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Dyes and Pigments 73 (2007) 76–80

DYES and PIGMENTS

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Exhaustion studies of spiroxazine dye having reactive anchor on polyamide fibers and its photochromic properties

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Received 30 March 2005; received in revised form 11 July 2005; accepted 18 October 2005
Available online 13 December 2005

Abstract

The photosensitive spiroxazine dye having reactive anchor within the dye molecule was prepared to provide the durable coloration properties caused by covalent bonding system. Spiroxazine exhaustions to the polyamide substrates and its photochromic effects within the fiber molecules were investigated and effects of the reactive system of spiroxazine dyeing were discussed. Successful spiroxazine exhaustions within the fiber molecules were determined by photochromic properties of the dyed substrates. With UV irradiation, photochromic behaviors appeared on the substrates was that of blue color. In addition, in the case of spiroxazine dyeing having reactive group within the molecule, it showed photochromic color forming behavior even after the sample was subjected to extraction process.

Keywords: Spiroxazine; Reactive anchor; Dichloro-*s*-triazinyl; Photochromism; Polyamide; Exhaustion; UV irradiation

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1. Introduction

In recent years, functional finishings, especially color forming reactions caused by incoming stimulus, are quite interesting research subjects to utilize chromism coloration technology on many application fields. In previous works [1], the spiroxazine dye, commonly used as non-textile colorant to the color forming or sensing areas, was applied to the fiber substrates. That was the interesting research area in creating the colorations with desired optical chromism properties through achieving a well-observed color occurring substrates. In addition, its application was very useful and convenient. As explained previously, for the most commonly used coloration process, dyeing and printing technique is generally enjoyed as considerable usage in many coloration areas. For insoluble solid particles, the most widely applied methods are conducted using solution dyeing and microcapsule binding methods [2–4]. In this context, satisfactory direct exhaustion of the spiroxazines was achieved from the previous works [1].

In this part of work, another novel spiroxazine dye introducing dichloro-*s*-triazinyl reactive group [5–8] to the spiroxazine dye molecule was designed and its corresponding exhaustion and fixation behaviors were discussed. Successful coloration and its strong covalent bonding were clearly observed. These results were also confirmed from photographs and absorption spectra by photochromic reaction. The aim of this work, in this context, is to provide more strong interactions between spiroxazine dyes and fiber substrates.

2. Experimental

Melting points were determined using an Electrothermal IA 900. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass analysis was recorded using a Shimadzu QP-1000 spectrometer with an electron energy of 70 eV and direct sample introduction. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard.

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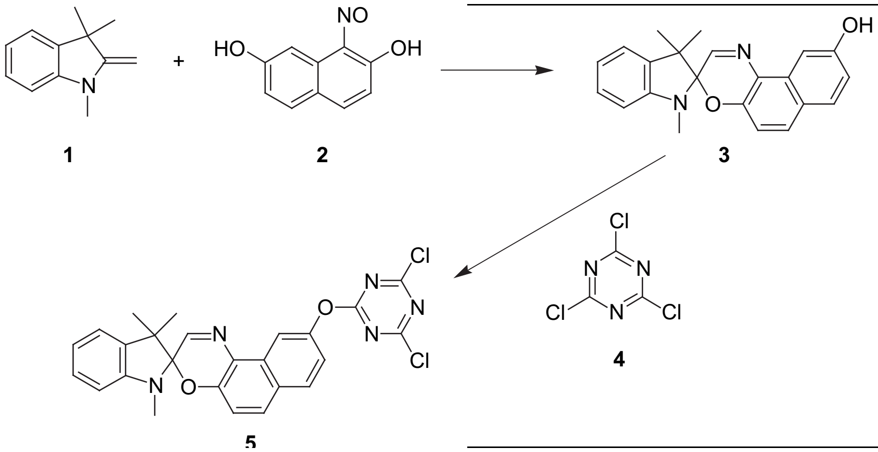
doi:10.1016/j.dyepig.2005.10.012

