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Synthesis of Benzisothiazole−Azo Disperse Dyes for High Resistance to Alkaline Treatments and Peroxide Bleaching of Polyester and Polyester/Cotton Fabric

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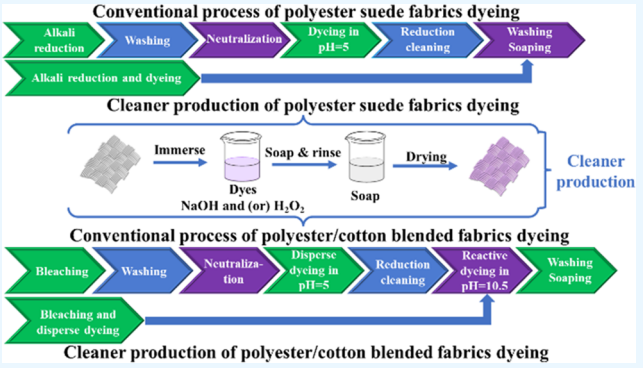
ABSTRACT: We proposed in this paper to design and synthesize a series of benzisothiazole-based heterocyclic azo disperse dyes with high resistance to alkali and peroxide. These newly synthesized disperse dyes were confirmed using ^{1}H nuclear magnetic resonance (^{1}H NMR), mass spectroscopy, and a UV−visible spectrophotometer. The resistances to alkali and peroxide were examined by dyeing polyester fabric with these synthesized disperse dyes in sodium hydroxide solution and alkaline hydrogen peroxide solution, respectively. It was found that the disperse dyes having cyano and hydroxyl groups exhibited poor resistance to alkali and peroxide. When the cyano and hydroxyl groups were substituted with ethyl, benzyl, and *p*-methylbenzyl groups, the synthesized disperse dyes exhibited extremely high resistance to alkali and peroxide. Utilizing the high resistance to alkali and peroxide of synthesized disperse dyes, the polyester suede fabric and polyester/cotton blended fabric could be produced by combining pretreatment with dyeing in one bath. From pilot-plant production based on 1-ton fabric, the one-bath process provided the advantages of saving electric power, steam, water, and man-hour.

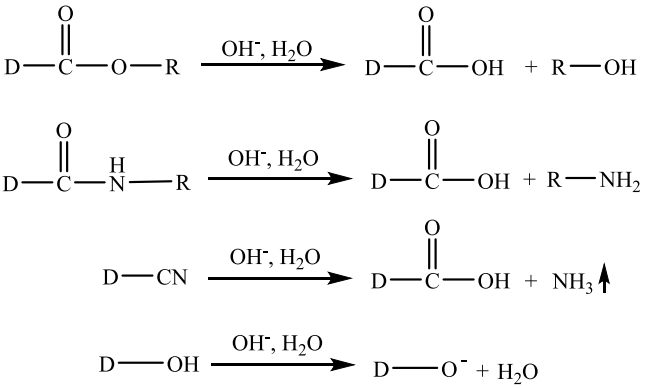


1. INTRODUCTION

The conventional production of polyester[1] and polyester/cotton blended fabrics[2] involves multistep wet processing, which is often operated in separate baths because of varying production conditions.[3] For example, polyester fabric requires alkaline pretreatment, and the residual alkali on the fabric must be completely neutralized with acid reagents and rinsed with a large amount of water before it is dyed with disperse dyes under acidic conditions.[4,5] Polyester/cotton blended fabric requires an even more complicated production process including, in turn, bleaching of cotton with alkaline hydrogen peroxide, dyeing of polyester with disperse dyes, and dyeing of cotton with reactive dyes,[6,7] which must be completely neutralized and rinsed at the end of each process step, otherwise the production quality will be impaired at the next process step.[8] Especially, when the polyester fabric is dyed with disperse dyes under acidic conditions, oligomers such as ring-trimers migrate[9] from polyester to deposit on the fabric detracting from the dyeing quality.[10,11] Therefore, the conventional production of polyester[12] and polyester/cotton blended fabric[13] is featured with high consumption of energy and water.[14−16]

One problem is that most disperse dyes contain auxochromic groups such as ester, amide, cyano, and hydroxyl that are sensitive to alkalis and tend to hydrolyze or ionize under alkaline conditions as shown in Scheme 1. In the first 20 years of the 21st century, much effort has been focused on the cleaner production of polyester fabric by synthesizing alkali-stable disperse dyes.[17−20] Dyeing of polyester fabric with these alkali-stable

Scheme 1. Mechanism of Various Groups in Alkali Conditions



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disperse dyes could be combined with scouring of polyester fabric in one bath, which shortens the process flow, reduces water and energy, and increases the production efficiency.[21,22] Especially, the problem of tar spots on polyester fabric was eliminated by dyeing in the alkali bath.[10,23] Among these alkali-stable disperse dyes, heterocyclic azo disperse dyes[24] have attracted much attention due to their bright shades, high molar extinction coefficients,[25] and excellent colorfastness.[26] However, most of the alkali-stable disperse dyes have limitations in alkali resistance[18,27] so the dyeing of polyester fabric with alkali-stable disperse dyes cannot be combined with alkali reduction treatment in one bath, which often requires a concentration of 10 g/L sodium hydroxide or higher.[22,28,29] Especially, the peroxide resistance of these alkali-stable disperse dyes cannot meet the requirement of the one-bath process of cotton/polyester blended fabric for bleaching with hydrogen peroxide and dyeing with disperse dyes. Our previous research focused on benzothiazole-azo disperse dyes and their resistance to alkali and peroxide. The results showed that the synthesized benzothiazole-azo disperse dyes are stable under the dyeing conditions of 10 g/L sodium hydroxide and 5 g/L hydrogen peroxide,[30] which can be applied not only for dyeing and alkaline reduction of polyester fabric in one bath but also for dyeing and peroxide bleaching of polyester/cotton blend fabric in one bath.[31]

