THE PRE-TREATMENT AND AFTER-TREATMENT OF LYOCELL: THE SYNTHESIS, APPLICATION AND EVALUATION OF NOVEL ACRYLAMIDO AGENTS

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ABSTRACT

Lyocell is made from wood pulp by an environmental friendly ' solvent spinning' process. Lyocell fibres posses several superior characteristics over other man-made cellulosic fibres, such as viscose and modal, including high dry and wet tenacity, good drapeability and lower shrinkage. Nevertheless, in wet processing, lyocell fibres are known to be prone to fibrillation, which poses problems for the appearance, surface properties and garment structure. Accordingly, this thesis explores the possibility of cross-linking lyocell with novel, commercially-viable agents, during either pre-treatment or after-treatment, in order to overcome this fibrillation propensity, while offering technical benefits over the currently used cross-linking agents.

One novel, colourless, water soluble, cross-linking agent, 2,4-diacrylamido-benzenesulphonic acid has been synthesized. Evaluation of this agent uncovered an unexpected instability of the cross-link with lyocell to high temperature polyester dyeing conditions. A subsequent investigation led to the identification of a neighbouring group participation mechanism. Consequently, it has been proposed that benzeneacrylamido cross-linking agents, designed to be hydrolytically stable to a range of high temperature polyester dyeing conditions, should be devoid of *ortho* sulpho or *ortho* carboxyl substituents.

To this end, a series of agents, based on readily available sulphonated aromatic amines and devoid of the *ortho* sulpho group, have been synthesized and the wet abrasion resistance (fibrillation protection) and dyeing properties of the cross-linked lyocell fibres evaluated. In addition, 2,4-diacrylamidobenzenesulphonic acid has been applied to woven lyocell fabric and evaluated as an alternative to conventional DMDHEU resins. This agent exhibits promising features as a potentially industrially-viable chemical, useful for both the pre-treatment and after-treatment of lyocell.

DECLARATION

I certify that no portion of this work has been submitted in support of an application for another degree or qualification of this or any other university, or other institution of learning.

Yan Su

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INTRODUCTION

Lyocell is a solvent-spun, regenerated cellulose fibre whose 'closed-loop' method of manufacture enables virtually complete recovery of the organic solvent. The resultant lyocell fibres are structurally different from conventional viscose and display superior dry and wet strength and lower shrinkage. Moreover, they are also noted for their bulkiness, drape and soft handle. Because of these desirable qualities, demand for lyocell is strong and its applications are expanding. However, lyocell does have one major technical defect compared to viscose and modal, i.e. it displays a distinct tendency to fibrillate in the swollen state under wet abrasion.

Accordingly, this project focuses on the synthesis, application and evaluation of novel acrylamido compounds in the pre-treatment and after-treatment of lyocell to overcome this fibrillation propensity.

In this research, a novel, colourless, water soluble, cross-linking agent, 2,4-diacrylamidobenzenesulphonic acid was synthesized and applied to lyocell. The cross-linked lyocell fibres exhibited good fibrillation resistance with stable lyocell-O-agent bonding to subsequent hot exhaust reactive dyeing conditions. However, the fibre-agent bonds showed some instability to polyester dyeing conditions. This was rationalised in terms of hydrolysis of the amide bond *ortho* to the sulphonic acid group *via* a neighbouring group participation mechanism (chapter 4). The feasibility of the above mechanism was further confirmed by examining a number of related benzeneacrylamido derivatives (chapter 5). Based on this understanding, new cross-linking agents, devoid of an *ortho* sulpho group, to ensure that the subsequent cross-linked fibre could be blended with polyester, were synthesized and evaluated (chapter 6). Moreover, lyocell treated with 2,4-diacrylamidobenzenesulphonic acid was subsequently dyed with a series of cellulose reactive dyes, and its dyeing performance was compared

to that of untreated lyocell (chapter 7). Furthermore, this agent with the potential of being commercially viable was applied to dyed woven lyocell fabric by both an exhaustion and a continuous process, and subsequently evaluated as an alternative finishing agent to the conventional DMDHEU resins for the after-treatment of lyocell. The assessment was carried out by six methods: Martindale abrasion test, dry crease resistance test, tensile strength test, repeated laundering test, scanning electron microscopy (SEM) test and handle test (chapter 8).

AIM OF PROJECT

The primary aim of this project was to identify novel acrylamido compounds for the pre-treatment of lyocell to overcome its fibrillation propensity, to evaluate the technical properties of the correspondingly treated lyocell, and determine whether such a compound could replace commercial DMDHEU resins for the after-treatment of lyocell.

The specific objectives are:

- To synthesise the novel cross-linking agent, 2,4-diacrylamidobenzene-sulphonic acid, and apply it to lyocell fibres/fabrics;
- To investigate the cause for the loss of fibrillation protection of the afore-mentioned lyocell under high temperature (HT) polyester dyeing conditions;
- To further the understanding of the neighbouring group participation mechanism as the cause for losing fibrillation protection under HT conditions;
- To design and synthesise novel, commercially-viable cross-linking agents for the pre-treatment of lyocell;
- To apply the said agents to lyocell using conventional dyehouse processes;
- To investigate the effect of said agents on the protection of lyocell against fibrillation;
- To examine the dyeing properties of the treated lyocell with cellulose reactive dyes;
- To evaluate the novel cross-linking agent 2,4-diacrylamidobenzene-sulphonic acid as an alternative to Fixapret CP and Fixapret ECO (DMDHEU resins) for the after-treatment of lyocell, in order to convey fibrillation protection and crease-recovery properties.

CHAPTER 1

INTRODUCTION

1.1 Cellulose

Cellulose is the most abundant of all naturally occurring organic polymers, billions of tonnes being produced by photosynthesis annually throughout the world [1]. It was first recognised in 1838 as the common structural material of many of the higher land plants by Payen, who invented the name cellulose [2].

The chemical structure of cellulose may be conveniently described as a condensation polymer of ß-D-glucopyranose with 1,4- glycosidic linkages [3]. The repeating units of cellulose are called cellobiose units, each of which consists of two glucose units, shown in Figure 1.1.

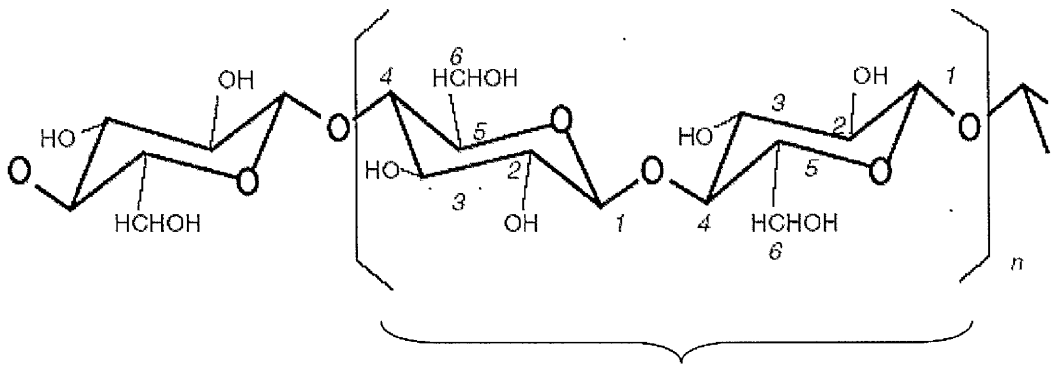


Figure 1.1 Structure of cellulose

Cellulose is insoluble in water and in most organic solvents. It is also susceptible to hydrolysis by hot dilute solutions of mineral acids. Like all alcohols, it is sensitive to oxidation by molecular oxygen under alkaline

conditions. In the absence of oxygen, cellulose exhibits excellent stability towards alkaline solutions. The most important groups in this natural polymer are the hydroxyl groups. These groups allow hydrogen bonding to occur between polymer chains. Van der Waals forces are also present in the chains but they are overshadowed by hydrogen bonding effects [2].

1.2 Regenerated cellulosic fibre

Wood is the most abundant source of cellulose. Continuous filaments of cellulose can be regenerated from specially purified wood pulp after dissolving them in a suitable solvent. Though the main raw material of regenerated cellulosic fibre is wood pulp, in the past cotton linters have also been used for the manufacture of regenerated cellulosic fibre.

1.2.1 Cuprammonium

Cuprammonium rayon (cupro) was produced from a solution of cellulosic materials in cuprammonium hydroxide at a low temperature in a nitrogen atmosphere, followed by extruding through a spinneret into a sulfuric acid solution to decompose the cuprammonium complex of cellulose. This is an expensive process with the environmental problem of copper in the waste stream [4,5].

1.2.2 Viscose

The viscose process [6] was discovered by Cross and Bevan in 1892, but it

was not until 1910 that appreciable quantities of regular viscose were produced. The dissolved pulp, used for the production of viscose, is either cotton linters or specially purified wood pulp. The first stage of the manufacture of viscose is the production of alkali cellulose, during which pulp is saturated with sodium hydroxide solution for an hour, pressed to remove excess solution and then the treated cellulose is cut up in a shredder to form powdery fragments. The powdery fragments are left for a day so that cellulose can react with caustic soda to form alkali cellulose. Afterwards, alkali cellulose is mixed with carbon disulphide (CS_2) to form sodium cellulose xanthate solution (Figure 1.2). This viscous cellulose solution can be coagulated in an ammonium sulphate bath and then converted back to pure white cellulose using dilute sulphuric acid [7].

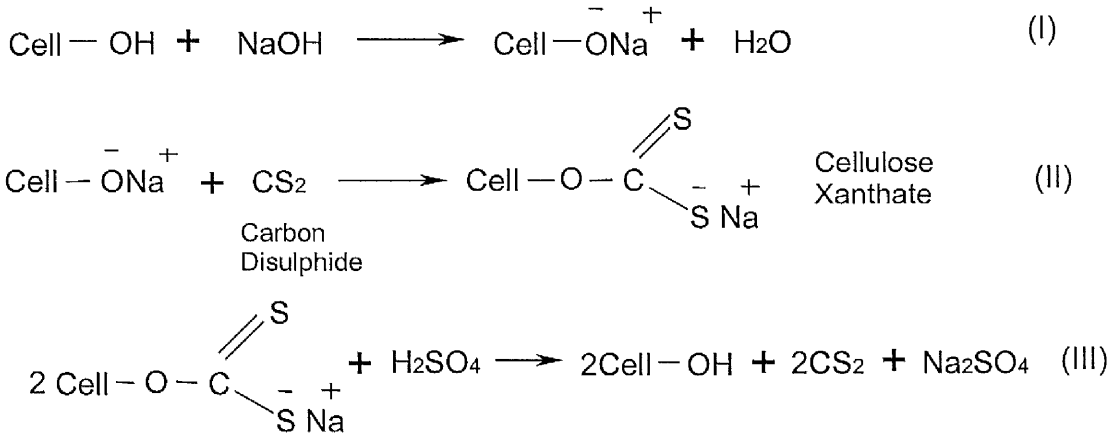


Figure 1.2 Viscose production process

The polynosic process developed by Tachikawa includes several modifications of the viscose process. The cellulose is xanthated to a high

degree with excess of CS_2 and the xanthate is dissolved in a diluted NaOH. The solution is then spun in a "cold, low-acid, low- salt, zinc-free spinbath" and stretched to produce polynosic fibres. The fibre has a fibrillar structure, high dry and high wet strength, a low elongation rate, a relatively low water retention and a very high wet modulus [8]

1.2.3 Regeneration from amine oxide solution: Lyocell

It is well known that the viscose process is environmentally hazardous. Accordingly, solvent spinning of cellulose from an amine oxide solution as an alternative to the viscose process has been a most important development in the production of regenerated cellulosic fibres.

Lyocell is a solvent spun regenerated cellulosic fibre whose "closed-loop" method of manufacture enables almost complete recovery of the organic solvent [9,10]. The raw material for lyocell is wood, the most abundant resource of cellulose in nature and the organic solvent used for dissolving the wood-pulp is N-methyl-morpholine-N-oxide (NMMO) (Figure 1.3). The solvent itself is non-toxic and all the effluent produced is non-hazardous [11, 12].

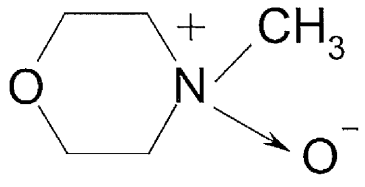


Figure 1.3 Chemical structure of NMMO

1.3 Dyes for cellulose

Several classes of dye can be used to dye cellulose, namely direct, vat, sulphur, azoic and reactive colourants [13]. The dyes fall into two major groups: non-ionic and anionic. Direct and reactive dyes are anionic, whilst vat, sulphur and azoic dyes are non-ionic in nature.

1.3.1 Direct dyes

The discovery by Böttiger of the dye, Congo Red, in 1884 was a landmark because this was the first dye to be used for colouring cellulose by a simple one-bath operation (i.e. directly) in the absence of a mordant; hence the term 'direct dye' [14]. Direct dyes are water-soluble with good substantivity for cellulosic fibres. Approximately 50% of all direct dyes are disazo structures, a typical example being the symmetrical dianisidine derivative, C.I. Direct Blue 1 (Figure 1.4).

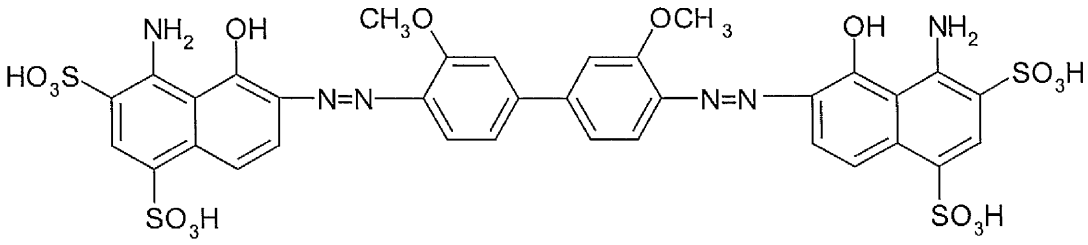


Figure 1.4 C.I. Direct Blue 1

There are basically three sub-divisions of direct dyes, with respect to their method of application: (a) those that migrate and level well, even in the presence of excess electrolyte, (b) those that level poorly, but whose

exhaustion may be controlled by careful addition of electrolyte, and (c) those that have poor levelling properties, but are satisfactorily exhausted by slowly increasing the dyebath temperature to the boil without addition of an electrolyte [15].

1.3.2 Vat dyes

Vat dyes are water-insoluble compounds that contain anthraquinone or indigoid type ring structures. Carbonyl groups in these structures are reduced to their soluble or leuco form in the dyebath with sodium hydroxide and sodium dithionite ($Na_2S_2O_4$), then insolubilized in the fibre by oxidation with air or with various oxidizing agents [16]. This reduction and oxidation scheme for vat dyes is shown in Figure 1.5.

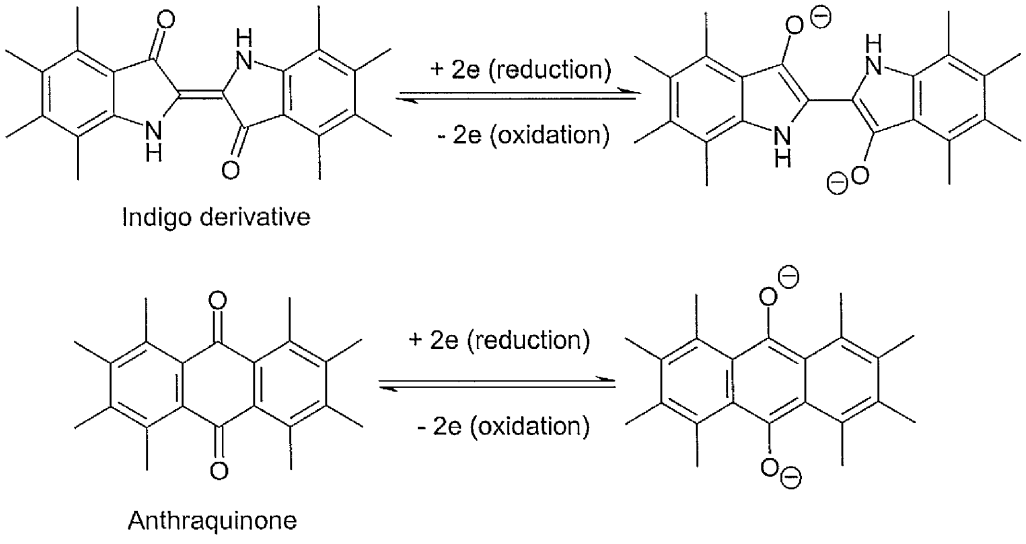


Figure 1.5 Reduction and oxidation scheme for vat dye

Immobilization in the fibre is completed by a boiling treatment which serves to aggregate the dyestuff molecules. This aggregation process is responsible for imparting the characteristic shade and fastness profile to the vat dyestuff [17].

1.3.3 Sulphur dyes

Sulphur dyes are made from organic compounds containing nitro and amino groups by reactions with sulphur or sodium sulphide at high temperature [18].

They are water-insoluble after application to cellulosic fibres. The application of sulphur dyes uses the same principles as those used for vat dyes. Reduction of the disulphide linkage in the molecule by the reducing agent gives the water soluble and cellulose-substantive leuco form. The two most important reducing agents for sulphur dyes are sodium sulphide (Na_2S) and sodium hydrosulphide (NaHS). After penetrating into the fibre in the soluble form, they are converted to their original insoluble forms by oxidation [19, 20]. This reduction and oxidation scheme for sulphur dyes is shown in Figure 1.6.

$$\underset{\text{Sulphur dye}}{Dye-S-S-Dye} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \underset{\text{Leuco form}}{Dye-S^{-} + {}^{-}S-Dye}$$

Figure 1.6 Reduction and oxidation scheme for sulphur dyes

1.3.4 Azoic dyes

Insoluble azoic dyes are synthesized inside cellulosic fibres as a result of a stoichiometric chemical reaction between a diazonium salt and a coupling component. After easy penetration of a coupler and a diazonium salt into the pores of cellulosic fibres, a dye is formed which is trapped in the fibre [21]. The most common type of diazotisation and coupling reactions used for azoic dye production are shown in Figure 1.7.

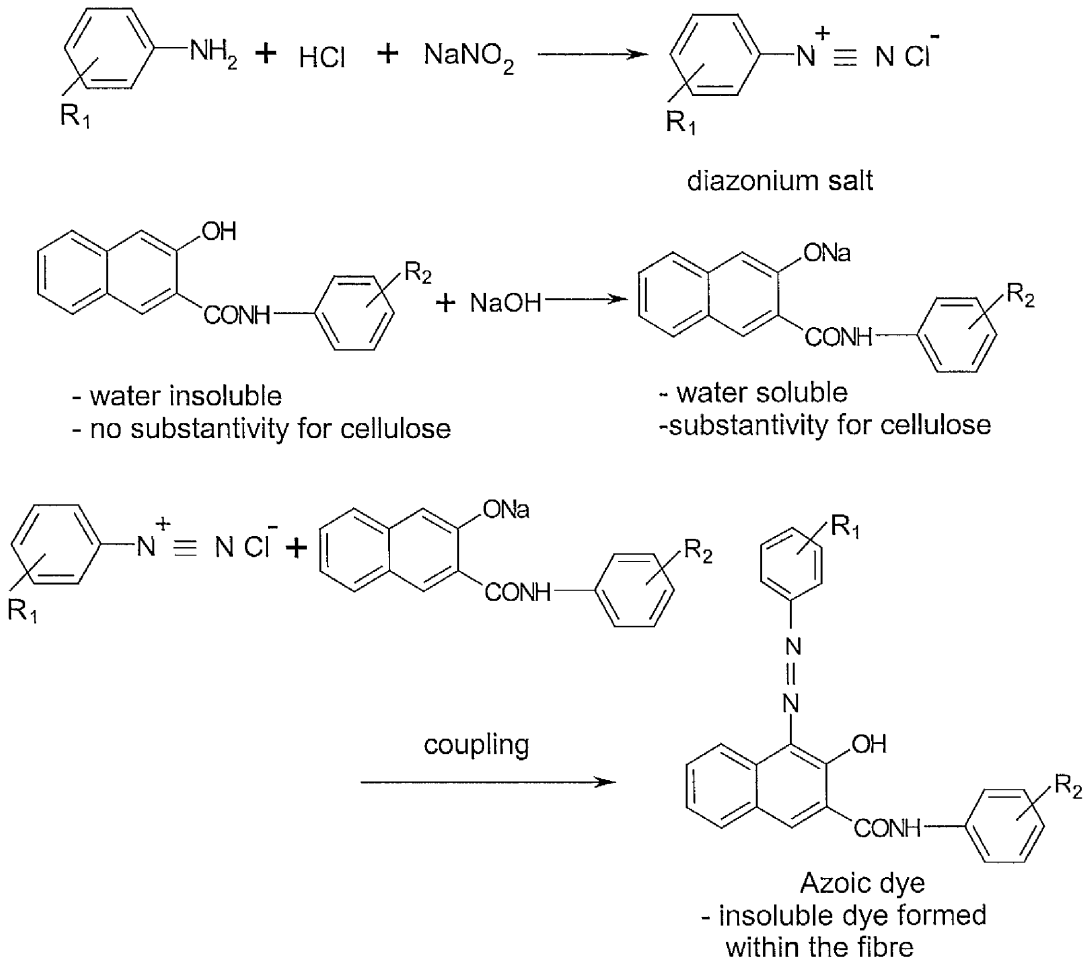
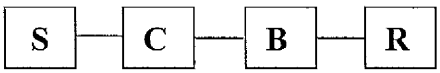


Figure 1.7 Diazotisation and coupling reaction for azoic dye formation

Textiles dyed with azoics have good fastness to washing, light and bleaching. They are particularly well represented in the orange, red, bordeaux and dark blue shade areas [22, 23]. However, their application is difficult and many diazo components are environmental unfriendly.

1.3.5 Reactive dyes

Reactive dyes are water-soluble compounds which react with hydroxyl groups of cellulose to become covalently bonded to the cellulosic fibre [24]. In general, reactive dyes for cellulose have certain characteristic structural features. Each of these features can influence the dyeing and fastness properties [25].



S is one or more solubilising sulphonic acid groups.

C is the chromogen, contributing the colour and much of the substantivity for cellulose.

B is the bridging group, linking the reactive system with the chromophore.

R is the reactive group, enabling the dye to form a covalent bond with cellulose.

In some cases the reactive group is attached directly, i.e. without a bridge, to the chromogenic system. Due to the incorporation of one or more negatively charged solubilising groups, there is an electrostatic repulsion between negatively charged dye and negatively charged cellulose. Thus, a

large amount of salt (sodium chloride or sodium sulphate) is added to the dyebath to increase dye exhaustion onto the cellulose. Alkali, such as sodium carbonate, is added to produce cellulosate anions which react with the dye [26].

There is, however, always the certainty that the dye reacts with water in the dye bath instead of with cellulose. But reactive dyeing is possible as several factors favour the reaction between the reactive dye and the cellulose. Because the pK_a of the cellulose is lower than that of water, ionization of cellulose occurs preferentially [27]. Also, because the dye is physically adsorbed onto cellulose, and the cellulosate anion is a much better nucleophile than hydroxide, the rate of reaction between the dye and cellulose is much greater than that between the dye and water [27, 28].

The nature of the reactive group in the dye molecule determines the level of its reactivity. The reactive group must exhibit adequate reactivity towards cellulose but lower reactivity towards water, since hydrolysis in water can inactivate the reactive group. Reactive groups are electrophilic in nature and can be classified into two main types [29]:

1) those reacting by nucleophilic substitution (Figure 1.8)

2) those reacting by nucleophilic addition to a carbon-carbon double bond (Figure 1.9)

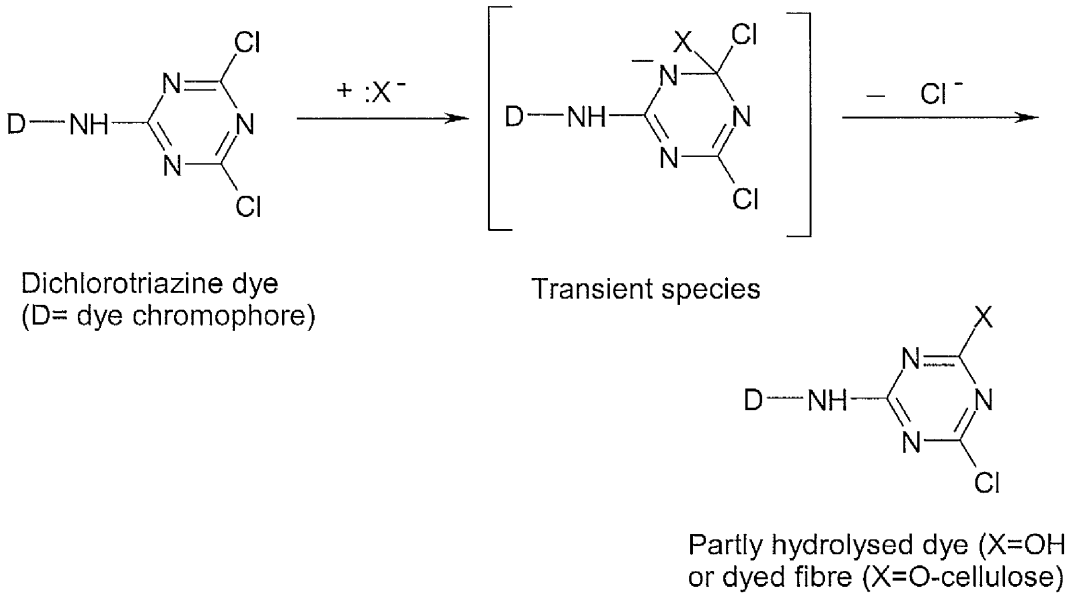


Figure 1.8 Nucleophilic substitution

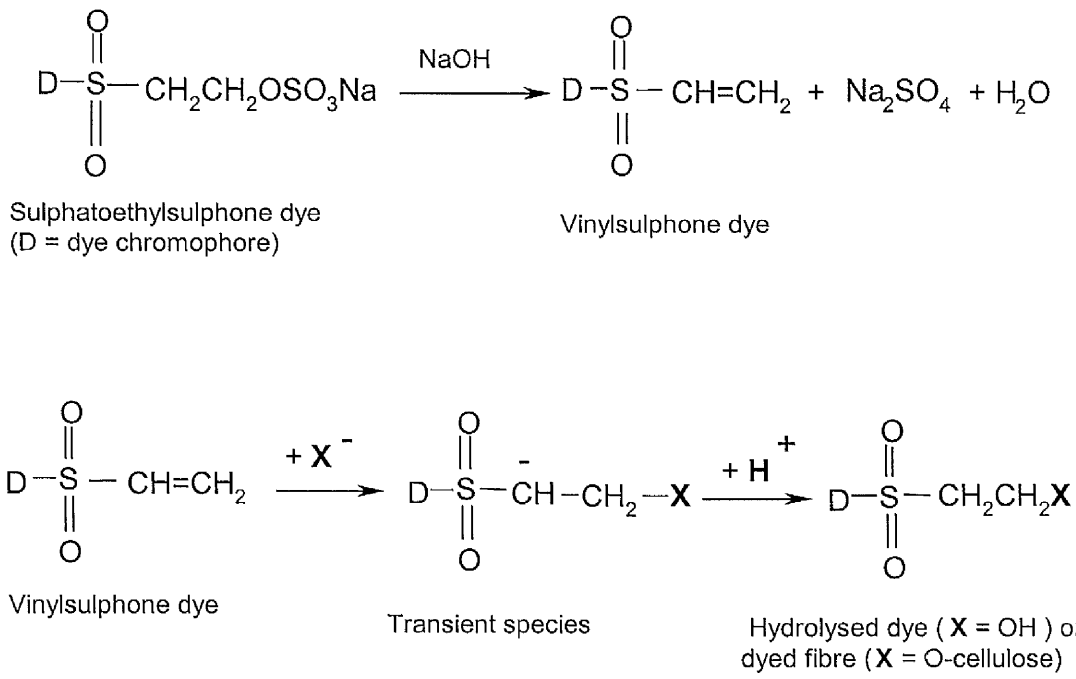


Figure 1.9 Nucleophilic addition

1.3.6 Technical properties of cellulosic dyes

A comparative assessment of the general performance of the different cellulosic dye classes is shown in Table 1.1 [30]

Table1.1

Advantages and disadvantages of the different dye classes used on cellulose

Dye Class	Advantages	Disadvantages
Direct	➢ Cheap and easy to apply ➢ Wide range of shades available	➢ Poor wet fastness properties even when after-treated
Reactive	➢ Economical and easy to apply ➢ Full shade gamut available ➢ High wet fastness profile	➢ Modest fastness to light and chlorine-containing agents
Vat	➢ High light, wet and bleach Fastness	➢ Limited shade range (mainly dull) ➢ Expensive
Sulphur	➢ Very economical when used to dye heavy dull shade, notably navy and black ➢ High conventional wet fastness Levels	➢ Limited shade (dull) range ➢ Environmental drawbacks ➢ Sensitive to oxidative bleach-containing detergents
Azoic	➢ Very economical in heavy shades ➢ High light and conventional wet Fastness	➢ Difficult to apply ➢ Environmental drawbacks ➢ Poor fastness to oxidative bleaching agents

1.4 Lyocell

A brief history of the development of lyocell is outlined below:

1. "Lyocell" is the generic name and the first commercially available solvent-spun cellulose fibre [31].
2. "Tencel" is the first commercialised lyocell (staple) fiber by Courtaulds [32].
3. Courtaulds constructed its semi-commercialised plant in the UK in 1988, and went into full production via its commercial plant in the USA in 1992 [32].
4. Lenzing took a licence on the basic patents in 1988, and since 1990 ran a pilot plant, before going into commercial production in 1998. Its staple fibre was termed "Lyocell" [33].
5. Courtaulds and Akzo Nobel announced a feasibility study of lyocell filament yarn which was completed in 1996. The filament yarn was termed "NewCell" [34].
6. Lenzing acquired Tencel Ltd from Courtaulds in 2004. "Tencel" is now used as the brand name for all Lenzing's lyocell fibres.

1.4.1 Lyocell fibre manufacturing

1.4.1.1 Preparing the wood pulp

The hardwood trees grown for lyocell are first cut to 20 ft (6.1m) lengths and debarked by high-pressure jets of water. Next, the logs are fed into a

chipper, a machine that chops them into squares slightly bigger than postage stamps. Mill workers load the chips into a vat of chemical digesters that soften them into a wet pulp. This pulp is washed with water, and may be bleached. Then, it is dried into a huge sheet which is rolled onto spools. The sheet of cellulose has the consistency of thick poster board paper. The roll of cellulose is enormous, weighing some 500 lb (227 kg) [35, 36].

1.4.1.2 Dissolving the cellulose

At the lyocell mill, several spools of cellulose are unrolled and broken into one inch squares. These squares are then loaded into a heated, pressurized vessel filled with amine oxide [36, 37].

1.4.1.3 Filtering

After a short time soaking in the solvent, the cellulose dissolves into a clear solution. It is pumped out through a filter, to insure that all the chips are dissolved [37].

1.4.1.4 Spinning

The solution is pumped through spinnerets. These are devices used with a variety of man-made fibers. Something like a showerhead, the spinneret is pierced with small holes, and when the cellulose is forced through it, long strands of fiber come out. The fibers are then immersed in another solution of amine oxide, diluted this time. This sets the fiber strands. Then, they are washed with de-mineralized water [38].

1.4.1.5 Treatment

After washing the fibre is treated in a number of ways [39]:

- The fibre could be bleached if required.
- Soft finish is always applied to make processing easier.
- An antistat is applied.
- Other treatments to give specific fibre properties can also be performed.

1.4.1.6 Drying and finishing

The lyocell fiber is next sent to a drying area, where water is evaporated from it. The strands at this point are passed to a finishing area, where lubricants are applied. This may be soap or silicone or other agent, depending on the future use of the fiber. This step is basically a detangler, making the future steps of carding and spinning into yarn easier.

1.4.1.7 Final steps

The dried, finished fibers are at this stage in a form called tow. Tow is a large untwisted bundle of continuous length filaments. The bundles of tow are taken to a crimper, a machine which compresses the fiber, giving it texture and bulk. The crimped fiber is carded by mechanical carders, which perform an action like combing, to separate and order the strands. The carded strands are cut and baled for shipment to a fabric mill. The entire manufacturing process, from unrolling the raw cellulose to baling the fiber, takes only about two hours. After this, the lyocell may be processed in a wide assortment of ways. It may be spun with another fiber, such as cotton

or wool. The yarn can be woven or knit like any other fabric, and given a variety of finishes, from soft and suede-like to silky [38].

1.4.1.8 Recovery of the solvent

The amine oxide used to dissolve the cellulose and set the fiber after spinning is recovered and re-used in the manufacturing process. The dilute solution is evaporated, removing the water, and the amine oxide is routed for re-use in the pressurized vessel. Ninety-nine percent of the amine oxide is recoverable in the typical lyocell manufacturing process [38-39].

