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Grafting printing of cellulose fabric with the reactive disperse dyes containing N-substituted 3-chloro-2-hydroxypropyl group

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ABSTRACT

The printed cellulose and its blend materials have wide applications in many high-tech fields. Six new reactive disperse dyes (D1–D6) containing a 3-chloro-2-hydroxypropyl group based on epichlorohydrin were designed and synthesized. The electronic absorption spectra and their grafting printing property for cotton fabrics were investigated. The grafting mechanism on cotton fabric was also discussed. The results show that these dyes had larger bathochromic shifts in stronger polar solvent, dimethylformamide, than in the weaker polar solvents, acetonitrile and acetone. 3-Chloro-2-hydroxypropyl functional group of the dyes could form covalent bond with the hydroxyl group on cellulose by a nucleophilic substituted reaction. The good color yields of D1–D6 on printed cotton fabric were obtained by curing at 170–180 °C. The reactive disperse dyes for printing cellulose fabric had good building up and better printing property. The light fastness, rubbing fastness and fastness to perspiration of the printed fabric were good. The reactive disperse dyes have potential application in cleaner production of printing cotton and cotton/polyester blend fabrics.

1. Introduction

Cotton cellulose is highly appreciated natural material for its outstanding characteristics, such as biodegradable, comfortable hand, and excellent softness for garment industry (Gouda & Keshk, 2010; Hou & Sun, 2013; Lam, Kan, & Yuen, 2011). Cotton fabric can be printed with reactive dyes because of the presence of numerous —OH groups on cellulose macromolecules. The printed cotton fabrics have wide applications in the different productions, such as biological technology, home textile, garment, and composite materials (Hou, Zhang, & Wang, 2012; Ibahim, Eid, Abd El-Aziz, & Abou-Elmaaty, 2013; Kumbasar, 2007; Rebeka, Sonja, & Romano, 2007). Reactive dyes, mainly containing monochloro-triazine reactive group, are widely used for dyeing and printing of cotton fabric and its blends. Although the reactive dyes could form covalent bond with fiber, the fastness property of the printed cotton fabrics with these dyes is not desirable, especially washing fastness and wet rubbing fastness. Some investigations on improving washing fastness and wet rubbing fastness properties of reactive dyes on cotton fabric have already been carried out (Wang & Lewis, 2002; Xie, Gao, Li, & Wang, 2014; Xie, Hou, & Zhang, 2006). Meantime, since the fixation of the traditional reactive dyes on cellulose materials is only about 60–80%, a large amount of effluent arises from washing-off. Unfixed reactive dyes in wastewater may further pose an environmental hazard (Burkinshaw & Salihu, 2013). Some novel structure dyes and new printing methods for cotton fabric have been developed (Hakeim, Abdou, El-Gammal, & El-Naggar, 2012; Hinks, Rashad, & El-Shafei, 2002; Kanik & Hauser, 2003). In our previous research work, the modified cellulose with a 1,3,5-triazine derivative containing the multi reactive groups has been investigated (Xie, Hou, & Wang, 2008; Xie, Liu, & Wang, 2009). The apparent color strength of the reactive dyes on the modified cellulose fabric is higher than that on the unmodified cellulose fabric. The wet rubbing and washing fastnesses of the modified printed cellulose fabrics are better than those of the printed unmodified cellulose fabric.

Reactive disperse dyes are the novel structure dyes containing reactive group without water-soluble group, such as $-SO_4^{2-}$. So, they can be used to dye not only cellulose but also polyester (PET) fabrics. Especially, it is important to dye and print polyester/cotton blend fabric (Burkinshaw & Collins, 1994; Gao, Cui, Huang, Yang, & Lin, 2014; Kraan, Fernandez-Cid, Woerlee, Veugelers, & Witkamp, 2007). So far, different reactive groups have been introduced to reactive disperse dyes, such as β-sulphatoethylsulphonyl, a,b-dibromopropionylamido, dichloro-s-triazinyl, acetoxyethylsulphone and so on (Bae, Kim, & Park, 2007; Kima & Sonb, 2005; Lee, Han, Lee, Choi, & Kim, 2003; Son, Park, Park, Shin, & Kim, 2007). Although the dyeing property of cotton

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or polyester fabric has been paid attention, the report of printing property for cotton fabric with reactive disperse dyes is scarce.

