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Synthesis and application of disperse dyes based on 1,4-bis(benzothiazol-2-yl)benzene to polyethylene terephthalate

M. Humphreys[a], N. Hall[b], D.A.S. Phillips[a], J.A. Taylor[a,*]

[a]Department of Textiles, UMIST, P.O. Box 88, Manchester M60 1QD, UK
[b]Dystar UK Ltd, P.O. Box 63, Earl Road, Cheadle Hulme, Cheshire SK8 6GH, UK

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Abstract

Two novel water-insoluble dyes based on the 1,4-bis(benzothiazol-2-yl)benzene chromophore have been synthesised and applied to polyethylene terephthalate (PET) by exhaust dyeing. The dyes exhibited high levels of heat and wet-fastness but light fastness was very poor.

Keywords: Disperse dyes; Polyester; PISYSTEM; Molecular modelling

1. Introduction

1,4-Bis(benzothiazol-2-yl)benzene (BBTB) (Fig. 1) has previously been synthesised by several workers [1–4] but, unlike the related 2-aminobenzothiazoles [5], has never before been used as an intermediate for the preparation of disperse dyes. Structurally similar benzoxazole compounds [6,7] have seen extensive use as fluorescent brightening agents for plastics and textiles.

Andreeshchev et al. [3] reported that BBTB displays an absorbance maximum (λ_{max}) at 352 nm and a molar extinction coefficient (ϵ_{max}) of 56,000 $dm^3\ mol^{-1}\ cm^{-1}$ in dioxane. Molecular orbital calculations, made using the PISYSTEM [8,9] software package, also suggested an absorbance maximum in the ultra-violet region, but at a predicted value of 382 nm. Molecular modelling with PISYSTEM98 suggested that, if strong electron donating groups were present in the benzothiazole ring, a substantial bathochromic shift would be observed, resulting in dyes with a yellow hue. Indeed Petitcolas et al. [2] synthesised, but did not fully characterise, a bis-diamino derivative of BBTB (Fig. 2, R = H), designated as 12,20-diamino BBTB for convenience.

Consequently, two novel bis-dialkylamino derivatives of BBTB have been synthesized. The additional electron donating groups resulted in an expected bathochromic shift yielding molecules which absorbed in the 'visible' region of the electromagnetic spectrum, with an intensity comparable to that of many commercial disperse dyes. The synthetic pathway used is shown in Fig. 3.

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* Corresponding author. Tel.: +44-161-200-4112; fax +44-161-955-8150.
E-mail address: john.a.taylor@umist.ac.uk (J.A. Taylor).

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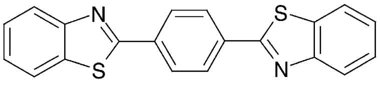

Fig. 1. Structure of BBTB.

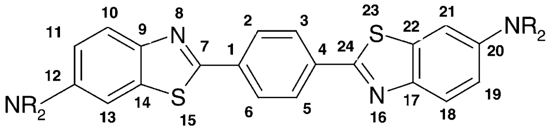

Fig. 2. Numbering system adopted for bis-dialkylamino derivatives of BBTB.

2. Experimental

2.1. Chemical synthesis

All melting points were determined using Stuart Scientific SMP3 digital melting point apparatus (heated block). Elemental microanalyses were performed on a Carlo-Erba 1108 elemental analyser. Thin-Layer Chromatography was performed using silica-coated aluminium plates (60-F_{254}, Merck). FTIR spectra were recorded on a Nicolet Magna 750 system. Mass spectra were obtained using a Micromass LCT Time-Of-Flight (electrospray, positive ion) mass spectrometer, a Micromass 70S Electron Impact Double Focusing High Resolution mass spectrometer or an AutospecEQ Fast Atom Bombardment (positive ion) mass spectrophotometer. Differential Scanning Calorimetry (DSC) was carried out using a Mettler DSC 30 set up (with Mettler TC15 controller and StarE software v6.1). All ^{1}H-NMR spectra were recorded at 300 MHz using a Bruker DPX 300 spectrometer, equipped with proton/carbon z-gradient dual probes. The numbering system used for ^{13}C-nmr analysis of compound 2.1.3 is based on that shown in Fig. 2. ^{13}C-NMR spectra were recorded at 100 MHz using a Bruker DPX 400 spectrometer.