1.4.2 Dyeing and finishing

The dyeing and finishing of lyocell fabrics is the key to their success. There are three characteristics of the fibres that can be manipulated to give fabrics with attractive and differentiated aesthetics – the ease of fibrillation, the high modulus and the wet swelling characteristics [40]. Fibrillation can yield the characteristic 'peach skin' surface touch of fabrics made from this fibre, but unwanted and uncontrolled fibrillation can also impair the fabric quality. Much of the dyeing and finishing development has been focused on this aspect.

Lyocell fibres can be dyed using the dye classes suitable for all other cellulose fibres. Direct, reactive and vat dyes are the principal classes of dyes used on lyocell. The application methods, technical properties and relative costs of the different dye classes are important parameters, which determine the choice of a particular dye to satisfy particular

techno-commercial requirements [40, 41].

A non-fibrillated aesthetic can be achieved either by avoiding fibrillation or removing it, once it has formed.The simplest way is to avoid the fibrillation forming and this can be done by dyeing without mechanical stress, such as by dyeing in open width by cold pad batch or fully continuous, by jig or beam dyeing or even dyeing in the yarn form on package or beam, i.e. anything that avoids a "rubbing" action on the fabric surface [35].

When a lyocell fibric is first subjected to water and mechanical action, the loose fibres on the fabric surface fibrillate and form easily seen pills. This is called primary fibrillation and is aesthetically unacceptable. Primary fibrillation is usually removed by enzymes, so that a clean surface is generated. Secondary fibrillation occurs in further wet processing, and since there are no longer any hairs, no pilling occurs, but only fibrillation at the high points of the fabric. A frosted appearance is given by softening and tumbling, which allows the surface fibrillation to lift.

Resins which can cross-link with the fabric are often used after dyeing. This embrittles the fibrils and enables any fibrillation that has occurred during the dyeing process to be easily removed. This process is particularly suited to woven fabrics which are usually prepared and dyed open width and so are free of fibrillation before dyeing. However, this will not normally be necessary for those fabrics designed to have a peach-skin finish.

1.4.3 Properties of lyocell

1.4.3.1 Physical properties

Lyocell fibres are structurally different from conventional viscose and display superior dry, wet and loop strength and low shrinkage [42] compared to the latter fibre. This marked improvement in the mechanical properties of lyocell [43, 44] compared to viscose, is a direct consequence of the solvent spinning technique used [45] in the lyocell process which results in longer crystallites, and shorter and better orientated amorphous regions [43]. Moreover, lyocell is also noted for its bulkiness, ability to drape and softness to handle. Table 1.2 summarizes some of the main technical properties of lyocell compared to other types of fibre [46, 47].

Table 1.2

Physical properties of lyocell compared with other fibres

	Lyocell	Viscose	Modal	Cotton	Polyester
Linear Density (dtex)	1.7	1.7	1.7	--	1.7
Dry tenacity (cN/tex)	40-42	20-24	34-36	20-24	50-55
Dry elongation (%)	13-15	20-25	13-15	7-9	25-30
Wet tenacity (cN/tex)	34-38	10-15	19-21	26-30	50-55
Wet elongation (%)	16-18	25-30	13-15	12-14	25-30
Water inhibition (%)	65-70	90-100	75-80	45-55	--

The dry tensile strength of lyocell is greater than that of any other man-made cellulosic staple fibre, approaching that of polyester. When lyocell fibre is wet, just after manufacture, it is swollen. Drying the fibre enables hydrogen bonding to occur, which allows the fibre to absorb less moisture when it is subsequently rewetted. The hydrogen bonds at the fibril surface, in the edges of the cellulose domains, may be less ordered, which gives water a gateway into the fibrils, but there will always be a region within the crystalline core of the fibril where water cannot reach. This is the only man-made cellulosic fibre that is stronger than cotton when wet, retaining 85% of its dry strength in wet state.

Lyocell also has a high modulus that leads to low shrinkage in water, enabling fabrics and garments to demonstrate good stability when they are washed [48]. Water absorption is measured via the imbibed water fraction and it is affected by the crystallinity. The higher the imbibed water fraction the more water it absorbs and the less crystalline is the fibre. Lyocell has an imbibed water fraction close to cotton's, whereas that of viscose is relatively high.

The conversion of fibre strength to yarn strength for lyocell is considerably higher than for most other fibre types. The smooth and straight character of the fibre and its round cross-section enables the fibres to be very closely packed in the yarn structure and the resulting high cohesion between parallel fibres adds to the strength of the yarn [46, 49].

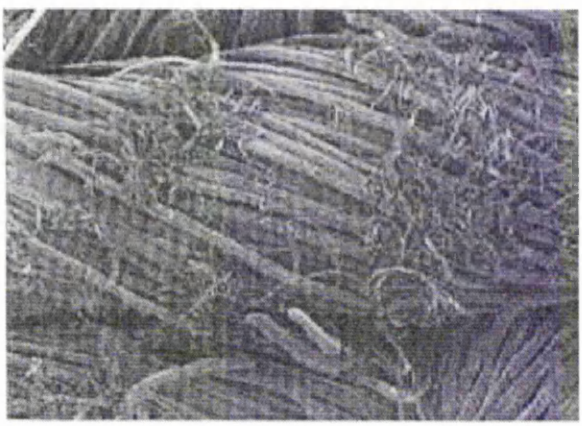
Yarn and fabric characteristics, in terms of performance and aesthetics, can be improved by blending lyocell fibre with other fibres. For example, at all blend levels, the stress-strain characteristics of lyocell supply strength to cotton-blend yarns, while the resulting fabrics benefit from increased softness. Long-staple lyocell can be blended with wool etc. to increase strength, as well as to produce finer yarns. Additionally, the fibrillation characteristics of lyocell increase the aesthetic possibilities of the blended fabric significantly [50].

1.4.3.2 Fibrillation

Fibrillation [47] is the abrading of small fibrillar hairs from the fibre surface of wet swollen lyocell, when the fibre is subjected to any kind of mechanical stress. The fibrils split lengthwise along the fibre axis and this change is brought about by an expansion of the less ordered interfibrillar zones, or voids, on swelling, and a reduction in the cohesive forces between the fibrils [44-47]. The shape of the voids is important. Lyocell is characterised by anisotropic, elongated voids which are absent in normal viscose and modal [45-47].

The samples in Figure 1.10 show an example of a non-fibrillated (a) and a highly fibrillated (b) lyocell fabric. The fibrils formed can be so fine that they become virtually transparent and give a frosty appearance to the fabric [9].

Non-fibrillated lyocell (a)



Highly fibrillated lyocell (b)

Figure 1.10 Non-fibrillated lyocell (a) and highly fibrillated lyocell (b)

Fibrillation is an ambivalent factor in lyocell finishing. It can have either a positive or a negative effect on the fabric appearance. On one hand, controlled fibrillation gives the fabric its characteristic soft "peach skin" touch. On the other hand, unwanted and uncontrolled fibrillation impairs the fabric quality, leading to local greying, a change of handle during laundry, and affects subsequent dyeing and finishing [51, 52].

1.4.3.3 Chemical properties

Lyocell degrades when in contact with hot diluted or concentrated mineral

acids. Alkalis cause swelling at first, reaching a maximum at 9% NaOH solution at 25°C, for example, and then the fibre ultimately disintegrates. Most common organic solvents and dry cleaning agents do not affect the fibres and they can be bleached with peroxide or hypochlorite. In addition, a full range of shades can be achieved using typical dyes used for cellulose, such as direct, reactive and sulphur. Lyocell fibres do not melt and are stable below 150°C, but above 170°C they begin to lose strength gradually. By 300°C decomposition becomes rapid and at 420 °C the fibres will ignite [53].

Lyocell biodegrades easily, producing only carbon dioxide and water, the constituents of plant life, from which it was originally made, and which can become food for microorganisms. Lyocell possesses extremely good dyeing characteristics [54]. The yield of reactive dyes on lyocell by all relevant dyeing methods is very good, particularly when they are applied by printing, where causticisation or mercerisation is no longer necessary to improve dye yields, as with conventional viscose or cotton. The dye yields of reactive dyes, such as Procion P (DyStar) used, on printed lyocell regular viscose and cotton were spectro-photometrically determined and quantified by Taylor and Mears [46]. All the fabrics were prepared using open-width bleaching and no caustic treatment was used (Table 1.3) [46, 55].

Table 1.3

Relative yields of reactive dyes in printing

Fibre	Colour yields		
	Navy	Red	Brown
Lyocell	198	189	199
Viscose	152	155	159
Cotton	100	100	100

The garment dye and wash process is ideal for the development of the soft, luxurious drape and hand characteristics of lyocell. However, not withstanding the advantageous properties mentioned above, there are also problems that arise with fabrics based on lyocell. One of the most striking disadvantages of lyocell fabrics is the fact that they do have poor abrasion resistance. Also, many companies are experiencing difficulties with the dyeing of lyocell. The lab-dyed samples produced are not representative of the bulk production due to the fibrillation behaviour of lyocell. Since smaller machines are used for processing in the labs, which tumbles the samples within the dye liquor, the areas of the sample that are in contact with the side of the machine fibrillate more than the rest of the fabric.

Variation in fibrillation appears as inconsistency in colour depth, which is also a problem in the bulk production. It is almost impossible to fibrillate different batches to exactly the same degree. However, lyocell production is an environmental friendly process, which gives it an advantage over

viscose. However, the process costs more, which makes the lyocell fibre relatively more expensive.

1.4.4 End uses

Lyocell was initially marketed as and can generally be found in high end designer apparel. Production costs are greater for lyocell than for cotton, making lyocell more expensive in finished garments. However, as production increases and costs decrease, it is expected that more lyocell will be used in moderately priced apparel. Currently, 90% of lyocell is used in women's wear. Its uses range from casual denim applications to tailored suits. A small percentage of lyocell is found in casual men's wear such as golf shirts. Other uses of lyocell products include industrial textiles, special types of papers and non-wovens, e.g. artificial leathers, filters, hygiene products, and medical wipes. Industrial uses include protective suits in the work-wear industry, coated fabrics, military fabrics, oil filters and ropes. Two cigarette manufacturers are now using lyocell to make ultra-low tar cigarettes. Lyocell can also be found in upholstery fabrics and window treatments [56,57].

1.4.5 Environmental benefits of lyocell

Lyocell is a 100% cellulosic fibre. Its raw material is wood from sustainable, managed forests. The fibre is fully biodegradable. On the contrary, synthetic fibres like polyester are produced from petroleum which is not renewable,

and the end product is generally not biodegradable, thus causing environmental problems [54, 58].

The production process of lyocell is environmental friendly. It is a modern closed loop solvent spinning process. The key feature is that the non-toxic solvent is almost completely recycled (>99%) [59]. This protects the environment and also saves water and energy. Such an environmental friendly production process is particularly a great advantage over viscose, of which the xanthation process results in serious pollution of the environment [59-62].

Lyocell also achieves far better ecological results than cotton. Good fibre yields from cotton require intensive irrigation, which constitutes an ecological and economic problem in many parts of the world. Moreover, the amounts of chemicals needed for the production of cotton are considerable: the cultivation of cotton demands significant amounts of toxic substances, such as pesticides, herbicides, insecticides and fertilizers. By comparison, only half the amount of chemical substances is required to manufacture lyocell, while the substances used represent less of an ecological hazard [63, 64].

CHAPTER 2

LITERATURE REVIEW

2.1 Fibrillation of lyocell

Lyocell has a tendency to fibrillate, especially under mechanical stress in the wet state. Fibrillation can be defined as the longitudinal splitting of a single fibre filament into microfibres of typically less than 1 to 4 microns in diameter (Figure 2.1). The splitting occurs as a result of wet abrasion against fabric or metal [47].

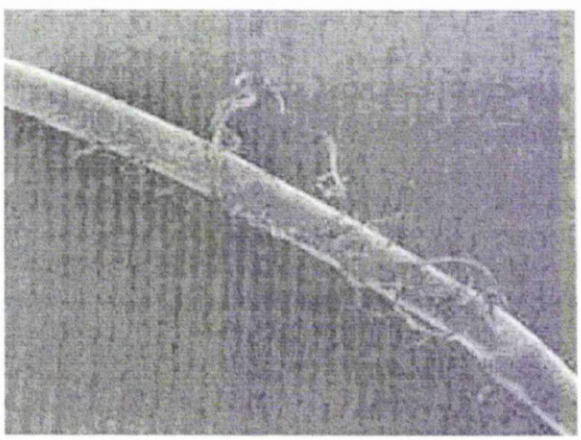


Figure 2.1 Fibrillation of lyocell fibre

Fibrillation has a positive side. If properly controlled during wet processing, deliberate (secondary) fibrillation can furnish fabrics with unusual sensory character, e.g. the production of microfibres on a lyocell fabric surface gives rise to the so-called "peach-skin" effect [65].

While fibrillation can be a useful property, for many outlets it poses problems in the appearance, surface properties and garment structure, and restricts wider use of lyocell. In particular, fabric dyed in dark hues, to medium / heavy depths, can develop a "frosty" appearance caused by

fibrils, so fine as to be virtually transparent, becoming detached from the fibre surface [65-67].

Consequently, it has been a major area of research to investigate the causes and effects of fibrillation and thereby prevent or minimise the fibrillation propensity of lyocell.

2.2 The cause of fibrillation

Lyocell is a cellulose regenerated fibre, with a complex structure consisting in microfibrils, highly oriented along the length of the fibre axis [68-70]. The fibrils split lengthwise along the fibre axis and this change is brought about by an expansion of the less ordered interfibrillar zones, or voids, on swelling, and a reduction in the cohesive forces between the fibrils [71, 72]. The properties of lyocell are defined at the stretching stage and during precipitation: in the crystalline area of the fibre very long crystallites form, which are very highly oriented in the longitudinal axis of the fibre but which have a low clustering rate. At the same time these fibres have, by comparison, a high amorphous orientation. A longitudinally stretched hollow system results with a relatively large pore volume compared to cotton [73, 74].

Processing of the fabric in rope dyeing equipment (jets, winches), where the fabric rubs against itself and metal, can lead to fibrillation. A number of factors will accelerate fibrillation, such as high pH, high temperature, lack of lubrication, high machine loadings and vigorous machine action [75, 40].

2.3 Positive use of lyocell fibrillation

2.3.1 Lyocell fabrics with peach-skin aesthetic

Lyocell's ability to fibrillate can be manipulated to give a variety of surface finishes and optical effects such as 'peach skin'. Used for high fashion apparel, the peach skin effect is obtained by a three-stage process: primary fibrillation, enzyme clean and secondary fibrillation [76, 77].

The most common method to achieve the peach-skin effect is using batchwise piece processing. Lyocell fabrics, in open width form, are pre-treated in 10 to 12% caustic soda. In caustic soda, lyocell swells very significantly in diameter but very little in length, thus its bulk and flexibility are significantly enhanced, and its wet stiffness is much reduced. Furthermore, the caustic treatment gives more rapid fibrillation removal in processing and a reduced tendency to fibrillation in domestic use [78]. During the mechanical action in the wet state in preparation and dyeing the surface hairs receive the majority of the abrasive action, therefore fibrillation will occur predominantly on these surface fibres. The fibrils formed are relatively long and are able to become entangled. Caustic treatment enables the surface fibres to be fibrillated to their maximum extent and therefore facilitates complete hair removal [79].

A cellulase enzyme is used to clean the fibrillated hairs from the surface of the fabric, with minimal effect on the bulk of the fabric. The hydrolytic fibre degradation involved in this process results in a loss of weight, typically 4%, and is accompanied by some reduction in fabric strength [80].

In order to generate a stable finished fabric appearance, it is necessary to fibrillate the fabric a second time. Secondary fibrillation can be produced by either a simple washing treatment or by jet-dyeing the fabric and it should be generated to a level that will not increase on subsequent washing. A small pile is created on the surface of the fabric which gives the special touch and feel characteristics known as 'Peach Skin'. The characteristics of this 'secondary' fibrillation are, however, very different to the 'primary' fibrillation. With the absence of surface hairs, fibrillation is confined to the yarn cross-over points and the high points of the fabric construction. Furthermore, the positioning of these fibrils means that they are physically unable to entangle and therefore pilling does not occur [80, 81].

While the traditional method of achieving a peach-skin effect involves many steps, a new method was developed which shortens the process considerably. The scheme of this method is shown in Figure 2.2. This involves one-bath fibrillation, dyeing, and enzyme treatment. In this one-bath dyeing method for achieving peach-skin effect, the processes of dye exhaustion and primary fibrillation are combined and generated at 130 ^{o}C. By carrying out the enzyme treatment within the dyeing cycle, it is possible to defibrillate lyocell when the dye is exhausted and not fixed. The pH conditions would remain the same from the beginning of the dyeing cycle until the enzyme treatment stage [82].

Following enzyme treatment, the denaturing of the enzyme was combined with the dye fixation step since conditions for both are the same. Since the dye fixation time is usually 45-60 minutes, there is sufficient time to generate secondary fibrillation on the fibre. Hence, when the dyebath is

dropped for the first time, the fabric would not only be dyed, but also it would have achieved the peach skin effect [81].

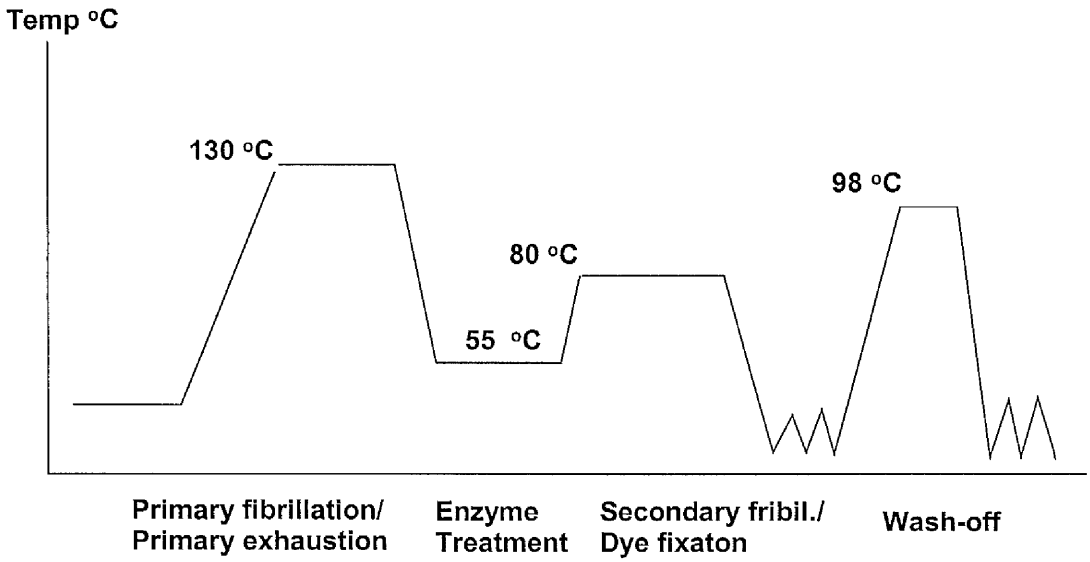


Figure 2.2 Novel one-bath dyeing and finishing route to achieve peach skin effect

2.3.2 Lyocell fabrics with patterned fibrillated portions

The fibrillation of lyocell was also skillfully manipulated to give fibrillated patterns on a piece of fabric, thus satisfying special aesthetic designs. As disclosed by a Japanese patent, lyocell fabrics with patterned fibrillated portions are prepared by printing fabrics with alkali pastes and fibrillating the fibers in the printed portions. A dyed woven lawn was printed with an aqueous composition containing 50% caustic soda, dried, treated with a neutralizing agent, soaped, and fibrillated in a washer for 1 hour at 60°C to give a fabric with patterned fibrillated portions [83].

2.4 Protection of lyocell against fibrillation

As fibrillation is, in many cases, undesirable and restricts the wide use of lyocell, various methods have been employed to prevent or reduce the fibrillation of lyocell. Cross-linking of lyocell is by far the major and most practical method for minimising lyocell fibrillation. In practice, two commercially available low-fibrillation lyocell fibres have been produced by cross-linking. Other methods of fibrillation reduction include application of multifunctional reactive dyes, resin finishing, use of enzymes to remove primary fibrillation, and variation of spinning conditions.

2.4.1 Application of cross-linking agents

Colourless reactive cross-linking agents offer the best and most versatile way to produce a low fibrillation lyocell. It has been a major research area, both for industry and academia, to find an ideal colourless cross-linking agent for lyocell. So far, two commercially available low fibrillation lyocell fibres have been produced by colourless cross-linking and much research is currently on-going.

2.4.1.1 Tencel LF

Tencel LF (formerly Lyocell LF) [84, 85] uses dichlorohydroxy-s-triazine as the cross-linking agent, shown in Figure 2.3. Lenzing AG currently employs an "in-line" cross-linking after-treatment of their "never dried" fibres to minimise the fibre's propensity to fibrillate. Pre-treatment of the fibre during the manufacturing process has proved the most successful way [85].

Figure 2.3 Tencel LF agent

Production of Tencel LF

As with the regular lyocell fibre, the production process for Tencel LF (Figure 2.4) is based on the principle of solvent spinning. In this respect the pulp is dissolved in the NMMO solvent. A highly viscous solution is produced by evaporating water, which is then extruded through spinnerets. Following stretching in an air gap the cellulose is precipitated into an aqueous solution of NMMO. Finally the product is cut and washed to recover the solvent [86].

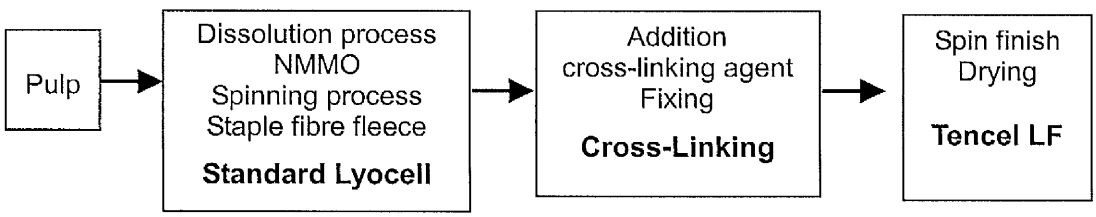


Fig. 2.4 The principle of production of Tencel LF by Lenzing

This fibre is then chemically cross-linked in an additional finishing step. The cross-linking agent, dichlorohydroxy-s-triazine, is introduced in this step. For the properties of the product, it is imperative decisive that this cross-linking takes place in a never dried condition, whereby the typical properties of lyocell are largely maintained. In the following step the soft finish is applied, which is necessary for spinning, and the fibre is dried [86, 87].

Properties of Tencel LF

Good anti-fibrillation properties are observed for Tencel LF even after repeated washing. As a result of the cross-linking agent the fibre has a more pronounced anionic character than normal lyocell, which can lead to a reduction in dyeing affinity with certain dyestuff groups (direct dyes). Using test methods developed at Lenzing, cellulosic fibres reveal fibrillation in line with the following sequence:

Viscose/Modal/Tencel LF Cotton Polynosics Standard Lyocell

No fibrillation ⟶ **Strong fibrillation**

Cross-linking leads to characteristic properties in Tencel LF which influences the fibre structure and the mechanical properties. It is well known that the mechanical strength of cross-linked fibres is influenced by the degree of substitution [86].

Table 2.1 shows the results of the fibre tests of Tencel LF in which the high relative wet strength characteristic of lyocell, the high transverse strength (loop and knot strength) or the high wet modulus are documented. As a result of cross-linking the tenacity and the elongation of the fibre are reduced, but to an acceptable level. From the water retention capacity and the swelling behaviour, it is possible to deduce that Tencel LF has a higher accessibility and a modified pore structure compared with standard lyocell [86, 88].

Table 2.1 Mechanical and structural parameters of Tencel LF compared with standard lyocell

	Tencel LF	Standard Lyocell
Tenacity cond. [cN/tex]	35-37	40-42
Elongation cond. [%]	9-11	15-17
Wet tenacity [cN/tex]	27-29	34-36
Wet elongation [cN/tex]	11-13	17-19
Loop strength cond. [cN/tex]	17	20
Pore volume [ml/g]	0.82	0.60
Inner surface [m^2/g]	507	374
Water retention capacity [%]	69	55
Thickness swelling in H_2O [%]*	34	15

cN/tex: centinewtons per tex

* after 5 minutes; laboratory test

The chemical stability of Tencel LF is very good in moderate temperature ranges in alkaline conditions. However, in acidic media Tencel LF is clearly much more sensitive. Finishing steps in the range of pH values around 4 can be readily carried out at moderate temperature. Lower pH values, however, quickly lead to a reduction in the protection against fibrillation.

2.4.1.2 Tencel A100

Tencel A100 [89, 90] uses 1,3,5-triacryloyl-hexahydro-s-triazine as the cross-linking agent, shown in Figure 2.5.

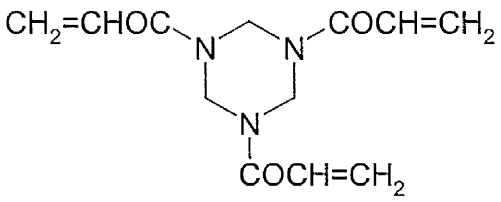


Figure 2.5 Tencel A100 agent

Production of Tencel A100

Tencel A100 is produced in the same spinning processes as standard lyocell. After spinning and washing, standard lyocell is dried, crimped and cut to staple fibre. Tencel A100, on the other hand, is treated in a bath with the cross-linking agent, 1,3,5-triacryloyl-hexahydro-s-triazine, after spinning and washing. It is subsequently steamed, washed, dried, crimped and cut to staple fibre.

Properties of Tencel A100

Since cross-linking of the fibre takes place in the wet state, its accessibility is higher than standard lyocell. The resultant open fibre structure has a positive influence on water retention (approximately 75% compared to 65% for standard lyocell). In spinning, Tencel A100 behaves like the standard variant and it can be processed by the usual spinning methods and machinery. The properties of standard lyocell such as high dry and wet strength and high cross-sectional swelling are likewise present in Tencel A100. As with standard lyocell, the circular cross-section of the fibre and its smooth surface gives fine, densely spun yarns which exhibit a slightly increased hairiness compared to standard lyocell, thus conferring a warm full handle [90, 91].

The open fibre structure has a positive influence on its dyeing properties. Higher colour yields and more brilliant colours are achieved in the dyeing of Tencel A100 compared with standard lyocell or other cellulosic fibres. The fibre can be dyed with reactive and direct dyes without any limitations. Hot dyeing methods with long migration times, as well as reduced and slower addition of alkali, are recommended when dyeing with reactive dyes. The colour fastness ratings achieved are similar to those of standard lyocell and are comparable to cotton and modal. The washability of Tencel A100 is superior to that of cotton and modal fibres.

1,3,5-Triacryloyl-hexahydro-s-triazine produces cross-links which are stable to acidic but show some instability to strong alkali environments. Depending on the temperature of treatment, the cross-linkage of Tencel A100 may be broken down during treatment in alkaline liquors, especially caustic soda. In the case of soda ash, treatment with 25 g/l and 95 °C is regarded as the limit. With caustic soda, the dosage is limited to 1 g/l at 95 °C. At 80 °C, however, the caustic soda concentration may be increased to 5 g/l. At lower temperature, higher concentrations can be used without damaging the fibre [91].

2.4.1.3 Other cross-linking agents

Much interest has also been shown in colourless agents carrying conventional fibre reactive groups for cellulose as potential anti-fibrillating agents, e.g. dichlorotriazines (DCT) [92], such as Sandospace R [93], and Cibatex AE 4425 [94].

Sandospace R (Sandospace is a trademark, Figure 2.6) is a colourless dichloro-s-triazine compound available from Clariant in the form of a paste and used to provide dye-resist on natural and synthetic polyamide fibres. It was applied to dried lyocell fibres by a pad-steam method. The treated fibre gave a lower fibrillation index compared to the untreated one [93].

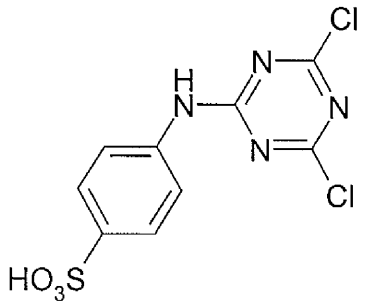
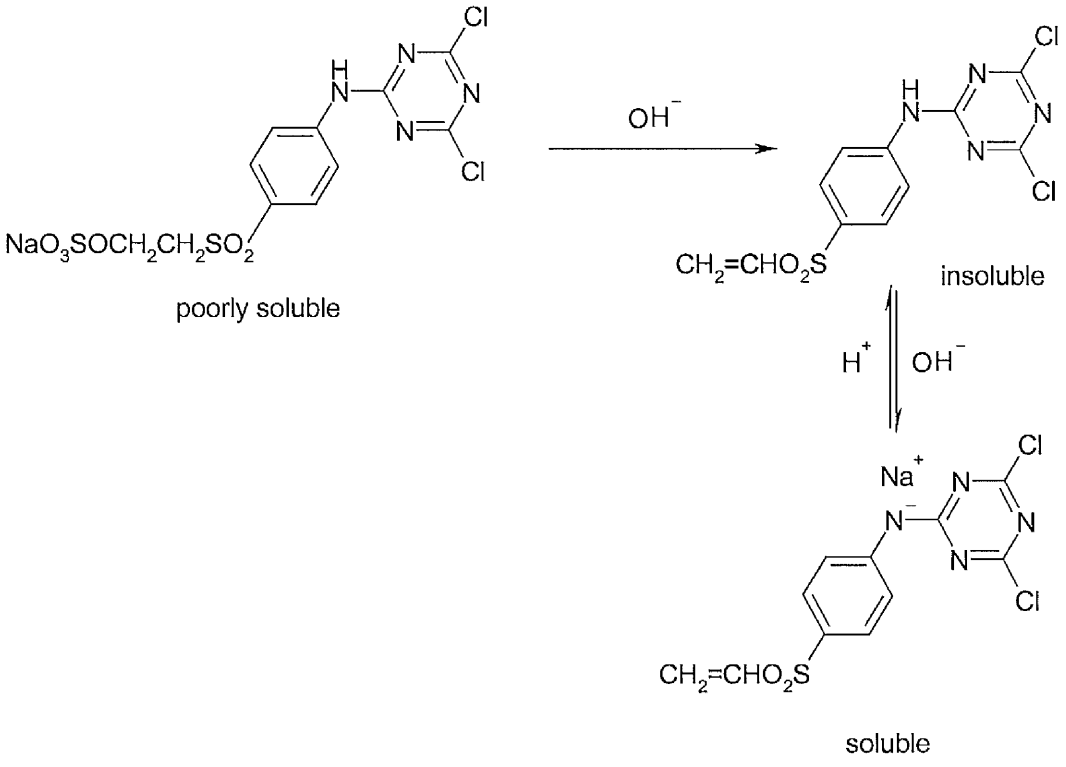


Figure 2.6 Sandospace R

2,4-Dichloro-6-[4-(β-sulfatoethylsulfonyl)anilino]-s-triazine (Cibatex AE 4425) gained commercial interest as a crosslinking agent to improve the wet abrasion resistance of lyocell fibers. The agent, which exhibits poor water solubility, was sold as an aqueous dispersion. During application to lyocell in the presence of alkali, the agent entered the solution phase before reaction with the fibers. HPLC analysis and solution studies supported the view that the two electrophilic species taking part in the crosslinking reaction are vinyl sulphone plus one of the chlorine atoms of the dichloro-s-triazine (DCT) residue and that preliminary hydrolysis of one of the chlorine atoms is not the cause of the observed solubility changes. Renfrew and Phillips showed that in alkali media, 2,4-dichloro-6-[4-(β-sulfatoethylsulfonyl)anilino]-s-triazine underwent the expected elimination reaction to give a less water soluble non-anionic vinyl sulphone species. As the pH was raised, the increased aqueous solubility of the cross-linking agent was the result of the deprotonation of the weakly acidic

arylaminodichloro-s-triazinyl group (Scheme 2.1) and not the formation of a chlorohydroxy-s-triazine derivative. Accordingly, the effective cross-linking groups were the vinylsulphone and dichloro-s-triazine functions [95].



Scheme 2.1

In addition to the above two commercially available compounds, other dichloro-s-triazine derivatives were also described in the patent as cross-linking agents for lyocell [96], shown in Figure 2.7. Cyanuric chloride was reacted with 4-aminobenzoic acid to give 2,4-dichloro-6-p-carboxyanilino-1,3,5-triazine. Reactive dyes could be co-applied with this agent to lyocell fabrics. 2,4-Dichloro-6-(2'-hydroxy)ethylamino-1,3,5-triazine was synthesized from cyanuric chloride and ethanolamine and applied to lyocell by an exhaustion method. In both cases, treated lyocell exhibited increased wet abrasion resistance over untreated fabrics.