In this paper, the reactive disperse dyes containing a 3-chloro-2-hydroxypropyl group were designed and synthesized. Their grafting printing property for cotton fabric was investigated and the grafting mechanism was also discussed.

2. Experimental

2.1. Materials

3-Nitroaniline, 4-nitroaniline, 2-bromine-4-nitro-aniline, 2-bromine-4, 6-dinitro-aniline, 3-[N-(3-chloro-2-hydroxypropyl)] amino acetanilide, and N-[[3-(3-chloro-2-hydroxypropyl) amino]-4-methoxyphenyl] acetanilide were obtained from Zhejiang Wanfeng Chemical Company, Shaoxing, China. 3-Amino-5-nitrobenzothiazole was obtained from Zhejiang Lianhua Chemical Company, Huangyan, China. Other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai, China. Scoured and bleached cotton fabrics were obtained from Zhejiang Jinqiu Textile Comoany, Shaoxing China).

FTIR spectrum was measured by an OMNI 98 Sampler of the Nexus-670 FTIR-Raman Spectrometer (Nicolet Analytical Instruments, Madison, WI). ^{1}H NMR spectrum was recorded on a Bruker Avance 400 (Bruker Co., Faellanden, Switzerland). Element analysis for C, H and N were performed on a Vario EL III (Elmentar Co., Germany). The visible spectra were measured using a Lambda 35 spectrophotometer (Perkin Elmer. Co.).

2.2. Synthesis of dyes

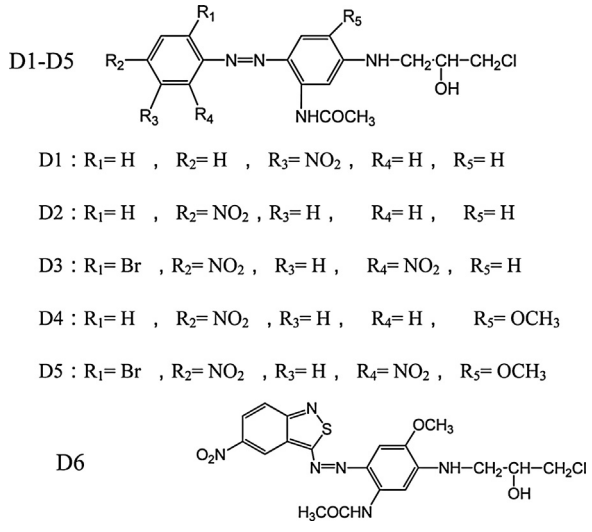
The chemical structures of the reactive disperse dyes containing reactive 3-chloro-2-hydroxypropyl groups are shown in Scheme 1.

2.2.1. Diazotization reaction

3-Nitroaniline (2.76 g, 0.02 mol) was dissolved in water (100 ml) and concentrated hydrochloric acid (36% w/v, 5 ml). The solution of sodium nitrite (1.5 g, 0.022 mol dissolved in water, 3.5 ml) was slowly added to the above solution at 0–5 °C and the diazotization reaction was continued for 1 h.

4-Nitroaniline (2.76 g, 0.02 mol) was dissolved in hot water at 65 °C (150 ml) and concentrated hydrochloric acid (36% w/v, 6 ml) until a clear solution was obtained. The solution of sodium nitrite (1.5 g, 0.022 mol dissolved in water, 3.5 ml) was rapidly poured into the above solution at 0–5 °C and the diazotization was continued for 1 h, then filtered to get clear solution.

2-Nromine-4,6-dinitro-aniline(5.24 g, 0.02 mol) was dissolved in sulphuric acid (98% w/v, 10.4 g) at 20 °C until a clear solution was obtained. Nitrosylsulfuric acid (M = 127, 40% w/w, 7.76 g) slowly added to the above solution at 50–55 °C and the diazotization was continued for 1 h. The diazotization of 3-amino-5-nitrobenzothiazole was carried out according to the previous work (Bae et al., 2007; Ho & Yao, 2006; Kima & Sonb, 2005).