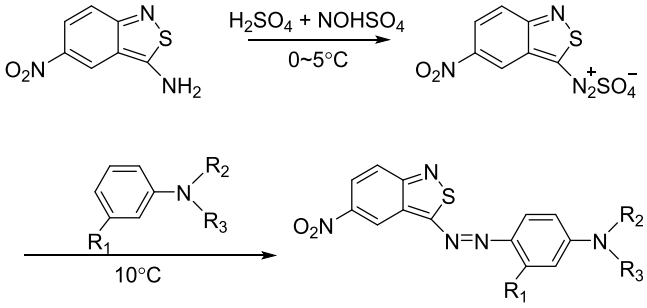
In this study, we proposed to synthesize a series of benzisothiazole-based heterocyclic azo disperse dyes that have high resistance to alkali reduction treatment and hydrogen peroxide bleaching. The high resistance to alkali reduction treatment allows for the polyester fabric to be processed for alkali reduction and dyeing in one bath, and the high resistance to hydrogen peroxide bleaching allows for the cotton/polyester blended fabric to be processed for hydrogen peroxide bleaching and dyeing in one bath. It is expected that the newly synthesized benzisothiazole-based heterocyclic azo disperse dyes will result in cleaner production, saving water and energy.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyester knitted greige fabric (100%, 188 g/m^2), polyester suede greige fabric (100%, 320 g/m^2), and polyester/cotton blended knitted greige fabric (polyester/cotton: 55/45, 260 g/m^2) were provided by Laimei Technology Co., Ltd. (Zhengjiang, China). All of the dye intermediates were provided by Penglai Jiaxin Dye Chemical Co., Ltd. (Shandong, China), including 3-amino-5-nitro-2,1-benzoisothiazole, *N*,*N*-diethylaniline, *N*-ethyl-*N*-hydroxyethylaniline, 2,2′-(phenylimino)diethanol, 2-(*N*-ethyl-*m*-toluidino)ethanol, *N*-(2-cyanoethyl)-*N*-benzyl-*m*-toluidine, *N*-cyanoethyl-*N*-benzylaniline, *N*-ethyl-*N*-cyanoethoxyethyl-*m*-methyl-aniline, *N*-ethyl-*N*-cyanoethoxyethyl-aniline, *N*-ethyl-*N*-*p*-methylbenzylaniline, *N*-ethyl-*N*-*p*-methylbenzyl-*m*-aniline, *N*-ethyl-*N*-benzyltoluidine, and *N*-benzyl-*N*-ethylaniline. All other chemical reagents (Analytical Reagent, AR) for the syntheses, dyeing, characterizations, and measurement of the dyeing properties were purchased commercially (Sinopharm Chemical Reagent Co., Ltd., China). Leveling agent NICCA SUNSOLT 7000Z (industrial reagent) was purchased from Rihua Chemical Co., Ltd. (Shanghai, China). Stabilizing agent DM1403 (industrial reagent) was purchased from Dymatic Co., Ltd. Other chemicals used in experiments were all laboratory reagent grade.

2.2. Synthesis and Characterization of Dyes. The benzisothiazole-based heterocyclic azo disperse dyes were synthesized as shown in Scheme 2.

Scheme 2. Synthesis of Benzisothiazole-Based Heterocyclic Azo Disperse Dyes



2.2.1. Preparation of Diazonium Salt. Concentrated sulfuric acid (50 mL) was slowly added to a solution of 5-nitro-3-aminobenzisothiazole (19.5 g, 0.1 mol). The temperature of the mixture was quickly dropped to 0−5 °C in an ice bath. An appropriate amount of nitrosyl sulfuric acid was added to the mixture for diazotization at 0−5 °C for 3 h. The reaction was monitored with starch-iodide paper. Once the nitrogen was consumed, the diazonium salt was obtained and used for coupling.

2.2.2. Coupling and Purification. Twelve coupling components with different substitute groups were used for synthesizing 12 different benzisothiazole-based heterocyclic azo disperse dyes, as shown in Table 1.

The coupling component was added to a mixture of water (60 mL), concentrated sulfuric acid (2 mL), and sulfamic acid (0.2 g, 0.02 mol) in a two-neck flask. The solution of the coupling component was cooled to 10 °C. The diazonium salt solution was added dropwise to the coupling solution with mechanical stirring at 10 °C, and the reaction mixture was stirred for 6 h. The reaction was monitored by thin layer chromatography (TLC). After the reaction was completed, the solution was neutralized with sodium hydroxide. The precipitated product was filtered, washed with water, and recrystallized from ethanol. The yield of each dye was then calculated.

2.2.3. Characterization. The melting points (MPs) were recorded on an X-4 micro-melting melting point apparatus (Yuhua Instrument Co., Ltd., China). ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded in $CDCl_3$ solution on an Avance III 400 MHz digital NMR spectrometer (Bruker, Switzerland). Chemical shifts (d) were relative to tetramethylsilane (TMS, d = 0.00) as an internal standard and were expressed in ppm. Mass spectra (MS) were recorded in positive electron spray ionization (ESI+) mode using a Waters (USA) MALDI Synapt Q-TOF mass spectrometer. The photophysical properties of the synthesized dyes were characterized in 1 cm quartz cells using a UV-2600 UV−vis spectrophotometer (Shimadzu, Japan) with acetone, ethanol, and *N*,*N*-dimethylformamide (DMF) as solvents. Characterization data of dyes are provided in the Supporting Information.

