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Design, synthesis of novel bisazo disperse dyes: Structure analysis and dyeing performance on PET



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ABSTRACT

To achieve bisazo disperse dyes with better dyeing performances, novel bisazo disperse dyes based on butane-1,4-diyl bis(ethyl(phenyl)carbamate) were synthesized by coupling with diazonium salts. Butane-1,4-diyl bis (ethyl(phenyl)carbamate) was prepared by condensation of 1,4-butanediol and N-ethyl-N-phenylglycinoyl chloride. N-ethyl-N-phenylglycinoyl chloride was achieved from N-ethyl-N-phenylglycine, which was hydrolyzed from ethyl N-ethyl-N-phenylglycinate. Compared with previously reported bisazo disperse dyes' low exhaustion, poor fastness performance or monotone color, constructed symmetrical bisazo disperse dyes exhibited excellent dyeing performance on polyethylene terephthalate (PET) fabrics, by introducing 1,4-butanediol as soft chain to lessen structure hardness of dye molecule and stronger hydrophobicity. Enhanced affinity between dye molecular and fiber was achieved by ester groups existing both in dye molecular and fiber, increased molecular size also enhanced stronger Van der Waals force and hydrogen bonding. Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance techniques (¹H NMR) were used to confirm the structures. Constructed bisazo disperse dyes were applied to estimate relationship between spectral properties and structures. Constructed bisazo disperse dyes were applied on polyethylene terephthalate (PET) fabric using conventional high temperature dyeing method under pressure, gave orange to blue shade with satisfying fastness properties. Quantum simulation was applied to provide a new guide line to evaluate structure-property relationship for dyestuffs.

1. Introduction

Azo disperse dyes play an important role in development of disperse dyes for coloring synthetic fibers [1,2]. Many studies about bisazo disperse dyes have been investigated to increase dye ability on PET fabric [3,4]. Dye chemists have been focused on improving tinctorial strength and fastness properties to fabrics over the years [5,6]. Low fastness and poor dyeing performance were attributed to weak dye-fiber affinity, disperse dyes containing multi-ester groups exhibited deeper and brighter intense hues, eater groups can also enhance dye-fiber affinity [6]. Increased molecular mass can also facilitate dye-fiber interaction, which help to reduce thermomigration of disperse dyes on hydrophobic fibers [7]. But Most developed bisazo disperse dyes are in rigid construction, leading to lower affinity with fabrics, which would increase burden of swage treatment [8,9].

disperse dyes are also good imitation of PET, which could help to boost dyeing performance and fastness properties. Increased molecular weight can enhance the fiber-dye intermolecular force to reduce the degree of thermomigration of dyes [13]. A wide range of color can also be achieved by varying diazonium components [14]. Dyed PET fabrics exhibit much better dyeing and fastness performance than previously reported bisazo disperse dyes [15–17][.] Quantum simulation was applied to discuss relationship between dyeing performance and structures of synthesized dyes [18]. Chromogenic moieties on both ends of symmetrical D1-D4 exhibited excellent coplanarity, which can enhance dye-fiber interaction, as PET also showed good coplanarity.

and soft alkane chains [12]. Those symmetric structure of biszao

2. Experimental

In this context, butane-1,4-diyl bis(ethyl(phenyl)carbamate) was designed as coupling compounds to enhance dye-fiber affinity and lessen chemical hardness of dye molecular, by inserted ester groups [10,11]

2.1. Materials and measurements

Polyester fabrics (plain weave, wrap/weft density 54/48 yarn/cm)

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Scheme 1. Synthsis route of ethyl N-ethyl-N-phenylglycinate.

were obtained from Zhejiang Xinfa Dyeing and Finishing Company, Shaoxing, China. N-ethylaniline (98%), 4-nitroaniline (99%), 2-amino-6-nitrobenzothiazole (99%), 3-amino-5-nitro(2,1)benzisothiazole (98%) and 2-amino-3,5-binotro-thiophene (95%) were obtained from Zhejiang Wanfeng Chemical Company, Shaoxing, China. Ethyl chloroacetate (98%), Oxalyl chloride (98%) and 1,4-butanediol (99%) were purchased from Shanghai Titan Scientific Co. Ltd., Shanghai, China. All the other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai, China. All chemicals were used as received without further purification.