Scheme 1. Chemical structures of D1–D6.

2.2.2. Coupling reaction

3-[N-(3-chloro-2-hydroxypropyl)] amino acetanilide (0.02 mol) was dissolved in acetic acid (15 ml) and ethanol (5 ml) at 40–50 °C until a clear solution was obtained. The solution was cooled to 0–5 °C, and the diazonium compounds were gradually added, respectively. The temperature of the mixture was maintained below 5 °C for 2 h. The pH value was adjusted to 6 by adding acetate sodium solution. After the coupling reaction was completed, the solution was heated to 60–70 °C for 1 h. Then the desired dyes were filtered and washed with water. The purification was accomplished by recrystallization with ethanol and dried.

Coupling reaction of N-[[3- (3-chloro-2-hydroxypropyl) amino]-4-methoxyphenyl] acetamide was carried out with the similar method. Six reactive disperse dyes were obtained. All the dyes were recrystallized from ethanol. Their structures were characterized by element analysis, FTIR and H NMR.

D1: Yield 89%. Element analysis: Calc: C 52.15, H 4.63, N 17.89; Found: C 52.10, H 4.64, N 17.50. FTIR (KBr, cm^{-1}), 3404, 3348, 3090, 2946, 2882, 1676, 1627, 1531, 1356, 1310. ^{1}H NMR (DMSO-d_6, ppm): 10.48 (s, 1H, —NHCO), 8.54-6.90 (t, 7H, Ar-H), 6.83–6.40 (d, 1H, —CHOH), 5.67–5.37 (m, 1H, —CH_2—C*H*—CH_2), 4.18–3.53 (m, 4H, —*CH_2*CH*CH_2*), 2.224 (s, 3H, —$COCH_3$), 1.229 (t, 1H, —N*H*CH_2).

D2: Yield 91%. Element analysis: Calc: C 52.15, H 4.63, N 17.89; Found: C 51.96, H 4.66, N 17.34. FTIR (KBr, cm^{-1}), 3413, 3337, 3092, 2939, 2853, 1677, 1627, 1508, 1369, 1338. ^{1}H NMR (DMSO-d_6, ppm): 10.507 (s, 1H, —NHCO), 8.49–7.30 (m, 7H, Ar-H), 6.72–6.39 (d, 1H, O*H*), 5.67–5.50 (m, 1H, —CH_2C*H*CH_2), 3.99–3.44 (m, 4H, —*CH_2*CH*CH_2*), 2.23 (s, 3H, —$COCH_3$), 1.236 (s, 1H, —NH).

D3: Yield 87%. Element analysis: Calc: C 39.60, H 3.12, N 16.31; Found: C 39.24, H 3.09, N 16.37. FTIR (KBr, cm^{-1}), 3444, 3265, 3088, 3014, 2941, 2873, 1675, 1616, 1532, 1320. ^{1}H NMR (DMSO-d_6, ppm): 10.18–9.7 (b, 1H, —NH), 8.90–7.43 (m, 5H, Ar-H), 6.82–6.46 (d, 1H, —CHO*H*), 5.74–5.48 (m, 1H, —CH_2—C*H*—CH_2), 4.15–3.46 (m, 4H, —*CH_2*—CH—C*H_2*), 2.21 (s, 3H, CH_3), 1.23 (s, 1H, —NH).

D4: Yield 94%. Element analysis: Calc: C 51.29, H 4.78, N 16.63; Found: C 50.41, H 4.72, N 17.22. FTIR (KBr, cm^{-1}), 3414, 3016, 2939, 2850, 1667, 1616, 1510, 1325, 1373. ^{1}H NMR (DMSO-d_6, ppm): 10.07 (s, 1H, —NH), 8.42–7.22 (m, 6H, Ar-H), 5.89–5.25 (br, 1H, —OH), 4.11–3.95 (t, 1H, —N*H*CH_2), 3.95–3.76 (s, 3H, —OCH_3), 3.74–3.59 (m, 2H, —NHC*H_2*), 2.38–2.14 (s, 3H, —$NHCOCH_3$), 2.10–1.83 (m, 1H, —CH_2C*H*CH_2), 1.54–1.14 (d, 2H, —CH_2Cl).