2.2.4. Milling of Dyes. The purified dyes were milled with sodium lignin sulfonate (1:1, w/w) at 500 r/min for 8 h at 25 °C using a spherical grinder with the addition of a fixed amount of water (to ensure a solid content of 45%) and zirconium beads. The milled dyes were dried and then mixed at a high speed for 20 min to obtain the final dye powder.

2.3. Dyeing Experiments. *2.3.1. Tests of Resistance of the Synthesized Disperse Dyes to Alkali and Peroxide.* The dye bath was prepared by adding 2.0% of a synthesized disperse dye on weight of fabric and 1 g/L leveling agent. A 5 g sample of

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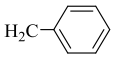
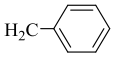
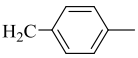
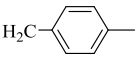
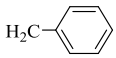
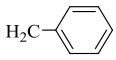
Table 1. Substitute Groups of the Coupling Component for Target Dye

Term for target dye	Substitute groups of coupling component		
	R_1	R_2	R_3
D1	H	CH_2CH_3	CH_2CH_3
D2	H	CH_2CH_3	CH_2CH_2OH
D3	H	CH_2CH_2OH	CH_2CH_2OH
D4	CH_3	CH_2CH_3	CH_2CH_2OH
D5	CH_3	CH_2CH_2CN	
D6	H	CH_2CH_2CN	
D7	H	CH_2CH_3	$C_2H_4OC_2H_4CN$
D8	CH_3	CH_2CH_3	$C_2H_4OC_2H_4CN$
D9	H	CH_2CH_3	
D10	CH_3	CH_2CH_3	
D11	H	CH_2CH_3	
D12	CH_3	CH_2CH_3	

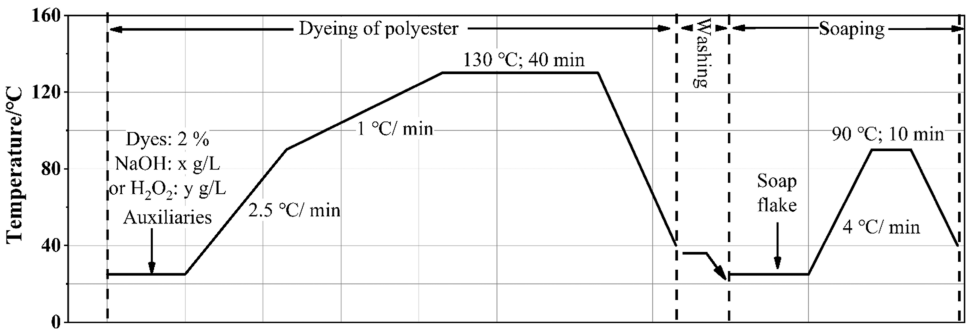


Figure 1. Process diagram of dyeing for polyester.

polyester fabric was added to the dye bath at a liquor-to-goods ratio of 20:1. Various concentrations of sodium hydroxide (0−10 g/L) or a buffer solution (0.05 M, pH 8−13) were added to the dye bath to investigate the resistance of the synthesized disperse dyes to alkali. Various concentrations of hydrogen peroxide (35% w/w, 0−5 g/L) were added to the dye bath at pH 11 (0.05 M buffer solution) to investigate the resistance of the synthesized disperse dyes to peroxide. The dye bath buffered at pH 5 was used as a standard reference. The dyeing experiments were conducted in an Ahiba IR Dyeing Machine (Datacolor, USA). The dyed fabric was cleaned through a soaping process. The process diagram for dyeing is shown in Figure 1.

2.3.2. Pilot-Plant Production. 2.3.2.1. Pilot-Plant Production of Polyester Suede Fabric. The conventional production of polyester suede fabric includes alkaline reduction (Stage I) and dyeing (Stage II) as shown in Figure 2. The polyester suede greige fabric (1000 kg) was immersed in a 10 g/L NaOH solution at a liquor-to-goods ratio of 20:1 for the alkaline reduction process, which was carried out according to the procedure (Stage I) as shown in Figure 2. When the alkaline reduction was completed, the polyester suede fabric was rinsed in hot water and neutralized with acetic acid. The polyester suede fabric was then dyed at pH 5 with a synthesized disperse dye (e.g., D12) in an amount of 2% on weight of fabric. The process of dyeing was carried out according to the procedure (Stage II) as shown in Figure 2. When the dyeing was completed, the polyester suede fabric was treated in a reduction cleaning bath with the addition of 2 g/L $Na_2S_4O_2$ and 2 g/L NaOH at 85 °C for 10 min. Then, the fabrics were thoroughly rinsed with water and dried.

A one-bath process for production of polyester suede fabric was designed using a newly synthesized disperse dye (e.g., D12) as shown in Figure 3. The polyester suede greige fabric (1000 kg) was immersed in a 10 g/L NaOH solution, 2% of D12 based on weight of fabric, and other dyeing auxiliaries. The one-bath process was carried out according to procedure (a) in Figure 3. When the one-bath process was completed, the polyester suede fabric was cleaned through a soaping process, thoroughly rinsed with water, and dried.

