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Dyes and Pigments 43 (1999) 51–58

DYES and PIGMENTS

Modification of cotton cellulose with sodium benzoylthioglycollate and its effect on its dyeability with disperse dyes

Part 1: synthesis and characterisation of sodium benzoylthioglycollate

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Received 25 February 1999; accepted 17 March 1999

Abstract

The extensive amount of work which has been carried out to increase disperse dye substantivity for cellulosic fibres is critically assessed. From the viewpoint of the practical colourist it is important that such systems should be operable in aqueous media. A water soluble acylating agent, sodium benzoylthioglycollate, (BTG) was therefore synthesised and characterised. The stability of BTG to hydrolysis in aqueous media was determined, together with its reactivity towards other nucleophiles. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cotton modification; Benzoylthioglycollate; Synthesis; IR characterisation

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1. Introduction

Non-ionic disperse dyes have little substantivity for cellulosic fibres. Modification of such fibres to increase the substantivity of non-ionic disperse dyes is desirable for two major reasons. Firstly, disperse dyes are widely employed in the sublimation transfer printing process and so suitable modification of cellulosic fibres should provide an extended use of this process. Secondly, polyester/cotton blend fabrics are highly popular apparel fabrics, and a method to dye such fabrics with a single class of dye would be valuable. At the present time, the polyester part of the blend is dyed using disperse dyes, whilst the cotton part of the blend is frequently dyed using water soluble reactive dyes. Such processes are expensive and time consuming, especially if using two step methods involving first dyeing the polyester portion with the disperse dye at 130°C, reduction clearing, dropping and resetting the bath, reactive dyeing the cotton portion and finally clearing unfixed dye.

A number of workers have shown that increasing the hydrophobic character of cotton cellulose and natural keratin fibres gives a fibre which is more readily dyeable with disperse dyes. The

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PII: S0143-7208(99)00036-4

hydrophobic character of such fibres can be increased by reactions that incorporate bulky aryl residues in the fibres. Natural cellulosic fibres may be acylated by the Shikibo-Uni process[1,2] involving sequential treatment with 20% aq. sodium hydroxide and benzoyl chloride. The use of benzoyl chloride as an acylating agent is unsatisfactory due to its hazardous and lachrymatory nature.

Thomas [3] demonstrated that activated phenolic or mercapto esters of carboxylic acids reacted with cellulose at high temperatures (150–200°C) to form the cellulose-carboxylic acid ester. The esters employed were water soluble due to the presence of pendant carboxylate groups, and so may be applied to cellulosic fabrics under mill processing conditions, the reaction with cellulose being promoted by a baking procedure in thermosol equipment. Typical examples of such water soluble reactive esters are sodium benzoylthioglycollate (BTG) and sodium benzoylsalicylate. The essential reactions involved can be represented by Scheme 1.

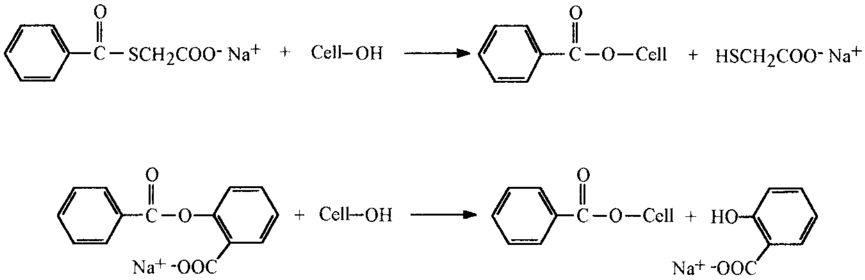
Eastall [4] found that wool fibres modified with BTG showed improved disperse dye uptake and the resulting dyed modified wool fibres showed improved wash fastness and improved resistance to felting during washing.

Baumann and Korte [5] showed that cellulosic fibres acylated with various aliphatic and aromatic acid chlorides exhibited enhanced disperse dye substantivity. The disperse dye substantivity for cellulose modified with aliphatic acid chlorides increased as the chain length of the aliphatic residue increased [5], maximum substantivity being achieved at a chain length of at least 11 carbon atoms. Aromatic substituents on the fibre produced high disperse dye substantivity and such dyeings exhibited better wash fastness than the corresponding dyeings produced on fibres modified with aliphatic substituents [6,7].

