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Dyes and Pigments 65 (2005) 261–266

DYES and PIGMENTS
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Synthesis of a novel bridge compound having hetero-bi-functional reactive groups. Part 1: its adsorption properties

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Received 12 February 2004; received in revised form 11 May 2004; accepted 28 July 2004
Available online 4 October 2004

Abstract

A novel bridge compound having hetero-bi-functional reactive groups was synthesized. It was designed to contain two different reactive groups such as α,β-dibromopropionylamido and dichloro-*s*-triazinyl group within the molecular structure. The α,β-dibromopropionylamido group shows considerable reactivity towards amines or amino groups at acidic condition and high temperature. In contrast, the dichloro-*s*-triazinyl group has reactivity towards hydroxyl groups at alkaline condition and room temperature. In order to examine whether as a bridge the compound could combine dyes containing amino groups with cellulosic substrates, a disperse dye containing amino group was tried to dye the cotton fibers pretreated with the reactive compound. In this context, it was investigated that the synthesized compound was treated by using several experimental conditions such as temperature, pH, neutral salt, treatment time and concentration of the compound. It was also found that the compound of hetero-bi-functional reactive groups showed the feasibility as a bridge agent to combine the cellulosic fibers and the disperse dyes having amino groups.

Keywords: Hetero-bi-functional; Bridge; Cellulosics; Disperse dyes; Amino groups

1. Introduction

Over the years a number of researches on the finishing of cotton fibers have been carried out to examine and enhance dye build-up properties. The focus of most studies was chemical modification of the fiber itself. These attempts involved the cationization of cotton fibers to increase the adsorption of anionic materials [1–5] and the anionization to improve affinity of cationic materials [6–9]. Despite relatively easy methods, weak interaction forces are the disadvantages of these modifications. Otherwise the crosslinking agents may be considered to trap dyes or compounds within the crosslinked structures. However, this crosslinking method could not offer the controlled reaction to the specific sites of the substrates. In addition, the crosslinking treatment could impart a harsh handle and a shade change to the substrates.

In this context, a novel bridge compound having hetero-bi-functional reactive groups was prepared. It was designed to contain two different reactive groups, namely α,β-dibromopropionylamido and dichloro-*s*-triazinyl group. The α,β-dibromopropionylamido group, which is a common reactive group used for commercial *Lanasol* reactive dyes for wool, shows a great reactivity towards amines or amino groups at acidic condition and high temperature (90–100 °C) [10,11]. In contrast, the dichloro-*s*-triazinyl group, which is a popular reactive group used for *Procion MX* reactive dyes for cellulosics, has a reactivity with hydroxyl groups at alkaline condition and room temperature (20–30 °C) [12–14]. Thus, as a bridge this

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doi:10.1016/j.dyepig.2004.07.023

novel compound having hetero-bi-functional reactive groups could combine the substances containing amino group with the fiber substrates having hydroxyl groups. There are a variety of materials containing the amino and/or hydroxyl groups, such as dyes, pigments, surfactants, chitosan, amino acid, proteins, and other organic compounds. This bi-functional reactive bridge compound makes it possible for those materials to be fixed to the fibers by formation of covalent bonds.

The aim of this part of the study was to synthesize the hetero-bi-functional reactive compound and to modify the cotton fibers using this compound. Furthermore, the purposes were to examine the use of such hetero-bi-functional reactive agent on to cotton fibers and to explore application factors such as temperature, pH, neutral salt and treatment time. Finally the disperse dye containing amino groups was tried to dye the modified cotton fibers using the reactive agent. It was concerned that the bridge compound combined the dye containing amino group with cellulosic fibers and corresponding results were discussed.

2. Experimental

2.1. Synthesis of hetero-bi-functional reactive compound (sodium-2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate, DBDCBS)

The synthesis scheme is shown in Fig. 1. Sodium carbonate (3.39 g, 0.032 mol) and 2,5-diaminobenzenesulfonic acid (**1**, 5.65 g, 0.03 mol) were dissolved in distilled water (40 ml) in order to change the sulfonic acid of **1** to sodium salt (**2**) and the solution (solution 1) was then cooled to 0–5 °C. 2,3-Dibromopropionylchloride (**3**, 7.51 g, 0.03 mol) in acetone (10 ml) was added dropwise to solution 1 for 30 min to produce sodium-2-amino-5-(2,3-dibromopropionylamino)-benzenesulfonate (**4**). The reaction mixture was further stirred for 1 h maintaining the temperature 0–5 °C in an ice-bath. The solid suspended solution was filtered and washed with a small amount of acetone.