2.3.2.2. Pilot-Plant Production of Polyester/Cotton Blended Fabric. The conventional production of polyester/cotton blended fabric includes bleaching of the cotton component (Stage I) and dyeing of the polyester component (Stage II) as shown in Figure 4. The polyester/cotton blended

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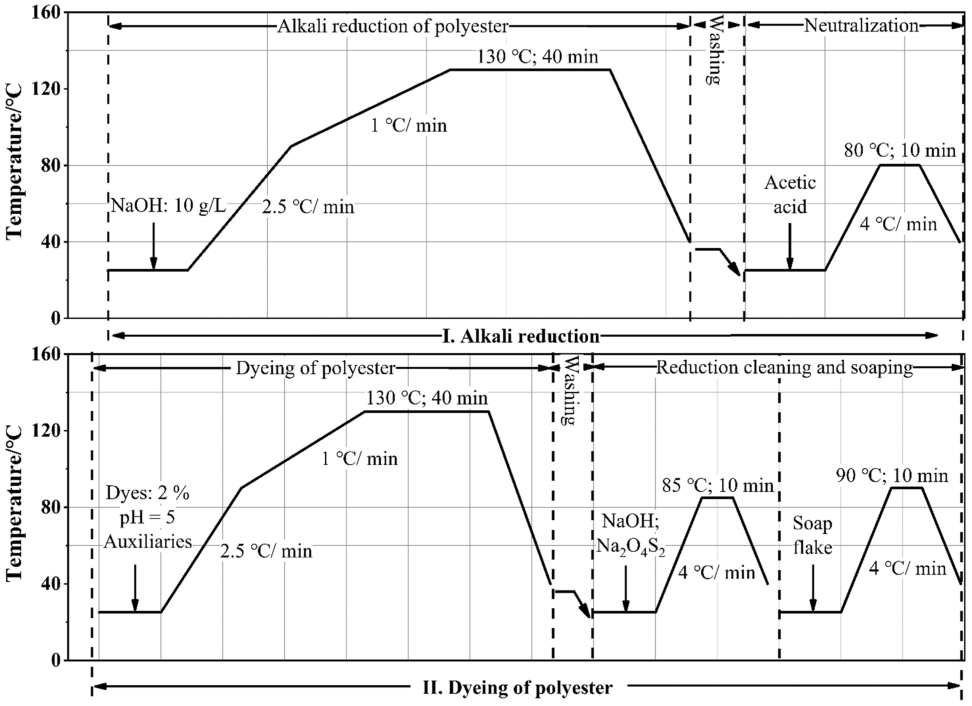

Figure 2. Process diagrams of conventional production of polyester suede fabric.

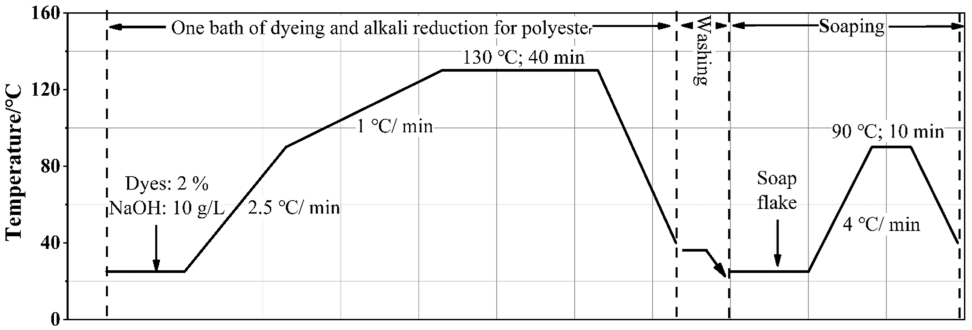

Figure 3. Process diagrams of one-step dyeing of polyester suede fabric.

greige fabric (1000 kg) was immersed in a bleaching bath containing 5 g/L hydrogen peroxide (35% w/w), 2 g/L sodium hydroxide, and other auxiliaries at a liquor-to-goods ratio of 20:1. The process of bleaching was carried out according to the procedure (Stage I) shown in Figure 4. When the bleaching was completed, the polyester/cotton blended fabric was neutralized with acetic acid and thoroughly rinsed with water. The polyester/cotton blended fabric was then dyed at pH 5 with a synthesized disperse dye (e.g., D12) in an amount of 2% on weight of fabric. The process of dyeing was carried out according to the procedure (Stage II) shown in Figure 4. When the dyeing was completed, the polyester/cotton blended fabric was treated in a reduction cleaning bath with the addition of 2 g/L $Na_2S_4O_2$ and 2 g/L NaOH at 85 °C for 10 min. The polyester/cotton blended fabric was then thoroughly rinsed with water and dried.

A one-bath process for production of polyester/cotton blended fabric was designed using a newly synthesized disperse dye (e.g., D12) as shown in Figure 5. The polyester/cotton blended greige fabric (1000 kg) was immersed in the process bath containing 5 g/L hydrogen peroxide (30% w/w), 2 g/L sodium hydroxide, 2% of D12 based on weight of fabric, and other dyeing auxiliaries at a liquor-to-goods ratio of 20:1. The one-bath process was carried out according to the procedure (a) in Figure 5. When the one-bath process was completed, the polyester/cotton blended fabric was cleaned through a soaping process, thoroughly rinsed with water, and dried.

2.4. Measurements. *2.4.1. Color Strength and Color Difference.* The color strength (K/S value) of the dyed fabrics and color difference (ΔE_{CMC}) between dyed fabrics were, respectively, measured according to the standard of AATCC Evaluation Procedure 6−2016 with the settings of the CIE Illuminant D65 and the CIE 1964 Standard Observer. The degree of whiteness of the bleached polyester/cotton blended fabric was measured using the CIE whiteness index (WI) according to the AATCC Test Method 110−2010.

2.4.2. Colorfastness. The colorfastness to washing, sublimation, rubbing, and light was measured in terms of AATCC TM 61−2009, ISO 105-X11:1994, ISO 105-X12:2016, and ISO 105-B02:2014, respectively.