Various workers have investigated other reactive compounds for the partial modification of cellulosic fibres. Terephthalic acid half ester acid chlorides ($ROCOC_6H_4COCl$) of *n*-butanol, benzyl alcohol and cyclohexanol have been used to modify cellulose [8]. These compounds gave a degree of substitution (D.S.) of 0.14 regardless of the type of acyl residue. They also imparted improved crease resistance properties to the modified fibre, indicating that cross-linking had occurred. Dicarboxylic acid half ester amides ($H_2N\text{-}CO\text{-}RCO_2R$) and acid anhydrides have also been used to modify cellulose [8] to change its dyeing properties.

Cellulose can also be modified by reaction with acrylonitrile [6,7,9]; such cyanoethylated cellulosic fibres, with a D.S. of 0.1 and above, exhibit good dyeability with disperse dyes. The brilliance of colour of the dyeings was similar to that obtained for polyester, but the wet fastness properties of such dyeings was poor. Cellulose can be modified using acetic anhydride at room temperature. After 4 min, a degree of substitution of 0.1 is obtained, whilst after 12 min a degree of substitution of 0.158 is obtained [6–9]. Further reaction leads to a degree of substitution of 2.5 and eventually to a maximum value of 3, resulting in a modified fibre which may be disperse dyed to give dyeings of excellent colour yield and wash fastness.

Blanchard et al. [10] studied the modification of cotton and polyester/cotton blends to produce a substrate suitable for sublimation transfer printing with disperse dye printed papers. The fabrics were modified using water soluble ethylene and propylene



Scheme 1. The reactions of sodium benzoylthioglycollate and sodium benzoylsalicylate with cellulose.

glycols and a dimethyloldihydroxyethylene urea cross-linking agent. Propylene glycol gave the best results, in terms of colour yield, on transfer printing the modified fabrics. Transfer printing 50:50 polyester/cotton blend and 100% cotton fabrics modified by this method produced similar prints, but the prints on 50:50 polyester/cotton blend fabrics showed better wash fastness. The fabrics were also modified with melamine-formaldehyde resins in the presence of glycols. Modified polyester/cotton blend fabrics gave the best results, the modified pure cotton fabrics giving poor wash fastness tests.

In-situ interfacial polymerisation [10] has also been used to modify cellulose. The polymers were formed on the fibre surface by reactions between di-acid chlorides and bisphenols or between acid chlorides and diamines. The resulting modified fabric gave good transfer prints.

Isocyanates, s-triazine derivatives and sulphonyl chlorides have also been used to modify cellulosic fabrics to enhance disperse dyeability [6,7].

In addition to showing improved disperse dye substantivity and improved wash fastness of disperse dyeings, cellulosic fabrics modified by incorporation of bulky hydrophobic residues possess improved thermal stability, improved crease and wrinkle resistance, and show a slight decrease in water retention properties.

Einsele et al.[6,7] showed that a degree of substitution between 0.15 and 0.25 for benzoylated cellulosic fabrics gave optimum disperse dye substantivity. According to Thomas [3] such benzoylated cellulose fabrics could also be dyed with selected acid and 2:1 premetallized dyes. For a degree of substitution of 0.12, approximately 3% of the cellulose hydroxyl groups would be modified. A degree of substitution in the region of 0.12–0.15 is required to give a modified fibre which can be effectively transfer printed with sublimable disperse dyes [7,11]. In order to achieve good wash fastness properties, a degree of substitution in the range of 0.3–0.4 is required.

Baumann et al. [8] showed that for acylated cellulose approximately 30% of the ester groups originally present are hydrolysed when washing under strong alkaline conditions. After 5 washes, 60–70% of the ester groups present will have been hydrolysed. After 10 washes, no further significant hydrolysis occurs. Thus, new alkali stable bridging groups should be developed for commercial application of such fibre modifications.