In the second reaction step, 2,4,6-trichloro-1,3,5-triazine (**5**, 2.95 g, 0.016 mol) was dissolved in acetone (20 ml) and this solution was poured in distilled water (20 ml) with crushed ice (20 g). Hydrochloric acid aqueous solution (2 N, 0.2 ml) was added to the system (pH 1–2). The reaction system (solution 2) was stirred maintaining the temperature 0–5 °C in the ice-cooled bath. An aqueous solution (20 ml) of **4** (6.79 g, 0.016 mol) obtained in the first reaction was slowly added into solution 2 to produce the final product, namely sodium-2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate (**6**, DBDCBS). And then 20% aqueous solution of sodium carbonate was slowly added to the reaction mixture to get a pH of 6. The reaction mixture was stirred at 0–5 °C for 1 h. After the reaction was completed, the precipitated solid was filtered, washed with a small amount of ice-cooled water and acetone (yield 75%, 6.86 g).

HPLC/MS (negative mode, *m*/*z*, relative intensity): 545.8 ($[M-Na]^-$, 37.7), 547.8 ($[M-Na+2]^-$; isotopic peak, 100.0), 549.8 ($[M-Na+4]^-$; isotopic peak, 92.8), 551.8 ($[M-Na+6]^-$; isotopic peak, 36.9).

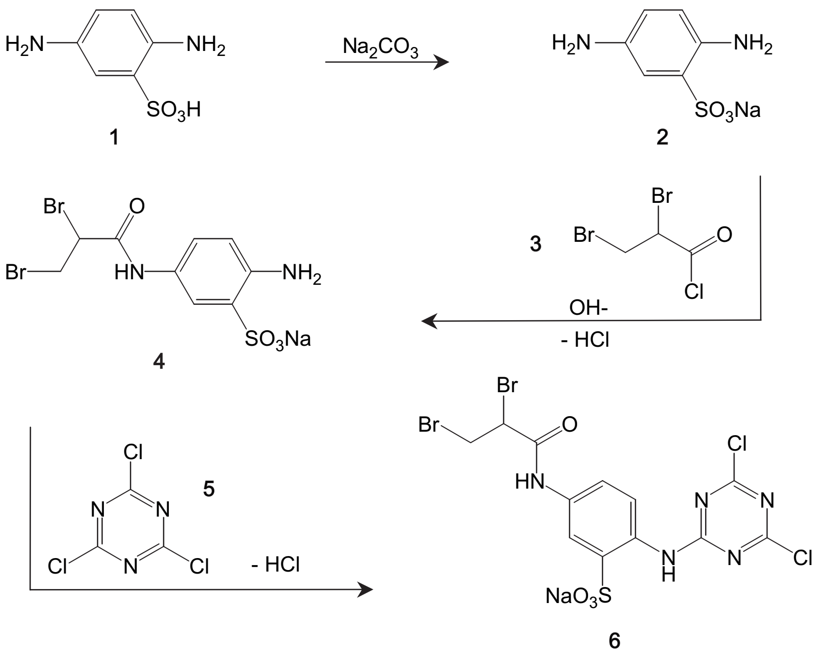


Fig. 1. Synthesis scheme of hetero-bi-functional reactive compound (sodium-2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate, DBDCBS).

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.85–4.08 (Br(CH$_2$)–, m, 2H), 4.77–4.83(–CHBr–, m, 1H), 7.61–7.98(aromatic, m, 3H), 10.71–10.76(–NHCO–, s, 1H), 10.82–10.93(–NH–, s, 1H).

Elemental analysis: Calculated for $C_{12}H_8Br_2Cl_2N_5NaO_4S$: C, 25.20; H, 1.41; N, 12.24; S, 5.61%. Found: C, 25.65; H, 1.48; N, 12.52; S, 5.85%.

UV–vis: λ_{max} (H_2O) 298.0 nm, ε(H_2O): 1.58×10^4.