FT-IR spectra were measured using a Spectrum Two FT-IR spectrometer (PerkinElmer *Perkin Elmer* Inc, Liantrisant, UK) scanning between 4000 and 500 cm^{-1.1}H NMR (400 MHz) were recorded on a Bruker AV 400 (Bruker Co., Faellanden, Switzerland), using chloroform*d* (CDCl₃) as the solvents at room temperature (25 °C). The visible absorption spectra were measured using UV–vis spectrometer (Hitachi Limited, Japan). Melting points were measured by open capillary method with a Mel-Temp capillary melting point apparatus (Shanghai Precision and Scientific Instruments, China). Size distribution and zeta potential of aqueous dispersions were measured with a Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., United Kingdom) at 25 °C.

2.2. Preparation of intermediates

2.2.1. Synthesis of ethyl N-ethyl-N-phenylglycinate (I)

N-ethylaniline (24.40 g/0.20 mol) and sodium carbonate (Na₂CO₃, 10.60 g/0.10 mol) were added in three-necked, round bottomed flask containing 100 mL N,N-Dimethylformamide (DMF) at room temperature (RT). Ethyl chloroacetate (49.02 g/0.40 mol) was dropwise added into reaction mixture under constant stirring. The reaction mixture was heated to 110 °C stirred for 1 h, thin layer chromatography (TLC) method (toluene:acetone:acetic acid = 20:1:1 v/v) was applied to monitor the reaction. After the end of the reaction, the reaction mixture was added into ice slurry under stirring, then 100 mL dichloromethane (CH₂Cl₂) was added into mixture and fully mixed. The mixture was transferred into separating funnel and the lower organic liquid was kept. The organic layer was washed three times using 200 mL deionized (DI) water. The organic solution was evaporated under vacuum to remove solvent and excess ethyl chloroacetate. The ethyl N-ethyl-N-phenylglycinate (I, Scheme 1) was obtained as yellow liquid, 98.87% yield. ¹H NMR (CDCl₃, δ_H, ppm): 7.19–7.23 (m, 2H, Ar–H), 6.69–6.73 (t, 1H, Ar-H), 6.60-6.65 (d, 2H, Ar-H), 4.16-4.22 (q, 2H, -CH₂-), 4.01 (s, 2H, -CH2-), 3.44-3.49 (q, 2H, -OCH2-), 1.24-1.27 (t, 3H, -CH3) 1.19-1.22 (t, 3H, –CH₃). Main FT-IR absorption peaks (v, cm⁻¹): 2976, 2935, 1740, 1600, 1504, 1383, 1361, 1183, 1266, 1129, 1030.

2.2.2. Synthesis of N-ethyl-N-phenylglycine (II)

Sodium hydroxide (NaOH, 12 g/0.30 mol) was dissolved into mixture of ethanol (80 mL) and DI water (100 ml) at RT in a threenecked, round-bottomed flask. N-ethyl-N-phenylglycine (I, 41.40 g/ 0.20 mol) was slowly added into the reaction mixture under constant stirring. The reaction mixture was refluxed for 1 h. The same TLC method was applied to estimate the reaction. The mixture was cooled to RT after the end of the reaction, and hydrochloric acid was used to regulate pH to 5. CH₂Cl₂ (100 mL) and saturated brine (200 mL) was added into and mixed completely. The mixture was transferred into separating funnel and the organic liquid was kept. The organic layer was yellowish and washed three times using 200 mL brine. The organic solution was evaporated under vacuum to remove solvent. The N-ethyl-N-phenylglycine (II, Scheme 2) was achieved as honey-like viscous liquid, 81.17% yield. ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm): 7.12–7.16 (m, 2H, Ar–H), 6.56–6.62 (m, 3H, Ar–H), 4.11 (s, 2H, –CH₂-), 3.37–3.43 (q, 2H, –OCH₂-), 1.17–1.20 (t, 3H, –CH₃). Main FT-IR absorption peaks (ν , cm⁻¹): 3050, 2973, 2929, 2881, 1726, 1598, 1502, 1382, 1352, 1193, 1263, 1127, 1074, 1029.

2.2.3. Synthesis of N-ethyl-N-phenylglycinoyl chloride (III)

Oxalyl chloride (15.23 g/0.12 mol) was added dropwise to the mixture of N-ethyl-N-phenylglycine (II, 1.79 g/0.10 mol) and DMF (0.73 g/0.01mol) in CH₂Cl₂ at 0 °C. Resulting solution was warmed to RT and continued stirred for 6.5 h. The same TLC method was applied to confirm the reaction. Solvent and excessed oxalyl chloride were removed under reduced pressure to afford N-ethyl-N-phenylglycinoyl chloride (III, Scheme 3). The product was yellowish soft blocks, 98.73% yield.

