were expressed by  $L^*a^*b^*$  and  $C^*h^*$ .

### 2.7 Fastness

Color fastnesses of the dyes were tested on the fabrics dyed with 5% owf dyes at 130°C. The wash and light fastness were examined by the procedures of ISO 105-C06 A1S and ISO 105 B02 (63°C, 20hrs, water-cooled xenon-arc lamp, continuous light) respectively.

## 3. Results and Discussion

### 3.1 Synthesis and analysis of dyes

The aim of this study is to synthesize red dyes for unmodified pure propylene fibers. In the previous study<sup>12</sup>, it was concluded that the super hydrophobic dyes having a di-n-hexyl group had high affinity toward polypropylene fibers.

Therefore, in this study also, *N,N*-di-n-hexylaniline was coupled to various diazo components having different substituents such as hydrogen(-H, unsub-

stituted), methoxy(-OCH<sub>3</sub>), chloro(-Cl), nitro(-NO<sub>2</sub>), and cyano(-CN) groups which could be expected to make red chromophores.

To verify the structure of dyes, the proton NMR spectrometry, mass spectrometry, and elemental analysis were performed. Table 1 summarizes the NMR analysis data. As expected, the NMR data show mainly apparent two kinds of hydrogen peaks, such as aliphatic hydrogens appeared in around  $\delta$  1.0~3.0 ppm and aromatic hydrogens in around  $\delta$  7.0~8.0 ppm.

In Table 2, the mass data of dyes were presented. The obtained m/z values of molecular ions of dyes were perfectly matched with the calculated exact molecular mass.

The additional analysis to verify the structure of dyes was the elemental analysis which was carried out for 3 species of atoms such as carbon,

nitrogen, and hydrogen. The elemental analysis data appeared in Table 3 were matched well with the calculated values.

Fig. 1 shows the UV-Vis. spectra of the dyes having different substituents on diazo components. Compared with the unsubstituted dye (-H, dye A), the dye B(-OCH<sub>3</sub>) shows hypsochromic shift and the dye C(-Cl), D(-NO<sub>2</sub>), and E(-CN) show bathochromic shift. In order to achieve bathochromic shift of monoazo dyes, electron withdrawing groups such as nitro group(-NO<sub>2</sub>) are substituted on diazo components and electron donating groups, for example alkyl amine(-NR<sub>2</sub>), are substituted on coupling components. This bathochromic shift is generally enhanced by additional substitution with electron withdrawing groups on ortho position of diazo components<sup>19)</sup>. In Fig. 1, therefore, it can be demonstrated that since the chloro(-Cl), nitro

**Table 1.** <sup>1</sup>H NMR data of the dyes

Dye	Substituent	Chemical shift (CDCl <sub>3</sub> , ppm)
A	-H	0.9(6H, t, -CH <sub>3</sub> ), 1.3(12H, m, Ar-N-C-C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C), 1.5(4H, m, Ar-N-C-CH <sub>2</sub> -C-C-C), 3.3(4H, t, Ar-N-CH <sub>2</sub> -C-C-C-C-C), 6.6(2H, d, Ar-H), 7.8(2H, d, Ar-H), 8.3(4H, d, Ar-H)
B	-OCH <sub>3</sub>	0.9(6H, t, -CH <sub>3</sub> ), 1.3(12H, m, Ar-N-C-C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C), 1.5(4H, m, Ar-N-C-CH <sub>2</sub> -C-C-C-C), 3.3(4H, t, Ar-N-CH <sub>2</sub> -C-C-C-C-C), 4.0(3H, s, -O-CH <sub>3</sub> ), 6.6(2H, d, Ar-H), 7.6(1H, d, Ar-H), 7.9(4H, d, Ar-H)
C	-Cl	0.9(6H, t, -CH <sub>3</sub> ), 1.3(12H, m, Ar-N-C-C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C), 1.5(4H, m, Ar-N-C-CH <sub>2</sub> -C-C-C-C), 3.3(4H, t, Ar-N-CH <sub>2</sub> -C-C-C-C-C), 6.7(2H, d, Ar-H), 7.8(1H, d, Ar-H), 7.9(1H, d, Ar-H), 8.1(2H, d, Ar-H), 8.4(1H, s, Ar-H)
D	-NO <sub>2</sub>	0.9(6H, t, -CH <sub>3</sub> ), 1.3(12H, m, Ar-N-C-C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C), 1.5(4H, m, Ar-N-C-CH <sub>2</sub> -C-C-C-C), 3.3(4H, t, Ar-N-CH <sub>2</sub> -C-C-C-C-C), 6.7(2H, d, Ar-H), 7.9(3H, d, Ar-H), 8.4(1H, d, Ar-H), 8.6(1H, s, Ar-H)
E	-CN	0.9(6H, t, -CH <sub>3</sub> ), 1.3(12H, m, Ar-N-C-C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C), 1.5(4H, m, Ar-N-C-CH <sub>2</sub> -C-C-C-C), 3.3(4H, t, Ar-N-CH <sub>2</sub> -C-C-C-C-C), 6.7(2H, d, Ar-H), 7.9(3H, d, Ar-H), 8.3(1H, d, Ar-H), 8.5(1H, s, Ar-H)