2.2. Optimum treatment conditions of DBDCBS on cotton fiber

To determine the optimal treatment conditions, scoured and rinsed cotton fabrics (warp 20 tex/yarn 28 yarns/cm, weft 16 tex/yarn 27 yarns/cm, 100 ± 5 g/m^2) were treated with DBDCBS (1–50% owf) at various temperatures (30–80 °C) and pH values (7–12) for 1 h. The liquor ratio was 1:20 and sodium sulfate (0–300 g/l) was used as a neutral salt. The pH was adjusted using sodium carbonate (0–10 g/l). At the end of the treatment, the fabrics were removed and rinsed thoroughly in boiling water.

Absorbance measurements of the original bath and the exhausted bath were carried out using a UV–vis spectrophotometer. Using a previously established absorbance/concentration relationship at the λ_{max} of DBDCBS, the quantity of DBDCBS in solution was calculated and the extent of exhaustion (%E) achieved was determined using Eq. (1), where D_0 and D_t are the quantities of DBDCBS initially in the bath and in the final bath, respectively.

$$\%E=\frac{(D_0-D_t)}{D_0}\times 100 \qquad (1)$$

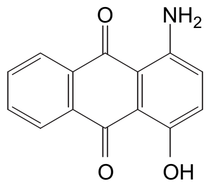
Unfixed DBDCBS from the fabrics was extracted using 25% aqueous pyridine solution and then measured spectrophotometrically. The extent of fixation (%F) and fixation efficiency (%EF) were calculated using Eqs. (2) and (3), respectively, where D_e is the amount of extracted DBDCBS.

$$\%F=\frac{(D_0-D_t-D_e)}{(D_0-D_t)}\times 100 \qquad (2)$$

$$\%\mathrm{EF}=\frac{(E\times F)}{100} \qquad (3)$$

2.3. Disperse dyeing on DBDCBS treated cotton fibers

The cotton fibers (1.0 g) pretreated with DBDCBS (10% owf) under optimal conditions were dyed with a disperse dye shown in Fig. 2.



1-Amino-4-hydroxy anthraquinone (AHAQ)

Fig. 2. Disperse dye used in the study.

The dyeing was carried out at 100 °C and pH 3 with acetic acid for 1 h. The liquor ratio was 1:50. At the end of dyeing, the dyed samples were washed with acetone in order to eliminate unfixed dyes from the fibers. Thereafter the samples were washed with plenty amount of water and dried in the open air.

2.4. Measurement of color strength

Color strengths (fk values) of dyeings were determined using a *Datacolor SF 600 plus* spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10° standard observer.

3. Results and discussion

3.1. Synthesis of DBDCBS

A novel bridge compound possessing hetero-bifunctional reactive groups was synthesized using two reaction steps. The first step was to synthesize the compound **4** and the second step was carried out to produce the compound **6**. Herein, the reverse step of the reaction was not recommended. This reason can be explained by the fact that the chlorine groups of **5** having reactivity towards cellulosic fibers were highly susceptible to hydrolysis reaction [13,14]. Thus, this attribute of cyanuric chloride could influence the final product to be inactive to the reaction with cellulosic molecules.

The equimolar amounts of compound **1** and **3** were reacted in an ice-bath to produce **4** containing an α,β-dibromopropionylamido group. This group shows greater reactivity towards amines or amino groups of substances at acidic condition and high temperature (90–100 °C) [10,11]. A similar reaction mechanism is generally observed from the reactive group, namely α-bromoacrylamide group, which is commonly used for commercial reactive dyes (*Lanasol* dyes) for wool fibers.

In the following step, the equal molar amounts of compound **4** and **5** were reacted in an ice-bath to produce the final product **6** containing a dichloro-*s*-triazinyl reactive group as well as an α,β-dibromopropionylamido reactive group. The dichloro-*s*-triazinyl group, which is a common reactive group used for *Procion MX* dyes, has a greater reactivity towards hydroxyl groups of cellulosic fibers at alkaline condition and room temperature (20–30 °C). This reactive group can be covalently bonded to the cellulosic fibers by nucleophilic substitution reaction at room temperature [13,14]. Thus, reaction mechanism of the synthesized compound may be similar to that of commercial reactive dyes such as *Lanasol* and *Procion MX* dyes. Consequently, the dichloro-*s*-triazinyl reactive side of this bi-functional bridge compound could react with primary amines in polyamide fibers or hydroxyl groups in cellulosic fibers. In the case of the α,β-dibromopropionylamido group, after treatment of the dichloro-s-triazinyl reactive group to the substrates this reactive group still remained active to the amine groups. In this context, these DBDCBS treated fibers could link with disperse dyes containing amino groups in the structure. The corresponding reaction mechanism is shown in Fig. 3.