All reagents were purchased from Aldrich, Acros, Fisher or Lancaster and used without further purification.

2.1.1. *1,4-bis(benzothiazol-2-yl)benzene [Structure 2.1.1, Fig. 3]*

Polyphosphoric acid (125 cm^{3}) was heated and stirred at 70 °C for 1 h. Terephthalic acid (0.1 mol, 16.6 g) was added and the mixture stirred

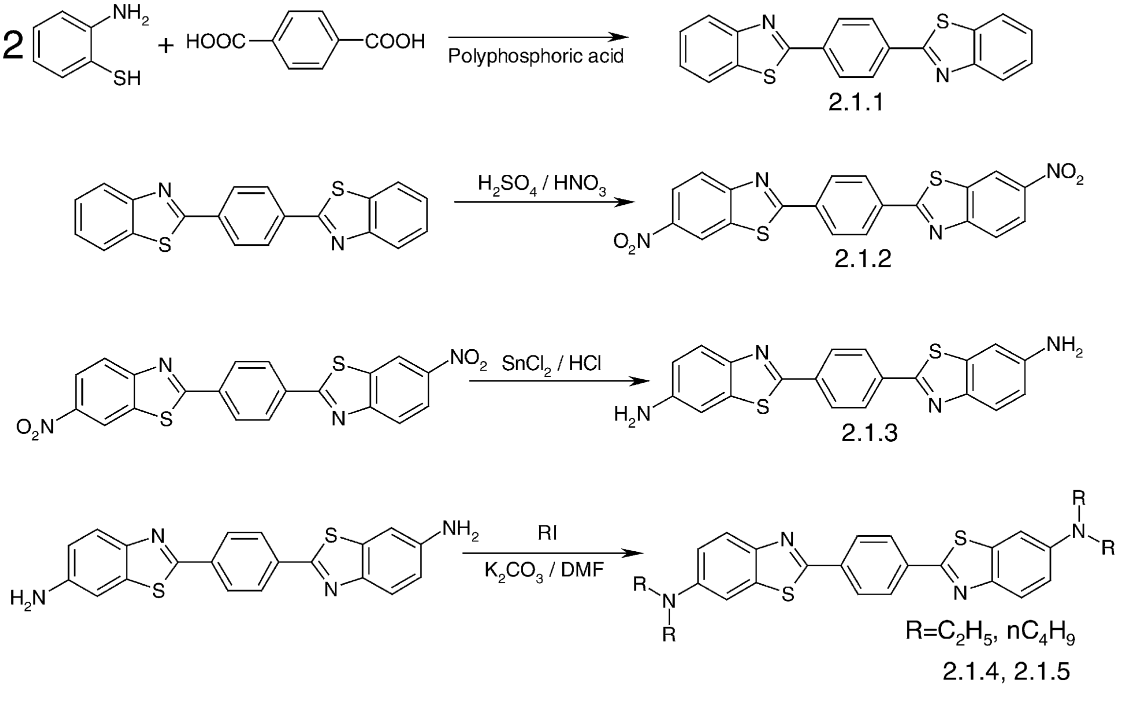

Fig. 3. Synthetic route to 12,20-dialkylamino BBTB dyes.

for 15 min. 2-aminothiophenol (0.2 mol, 25.1 g) was added dropwise over 10 min. The temperature was raised to 150 °C and maintained at this temperature for 2 h with efficient stirring before cooling to room temperature. The resulting reaction mixture was stirred with iced-water (1.5 dm^3) for 1 h, neutralised with dilute sodium hydrogen carbonate solution, filtered and oven dried overnight. The solid was crystallised from dimethylformamide (200 cm^3). Finally the filtered product was washed with methanol (100 cm^3) and dried in a vacuum oven at 100 °C to yield 1,4-bis(benzothiazol-2-yl)benzene as colourless needles (15.69 g, 46%), m.p. 263 °C, lit. 263 °C [1]; Found: C, 69.1; H, 3.6; N, 7.9; S, 18.6%. $C_{20}H_{12}N_2S_2$ requires C, 69.8; H, 3.5; N, 8.1; S, 18.6%; *m/z* (EI) 344(100%).