D5: Yield 89%. Element analysis: Calc: C 39.63, H 3.33, N 15.42; Found: C 39.56, H 3.22, N 16.22. FTIR (KBr, cm^{-1}), 3432, 3007, 2927, 2856, 1620, 1575, 1521, 1380, 1316, ^{1}H NMR (DMSO-d_6, ppm): 9.27 (br, 1H, —NH), 9.79–8.69 (d, 2H, Ar-H), 7.77 (s, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 5.72–5.54 (d, 1H, —OH), 4.06–3.97 (t, 1H, —N*H*CH_2), 3.88 (s, 3H, —OCH_3), 5.74–5.54 (m, 2H, —NHC*H_2*), 2.27–1.92 (s, 3H, —$COCH_3$), 2.08–1.86 (m, 1H, —CH_2—C*H*—CH_2), 1.28–1.21 (d, 2H, —CH_2Cl).

D6: Yield 83%. Element analysis: Calc: C 47.65, H 3.97, N 17.55; Found: C 47.21, H 3.89, N 17.86. FTIR (KBr, cm^{-1}), 3445, 3007, 2920, 2859, 1687, 1607, 1541, 1314. ^{1}H NMR (DMSO-d_6, ppm): 10.06–9.69 (br, 1H, —NH), 9.06 (s, 1H, Ar-H), 8.26–8.09 (d, 1H, Ar-H), 7.86–7.62 (dd, 2H, Ar-H), 7.45 (s, 1H, Ar), 5.67 (s, 1H, —OH), 4.11–3.84 (s, 3H, —OCH_3), 3.84–3.50 (dd, 2H, —$NHCH_2$), 2.36–2.17

Table 1
Spectrum data of the reactive disperse dyes in three solvents.

Dye	M.P. (°C)	λ_{max} (nm)			ε (L mol^{-1} cm^{-1})		
		DMF	ACN	AT	DMF	ACN	AT
D1	140–142	472	458	462	27,679	27,734	26,541
D2	152–154	500	470	482	30,674	30,541	31,197
D3	180–182	584	568	572	29,607	29,489	28,283
D4	172–174	508	486	494	37,584	35,739	36,607
D5	238–240	596	580	586	31,284	31,122	30,196
D6	226–228	654	630	636	51,734	51,510	52,283

(d, 2H, —CH_2Cl), 2.06–1.88 (m, 1H, —CH_2—C*H*—CH_2), 1.24 (s, 3H, —CH_3), 1.01–0.71 (t, 1H, —$NHCH_2$).

2.3. Printing paste

The reactive disperse dye (75 g), the dispersing agent MF (45 g), and water (180 ml) were added to a grinding mill (8.5 cm inner diameter), and the mixture was stirred for 15 min. Then, the grinding material, silica sand (density 2.66 g/cm^3, the fineness 100–150 mesh) 600 g, were added and subsequently grinded for 30 min at 30 °C with 1260 r/min. Then, the mixture was filtered and dried at 75 °C.

The printing pastes of D1–D6 were respectively formulated according to the following recipe: dyes, 80 g (including synthesized dye and dispersing agent MF), sodium alginate paste (40 g/L) 60 g, urea 60 g, and resist salt S 15 g, the amount of sodium carbonate increased with the reactive disperse dyes. A certain amount of water was added for total 1000 g.

2.4. Printing

Flat screen-printing method according to the previous description was applied to fabric (Xie et al., 2009). The printed samples were cured at different temperature for 7 min or steamed at 105 °C for 12 min. The printed fabric was washed with soaping agent, 5 g/L, at 98 °C for 15 min. Then all the printed fabrics were rinsed thoroughly with cold water and dried.