Considering this reaction mechanism, this novel approach could be used in one-bath/one-stage dyeing process for PET/cotton blends. In addition, it is proposed that the durable wash fastness properties could be obtained by virtue of the covalent nature of the bonds.

3.2. Optimum treatment conditions of DBDCBS

As a bridge compound between fiber substrates and dye molecules, firstly DBDCBS was exhausted to the cotton fibers where the first covalent bonds of DBDCBS could be produced. In this reaction step, the dichloro-*s*-triazinyl reactive group of DBDCBS was reacted with the hydroxy group of the cotton substrates. This reaction for introducing covalent bonds to the cotton substrates could be explained by the view of its mechanism to be like commercial reactive dyes that involve the nucleophilic reaction of dichlorotriazinyl dyes, namely *Procion* cold type dyes. However, the opposite side, α,β-dibromopropionylamido group, remained unreacted and undamaged state, which is supposed to react with materials containing amino groups. In this study, the disperse dye was chosen to use. This stepwise reaction is possible because the α,β-dibromopropionylamido group does not react with hydroxyl groups of cellulose molecules and water [11]; this reactive group only reacts with amino groups at acidic condition and a higher temperature.

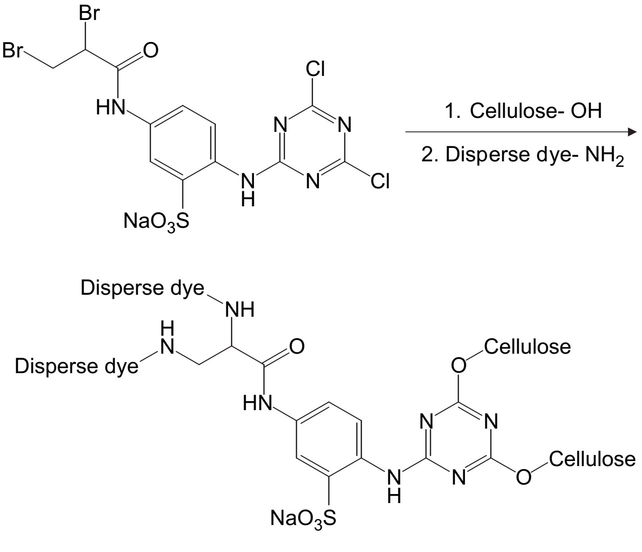


Fig. 3. Reaction mechanism of DBDCBS with cellulose fibers and disperse dyes containing amino groups.

To determine the optimum treatment condition of DBDCBS on cotton fibers, the exhaustion (%*E*) and fixation (%*F*) were obtained at various temperatures. DBDCBS (1.0% owf), 5 g/l of sodium carbonate and 100 g/l of sodium sulfate were used. In the temperature ranges of 30–80 °C (Table 1), it is evident that %*E* and % EF of the treatment greatly increased with decreasing temperature. In the case of fixation, %*F* was obtained with similar values at all temperatures. It is concluded that most of the DBDCBS that was exhausted underwent reaction to give the high fixation levels seen. This finding represents that the reaction efficiency for forming covalent bonds between DBDCBS and cellulosic fibers depends on the exhaustion (%*E*) characteristic. The highest exhaustion was achieved at a temperature of 30 °C.

This higher reactivity at lower temperature could be explained by the fact that the two electronegative chlorines of the DBDCBS agent increased the reactivity of the *s*-triazinyl group with cellulosic substrates even at room temperature [12–14]. At higher temperature, the adsorption or affinity towards cotton fiber was very low and moreover the hydrolysis of the reactive group severely occurred, which could make the reactive group inactive to the fiber substrates. These effects confirm the same view of its mechanism like commercial reactive dyes.