2.4.3. Alkaline Reduction Rate. The alkali reduction rate (w %) was calculated using eq 1:

$$w\ \% = \frac{m_0 - m_1}{m_0} \times 100 \quad (1)$$

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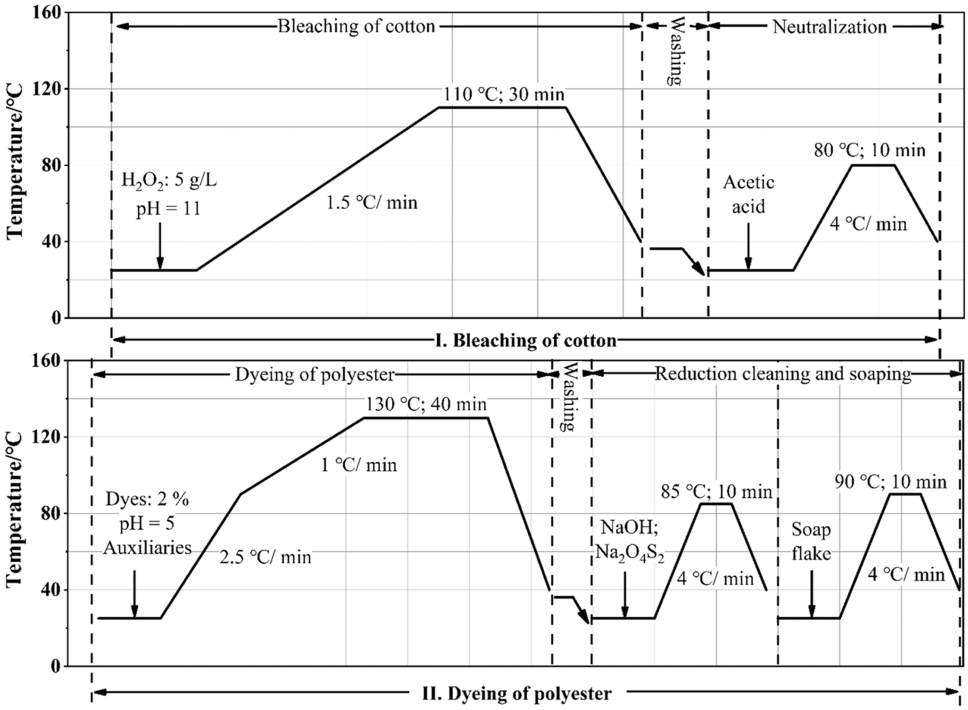

Figure 4. Process diagrams of conventional dyeing of polyester/cotton blended fabric.

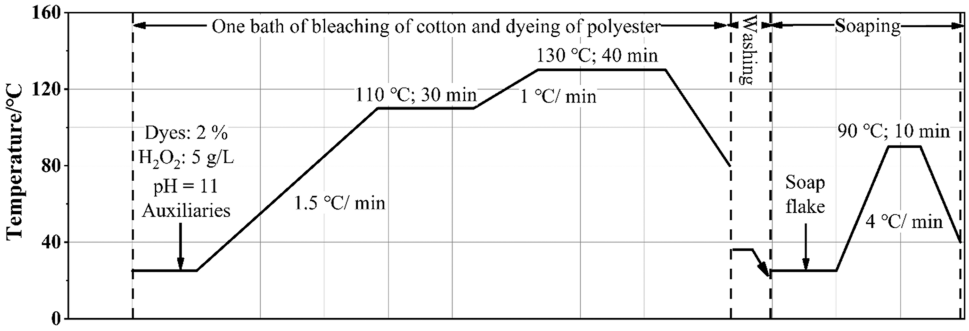

Figure 5. Process diagrams of one-bath dyeing of polyester/cotton blended fabric.

Table 2. Absorption Maximum Wavelength and Molar Extinction Coefficient of the Synthesized Dyes in Various Solvents

	acetone		ethanol		DMF	
dye	λ_{max}, nm	$\varepsilon \times 10^4$, L/(mol·cm)	λ_{max}, nm	$\varepsilon \times 10^4$, L/(mol·cm)	λ_{max}, nm	$\varepsilon \times 10^4$, L/(mol·cm)
D1	601.5	2.90	599.5	2.54	614.5	3.41
D2	600.0	3.45	598.0	3.14	615.0	3.75
D3	616.0	3.71	611.5	3.76	630.5	4.43
D4	615.5	3.34	610.0	2.91	630.0	3.49
D5	582.0	2.08	568.0	2.91	595.5	2.79
D6	568.0	2.32	564.0	2.65	582.0	2.16
D7	595.0	2.67	591.5	2.65	608.5	2.75
D8	611.5	3.01	595.0	3.74	623.0	2.82
D9	598.0	3.71	596.0	3.14	606.0	3.75
D10	607.0	2.13	603.5	1.19	621.0	2.43
D11	590.5	3.06	587.0	2.19	603.5	3.39
D12	599.5	3.98	597.0	2.59	612.0	3.99

where m_0 and m_1 are the dry weight of polyester fabric before and after alkaline reduction, respectively.

2.4.4. Bursting Strength. The bursting strength of polyester and polyester/cotton fabrics dyed by the conventional method and the one-bath method was measured using an electronic strength tester HD 026N (Nantong Hongda Experimental Instrument Co., Ltd., China) according to the steel ball method described in ISO 3303-1: 2012(E), and the strength loss rate (l %) was measured and calculated using eq 2:

