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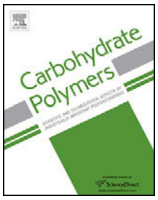

Grafting printing of cellulose fabric with the reactive disperse dyes containing N-substituted 3-chloro-2-hydroxypropyl group

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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.).

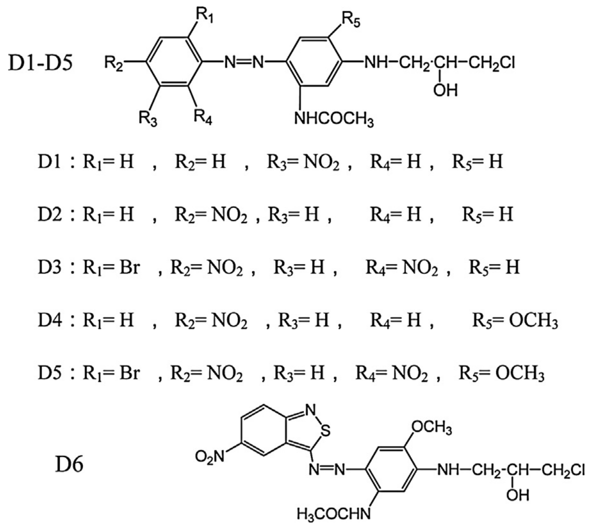
2.2. Synthesis of dyes

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.



D1 : R$_1$= H , R$_2$= H , R$_3$= NO$_2$, R$_4$= H , R$_5$= H

D2 : R$_1$= H , R$_2$= NO$_2$, R$_3$= H , R$_4$= H , R$_5$= H

D3 : R$_1$= Br , R$_2$= NO$_2$, R$_3$= H , R$_4$= NO$_2$, R$_5$= H

D4 : R$_1$= H , R$_2$= NO$_2$, R$_3$= H , R$_4$= H , R$_5$= OCH$_3$

D5 : R$_1$= Br , R$_2$= NO$_2$, R$_3$= H , R$_4$= NO$_2$, R$_5$= OCH$_3$

Scheme 1. Chemical structures of D1–D6.

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).

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, $-CH_2-CH-CH_2$), 4.18–3.53 (m, 4H, $-CH_2CHCH_2$), 2.224 (s, 3H, $-COCH_3$), 1.229 (t, 1H, $-NHCH_2$).

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, OH), 5.67–5.50 (m, 1H, $-CH_2CHCH_2$), 3.99–3.44 (m, 4H, $-CH_2CHCH_2$), 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, —CHOH), 5.74–5.48 (m, 1H, $-CH_2-CH-CH_2$), 4.15–3.46 (m, 4H, $-CH_2-CH-CH_2$), 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, $-NHCH_2$), 3.95–3.76 (s, 3H, $-OCH_3$), 3.74–3.59 (m, 2H, $-NHCH_2$), 2.38–2.14 (s, 3H, $-NHCOCH_3$), 2.10–1.83 (m, 1H, $-CH_2CHCH_2$), 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, $-NHCH_2$), 3.88 (s, 3H, $-OCH_3$), 5.74–5.54 (m, 2H, $-NHCH_2$), 2.27–1.92 (s, 3H, $-COCH_3$), 2.08–1.86 (m, 1H, $-CH_2-CH-CH_2$), 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