2.1. Synthesis of spiroxazine dye **3**

Spiroxazine dye **3** was prepared using 1,3,3-trimethyl-2-methyleneindoline **1** and 1-nitroso-2,7-dihydroxynaphthalene **2** according to the described method [9,10]. Yield: 4.33 g (58%); m.p.: 212–214 °C; MS *m/z* (M^+): 344; Anal. calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13%. Found: C, 76.89; H, 4.97; N, 8.59%; ^1H NMR ($CDCl_3$, δ ppm): 1.36 (s, 6H), 2.76 (s, 3H), 6.58 (d, $J = 7.8$ Hz, 1H), 6.84 (d, $J = 8.84$ Hz, 1H), 6.90 (t, $J = 7.46$ Hz, 1H), 7.02 (d, $J = 8.68$ Hz, 1H), 7.22 (d, $J = 7.40$ Hz, 1H), 7.58 (d, $J = 8.6$ Hz, 1H), 7.65 (d, $J = 8.56$ Hz, 1H), 7.71 (s, 1H), 7.88 (s, 1H).

2.2. Synthesis of spiroxazine dye **5**

Cyanuric chloride 6.61 g (35.85 mmol) **4** was dissolved in 120 ml of acetone. Temperature of the solution was maintained at 0–5 °C. The prepared dye **3** (12.33 g) (35.85 mmol) was added into the solution, which was then stirred for 2.5 h. Na_2CO_3 (40 ml) (0.98 N) was added into the solution and stirred for 1.5 h. After completion of reaction, this solution was poured into 500 ml of H_2O. The resulting solid **5** was filtered and obtained. Yield: 13.3 g (75.5%); m.p. 140 °C; MS *m/z* (M^+) 492; Anal. calcd for $C_{25}H_{19}Cl_2N_5O_2$: C, 60.99; H, 3.89; N, 14.22. Found: C, 60.01; H, 3.76; N, 14.13; ^1H NMR ($CDCl_3$, δ ppm): 1.36 (s, 6H), 2.77 (s, 3H), 6.59 (d, $J = 7.52$ Hz, 1H), 6.91 (t, $J = 7.56$ Hz, 1H), 7.05 (d, $J = 8.52$ Hz, 1H), 7.09 (d, $J = 7.04$ Hz, 1H), 7.17 (d, $J = 9.04$ Hz, 1H), 7.23 (t, $J = 7.52$ Hz, 1H), 7.70 (d, $J = 8.52$ Hz, 1H), 7.72 (s, 1H), 7.83 (d, $J = 9$ Hz, 1H), 8.32 (s, 1H).



2.3. Materials

Polyamide filament taffeta (warp 75 denier/yarn 107 yarns/in., weft 75 denier/yarn 97 yarns/in., 70 ± 5 g/m^2) was used in this experiment. The prepared two spiroxazine dyes were used. All other chemicals used were laboratory grade reagents.

2.4. Exhaustion

Polyamide fiber was dyed in sealed, stainless steel dye pots of 120 cm^3 capacity in a laboratory-scale dyeing machine (ACE-6000T). Samples were placed in a 40 °C dyebath of 50:1. After 10 min, the temperature was raised until the range of temperatures of 80–110 °C was reached. At these temperatures, the exhaustion of spiroxazine dyes was continued for 1 h. At the end of exhaustion, the dyed samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air.