2.5. Measurement

2.5.1. Color yield analysis

The color yield (K/S) of the printed sample was determined by Datacolor SP600+ spectrophotometer (Datacolor, Switzerland). The dye absorbance was measured in the visible spectrum region 380–720 nm. The reflection spectrum and the color parameters *L*, *a*, *b*, and *C* of the printed samples were measured under illuminant D65 using the 10° standard observer in the visible spectrum region 380–700 nm. The reflectance at λ_{max} was used to calculate the color yield of the printed fabric by the Kubelka–Munk Equation (1).

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

where *K* is the absorption coefficient of the substrate, *S* is the scattering coefficient of the substrate and R is the reflectance of the printed fabric at λ_{max}.

2.5.2. Dye fixation

The dye fixation ratio (*F*%) was measured and calculated using Eq. (2) (Ahmed, Youssef, El-Shishtawy, & Mousa, 2006).

$$F\% = \frac{(K/S)\ \text{after}_{DMF}}{(K/S)\ \text{after}_{soaping}} \times 100\% \quad (2)$$

where *K*/*S* after dimethylformamide (DMF) and *K*/*S* after soaping are *K*/*S* values of the printed fabrics after and before extracted with 50% DMF for 10 min (liquor ratio 20:1), respectively.

2.6. Fastness property

Fastness properties to washing, dry and wet rubbing, perspiration, and light were evaluated according to the respective international standards: ISO 105-C04 (1989), ISO 105-X12 (2001), ISO 105/E04 (1994); ISO 105-B02 (1994), respectively.

3. Results and discussion

3.1. Spectral property of the reactive disperse dyes

The melting points and electric absorbance spectra of the reactive disperse dyes were measured. The data, melting points (m.p.), maximum absorption wavelength (λ_{max}) and the molar extinction coefficient (ε) of them in dimethylformamide (DMF), acetone (AT) and acetonitrile (ACN), are summarized in Table 1. The maximum absorption of these dyes was at 458–654 nm, which was orange to blue shade. Comparing the maximum absorptions (λ_{max}) and the extinction coefficients (ε) of D3 and D5 with those of D2 and D4, the bathochromic and hyperchromic effect were observed, respectively. The bathochromic effect could be attributed to the electron donor group of methoxy at the *o*-position of the coupling component. D1 showed a hyperchromic shift of 28 nm in compare with D2, due to electron withdrawing effect of nitro group at the *m*-position rather than *p*-position of the diazonium component. Amino-substituted benzoisothiazole (D6) exhibited more significant hyperchromic effect than that of the dyes, D1-D5. The higher tinctorial strength of D3 and D5 than that of D2 and D4 should be due to the intramolecular hydrogen bond between the acetylamino group and the azo linkage.

In order to investigate the solvent effect on absorption spectra of the dyes, λ_{max} in three solvents, 1×10^{-5} mol/L, with different polarity was recorded. It is found that λ_{max} of D1–D6 increased in the order: DMF > AT > ACN. Dyes showed larger bathochromic shift in the stronger polar solvent, DMF, than in the weaker polar solvents, such as ACN and AT. For example, the λ_{max} of D6 was at 654 nm in DMF, 636 nm in AT, 630 nm in ACN. D1–D6 in various solvents exhibited different maximum absorption band. It can be interpreted in terms of intramolecular hydrogen bond (hydroxyl), electron donation factors (secondary amine) and dipole–dipole interaction between the dyes and polar solvents (Airinei, Homocianu, & Dorohoi, 2010; Mohammadi, Yazdanbakhsh, & Farahnak, 2012).