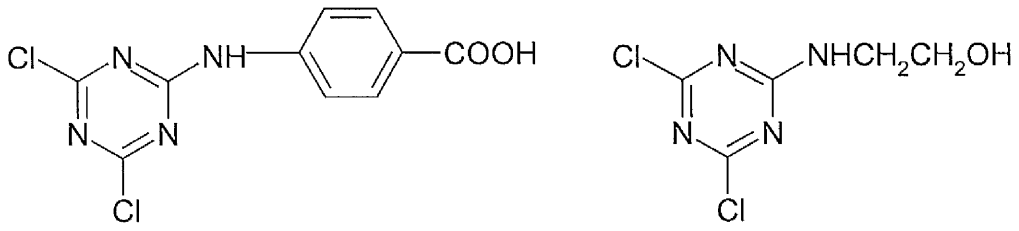


Figure 2.7 Dichloro-s-triazine derivatives

The familiar combination of halo-s-triazine and vinyl sulphone reactive groups [96-99] has furnished a series of potential cross-linking agents. They can increase fibrillation protection, as shown by several representative examples in Figure 2.8.

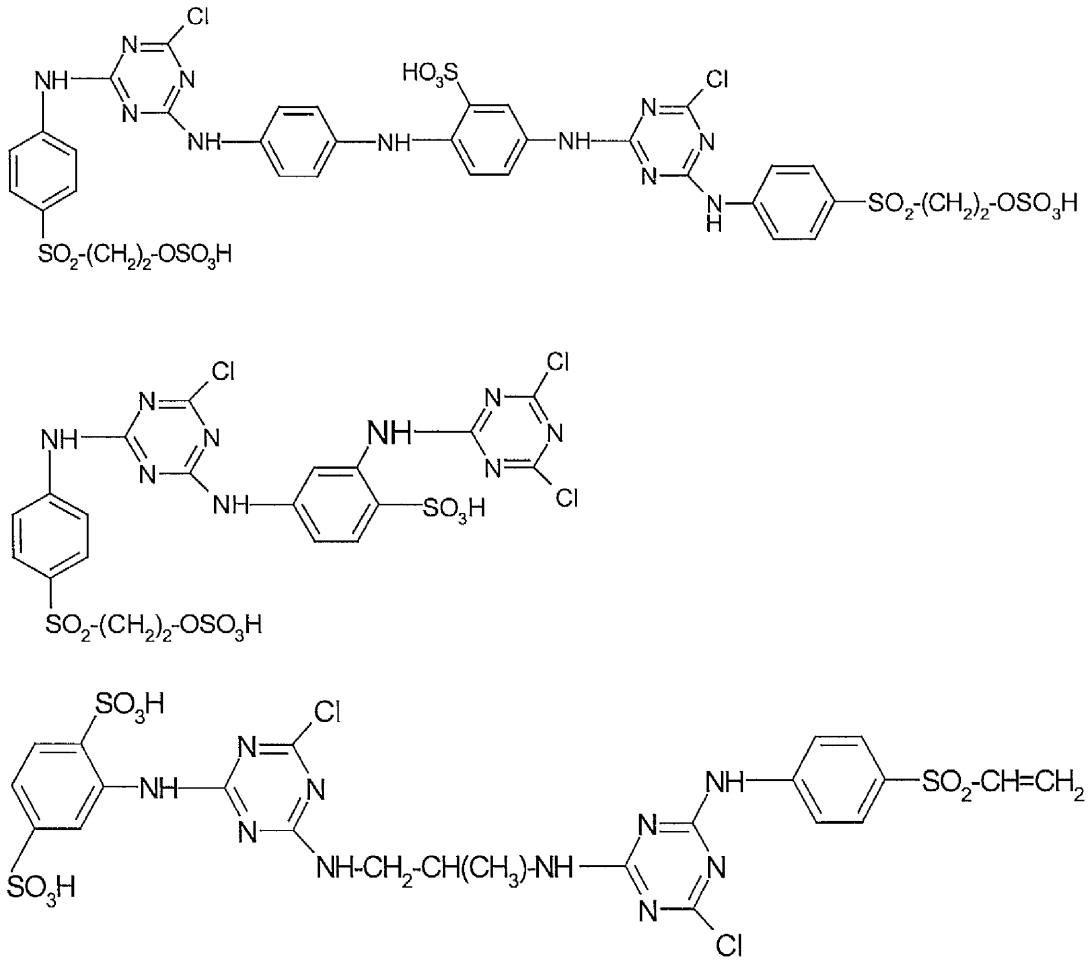


Figure 2.8 Cross-linking agents with halo-s-triazine and vinyl sulphone reactive groups

Bifunctional monofluoro-s-triazine derivatives were also synthesized [100]. 2,5-Anilinedisulphonic acid was reacted with cyanuric fluoride and 1,2-diaminopropane to give the intermediate 2-(2',5'-disulpho)anilino-4-(2''-amino-4''-methyl)ethylamino-6-fluoro-1,3,5-triazine, which on treatment with aniline-2-sulphonic acid yielded the cross-linking agent shown in Figure 2.9. Lyocell treated with this agent gave fibrillation resistance values about 1.5 times higher than that of the untreated fabric. The fabric could also be simultaneously dyed with reactive dyes during the treatment with this agent.

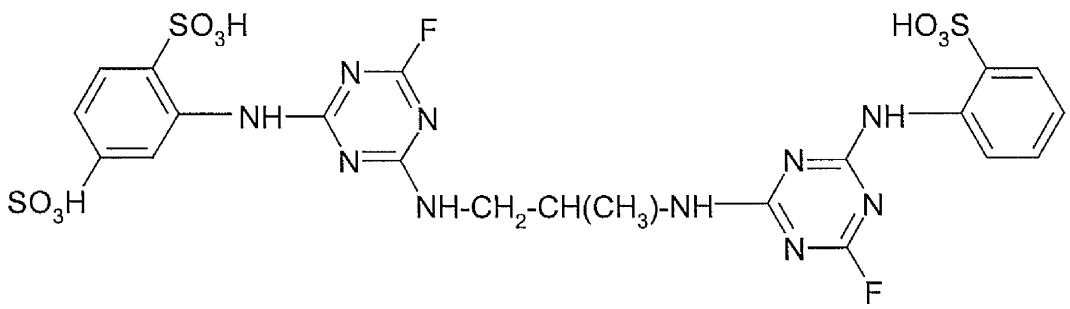


Figure 2.9 Bifunctional monofluoro-s-triazine cross-linking agent

Cross-linking agents prepared by the combination of halo-s-triazine and acrylamido groups [100, 101] have also been claimed in patents, as shown by the following representative examples in Figure 2.10. Treatment of the lyocell substrate with both agents resulted in a fibre, which showed good resistance against wet abrasion (fibrillation).

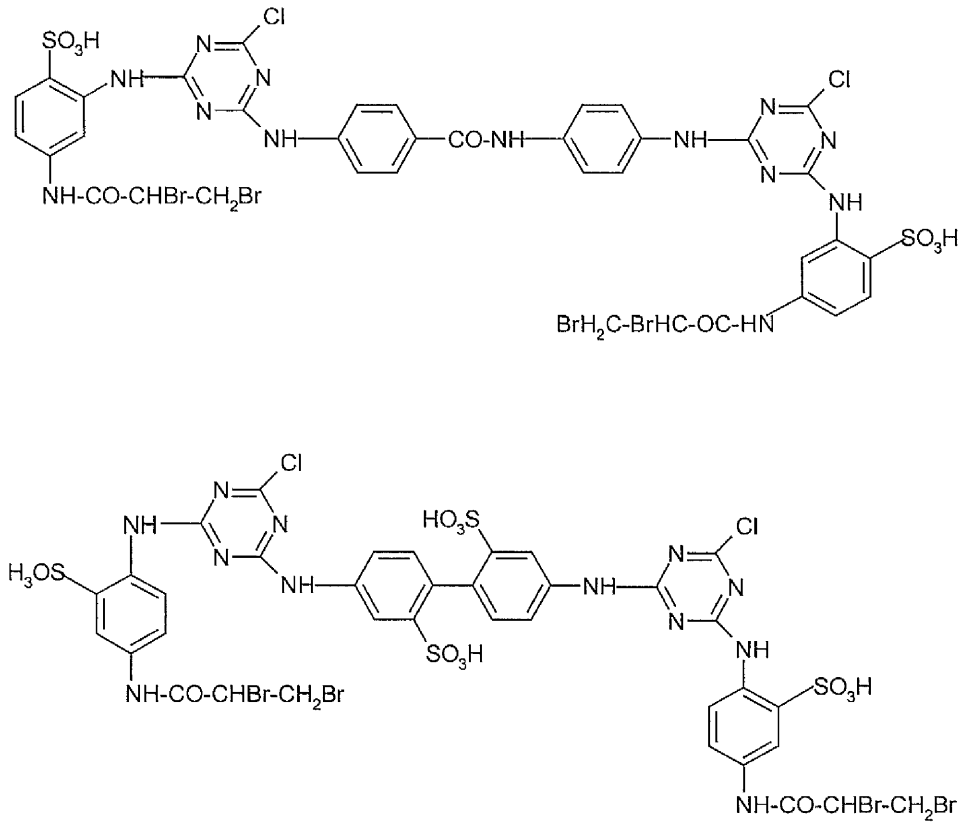
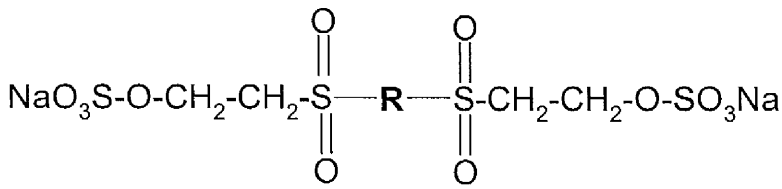


Figure 2.10 Cross-linking agents with halo-s-triazine and acrylamido groups

A paper by Mieck et al [101] describes the synthesis and application of bis-sulphatoethylsulphones (masked vinyl sulphones) attached to bridging groups of different size. All of the cross-linking agents (Figure 2.11) were successful in reducing the wet abrasion of lyocell and if the concentration of cross-linking agent on the fibre was used as the basis of comparison, the different structures had a similar effect. Accordingly, for swollen lyocell the molecular dimensions of a bis-vinyl sulphone cross-linking agent do not appear to be a critical factor.



R: Bridge Group	Name
$-CH_2-$	Methyl
$-(CH_2)_2-$	Ethyl
$-(CH_2)_6-$	Hexyl
$-(o-C_6H_4)-$	Ortho-substituted aromatic ring
$-(m-C_6H_4)-$	Meta-substituted aromatic ring
No bridge	Bis-vinylsulphone

Figure 2.11 Cross-linking agents with bis-sulphatoethylsulphones

2.4.2 Application of multi-functional reactive dyes

Specific multifunctional reactive dyes have a favourable effect on the fibrillation behaviour typical of the lyocell fibre. Some studies have shown that this effect can be produced by inter-fibrillar cross-linking of the reactive groups of these dyes with adjacent cellulose chains [102].

The most often used bi-functional dye for cross-linking lyocell is C.I. Reactive Black 5 (Figure 2.12), which has two masked vinyl sulphone groups separated by the chromophore. The fibrillation of lyocell decreases markedly with increasing depth of shade [101,103, 104].

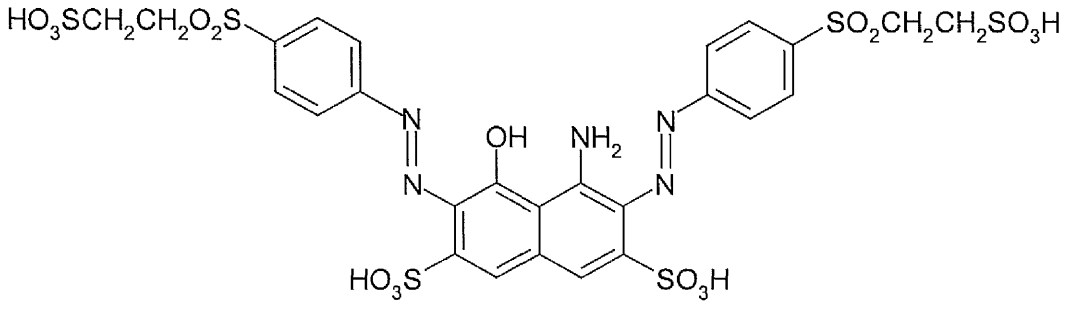


Figure 2.12 Reactive Black 5

However, a different VS-dye with a triphenodioxazine chromophore (Figure 2.13) does not increase the wet abrasion index even in deep dyeings [105].

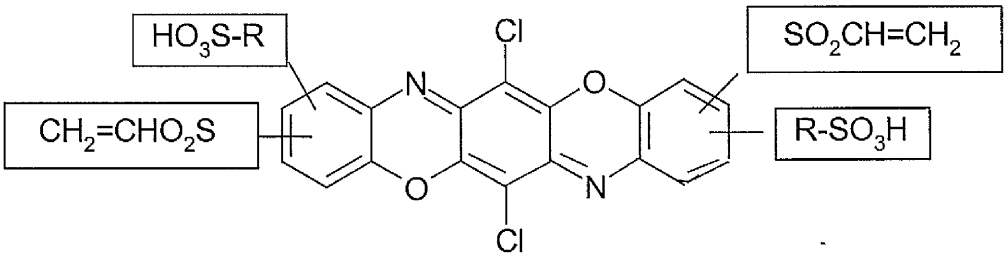


Figure 2.13 Bi-functional VS-triphenodioxazine blue dye

M. Nicolai et al [106] concluded that the existence of two or more reactive groups can not be the sole condition for the cross-linking reaction. The important factor is the internal mobility of the chromophore. As in this case, the VS-dye with a triphenodioxazine chromophore is a polynuclear condensed aromatic system which is a highly rigid structure compared to C.I. Reactive Black 5. So a second reactive group may not be bonded to lyocell due to steric reasons and will usually hydrolyze. In addition, it is possible that the dye may react with the two hydroxyl groups of the same molecular chain of lyocell instead of linking two different molecular chains because of steric factors. In either case, cross-linking will not occur and therefore fibrillation will not change.

It was also found that bi-functional dyes with two monochloro-s-triazine groups, e.g. C.I. Reactive Red 120 (Figure 2.14), which is a hot dyeing, exhaust dye in the Procion H-E range (Dystar), only produce a moderate increase in the wet abrasion index [107]. Even here, the bi-functional anchor component in the middle of the dye containing two rigid MCT-groups

linking two chromophores may not be in a position to react preferentially by cross-linking [106].

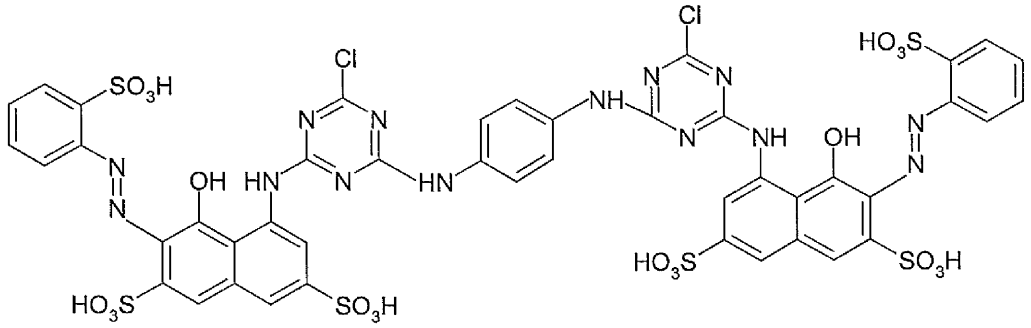


Figure 2.14 C.I. Reactive Red 120

Dyes which contain the bi-functional monochlorotriazine/vinyl sulphone reactive groups (Figure 2.15) were also studied. Dyes of this type have been included in the Sumifix Supra (Sumitomo) and Remazol (DyStar) ranges. A certain increase in the wet abrasion index with increasing depth of shade was found, but this trend was distinctively lower than that with Reactive Black 5 [105, 107].

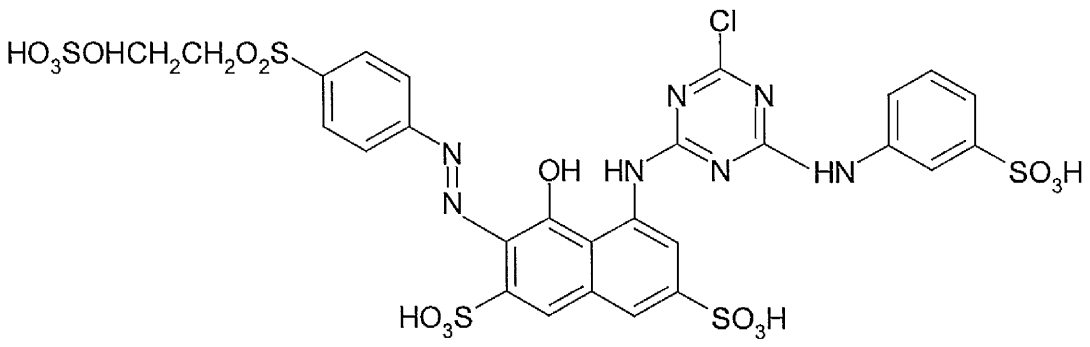


Figure 2.15 Bi-functional MCT/VS red dye

In contrast to MCT/VS dyes, dyes with groups of similar reactivity groups, e.g. monofluoro-s-triazine/vinyl sulphone, as included in the Cibacron C

range (Figure 2.16), only produce a moderate increase of fibrillation protection [106, 108].

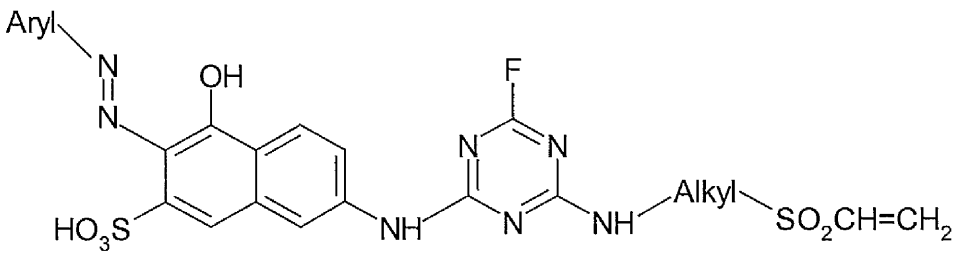


Figure 2.16 Orange bi-functional MFT/VS reactive dye

A tri-functional VS/VS/MCT red dye, C.I. Reactive Red 228, Cibacron Red C-2G (Figure 2.17) based on H-acid was found to increase the wet abrasion index of lyocell in a similar manner to C.I. Reactive Black 5 [108].

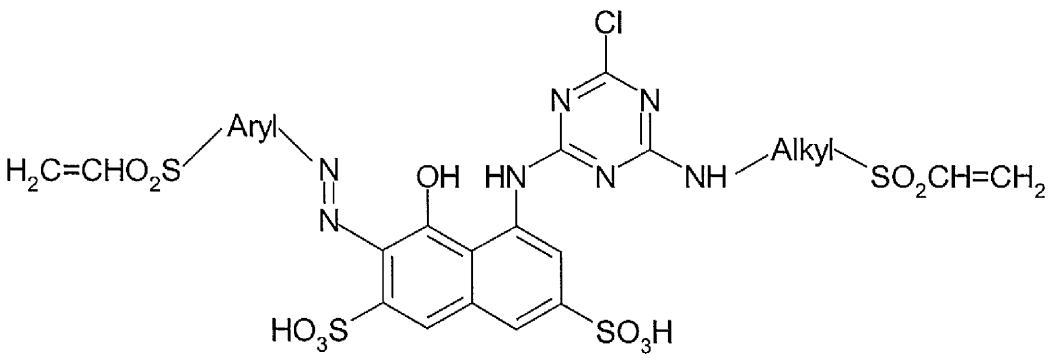


Figure 2.17 Tri-functional VS/VS/MCT red dye

(converted to vinyl sulphone form)

In conclusion, whether, and to what extent, the fibrillation propensity of lyocell is reduced by dyeing with bi- and multi-functional reactive dyes depends on the dye constitution, the dyeing method and the depth of shade. Dyes with the same and similar reactivity groups which possess a

certain mobility and avoid strong absorption in the fibre pores give the best results [105, 108].

2.4.3 Application of resins

Resins, which can cross-link lyocell fabric, are used after dyeing. This embrittles the fibrils and enables the removal of fibrils, from the fibre surface, which have been generated during the dyeing process. This process is particularly suited to woven fabrics as these are prepared and dyed open width and so are free of fibrillation before dyeing [80, 109]. Agster showed that, compared to other regenerated cellulose fibers (e.g. modal or viscose), lyocell requires distinctly lower quantities of resins in order to achieve the same, or sometimes even better, technological ratings [110].

Lyocell fabrics with improved fibrillation resistance and pill resistance were prepared by cross-linking with formaldehyde resins. N,N'- Dimethylol-4,5-dihydroxyethylene urea (DMDHEU) is the most widely used commercial cross-linking agent. It is made by reacting 1 mole of urea with 1 mole of glyoxal and the product with 2 moles of formaldehyde, as shown in Figure 2.18 [111].

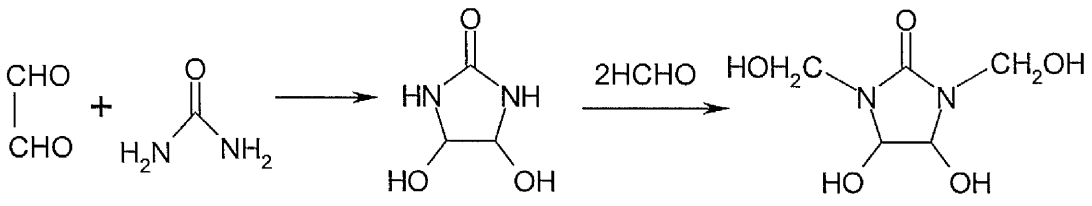


Figure 2.18 Synthesis of DMDHEU

This agent exhibits high acid hydrolytic stability and relatively low reactivity. It is generally accepted that all four hydroxyl groups are capable of reacting with cellulose but it is the pendant N-hydroxymethyl groups that are the

primary source of cross-linking reactivity, shown in Figure 2.19 [111]. The single-end reacted product is bound to the cellulose but bears an unreacted N-hydroxymethyl group on the ring capable of producing crosslinking [112, 113]

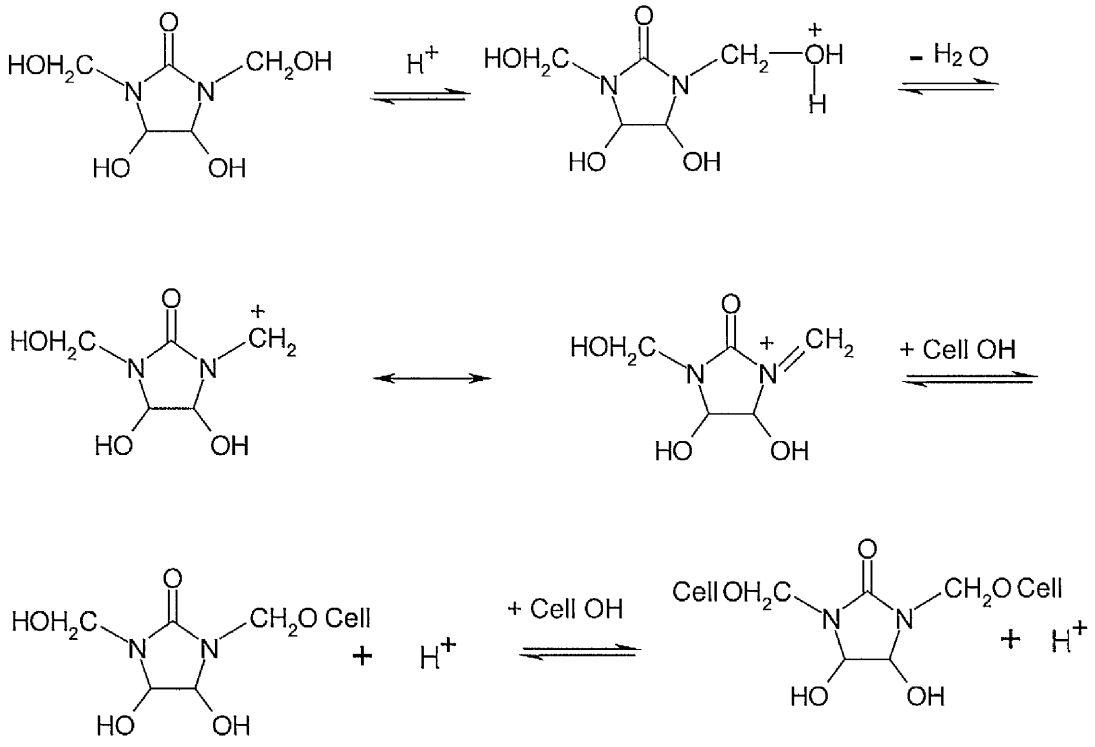


Figure 2.19 Reaction of cellulose with DMDHEU

Formaldehyde addition products, widely used as cross-linking agents for durable press/wrinkle resistant finishing, continuously release formaldehyde vapour during durable press finishing (curing) of lyocell fabric, subsequent storage of the treated fabric, manufacture and retailing of the resulting garment, and finally during use of the garment or textile by the consumer [114, 115]. The release of formaldehyde into the air from curing is subject to a limit of 20 ppm in some European countries [116, 117].

Therefore, low and no formaldehyde resins are also used to reduce the fibrillation tendency of lyocell. Various categories of such resins have all been described as alternative approaches to minimising the wet abrasion of lyocell. These include:

1) The use of low and zero formaldehyde resins to facilitate wet and dry cross-linking [118].

2) N-Methylol resins [119], including N-methylol ethers of carboxylic acid amides, urethanes, ureas and aminotriazines [120].

3) Dialdehydes [120].

4) Mixtures of polyurethanes and isocyanates [120].

5) Reactive sulphonium salts [121].

6) Amino-, polyalkylene oxide, epoxy- or carboxyl functionally modified self-cross-linking polysiloxanes [122].

7) Aliphatic ethers containing two to six chlorohydrin groups [123].

In particular, the reactive resin finishing is another practiced method for fibrillation protection besides the above mentioned cross-linking compounds. The positive effects of resin finishing are better crease recovery, no pilling, and reduced fabric shrinkage. The negative effects are mainly the losses of tear strength, tensile strength, abrasion resistance and modifications of handle. The performance is affected by resin formulation, application levels and wet processing carried out on the fabric prior to finishing. Low add-on levels of resin are recommended to achieve high easy care performance while minimising the losses of other physical parameters [124-126].

2.4.4 Modification of the manufacturing processes

The spinning process determines the fibrillar structure of lyocell, which is responsible for high fibre tenacity but low lateral cohesion. Modifications of the spinning process are expected to provide a fundamental solution to the fibrillation of lyocell, but to date this objective has not been fully achieved [127-129].

Various trials have been conducted to modify the manufacturing process of lyocell, with the aim of reducing or preventing the fibrillation of lyocell fibres. A German patent claimed that the tendency to fibrillation can be reduced by treating the fibers with an aqueous NMMO solution after spinning. The extent of dissolution of the surface of the fibers was controlled by the dwell time of the fibers in the solvent, its concentration and temperature. Lyocell fibres produced by this route exhibited a significantly reduced tendency to fibrillation [130].

A similar approach was described in another patent. The fibrillation tendency of lyocell was reduced by controlling the crystal morphology, i.e., by providing a skin/core structure to a lyocell filament spun from a cellulose solution in an amine oxide solvent. Such structure was achieved by passing the filament through a regeneration bath containing a 60% NMMO solution, and washing the filament in an aqueous medium. The relative degrees of crystallinity of the skin and core elements of the filament may be controlled by varying the concentration of the amine oxide solution, the temperature of the solution and the residence time of the filament in the solution [131].

The spinning process was modified by the use of a die. A solution of cellulose in a tertiary amine N-oxide was extruded by way of a die through

an air-gap into a coagulating bath, air being supplied to and discharged from the air-gap that comprised a first region adjacent the face of the die and a second region more remote from the face of the die. The moisture content of the air supplied to the first region was of a lower value compared to the air to the second region. Lyocell fibres produced by this route exhibited reduced tendency to fibrillation [132].

A cross-linking catalyst can be added to the cellulose solution. The method was characterized in that the cellulose solution contains a substance which activates the cross-linking agent. Thus a suspension of cellulose in aqueous NMMO and containing poly(diallyldimethylammonium chloride) crosslinking catalyst was converted to a solution and spun to a fibre containing this compound. After converting this compound to the active hydroxy form, aqueous di-sodium tris(β -sulphatoethyl)sulphonium salt was added and the fiber dried. The resultant fiber exhibited a strongly reduced tendency for fibrillation. This method enables lyocell fibres to be produced with accurately controllable fibrillation characteristics [133].

Finally, a comprehensive study has been made of the influence of various process parameters on the fibrillation characteristics of lyocell fibers, which are spun from a solution of cellulose in N-methyl-morpholine-N-oxide (NMMO). The important parameters were related to the spinning condition and the spin-bath:

1) The air gap, particularly its length, temperature, and humidity.
2) The line speed, i.e. the spinning speed, which affects the residence time of the filament in the air gap.

3) The draw ratio, as it is well known that lowering the draw ratio reduces the orientation of the polymer in the resultant fibre.
4) The cellulose content of the polymer solution, which determines the solution viscosity.
5) The water content of the polymer solution, as decreasing water content has been shown to increase birefringence and hence the orientation of the polymer.
6) Coagulation bath concentration, using 25% NMMO in the coagulant instead of the usual water.
7) Coagulation bath temperature, at 2 °C (using floating ice on the spin-bath surface), 20 °C and 50 °C.

Fibrillation was induced in the fibers by an ultrasonic treatment and compared by defining a fibrillation index from optical micrographs. By selecting combinations of the parameters described above, fibrillation can either be increased or decreased without significantly affecting the tensile properties of the fibers.

2.4.5 Application of enzymes

Enzymes are mainly used to 'polish' the fabric surface after primary fibrillation [134]. Cellulases are highly specific enzymes that can catalyse the hydrolysis of the 1,4-β-glucosidic bonds within a cellulose chain. The number of bonds split by enzymes can thus be controlled by varying the treatment time and/or enzyme quantity [135].

Enzymes can only work if the pH value and temperature are optimally adjusted. Therefore, effective buffer and temperature control systems are

essential. At the end of enzyme treatment an enzyme stop is performed by raising the temperature and pH value [136].

Enzymes cannot prevent the recurrence of fibrillation of the fibres. They are mainly used after the primary fibrillation step, to remove as many of the inadequately bound-in fibre tips as possible. The purpose of enzymatic defibrillation is to 'polish' the fabric surface and facilitate subsequent dyeing, secondary fibrillation, or finishing [137, 138].

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Measurement of Wet Abrasion Resistance (NSF)

The propensity to fibrillate was determined using an instrument (Delta 100) manufactured by Lenzing AG. The instrument consists of a 10mm diameter shaft with a sandblasted surface which can rotate at 100-500 rpm. The shaft is horizontally mounted and sits in a small trough of deionised water, which is constantly being replenished. This trough ensures that the shaft has a constant film of water over its surface. In addition the shaft can oscillate 10 mm min^{-1} along the axis of rotation. This ensures that a fibre sample is subjected to a more even abrasion from the shaft.

The fibres being tested are held in contact with the bar and their contact angle can be adjusted from 0^{o} – 100^{o}. To apply a degree of tension, weights in the form of clips are attached to the lower end of each fibre. During the testing process as each individual fibre breaks, the respective clip falls into a channel below, which guides the clip to a detector. 20 samples are measured at any one time. The usual settings are 50 mg weights, 40^{o} contact angle, 500 rpm and with the shaft oscillation operating. The whole process of instrument control and data processing is achieved by use of a PC.

3.2 High Pressure Liquid Chromatography

High Pressure Liquid Chromatography (HPLC) is used to separate components of a mixture based on a variety of chemical interactions

between the substance being analyzed and the chromatography column [139]. It is applicable to all kinds of ionic and organic compounds whether they are coloured or not.

In HPLC the reaction mixture is carried through the packed column or capillary tube which is under high pressure. The stationary phase is column-packing material and the most popular is a silica gel to which is attached a C18 alkyl chain hydrocarbon.

After separation, the solution passes through a spectrophotometer cell that operates over the range 190-700 nm. Different compounds have different retention times on the column and therefore exit at different times from the column. Consequently, the number of the revealed peaks within the set time is equal to the number of the possible components in the reaction solution.

The HPLC instrument contains a pump, an injector, a column, a detector and a collector. The pump pushes solvent out to the column from the reservoir. Samples are injected into the instrument via an injection port, which consists of an injection valve and the sample loop. The sample is typically dissolved in the mobile phase before injection into the sample loop. The columns are constructed of stainless steel to cope with the back-pressure and are glass lined to prevent metal catalyst of solvent-solute reactions at the high column pressures. The detector emits a response due to the eluting sample and subsequently signals a peak on the chromatogram. It is positioned immediately after the stationary phase in order to detect the compounds as they elute from the column. The bandwidth and height of the peaks may usually be adjusted using the

coarse and fine-tuning controls and the detection and sensitivity parameters may also be controlled. The collector simply gathers the results of the analysis.