2.2.4. Synthesis of butane-1,4-diyl bis(ethyl(phenyl)carbamate) (IV)

1,4-Butanediol (2.25 g/0.025 mol) and trimethylamine (Et₃N, 8.10 g/0.08 mmol) was dissolved in 100 mL CH_2Cl_2 at RT, and cooled to 0 °C. N-ethyl-N-phenylglycinoyl chloride (III, 19.80 g/0.1 mol) was slowly added into reaction solution under constant stirring. Resulting suspension was warmed to RT and continued stirred overnight. TLC method (hexane:ethyl acetate: acetic acid = 2:1:1) was applied to detect the reaction. Solvent and excessed Et₃N were removed under vacuum. Acetone (40 mL) was added into mixture and disperse completely. The mixture was filtered, and filtrate was evaporated under vacuum to remove the solvent. The excessed N-ethyl-N-phenylglycinoyl chloride (III) was separated out using DI water and chloroform extraction method. The organic layer was evaporated under vacuum to give desired product. Butane-1,4-diyl bis(ethyl(phenyl)carbamate) (IV, Scheme 4) was brown viscous mucus, 77.45% yield. ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm): 7.22-7.26 (m, 4H, Ar-H), 6.74-6.78 (t, 2H, Ar-H), 6.67-6.72 (t, 4H, Ar-H), 4.15-4.18 (t, 2H, -CH2-), 4.04 (s, 2H, -CH2-), 4.02 (s, 2H, -CH2-), 3.58-3.61 (t, 2H, -CH2-), 3.44-3.51 (m, 4H, -CH2-), 1.69-1.71 (t, 2H, -CH2-), 1.56-1.60 (t, 2H, -CH2-), 1.51-1.55 (t, 2H, -CH2-), 1.22-1.24 (t, 3H, -CH₃), 1.19-1.21 (t, 3H, -CH₃). Main FT-IR absorption peaks (v, cm-1): 2966, 2928, 1737, 1662, 1599, 1503, 1386, 1347, 1271, 1180, 1125, 1038.



Scheme 2. Synthsis route of N-ethyl-N-phenylglycine.



Scheme 3. Synthsis route of N-ethyl-N-phenylglycinoyl chloride.



Scheme 4. Synthsis route of butane-1,4-diyl bis(ethyl(phenyl)carbamate).



Scheme 5. Chemical structures of the synthesized bisazo disperse dyes.

2.3. Preparation of bisazo disperse dyes

Aromatic amines were diazotized according to previously reported methods [6,13]. Diazonium salts were coupled with coupling components to achieve desired bisazo disperse dyes. The chemical structures of the designed bisazo disperse dyes are shown in Scheme 5.

2.3.1. Synthesis of bisazo disperse dye D1

4-nitroaniline (0.56 g/4 mmol) was disperse in 1.50 mL water and 0.75 ml HCl (36%, v/v) at RT under constant stirring. After fully mixed for 30 min, sodium nitrite solution (0.5 g, 30%, w/w) was quickly added into the cooled suspension at 0–5 °C. The mixture was stirred for 1 h at 0–5 °C. Sulphamic acid was added to eliminate excessed nitrous acid. The resulting diazonium salt solution was dropwise added into cooled butane-1,4-diyl bis(ethyl(phenyl)carbamate) (**IV**, 0.79 g/2 mmol) solution in ethanol at 0–5 °C. The reaction mixture was warmed to 10–15 °C and stirred for 4 h. The reaction mixture was dispersed thoroughly in water and filtered to obtain the precipitate. The crude product was recrystallized from ethanol to get D1, 89.40% yield. Mp: 182–184 °C. ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm): 8.44–8.48 (m, 2H, Ar–H), 8.31–8.34 (m, 2H, Ar–H), 8.25–8.27 (m, 2H, Ar–H), 6.85–6.90 (m, 2H,

Ar–H), 4.39 (s, 2H, –CH₂-), 4.23–4.27 (t, 2H, –CH₂-), 3.71–3.75 (t, 2H, –CH₂-), 3.66–3.70 (t, 2H, –CH₂-), 1.35–1.38 (t, 3H, –CH₃). Main FT-IR absorption peaks (ν , cm⁻¹): 2968, 2931, 1736, 1593, 1511, 1384, 1327, 1249, 1188, 1131.