2.1.2. 1,4-bis(6-nitrobenzothiazol-2-yl)benzene [Structure 2.1.2., Fig. 3]

1,4-Bis(benzothiazol-2-yl)benzene (8.4 g, 0.024 mol) was added cautiously to concentrated sulphuric acid (100 g, 55 cm^3) at 8 °C and stirred for 15 min. A mixture of concentrated nitric acid (5.1 g) in concentrated sulphuric acid (5g) was added dropwise below 8 °C and the reaction mixture stirred for 1 h at 0 °C. This mixture was added slowly, with stirring, to iced water (500 m^3) and neutralised with aliquots of sodium hydrogen carbonate solution. The solid was collected by filtration, crystallized from nitrobenzene, washed with cold methanol and dried in a vacuum desiccator at 100 °C yield to 1,4-bis(6-nitrobenzothiazol-2-yl)benzene as a yellow solid (5.98 g, 57%) m.p.> 300 g; Found. C, 55.3; H, 2.3; N, 12.9; S, 14.8. $C_{20}H_{10}N_4O_4S_2$ requires C, 54.8; H, 2.4; N, 12.7; S, 14.6%; m/z EI) 434(100%); ν_{max}(nujol)/cm^{-1} 1347(s, N=O), 1525(s, N=O).

2.1.3. 1,4-bis(6-aminobenzothiazol-2-yl)benzene [Structure 2.1.3., Fig. 3]

1,4-Bis(6-nitrobenzothiazol-2-yl)benzene (1 g, 0.003 mol), tin(II)chloride (6.1 g) and concentrated hydrochloric acid (15 cm^3) were heated under reflux for 4 h. The reaction mixture was then drowned into iced water (750 cm^3) and neutralised with sodium hydrogen carbonate solution. The crude product was crystallised from dimethylformamide, filtered, washed with cold methanol and dried in a vacuum oven at 100 °C to yield 1,4-bis(6-aminobenzothiazol-2-yl)benzen*e* as yellow needles (0.72 g, 84%), m.p.(DSC) 320 °C; Found: C, 64.1; H, 3.9; N, 15.3; S, 16.9. $C_{20}H_{14}N_4S_2$ requires C, 64.1; H, 3.8; N, 15.0; S, 17.1%; m/z (FAB) 375 (M+, 100%) ν_{max}(nujol)/cm^{-1} 3323(*m*, N-H), 3404(*m*, N-H); λ_{max}(DMF)/nm 414, ϵ_{max}(DMF)/dm^3 mol^{-1} cm^{-1} 39000, $\Delta\lambda_{1/2}$ / nm 78; δ_H(300MHz), d_6-DMSO; 5.58 (4H, *br s*, N-H), 6.83 (2H, dd, *J* 2.64 and 9.04 Hz, aromatic), 7.12 (2H, *d*, *J* 2.64 Hz, aromatic), 7.74 (2H, *d*, *J* 9.04 Hz), 8.08 (4H, *s*, phenyl-H); δ_C(100 MHz), d_6-DMSO; 104 (2C-13,21), 115.8 (2C-11,19), 123.8 (2C-10,18), 127.5 (4C-2,3,5,6), 135 (2C-14,22) 137 (2C-1,4), 145.6 (2C-9,17) 148.2 (2C-12,20) 159.7 (2C-7,24).

*2.1.4. 1,4-bis(6-*N,N*-diethylaminobenzothiazol-2-yl)benzene [Structure 2.1.4., Fig. 3]*