3.2. Grafting of the dyes on cellulose fabric

The macromolecular structure of cellulose has numerous hydroxyl groups (—OH). Cellulose fabrics can be chemically grafted with the compounds containing reactive group. The synthesized dyes contained 3-chloro-2-hydroxypropyl, which can convert to

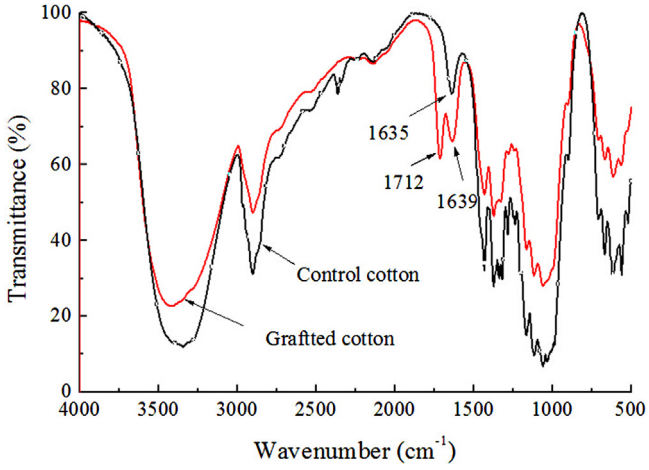


Fig. 1. FTIR spectra of the grafted and control cotton samples.

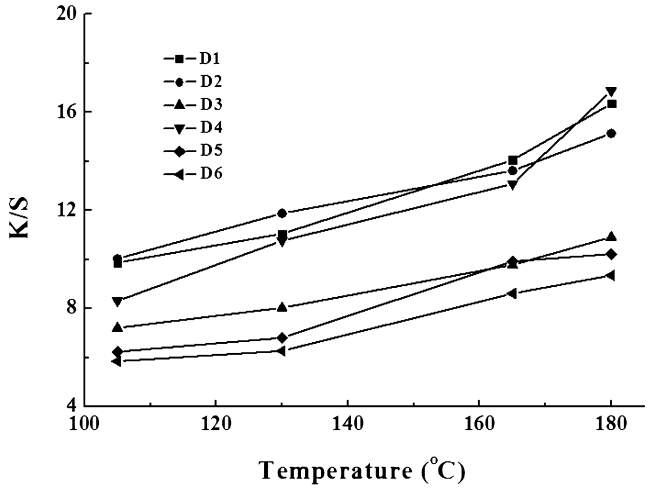


Fig. 2. Color yield at various temperatures (dyes, 80 g/L).

epoxy group under the alkaline condition. The epoxy group can be used to graft cellulose. Flat screen-printing method was applied to cotton fabric. D6, 80 g/L, was applied to print cotton fabric. The printed sample was carried out by steaming at 105 °C for 12 min. The sample was washed using soaping agent, 5 g/L, at 98 °C for 15 min and then were rinsed thoroughly with 50% DMF aqueous solution. FTIR spectra of the printed cotton and control samples were measured and shown in Fig. 1.

FTIR spectrum of the grafted cellulose assured the presence of —C=O at 1712 cm^{-1}. It should be attributed to —$NHCOCH_3$ group in the dye structure. Meantime, there was a stronger peak at 1639 cm^{-1}, which was attributed to —N=N—. FTIR spectrum of the grafted cellulose demonstrates that the dye was grafted to cellulose. This confirms that the dye was able to form covalent bond with cellulose fiber. The grafting reaction of cellulose with D6 is shown in Scheme 2.

3.3. Printing property of the reactive disperse dyes for cotton fabric

The temperature is a crucial factor for the cellulose grafting reaction. The color yields (*K*/*S* value) of D1–D6 on cotton fabric at various temperatures were measured and shown in Fig. 2. The printing color yields rapidly increased with temperature. It can be seen that *K*/*S* value was significantly affected by temperature. The good color yields of D1–D6 on cotton fabric were obtained at 170–180 °C. *K*/*S* values of the samples using D1, D2, and D4 were higher than those of the samples using D3, D5, and D6. A possible explanation for this phenomenon is that the functional epoxy group began to react with cotton fabric when the curing temperature exceeded 130 °C. 160–180 °C was suitable reactive temperature for the grafting printing of cotton fabric using the reactive disperse dyes containing 3-chloro-2-hydroxypropyl. The fixation rates