In the current study, HPLC was performed with a Hewlett Packard 1100 series fitted with a quaternary pump. The column was a 10 cm Pursopher RP-18 (5µm) packing and a LiChrocart 125-4 HPLC column cartridge; solvent A, acetonitrile; solvent B, water with 0.25% dicyclohexyl-ammonium phosphate (CHAPS); flow rate 2 ml/min; temperature 40°C; injection volume 5 µl; samples were analysed using a diode array detector. The following gradient programme was used:

Programme A (Flow 2 ml/min):

Min.	% A	% B
0	30	70
5	50	50
6	40	60
7	30	70

Stop time 7

Programme B (Flow 2 ml/min):

Min.	% A	% B
0	15	85
8	50	50
10	15	85

Stop time 10

Programme C (Flow 1 ml/min):

Min.	% A	% B
0	75	25
9	85	15

12	90	10
12.5	75	25
14	75	25

Stop time 14

Retention times (t_R) are in minutes.

3.3 Mass Spectrometry

Mass spectrometry is a highly sensitive analytical technique used to identify unknown compounds and to quantify known materials. This combined separation and detection method is based on the generation of gaseous ions from molecules, the subsequent separation of these ions according to their mass-to-charge (m/z) ratio and the detection of these ions. A mass spectrometer can separate charged atoms or molecules according to their mass [140].

The following methods were used:

Method A:

Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-flight mass spectrometer fitted with a Z-Spray electrospray ion source operating in negative mode at 3kV needle potential. Nitrogen was used as a drying and sheath gas. Data was stored in the continuum mode on a Micromass Instruments MassLynx data station utilizing Version 3.5 software pack. Infusion was at a rate of 20μl/minute with a Harvard Instruments syringe pump utilized for sample introduction.

Method B:

FAB mass spectra were recorded with a VG 70-70 EG high resolution mass spectrometer run in positive ion mode using m-nitrobenzylalcohol as

FAB matrix. The instrument was run as a double focusing instrument and calibrated with cesium iodide over the desired mass range.

Mass Spectrometry were carried out by Hall Analytical, at Hall Analytical Laboratories Ltd., Millbrook Business Centre, Unit A, Floats Road, Manchester, M23 9YJ

3.4 UV/Visible Spectroscopy

Ultraviolet-Visible spectroscopy (UV-vis) is a reliable and accurate analytical laboratory assessment procedure that measures the absorption, transmission and emission of ultraviolet and visible light wavelengths by matter [141].

Ultraviolet spectra were taken with a Camspec M350 Double Beam UV-Visible Spectrophotometer in this research.

3.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR data were recorded on a Bruker Avance at 300 MHz for ^{1}H NMR and at 75.47 MHz for ^{13}C NMR in D_2O unless otherwise stated. Chemical shifts, relative to TMS as the internal standard, are given in δ values. Coupling constants are given in Hertz. ^{13}C peaks were assigned by means of APT, HMQC and HMBC experiments.

3.6 Elemental Analysis

Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried on a Carlo Erba EA1108 elemental analyzer at the Department of Chemistry, University of Manchester.

3.7 Nitrogen Analysis

Nitrogen analysis of treated lyocell fabrics was performed with a LECO FP 328 nitrogen analyser in Lenzing AG, Austria.

Principle:

Sample (solid or liquid) is contacted with oxygen and burned at 950°C.

20 ml of the burning gas are injected into a helium gas flow via a sample loop.

The gas is reduced on a heated copper catalyst (750°C) and CO_2 and moisture are eliminated by an adsorber.

Detection is performed via thermal conductivity detectors.

3.8 Application Methods

3.8.1 Exhaustion Process

In the conventional form, the exhaust application procedure for cellulose fibres (fabrics) normally consists of four main stages [142]:

1. Exhaustion from an aqueous bath, containing electrolyte, normally under neutral conditions.

2. Addition of alkali to promote further uptake and chemical reaction of absorbed dye or agent with the fibre at the optimal pH and temperature.

3. Washing of the dyed material to remove electrolyte, alkali and unfixed or hydrolysed dye.

4. Drying of the material.

The application procedures were conducted in sealed stainless steel dye pots housed in a Mathis Labomat BFA 12 dyeing machine.

3.8.2 Continuous Process

The fabric or fibre passes through different pieces of equipment at various steps of the application process [143]:

1. Impregnation of the well-prepared fabric/fibre in a padding solution at ambient temperature.

2. Uniform squeezing of surplus liquor from the fabric/fibre as it passes through the mangle nip. Mangle pressure are set to give a liquor pick-up of 80%-100% at a constant padding temperature of 20-25°C.

3. Fixation of the dye/cross-linking agent by thermofixation, steaming or batching. For steam fixation a 2nd padding operation involving alkali and saturated salt solution is required.

4. Washing off unfixed and hydrolysed dye/cross-linking agent.

5. Drying of the material.

The continuous processes employed in this research are: Pad-Steam; Pad-Dry-Chemical Pad-Steam and Pad-Dry-Bake.

3.8.2.1 Pad-Steam

This method is adapted from Lenzing's method of fixing colourless cross-linking agents to lyocell and is a single padding method. The "never-dried" lyocell fibre was padded with agent, sodium hydroxide and sodium sulphate at room temperature and fixation takes place in saturated steam for 5mins. The treated fibre was rinsed in hot running water for 5 minutes, soaped at the boil for 10 minutes (Cibapon R: 1g/l; liquor ratio: 50:1) and rinsed in cold running water for 5 minutes.

3.8.2.2 Pad-Dry-Chemical Pad-Steam

The first practical dyeing method devised for reactive dyes involved padding in a neutral dye solution and then in a dilute solution of caustic soda in saturated brine. This sequence showed a severe problem of dye bleeding in the alkali solution, even at the maximum salt concentration, which resulted in loss of fixation. This unsatisfactory 'wet-on-wet' sequence was soon replaced by the 'wet-on-dry' technique: pad (neutral dye solution)-dry-pad (caustic soda in brine)-steam-wash. In this process, after padded in a neutral dye solution, the materials were passed through the drying zone, and then padded in a mixture of alkali solution and saturated brine. After intermediate drying in a hot flue, highly efficient absorption of the alkali/salt liquor is achieved and few colour-bleeding problems are encountered. The fixation takes place in the superheated steam. Washing off follows as described in the above section.

3.8.2.3 Pad-Dry-Bake

In this sequence, the fabrics were typically padded with agent or dye, 10-20 g/l sodium carbonate and 100-200 g/l urea. Little fixation takes place during intermediate drying; this stage is not particularly critical, except that precautions are essential to minimise dye migration. The dried fabric is led directly into the thermofixation unit where baking take place. A typical baking treatment is between 30 seconds and 3 minutues at 160-200°C. Washing off follows as described above.

3.9 Measurement of Colour Strength (K/S)

In this research, K/S values were measured using a Datacolor International Spectraflash 600 spectrophotometer. Dyed fibres were torn and folded until no further light penetrated them. The average of four reflectance measurements, taken at different positions on the sample, were processed to give the K/S value at the wavelength of maximum absorption.

K/S value is based on the equation suggested by Kubelka-Munk that the concentration of dye on a substrate is directly proportional to the ratio of the light absorbed (by the dye) and light scattered (by substrate). It can be represented mathematically as [144]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = ac \text{ (at a particular wavelength)}$$

Where,

K = absorption coefficient

S = scatter coefficient

R = reflectance, expressed as a fractional value

a = constant

c = the concentration of the dye in the substrate

The utility and application of this important equation has been critically reviewed by Nobbs. It can be used in conjunction with CIELab systems or other related colour systems to match a given colour standard.

3.10 Dry Crease Resistance Test

Creases in textile fabrics diminish at varying rates on the removal of the creasing forces. The magnitude of the crease recovery angle is an indication of the ability of a fabric to recover from accidental creasing.

This test was carried out according to British Standard EN 22313:1992 under standard laboratory conditions (20±2°C; 65±2% relative humidity), with the fabrics being conditioned in this environment for at least 24 hours prior to testing. The 40 mm x 15 mm samples were carefully creased by folding in half, loaded with 10 Newtons and maintained for 5 mins. The load was removed and the sample transferred to the fabric clamp on the instrument and allowed to recover from creasing. As it recovered, the dial of the instrument was rotated to keep the free edge of the specimen in line with the reference edge. After the removal of the load, the recovery angle in degrees was read on the scale after 5 mins, 15 mins, 30 mins and 60 mins respectively.

Six samples for warp direction and six samples for weft direction were tested. Mean values were calculated in both warp and weft directions.

3.11 Tensile Strength Test

The woven lyocell fabrics used in this study were characterized in terms of their tensile properties. This test was carried out according to British Standard EN ISO 13934-1:1999, using an Instron Model 5546 tensile tester, under standard laboratory conditions (20±2°C; 65±2% relative humidity). The fabric was clamped vertically at each end between the Instron jaws without any tension being introduced into the sample. During

operation, the upper movable jaws moved upward extending the sample. A fabric test specimen was extended at a constant rate until it ruptured.

A full-scale load of 1 kN was used and crosshead speed was set at 100 mm/min. A 200 mm x 60 mm template was used to mark out the fabric. The sample strips were reduced to 50 mm width by removing threads from each side of the strip. Four strips of the warp direction for each sample were tested.

3.12 Repeated Laundering Test

A repeated laundering test method based on AATCC124 was designed to evaluate the fibrillation protection and the smoothness appearance of flat fabric specimens after repeated home washing. This test was conducted in a domestic washing machine (BOSCH, WFB 2000). 25 x 25 cm fabric specimens cut parallel to the fabric length and width were prepared.

Automatic Washing Conditions:

Temperature: 60°C

Wash Time: 30 min

Rinse Time: 40 min

Spin Speed: 650 rpm

Final Spin Cycle: 8 min

1993 AATCC Standard Reference Detergent: 40 g

Wash Load Ballast: 50/50 Poly/Cotton 1.75 kg

Dryer (Tumble dry):

Temperature: 60°C

Time: 20 min

Number of laundering cycles: 1, 5, 10, 15

3.13 Martindale Abrasion Test

The Martindale test was carried out according to BS EN ISO 12947-3:1999 using the standard crossbred worsted abradant material. The standard abradant was replaced at the start of each test.

The test samples were exposed to a standard laboratory condition (20±2°C; 65±2% relative humidity) for at least 24 hours prior to testing. Four fabric samples were cut in a circular shape with a 38 mm diameter. Each individual sample was mounted in a sample holder on the abrasion machine, and a piece of polyurethane foam with circular 38 mm diameter was placed behind the sample to act as backing. Each sample holder was clamped on the moving plate under a load of 12 KPa. Samples were abraded with a cyclic planar motion, which results from two simple harmonic motions at right angles to each other. While remaining in the sample holder, samples were examined at suitable intervals using a low power stereomicroscope to check whether two threads were broken (End Point Method). The mean value of the number of cycles required for the second thread of the four samples of each fabric to break down was reported.

3.14 Scanning Electron Microscopy

The scanning electron microscope (SEM) is one of the most versatile instruments to analyze and characterize the surface features of an object.

The basic components of the SEM are the lens system, an illumination system, which include the electron guns, and the condenser. These

components were successfully assembled for the first time in 1965 by the Cambridge Scientific Instrument in their Mark I instrument [145]. In SEM, images are formed by the collection and amplification of electrons back scattered or emitted from the surface of a bulk specimen when a high energy electron beam is scanned across its surface. The resolution of SEM is vastly superior (about 15nm) to light microscopy with its depth of field also up to several millimetres.

In this research, the scanning micrographs were obtained with an SM-300 Scanning Electron Microscope operating at 5 kV. Fabric samples were fixed on stubs using copper adhesive tape to increase the conductivity of the sample. Due to the extremely low conductivity of fabrics, samples were also pre-coated with a thin layer (20nm) of gold in a coating unit at 2.4 kV, 18-30mA for 3 mins. Magnification was 300 times. Significant evidence of fibrillation was found on the untreated samples after 10 and 15 laundering tests and remarkable differences were showed on the surface of treated and untreated woven lyocell fabric.

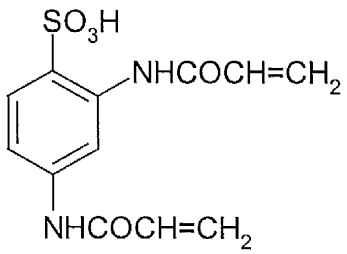
CHAPTER 4

PROTECTION OF LYOCELL AGAINST FIBRILLATION; MODE OF ACTION OF 2,4-DIACRYLAMIDOBENZENESULPHONIC ACID

4.1 Introduction

Lyocell is the first solvent spun cellulosic fibre made on a commercial scale. It is structurally different from conventional viscose and displays superior properties such as dry and wet strength and lower shrinkage. However it does have one major technical defect: it has a distinct tendency to fibrillate in the swollen state.

To overcome this fibrillation propensity, the CD laboratory of the University of Manchester has identified a potential cross-linking agent for lyocell: **2,4-diacrylamidobenzenesulphonic acid (I),** with a view to replace or supplement the commercial agents currently used by Europe's only lyocell manufacturer, Lenzing AG.



(I)

Treatment of the never-dried lyocell substrate with this agent resulted in a fibre which showed excellent resistance to wet abrasion (fibrillation) but

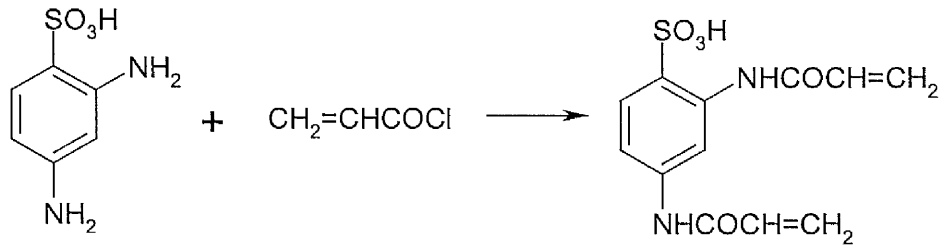
unexpectedly exhibited a significant loss of protection against wet abrasion after high temperature (HT) processing under acidic conditions. Accordingly, the cross-linked fibre could not be blended with polyester.

This work was undertaken to understand the nature of, and find solutions to, the above problem, with a view to re-establishing 2,4-diacrylamido-benzenesulphonic acid as a suitable technical replacement for existing cross-linking agents for lyocell.

4.2 Experimental

4.2.1 Syntheses

4.2.1.1 2,4-Diacrylamidobenzenesulphonic acid (I)

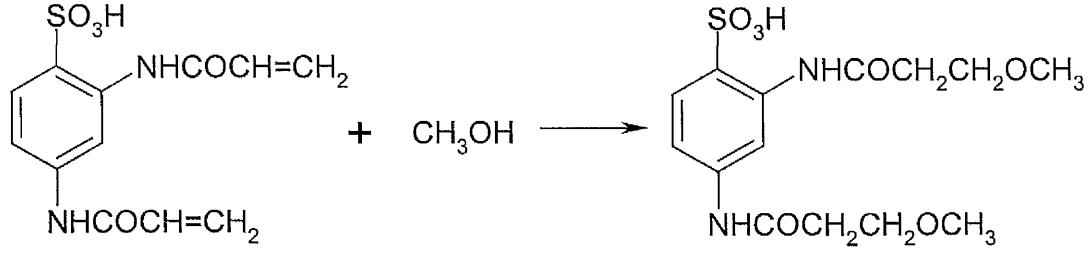


(I)

To a solution of 2,4-diaminobenzenesulphonic acid (9.6 g; 98 % strength; 0.05 mol) in water (150 ml) was added caustic soda to give a clear solution and pH 5.5. The solution was cooled to 2 °C and acryloyl chloride (19 ml; 96 % strength; 0.23 mol) was added dropwise, with stirring, while maintaining a pH of 3.0-4.0 with a sodium carbonate solution. The reaction mixture was filtered to remove a small quantity of white solid and sodium chloride (20 %w/v) was added to the filtrate. The precipitate so formed was filtered off, washed with 20 % brine (20 ml), pulled down and oven-dried to give the product (11 g). A small portion was lixiviated in ice cold water,

filtered and dried. Found C, 42.2; H, 3.1; N, 8.0; S, 8.7. $C_{12}H_{11}N_2O_5SNa$ (93 % pure) requires C, 42.2; H, 3.2; N, 8.5; S, 9.4 %. HPLC showed a single peak at t_R = 0.97 and mass spectral analysis (method B) gave a molecular ion at m/z 319 $(M+H)^+$ (35). ^1H (300 MHz,): δ (ppm) = 5.69-5.73 (1 H, t, J 5.6 Hz, -CH=), 5.79-5.83 (1 H, dd, J 2.6 and 8.3 Hz, -CH=), 6.16 (2 H, d, J 5.6 Hz, CH_2=), 6.21 (2 H, m, CH_2=), 7.17-7.21 (1 H, dd, J 1.5 and 8.7 Hz, ^{Ar}H), 7.59 (1 H, d, J 8.7 Hz, ^{Ar}H), 8.09 (1 H, s,^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 114.6, 116.5, 128.5, 128.8, 129.2, 129.3, 130.6, 131.3, 134.5 and 140.8 (10 C, ^{Ar}C and 2 x -CH= and 2 x =CH_2), 166.4 and 166.6 (2 C, C=O).

4.2.1.2 2,4-Bis-(γ-methoxypropionamido)benzenesulphonic acid (II)

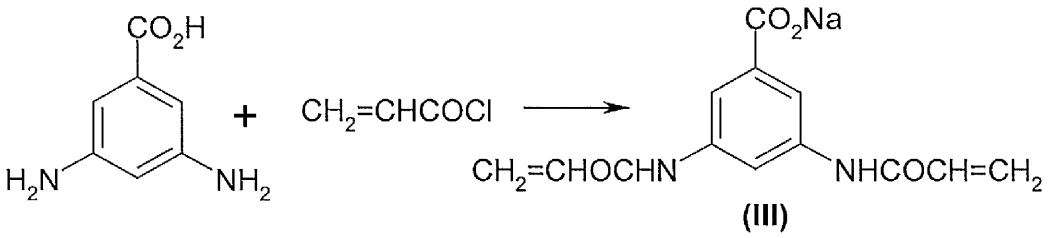


(II)

To 2,4-diacrylamidobenzenesulphonic acid (I; 10 g; 77.9 % strength) was added methanol (60 ml), water (60 ml) and sodium carbonate (2 g) and the reaction mixture heated under reflux for 48 hrs. The solvent was removed under vacuum with a rotary evaporator to give an off-white solid (8.2 g) which was lixiviated with acetone (100 ml), filtered and oven-dried at 40 °C. HPLC showed a single peak at t_R = 0.87 and mass spectral analysis (method A) gave ions at m/z 359 $(M-H)^-$(100), 327 $(M-H-CH_3OH)^-$ (42). ^1H (300 MHz): δ (ppm) = 2.51 (2 H, t, J 5.6 Hz, -CH_2C=O), 2.58 (2 H, t, J 5.6

Hz, -CH_2C=O), 3.19 (3 H, s, OCH_3), 3.22 (3 H, s, OCH_3), 3.58-3.64 (4 H, m, 2 x CH_2O), 7.20 (1 H, d, J 8.7 Hz, ^{Ar}H), 7.62 (1 H, d, J 8.7 Hz, ^{Ar}H) and 7.94 (1 H, s, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 37.1 and 37.5 (2 C, 2 x OCH_3), 58.5 (2 C, 2 x -CH_2), 68.1 and 68.4 (2 C, 2 x -CH_2O), 115.9, 117.1, 128.5, 129.6, 134.5 and 140.7 (6 C, ^{Ar}C), 168.3 and 172.8 (2 C, 2 x C=O).

4.2.1.3 3,5-Diacrylamidobenzoic acid (III)

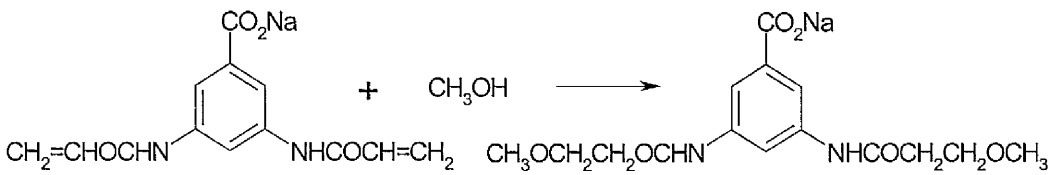


(III)

To a solution of 3,5-diaminobenzoic acid (43.5 g; 0.29 mol) in water (600 ml) was added hydrochloric acid (32 %; 50 ml) and the suspension stirred for 1 hour. The solution, pH 2.5, was filtered to remove a small quantity of undissolved solid and the pH raised to 3.1 with sodium hydroxide solution. The solution was cooled to 10 °C and acryloyl chloride (60 ml; 96 % strength; 0.7 mol) was added dropwise, with stirring, over 1 hour, while maintaining a pH of 3.0-4.0 with sodium carbonate solution, to give a grey solid. The solid, which gave a positive Ehrlich's test was filtered off, was re-dissolved in water (500 ml) and the pH raised to 10 with sodium carbonate solution. Further acryloyl chloride (12 ml; 96 % strength; 0.15 mol) was added and the pH allowed to fall. Sodium carbonate solution was added to raise the pH to10.7 and sodium chloride (10 %w/v) added to give a grey solid. The solid was filtered off, washed with brine (20 %; 400 ml), pulled down and oven-dried to give the product (51 g). HPLC showed a single

peak at t_R = 0.84 and mass spectral analysis (method B) gave a ions at m/z 305 $(M+Na)^+$(92), 283 $(M+H)^+$ (78). There was also a sodiumated dimer ion at m/z 587 $(2M+Na)^+$ (15). ^1H (300 MHz, NaOD): δ (ppm) = 5.50-5.54 (2 H, t, J 6.0 Hz, 2 x CH=), 5.97 (4 H, d, J 5.6 Hz, 2 x CH_2), 7.33 (2 H, s, ^{Ar}H) and 7.48 (1 H, s, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 115.1, 117.5, 128.5, 130.6, 137.9 and 138.0 (10 C, ^{Ar}C, -CH= and -CH_2=), 166.4 (2 C, C=O) and 171.1 (1 C, COOH).

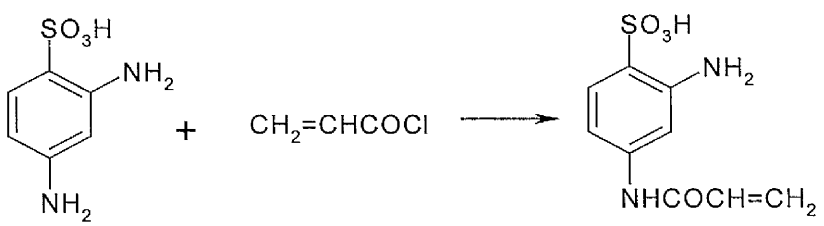
4.2.1.4 3,5-Bis-(γ-methoxypropionamido)benzoic acid (IV)



(IV)

To 3,5-diacrylamidobenzoic acid (0.7 g; 93.1% strength) and sodium carbonate (0.6 g) was added a mixture of methanol (24 ml) and water (12 ml) and the reaction mixture refluxed for 48 hrs. The solvent was removed on a rotary evaporator to give an off-white solid which was washed with acetone (20 ml), filtered and oven-dried at 40 °C to give the product (0.3 g). HPLC showed a single peak at t_R = 0.71 and mass spectral analysis (method A) gave a molecular ion at m/z 323 $(M-H)^-$(100).

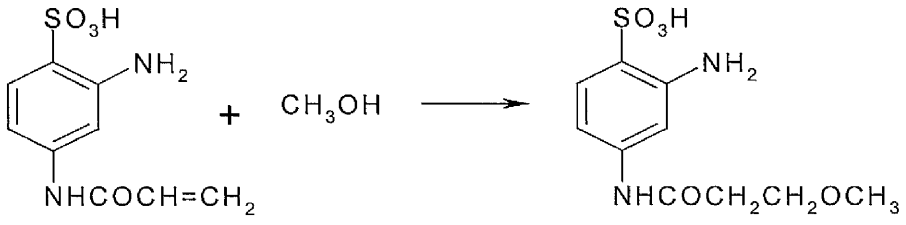
4.2.1.5 2-Amino-4-acrylamidobenzenesulphonic acid (V)



(V)

To water (200 ml) was added m-phenylenediaminesulphonic acid (94 g; 0.5 mol) and the pH was adjusted to 6.5. Acryloyl chloride (44 ml; 96 % strength; 0.51 mol) was added dropwise, at 0-3 °C, while maintaining the pH at 4.7-5.6 with a sodium carbonate solution (2 M). The reaction was stirred for 2 hrs, and salt (30 %w/v) added and stirring continued for a further 1 hr. The precipitate which formed was isolated by filtration, washed with saturated brine and dried at 40 °C to give the product (74.3 g). HPLC showed a single peak at t_R = 0.74 and mass spectral analysis (method A) gave a molecular ion at m/z 241 $(M-H)^-$(94). ^1H (300 MHz): δ (ppm) = 5.88-5.91 (1 H, dd, J 1.9 and 9.8 Hz, CH=), 6.31-6.37 (1 H, dd, J 1.5 and 16.9 Hz, CHH=), 6.40-6.48 (1 H, dd, J 9.8 and 16.9 Hz, CHH=), 6.92-6.96 (1 H, dd, J 1.9 and 8.7 Hz, ^{Ar}H), 7.17 (1 H, d, J 1.9 Hz, ^{Ar}H) and 7.62 (1 H, d, J 8.7 Hz, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 109.4, 110.6, 119.4, 128.7, 129.1, 130.6, 141.0 and 145.0 (8 C, ^{Ar}C, -CH= and $-CH_2=$), and 167.1 (1 C, C=O).

4.2.1.6 2-Amino-4-(γ-methoxypropionamido)benzenesulphonic acid (VI)

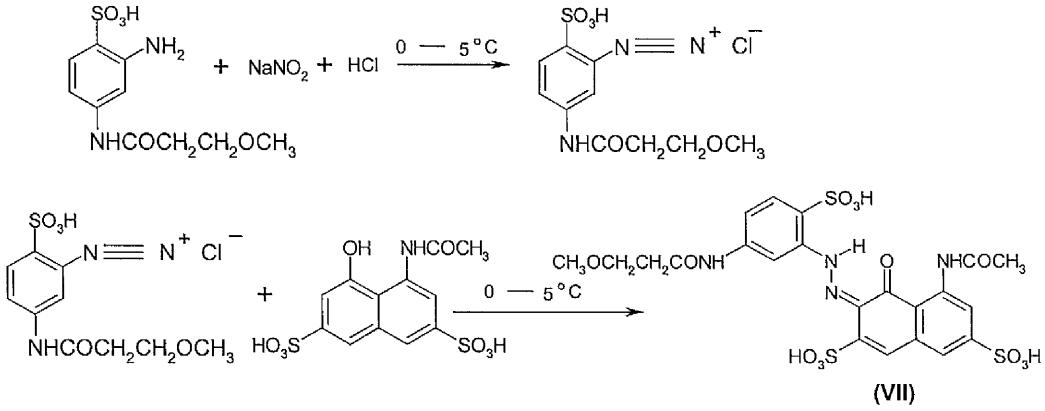


(VI)

To methanol (50 ml) and water (50 ml) was added, with stirring, 2-amino-4-acrylamidobenzenesulphonic acid (7 g) and sodium carbonate (1.8 g). The reaction mixture was heated under reflux for 48 hrs and the solvent (50 ml)

removed on a rotary evaporator. Salt (20 %w/v) was added to the remaining solution and the resulting precipitate isolated by filtration. The solid was dried at 40 °C to give the product (5.23 g). HPLC showed a single peak at t_R = 0.71 and mass spectral analysis (method A) gave a molecular ion at m/z 273 $(M-H)^-$(100). ^1H (300 MHz): δ (ppm) = 2.49 (2 H, t, J 5.6 Hz, $CH_2C=O$), 3.21 (3 H, s, OCH_3), 3.60 (2 H, t, J 5.6 Hz, CH_2O), 6.67 (1 H, d, J 8.3 Hz, ^{Ar}H), 6.92 (1 H, s, ^{Ar}H) and 7.43 (1 H, d, J 8.3 Hz, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 37.2 (1 C, OCH_3), 58.6 (1 C, CH_2), 68.6 (1 C, CH_2O), 109.6, 110.8, 127.2, 128.8, 141.2 and 145.3 (6 C, ^{Ar}C) and 165.1 (1 C, C=O).

4.2.1.7 8-Acetylamino-2-[5' (3''-methoxy)propionamido-2'-sulpho]phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (VII)



To water (20 ml) was added 2-amino-4-acrylamidobenzenesulphonic acid (4 g; 50.3 %; 7.6 mmol) and the solution cooled to 0-5 °C in an ice bath. Concentrated hydrochloric acid (4 ml) was added dropwise and pH dropped from 10.4 to 1, followed by sodium nitrite solution (6.8 ml; 1 M) while maintaining a temperature of 0-5 °C. After 30 minutes the reaction mixture was added to a solution of acetyl H-acid (2.75 g; 7 mmol) dissolved

water (20 ml), at 0-5 °C, and the pH was adjusted to 6.5 with a sodium carbonate solution (2 M). Potassium chloride (15 %w/v) was added and the reaction mixture stirred for a further 1 hr. The solid so formed was isolated by filtration, and air-dried to give a red solid (1.9 g). HPLC showed a single peak at t_R = 1.63, and mass spectral analysis (method A) gave ions at m/z 699 $(MNa_2\text{-}H)^-$(6), 683 $(MK\text{-}H)^-$(15), 667 $(MNa\text{-}H)^-$(48), and 645 $(M\text{-}H)^-$(85). ^1H (300 MHz): δ (ppm) = 2.37 (3 H, s, $CH_3C{=}O$), 2.66 (2 H, s, $CH_2C{=}O$), 3.34 (3 H, s, OCH_3), 3.74 (2 H, s, OCH_2), 7.42-7.68 (5 H, m, ^{Ar}H) and 8.82 (1 H, s, ^{Ar}H).

4.2.1.8 Diazotisation and coupling of the reaction mixture obtained after subjecting compound (II) to 130 °C and pH 4.5 for 1 hour.

Compound II (0.5 g; 79.6 %; 1 mmol) in pH 4.5 buffer solution (15 ml) was heated to 130 °C for 1 hr and the resultant solution cooled to 0-5 °C in an ice bath. Concentrated hydrochloric acid (4 ml) was added dropwise and the mixture titrated with standard 0.1 M sodium nitrite solution (2.8 ml). Excess nitrous acid was destroyed with sulphamic acid. The diazotisation solution was added to a suspension of acetyl H-acid (0.11 g, 0.3 mmol) at 0-5 °C and the pH raised to 6.5 with a sodium carbonate solution (2 M) to give a red dye. HPLC (programmes A,B and C) showed the dye to be identical to compound (VII).

4.2.3 Application of cross-linking agents to lyocell

Experiments were performed with "never-dried" lyocell fibres (1.3 dtex; 40mm staple) provided by Lenzing.

Cross-linking agents used:

2,4-diacrylamidobenzenesulphonic acid (I)

3,5-diacrylamidobenzoic acid (III)

Pad-Steam Method

Padding solutions were prepared using distilled water with the following composition:

Agent (x g/l, at 100 % strength) *

Sodium hydroxide (4 g/l)

Sodium sulphate (100 g/l)

"Never-dried" lyocell fibre was then impregnated in the pad liquor for 5 minutes at room temperature.

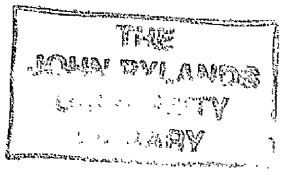
The fibre was squeezed at 3 bar pressure and 2 m/min speed.

The padded fibre was steamed at 100°C for 5 minutes.

After steaming, the fibre was rinsed in hot running water for 5 minutes, soaped at the boil for 10 minutes (soap concentration 1g/l; liquor ratio 50:1) and rinsed in cold running water for 5 minutes.

The washed fibre was air dried.

* (X=10, 20, 30, 40)



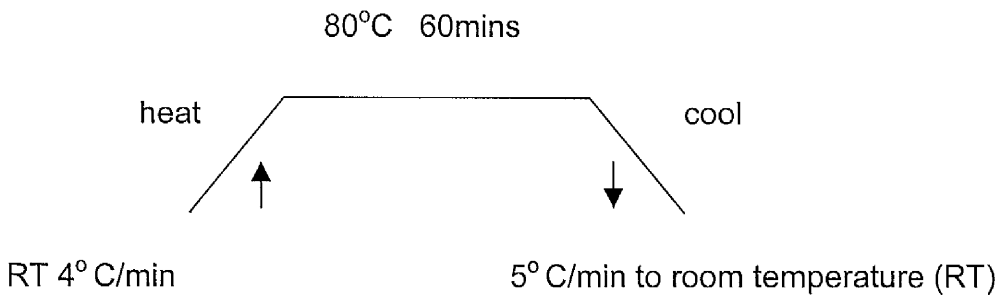
(The recipe of padding liquor and the Pad- Steam application process are adapted from Lenzing's standard application procedure for cross-linking chemicals.)