3. Results and discussion

3.1. Exhaustion studies

For further researches on the spiroxazine exhaustion to the fiber substrates, durable bonding system between spiroxazine compounds and fiber substrates was designed by introducing a reactive group within the dye molecule. In the previous paper [1], the interesting approach using direct exhaustion method of non-textile dye, spiroxazine compound, was presented, which provided more convenient way than conventional procedures [2–4]. In this part of the work, another novel approach of employing the spiroxazine compound having dichloro-*s*-triazinyl reactive group is proposed. In previous works, successful spiroxazine exhaustion within the fiber molecules was determined by photographs and absorption spectra caused by photochromic reaction. Thus, to introduce more strong bonding interactions between spiroxazine dyes and fiber substrates is the aim of this work. For this purpose, dichloro-*s*-triazinyl reactive group was adopted, which was commonly used as a traditional reactive dye system for textile dyeings. Fig. 1 represents the model of reversible photoconversion of ring-closed colorless and ring-opened colored spiroxazine dyes within the fiber molecules where dichloro-*s*-triazinyl reactive anchor is covalently bonded to the polyamide substrates.

The photochromic reaction is caused by the reversible heterolytic cleavage of the C(spiro)–O bond under UV irradiation,

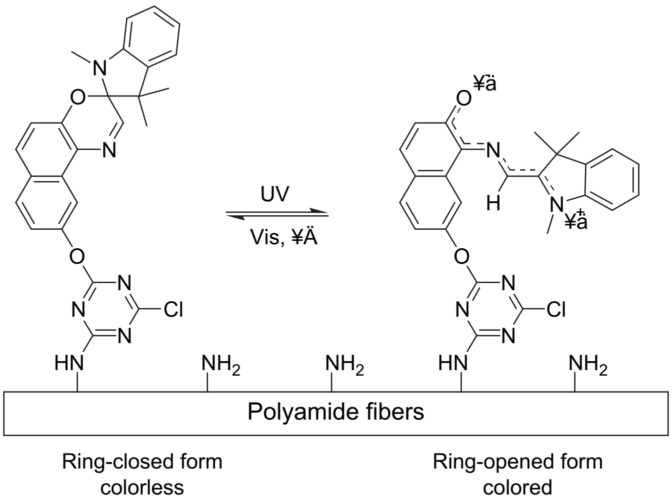


Fig. 1. Reversible photoconversion structures between ring-closed colorless and ring-opened colored spiroxazine forms.

yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark. Electronic absorption spectral changes of spiroxazine **5** upon UV irradiation in DMF are depicted in Fig. 2. After UV irradiation, an absorption maximum of 600 nm was observed. The new band is ascribable to the generation of the open merocyanine form from the closed spiro form. The original spectral pattern was reversibly recovered within 10 s.

In order to examine the effect of reactive anchor within the dye structure on exhaustion behaviors, polyamide fibers were dyed with prepared two spiroxazine dyes at various temperatures (80–110 °C). The 2% owf of spiroxazines was used. Employed exhaustion method was followed as mentioned above. Fig. 3 shows the absorption spectra of spiroxazine dyeings on polyamide fibers at various temperatures. To measure absorbance, dyed samples were extracted using DMF solution at 90 °C for 5 h to determine the absorption spectra in which dye exhaustion behaviors can be considered.

Generally, in the case of dye **3**, the absorbance of extracted dye solution increased with increasing application temperatures. This finding represents that dye adsorption onto fiber substrates was more favorable at higher temperature than at lower temperature. Within the lower range of exhaustion temperatures (80–90 °C), these conditions had a little effect on the spiroxazine dye uptake to the substrates. Especially, higher exhaustion was obtained at 110 °C. In this context, it is thought that in terms of the effect of dyeing temperatures, the adsorption behavior of the spiroxazine dye **3** onto polyamide fibers is following a similar exhaustion mechanism to be like commercial disperse dyes, which commonly involved a high-pressure and a high-temperature dyeing method. On the contrary, spiroxazine dye **5** having reactive anchor showed different exhaustion behaviors in the range of temperatures (80–110 °C). The absorption spectra showed similar values for all temperature ranges. This finding proposes that the extracted dye amount is relatively low for all dyeing temperatures and most of dye amounts remain within the fiber substrates owing to the formed covalent bonds. This covalent reactive system can be explained that the two electronegative chlorines of the reactive anchor can give higher reactivity of the *s*-triazinyl group with polyamide substrates even at low temperatures [6,11,12]. This effect confirms the view of its mechanism to be like commercial reactive dyes that involve the nucleophilic reaction of dichlorotriazine dyes, namely *Procion* cold type dyes. Commonly, due to higher reactivity, the dichloro-*s*-triazinyl reactive group of *Procion* dyes can be easily reacted with the hydroxyl group of the cellulosic substrates even at lower temperatures.