2. Experimental

2.1. Materials

All chemicals employed were of laboratory reagent grade unless otherwise stated.

2.2. Preparation and characterisation of benzoylthioglycollic acid

Benzoylthioglycollic acid was prepared by the reaction of sodium thioglycollate with benzoyl chloride at 0–5°C [3,4] (Scheme 2). Thioglycollic acid (92 g, 1 mol) was added to a cold solution of sodium hydroxide (80 g, 2 mole) in water (440 ml). The sodium thioglycollate solution produced was cooled to below 5°C and benzoyl chloride (140.5 g, 1 mol) was added dropwise with thorough stirring. The reaction was allowed to proceed until a constant pH between 5 and 6 was obtained. Conc. HCl (1 mol) was then gradually added to the solution to precipitate the free benzoylthioglycollic acid. The precipitate was collected, washed with water, dried and then purified by recrystallisation from toluene.

2.3. Spectroscopy

IR spectra were obtained (KBr) on a Unicam SP1100 infra-red spectrophotometer, and electronic spectra on a Pye-Unicam SP800A spectrophotometer (10 mm quartz cells).

2.4. High performance liquid chromatography (HPLC)

Reverse phase ion-pair HPLC was used to detect and quantify sodium benzoate and sodium thioglycollate in solution. The analysis was carried out on a Perkin–Elmer series 10 liquid chromatograph, in combination with a Perkin–Elmer LC-75 spectrophotometric detector. The analysis was carried out using a Hypersil MOS 5 μm (C8 bonded) chromatographic column, with a flow rate of 2 ml/min. Eluents based on HPLC grade methanol/water mixtures were used for the analysis, tetrabutylammonium bromide being added as the ion-pair reagent. Detection of the eluting species was carried out at a wavelength of 235 nm.

2.5. Hydrolysis of sodium benzoylthioglycollate

The extent of hydrolysis of sodium benzoylthioglycollate was investigated under both acidic and alkaline conditions. BTG (0.5 g) was dissolved in a minimum quantity of 10% w/v aq. sodium carbonate adjusted to the desired pH value using 10% w/v aq. sodium carbonate or 10% v/v aq. acetic acid and then made up to 100 ml with deionised-distilled water. BTG solutions adjusted to the desired pH were left to stand at room temperature and, after 24 h, samples were analysed by HPLC; the extent of hydrolysis was determined by following the amount of sodium benzoate produced during the hydrolysis reaction. The extent of hydrolysis of BTG at 100°C was determined over a period of 4 h.

The alkaline solution hydrolysis may be represented as shown in Scheme 3.

2.6. Nucleophilic substitution with amines

Model reactions between BTG and benzylamine were carried out using different temperature and pH conditions. The reaction product is *N*-benzylbenzamide, which is water insoluble (Scheme 4).

BTG (0.5 g) was dissolved in a minimum quantity of 10% w/v aq. sodium carbonate, adjusted to the required pH value and made up to 50 ml with deionised-distilled water. An equimolar quantity of benzylamine (0.28 ml) was mixed with water, adjusted to the desired pH value and made up to 50 ml with deionised-distilled water. The benzylamine solution was then added to the BTG solution and the mixture heated at various temperatures (see Fig. 3) in a water bath for 1 h. After 1 h the reaction was stopped and the water insoluble *N*-benzylbenzamide was collected by filtration and dried to constant weight.

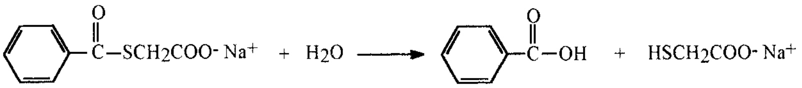
The reaction of BTG and benzylamine was repeated in the presence of nicotinic acid (0.1 g), since this tertiary amine has been shown to catalyse the reaction of monochlorotriazine dyes with cellulose[12]. It was expected that BTG would react first with nicotinic acid to form a highly reactive quaternary species.