**Table 2.** Molecular ion peaks of the dyes

Dye	Substituent	Exact molecular mass calculated	m/z values of molecular ions obtained
A	-H	410.27	410
B	-OCH <sub>3</sub>	440.28	440
C	-Cl	444.23	444
D	-NO <sub>2</sub>	455.25	455
E	-CN	435.26	435

**Table 3.** Elemental analysis data of the dyes

Dye	Substituent	Molecular formula	Calculated	Obtained
A	-H	C <sub>24</sub> H <sub>34</sub> N <sub>4</sub>	C 70.21, H 8.35, N 13.65	C 70.11, H 8.80, N 13.44
B	-OCH <sub>3</sub>	C <sub>25</sub> H <sub>36</sub> N <sub>4</sub> O	C 68.15, H 8.24, N 12.72	C 67.80, H 8.33, N 12.24
C	-Cl	C <sub>24</sub> H <sub>33</sub> N <sub>4</sub> Cl	C 64.78, H 7.47, N 12.59	C 64.04, H 7.73, N 12.81
D	-NO <sub>2</sub>	C <sub>24</sub> H <sub>33</sub> N <sub>5</sub> O <sub>2</sub>	C 63.28, H 7.30, N 15.37	C 62.80, H 7.30, N 15.20
E	-CN	C <sub>25</sub> H <sub>33</sub> N <sub>5</sub>	C 68.94, H 7.64, N 16.08	C 68.54, H 8.20, N 15.10

(-NO<sub>2</sub>), and cyano(-CN) groups of the dye C, D, and E are electron withdrawing groups, the bathochromic effect was enhanced by them.

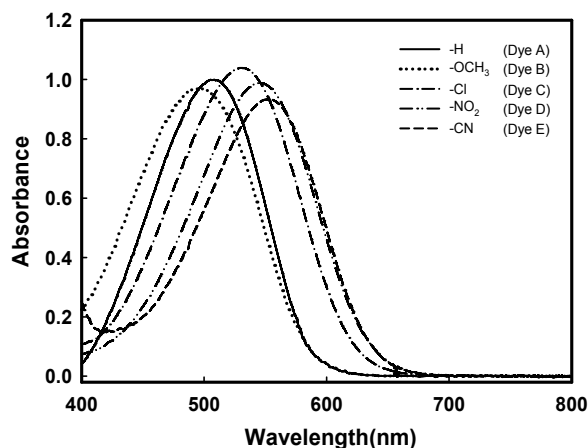
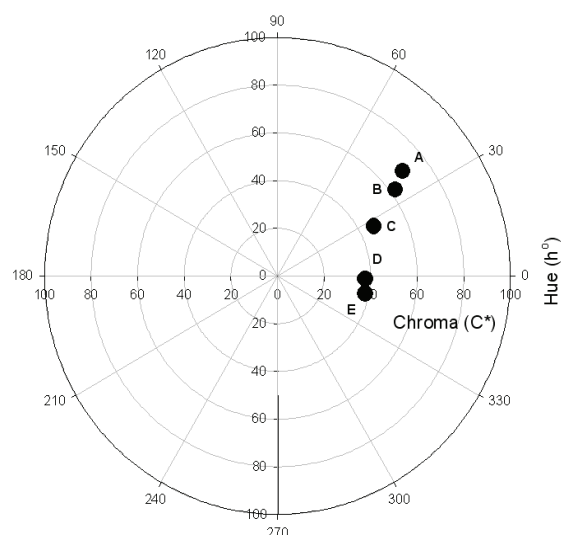
In contrast, the methoxy group (-OCH<sub>3</sub>) of dye B is a electron donating group, which means the hypsochromic effect of methoxy group offset the bathochromic effect of electron withdrawing nitro group substituted para position of diazo component.