4.2.4 High temperature treatment

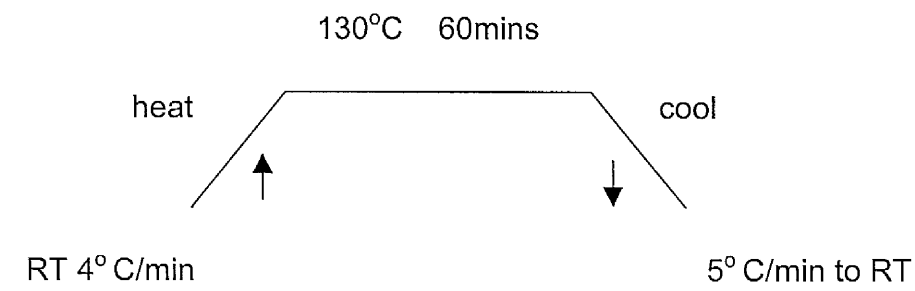
4.2.4.1 High temperature treatment of cross-linked lyocell

Cross-linked, "never-dried" lyocell was treated in the following manner: (a) at 80 °C and pH 11 for 60 minutes (to simulate hot reactive dyeing) ; (b) at 130 °C and, in turn, in buffer solutions of pH 4.5, 5.0, 6.0 and 7.5 for 60 minutes (to simulate HT dyeing of the polyester component of a polyester / lyocell blend). The treatments were performed in sealed stainless steel dye pots housed in a Mathis Labomat BFA 12 dyeing machine.

(a) Hot Reactive Dyeing Profile at pH 11



(b) High Temperature Polyester Dyeing Profile



4.2.4.2 High temperature treatment of model compound representing "lyocell-O-agent"

Each model "lyocell-O-agent" compound (0.5 g), in pH 4.5 buffer solution (20 ml), was heated at 130 °C for 60 minutes, the same with manner (b).

4.2.4.3 Preparation of buffer solutions

pH=4.5: 50ml of 0.1 molar potassium hydrogen phthalate + 8.7ml of 0.1 molar NaOH;

pH=5.0: 50ml of 0.1 molar potassium hydrogen phthalate + 22.6ml of 0.1 molar NaOH;

pH=6.0: 50ml of 0.1 molar potassium dihydrogen phosphate + 5.6ml of 0.1 molar NaOH;

pH=7.5: 50ml of 0.1 molar potassium dihydrogen phosphate + 40.9ml of 0.1 molar NaOH.

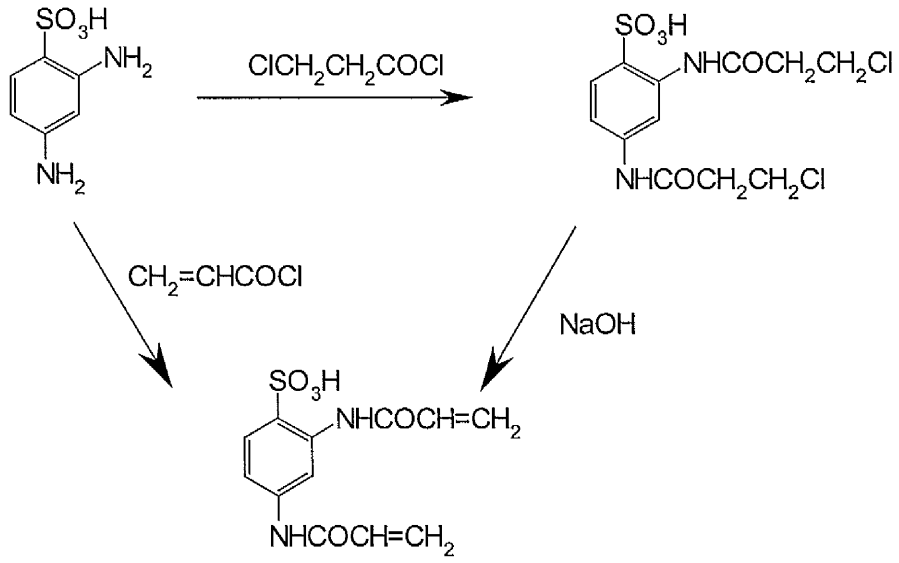
4.3 Results and discussion

4.3.1 Technical assessment of novel cross-linking Agent (I)

4.3.1.1 Advantages of cross-linking Agent (I)

To design a cross-linking agent the presence of an anionic group was considered essential to satisfy the criteria of good water solubility, low vapour pressure and low toxicity. Acrylamido reactive groups were selected for the cross-linking reaction. Although the Michael addition products are susceptible to base catalysed β-elimination they are more robust than the related vinyl sulphone products. Triazine chemistry was

ruled out on the basis of the sensitivity of alkyl triazinyl ethers to hot acid environments. 2,4-Diaminobenzenesulphonic acid was selected as starting material being a low cost industrial scale intermediate. Acryloylation of this intermediate furnishes the novel cross-linking agent (I; Scheme 4.1)



Agent (I)

Scheme 4.1

The cross-linking Agent (I) can be prepared directly with acryloyl chloride as acrylating agent, or indirectly with 3-chloropropionyl chloride followed by base catalysed β-elimination. All reactions were performed in water as solvent.

Agent (I) is colourless with good water solubility and was applied to both dry and never-dried lyocell by a pad-steam method. The wet abrasion values (NSF) were measured with a Delta 100 instrument (see Chapter 3 Experimental). Such values are a good indicator [72, 106] of fibre cross-linking and are shown in Figure 4.1.

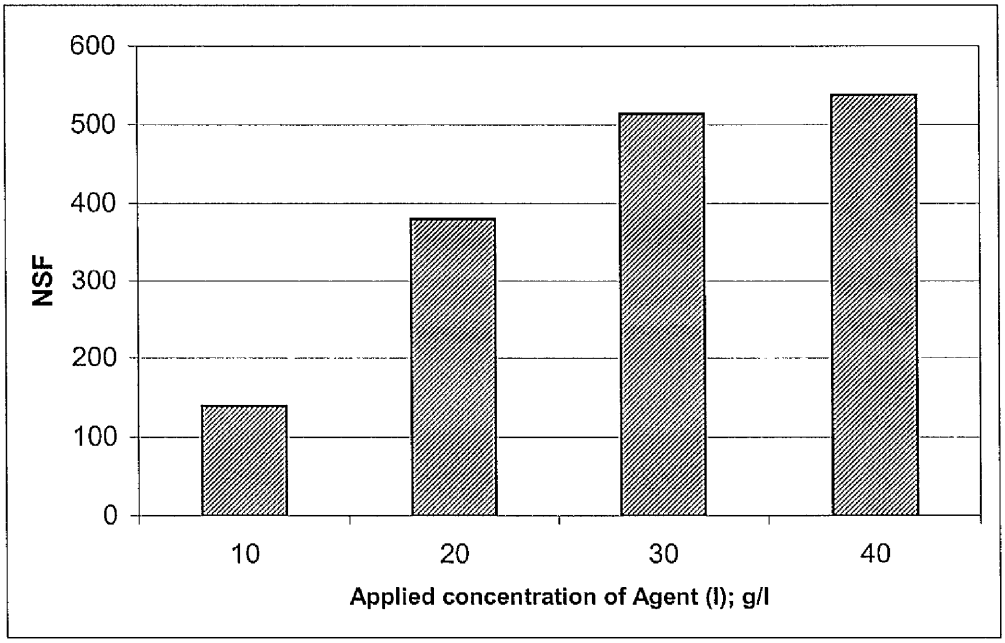


Figure 4.1 Wet abrasion resistance (NSF) of lyocell cross-linked with different concentrations of Agent (I)

As can be seen from Figure 4.1, the wet abrasion resistance of lyocell increases as the concentration of Agent (I) increases. The NSF values gradually reach a plateau with increasing concentrations of Agent (I), indicating that there is an optimal concentration for the application of Agent (I) to achieve the best results. Furthermore, Agent (I) proved to be a good cross-linking agent giving NSF values comparable to those exhibited by commercial agents Tencel LF and Tencel A100.

4.3.1.2 Stability of the lyocell-O-agent bonding

To evaluate the stability of the lyocell-O-agent bonding, the cross-linked fibre was subjected, in turn, to hot reactive dyeing conditions (1 hour at 80°C and pH 11) and to polyester dyeing conditions (1 hour at 130°C and over a range of pH values) and the NSF values re-measured. The results are shown in Figures 4.2 and 4.3.

Figure 4.2 shows lyocell–O-Agent (I) bonds to be stable to hot reactive dyeing conditions. The slight increase in NSF values at the higher concentrations may be attributed to some mono attached agent undergoing cross-linking.

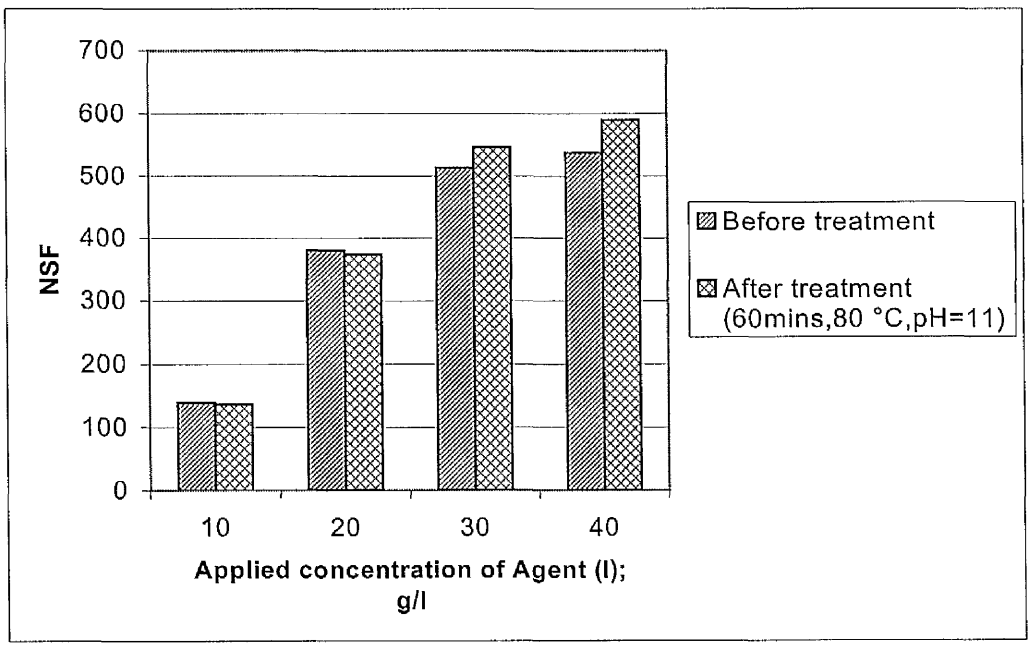


Figure 4.2 Wet abrasion resistance (NSF) of cross-linked lyocell after treatment under hot reactive exhaust dyeing conditions

Figure 4.3 shows significant instability of the lyocell-O-Agent (I) bonds to high temperature (HT) polyester dyeing conditions at pH 4.5 and 5.0. This was particularly so at pH 4.5 and 40 g/l applied agent where approximately 50% reduction in NSF value was found. Consequently, investigation was carried out to find out why the lyocell-O-Agent (I) bonding was not stable to HT polyester dyeing conditions, particularly at the more acidic pH values.

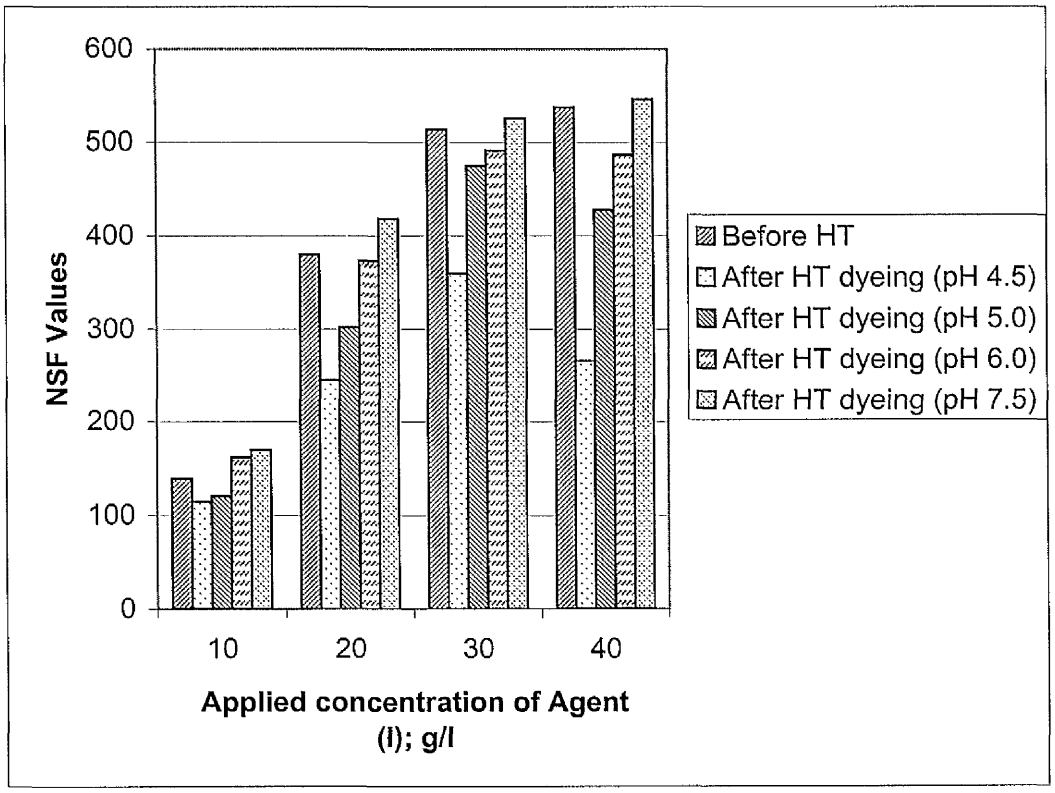


Figure 4.3 Wet abrasion resistance (NSF) of cross-linked lyocell under HT polyester dyeing conditions (1 hour at 130 °C), carried out at different pH values

4.3.2 Investigation of the instability of the lyocell-O-agent bonding under high temperature (HT) polyester dyeing conditions

The instability of lyocell-O-Agent (I) bonding to high temperature polyester dyeing conditions was initially unexpected, as the structurally related 1,3,5-triacryloyl-hexahydro-s-triazine gives stable lyocell-O-agent bonding under the same conditions. Nitrogen analysis of the lyocell fibre, cross-linked with Agent (I), before and after HT polyester dyeing conditions was unchanged, indicating that despite the fall in NSF values, the cross-linking agent was still attached to the fibre.

4.3.2.1 Amide bond cleavage via a neighbouring group participation mechanism

To investigate what may have occurred, a model ether (II) was synthesised to simulate the attachment of lyocell to Agent (I) and then the model compound subjected to high temperature treatment over a range of acid pH values.

At pH 4.5 and 5.0 the appearance of a small new peak at t_R 0.65 was observed by HPLC (Agent II; t_R 0.87). In addition, it was also found that the more acidic the pH, the greater the percentage of this small new peak, as shown by Table 4.1. The evidence suggested that a reaction had taken place during the HT treatment, with the lowest pH being most favourable.

Table 4.1
Ratio of new peak observed by HPLC

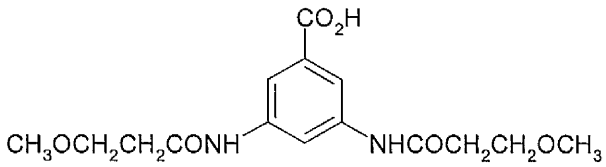
pH	Ratio of new peak to original peak *
5	13.5%
4.5	24.3%
4	32.6%

* Ratio of new peak to original peak= (Area percentage of the new peak) / (Area percentage of the original peak)

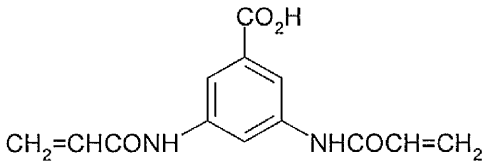
Moreover, subjecting cross-linking Agent (I) to a similar treatment also brought about a chemical change and a lower retention time product was also detected by HPLC.

At this stage it was suspected that the presence of the sulphonic acid group was exerting a neighbouring group influence on the stability of

Agents (I) and (II). Accordingly, Agent (IV) was synthesised and subjected to high temperature treatment as before (see 4.2 Experimental).



Agent (IV)



Agent (III)

For Agent (IV) at pH 4.5, 5.0 and 6.0 no chemical change was observed after one hour at 130°C supporting the view that degradation of Agents (I) and (II) was related to the presence of the *ortho* sulphonic acid group. Further support was given by the application of cross-linking Agent (III) to lyocell, followed by treatment of the cross-linked fibres for one hour at 130°C, and pH 4.5. No significant decrease in NSF values was found (Figure 4.4).

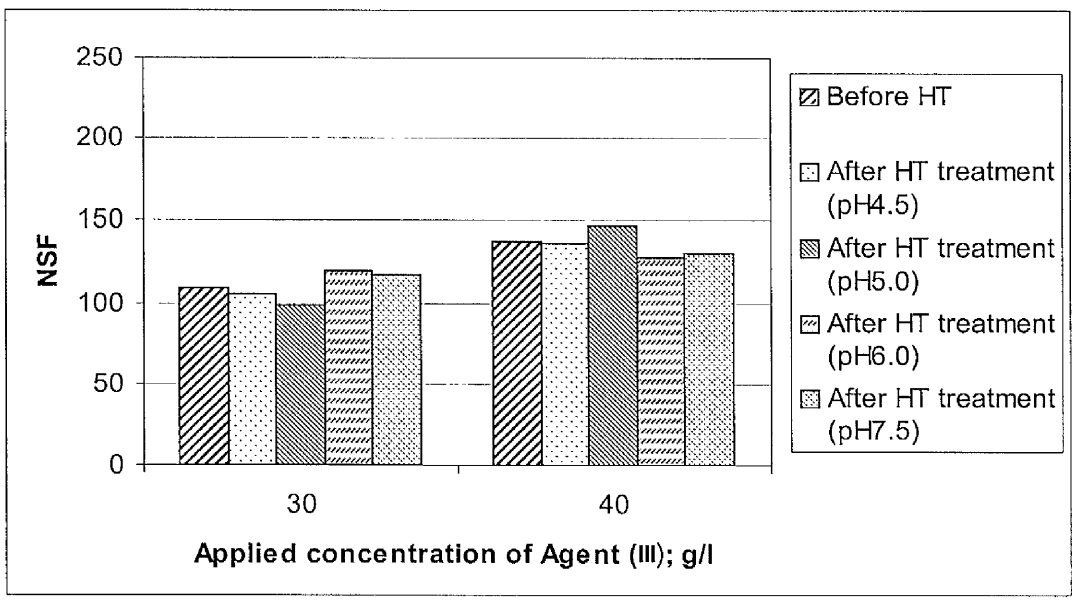
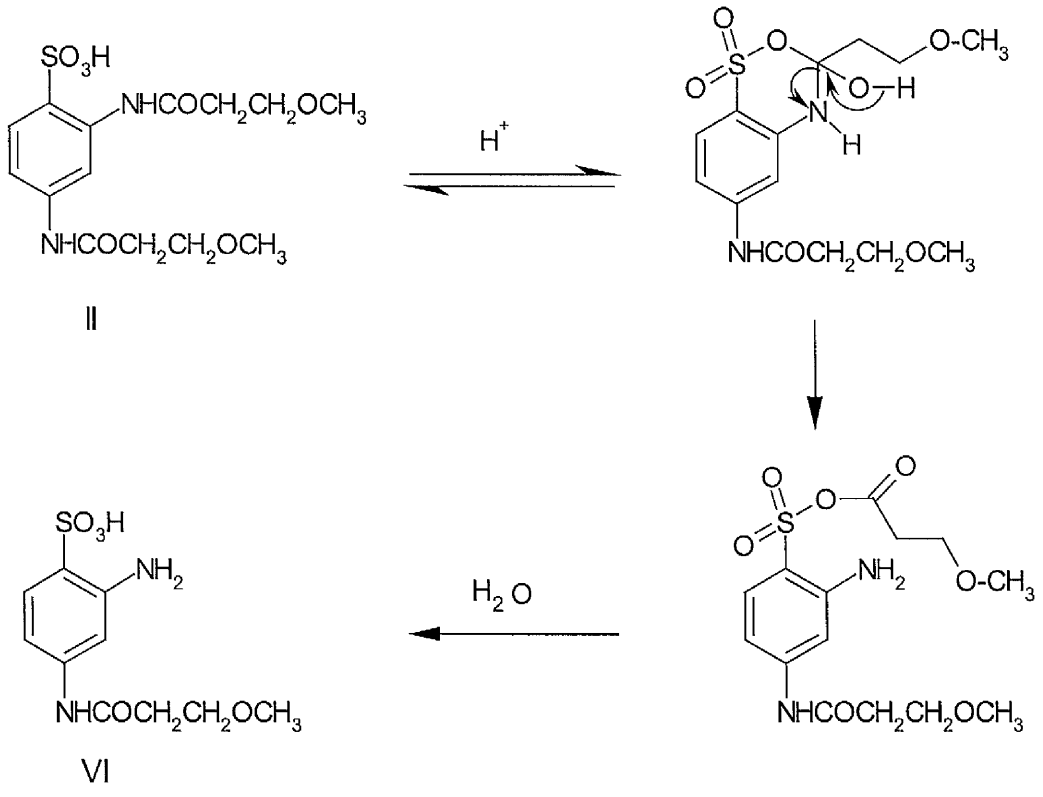


Figure 4.4 Wet Abrasion resistance (NSF) of lyocell, cross-linked with Agent (III), after HT (130°C) polyester dyeing conditions for 60mins at different pH values .

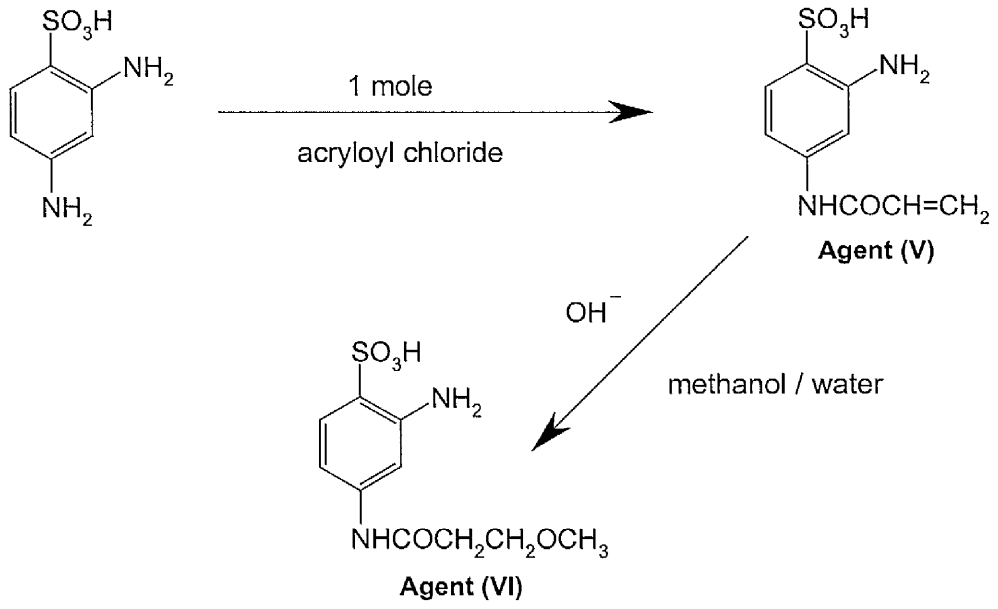
Initial findings suggested that, under high temperature polyester dyeing conditions, hydrolysis of the amide link *ortho* to the sulphonic acid group may be taking place. The sterically favourable position of the SO_3^- group can furnish a six-membered intermediate on protonation of the amide group (Scheme 4.2). It is known that the neighbouring group mechanism operates effectively only for certain ring sizes with the most rapid reactions occurring for 3, 5 and 6 membered rings [146]. Anchimeric assistance by sulphonic acid groups has not been reported previously. Scheme 4.2 shows protonation of the amide group on the carbonyl oxygen atom, although some amides can protonate on nitrogen [147].



Scheme 4.2

4.3.2.2 Investigation of the hydrolysis product

To further investigate the anchimeric assistance hypothesis, 2-amino-4-(γ-methoxy-propionamido)benzene sulphonic acid (VI; Scheme 4.3) was synthesised and the product shown to be identical, by HPLC, to the hydrolysis product formed by subjecting Agent (II) to HT polyester dyeing conditions at pH 4.5. However, formation of the other isomer of (VI) could not be completely ruled out.



Scheme 4.3

The reaction mixture obtained by subjecting a solution of the model bis-methyl ether (II) to HT polyester dyeing conditions (60mins @ 130°C) at pH 4.5 was titrated with sodium nitrite solution (see 4.2 Experimental) to determine the concentration of primary amine present. The results are shown in Table 4.2.

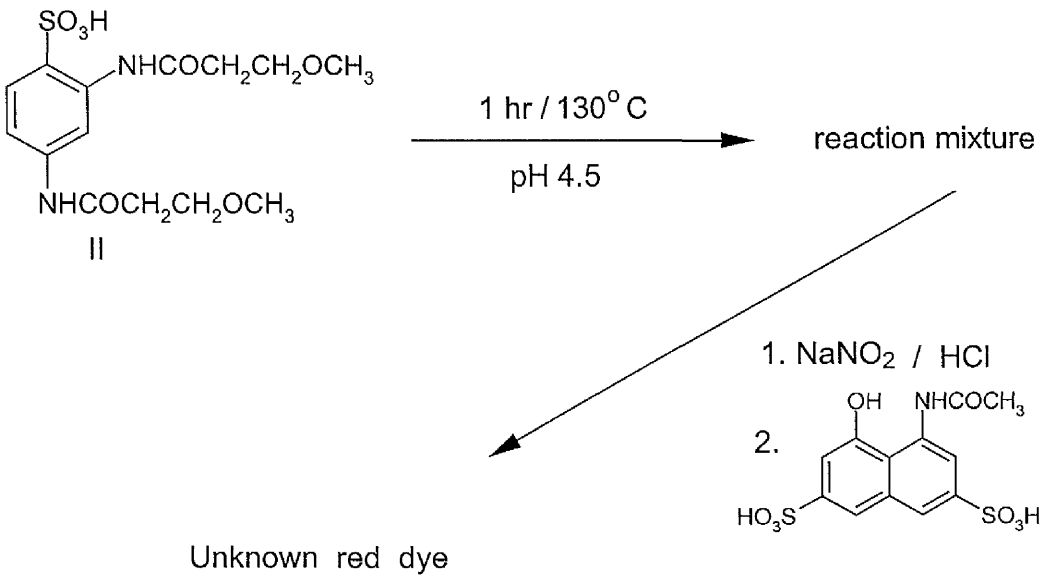
Table 4.2

Titration of the reaction mixture obtained from high temperature treatment of Agent (II) for 1 hour at 130°C and pH 4.5.

No.	Weight of Agent (II) subjected to HT acidic dyeing conditions	Titre (0.1 M $NaNO_2$)	Percentage of primary amine in reaction mixture
1	0.5 g (strength 73.0 %)	2.6 ml	27.2 %
2	0.5 g (strength 73.0 %)	2.75 ml	28.8 %

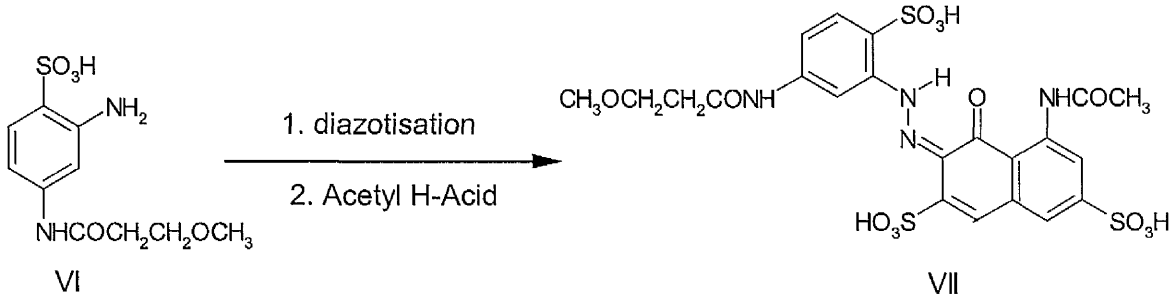
Accordingly, subjecting the model compound to polyester dyeing conditions at pH 4.5, resulted in approximately 28% amide hydrolysis. Consequently, if a similar hydrolysis took place for lyocell, cross-linked with the bis-acrylamido Agent (I), a significant reduction in NSF would be expected.

To further investigate the product of the bond cleavage reaction, the diazo solutions from the sodium nitrite titrations were coupled with acetyl H-acid (8-acetylamino-1-naphthol-3,6-disulphonic acid) to give an unknown red dye (Scheme 4.4).



Scheme 4.4

The anticipated product formed in Scheme 4.4 above was unambiguously synthesised as shown in Scheme 4.5.



Scheme 4.5

Dye (VII) and the unknown dye (Scheme 4.5) were analysed individually and in admixture using three different HPLC programmes (see Chapter 3 Experimental) and the results shown in Table 4.3. HPLC analyses of the mixture resulted in a single peak for the three methods used. Virtually identical retention times, t_R, for the individual analyses and the appearance

only of a single peak for the mixtures strongly supported the hypothesis that the unknown dye (Scheme 4.4) and dye VII (Scheme 4.5) were identical.

Table 4.3
HPLC Retention Times

Programme	Dye VII t_R	Unknown Dye t_R	Mixture t_R
A	0.77	0.77	0.82
B	4.97	4.99	4.98
C	1.62	1.60	1.71

Virtually superimposible visible spectral curves for dye (VII; λ_{max} 503), and for a solution of the unknown red dye (λ_{max} 505), prepared as shown in Scheme 4.5, provided additional support.

4.4 Conclusions

2,4-Diacrylamidobenzenesulphonic acid (Agent I), applied by a pad-steam process, is an effective cross-linking agent for lyocell. The lyocell-O-agent bonds, so generated, are stable to hot reactive dyeing but show some instability to HT polyester dyeing conditions, particularly at pH 4.5. This has been rationalised in terms of acid catalysed hydrolysis of the amide bond *ortho* to the sulphonic acid group via a neighbouring group participation mechanism.

CHAPTER 5

STABILITY OF BENZENEACRYLAMIDO DERIVATIVES TO HIGH TEMPERATURE ACIDIC ENVIRONMENTS

5.1 INTRODUCTION

This work was undertaken to further test the validity, and to explore the generality, of the hypothesis proposed in the previous chapter, i.e. the neighbouring group participation mechanism that results in the hydrolysis of amide bonds.

To this end, a series of benzeneacrylamido derivatives, each with at least one sulpho or carboxyl group, has been synthesised. The carboxylic acid group was *ortho* to the amide bond for compound **2-acrylamidobenzoic acid (I)**. The sulphonic acid groups were either *meta* or *para* to the amide bond for compounds **3-acrylamidobenzensulphonic acid (III)** and **4-acrylamidobenzenesulphonic acid (VII)** respectively, while *ortho* for compound **2-acrylamidobenzenesulphonic acid (V)**.

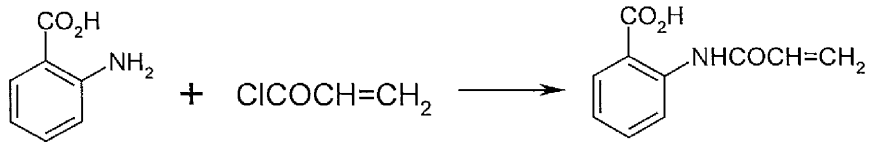
Similar to previous studies, these compounds were converted to their corresponding methyl ethers, and each derivative was dissolved in pH 4.0 buffer solution and subjected to high temperature (HT) polyester dyeing conditions (130 ^{o}C) for one hour.

Three techniques were used to investigate the stability of the amide bond under HT treatment conditions. The products obtained after HT treatment were analysed by HPLC to detect the formation of new band. They were also titrated with sodium nitrite solution to test the generation of aromatic primary amine. Furthermore, an unknown dye was synthesised by diazotisation of each hydrolysed product with sodium nitrite solution and coupling with 8-acetylamino-1-naphthol-3,6-disulphonic acid (Acetyl H-Acid). The dye's retention time and visible spectral curves were compared with that of the anticipated product.