3. Results and discussion

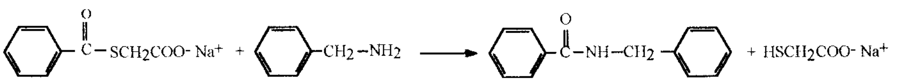
3.1. BTG preparation

The yield of benzoylthioglycollic acid produced varied between 75 and 95%. A melting range of

Scheme 2. Preparation of sodium benzoylthioglycollate.



Scheme 3. The hydrolysis of sodium benzoylthioglycollate.



Scheme 4. The reaction of sodium benzoylthioglycollate with benzylamine.

106–107°C was obtained for the recrystallised solid (literature 107°C [4]).

The UV spectrum of sodium benzoylthioglycollate showed two wavelengths of maximum absorption, one at 239 nm and one at 268 nm, that of sodium benzoate showed one absorption peak at a wavelength of 224 nm and that of sodium thioglycollate gave no pronounced absorption peaks.

The IR absorption frequencies of some of the functional groups in sodium benzoate, sodium benzoylthioglycollate, sodium thioglycollate, thioglycollic acid, benzoic acid and benzoylthioglycollic acid are given in Table 1.

Benzoic acid exhibited a strong IR absorption at 1695 cm^{-1} due to the stretching of the carbonyl component of the carboxylic acid group. Sodium benzoate showed two strong peaks at 1597 and 1430 cm^{-1} due to the respective asymmetric and symmetric stretching absorptions of the ionised carboxylate group. Sodium thioglycollate gave two strong peaks at 1585 and 1400 cm^{-1}, due to the asymmetric and symmetric stretching absorptions of the carboxylate group and thioglycollic acid exhibited a very strong absorption of 1720 cm^{-1}, due to the stretching of the carbonyl component of the carboxylic acid group.

Sodium benzoylthioglycollate showed two IR absorption bands at 1610 and 1400 cm^{-1}, due to the respective asymmetric and symmetric stretching of the ionised carboxylate group. A strong absorption also occurred at 1665 cm^{-1} due to the stretching of the carbonyl group in the thio-ester linkage, $-COS-$. Benzoylthioglycollic acid exhibited two strong absorption peaks at 1710 and 1665 cm^{-1}. The absorption band at 1665 cm^{-1} was again attributed to the stretching of the carbonyl group of the thio-ester linkage, whilst the absorption at 1710 cm^{-1} was attributed to the stretching of the carbonyl component of the carboxylic acid group.

The hydrolysis experiments at room temperature indicated that even under strongly alkaline conditions, the rate of hydrolysis was exceedingly slow, only 3% hydrolysis occurring after 24 h at pH 11. The extent of hydrolysis of sodium benzoylthioglycollate at 100°C was determined over the pH range 4–10.46 and a period of 0–4 h. The results are shown in Figs. 1 and 2. Unlike room temperature, significant hydrolysis occurred at the boil, especially under alkaline conditions. The amount of hydrolysis occurring also increased as the reaction times were prolonged.

The yields of *N*-benzylbenzamide formed during the model reactions between BTG and benzylamine were calculated and the results are represented graphically in Fig. 3. The yields of *N*-benzylbenzamide formed in the presence of nicotinic acid were also calculated and the results are shown in Fig. 4, together with the corresponding results obtained in the absence of nicotinic acid.

Model reactions of BTG with benzylamine indicated that, in general, higher yields of *N*-benzylbenzamide were produced as the pH at which the reaction was carried out increased. Higher yields of *N*-benzylbenzamide were also obtained by increasing the reaction temperature. By incorporating nicotinic acid in the reaction mixture, higher

Table 1
Carboxylate and carbonyl infrared absorption frequencies of sodium benzoate, sodium thioglycollate, sodium benzoylthioglycollate, benzoic acid, thioglycollic acid and benzoylthioglycollic acid