### 3.2 Color values and color strength

To examine the color values and color strength of the dyes, dyeing was carried out in 5% owf dye dispersion solution at 130°C for 1 hour. The  $C^*h^\circ$  values of the dyeings are shown in Fig. 2. Dye A and B exhibited red color with slightly orange hue. Dye C showed high chroma red color. Meanwhile, dye D and E displayed purplish red color.

Fig. 3 shows the color strength of the red dyes on unmodified pure polypropylene fabrics. The dye showing the strongest color on polypropylene was dye C which was substituted with chloro group. Although the dye A and B displayed a little lower color strength than dye C, they still showed enough color strength on polypropylene fabric. Dye D and E showed relatively lower color strength on the fabric among the dyes used in this experiment. Nevertheless, all the 5 dyes have strong affinity toward unmodified pure polypropylene fiber and exhibited deep shade of dyeings practically. This is attributed that the di-n-hexyl group substituted on the coupling component imparts strong hydrophobicity to the dyes, which gives

high affinity toward extreme hydrophobic polypropylene fiber. The color values and color strength of the dyeings were summarized in Table 4.

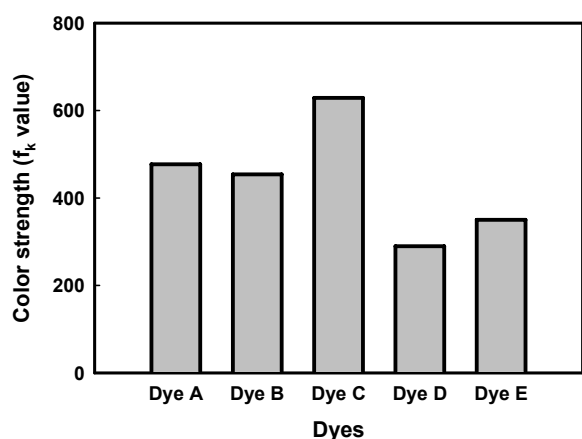

**Fig. 1.** UV Vis. spectra of the dyes.

**Fig. 2.** Color values ( $C^*h^\circ$ ) of polypropylene fabrics dyed with 5% owf dyes at 130°C.

**Table 4.** Color values and color strength of polypropylene fabrics dyed with 5% owf dyes at 130°C

Dye	Substituent	Color value					Color strength ( $f_k$ value)
		$L^*$	$a^*$	$b^*$	$C^*$	$h^\circ$	
A	-H	41.58	53.81	44.02	69.53	39.27	477.30
B	-OCH <sub>3</sub>	38.25	50.56	36.09	62.13	35.51	454.00
C	-Cl	28.15	41.42	20.82	46.36	26.68	629.10
D	-NO <sub>2</sub>	28.69	37.71	-0.79	37.73	358.8	289.70
E	-CN	29.43	37.73	-7.53	38.49	348.7	350.20

**Table 5.** Color fastnesses of the polypropylene fabrics dyed with 5% owf dyes at 130°C

Color fastness		Dye A	Dye B	Dye C	Dye D	Dye E	
		(-H)	(-OCH <sub>3</sub> )	(-Cl)	(-NO <sub>2</sub> )	(-CN)	
Washing	Change in color	4~5	4~5	4~5	4~5	4~5	
	Staining	Acetate	4~5	4~5	4~5	4~5	4~5
		Cotton	4~5	4~5	4~5	4~5	4~5
		Nylon	4~5	4~5	4~5	4~5	4~5
		Polyester	4~5	4~5	4~5	4~5	4~5
		Acrylic	4~5	4~5	4~5	4~5	4~5
		Wool	4~5	4~5	4~5	4~5	4~5
Light	Change in color	4	4	3~4	1~2	2	



**Fig. 3.** Color strength of polypropylene fabrics dyed with 5% owf dyes at 130°C.

### 3.3 Color fastness

Fastnesses to washing and light of the dyed fabrics were tested and presented in Table 5. Fastness to washing was very good for all the 5 red dyes showing ratings 4~5 in both color change and staining. This is also because the di-n-hexyl group substituted on the coupling component imparts strong hydrophobicity to the dyes, which gives high affinity toward extreme hydrophobic polypropylene fiber.

In case of fastness to light, the dye A and B exhibited good ratings 4 and dye C showed ratings 3~4. However, the dye D and E showed very poor fastness of ratings 1~2 and 2, respectively. Consequently, the only 3 dyes, A, B, and C, can be used to dye unmodified pure polypropylene fibers practically.