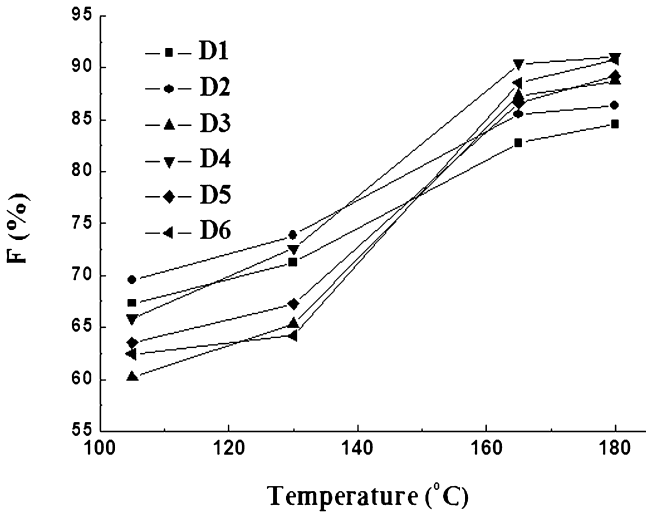
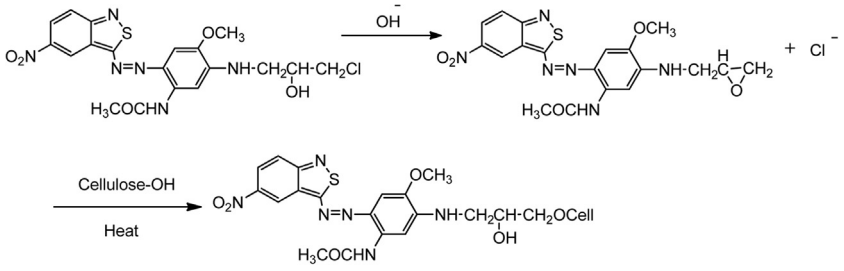


Fig. 3. Fixation at various temperatures.

on cotton fabric at different temperatures are shown in Fig. 3. The fixation rates were in agreement with *K*/*S* values of D1–D6. With temperature rising, the fixation rates also rapidly increased. Because of lower molecular weights and lower melt points of D1, D2, and D4, they exhibited higher color yield at low temperature than that of D3, D5, and D6.

The effect of the dye concentration on *K*/*S* value and fixation on cotton fabric were also investigated. The results are shown in Figs. 4 and 5. The *K*/*S* values of all printed samples obviously increased with increasing the dyes concentration. It indicates that the synthesized reactive disperse dyes for cotton fabric printing



Scheme 2. Grafting mechanism of cellulose with the dye D6.

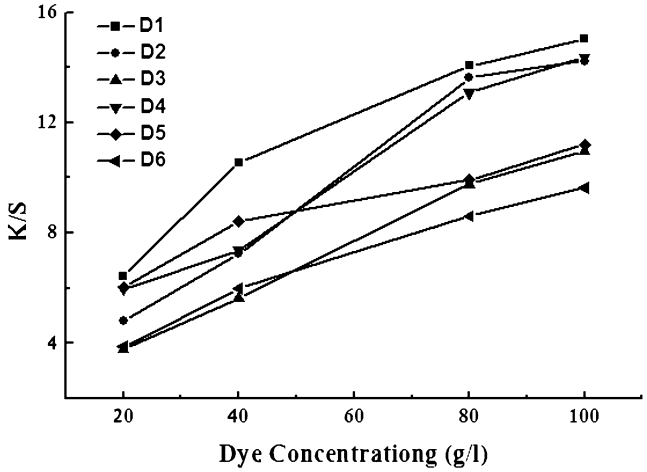


Fig. 4. Building up property of D1–D6 for printing.