5.2 Experimental

5.2.1 Syntheses

5.2.1.1 2-Acrylamidobenzoic acid (I)



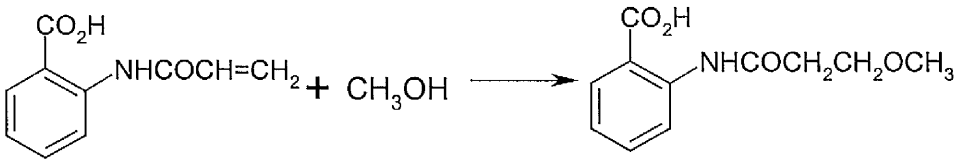
(I)

To anthranilic acid (14 g; strength 98 %; 0.1 mol) in deionised water (60 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0-5 °C and acryloyl chloride (10.46 ml; d = 1.114; strength 98 %; 0.124 mol) added dropwise, with stirring, while maintaining a pH of 4.5-5.5 with sodium carbonate solution (2 M). The reaction was continued for 35 hours to give a white precipitate. HPLC of the

reaction mixture showed 85 % conversion to a new product, t_R = 1.65 (starting material; t_R = 1.22). The precipitate was filtered off, washed with 10% brine, and air dried to give a white solid (18.9 g). HPLC showed a single peak at t_R = 1.59, mass spectral analysis gave ions at m/z 190 $(M-H)^-$(88) and 146 $(M-H-CO_2)^-$(100).

^{1}H (300 MHz, D_2O and NaOD): δ (ppm) = 5.55-5.58 (1 H, dd, *J* 2.3 and 9.0, CH=), 6.93-6.09 (2 H, m, CH_2=), 6.84-6.89 (1 H, td, *J* 0.76 and 7.5, ^{Ar}H), 7.11-7.16 (1 H, tt, *J* 0.75 and 7.5, ^{Ar}H), 7.56-7.59 (1 H, dd, *J* 1.5 and 7.9, ^{Ar}H) and 7.84 (1 H, d, *J* 8.3, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 120.8, 124.1, 124.9, 127.8, 131.0, 132.0, 132.2 and 138.4 (8 C, 6 x ^{Ar}C, CH= and CH_2=), 174.7 and 166.4 (2 C, C=O and COONa).

5.2.1.2 2-(*γ*-Methoxy)propionamidobenzoic acid (II)



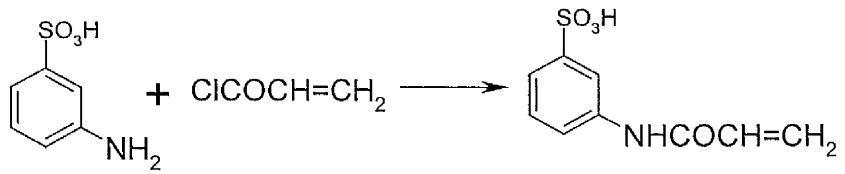
(II)

To methanol (100 ml) and water (50 ml) was added, with stirring, 2-acrylamidobenzoic acid (8.0 g) and sodium carbonate (1.6 g) and the reaction mixture heated under reflux for 40 hrs. The solvent was removed on a rotary evaporator to give a solid, which was lixiviated in acetone (100 ml), filtered off, and oven dried, at 40 °C, to give the product (8.1 g). HPLC

showed a single peak at t_R = 1.68, mass spectral analysis gave ions at m/z 244 $(M-2H+Na)^-$(5) and 222 $(M-H)^-$(100).

^1H (300 MHz): δ (ppm) = 2.57 (2 H, t, *J* 6.0, $CH_2C=O$), 3.25 (3 H, s, OCH_3), 3.65 (2 H, t, *J* 6.0, CH_2O), 7.04-7.1 (1 H, td, *J* 1.1 and 7.9, ^{Ar}H), 7.31-7.37 (1 H, td, *J* 1.5 and 7.15, ^{Ar}H), 7.70 (1 H, dd, *J* 1.5 and 7.54, ^{Ar}H) and 7.97 (1 H, d, *J* 7.91, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 38.0 (1 C, OCH_3), 58.5 (1 C, $CH_2C=O$), 68.4 (1 C, CH_2O), 121.4 and 124.5 (2 C, 2 x ^{Ar}C), 125.0 (1 C, ^{qAr}C), 130.8 and 131.9 (2 C, 2 x ^{Ar}C), 136.0 (1 C, ^{qAr}C), 167.9 and 175.0 (2 C, C=O and COOH).

5.2.1.3 3-Acrylamidobenzensulphonic acid (III)



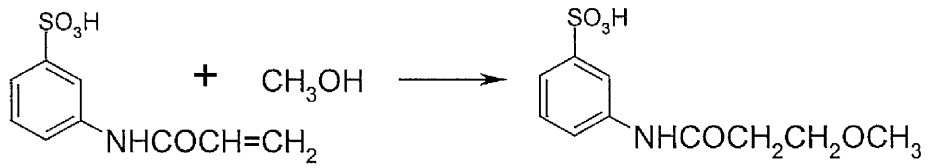
(III)

To *m*-aminobenzenesulphonic acid (17.3 g; strength 98 %; 0.1 mol) in deionised water (50 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0-5 °C and acryloyl chloride (8.5 ml; strength 98 %; d = 1.1; 0.1 mol) added dropwise, with stirring, while maintaining a pH of 4.5-5.5 with sodium carbonate solution (2 M). The reaction was continued for 24 hours and HPLC showed 94 % conversion to a new product, t_R = 0.86 (starting material, t_R = 0.66). Sodium chloride (82.5 g; 25 %w/v) was added portionwise, with stirring, to give a

precipitate which was filtered off, and oven dried at 40 °C to give a white solid (8.1 g). HPLC showed a single peak at t_R = 0.88 and mass spectral analysis gave a molecular ion at m/z 226 $(M-H)^-$(100).

^{1}H (300 MHz): δ (ppm) = 5.70-5.74 (1 H, dd, *J* 3.3 and 8.3, CH=), 6.14-6.28 (2 H, m, CH_2=), 7.34 (1 H, t, *J* 7.9, ^{Ar}H), 7.45 (2 H, t, *J* 7.9, ^{Ar}H) and 7.86 (1 H, s, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 118.3, 122.4, 124.2, 129.1, 130.2, 130.5 (6 C, 6 x ^{Ar}C), 137.8 and 143.5 (2 C, 2 x ^{qAr}C), and 167.1 (1 C, C=O).

5.2.1.4 3-(γ-Methoxy)propionamidobenzenesulphonic acid (IV)



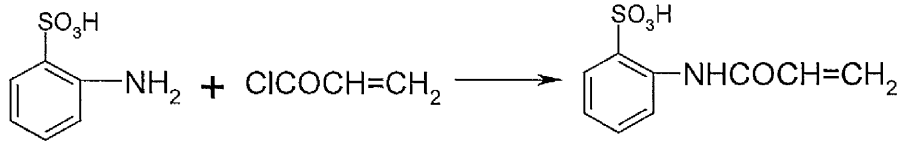
(IV)

To methanol (60 ml) and water (30 ml) was added, with stirring, 3-acrylamidobenzenesulphonic acid (2.5 g) and sodium carbonate (0.5 g) and the reaction mixture heated under reflux for 40 hrs. The solvent was removed on a rotary evaporator to give a solid which was lixiviated in acetone (80 ml), filtered off, and oven dried, at 40 °C to give the product (1.28 g). HPLC showed a single peak at t_R = 0.92, mass spectral analysis gave a molecular ion at m/z 258 $(M-H)^-$(100) and 226 $(M-H-CH_3OH)^-$(75).

^{1}H (300 MHz): δ (ppm) = 2.56 (2 H, t, *J* 6.02, CH_2C=O), 3.25 (3 H, s, OCH_3), 3.65 (2 H, t, *J* 6.03, CH_2O), 7.38 (1 H, t, *J* 7.91, ^{Ar}H), 7.45-7.49 (2 H, m, ^{Ar}H)

and 7.78 (1 H, s, 2-^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 36.9 (1 C, OCH_3), 58.4 (1 C, $CH_2C{=}O$), 68.4 (1 C, CH_2O), 118.6, 122.4, 124.6 and 130.2 (4 C, 4 x ^{Ar}C), 137.7 and 143.5 (2 C, 2 x ^{qAr}C), 168.1 (1 C, C=O).

5.2.1.5 2-Acrylamidobenzenesulphonic acid (V)

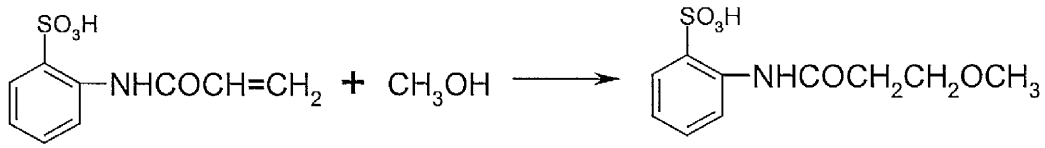


(V)

To orthanilic acid (14.3 g; strength 80.6 %; 0.067 mol) in deionised water (60 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0-5 °C and acryloyl chloride (10.5 ml; d = 1.114; strength 98 %; 0.127 mol) added dropwise, with stirring, while maintaining a pH of 4.5-5.5 with sodium carbonate solution (2 M). The reaction was continued for 35 hrs, and HPLC showed 81 % conversion to a new product, t_R = 0.99 (orthanilic acid, t_R = 0.76). Salt (15 %w/v) was added and the reaction mixture stirred for a further 30 mins. The precipitate was filtered off, washed with 20 % brine and air dried to give a white solid (18.9 g). HPLC showed a single peak at t_R = 0.98 and mass spectral analysis gave a molecular ion at m/z 226 $(M-H)^-$(100).

^{1}H (300 MHz): δ (ppm) = 5.84 (1 H, m, CH=), 6.23-6.41 (2 H, m, CH_2=), 7.28 (1 H, t, *J* 7.5, ^{Ar}H), 7.48-7.53 (1 H, td, *J* 0.75 and 7.54, ^{Ar}H), 7.80 (2 H, d, *J* 7.91, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 125.4, 126.4, 127.8, 129.2, 131.0, 132.7, 133.5 and 134.6 (8 C, 6 x ^{Ar}C, CH= and CH_2=), and 167.3 (1 C, C=O).

5.1.2.6 2-(γ-Methoxy)propionamidobenzenesulphonic acid (VI)

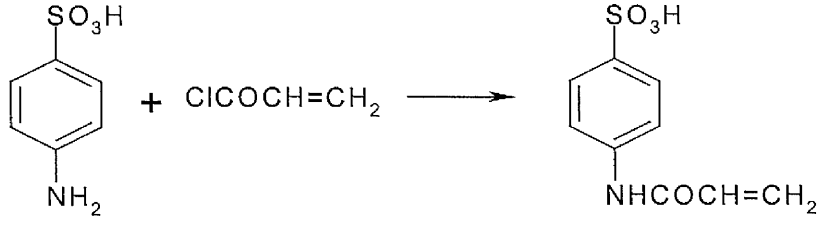


(VI)

To methanol (110 ml) and water (50 ml) was added, with stirring, 2-acrylamidobenzenesulphonic acid (12 g) and sodium carbonate (1.8 g). The reaction mixture was heated under reflux for 40 hours and then the solvent removed on a rotary evaporator to give a white solid. The solid was lixivated in acetone (100 ml), filtered off, and oven dried at 40 °C to give the product (14.8 g). HPLC showed a single peak at t_R = 0.92, mass spectral analysis gave ions at m/z 258 $(M-H)^-$(56) and 226 $(M-H-CH_3OH)^-$(9).

^1H (300 MHz): δ (ppm) = 2.65 (2 H, t, *J* 5.7, $CH_2C=O$), 3.31 (3 H, s, OCH_3), 3.70 (2 H, t, *J* 5.8, CH_2O), 7.26 (1 H, t, *J* 7.53, ^{Ar}H), 7.45-7.51 (1 H, td, *J* 1.1 and 7.91, ^{Ar}H), 7.74-7.80 (2 H, td, *J* 1.1 and 7.91, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 37.3 (1 C, OCH_3), 58.5 (1 C, $CH_2C=O$), 68.2 (1 C, CH_2O), 125.7, 126.3, 127.7 and 132.6 (4 C, 4 x ^{Ar}C), 133.5 and 134.6 (2 C, 2 x ^{qAr}C), 173.3 (1 C, C=O).

5.2.1.7 4-Acrylamidobenzenesulphonic acid (VII)

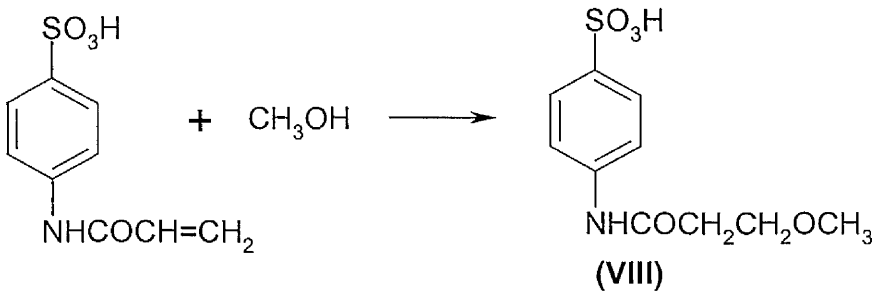


(VII)

To sulphanilic acid (14.58 g; MW = 173.19; strength 99 %; 0.083 mol) in deionised water (50 ml) was added sodium hydroxide solution (2 M) to give a clear solution at pH 6.5. The solution was cooled to 0-5 °C and acryloyl chloride (20.5 ml; MW = 90.51; d = 1.114; strength 96 %; 0.24 mol) added dropwise, with stirring, while maintaining a pH of 4.5-5.5 with a sodium carbonate solution (2 M). The reaction was continued for 24 hours and HPLC showed 93 % conversion to a new product, t_R = 0.77 (starting material; t_R = 0.98). Salt (18 % w/v) was added and the reaction mixture stirred for a further 30 mins. The precipitate was filtered off, and then dried in the air to give a white solid (8.26 g). HPLC showed a single peak at t_R = 0.78 and mass spectral analysis gave a molecular ion at m/z 226 $(M-H)^-$ (100).

^1H (300 MHz): δ (ppm) = 5.77-5.81 (1 H, dd, *J* 2.64 and 9.04, CH=), 6.20-6.35 (2 H, m, CH_2=), 7.54 (2 H, d, *J* 8.66, ^{Ar}H), 7.67-7.72 (2 H, dt, *J* 1.88 and 8.67, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 121.4 and 126.9 (4 C, 4 x ^{Ar}C), 129.4 and 130.6 (2 C, 2 x C=C), 138.71 and 140.2 (2 C, 2 x ^{qAr}C), 167.2 (1 C, C=O).

5.2.1.8 4-(*γ*-Methoxy)propionamidobenzensulphonic acid (VIII)



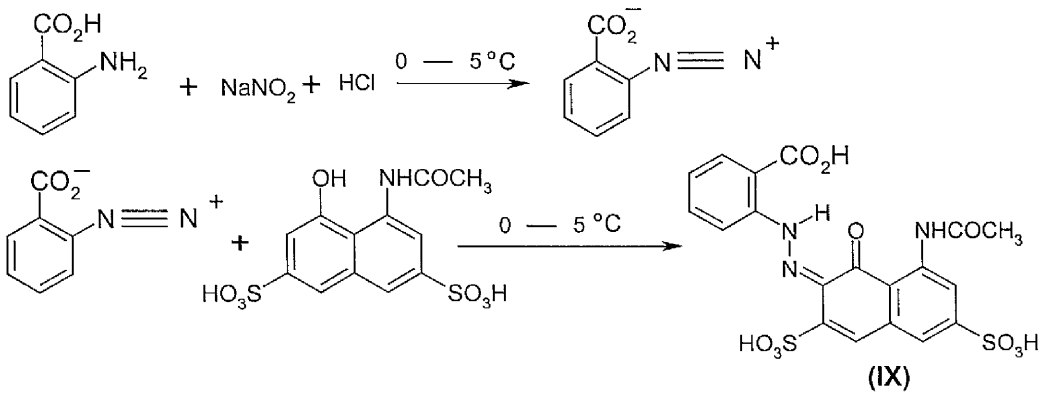
(VIII)

To methanol (80 ml) and water (40 ml) was added, with stirring, 4-acrylamidobenzenesulphonic acid (5.3 g) and sodium carbonate (1.45 g) and the reaction mixture heated under reflux for 35 hrs. The solvent was removed on a rotary evaporator to give a solid which was lixiviated in acetone (80 ml), filtered off, and oven dried, at 40 °C to give the product (6.7 g). HPLC showed a single peak at t_R = 0.85, mass spectral analysis gave a molecular ion at m/z 258 (M-H)$^-$ (100) and 226 (M-H-CH_3OH)$^-$ (38).

^{1}H (300 MHz): δ (ppm) = 2.64 (2 H, t, *J* 6.02, CH_2C=O), 3.29 (3 H, s, OCH_3), 3.70 (2 H, t, *J* 6.02, CH_2O), 7.51 (2 H, d, *J* 8.67, ^{Ar}H), 7.70 (2 H, d, *J* 8.67, ^{Ar}H). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 37.1 (1 C, OCH_3), 58.5 (1 C, CH_2C=O), 68.5 (1 C, CH_2O), 121.6 and 126.9 (4 C, 4 x ^{Ar}C), 138.71 and 140.02 (2 C, 2 x ^{qAr}C), 167.42 (1 C, C=O).

5.2.1.9

8-Acetylamino-2-(2'-carboxy)phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (IX)



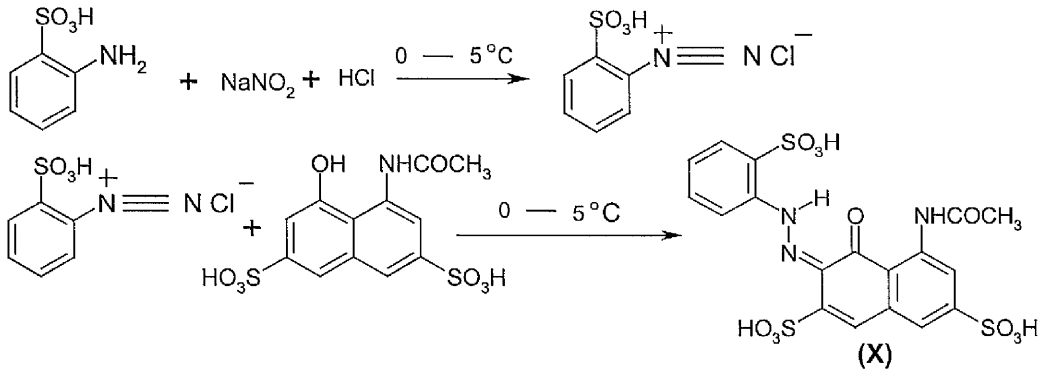
(IX)

To water (30 ml) was added anthranilic acid (0.98 g; strength 98 %; 7 mmol)

and the solution was cooled to 0-5 °C in an ice bath. Concentrated hydrochloric acid (4 ml) was added dropwise followed by sodium nitrite solution (7 ml; 1 M) with stirring while maintaining a temperature of 0-5 °C. After 25 mins the reaction mixture was added to a solution of acetyl H-acid (2.82 g; MW = 405; 7 mmol) dissolved in water (15 ml) at 0-5 °C, and the pH was adjusted to 6.5 with a sodium carbonate solution (2 M). Potassium chloride (17 % w/v) was added and the reaction mixture stirred for a further 1 hr. The solid so formed was isolated by filtration, and air dried to give a red solid (1.42 g). HPLC showed a single peak at t_R = 1.62, mass spectral analysis gave a molecular ion at m/z 508 $(M-H)^-$(100) and 530 $(M-2H+Na)^-$(30).

^{1}H (300 MHz): δ (ppm) = 2.05 (3 H, s, CH_3), 6.89 – 6.95 (1 H, t, *J* 7.9, ^{Ar}H), 7.15 (1 H, d, *J* 7.9, ^{Ar}H), 7.38 – 7.43 (1 H, t, *J* 7.5, ^{Ar}H), 7.54 (2 H, d, *J* 5.27, ^{Ar}H), 8.06 (1 H, d, *J* 5.3, ^{Ar}H) and 8.30 (1 H, s, ^{Ar}H).

5.2.1.10 8-Acetylamino-2-(2′-sulpho)phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (X)



To water (35 ml) was added orthanilic acid (2 g; strength 95 %; 11 mmol)

and the solution cooled to 0-5 °C in an ice bath. Concentrated hydrochloric acid (5 ml) was added dropwise followed by sodium nitrite solution (11 ml; 1 M), with stirring, while maintaining a temperature of 0-5 °C. After 30 mins the reaction mixture was added to a solution of acetyl H-acid (4.5 g; 11 mmol) dissolved in water (20 ml) at 0-5 °C, the pH adjusted to 6.5 with sodium carbonate solution (2 M) and stirring continued for 3 hrs. Potassium chloride (18 %w/v) was added and the reaction mixture stirred for a further 1 hr. The solid so formed was isolated by filtration, and air dried to give a red solid (2.1 g). HPLC showed a single peak at t_R = 1.65, mass spectral analysis gave ions at m/z 566 $(M-2H+Na)^-$(10) and 544 $(M-H)^-$(100).

^{1}H (300 MHz, D_2O): δ (ppm) = 2.31 (3 H, s, CH_3), 7.21 (1 H, t, *J* 7.54, ^{Ar}H), 7.52 (1 H, t, *J* 7.91, ^{Ar}H), 7.62-7.74 (3 H, m, ^{Ar}H), 8.01 (1 H, d, *J* 8.29, ^{Ar}H), 8.77 (1 H, s, 8-H).

5.2.1.11 Diazotisation and coupling of the reaction mixture obtained after subjecting Agents (II and VI) to 130 °C and pH 4.0 for 1 hour.

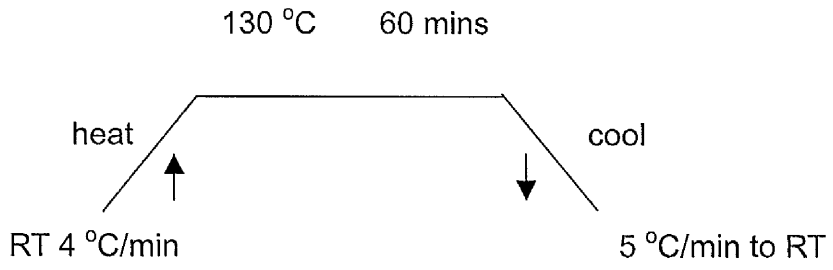
Both Agent II and Agent VI (0.5 g) were, in turn added to a pH 4.0 buffer solution (20 ml), which were heated to 130 °C for 1 hr and the resultant solution cooled to 0-5 °C in an ice bath. Concentrated hydrochloric acid (2 ml) was added dropwise and the mixture titrated with standard 0.1 M sodium nitrite solution to a positive 15 minute sulphone indicator end-point. Excess nitrous acid was destroyed with sulphamic acid. The diazotisation

solution was added to a suspension of acetyl H-acid (0.093 g) at 0-5 °C and the pH raised to 6.5 with a sodium carbonate solution (2 M) to give a red dye.

5.2.2 High temperature treatment

Each γ-methoxypropionamido compound (0.5 g), in pH 4.0 buffer solution (20 ml), was heated at 130 °C for 60 minutes, in a sealed stainless steel dye pot housed in a Mathis Labomat BFA 12 dyeing machine using the profile shown below. The solutions were cooled, and analysed by HPLC and by titration with sodium nitrite solution.

"High Temperature Treatment" Profile



5.2.3 Sodium nitrite titration

Each solution from the HT treatment above was titrated with 0.1 M standard sodium nitrite solution. A blank titration was performed on each starting material. Only compounds (II and VI) gave significant titrations. For the other compounds tested, one or two drops of sodium nitrite solution were

needed to reach the end point indicating that a trace only of primary amine was formed during HT treatment in the acidic environment.

5.2.4 HPLC results

Following HT treatment, each γ-methoxypropionamido compound listed above was analysed by HPLC. Only compounds (II and VI) showed the presence of a new peak. Before HT, compound (II) gave a peak at $t_R = 1.68$ and after HT treatment a new peak appeared at $t_R = 1.09$. For compound (VI; $t_R = 0.92$), a second peak at $t_R = 0.84$ was formed.

5.3 Results and discussion

Previous studies showed that, lyocell fibre pre-treated with 2,4-diacrylamido benzenesulphonic acid, underwent a loss of NSF after HT treatment under acidic conditions. NSF or wet abrasion resistance values have been shown to be a good measure of fibre cross-linking [42]. As elemental analysis of the fibre showed no loss of nitrogen, it was suggested that the sulphonic acid group *ortho* to one of the amide links was responsible for the observed hydrolytic instability of the cross-linking agent.

Accordingly, to further test the validity, and to explore the generality, of this hypothesis, a series of mono- and bis-acrylamido derivatives were synthesised, converted to their corresponding methyl ethers and the latter compounds subjected to HT polyester dyeing conditions. A pH value of 4.0

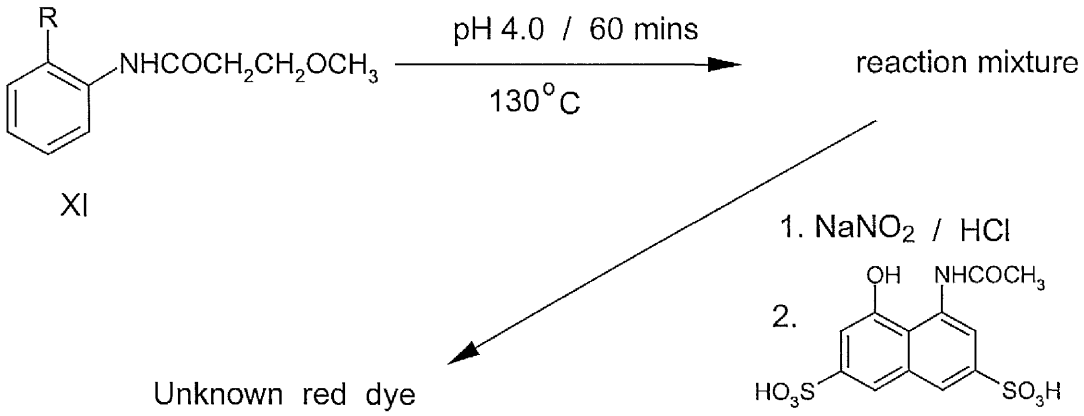
was chosen for the HT treatment in order to subject the agents to the most severe acidic conditions encountered during polyester dyeing.

Compounds (IV and VIII) with sulphonic acid groups *meta* or *para* to the amide bond, are unable to participate in a neighbouring group hydrolysis mechanism. Each compound in this series was dissolved, in turn, in the buffer solution and subjected to the HT dyeing conditions (see Experimental). No new band was detected by HPLC and titration with sodium nitrite solution revealed only a trace of aromatic amine had been produced. Accordingly, the *γ*-methoxypropionamido compounds (IV and VIII) proved to be, for all practical purposes, stable to HT polyester dyeing conditions.

Treatment of compounds (II and VI), which contain either a carboxylic or a sulphonic acid group positioned ortho to the amide group, i.e. in a similar situation to that found in 2,4-diacrylamidobenzenesulphonic acid, produced a different outcome. In this case HPLC following HT treatment of compound (II; $t_R = 1.68$), with an *ortho* carboxyl group, furnished a new HPLC peak at t_R = 1.09 after the HT treatment. Sodium nitrite titration showed 18.2 % hydrolysis had occurred. Similarly compound (VI), showed the presence of a new peak at $t_R = 0.84$, and titration with sodium nitrite solution determined that 23.8 % hydrolysis had occurred.

5.3.1 Investigation of the hydrolysis product

To further investigate the products of hydrolysis, the diazo solutions from the sodium nitrite titrations of *γ*-methoxypropionamido derivatives (II and VI) were coupled, in turn, with 8-acetylamino-1-naphthol-3,6-disulphonic acid (Acetyl H-Acid) to give an unknown red dye (Scheme 5.1).



R=CO_2H or SO_3H

Scheme 5.1

The anticipated products (IX and X) formed in Scheme 5.1 were un-ambiguously synthesised, their retention times compared with those of the unknown products by HPLC and the results listed in Tables 5.1 and 5.2.

Virtually identical retention times for the individual analyses, and the appearance only of a single peak for the mixtures, strongly supported structural assignments (IX and X) for the unknown dyes.

Table 5.1

HPLC retention times

Programme	Dye IX t_R	Unknown dye t_R	Mixture t_R
A	1.49	1.42	1.47
B	4.71	4.70	4.70
C	0.79	0.79	0.79

Table 5.2

HPLC retention times

Programme	Dye X t_R	Unknown dye t_R	Mixture t_R
A	0.79	0.79	0.79
B	4.89	4.92	4.90
C	1.65	1.61	1.69

Additional support was provided by comparing the visible spectral curves of the unknown dyes (XI, where R = CO_2H; Scheme 5.2), λ_{max} 533 nm, and (XI, where R = SO_3H; Scheme 5.2), λ_{max} 503 nm with those of dye (IX), λ_{max} 534 nm and dye (X), λ_{max} 505 nm.

5.4 Conclusions

The methyl ethers of a number of benzeneacrylamido derivatives, with sulpho groups *meta* and *para* to the amide links proved to be hydrolytically stable to the HT polyester dyeing conditions at pH 4.0. Two other derivatives, one with an *ortho* sulpho substituent and the other with an *ortho*

carboxyl group underwent significant amide hydrolysis during the HT treatment. This is consistent with a neighbouring group participation mechanism and confirms previous findings [148]. In order to furnish a benzeneacrylamido cross-linking agent, for lyocell fibres, which is hydrolytically stable to a range of HT polyester dyeing conditions, the absence of *ortho* sulpho or *ortho* carboxyl groups is necessary.

CHAPTER 6

SYNTHESIS AND EVALUATION OF NOVEL ACRYLAMIDO BASED CROSS-LINKING AGENTS

6.1 Introduction

Previous evidence suggested that, under high temperature polyester dyeing conditions, hydrolysis of the amide link *ortho* to the sulphonic acid group was taking place *via* a neighbouring group participation mechanism. Based on the understanding derived from the above investigation, further work was undertaken to synthesise and evaluate new cross-linking agents, devoid of the *ortho* sulpho structure to make sure that the subsequent cross-linked fibre would be sufficiently stable to permit blending with polyester.

To this end, a series of sulphonated diamino compounds, with both amino groups *meta* to the sulphonic acid groups, was chosen as precursors. Subsequent acryloylation of the sulphonated diamino precursors furnished the novel cross-linking agents, which were applied to lyocell by a pad-steam method.

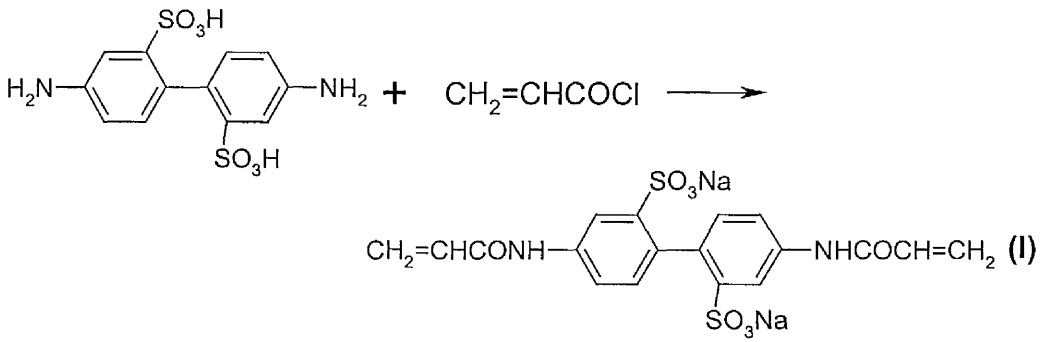
The stability of the lyocell-O-agent bonding under high temperature (HT) polyester dyeing conditions was tested in the same way as described in previous chapters. Following application of cross-linking agents to lyocell,

the wet abrasion resistance of the cross-linked fibre was measured to indicate the effectiveness of these new agents in preventing lyocell fibrillation.

6.2 Experimental

6.2.1 Syntheses

6.2.1.1 4,4'-Diacrylamidobiphenyl-2,2'-disulphonic acid (I)



To 4,4'-diaminobiphenyl-2,2'-disulphonic acid (15.8 g; strength 96 %; 0.05 mol) in water (50 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0-5 °C and acryloyl chloride (11.8 ml; d = 1.1; strength 96 %; 0.07 mol) added dropwise, with stirring, while maintaining a pH of 4.5-5.5 with a sodium carbonate solution (2 M). The reaction was continued for 48 hours and HPLC showed 98 % conversion to a new product t_R = 1.02 (4,4'- diaminobiphenyl-2,2' - disulphonic acid compound, t_R = 0.61). Sodium chloride (20 g; 10 %w/v) was added portionwise to give a precipitate which was filtered off, and oven dried at 40 °C to give a white solid (22.6 g). HPLC showed a single

peak at t_R = 1.09 and mass spectral analysis gave ions at m/z 473 $(M-2H+Na)^-$(68) and 451 $(M-H)^-$(75).