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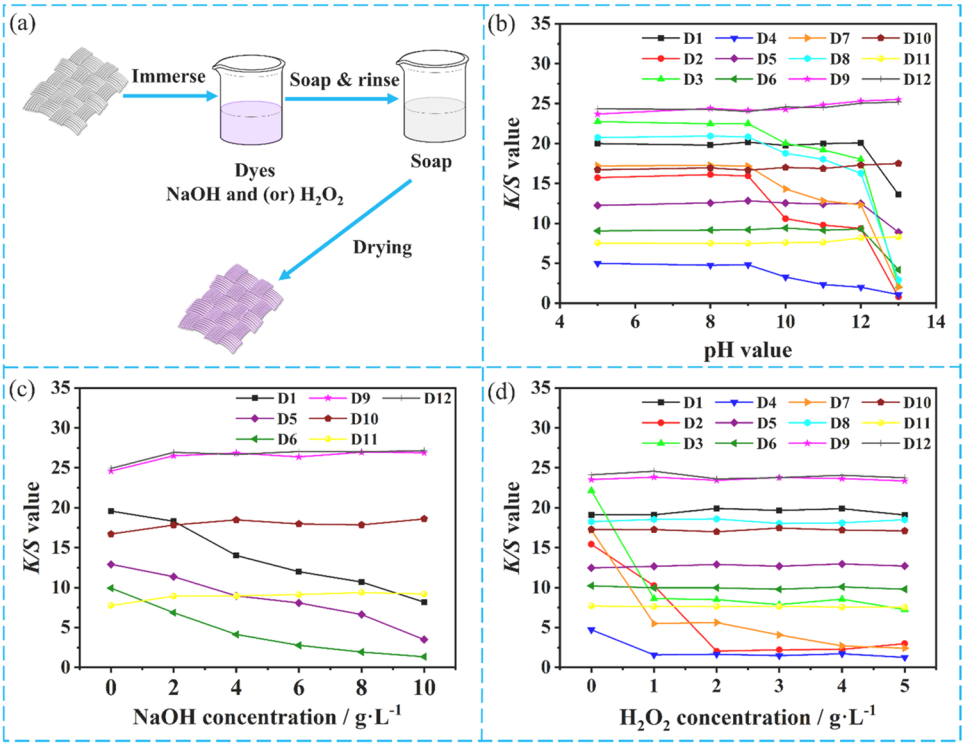

Figure 6. (a) Process diagrams of tests of resistance to alkali and peroxide; (b) *K*/*S* curves of the dyed polyester fabrics with D1−D12 under different pH values; (c) *K*/*S* curves of the dyed polyester fabrics with D1, D5−D6, and D9−D12 under different NaOH concentrations; and (d) *K*/*S* curves of the polyester fabrics dyed with D1−D12 under different H_2O_2 concentrations.

$$l\,\% = \frac{S_0 - S_1}{S_0} \times 100 \qquad (2)$$

where S_0 and S_1 are the bursting strength of the polyester fabric before and after alkali reduction, respectively.

3. RESULTS AND DISCUSSION

3.1. Photophysical Properties of Dyes. Photophysical properties of the synthesized disperse dye powder in acetone, ethanol, and DMF were measured. The absorption maximum wavelength (λ_{max}) and molar extinction coefficient (ε) of these synthesized disperse dyes in various solvents are shown in Table 2.

As shown in Table 2, the λ_{max} of D1 to D12 in acetone ranging from 568 to 616 nm indicated a hue from greenish to purplish-blue. The dominant hue of all of the synthesized disperse dyes was blue as they have the same diazo component. The maximum extinction coefficients of most synthesized disperse dyes are more than 20 000 L/(mol·cm), indicating that they have excellent chromogenic properties and can provide strong color strength. The difference in λ_{max} of the dyes was mainly caused by the different substituents in the coupling component. The introduction of hydroxyl groups in D3 and D4 increased the hydroxyl polarity of dyes, leading to a bathochromic shift (+15.5 nm, D3; +15 nm, D4) and an increase in molar extinction coefficient of dyes. The introduction of cyano groups caused a hypochromatic shift (−22.5 nm, D6; −17.5 nm, D5) due to their electron-accepting effect.

The λ_{max} of all of the synthesized disperse dyes in DMF showed bathochromic shifts compared with that in ethanol and acetone, due to the polarity differences of the three solvents. For all of the synthesized dye molecules assigned to the $\pi-\pi^*$ transition system, the ground state was less polar than the excited state. Hence, with the increase of the polarity of the solvent (ethanol < acetone < DMF), the energy of the ground state was almost unaffected while the energy of the excited state decreased, which led to a hyperchromic effect.[19]

3.2. Resistance to Alkali. The alkaline resistance of the synthesized disperse dyes was examined by the dyeing of polyester fabric (Figure 6a) at various pH values. The color strength (*K*/*S* value) of the dyed polyester fabric was measured as an indicator of alkaline resistance. As shown in Figure 6b, the *K*/*S* values of the polyester fabric dyed with each synthesized disperse dye are stable in the range of pH 5−9, indicating that all of the 12 synthesized disperse dyes have alkaline resistance. However, the *K*/*S* values of the polyester fabrics dyed with D2, D3, D4, D7, and D8 decreased as the pH increased from 9 to 13. This is mainly due to the fact that the hydroxyl groups in D2, D3, and D4 were ionized and the cyano group in D7 and D8 hydrolyzed under stronger alkaline conditions. Though D5 and D6 have a cyano group, they have better alkaline resistance than D7 and D8. This may be ascribed to the introduction of the benzene group, which can provide good coplanarity to the adjacent cyano group, enhance the $\pi-\pi$ stacking interaction between two adjacent dye molecules, and protect the cyano group from hydrolysis under alkaline conditions.[1] However, as the pH increased up to 13, the hydrolysis of the cyano group in D7 and D8 occurred, resulting in a decrease in dyeing performance. Among these synthesized disperse dyes, D9−D12 exhibited excellent dyeing performance in a wide range of pH values, which might be the ideal candidates for alkaline-resistant disperse dyes.