Sample	Absorption frequency (cm^{-1})	Functional group
Benzoic acid	1695	C=O of $-COOH$
Sodium benzoate	1597	$-COO^-$ group
Sodium thioglycollate	1585	$-COO^-$ group
	1400	$-COO^-$ group
Thioglycollic acid	1720	C=O of $-COOH$
Sodium benzoylthioglycollate	1665	C=O of $-COS-$
	1610	$-COO^-$ group
	1400	$-COO^-$ group
Benzoylthioglycollic acid	1710	C=O of $-COOH$
	1665	C=O of $-COS-$

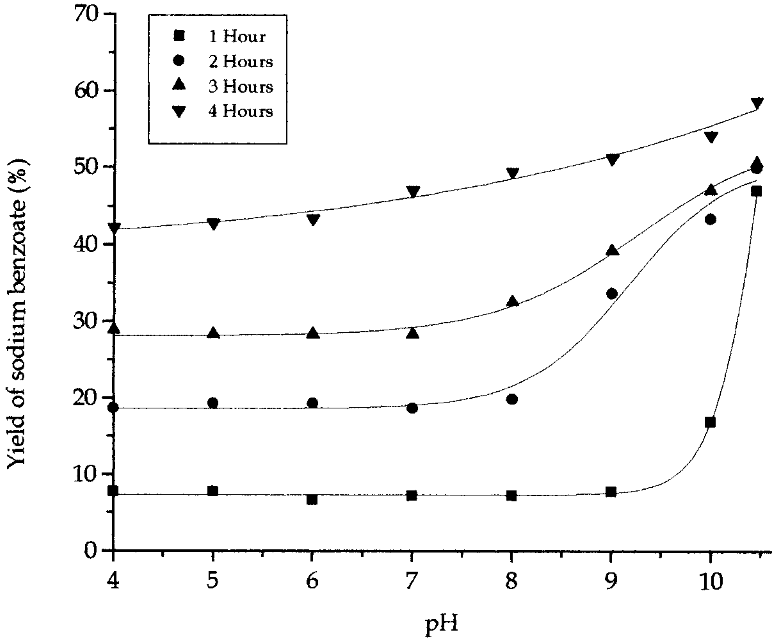


Fig. 1. The effect of pH on the hydrolysis of BTG at 100°C.

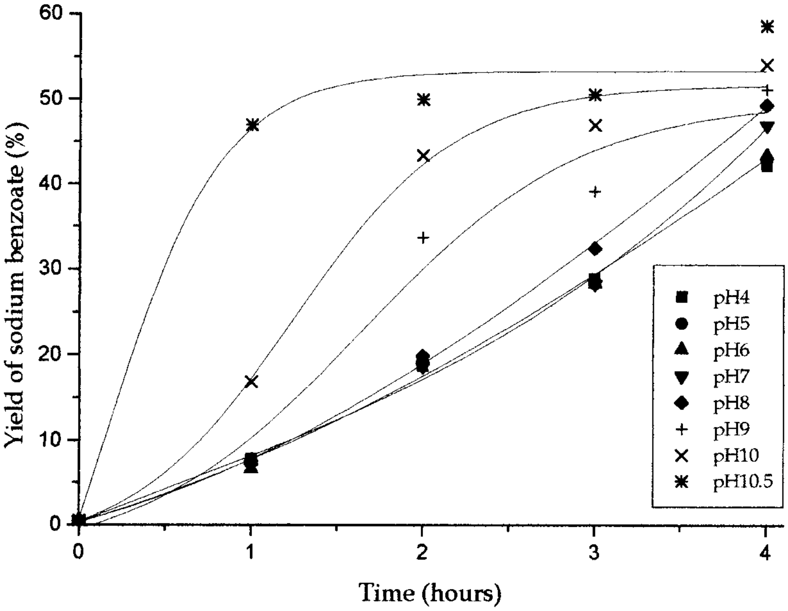


Fig. 2. The effect of time on the hydrolysis of BTG at 100°C.