To enhance the reactivity of the dichloro-*s*-triazinyl group of DBDCBS towards cotton fibers, the addition of alkali was attempted [12–14]. Table 2 shows the effect

Table 1
Effect of application temperatures on %*E*, %*F*, and %EF of DBDCBS

Temperature (°C)	%*E*	%*F*	%EF
30	88.2	95.3	84.0
40	82.5	94.4	77.8
50	76.1	95.9	73.0
60	72.3	96.1	69.5
70	66.0	95.4	62.9
80	45.9	93.9	43.1

Table 2
Effect of application pHs on %*E*, %*F*, and %EF of DBDCBS

pH	%*E*	%*F*	%EF
7	38.1	60.5	23.1
8	49.4	79.9	39.4
9	85.0	94.2	80.1
10	88.2	95.5	84.2
11	88.5	95.2	84.3
12	88.5	95.7	84.7

of application of pHs on %*E*, %*F* and %EF of DBDCBS. DBDCBS (1.0% owf) was treated on to cotton fabrics at 30 °C and 100 g/l of sodium sulfate was used. As the pH increased up to a pH of 9, %*E*, %*F*, and %EF were highly increased, but further pH increase did not influence the reaction properties. In the alkaline conditions, the hydroxyl groups within the cotton fibers were ionized to cellulosate anions and the nucleophiles attack the carbon atom of the dichloro-*s*-triazinyl group. However, as predicted, both acidic and neutral treatment conditions did not result in a significant production of nucleophiles, and provided a smaller chemical reaction.

Neutral salts (Na_2SO_4) could affect the exhaustion properties of DBDCBS on to the cotton fibers in the same manner with common reactive dyeings [12–14]. DBDCBS (1.0% owf) was treated on to cotton fabrics at 30 °C and 5 g/l of sodium carbonate was used. The effect of the addition of sodium sulfate on %*E*, %*F* and %EF is shown in Table 3.

Table 3 shows that %*E* and %EF gradually increased with increasing concentration of sodium sulfate and that maximum values of %EF were obtained at salt concentration of 200–300 g/l. However, %*F* values remained the same at all concentrations of sodium sulfate. It is proposed that the neutral salt significantly improved the exhaustion properties (%*E*) and that the salt addition imparted little influence to the fixation (%*F*) of DBDCBS. Because the positive sodium ions neutralized the negative charges on the surface of cotton fibers, the salt promoted substantivity of DBDCBS to the cotton fiber surface due to the reduction in the ionic repulsion forces between the fiber substrates and the negative DBDCBS [15].

Table 3
Effect of neutral salt on %*E*, %*F*, and %EF of DBDCBS

Concentration of Na_2SO_4 (g/l)	%*E*	%*F*	%EF
0	31.1	96.0	29.8
10	43.6	95.6	41.7
20	48.0	95.1	45.7
40	61.5	95.1	58.5
70	79.3	95.5	75.7
100	88.4	95.7	84.6
150	94.0	95.4	89.7
200	98.2	95.1	93.4
300	99.1	96.7	95.9

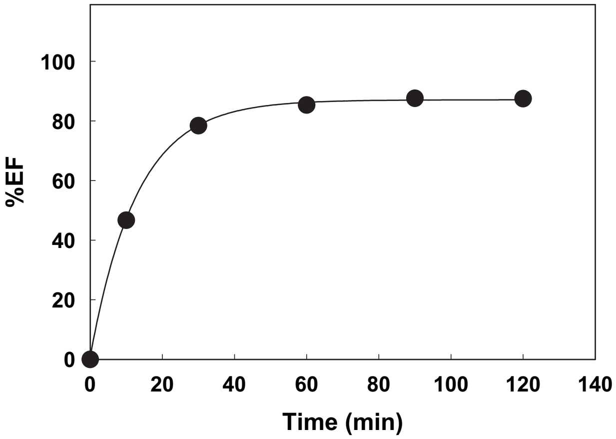


Fig. 4. Effect of treatment time on %EF of DBDCBS.

Meanwhile, from the industrial point of view, because 200–300 g/l of the salts were practically too excessive to employ, 100 g/l of sodium salt was considered to be appropriate and used in subsequent experiments. In the case of treatment time, proper fixation efficiency was sufficiently achieved in 1 h (Fig. 4).