1,4-Bis(6-aminobenzothiazol-2-yl)benzene (3 g, 0.008 mol) and potassium carbonate (33.12 g, 0.24mol) were vigorously stirred for 30 min at 70 °C in dimethylformamide (100 cm^3). Iodoethane (37.44 g, 0.24 mol) was added dropwise. The temperature was elevated to, and maintained at, 100 °C for 24 h and the reaction followed by TLC (Eluent: toluene: ethyl acetate, 50:50). After cooling, the reaction mixture was drowned into 200 cm^3 of hot water, to yield a crude orange dye. This was collected by filtration and crystallised from toluene to yield [1,4]bis(6-*N*,*N*-diethylaminobenzothiazol-2-yl)benzene as bright orange needles (1.9 g, 50%), m.p. 246–248 °C; Found C, 69.1; H, 6.3; N, 11.5; S, 12.9. $C_{28}H_{30}N_4S_2$ requires C, 69.1; H, 6.2; N, 11.5; S, 13.2%; *m/z* (EI) 486(100%); λ_{max}(DMF)/nm 440, ϵ_{max}(DMF)/dm^3 mol^{-1} cm^{-1} 43000, $\Delta\lambda_{1/2}$ /nm 80; δ_H(300 MHz), $CDCl_3$; 1.25, (12H, *t*, *J* 7.16Hz, CH_2CH_3), 3.46, (8H, quartet, *J* 7.16 Hz, CH_2CH_3), 6.93 (2H, dd, *J* 2.64 Hz and 9.04 Hz, aromatic), 7.09 (2H, *d*, *J* 2.64 Hz, aromatic), 7.91 (2H, *d*, *J* 9.04 Hz, aromatic), 8.10 (4H, *s*, phenyl-H).

*2.1.5. 1,4-bis(6-*N,N*-dibutylaminobenzothiazol-2-yl)benzene [Structure 2.1.5., Fig. 3]*

1,4-Bis(6-aminobenzothiazol-2-yl)benzene (2 g, 0005 mol) and potassium carbonate (22.15 g, 0.16 mol) were vigorously stirred for 30 min at 70 °C in dimethylformamide (100 cm^3). 1-Iodobutane (29.49 g, 0.16 mol) was added dropwise and the reaction mixture heated under reflux for 11 h, the reaction being followed by TLC (Eluent: toluene: ethyl acetate 50:50). The mixture was poured, with stirring, into 500 cm^3 of hot water and extracted with chloroform (4×100 cm^3). The combined chloroform extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. The residual solid was crystallised from acetonitrile to yield 1,4-bis(6-*N*,*N*-dibutylaminobenzothiazol-2-yl)benzene as bright orange fine needles (2.1 g, 66%), m.p. 139 °C; Found C, 72.2; H, 7.5; N, 9.3; S, 10.6. $C_{36}H_{46}N_4S_2$ requires C, 72.2; H, 7.7; N, 9.4; S, 10.7; *m*/*z* (FAB) 599 (M+, 100%); λ_{max}(DMF)/nm 444, ϵ_{max}(DMF)/dm^3 mol^{-1} cm^{-1} 54000, $\Delta\lambda_{1/2}$ /nm 82; δ_H(300 MHz), d_6-Acetone; 0.97 (12H, *t*, *J* 7.35 Hz, $NCH_2CH_2CH_2CH_3$), 1.42 (8H, sextet, *J* 7.35 Hz, $NCH_2CH_2CH_2CH_3$), 1.65 (8H, quintet, *J* 7.35 Hz, $NCH_2CH_2CH_2CH_3$), 3.45 (8H, *t*, *J* 7.35 Hz, $NCH_2CH_2CH_2CH_3$), 7.01 (2H, *dd*, *J* 2.64 and 9.04 Hz, aromatic), 7.28 (2H, d, *J* 2.64 Hz, aromatic), 7.84 (2H, d, *J* 9.04Hz, aromatic), 8.15 (4H, s, phenyl-H).

2.2. UV/Visible properties of the novel dyes

2.2.1. PISYSTEM98© colour prediction [8]

Based on molecular orbital theory, this simple computer program has the ability to predict the approximate absorption maximum of a conjugated molecule in an inert solvent. Two quantities are calculated, viz the absorption maximum (λ_{max}) and the oscillator strength (*f*) of the molecule. Griffiths [10] has described in detail how the oscillator strength relates to the molar extinction coefficient of a chromophore. In general, if the value of *f* is predicted to be high, the dye should be strong and bright (i.e. exhibit a narrow band width in its visible absorption spectrum).

2.2.2. UV/Visible dye spectra

UV/Visible spectra were recorded on a Camspec M350 Double beam UV-Visible spectrophotometer. All measurements were made in dimethylformamide in the wavelength range 350–700 nm. The *measured* values of absorption maximum (λ_{max}), molar extinction coefficient (ϵ_{max}) and half-band width ($\Delta\lambda_{1/2}$), with the *calculated* values of absorption maximum and oscillator strength (*f*), are shown in Table 1.