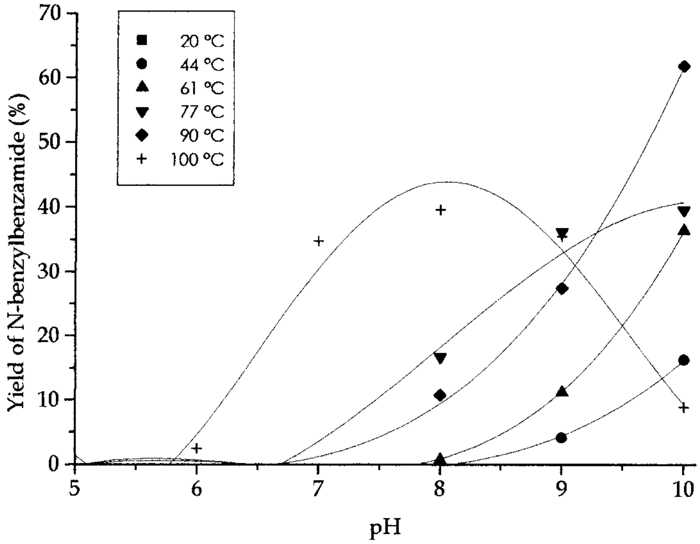


Fig. 3. The effect of pH on the reaction between BTG and benzylamine.

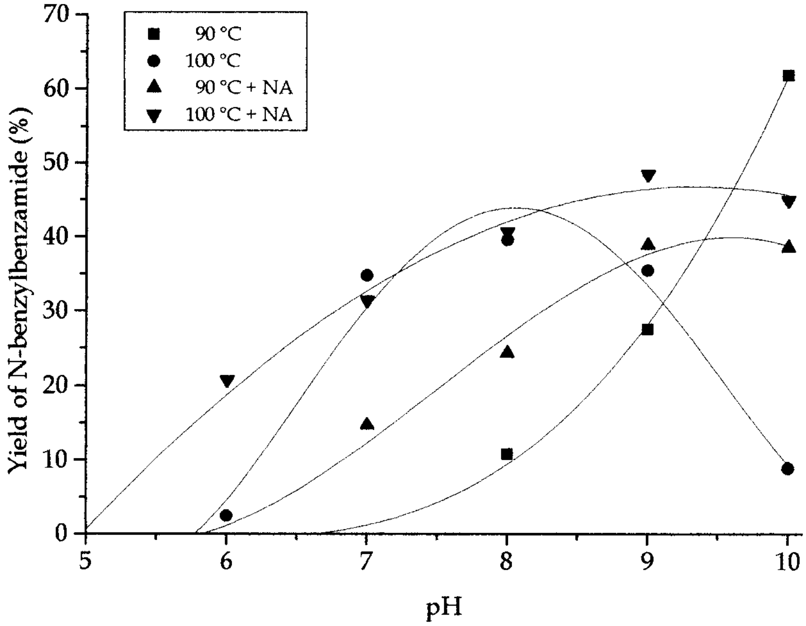
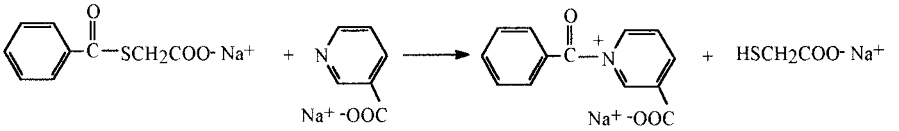


Fig. 4. The effect of pH on the reaction between BTG and benzylamine in the presence of nicotinic acid (NA).



Scheme 5. Proposed reaction of sodium benzoylthioglycollate with nicotinic acid.

yields of *N*-benzylbenzamide were obtained relative to the reaction in the absence of nicotinic acid.

The reaction Scheme 5 for the formation of the more reactive quaternary species is proposed.

The intermediate quaternary benzoyl pyridinium derivative would be expected to show increased reactivity towards nucleophiles.

4. Conclusions

The results obtained indicate that a water soluble benzoylating agent (BTG) which is relatively stable in aqueous media could be prepared. BTG can be qualitatively and quantitatively determined by HPLC, thus providing a convenient method to follow any hydrolysis reactions in solution.

Model reactions of BTG with benzylamine produced a secondary amide, indicating that BTG readily undergoes nucleophilic substitution reactions.

The application of BTG in cotton fabric modification will be discussed in a subsequent paper.

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