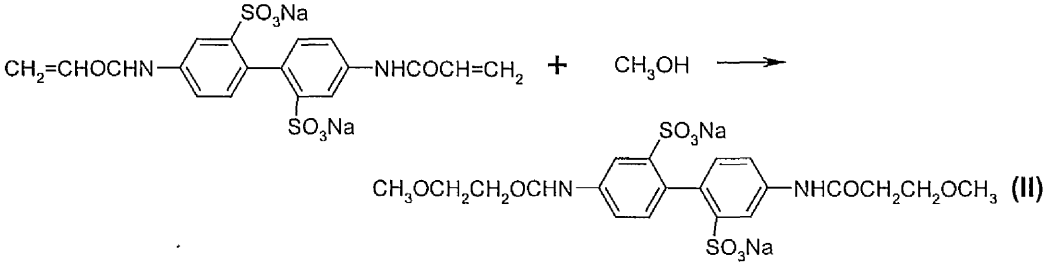
^1H (300 MHz): δ (ppm) = 5.75-5.79 (2 H, dd, *J* 2.3 and 9.0, 2 x CH=), 6.20-6.36 (4 H, m, 2 x CH_2=), 7.11 (2 H, d, *J* 8.3, 2 x H-*m*-$ArSO_3Na$), 7.42 (2 H, dd, *J* 1.9 and 8.3, 2x H-*p*-$ArSO_3NaAr$), 8.05 (2 H, d, *J* 1.9, 2 x H-*o*-$ArSO_3NaAr$). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 119.9 and 122.6 (4 C, 2 x CH_2= and 2 x CH=), 129.1, 130.7, 133.2, 134.1, 136.9 and 141.6 (12 C, 12 x ^{Ar}C), 167.1 (2 C, 2 x C=O).

Elemental Analysis:

Element	Expected	Found
%C	42.9	27.3
%H	4.3	3.1
%N	5.0	3.4
%S	11.4	7.9

The strength of the compound I was therefore calculated to be 67.6%.

6.2.1.2 4,4'-(*γ*-Dimethoxy)propionamidobiphenyl-2,2'-disulphonic acid (II)



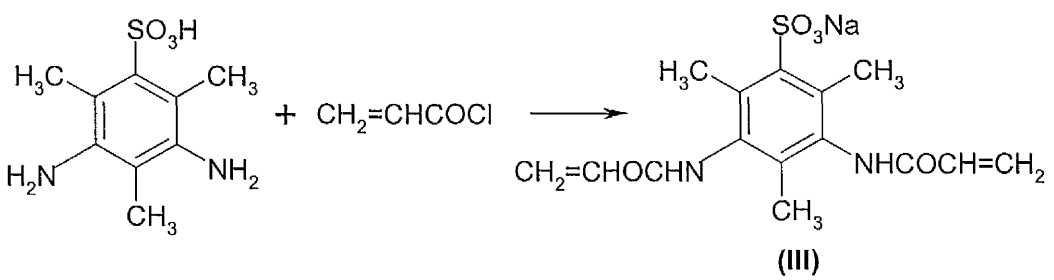
(II)

To methanol (50 ml) and water (25 ml) was added, with stirring, 4,4'-diacrylamidobiphenyl-2,2'-disulphonic acid (4 g) and sodium carbonate (0.8

g) and the reaction mixture heated under reflux for 48 hrs. The solution so formed was evaporated to dryness on a rotary evaporator to give an off-white solid. The product was lixivated in acetone, filtered off and oven-dried at 40 °C to give the product (2.1 g). HPLC showed a single peak at t_R = 1.09 and mass spectral analysis gave ions at m/z 515 $(M-H)^-$(100) and 483 $(M-H-CH_3OH)^-$(35).

^1H (300 MHz): δ (ppm) = 2.60 (4 H, t, *J* 6.0, 2 x $CH_2C=O$), 3.27 (6 H, s, 2 x OCH_3), 3.69 (4 H, t, *J* 6.0, 2 x CH_2O), 7.18-7.22 (2 H, dd, *J* 3.4 and 8.3, 2 x H-*m*-$ArSO_3Na$), 7.44-7.47 (2 H, dd, *J* 1.9 and 8.3, 2x H-*p*-$ArSO_3NaAr$), 7.92 (2 H, d, *J* 1.9, 2 x H-*o*-$ArSO_3NaAr$). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 37.0 (2 C, 2 x OCH_3), 58.5 (2 C, 2 x $CH_2C=O$), 68.5 (2 C, 2 x CH_2O), 120.3, 123.1, 133.0, 134.2, 136.9 and 141.7 (12 C, 12 x ^{Ar}C), 167.8 (2 C, 2 x C=O).

6.2.1.3 3,5-Diacrylamido-2,4,6-trimethylbenzenesulphonic acid (III)



(III)

To 3,5-diamino-2,4,6-trimethylbenzenesulphonic acid (9.2 g; strength 96 %; 0.04 mol) in water (50 ml) was added sodium carbonate solution (2 M) to give a clear solution and pH 9.0. The solution was cooled to 0-5 °C and

acryloyl chloride (8.46 ml; d = 1.114; strength 96 %; 0.1 mol) added dropwise, with stirring, while maintaining a pH of 4.5-5.5 with a sodium carbonate solution (2 M). The reaction was left to stir for 24 hrs. The resultant solution was evaporated on a rotary evaporator to give a solid. The solid was washed with acetone (80 ml), filtered off, and oven dried, at 40 °C, to give a yellow solid (12.5 g). HPLC showed a single peak at t_R = 0.78 and mass spectral analysis gave a molecular ion at m/z 337 $(M-H)^-$ (100).

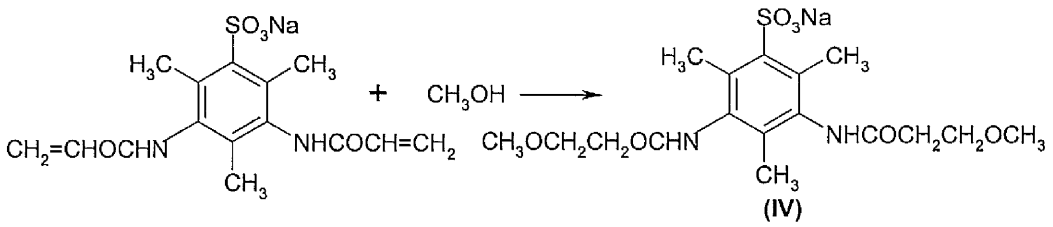
^1H (300 MHz, NaOD): δ (ppm) = 2.08 (3 H, s, CH_3-*p*-SO_3Na), 2.39 (6 H, s, 2 x CH_3-*o*-SO_3Na), 5.68-5.72 (2 H, dd, *J* 1.9 and 10.2, 2 x C*H*H=), 6.16-6.22 (2 H, dd, *J* 1.9 and 16.9, 2 x CH*H*=), 6.45-6.54 (2 H, dd, *J* 10.2 and 16.9, CH=). ^{13}C (75.5 MHz, NaOD): δ (ppm) = 13.8 (1 C, CH_3-*p*-SO_3Na), 17.2 (2 C, 2 x CH_3-*o*-SO_3Na), 122.0 and 126.4 (2 C, 2 x $CH=CH_2$), 131.8, 133.1 and 133.5 (6 C, 6 x ^{Ar}C) and 167.2 (2 C, 2 x C=O).

Elemental Analysis:

Element	Expected	Found
%C	62.8	50.0
%H	6.5	5.0
%N	7.8	6.2
%S	8.9	7.0

The strength of the compound III was calculated to be 79.6%.

6.2.1.4 3,5-(γ-Methoxy)propionamido-2,4,6-trimethylbenzene sulphonic acid (IV)

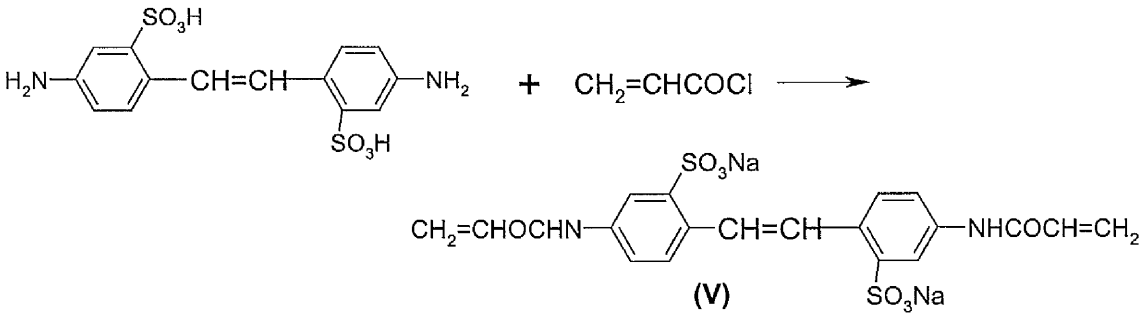


(IV)

To methanol (70 ml) and water (35 ml) was added, with stirring, 3,5-diacrylamido-2,4,6-trimethylbenzenesulphonic acid (5.0 g) and sodium carbonate (1.0 g). The reaction mixture was heated under reflux for 48 hours and then the solvent removed on a rotary evaporator to give a solid. The solid was lixivated with acetone (80 ml), filtered off, and dried in an electric oven at 40 °C to give the product (5.1 g). HPLC showed a single peak at t_R = 0.73 and mass spectral analysis gave ions at m/z 401 $(M-H)^-$ (100) and 369 $(M-H-CH_3OH)^-$(52).

^1H (300 MHz): δ (ppm) = 1.97 (3 H, s, CH_3-*p*-SO_3Na), 2.37 (6 H, s, 2 x CH_3-*o*-SO_3Na), 3.69 (4 H, t, *J* 6.0, 2 x CH_2CO), 3.32 (6 H, s, 2 x OCH_3), 3.73 (4 H, t, *J* 6.0, 2 x CH_2O). ^{13}C (75.5 MHz, D_2O): δ (ppm) = 13.8 (1 C, CH_3-*p*-SO_3Na), 16.8 (2 C, 2 x CH_3-*o*-SO_3Na), 36.1 (2 C, 2 x OCH_3), 58.4 (2 C, 2 x $CH_2C=O$), 68.6 (2 C, 2 x CH_2O), 127.0, 133.4, 135.7 (6 C, 6 x ^{Ar}C) and 167.9 (2 C, 2 x C=O).

6.2.1.5 4,4'-diacrylamido-2, 2'-stilbenedisulphonic acid (V)



(V)

To 4,4'-diamino-2,2'-stilbenedisulphonic acid (18.88g; strength 98%; 0.05m) in deionised water (50 ml) was added sodium hydroxide (2M) to give a clear solution and pH 6.5. The solution was cooled to 0—5°C and acryloyl chloride (15 ml; d=1.114; strength 98%) added dropwise, with stirring, while maintaining a pH of 4.5—5.5 with sodium carbonate solution (2M). HPLC showed the steady disappearance of the starting 4,4'-diamino-2, 2'-stilbenedisulphonic acid compound, t_R=0.56 and t_R=0.65 (CIS and TRANS isomers). The reaction was continued for 48hrs, and the formation of new peaks at t_R=0.94 and t_R=1.42. HPLC showed 96% conversion to the desired product. The precipitate so formed was isolated by filtration and dried in an electric oven at 40 °C to give a bright yellow solid (29.53g). HPLC showed two peaks at t_R=0.84 (percentage of peak area 18.7%) and t_R=1.34 (percentage of peak area 75.0%), mass spectral analysis gave a molecular ion at m/z 478$(M-H)^-$(100).

6.2.2 Application of cross-linking agents to lyocell

Experiments were performed with "never-dried" lyocell fibres (1.3 dtex;

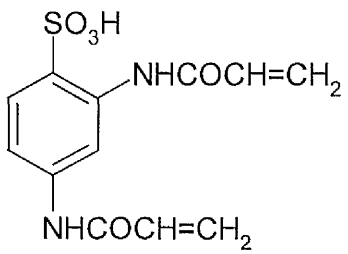
40mm staple) provided by Lenzing.

6.2.2.1 Cross-linking agents used:

4,4'-diacrylamidobiphenyl-2,2'-disulphonic acid (I)

3,5-diacrylamido-2,4,6-trimethylbenzenesulphonic acid (III)

2,4-diacrylamidobenzenesulphonic acid(VI)



VI

6.2.2.2 Pad-Steam Method

1) Padding solutions were prepared using distilled water with the following composition:

agent (X g/l, at 100 % strength) *

Sodium hydroxide (4 g/l)

Sodium sulphate (100 g/l)

2) "Never-dried" lyocell fibre was then impregnated in the pad liquor for 5 minutes at room temperature.

3) The fibre was squeezed at 3 bar pressure and 2 m/min speed.

4) The padded fibre was steamed at 100°C for 5 minutes.

5) After steaming, the fibre was rinsed in cold running water for 5 minutes,

soaped at the boil for 15 minutes (soap concentration 1g/l; liquor ratio 50:1) and rinsed in cold running water for 5 minutes.

6) The washed fibre was dried in 60°C oven to constant weight.

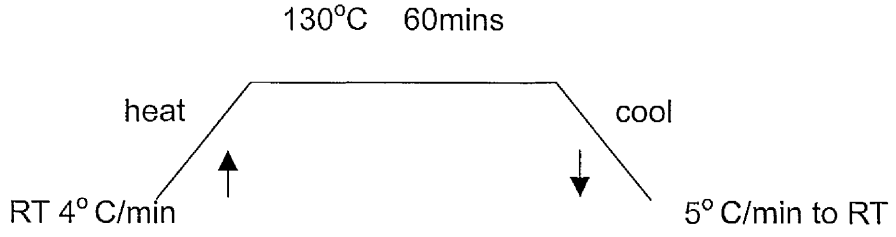
* (X=10, 20, 30, 40)

(The recipe for the padding liquor and the Pad-Steam application process were adapted from Lenzing's standard application procedure for cross-linking chemicals.)

6.2.3 High temperature treatment

The model compounds (II) and (IV) (0.5 g) were heated, in turn, at 130 °C in pH 4.0 buffer solution for 60 minutes (to simulate HT dyeing of the polyester component of a polyester / lyocell blend). The treatments were performed in sealed stainless steel dye pots, housed in a Mathis Labomat BFA 12 dyeing machine.

High Temperature Polyester Dyeing Profile



6.2.4 Nitrogen analysis

Nitrogen analysis of lyocell fibre treated with compounds (I) and (III) was performed with a LECO FP 328 nitrogen analyser by Lenzing AG, Austria.

6.3 Results and discussion

6.3.1 Criteria of an ideal cross-linking agent for lyocell

An ideal cross-linking agent for lyocell needs to satisfy many application, technical and environmental criteria as well as being cost effective for the fibre manufacturer or the dyer and finisher. Some of the important technical/commercial features of an ideal cross-linking agent for lyocell are shown in Table 6.1.

Table 6.1

Criteria for an Ideal Cross-Linking Agent for Lyocell

Good water solubility
Colourless on fibre
Substantive
Reactive yet stable to handling/storage
Reactive groups of equal reactivity
Easy/versatile application
High wet abrasion resistance properties
Stable agent-lyocell bonding
No yellowing in UV light
No change to fibre's mechanical properties
Low vapour pressure
Non-toxic
Biodegradable
Low Cost

6.3.2 Technical assessment of novel cross-linking agents

The sulphonated diamino precursors to Agents (I), (III) and (V) are all commonly used in reactive dye manufacturing. Agent (V) was not chosen for cross-linking lyocell because it was yellow. Agents (I) and (III) were examined as potential cross-linking agents for lyocell and their stability to HT polyester dyeing conditions was investigated.

6.3.2.1 Stability of the lyocell-O-Agent (I and III) bonding

To evaluate the stability of the lyocell-O-agent bonding, the corresponding model ethers (II) and (IV) were synthesised to simulate the attachment of Agents (I) and (III) to lyocell and then the model compounds subjected to high temperature treatment at pH 4.0.

For Agents (II) and (IV), at pH 4.0, no chemical change was observed after high temperature treatment. HPLC analysis of both compounds before and after HT treatment gave identical results. Furthermore, virtually no sodium nitrite solution was consumed during titration of the products obtained after HT treatment, showing that no free amine was generated, thus demonstrating stability of the methyl ethers of Agents (I) and (III) and by inference the lyocell-O-agent bonding, to HT polyester dyeing conditions. This result further confirms the previous conclusion, i.e. to furnish a benzeneacrylamido cross-linking agent, for lyocell fibres, which is hydrolytically stable to a range of HT polyester dyeing conditions, the absence of an *ortho* sulpho group is necessary.

6.3.3 Examination of wet abrasion resistance (NSF) of cross-linked lyocell

After re-adjusting the Delta 100 instrument due to a technical problem, there was an obvious change in all NSF values. This may be due to changes in machine operating conditions such as the wetness of the rolling bar. So, the NSF values of all samples, before and after HT treatment, were re-measured under the same new conditions.

Table 6.2 summarises the NSF values of "never-dried" lyocell treated, in turn, with the three cross-linking Agents (I), (III) and (VI) at two different concentrations.

Table 6.2

NSF values of lyocell treated with 3 cross-linking agents

Concentration of applied agents	NSF					
	Agent (I)		Agent (III)		Agent (VI)	
30 g/l	47	45	47	51	192	178
	47		55		162	
	42		52		181	
40 g/l	69	67	76	66	227	241
	74		66		256	
	57		55		242	

(NSF value of untreated lyocell: **27**)

The NSF values of both cross-linked fibre (Agent I and III) were less than one third that of lyocell cross-linked with Agent (VI). Following each application, the degree of substitution (DS) of the cross-linking agent on lyocell was determined (Table 6.3). Nitrogen analysis results showed that the fixation (degree of substitution) of both Agents (I) and (III) was very low, which probably resulted in the lower NSF values of this cross-linked fibre.

Table 6.3

Degree of substitution of lyocell

Samples	Nitrogen %	Degree of substitution (mol %)[1]
Lyocell (treated with Agent **I**)	0.431	0.84
Lyocell (treated with Agent **III**)	0.071	0.14

[1] moles of agent / mole of cellulose*100

6.4 Conclusions

Three novel aromatic acrylamido cross-linking agents, each devoid of a sulpho group *ortho* to the acrylamido group, were synthesised and applied to lyocell. The agents were based on a series of readily available sulphonated aromatic diamino precursors. The corresponding model ethers were synthesised to simulate attachment of the agents to lyocell. The ethers proved to be hydrolytically stable, thus by inference showing the stability of the lyocell-O-agent bonding under high temperature polyester dyeing conditions. This was consistent with previous findings.

One cross-linking Agent (V) was not evaluated due to its yellow colour. Lyocell cross-linked with the other two Agents (I and III) showed an inferior wet abrasion resistance compared to Agent (VI). The poor performances of Agents (I) and (II) were rationalized in terms of low fixation to lyocell by the Pad-Steam method.

CHAPTER 7

EFFECT OF LYOCELL, CROSS-LINKED WITH 2,4-DIACRYLAMIDO- BENZENESULPHONIC ACID, ON SUBSEQUENT DYEING WITH REACTIVE DYES

7.1 Introduction

Initially it was expected that the colour yield of anionic reactive dyes could be reduced when dyeing an anionically cross-linked lyocell fibre. Therefore, this work was undertaken to further evaluate the effect of 2,4-diacrylamido-benzenesulphonic acid (I) on subsequent dyeing with reactive dyes. A series of reactive dyes were applied to both standard lyocell and lyocell cross-linked with Agent (I) and the visual colour yields of the dyed fibre compared.

7.2 Experimental

7.2.1 Application of cross-linking Agent (I) to lyocell

Experiments were performed with "never-dried" lyocell fibres (1.3 dtex; 40mm staple) provided by Lenzing, Agent (I) being applied by a Pad-Steam method.

Padding solutions were prepared using distilled water with the following composition:

Agent I (30 and 40 g/l, at 100 % strength)

Sodium hydroxide (4 g/l)

Sodium sulphate (100 g/l)

"Never-dried" lyocell fibre was then immersed in the pad liquor for 5 minutes at room temperature.

The fibre was squeezed at 3 bar pressure and 2 m/min speed.

The above fibre was steamed at 100°C for 5 minutes.

After steaming, the fibre was rinsed in hot running water for 5 minutes, soaped at the boil for 10 minutes (soap concentration 1g/l; liquor ratio 50:1) and rinsed in cold running water for 5 minutes.

The washed fibre was air dried.

(The recipe for the padding liquor and the Pad-Steam application process were adapted from Lenzing's standard application procedure for cross-linking chemicals.)

7.2.2 Dyeing of cross-linked lyocell with cellulose reactive dyes

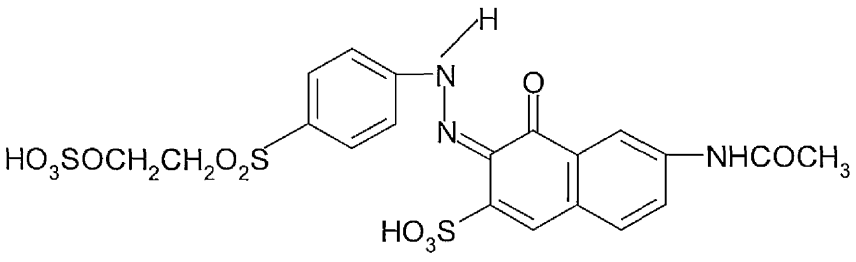
All dyeings were carried out in sealed stainless steel dye pots housed in a Mathis Labomat BFA 12 dyeing machine.

7.2.2.1 Cellulose reactive dyes

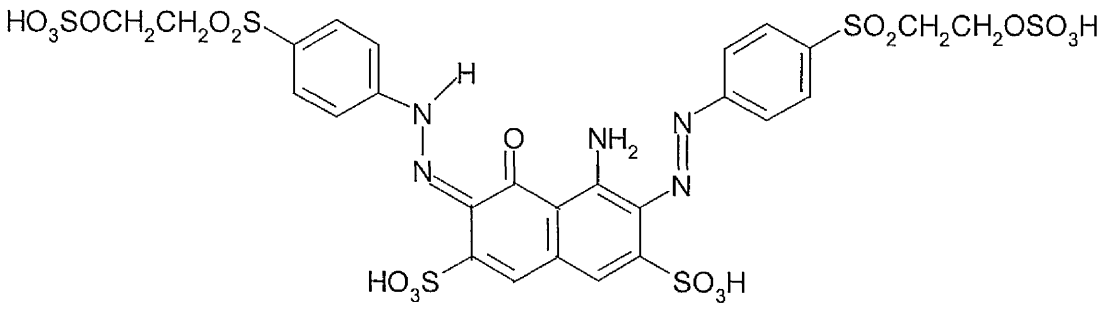
A series of cellulose reactive dyes with different numbers of sulphonic acid groups were used: Everzol Brill. Orange 3R (C.I. Reactive Orange 16), C.I.

Reactive Black 5, Everzol Red 3BS H/C (C.I. Reactive Red 239), and Procion Red H-E7B (C.I. Reactive Red 141).

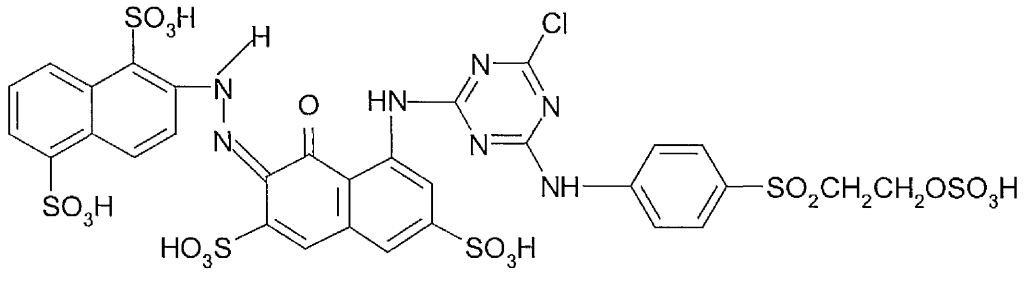
Their structures are shown below. They were applied, in turn, to both standard lyocell and lyocell fibre treated with Agent (I).



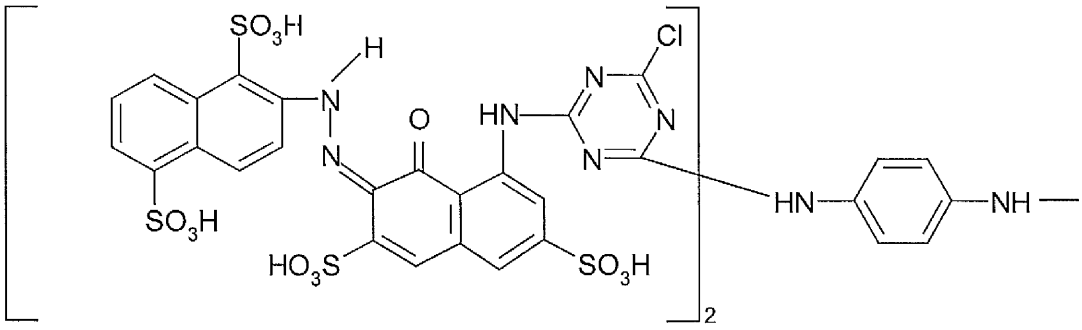
Everzol Brill. Orange 3R (C.I. Reactive Orange 16)



C.I. Reactive Black 5



Everzol Red 3BS H/C (C.I. Reactive Red 239)

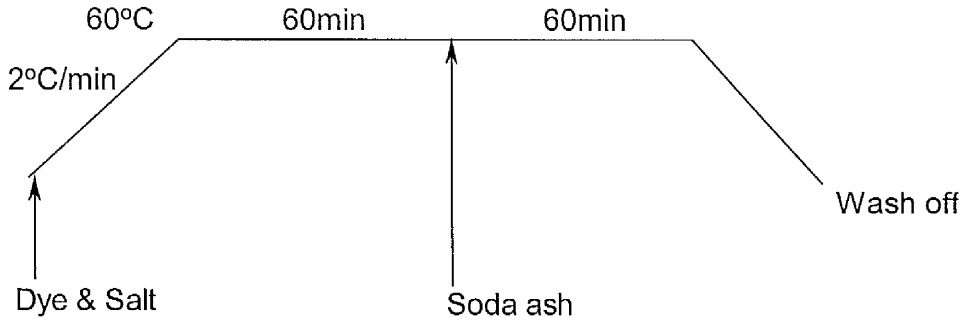


Procion Red H-E7B (C.I. Reactive Red 141)

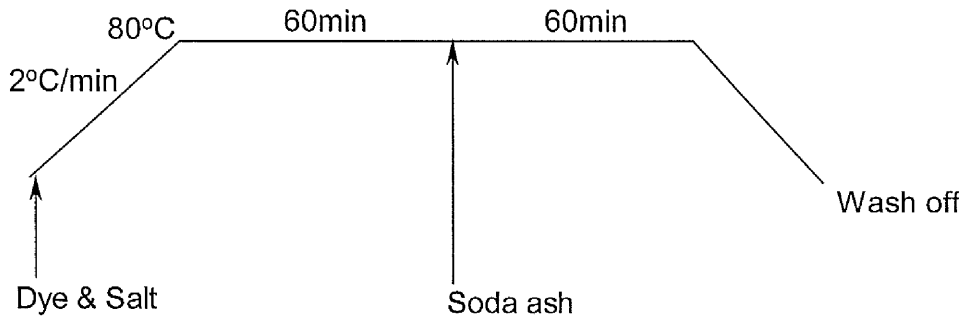
7.2.2.2 Conventional dyeing

Both standard and cross-linked lyocell fibre (2 g) were dyed by the dye manufacturers' recommended method, at a liquor ratio 20:1 with 2%, 4% and 6% dye on mass of fibre, in the presence of appropriate amounts of salt and alkali. The dyeing profiles employed are shown in Figure 7.1.

C.I. Reactive Black 5, Everzol Red 3BS (C.I. Reactive Red 239) and Everzol Brill. Orange 3R (C.I. Reactive Orange 16)



Procion Red H-E7B (C.I. Reactive Red 141)



Depth of Shade	Salt (g/l)	Soda Ash (g/l)
2% omf	50	20
4% omf	60	20
6% omf	80	20

Figure 7.1 Dyeing profiles for cellulose reactive dyes

7.3 Results and discussion

Cross-linking Agent (I) was applied to lyocell by a pad-steam method. Four reactive dyes, each containing a different number of sulphonic acid groups (Table 7.1), were chosen to dye the cross-linked fibre, with a view to investigating the effect of an anionic cross-linking agent on subsequent dyeing with reactive dyes.

Table 7.1

Number of sulphonic acid groups

Name of Dye	Number of Sulphonic Acid Groups
C.I. Reactive Orange 16	1
C.I. Reactive Black 5	2
C.I. Reactive Red 239	4
C.I. Reactive Red 141	8

Table 7.2 shows the visual colour yields (K/S values) of standard lyocell and the cross-linked lyocell fibre, each dyed, in turn, with the above four reactive dyes to 2% omf depth of shade as described in the Experimental section.

Initially it was expected that introduction of anionic cross-linking agents to lyocell might exert some repulsion on anionic reactive dyes, thus resulting in reduced colour yields. However, this adverse effect was not observed, as shown in Table 7.2. Although there was a slight drop of K/S values in a few cases, such a reduction was only marginal, which had no obvious effect on the visual colour yield. Consequently there is no strong evidence to suggest that the introduction of an anionic cross-linking Agent (I) will reduce the visual colour yield of a subsequent dyeing with reactive dyes. Moreover, K/S values of the fibre treated with 40 g/l agent were marginally increased than that of 30 g/l agent applied.

Table 7.2
Colour yield of lyocell treated with Agent (I)
dyed to 2% omf depth of shade

Dye 2% omf	K/S		
	Untreated Lyocell	Lyocell treated with Agent (I)	
		30 g/l	40 g/l
C.I. Reactive Orange 16	11.8	10.4	11.2
C.I. Reactive Black 5	23.2	21.7	23.0
C.I. Reactive Red 239	17.7	15.9	16.3
C.I. Reactive Red 141	11.6	10.8	11.4

Further support was given by dyeing of lyocell cross-linked with Agent (I) to other depths of shades. Table 7.3 and 7.4 show, respectively, the K/S values of the standard and the cross-linked lyocell fibre, each dyed, in turn, with 4% omf and 6% omf depth of the above four reactive dyes using the dye manufacturers' recommended methods (see Experimental). Again, no evidence was found to show that the anionic cross-linker (I) has any obvious adverse effect on subsequent visual colour yields with reactive dyes. Accordingly, any repulsion between the anionic cross-linking Agent (I) and anionic reactive dyes does not materially alter dyeing performance, e.g. a dyeing with 6% omf C.I. Reactive Red 141 (8 sulphonic acid groups) showed no loss of colour yield after pre-treatment with 40 g/l Agent (I).

Table 7.3

Colour yield of lyocell treated with Agent (I)

dyed to 4% omf depth of shade

Dye 4% omf	K/S		
	Untreated Lyocell	Lyocell treated with Agent (I)	
		30 g/l	40 g/l
C.I. Reactive Orange 16	19.9	18.9	19.8
C.I. Reactive Black 5	27.9	29.7	30.6
C.I. Reactive Red 239	25.7	24.3	25.4
C.I. Reactive Red 141	24.5	23.9	24.4

Table 7.4

Colour yield of lyocell treated with Agent (I)

dyed to 6% omf depth of shade

Dye 6% omf	K/S		
	Untreated Lyocell	Lyocell treated with Agent (I)	
		30 g/l	40 g/l
C.I. Reactive Orange 16	25.1	23.2	24.2
C.I. Reactive Black 5	32.2	32.2	33.3
C.I. Reactive Red 239	29.3	26.9	27.7
C.I. Reactive Red 141	29.1	28.4	29.1

7.4 Conclusions

Lyocell fibres cross-linked with Agent (I) were dyed in turn with four reactive dyes, containing different numbers of sulphonic acid groups, with the aim of investigating the effect of an anionic cross-linking agent on subsequent dyeing with reactive dyes. The obtained visual colour yields were then compared with dyed standard lyocell. No evidence was found to suggest that the introduction of the anionic cross-linking Agent (I) would reduce the visual colour yield of a subsequent dyeing with reactive dyes.

CHAPTER 8

EVALUATION OF 2,4-DIACRYLAMIDOBENZENESULPHONIC ACID AS AN ALTERNATIVE TO FIXAPRET CP AND FIXAPRET ECO (DMDHEU) RESINS FOR THE FINISHING OF LYOCELL

8.1 Introduction

8.1.1 Overview of resin finishing

Resin finishing of lyocell is of great importance, not only to prevent further fibrillation during household laundering, but also to increase its dimensional stability, durability, and easy of ironing.