Fig. 5 shows the build-up properties of DBDCBS using different application amounts. At about 10–20% owf of the agent, the fixed amount of DBDCBS reached the maximum range of values. Considering the practical application efficiency of DBDCBS, the optimum quantity was considered to be 10% owf of DBDCBS.

3.3. Disperse dyeing to the DBDCBS treated cotton fiber

Disperse dye shows a great affinity towards hydrophobic fibers such as polyester and nylon, but it does not provide adsorption substantivity on to cellulosic fibers.

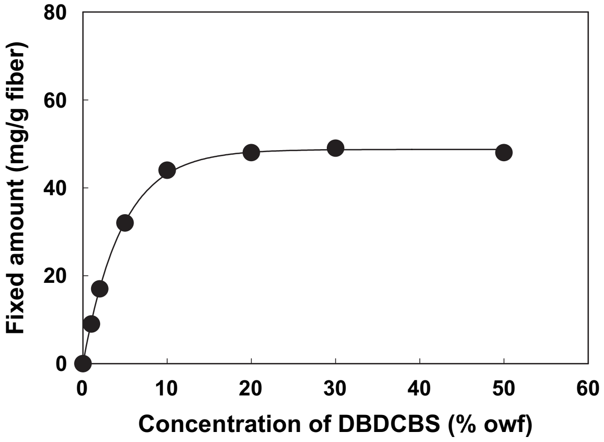


Fig. 5. Build-up property of DBDCBS on to cotton fibers.

Table 4
Color strengths (fk values) of the disperse dyeing on the DBDCBS treated cotton fibers

DBDCBS	*L**	*a**	*b**	fk
Untreated	89.67	12.77	−6.03	0.78
Treated	70.22	32.81	10.22	14.73

Even though a little amount of disperse dyes are temporarily adsorbed on to the cellulosic fibers, the dyes will be easily desorbed out of the substrates in washing or soaping process [16]. However, it is found that the modified cotton fibers with the DBDCBS agent imparted strong attraction forces to the disperse dye which has amino group in the dye molecule. The dichloro-*s*-triazinyl reactive group of DBDCBS was linked with the hydroxy groups of the cotton fibers and the other reactive part, namely α,β-dibromopropionylamido group, remained unreacted and undamaged, which may react with compounds containing amino groups. In this study, the disperse dye of 1-amino-4-hydroxy anthraquinone (AHAQ) was chosen to examine the dyeing effect imparted by the amino substituent.

The DBDCBS treated samples were dyed with this disperse dye using a pH of 3 at 100 °C for 60 min. At the end of dyeing, the dyed samples were washed with acetone and more washing with DMF at 95 °C for 30 min was then carried out to eliminate unfixed dyes on the fiber surfaces. The dyeing result is shown in Table 4.

From the color strengths (fk values), the disperse dye was not dyed on to the untreated cotton fibers. Virtually, it remained as an original white shade of fabrics after washing with hot DMF. Meanwhile, the AHAQ was considerably dyed on to the DBDCBS treated fabrics. This satisfactory dyeing result with AHAQ was attributable to strong affinity between amino groups of the dye and α,β-dibromopropionylamido groups of the DBDCBS treated samples. This reaction mechanism of the α,β-dibromopropionylamido group is similar to that of the α-bromoacrylamide group which is commonly used for commercial reactive dyes for wool, namely *Lanasol* dyes. Thus, the treated sample showed high reactivity towards the amino group of the dye at acidic condition and high temperature (90–100 °C).

4. Conclusions

A novel hetero-bi-functional reactive compound was synthesized and characterized. In addition, its reaction characteristics to the cotton fibers were investigated. Consequently, the dichloro-*s*-triazinyl reactive group of the bridge compound was reacted with hydroxyl groups of the cotton fibers at low temperature and alkaline condition. The salt addition promoted substantivity of DBDCBS to the cotton fiber surface due to the reduction in the ionic repulsion forces between the fiber substrates and the negative DBDCBS. In the case of treatment time, proper fixation efficiency was sufficiently achieved in 1 h. Considering the practical application efficiency of DBDCBS, the optimum quantity was considered to be 10% owf of DBDCBS. The disperse dye having amino groups was linked with the α,β-dibromopropionylamido reactive group of the synthesized agent at high temperature and acidic condition. In addition, it is proposed that the durable wash fastness property could be obtained by virtue of the covalent nature of the bonds.

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