## 4. Conclusions

The new red dyes having a di-n-hexyl substituent were synthesized by combination with various diazo components. The color values and fastnesses of the dyeings were examined on unmodified pure polypropylene fiber. Compared to the unsubstituted dye, the dye having electron donating group on ortho position of the diazo component showed hypsochromic shift. The dyes having electron withdrawing groups showed bathochromic shift. All the 5 dyes exhibited strong affinity toward unmodified pure polypropylene fiber and deep shade of dyeings practically. Fastness to washing was very good for all the 5 dyes. Fastness to light was good enough except for two purplish red dyes.

## References

1. S. B. Warner, "Fiber Science", Prentice Hall, Inc., Englewood Cliffs, pp.123-143, 1995.
2. R. W. Moncrieff, "Man-Made Fibres", The Whitefriars Press Ltd., London, pp.609-627, 1975.
3. I. S. Cho, D. S. Jang, B. Y. Seo, S. J. Park, K. M. Cho, and Y. B. Shim, "Practical Dyeing", Hyungseul Publish Co., Korea, pp.451-458, 2000.
4. R. Shishoo, "Textiles in Sport", Woodhead Publishing Ltd., Cambridge, pp.1-11, 2005.
5. S. B. Warner, "Fiber Science", Prentice Hall, Inc., Englewood Cliffs, pp.230-244, 1995.
6. I. S. Cho, D. S. Jang, B. Y. Seo, S. J. Park, K. M. Cho, and Y. B. Shim, "Practical Dyeing", Hyungseul Publish Co., Korea, pp.397-399, 2000.
7. M. Ahmed, "Polypropylene Fibers - Science and Technology", Elsevier Scientific Publishing Co., New York, pp.462-501, 1982.
8. E. R. Trotman, "Dyeing and Chemical Technology of Textile Fibres", Wiley-Interscience, New York, pp.497-498, 1984.
9. T. K. Kim, S. H. Yoon, J. P. Hong, H. J. Kim, and J. S. Bae, Coloration of Pure Polypropylene Fiber with Super Hydrophobic Dyes, *Textile Coloration and Finishing(J. Korean Soc. Dyers & Finishers)*, **18**(5), 30-34(2006).
10. T. K. Kim, J. S. Jung, S. H. Yoon, M. K. Kim, and Y. A. Son, The Coloration Properties of Alkyl-substituted Anthraquinoid Dyes for Pure Polypropylene Fiber, *Textile Coloration and Finishing(J. Korean Soc. Dyers & Finishers)*, **19**(6), 28-34(2007).
11. T. K. Kim, J. S. Jung, S. I. Son, S. H. Yoon, M. K. Kim, and J. S. Bae, Synthesis and Application of Alkyl-substituted Disazo Yellow Dye for Unmodified Polypropylene Fiber, *Fibers and Polymers*, **9**(5), 538-543(2008).
12. T. Kim, J. Jung, K. Jang, S. Yoon and M. Kim, Synthesis and Application of Alkyl-substitution High Chroma Yellow Dyes for Unmodified Polypropylene Fiber, *Fibers and Polymers*, **10**(2), 148-153(2009).
13. K. Holmberg, "Handbook of Applied Surface and Colloid Chemistry", John Wiley & Sons Ltd., England, pp.45-52, 2002.
14. R. Arshady, "Microspheres Microcapsules & Liposomes, Vol. 2", Citrus Books Ltd., London, pp.436-544, 1999.
15. M. J. Rosen, "Surfactants and Interfacial Phenomena", 3rd ed., John Wiley & Sons Ltd., New Jersey, pp.415-427, 2004.
16. W. Baumann, B. T. Groebel, M. Krayner, H. P. Oesch, R. Brossman, N. Kleinmeier and A. T. Leaver, Determination of Relative Colour Strength and Residual Colour Difference by Means of Reflectance Measurements, *J. Soc. Dyers Colour.*, **103**, 100-105(1987).
17. Hans G. Völz, "Industrial Color Testing, Fundamentals and Techniques", VCH, New York, pp.93-98, 1995.
18. E. R. Trotman, "Dyeing and Chemical Technology of Textile Fibres", Charles Griffin & Company Ltd., New York, pp.566-569, 1984.
19. S. Kim, Y. Son and J. Bae, "Dye Chemistry", Doseochulpan Green Publish Co., Korea, pp.223-257, 2005.