2.3. Application of synthesised novel dyes to polyester

The dialkylamino dyes (structures 2.1.4. and 2.1.5., Fig. 3) were applied to knitted polyester by an exhaustion process at a liquor ratio of 1:25 using a Roaches–Rotec machine. The (visual) build-up properties of the dyes were examined by application at 0.1, 0.5, 1.0, 2.0 and 4.0% omf. Dyes 2.1.4. and 2.1.5. were formulated as 2% dispersions by milling overnight with pea gravel at room temperature in the presence of a dispersing agent (Surfynol 104E, 1 drop, Air Products). Each dyebath contained a 2 g sample of polyester; the requisite amount of dye dispersion and dispersing agent (Matexil DA-N (0.5 cm^3), Uniqema), the pH being adjusted to four with a potassium hydrogen phthalate (BDH) buffer.

The greenish-yellow hydrazo-pyridone dyestuff, Dispersol®Yellow C-5G[1] (Dystar, C.I. Disperse Yellow 119, $C_{15}H_{13}N_5O_4$, $M_R = 327$), was used as a control against which to compare the shade and fastness properties of the novel dyes (see Section 2.4). A sample of the commercial dye was dispersed thoroughly, with stirring, in water, before being collected by filtration and dried overnight under vacuum at 40 °C. The material was used to make a 2% dispersion as described above.

All dyeings were carried out using the profile outlined in Fig. 4, where *T* represents the maximum dyeing temperature in degrees Celsius and *D* represents the dyeing time (in minutes) at the

Table 1
UV/Visible spectral properties of the novel dyes

Compound	λ_{max} (DMF)/nm	ϵ_{max} (DMF)/dm^3 mol^{-1} cm^{-1}	$\Delta\lambda_{1/2}$ /nm	λ_{max} (calc)[a]/nm	*f*(calc)[a]
2.1.3	414	39,000	78	450	1.41
2.1.4	440	43,000	80	542	1.36
2.1.5	444	54,000	82	542	1.36
Dispersol® Yellow C-5G	440	30,000	77	479	0.81

[a] Calculated using PISYSTEM98.

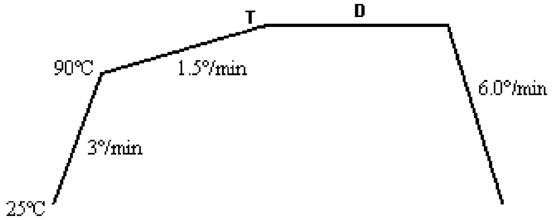

Fig. 4. Dyeing profile used to assess novel dialkylamino BBTB disperse dyes 2.1.4. and 2.1.5.

maximum dyeing temperature.After dyeing, the samples were reduction cleared at 70 °C for 30 min using a solution of 6 g/l NaOH (70 °Tw) and 3 g/l sodium metabisulphite.

A Spectroflash 600 spectrophotometer (with Datacolor v2.1 analytical software) was used to measure visual colour yield, expressed in terms of a K/S value.

2.4. Determination of fastness

The novel dyes 2.1.4. and 2.1.5., together with Dispersol® Yellow C-5G, as control (CTL), were dyed to achieve an approximate K/S value of 10.

These samples (of equal visual depth of shade) were used to assess the wash, heat and light fastness of the novel dyes. The results are shown in Table 2.

2.4.1. Fastness of novel dyes to washing

The ISO CO6/C2S wash fastness test [11], using a Roaches Washtec-P apparatus, was carried out on a sample of dyed polyester which had been heat set at 180 °C for 45 s after reduction clearing. The adjacent fabric used in the test was an SDC multifibre strip and staining was assessed using grey scales (1-severe staining, 5-no staining). The results are shown in Table 2.

2.4.2. Fastness of novel dyes to heat (sublimation)

After reduction clearing, samples of dyed polyester were placed against a piece of adjacent plain polyester. A Roaches dual contact hotplate was used to conduct the heat fastness tests, the upper plate being heated to either 180 or 210 °C with the samples placed on a heat protective mat. The composite samples were pressed between the two plates for 30 s at the defined temperature. The adjacent polyester samples were then visually assessed for staining using grey scales. The results are shown in Table 2.