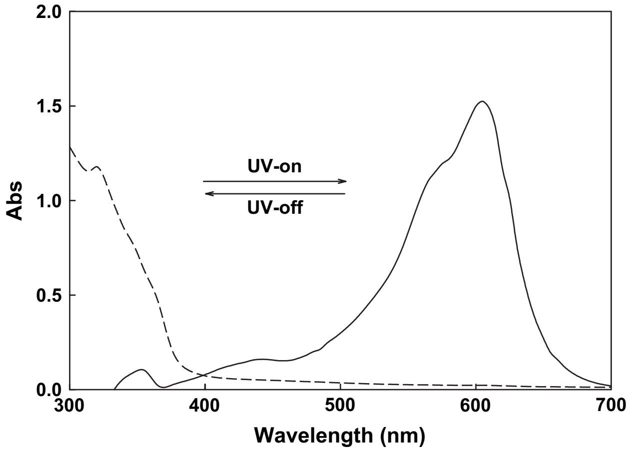


Fig. 2. UV–vis spectra of spiroxazine **5** before and after UV irradiation in DMF.

To support the effect of temperatures on spiroxazine dye exhaustions, the adsorbed amounts of dyes were determined and compared. To calculate dye amounts, absorbance measurement was conducted. Absorbance measurements of the extracted spiroxazine dye solutions were carried out using a UV–vis spectrophotometer. Using a previously established absorbance/concentration relationship at the $\lambda_{\max}$ of the spiroxazine dyes, the quantity of spiroxazine dyes in solution was calculated. Figs. 4 and 5 show the extracted dye amounts for all dyeing temperatures. Fig. 4 shows that the extracted amount of spiroxazine dye **3** increased with increasing exhaustion temperatures to be like conventional dyeing systems. In the case of spiroxazine dye **5**, little effect on extracted dye amount was observed at all ranges of temperatures, which is attributable to the remaining covalent bonding characteristics.

3.2. Effect of alkali addition on fixation

To achieve higher covalent bond fixation, an attempt was made to modify the exhaustion method using alkali addition to the dyebath in the processing stages. To enhance the reactivity of the dichloro-*s*-triazinyl group of the spiroxazine dye towards polyamide fibers, the addition of alkali was used [6,11,12]. In this way, it is proposed that initial exhaustion of the spiroxazine dye and subsequent dye–fiber fixation might be easily achieved, each at a suitable pH, and result in greater overall fixation efficiency. Essentially, this approach would parallel the dyeing process of cellulosic reactive dyeing in which alkali is commonly added at the later steps of the dyeing to expedite dye fixation.