The alkaline resistance of D1, D5, D6, and D9−D12 was further examined by adding various amounts of sodium hydroxide to dyeing baths (Figure 6a). The color strength of the dyed polyester fabric is shown in Figure 6c. It can be seen

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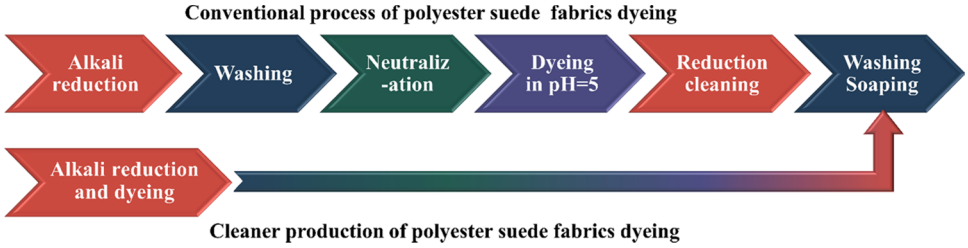
Scheme 3. Dyeing Procedures of Polyester Suede Fabrics



that the color strengths of polyester fabrics dyed with D1, D5, and D6 decreased as the concentration of sodium hydroxide increased. The decreasing performance of D1, D5, and D6 was ascribed to their instabilities in a strongly alkaline bath. Though D1, D5, and D6 are stable at pH 12 (as shown in Figure 6b), they may undergo chemical changes in the presence of a strong alkali such as sodium hydroxide. Comparatively, the dyes of D9−D12 exhibited excellent dyeing performance and were quite stable in the range of 0−10 g/L sodium hydroxide. This indicates that the dyes of D9−D12 have excellent alkaline resistance and can be used for dyeing polyester fabric with the addition of sodium hydroxide.

3.3. Resistance to Peroxide. The peroxide resistance of the synthesized disperse dyes was examined by the dyeing of polyester fabric in an alkaline bath containing various concentrations of hydrogen peroxide (Figure 6a), and the results are shown in Figure 6d. In the alkaline dyeing bath, hydrogen peroxide dissociated into perhydroxyl anions (HOO^-) by reaction with hydroxyl anions (HO^-). Therefore, HOO^- and HO^- are two main types of species that may potentially attack auxochromes (e.g., cyanoethyl and hydroxylethyl) and chromophores (e.g., azo) of these dyes. As shown in Figure 6d, the color strength of polyester fabric dyed with D2, D3, D4, and D7 decreased drastically as the concentration of hydrogen peroxide increased, which was mainly caused by ionization of the hydroxylethyl group and hydrolysis of the cyanoethyl group under alkaline conditions. D8 had higher alkaline resistance than D7 because of the methyl group in the ortho-position of the azo group, which may enhance the dye's stability by its electron-donating effect. It seems that HOO^- does not destroy the azo group of the disperse dyes.

3.4. Performance of Pilot-Plant Production of Polyester Suede Fabric. The conventional production of the polyester suede fabric includes the processes of alkaline reduction, washing, neutralization, dyeing at pH 5, reduction cleaning, soaping, and washing, as shown in Scheme 3. Using the synthesized alkaline-resistant disperse dyes, the processes of alkaline reduction and dyeing can be combined into one bath, but the processes of washing, neutralization, and reduction cleaning are excluded from the production of the polyester suede fabric. The combined process was examined by producing 1 ton of polyester suede fabric in comparison with the conventional production. As shown in Table 3, the alkaline reduction rate, strength loss rate, and color appearance of polyester suede fabric produced by the combined process were close to the alkaline reduction rate and color appearance of polyester suede fabric produced by the conventional process. Figure 7 shows that the colorfastnesses of the two polyester suede fabrics were similar. This indicates that the combined process could meet the requirement for production of polyester suede fabric.

3.5. Performance of Pilot-Plant Production of Polyester/Cotton Blended Fabric. The conventional production

Table 3. Performance Comparison of Dyed Polyester Suede Fabrics with Conventional and One-Step Processes

	alkali reduction rate (w %)	strength loss rate (l %)	λ_{max}, nm	K/S value	ΔE_{CMC}
conventional process	10.50	11.05	612.0	18.56	0.86
one-step process	9.15	9.31	612.0	19.68	

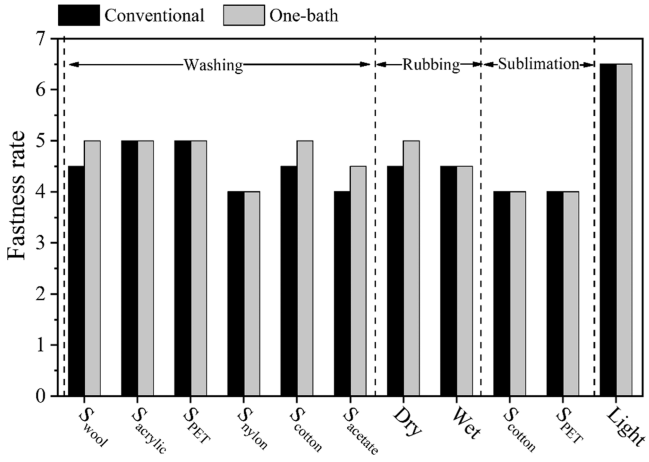


Figure 7. Colorfastness comparison of dyed polyester suede fabrics with conventional and one-step processes.

of polyester/cotton blended fabric includes the process of bleaching, washing, acidic neutralization, dyeing of polyester with disperse dyes at pH 5, reduction cleaning, dyeing of cotton with reactive dyes, soaping, and washing, as shown in Scheme 4. Using the synthesized disperse dyes, the bleaching of cotton and the dyeing of polyester can be combined into one bath, but the washing, acidic neutralization, and reduction cleaning are excluded from the production of the polyester/cotton blended fabric. The combined process was examined by producing 1 ton of polyester/cotton blended fabric in comparison with the conventional production. As shown in Table 4, the two production processes could provide the polyester/cotton blended fabric with a similar whiteness index, strength loss rate, and almost the same color appearance. The two dyed polyester/cotton blended fabrics had the same colorfastness as shown in Figure 8. This indicates that the combined process could meet the requirement for production of polyester/cotton blended fabrics.