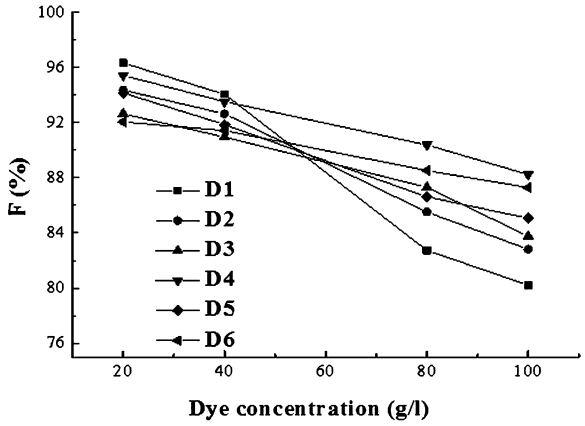


Fig. 5. Fixation of the reactive disperse dyes on cotton fabric at different dye concentrations.

had good building up. However, the fixation rates of them gradually decreased with increasing the dye concentration. It was in agreement with the references (Hrdina, Lunák-Jr, & Burgert, 1998; Xie & Hou, 2008).

3.4. Color data and fastness property of the printed fabric

The color parameters, *L*, *a*, *b*, were calculated by the tristimulus values *X*, *Y* and *Z*. *L* refers to brightness–darkness with values from 100 to 0 representing white to black. The colorimetric data of the samples printed with D1–D6, 20 g/L, 40 g/L and 80 g/L, respectively, are shown in Table 2. With increasing the dye concentration, the light (L^*) values slightly decreased, and the color (C) values obviously increased. The *a* values increased with increasing the dye concentration. The *b* values also increased with the dye concentrations. The *a* values run from negative (green) to positive (red). The *b* values run from negative (blue) to positive (yellow).

The fastness property of the printed cotton fabric with six synthesized reactive disperse dyes are summarized in Table 3. The light fastness, rubbing fastness and fastness to perspiration of the printed samples were good. However, washing fastness of the printed samples with D1 and D2 were slightly lower.

Table 2
Colorimetric data of the printed fabrics.

Dyes	Samples (g/L)	*L*	*a*	*b*	*C*
D1	20	88.25	29.41	43.09	52.16
	40	87.26	30.97	44.17	53.95
	80	85.73	31.83	44.91	55.05
D2	20	53.71	44.99	20.09	49.27
	40	52.83	45.21	20.42	49.61
	80	51.11	46.86	22.18	51.84
D3	20	47.61	0.63	−4.44	4.48
	40	46.74	0.99	−4.81	4.91
	80	46.36	1.87	−5.73	6.03
D4	20	50.36	38.46	22.92	44.77
	40	49.68	38.74	23.27	45.19
	80	48.42	40.21	24.63	47.15
D5	20	39.31	26.36	−1.34	26.39
	40	38.71	27.10	−1.47	27.13
	80	37.02	28.81	−2.32	28.90
D6	20	40.56	−41.87	−3.09	41.98
	40	39.82	−42.41	−2.92	42.51
	80	38.48	−44.96	−3.67	45.11

Table 3
Fastness properties of the printed cotton fabrics.

Samples	Light fastness	Rubbing fastness		Washing fastness		Fastness to perspiration	
		Dry	Wet	SC	SW	SC	SW
D1	2–3	4–5	3–4	2–3	2–3	4–5	3–4
D2	3–4	3–4	3–4	3	3	3–4	3
D3	4	3–4	3–4	4–5	4–5	5	5
D4	3	3–4	4	4–5	4–5	5	5
D5	3	4–5	4	4–5	4–5	5	5
D6	3–4	3–4	3	4–5	4–5	5	5

SC, staining on cotton; SW, staining on wool.

4. Conclusion

Six reactive disperse dyes, D1–D6 containing a 3-chloro-2-hydroxypropyl functional group were synthesized. The electronic absorption property of them exhibited solvent dependence, which showed larger bathochromic shifts in stronger polar solvent (DMF) than in the weaker polar solvents (ACN and AT). D1–D6 could form covalent bond with cotton fiber at the alkaline condition. The good color yields of them on cotton fabric were obtained at 170–180 °C. *K*/*S* values of the printed samples using D1, D2, and D4 were higher than those using D3, D5, and D6. The light fastness, rubbing fastness, washing fastness and fastness to perspiration of the printed samples were good. The reactive disperse dyes have potential application in cleaner production of cotton and cotton/polyester blend printed fabrics.

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