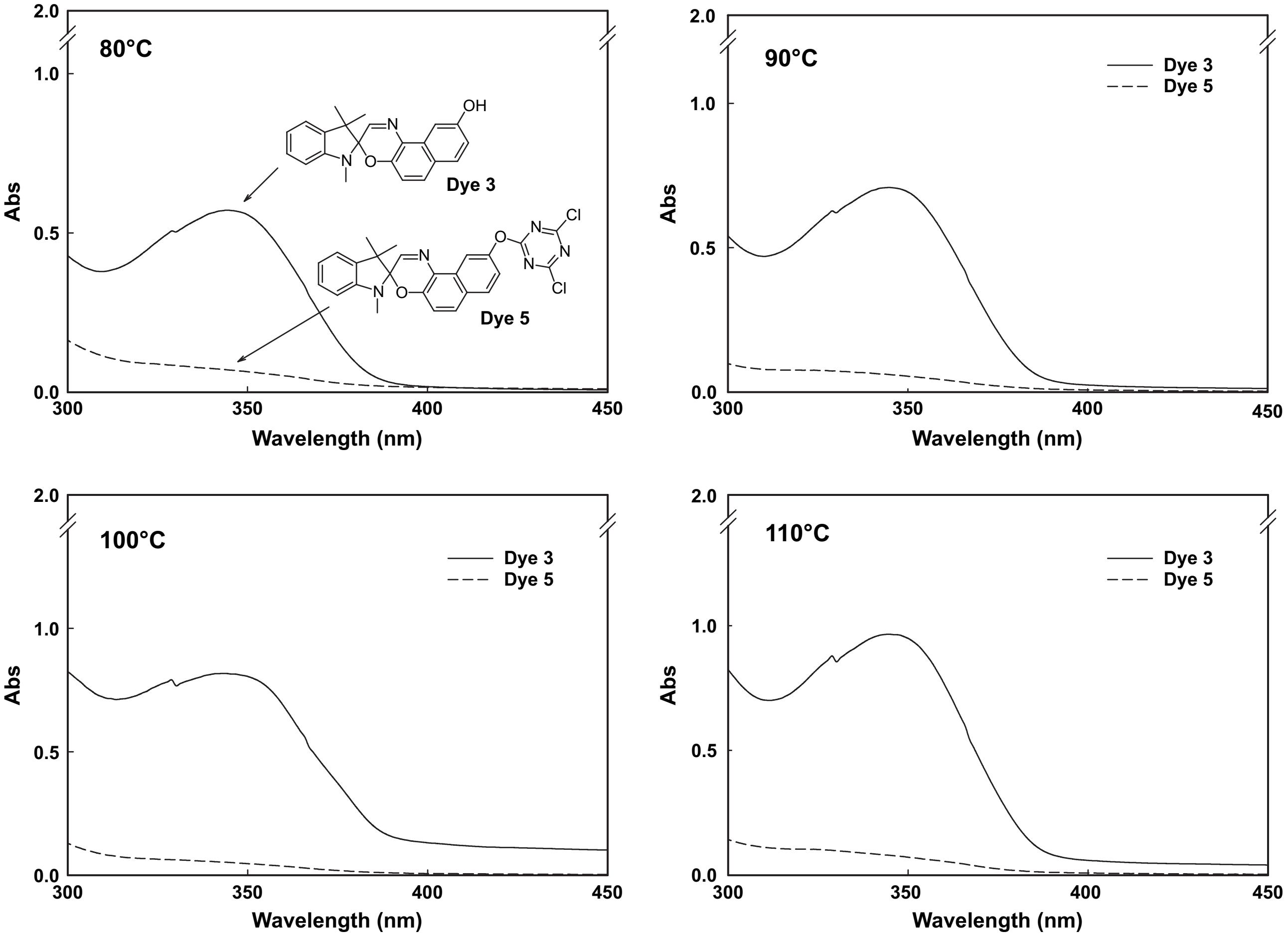


Fig. 3. Effect of temperatures on exhaustion with two spiroxazine dyes.

With the modification that 10 g/l Na_2CO_3 was added after 10, 30, 50 min at 100 °C, in common reactive dyeings on polyamide fibers, it was displayed that fixation increased by this alkali addition attempt; the fixation efficiencies obtained were more than 10% higher than those obtained using the dyeing achieved under fixed pH conditions [13]. However, in the case of spiroxazine dyes, similar low absorption spectra were determined at all stages of alkali addition (Fig. 6). Thus, it can be proposed that regardless of alkali addition, satisfactory covalent bondings were formed within the fiber substrates and corresponding low amount of extracted dyes responded to the absorption measurement.