2.4.3. Fastness of novel dyes to light

After reduction clearing, samples of dyed polyester were exposed to light from a xenon arc (Xenotest) for a total of 48 h, made in accordance with British Standard BS EN 20105, alongside a series of blue wool standards. Light fading was assessed on a scale of 1 (severe fading) to 8 (almost no fading). The results are shown in Table 2.

3. Results

3.1. Spectrophotometric analysis

Due to the very sparingly soluble nature of compounds 2.1.1. and 2.1.2., their UV/Vis spectral properties could not be accurately assessed. The observed spectrophotometric properties of compound 2.1.3. and the novel dyes 2.1.4. and 2.1.5., compared with their predicted values, are shown in Table 1.

Table 2
Fastness properties of the novel dyes 2.1.4. and 2.1.5. compared with C.I. Dispersol® Yellow C-5G

Dye	Washing (CO6/C2S)						Heat		Light
	Secondary cellulose acetate	Bleached unmercerised cotton	Nylon 6.6	Polyester (terylene)	Acrylic (courtelle)	Wool (worsted)	180 °C	210 °C	
2.1.4.	5	5	4/5	5	5	5	5	5	< 1
2.1.5.	5	5	4/5	5	5	5	5	5	< 1
Dispersol® Yellow C-5G (CTL)	5	5	5	5	5	5	5	4	8

3.2. Application of novel dyes 2.1.4. and 2.1.5. to polyester

3.2.1. Influence of dyeing temperature and time on visual colour yield (K/S) of dye 2.1.5

Figs. 5 and 6 illustrate the variations in colour yield with temperature (130 and 140 °C) and time, respectively. In each case 'applied depth of shade' refers to the weight of pure dye per 100 gm of polyester.

4. Discussion

4.1. Dye synthesis

Intermediates 2.1.1. and 2.1.2. were only sparingly soluble in most organic solvents, and could only be crystallised from highly polar solvents such as DMF. 2.1.2. was highly crystalline, with no clear melting point, even above

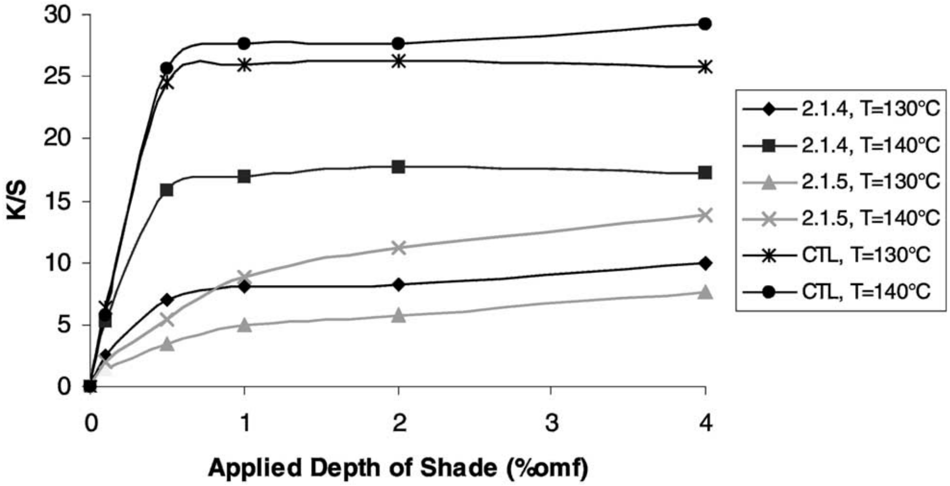

Fig. 5. The effect of maximum dyeing temperature, T °C, on visual colour yield for a dyeing time (D) of 60 min.