2.3.2. Synthesis of bisazo disperse dye D2

2-amino-6-nitrobenzothiazole was diazotized using nitrosylsulfuric acid (41%, w/w) as diazotization reagent in strong acid medium at 0–5 °C. The resulting diazonium salt was used in the coupling reaction with butane-1,4-diyl bis(ethyl(phenyl)carbamate) in the same condition as D1. Reaction mixture was added into water, then filtered to get crude product. Ethanol recrystallization method was applied to get purified D2, 83.65% yield. Mp: 102–104 °C. ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm): 8.75–8.77 (m, 1H, Ar–H), 8.33–8.36 (m, 1H, Ar–H), 8.12–8.16 (t, 1H, Ar–H), 7.99–8.04 (t, 2H, Ar–H), 6.72–6.77 (t, 2H, Ar–H), 4.23–4.26 (t, 2H, –CH₂-), 4.19 (s, 2H, –CH₂-), 3.63–3.68 (m, 2H, –CH₂-), 1.75–1.79 (t, 2H, –CH₂-), 1.31–1.35 (t, 3H, –CH₃). Main FT-IR absorption peaks (ν , cm⁻¹): 2969, 2872, 1738, 1597, 1552, 1512, 1406, 1363, 1326, 1273, 1188, 1140, 1108, 1073.



Fig. 1. Dyeing procedure of polyester using the synthesized dye.

2.3.3. Synthesis of bisazo disperse dye D3

3-amino-5-nitro(2,1) benzisothiazole was diazotized using nitro-sylsulfuric acid (41%, w/w) as diazotization reagent in concentrated sulfuric acid at RT. The resulting diazonium salt was used in the coupling reaction with butane-1,4-diyl bis(ethyl(phenyl)carbamate) in the same condition as D1. Water was added to precipitate the crude product. Pure D3 was derived from ethanol recrystallization method, 90.93% yield. Mp: 142–144 °C. ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm): 9.22 (s, 1H, Ar–H), 8.22–8.24 (t, 1H, Ar–H), 8.00–8.02 (m, 2H, Ar–H), 7.79–7.81 (t, 1H, Ar–H), 6.76–6.79 (m, 2H, Ar–H), 4.23–4.26 (t, 2H, –CH₂-), 4.21 (s, 2H, –CH₂-), 3.64–3.69 (m, 4H, –CH₂-), 1.32–1.35 (t, 3H, –CH₃). Main FT-IR absorption peaks (ν , cm⁻¹): 2967, 2930, 1735, 1591, 1506, 1401, 1309, 1242, 1196, 1111, 1065.

2.3.4. Synthesis of bisazo disperse dye D4

The same diazotization condition and coupling method as D3 to achieve D4 using 2-amino-3,5-binotro-thiophene as raw material, 95.47% yield. Mp: 108–110 °C. ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm): 8.38 (s, 1H, H of thiazole ring), 7.97–7.99 (d, 2H, Ar–H), 6.74–6.76 (d, 2H, Ar–H), 4.24–4.28 (t, 2H, –CH₂-), 4.22 (s, 2H, –CH₂-), 3.67–3.69 (t, 2H, –CH₂-), 3.64–3.66 (t, 2H, –CH₂-), 1.32–1.36 (t, 3H, –CH₃). Main FT-IR absorption peaks (ν , cm⁻¹): 3104, 2970, 2929, 1735, 1595, 1538, 1499, 1389, 1326, 1233, 1112, 1058, 1018.

2.4. Dyeing of PET using synthesized bisazo disperse dyes

PET fabrics were dyed using formulated dye, 0.5 g synthesized bisazo dye grinded with 0.5 g dispersant (Dispersant MF, anionic type) thoroughly, in a STARLET DL-6000 IR dyeing machine (Daelim Starlet Co., Ltd, South Korea) at a liquor ratio of 1:20. The dyeing profile was shown as Fig. 1.

The pH value of dye bath was adjusted to 4–5 using acetic acid solution (10%, v/v), and dye dosage was 1% (o.w.f.). Dyeing processes were commenced at 30 °C and raised at a rate of 2 °C/min to 130 °C, maintained for 60 min. Reduction cleaning of dyed PET fabrics were processed in an aqueous solution containing sodium dithionite (2 g/L) and sodium carbonate (2 g/L) at 85 °C for 15 min.

2.5. Color yield and levelness assessment

The colorimetric parameters of dyed polyester fabrics were determined by Datacolor SP 600 + spectrophotometer (Datacolor, Switzerland), under illuminant D65 using 10° standard observer in the visible spectrum region 380–720 nm. The measurements of the dyed samples were taken at least four different positions and averaged to achieve the final K/S value.