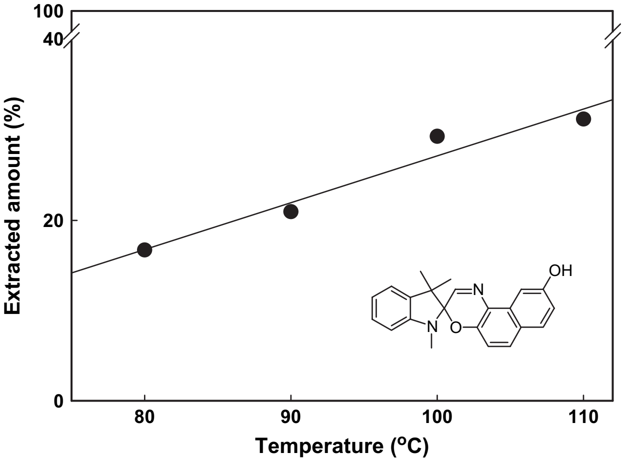


Fig. 4. Extracted amount of the spiroxazine dye **3**.

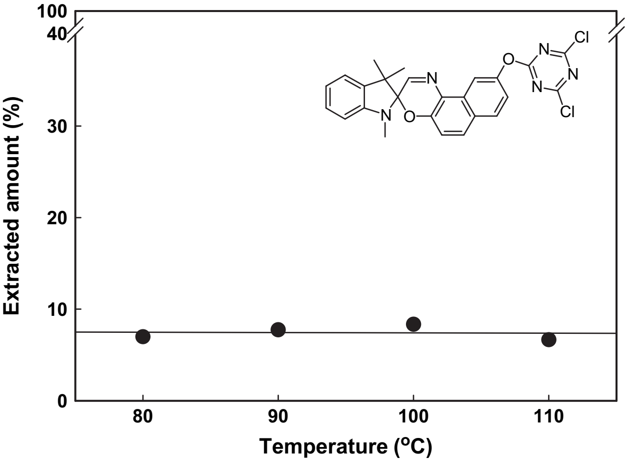


Fig. 5. Extracted amount of the spiroxazine dye **5**.

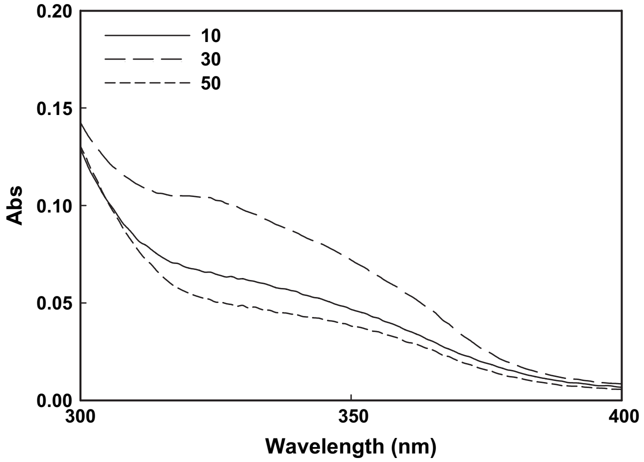


Fig. 6. Extracted absorption spectra of the spiroxazine **5** dye with alkali addition.

3.3. Photochoromic properties

As previously mentioned [1], the photochromic reaction of spiroxazine compound is generated by the reversible heterocyclic cleavage of the C(spiro)–O bond under UV irradiation, yielding the colored ring-opened form that can return to the colorless ring-closed form under visible light irradiation or in the dark. In other words, the spiroxazine dye linked to the fiber molecules with covalent bonding system does show the photochromic characteristics even after dyed samples are subjected to striping procedure. When UV ray of 365 nm was irradiated to the spiroxazine dyeings, the corresponding color occurring properties by photochromic reaction were clearly observed from both spiroxazine dyeings. However, after extraction stage, photochromic behavior was not determined from the dyeings with dye **3**. For dyeings with dye **5**, even though the color producing intensity was a little decreased, clear color forming property was still presented on the sample.

Acknowledgement

This research was supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

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