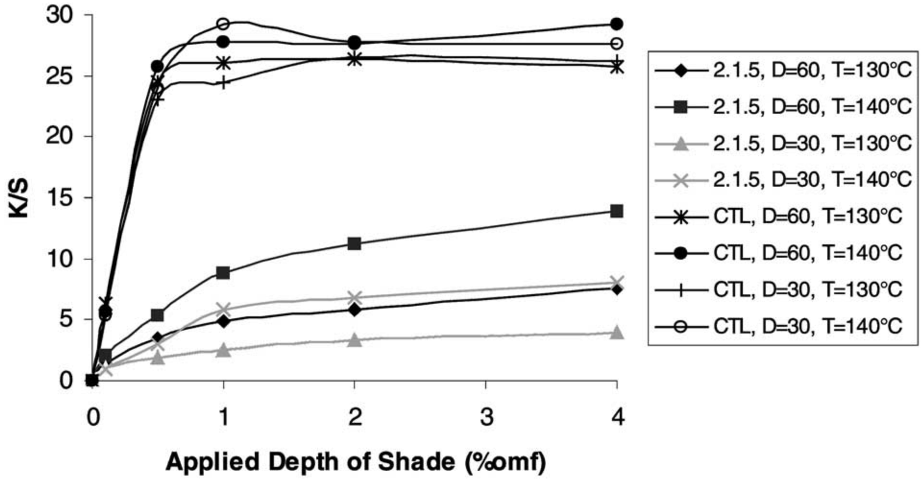

Fig. 6. The effect of dyeing time, D, on visual colour yield of dye 2.1.5. (at both 130 and 140 °C).

300 °C. The 12,20 substitution pattern of this material was proven by reduction of the nitro groups to form dye 2.1.3. Solubility of this material and the alkylated derivatives was greatly increased over that of 2.1.2., allowing the successive dye structures to be characterised by NMR.

4.2. Spectral analysis

The visible spectral properties of the BBTB dyes showed only a poor degree of correlation with those predicted using the PISYSTEM98 prediction programme (see Table 1). The bathochromic shift predicted by the programme on going from a diamino chromophore (dye 2.1.3., predicted $\lambda_{max} = 450$ nm) to a bis-dialkylamino chromophore (dyes 2.1.4., 2.1.5., predicted $\lambda_{max} = 542$ nm) was observed, but nothing like to the same extent [λ_{max}(DMF) 414 nm to 440, 444 nm resp.]. Indeed the programme predicted the novel dyes to be red, not greenish-yellow, in shade! In addition, the calculated oscillator strengths exhibited little correlation with the measured molar extinction coefficients, suggesting limited usefulness for the programme for predicting spectral properties of new chromophores. In practice, the novel, bis-dialkylamino substituted greenish-yellow dyes, although exhibiting much higher molar extinction coefficients than the hydrazo-pyridone control, were slightly duller in shade.

4.3. Dyeing properties

Fig. 5 indicates that the novel BBTB dyes 2.1.4. and 2.1.5. exhibit lower visual colour yield at the same applied depth than the tinctorially weaker Dispersol©Yellow C-5G. The visual colour yield of both BBTB dyes was increased by increasing the dyeing temperature (Fig. 6) and, as suggested by the performance of dye 2.1.5. (Fig. 5), the dyeing time. This suggests that the lower visual yields from the tinctorially stronger BBTB dyes may be, in part, attributable to their having lower aqueous solubility than the control; the novel dyes having molecular weights twice that of the hydrazo-pyridone control (Dye 2.1.4; $M_R = 486$, Dye 2.1.5; $M_R = 598$, Dispersol® Yellow C-5G; $M_R = 327$).

4.4. Fastness properties

The CO6/C2S wash fastness of the polyester, dyed with the BBTB dyes 2.1.4. and 2.1.5., was high after heat setting, although a trace inferior to that of the control. In practice however, the wet fastness of greenish-yellow disperse dyes is not regarded as a major problem by dyers and retailers.

The heat fastness of dyes 2.1.4. and 2.1.5. was also very high (category 'D'), their relatively large molecular weights inhibiting their propensity to sublime onto the adjacent polyester during the test. Their fastness was higher than the (category 'C') control dyestuff. Due to these high levels of heat/sublimation fastness, it could be assumed that the dyes would be particularly suited for application under high temperature thermofixation (continuous dyeing) conditions.

However, the light fastness of the BBTB dyes was catastrophically low, precluding any further interest in exploiting this type of substitution pattern as a commercially viable dyestuff. Photofading might well occur via singlet oxygen attack at the most electron-rich portions of the molecule, i.e. the electron-donating dialkylamino groups. This behaviour has been noted before in azo dye chemistry [12].

5. Conclusions

A novel class of disperse dye based on 1,4-bis(-benzothiazol-2-yl)benzene(BBTB) has been synthesised and applied to polyester under exhaust dyeing conditions. The dyes exhibited high heat and wash fastness properties but very low light fastness.

Acknowledgements

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