The dye exhaustion (E %) on PET was measured and calculated using equation (1):

$$E\% = \frac{n_0 A_0 - n_1 A_1}{n_0 A_0} \times 100\%$$
(1)

Where A_0 and A_1 are the absorptions before and after dyeing in their DMF solution and n_0 and n_1 are dilution ratios for dye liquor before and after dyeing, respectively.

The levelness of dyed samples was evaluated by comparing color differences. Five points on the dyed samples at 1% o.w.f. were measured. The first point was taken as the standard, the other four points were compared to give the ΔE values and averaged.

2.6. Fastness performance

Color fastness was evaluated according to the respective international standard methods. The fastness to rubbing was performed in a crockmeter (CM-5, Atlas Co., USA) with dry and wet samples according to ISO 105-X12 (2003), the staining on the white test cloth was assessed according to the gray scale. The fastness to washing was carried out by using a washing fastness apparatus (SW-12AII, Wenzhou Darong Textile Techology Co., Ltd, China) at 60 °C for 30 min according to ISO 105-C03 (2010), and staining on adjacent fabrics (Multifibre DW, Shanghai Textile Industry Institute of Technical Supercision, China) were applied to for the assessment of staining fastness, treated samples were also compared with original samples to evaluate their shade change. The sublimation fastness test was processed by using a sublimation tester (YG(B)605D, Wenzhou Darong Textile Techology Co., Ltd, China) to heat the samples at 180 °C and 210 °C for 30 s according to ISO105/P01 (1993), and adjacent fabrics of Multifibre DW were applied for assessment of staining fastness. The light fastness was performed by employing a light fastness tester (150S+, Altas Co. USA) with xenon lamps for a certain period of time according to ISO I05-B02 (2013), and blue scale was used for light fastness assessment.

2.7. Stability of dispersion and pH stability assessment

Stability of dispersion was determined by particle size distribution and zeta potential of bisazo disperse dye suspensions. Dye dispersions at 1 g/L were processed according to dyeing profile of Fig. 1 without PET, which was compared with milled bisazo disperse dyes bath without dyeing process. Particle size distribution and zeta potential of diluted dye suspensions at 0.2 g/L, before and after dyeing process, were measured to estimate stability of dispersion.

pH stability of dyeing bath was evaluated by adjust pH of dyeing bath according to dyeing profile of Fig. 1 at 1% o.w.f. The pH-value of the dye liquor was adjusted to 5.5 with CH₃COOH solution, 7 without other additives, 9, 11 and 13 using NaOH solution. Dyed fabric samples were reductive cleared and compared to evaluate pH stability of synthesized bisazo disperse dyes.



Fig. 2. The optimized geometries for D1-D4 and PET (front and side view).



Fig. 3. UV-Vis absorption for D1-D4 in their DMF solution.

2.8. Computational methods

The optimized geometries (Fig. 2) at ground state of designed disazo disperse dyes have been computed with DFT method at B3LYP/6-31G (d) level by Gaussian 16 program. It can be indicated that chromogenic moieties on both ends of symmetrical D1-D4 exhibited excellent coplanarity, which can enhance dye-fiber interaction, as PET also showed good coplanarity. The π electron distribution of dyes were analyzed with wavefunction analysis code Multiwfn to evaluate dyeing performance of synthesized dyes.

3. Results and discussions

As an attempt to generate disazo disperse dyes containing both ester group and soft chain in their structures, butane-1,4-diyl bis(ethyl (phenyl)carbamate) was designed and synthesized. Chloroactic acid was proposed as raw material to react with N-ethylaniline to obtain N-ethyl-N-phenylglycine (II). But carboxyl group of chloroactic acid exhibited much stronger polarity than ester group of ethylchloroacetate, leading to incomplete reaction with N-ethylaniline. Ethylchloroacetate was reacted with N-ethylaniline thoroughly, and product I was hydrolyzed into N-ethyl-N-phenylglycine (II) with acidification. Oxalyl chloride was applied as acylation reagent to give N-ethyl-N-phenylglycinoyl chloride (III), which is much easier to react with alcohol than carboxyl compounds. Diazonium was reacted with symmetrical butane-1,4-diyl bis (ethyl(phenyl)carbamate) (IV) to achieve novel bisazo disperse dyes.