3.6. Resource Consumption Estimation. Based on the pilot-plant production (e.g., 1-ton scale) of polyester suede fabric and polyester/cotton blended fabric in Jiangsu Lianfa Textile Co., Ltd. (Jiangsu, China), the consumption of resources such as electric power, steam, water, and man-hour was estimated as shown in Table 5. It can be seen that, in

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Scheme 4. Dyeing Procedures of Polyester/Cotton Blended Fabrics

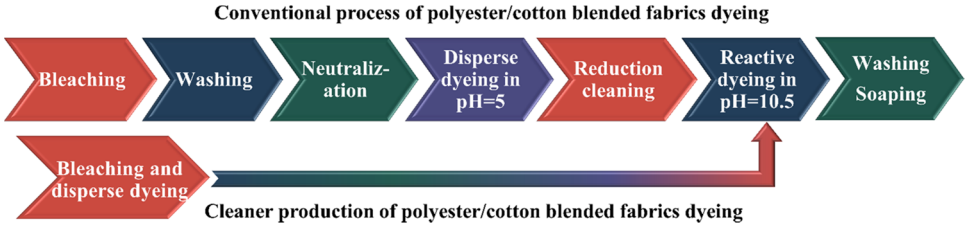

Table 4. Performance Comparison of Bleached Cotton Ingredient and Dyed Polyester Ingredient of Polyester/Cotton Blended Fabrics with Conventional and One-Bath Processes

			color appearance		
production	CIE WI	strength loss rate (l %)	λ_{max}, nm	K/S value	ΔE_{CMC}
conventional	79.86	12.48	612.0	18.96	0.35
one-bath	77.83	10.68	612.0	18.74	

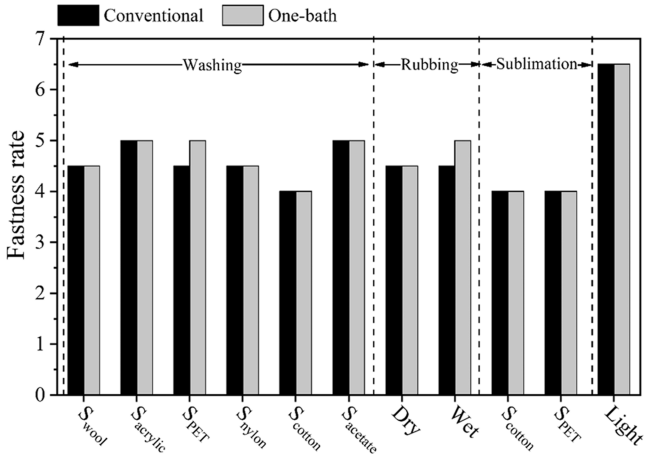

Figure 8. Colorfastness comparison of dyed polyester ingredients of polyester/cotton blended fabrics with conventional and one-bath processes.

Table 5. Resource Consumption in Production of Polyester Suede Fabric and Polyester/Cotton Blended Fabric

	production of polyester suede fabric			production of polyester/cotton blended fabric		
resource	conventional	one-bath	save rate (%)	conventional	one-bath	save rate (%)
electric power, kW·h	467	267	43	576	360	38
steam, ton	4.44	3.33	25	2.81	1.62	42
water, ton	56	28	50	90	60	33
man-hour, h	7	4	43	8	5	38

comparison with the conventional production processes, the newly designed production processes were shown to have great advantages such as saving 43% electric power, 25% steam, 50% water, and 43% man-hour in the production of polyester suede fabric and saving 38% electric power, 42% steam, 33% water, and 38% man-hour in production of polyester/cotton blended fabric. This can be mainly ascribed to the synthesized disperse dyes, which had good resistances to alkali and peroxide, allowing for the dyeing of polyester to be combined with alkaline reduction for the production of polyester suede fabric and combined with the bleaching of cotton for the production of polyester/cotton blended fabric. Therefore, the utilization of the synthesized disperse dyes resulted in cleaner production of polyester suede fabric and polyester/cotton blended fabric by saving energy and water and increasing production efficiency.

4. CONCLUSIONS

A new series of disperse dyes were designed and synthesized using 3-amino-5-nitro-2,1-benzoisothiazole as the diazo component. A total of 12 coupling components with various substituents were selected to obtain disperse dyes with high resistance to alkali and peroxide. These synthesized disperse dyes were confirmed by ^{1}H nuclear magnetic resonance and mass spectroscopy. UV−vis absorption spectroscopy showed that these synthesized disperse dyes gave colors from greenish to purplish-blue. The resistances of these disperse dyes to alkali and peroxide were examined by dyeing polyester fabric in sodium hydroxide and alkaline hydrogen peroxide solutions. It was found that the disperse dyes containing cyano and (or) hydroxyl groups exhibited poor dyeing performance under alkali conditions, which was ascribed to hydrolyzation of the cyano group and ionization of the hydroxyl group. The disperse dyes without cyano and hydroxyl groups exhibited great dyeing performance, indicating that these dyes were highly resistant to alkali and peroxide. One of these synthesized disperse dyes having high resistance to alkali and peroxide (e.g., D12) was used for the production of polyester suede fabric by combining alkaline reduction with dyeing in one bath and for the production of polyester/cotton blended fabric by combining the peroxide bleaching with dyeing in one bath. It was found from the results of pilot-plant productions that the newly designed processes could meet the production requirements and afforded enormous advantages in increasing production efficiency, conserving energy, and reducing emissions. Therefore, the synthesized disperse dyes with high resistance to alkaline and peroxide lead to the cleaner production of polyester and polyester/cotton blended fabrics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02720.

Characterization data and ^{1}H NMR and MS spectra of the synthesized dyes (PDF)

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Notes

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