3.1. Spectral properties of synthesized bisazo disperse dyes

Relationship between structure and color is an important part in both dye development and its commercialization. The absorption spectra of bisazo disperse dyes in their DMF solutions were shown in Fig. 3.

The color of the dye is correlated with both coupling component and diazo component. In this paper, synthesized bisazo disperse dyes' color was influenced by diazo compounds with fixed coupling component. The wavelength of absorption maxima (λ_{max}) and molar extinction coefficients (ε) of the four dyes were also compared to illustrate relationship between color and structure (Table 1).

The synthesized bisazo disperse dyes are symmetrical D- π -A (Donor- π -acceptor) structures. The λ_{max} of the bisazo disperse dyes ranged from 478 to 629 nm. Bathochromic shifts of the visible absorption band were observed, which was attributed to electronic transitions of whole conjugated structures in solvent. The bisazo disperse dyes also exhibited marvelous much higher ε values than reported bisazo disperse dyes [5,

Table 1

|--|

Dye	λ_{\max} (nm)				$arepsilon$ ($ imes$ 10 ⁴ L mol $^{-1}$ cm $^{-1}$)				
	DMF	CH ₃ OH	CH ₃ CN	CHCl ₃	DMF	CH ₃ OH	CH ₃ CN	CHCl ₃	
D1	478	460	460	460	4.55	4.43	4.42	4.33	
D2	540	530	525	523	7.44	6.99	7.29	7.15	
D3	592	575	575	569	4.77	4.57	4.51	4.45	
D4	629	615	605	605	5.21	5.43	5.17	5.03	



Fig. 4. Effect of dyeing time on the K/S value on PET fabrics.

 Table 2

 Dye exhaustion and levelness of bisazo disperse dyes.

Dye	D1	D2	D3	D4
E%	94.26	96.70	99.45	99.88
ΔE	0.46	0.32	0.21	0.30

8]. The higher ε values, the stronger chromophore, makes dyes more cost effective [19]. D2 exhibited much higher ε values, 70000, than other heterocylic bisazo disperse dyes. Carbocyclic D1 also achieved ε value at 45000, higher than reported carbocyclic bisazo disperse dyes [16,17].

3.2. Dyeing properties on PET fabrics

The synthesized bisazo dispersed dyes were applied at 1% (o.w.f) depth on polyester fabric. K/S was used to represent color depth of dyed PET fabrics, and data was curved in Fig. 4.

It can be indicated from Table 2 that ΔE of the dyed samples was less

than 0.5, the levelness was considered to be excellent. The exhaustion for synthesized bisazo disperse dyes was more than 94% using traditional high temperature dyeing under pressure. The high exhaustion of the dyes was attributed to enhanced dye-fiber affinity by stronger hydrogen bond and van der Waals force between fiber and synthesized dyes. Ester groups and larger molecular mass were the main factor to afford high exhaustion, soft hydrophobic alkyl chain also help to penetrate into fibers to achieve high exhaustion. The high exhaustion of those dyes can be attributed to chromogenic skeleton. As shown in Fig. 5, both PET and chromogenic skeleton exhibited coplanar structure, which facilitated π - π interaction between PET and dyes.

As shown in Fig. 6, synthesized bisazo exhibited different color yield with increased dye concentration. Heterocylic bisazo disperse dyes showed satisfying K/S values with increased dye concentration. D1 showed lower color yield than those heterocylic-containing bisazo disperse dyes.



Fig. 6. Build-up curves of bisazo disperse dyes.



Fig. 5. π electronic structure of D1-D4, and PET (front and side view).

Table 3

Particle size, Zeta potential of aqueous suspensions of bisazo disperse dyes.

Samples		average particle size (nm)	Zeta Potential (mV)
D1	before	588	-39.13
	after	420	-35.50
D2	before	594	-38.40
	after	539	-35.10
D3	before	357	-50.80
	after	294	-47.17
D4	before	220	-50.3
	after	216	-46.60



Fig. 7. K/S for D1-D4 dyed PET fabrics at different pH-values.

3.3. Stability of dispersion and pH stability

The stability of the bisazo dye dispersions were evaluated by measuring their particle size and Zeta potential (Table 3). The pH stability of dyeing bath was evaluated using dyed fabric samples dyed at pH = 5.5, 7, 9, 11, 13. K/S was used to represent color depth of dyed PET fabrics and compared to express pH stability of bisazo disperse dyes, as curved in Fig. 7.

As shown in Table 3, the bisazo dye bath exhibited good disperse stability, dye suspensions showed slightly decreased average particle size after high temperature and high pressure dyeing process. The average particle size of aqueous suspensions were at the range of 220–594 nm before dyeing, and 216–539 nm after dyeing process. Carbocyclic D1 showed the most obvious decreased average particle size, form 588 nm–420 nm. Heterocyclic D2-D4 showed relative less decreased average particle size. Zeta potentials of aqueous suspensions were around $-38 \sim -50$ mV, showed slightly change after dyeing process. The dye dispersions exhibited excellent disperse stability even processed by severe dyeing environment, average particle size <600 nm, far below 1 μ m.

Table 4

Fastness properties of dyed PET fabrics

As shown in Fig. 7, the bisazo disperse dyes showed poor dyeing performance under alkaline condition, which was attributed to ester groups in dye molecular structures. Ester groups can be hydrolyzed under high temperature and alkaline condition. D1-D3 showed different degrees of shade reduction with increased pH-value. D4 containing thiophene rings can be easily decomposed under alkaline condition [20, 21], showed the worst alkaline-resistance.

3.4. Fastness properties of dyed PET fabrics

Synthesized bisazo disperse dyes endowed a wide range of color ranging from orange to blue shade with good levelness, brightness and depth on the fabric. All the fastness properties of dyed PET fabrics using synthesized bisazo disperse dyes are shown in Table 4. Samples applied to estimate their rubbing, washing and sublimation fastness were 1% o. w.f. dyed PET fabrics, and 0.5% o.w.f. for light fastness.

As shown in Table 4, the dved PET fabrics exhibited excellent washing fastness and good to excellent sublimation fastness at 180 °C, which was attributed to enhanced dye-fiber affinity. Sublimation fastness tested at 210 °C showed obvious decreased level for staining on polvester. Rubbing fastness was designed to determine the amount of color transferred from surface of dved PET to another surface under rubbing. Synthesized dyes exhibited a moderate (3) to excellent (5) rubbing fastness, which was attributed to inadequate diffusion of dve into fibers. Commercial azo disperse dyes showed poor light fastness (\leq 3), which was attributed to diazo components were prone to photofading. The prepared dyes showed better light fastness, which might be ascribed to less prone to fading. Ester groups, polar group (-NO₂) existed in dye and large molecular mass help to reinforce hydrogen bond and van der Waals force between bisazo disperse dyes and PET. The dyed fabrics showed excellent washing fastness, no staining on adjacent fabrics, as well as barely shade change after treatment.

4. Conclusion

The novel symmetrical coupling component, butane-1,4-diyl bis (ethyl(phenyl)carbamate), has been synthesized using 1,4-butanediol as linker to react with synthesized N-ethyl-N-phenylglycinoyl chloride. Bisazo disperse dyes are synthesized using synthesized butane-1,4-diyl bis(ethyl(phenyl)carbamate) and characterized. These dyes give orange, red, purple and blue shades on PET fabrics having good fastness performance. The visible absorption and the shade of the dyed fabric are correlated with diazo components. Excellent levelness and exhaustion indicates the good penetration and affinity of these dyes to fabric. The high color yield is attributed to instrinsic conjugation structure of the bisazo disperse dyes.

CRediT authorship contribution statement

Shengli Wang: Synthesis of dyes, Data curation, Writing – original draft, preparation. **Linbo Gao:** Samples testing, Analysis. **Aiqin Hou:** Dyeing application. **Kongliang Xie:** Validation, Supervision, Reviewing. **Xiyu Song:** Quantum simulation, Writing – review & editing.

rashess properties of dyed i Er labries.										
Samples	Fastness to rubbing		Fastness to washing		Fastness to light	Fastness to sublimation				
			Change	Staining			180 °C		210 °C	
	Dry	Wet		SP	SC		SP	SC	SP	SC
D1	5	4	4–5	5	5	3–4	4	4–5	2–3	3–4
D2	3–4	4	4–5	5	5	4	4–5	5	3	4
D3	4	4–5	4–5	5	5	4	4–5	4–5	4	4–5
D4	3	4	4–5	5	5	4	4	4–5	2–3	4

SC = staining on cotton; SP = staining on polyester.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Cui ZH, Xia G, Gao JR, et al. Synthesis and properties of alkali-clearable azo disperse dyes containing a carboxylic ethyl ester group. Fibers Polym 2017;18(9): 1708–17.
- [2] Şener İzzet, Şener N, Gür M. Synthesis, structural analysis, and absorption properties of disperse benzothiazol-derivative mono-azo dyes. J Mol Struct 2018; 1174(15):11–7.
- [3] Qian HF, Feng GF, Bai G, et al. A contrastive study of adsorption behaviors on polyurethane fiber with diester/diurethane tethered and non-tethered azo disperse dyes. Dyes Pigments 2017;145:301–6.
- [4] Fang SJ, Feng GF, Guo YQ, et al. Synthesis and application of urethane-containing azo disperse dyes on polyamide fabrics. Dyes Pigments 2020;176:108225.
- [5] Metwally MA, Bondock S, El-Desouky SI, et al. Synthesis, structure investigation and dyeing assessment of novel bisazo disperse dyes derived from 3-(2'hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones. J Kor Chem Soc 2012;56(3):48–356.
- [6] Song XY, Chen HH, Hou AQ, et al. Relationship between the molecular structure, molecular polarities and dyeing properties of benzisothiazole dyes containing multi-ester groups for PET fabric. J Mol Liq 2020;296:111892.
- [7] Jiang H, Zhang L, Cai JF, et al. Quinoidal bithiophene as disperse dye: substituent effect on dyeing performance. Dyes Pigments 2018;151:363–71.
- [8] Bagdatli E, Ocal N. Synthesis, spectroscopic, and dyeing properties of new azo and bisazo dyes derived from 5-pyrazolones. J Heterocycl Chem 2012;49(5):1179–86.
- [9] Seferoğlu Zeynel, Ertan N. Synthesis of some novel bis(hetaryl)azo disperse dyes and investigation of their absorption spectra. Heteroat Chem 2010;18(6):622–30.

- [10] Cui ZH, Xia G, Gao JR, et al. Synthesis and properties of alkali-clearable azo disperse dyes containing a carboxylic ethyl ester group. Fibers Polym 2017;18(9): 1708–17.
- [11] Zhang Z, Hong X, Zheng C. Synthesis of single azo disperse dye containing double ester and determination of crystal structure. Kor J Chem Eng 2013;30(12): 219–2222.
- [12] Wessig P, Matthes A. Preparation of strained axially chiral (1,5)naphthalenophanes by photo-dehydro-Diels-Alder reaction. J Am Chem Soc 2011;133(8):2642–50.
- [13] Feng GF, Qian HF, Bai G, et al. Synthesis, characterization, and application of diester/diurethane tethered azo disperse dyes: a new strategy to improve dye's fastness properties. Dyes Pigments 2016;129:54–9.
- [14] Song XY, Hou AQ, Xie KL, et al. Synthesis and dyeing properties of new biheterocyclic disperse dyes containing pyridone group for polyester fabrics. Fibers Polym 2020;21(8):1743–9.
- [15] Rajesh HP, Kanuprasad DP, Dhirubhai JD, et al. Synthesis and dyeing performance of bisazo disperse dyes based on 3-[4-(4-amino-2-chlorophenoxy)anilino]phenol. J Saudi Chem Soc 2016;20:523–9.
- [16] Dixit BC, Patel DM. Assessment of dyeing properties of novel bisazo-bisazomethine disperse dyes on polyester fabric. J Chem Neuroanat 2012;8(3):1218–25.
- [17] Amer FA, Afsah ES, Soafan M. Synthesis of 4,4'-aryldihydrazono-3-(3'-pyridyl)-2pyrazolin-4,5-diones and 1-aryl-3-(3'-pyridyl)-4,4'-arylbisazo-5aryliminopyrazoles and their application as disazo disperse dyes. Part II. J Chem Technol Biotechnol 2010;30(1):78–84.
- [18] Lu T, Chen Q. A simple method of identifying π orbitals for non-planar systems and a protocol of studying π electronic structure. Theor Chem Acc 2020;139:25.
- [19] Müjgan M, Ezgi İ, Burcu A, et al. Synthesis, spectroscopic, thermal and electrochemical studies on thiazolyl azo based disperse dyes bearing coumarin. J Mol Struct 2016;1108:521–32.
- [20] Metwally MA, Abdel-Galil E, Metwally A, et al. New azo disperse dyes with thiazole, thiophene, pyridone and pyrazolone moiety for dyeing polyester fabrics. Dyes Pigments 2012;92(3):902–8.
- [21] Choi JH, Hong SH, Towns AD. High fastness heterocyclic azo disperse dyes bearing ester functions. Color Technol 2010;115(1):32–7.