Resins reduce the fibrillation of lyocell in two main ways. On one hand, resin finishing leads to less fibre swelling as a result of inter-fibrillar cross-linking. The formation of fibrils during laundering is thus inhibited. On the other hand, the high temperature, acid cross-linking process embrittles the fibre. The brittle areas can be regarded as breaking points. Therefore resin finishing enables any fibrillation, that has occurred during the dyeing and laundering process, to be easily removed [45, 135]. Resins, which can cross-link the fabric, are used after dyeing. For reasons of economy and comfort, the most common agents of this type are differently modified

dimethyol dihydroxyethylene urea molecules (DMDHEU), shown in Figure 8.1 [124, 125].

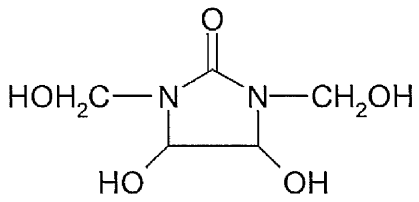


Figure 8.1 DMDHEU

However, formaldehyde, which is a threat to human health, can be released into the fabric after resin finishing. It is thus advantageous to identify other agents which can overcome this shortcoming without sacrificing the desirable qualities conferred by resin finishing.

8.1.2 Aim and methodology of the present work

A study was undertaken to evaluate 2, 4-diacrylamidobenzenesulphonic acid (I, shown in Figure 8.2) as an alternative finishing agent to Fixapret CP and Fixapret ECO resins. Fixapret CP contains DMDHEU in the form of a 75% solution and Fixapret ECO is modified DMDHEU with low levels of free formaldehyde.

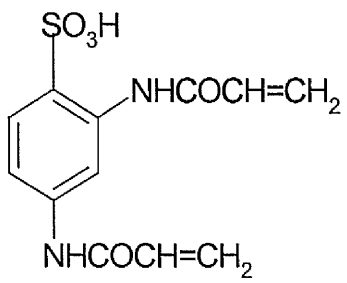


Figure 8.2 Agent (I)

The evaluation consisted of two steps. Firstly, a series of woven lyocell fabrics were dyed with C.I. Reactive Blue 19. Secondly, Agent (I) was applied to these dyed lyocell fabrics by both continuous and exhaustion processes.

There are two reasons for using C.I. Reactive Blue 19 (see Experimental). First of all, Reactive Blue 19 is a mono-functional dye and therefore is not able to cross-link with lyocell to provide fibrillation resistance. Furthermore, the use of a dyed substrate makes subsequent visual assessment of fibrillation easier. Following application of Agent (I) to the dyed woven lyocell fabrics, a six-test the assessment protocol was carried out, with a view to examining whether Agent (I) had the potential to be used as an alternative to DMDHEU resins.

- Martindale resistance test
- Dry crease resistance test
- Tensile strength test
- Repeated laundering test
- Scanning electron microscopy (SEM)
- Handle test

8.2 Experimental

Experiments were performed with woven lyocell fabrics, provided by Lenzing, after singeing and desizing.

8.2.1 Dyeing by Pad-Dry-Chemical Pad-Steam process

The cellulose reactive dye, C.I. Reactive Blue 19, was applied to woven lyocell fabrics. The chemical structure of C.I. Reactive Blue 19 is shown in Figure 8.3.

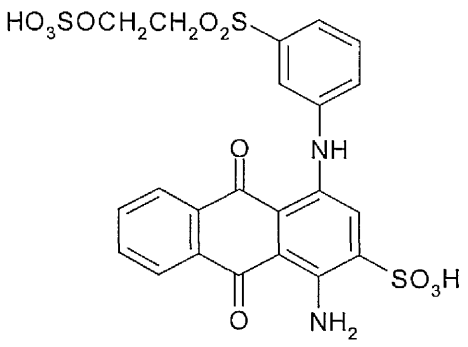


Figure 8.3 C.I. Reactive Blue 19

Dyeing profile:

Impregnation of the woven lyocell fabric in a 40 g/l neutral dye solution.

Uniform squeezing of surplus liquor from the fabric as it passes through the mangle nip at 2 m/min speed. The mangle pressure is set to give a wet pick-up of 75% at room temperature.

Drying of the padded fabric for 1 minute at 110°C.

Padding the dried fabric through 250 g/l common salt and 20 mls/l caustic soda mixture solution at approximately 100% pick-up.

Steaming for 45 seconds at 105°C.

Washing off:

- cold rinse
- neutralize with dilute acetic acid
- 2 soap boil treatments
- cold rinse until clear

Drying the fabric in air.

8.2.2 Application of resins/ cross-linker by a continuous (Pad- Dry- Bake) process

8.2.2.1 DMDHEU (Fixapret CP and Fixapret ECO)

Padding solutions were prepared using deionised water with the following composition in Table 8.1.

Table 8.1

The application recipe for DMDHEU

Resin	10 g/l	20 g/l	40 g/l	60 g/l	80 g/l
$MgCl_2$. $6H_2O$	7 g/l	7 g/l	8 g/l	12 g/l	16 g/l

(Agent at 100% strength; Active solids of Fixapret CP and Fixapret ECO: 65%)

Pad- Dry- Bake process

1) Pass the dyed woven lyocell fabric through the pad liquor at 2 m/min speed. The mangle pressure (3 bar) was set to give a wet pick-up of 80% at room temperature.

2) Dry the padded fabric for 1 minute at 110°C.

3) Bake for 1 minute at 170°C.

Calculation of fixed resin

The following parameters were assumed during the application procedure in order to achieve the desired levels of fixation:

'Solids content' of resin (65 %);

Bath concentration (60 g/l, 6%@ 100% pick-up);

Actual pick-up (80%);

Degree of cure (It is the efficiency of the reaction and can be calculated by taking a sample of undyed fabric after resination, together with the same fabric after resination and washing, and comparing the nitrogen contents. This will typically be about 90%).

The amount of resin fixed is calculated using the following equation:

Resin fixed =

Resin solid content x Bath concentration x Wet pick up x Degree of cure

= 65% x 6% x 80% x 90%

=2.8%

Only 60 g/l resin was evaluated, compared to various concentrations of Agent (I), because this is the common application level in industry, 2.8% of fixed product being normally sufficient to give full protection against fibrillation. Higher application levels may have a negative effect by reducing other physical parameters, such as tensile strength and abrasion resistance, excessively.

8.2.2.2 Agent I (2, 4-diacrylamidobenzenesulphonic acid)

Padding solutions were prepared according to the alkali/urea recommendations for Procion PX/Levafix PN dyes (see Table 8.2).

Table 8.2

Recipe for Agent (I) applied by a continuous process

Agent (I)	< 20 g/l	20-50 g/l	> 50 g/l
Urea (g/l)	100	150	200
Soda Ash (g/l)	10	15	20

(Agent at 100 % strength)

Pad- Dry- Bake process

1) Pass the dyed woven lyocell fabric through the pad liquor at 2 m/min speed. The mangle pressure (3 bar) was set to give a wet pick-up of 80% at room temperature.

2) Dry the padded fabric for 1 minute at 110°C.

3) Bake for 1 minute at 180°C.

4) Wash off:

- cold rinse
- neutralize

5) Dry the fabric in air.

8.2.3 Application of Agent (I) by an exhaustion process

The dyed woven lyocell fabric (20 g) was treated with 1%, 2%, 4%, 6% and 8% omf Agent (I), at 95 °C and at a liquor ratio of 20:1, using the appropriate amount of salt and alkali (see Table 8.3).

Table 8.3

Recipe for Agent (I) applied by an exhaustion process

Amount of Agent (I) applied (omf)	Concentration of Salt (g/l)	Concentration of Soda Ash (g/l)
1%	20	5
2%	40	10
4%	60	15
6%	60	15
8%	60	15

The application profile employed is shown in Figure 8.4. All applications were carried out in sealed stainless, steel dye pots housed in a Mathis Labomat BFA 12 dyeing machine.

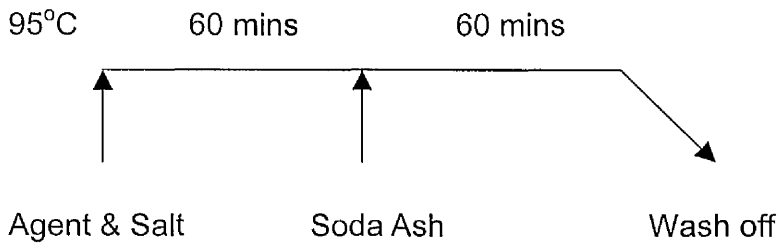


Figure 8.4 Exhaust application profile of Agent (I)

8.2.4 Treatment of dyed fabrics in absence of either DMDHEU or Agent (I)

Lyocell fabric, dyed with C.I. Reactive Blue 19, was treated both with and without Agent (I) and DMDHEU, to evaluate the effect of the chemicals and to investigate the influence of the blank application process on technical performance.

With regard to the treatment of dyed lyocell fabric with either Agent (I) or resins, the conditions used were the same as used for the application of the cross-linking chemical at 60g/l (for continuous process) and 6% omf (for exhaust process) respectively.

8.2.4.1 Blank process for DMDHEU application by a Pad-Dry-Bake process

Padding liquor (50 ml) was prepared using deionised water with 12 g/l magnesium chloride crystals (corresponding to the application recipe for 60

g/l DMDHEU). The application profile employed was exactly as described in Section 8.2.2.1.

8.2.4.2 Blank process for Agent (I) application by a Pad-Dry-Bake process

Padding liquor (50 ml) was prepared using deionised water with 200 g/l urea and 20 g/l soda ash (corresponding to the application recipe for 60 g/l agent I). The application profile employed was exactly as described in Section 8.2.2.2.

8.2.4.3 Blank process for Agent (I) application by an exhaustion method

The dyed woven lyocell fabric (20 g) was treated at 95 °C and a liquor ratio at 20:1 with 60 g/l common salt. After 60 mins, 15 g/l soda ash (corresponding to the application recipe of 6% omf Agent I) was added and fixation allowed to proceed for 60 mins. The application profile employed was exactly as described in Section 8.2.3.

8.2.5 Evaluation of the effect of a (commercial) detergent formulation on lyocell treated with Agent (I)

1993 AATCC Standard Reference Detergent (0.8 g), a non-phosphate, carbonate-containing powder, was mixed with 2,4-Bis- (*γ*-methoxypropion-amido)benzenesulphonic acid (0.1 g) in 100 ml water at 60 °C. This Agent (I) methyl ether is the "model compound" for "lyocell-O-agent", as described in Chapter 4, The resulting mixture was treated for 120 mins to simulate laundering conditions, as shown in Figure 8.5. The treatment was

performed in sealed stainless steel dyeing pots housed in a Mathis Labomat BFA 12 dyeing machine.

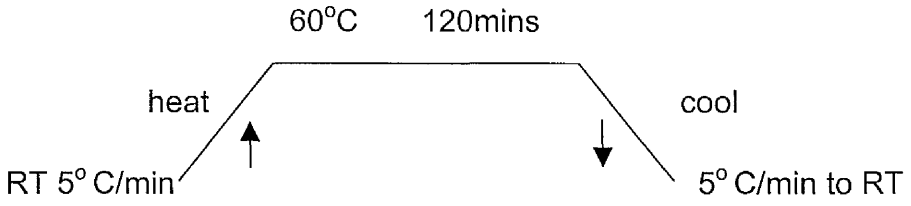


Figure 8.5 Simulated laundering treatment

The reaction mixture was analysed by HPLC, both before and after treatment, to evaluate the stability of Agent (I) methyl ether to repeated laundering, which indicates, in turn, the stability of lyocell, cross-linked with Agent (I) to repeated domestic laundering.

8.2.6 Fixation of Agent (I) on dyed lyocell fabric

In this study, fixation (F) was defined as the percentage of actual agent which was covalently fixed to the dyed lyocell fabric. The fixation value was obtained at the end of the application cycle, after removal of unfixed agent by washing off thoroughly.

8.2.6.1 Fixation of Agent (I) applied by an exhaustion process

Two vessels, $tube_I$ (without fabric) and $tube_{II}$ (with 5g fabric) were prepared. Each tube contained Agent (I), salt, and de-ionised water. The amount of solution (50 ml) in each tube was dependant upon the application recipe of Agent (I), as described in Table 8.3. The profile of the application by an exhaustion process was as shown before (in Section 8.2.3). After

application, the squeezed fabric from $tube_{II}$ was washed with de-ionised water (46 ml), the excess liquor in the fabric squeezed out and the optical density measured by UV spectroscopy. Washing-off was repeated until no absorption was detected. The optical density results were used to determine the amount of unfixed agent removed during washing off, allowing the true fixation to be calculated.

To ensure greater accuracy of the optical density measurement, the cross-linked fabric was squeezed to the same weight; thereby the amount of the excess liquor was effectively controlled.

All applications were performed in a Mathis Labomat BFA 12 laboratory scale exhaust dyeing machine.

Optical density determination (OD)

The optical densities of the collected solutions from the application process were measured with a Camspec M350 Double Beam UV-Visible Spectrophotometer. All readings were taken at ambient temperature. The fixation was calculated using Equation 1:

$$F\ (\%) = \left(\frac{OD_I - OD_{II} - OD_w}{OD_I}\right) x100$$

F: percentage of fixation

OD: optical density of Agent (I) in absence of fabric

I: $tube_I$ (without fabric) II: $tube_{II}$ (with 5g fabric)

W: wash off liquor (total)

Equation 1

8.2.6.2 Fixation of Agent (I) applied by a continuous process

The padding solution was applied to the dyed woven lyocell fabric (5 g) with a wet pick-up of 80%, the amount of solution being dependant upon the application recipe of Agent (I) for the continuous method. This means that padding solution (4g; 5g X 80%) was padded onto the fabric. For calculation purposes, the volume of a 4g padding solution was measured as follows: (1) a 10 ml accurate pipette was filled with padding solution; (2) 4g padding solution was then accurately pipetted a beaker placed on a sensitive balance; (3) the volume corresponding to the 4g padding solution was recorded through the pipette.

The amount of agent padded onto the fabric was thus calculated using the following Equation 2:

Weight of agent padded onto the fabric= Volume of liquor * Conc.

Equation 2

After application, the treated fabric was washed in 1000 ml water. The optical densities (OD) of the washed-off solution (containing unfixed agent) and the initial padding liquor were measured by a Camspec M350 Double Beam UV-Visible Spectrophoto-meter. As OD is proportional to concentration, therefore,

$$\frac{OD_i}{OD_w} = \frac{Conc._i}{Conc._w}$$

(I: initial; w: washing-off)

Similarly, the amount of unfixed agent was calculated using the following Equation 3:

Weight of agent unfixed = Volume of washing liquor * $Conc._w$

Equation 3

Washing off was repeated until no absorption was detected. The amount of unfixed agent removed during washing off was calculated in order to determine the fixation of agent, as shown by the following Equation 4:

$$F\ (\%) = \left(\frac{W_I - W_w}{W_I}\right) x100$$

W_I: Weight of agent padded onto the fabric

W_w: Weight of unfixed agent (total)

Equation 4

8.2.6.3 Evaluation of the effect of urea on fixation of Agent (I)

To evaluate the effect of urea on fixation of Agent (I), padding liquors were prepared using a constant concentration of urea with different concentration of Agent (I), as shown in Table 8.4.

Table 8.4

Application recipe for Agent (I) under constant concentration of urea

Agent (I)	10 g/l	40 g/l	60 g/l
Urea (g/l)	150	150	150
Soda Ash (g/l)	15	15	15

The application profile employed was exactly as described in Section

8.2.2.2, with the measurement of fixation as above.

8.2.7 Handle testing

'Handle', the term given to properties assessed by touch, depends upon subjective assessment of the fabrics. In this research, 10 observers rated each test specimen: resin finished fabric and Agent (I) treated fabric independently.

8.3 Results and discussion

8.3.1 Criteria for an ideal finishing agent for lyocell

The purpose of finishing textiles is to impart the special properties that they must possess to meet appropriate in-service requirements and secure customer satisfaction. Particular features of an ideal cross-linker / finishing agent for dyed lyocell are as follows:

1. High crease recovery
2. Little deterioration in physical properties
3. Minimum effect on handle
4. Little effect on shade and fastness of dyed fabrics or yellowing of whites
5. Low or zero formaldehyde level
6. Good dimensional stability
7. Low adverse environmental impact, both in the application of the resin and in the final make-up fabric / garment.
8. Ease of application and low cost

A technical assessment of Agent (I), as an alternative of DMDHEU (Fixapret CP and ECO) resins, is now discussed in detail.

8.3.2 Fixation of Agent (I) on dyed woven lyoceli fabric

The results for the fixation of Agent (I) to dyed woven lyocell fabric with C.I. Reactive Blue 19 by both continuous (Pad-Dry-Bake) and exhaustion processes are shown in Tables 8.5 and 8.6 respectively. Two features become evident through comparison of both tables.

Table 8.5

Fixation of Agent (I) applied by a Pad-Dry-Bake process

Conc. of Agent (I) Applied @ 80% pick-up	10 g/l	20 g/l	40 g/l	60 g/l
Urea	100 g/l	150 g/l	150 g/l	200 g/l
Fixation	67.2%	75.9%	75.2%	85.0%
Agent fixed (g/100g lyocell fabric)	0.52	1.15	2.24	3.72

Table 8.6

Fixation of Agent (I) applied by an exhaustion process

Amount of agent	1% omf	2% omf	4% omf	6% omf
Fixation	47.28%	45.1%	40.5%	41.98%
Agent fixed (g/100g lyocell fabric)	0.47	0.90	1.62	2.52

(omf: on mass fibre)

Firstly, Agent (I), applied by a continuous process (wet pick-up: 80%), exhibited a higher level of fixation than by an exhaustion process. This could be due to the low substantivity of Agent (I). The continuous dyeing method, in which the pad liquor is pushed onto the fabric through physical pressure, would compensate for the low substantivity of an agent for lyocell substrates.

Secondly, it was observed that, in general, the fixation level of Agent (I) to lyocell fabric by a continuous (Pad-Dry-Bake) process gradually increased with increasing concentrations of cross-linking agent applied (Table 8.5). By contrast, the fixation level by an exhaustion process decreased (Table 8.6).

To investigate the possible cause for the above-mentioned difference, it was noted that different concentrations of urea are employed during the application of Agent (I) to lyocell by the continuous process. Urea is well-known to be a potential swelling agent for cellulose and capable of breaking hydrogen bonds, aiding penetration and mobility of a dye/agent [149]. As can be seen from Table 8.5, the increased fixation of Agent (I) to lyocell corresponds with an increase in urea concentration. Therefore, it is possible that the concentration of urea may have an effect on the fixation level of Agent (I) during the Pad-Dry-Bake process.

Accordingly, it is desirable to examine the correlation between agent concentration and fixation level if a constant concentration of urea is

employed in the continuous process. To this end, 150 g/l urea and 15 g/l soda ash were used together with different concentrations of Agent (I) in the Pad-Dry-Bake process. Table 8.7 summarizes the fixation level of Agent (I) in the presence of a constant concentration of urea.

Table 8.7

Fixation of different concentrations of Agent (I) using a constant concentration of urea in the Pad-Dry-Bake process

Conc. of Agent (I) Applied	10 g/l	40 g/l	60 g/l
Urea	150 g/l	150 g/l	150 g/l
Fixation	78.1%	75.2%	74.3%

When the concentration of urea was maintained at 150 g/l, the fixation level of Agent (I) to lyocell by a Pad-Dry-Bake process gradually decreased with increasing concentration of Agent (I), as shown in Table 8.7. This trend was opposite to that observed in Table 8.5, where fixation level improved with increasing agent concentration, but was consistent with that shown in Table 8.6 where fixation level went down when agent concentration increased. Therefore, this indicates that fixation of Agent (I) to lyocell generally decreases with increasing concentration of Agent (I) applied. Furthermore, it shows that the use of increasing quantities of urea can effectively increase the percentage of Agent (I) fixation to lyocell by a Pad-Dry-Bake process.

8.3.3 Abrasion resistance of dyed woven lyocell fabric

8.3.3.1 Dry Martindale abrasion test

The number of rubs recorded using the 'two threads broken' was taken as the end point. Accordingly, the higher number of rubs the better abrasion resistance. This physical testing method is described in Chapter 3. All samples were tested by the Martindale abrasion tester under dry conditions, after being dyed with C.I. Reactive Blue 19.

Table 8.8 compares the dry abrasion resistance of the three types of treated lyocell, i.e. lyocell treated with Agent (I), Fixapret CP and Fixapret ECO, respectively, by the Pad-Dry-Bake process. Table 8.9 shows the dry abrasion resistance of lyocell treated with Agent (I) by an exhaustion process. It is clear from both tables that lyocell fabrics treated with Agent (I) achieved excellent abrasion resistance, especially when high levels of agent were applied.

Table 8.8

Dry abrasion resistance of lyocell, treated with 3 different cross-linking chemicals by a Pad-Dry-Bake process

Conc. Of Agent Applied	10 g/l	20 g/l	40 g/l	60 g/l	80 g/l
Number of rubs to end point (Fixapret CP)	12,000	11,250	10,250	9,500	7,250

Number of rubs (Fixapret ECO)	11,000	10,000	9,500	8,750	5,750
Number of rubs (Agent I)	13,400	14,500	16,250	16,750	17,500

(The number of rubs of untreated fabric: 13,000)

Table 8.9

Dry abrasion resistance of lyocell, treated with Agent (I) by an exhaustion process

Agent applied	1% omf	2% omf	4% omf	6% omf	8% omf
Number of rubs to end point	13,500	14,500	16,000	16,400	17,000

(The number of rubs of untreated fabric: 13,000)

These results show that lyocell, treated with Agent (I), is superior to Fixapret CP and Fixapret ECO finished lyocell in several aspects:

i) Compared with the untreated sample, finishing with Fixapret CP and Fixapret ECO decreased the abrasion resistance of dyed lyocell fabrics, whereas, application of Agent (I) increased the abrasion resistance of dyed lyocell fabrics.

ii) The abrasion resistance of dyed lyocell, cross-linked with Agent (I), increased with increasing concentrations of Agent (I) applied, whereas, for Fixapret CP and Fixapret ECO finished lyocell, the abrasion resistance decreased with increasing resin concentration.

iii) The highest rub number achieved by dyed lyocell fabric treated with Agent (I) was 17,500, compared with 12,000 for Fixapret CP finished dyed lyocell.

Furthermore, when comparing the abrasion resistance of fabrics treated with Agent (I) by a Pad-Dry-Bake process with that by an exhaustion process, it was observed that, at similar application levels, the number of rubs achieved was very similar for both application methods. In other words, the resulting abrasion resistance of the treated fabric was independent of the application method.

Finally, it was observed that the rub number of the samples finished with 80 g/l DMDHEU resins decreased dramatically compared with 40 and 60 g/l.

8.3.3.2 Wet Martindale abrasion test

The wet Martindale test is a measure of the fibrillation resistance of the fabric. This test method is essentially the same as the traditional dry Martindale test, except that samples are wet during the test.

Table 8.10 compares the wet abrasion resistance of the three types of treated lyocell, i.e. dyed lyocell treated with Agent (I), Fixapret CP and Fixapret ECO, respectively, by the Pad-Dry-Bake process. Table 8.11 shows the wet abrasion resistance of dyed lyocell treated with Agent (I) by an exhaustion process.

It was observed that all samples reached the end point much more rapidly in the wet Martindale test than in the dry Martindale test, as evidenced from

the fact that the rub number was considerably lower for the wet than for the dry test. The end point of the untreated lyocell fabric was only 510 rubs in the wet conditions, compared with 13,000 rubs in a dry test. Such a low rub number indicates poor fibrillation resistance, which highlights the major technical defect of lyocell, i.e. it has a distinct tendency to fibrillate in the swollen state.

Table 8.10

Wet abrasion resistance of dyed lyocell, treated with 3 different agents by a Pad-Dry-Bake process

Conc. of Agent Applied	10 g/l	20 g/l	40 g/l	60 g/l	80 g/l
Number of rubs to end point (Fixapret CP)	610	700	1150	1700	1900
Number of rubs (Fixapret ECO)	580	660	870	1040	1500
Number of rubs (Agent I)	580	650	730	950	1080

(Number of rubs of untreated woven lyocell fabric: 510)

Table 8.11

Wet abrasion resistance of dyed lyocell, treated with Agent (I) by an exhaustion process

Agent Applied	1% omf	2% omf	4% omf	6% omf	8% omf
Number of rubs to end point (Agent I)	570	650	700	880	960

(Number of rubs of untreated woven lyocell fabric: 510)

The fibrillation resistance of dyed lyocell fabrics can be improved by treatment with both Agent (I) and the resins. However, Table 8.10 shows that, in general, resin-finished dyed lyocell fabrics gave a higher rub number than those treated with Agent (I), this tendency becoming more pronounced when higher levels of resin were applied. For example, when lyocell was treated with 10 or 20 g/l of each agent, the resin-finished samples only gave a slightly higher rub number than Agent (I)-treated ones. However, if higher concentrations were employed, e.g. 60 or 80 g/l, the rub number was much higher for resin-finished samples than for Agent (I)-treated ones. Such a comparison indicates that resin-finished dyed lyocell fabrics offered inherently better protection against (wet) fibrillation than lyocell treated with Agent (I). As discussed above, lyocell finished with Fixapret CP and Fixapret ECO resins gave particularly good results in the wet Martindale test.

Furthermore, as a general trend, it was observed that, the higher the concentration of agent used, the higher the rub number achieved. This means that fibrillation resistance was improved with increasing concentrations of either Agent (I) or resins applied to the lyocell fabric.

8.3.3.3 Blank process in Martindale abrasion test

Tables 8.12 and 8.13 summarise the dry and wet Martindale abrasion results for samples of dyed lyocell after-treated using a blank finishing

process. The data shows that the rub number of the finished fabric samples was similar to that of the untreated fabric, the abrasion resistance of all samples subjected to a blank finishing process being essentially the same as that of the untreated fabric under both dry and wet test conditions. Therefore, the application process itself (in the absence of the cross-linking chemicals) did not have any influence on the dry abrasion and (wet) fibrillation resistance performance of dyed lyocell substrates.

Table 8.12

Dry Martindale abrasion results of dyed lyocell samples subjected to a blank finishing process

Blank Process	60 g/l DMDHEU Resin	60 g/l Agent (I) (Continuous process)	6% omf Agent (I) (Exhaustion process)
Number of rubs	12,800	12,800	13,000

(The number of rubs of untreated fabric: 13,000)

Table 8.13

Wet Martindale abrasion results of dyed lyocell samples subjected to a blank finishing process

Blank Process	60 g/l DMDHEU Resin	60 g/l Agent (I) (Continuous process)	6% omf Agent (I) (Exhaustion process)
Number of rubs	490	500	500

(Number of rubs of untreated woven lyocell fabric: 510)

8.3.4 Dry crease recovery angle of dyed woven lyocell fabric

Creases in textile fabrics diminish at varying rates on the removal of the creasing forces. The magnitude of the crease recovery angle is an indication of the ability of a fabric to recover from accidental creasing. The higher the dry crease recovery angle (CRA) of a fabric, the better its crease recovery. This physical testing was described in Chapter 3. All lyocell samples were tested for crease recovery after being dyed with C.I.Reactive Blue 19 (Tables 8.14 and 8.15).

Table 8.14

CRA of dyed lyocell, treated with 3 different agents, by a Pad- Dry- Bake process

Conc. of Agent Applied		Untreated Sample	60 g/l Fixapret CP	60 g/l Fixapret ECO	Agent (l)				
					10 (g/l)	20 (g/l)	40 (g/l)	60 (g/l)	80 (g/l)
CRA (°)	5 min	74	104	105	98	103	106	109	114
	15 min	78	109	108	103	107	109	114	118
	30 min	81	112	111	107	110	112	117	122
	60 min	81	112	111	107	110	113	117	122

Table 8.15

CRA of dyed lyocell, treated with Agent (I), by an exhaustion process

Agent applied (omf)		1%	2%	4%	6%	8%
CRA (°)	5 min	95	99	103	105	108
	15 min	100	103	106	110	113
	30 min	104	107	110	114	116
	60 min	104	107	110	114	117

These results show that, not surprisingly, a higher CRA was obtained for dyed woven lyocell fabric, treated with either Agent (I) or DMDHEU, than for the untreated sample. In the case of dyed lyocell fabrics, treated with equal or more than 40 g/l Agent (I) by the Pad-Dry-Bake process and those treated with equal or more than 6% omf Agent (I) by an exhaustion process, the CRA obtained was higher than that of dyed fabric finished with 60 g/l Fixapret CP or Fixapret ECO, which is the concentration commonly used in industrial DMDHEU finishing. Fabrics treated with lower concentrations of Agent (I) gave only slightly lower CRA values than those treated with 60 g/l Fixapret CP and Fixapret ECO. Increasing the amount of Agent (I) applied to the fabric resulted in better crease recovery. Such a trend was observed for both application methods.

The tests showed that after removal of the load, the CRA of all samples

showed a significant change in the first 5 mins, then increased only 3-5° in the next 10 mins and remained virtually unchanged after 30 mins.

8.3.5 Tensile strength of dyed woven lyocell fabric

The tensile strengths of all samples were measured in the warp direction. This physical testing was described in Chapter 3. All samples were tested for tensile strength after being dyed with C.I. Reactive Blue 19.

The effect of Agent (I), Fixapret CP and Fixapret ECO on the tensile strengths of dyed woven lyocell fabrics is presented in Tables 8.16 and 8.17. The results indicate that, after Fixapret CP and Fixapret ECO resins were applied to woven lyocell fabrics, the resultant tensile strength decreased compared with that of the untreated samples. The tensile strength value dropped (by almost 40%) from the original value of 10.5 kN/m (for the untreated sample) to 6.4 kN/m (for the 80 g/l Fixapret ECO finished sample). The low tensile strength of DMDHEU treated fabric is likely to be due to chemical degradation of cellulose by the acid-producing catalyst during curing of the dried fabric at high baking / curing temperature [150].

Table 8.16

Tensile strength (TS) of dyed lyocell, treated with 3 different agents, by a Pad- Dry- Bake process

Conc. of Agent Applied		10 g/l	20 g/l	40 g/l	60 g/l	80 g/l
T S	Agent (I)	12.6	12.3	11.6	11.2	11.0

(kN/m)	Fixapret CP	10.1	9.8	9.0	8.7	6.9
	Fixapret ECO	10.0	9.5	9.1	8.5	6.4

(Tensile strength of untreated woven dyed lyocell fabric: 10.5 kN/m)

Table 8.17

Tensile strength (TS) of dyed lyocell, treated with Agent (I), by an exhaustion process

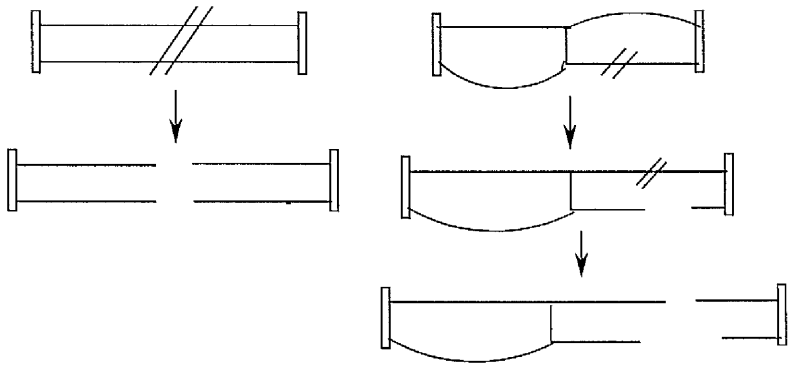
Agent (I) Applied	1% omf	2% omf	4% omf	6% omf	8% omf
T S (kN/m)	12.4	11.8	11.7	11.2	11.2

(Tensile strength of untreated woven dyed lyocell fabric: 10.5 kN/m)

With regard to application of cross-linking agents by either a Pad-Dry-Bake or an exhaustion process, the tensile strengths of all samples, treated with Agent (I), were higher than those of untreated woven dyed lyocell fabric, as well as Fixapret CP and Fixapret ECO finished fabrics. In other words, cross-linking with Agent (I) increased the tensile strength of woven dyed lyocell fabrics, whereas finishing with a DMDHEU resin decreased it.

Nevertheless, the tensile strength of the finished dyed fabrics generally decreased with increasing concentrations of applied Agent (I). Such a trend was observed for both application methods. This loss of tensile strength may be caused by the restriction of stress distribution within fibres due to their rigid cross-linking [150]. A mechanism has been proposed to explain why rigid cross-linking decreases tensile strength. This mechanism

considers the sharing of load between molecular chains or fibrils. An analogous system of two chains is shown in Figure 8.6. With a cross-link present, each chain breaks separately, and the strength will be half the value that it would be without the cross-link when both chains have to be broken together [151].



(a) (b)

Figure 8.6 Rupture of two chains: (a) without link; (b) with a cross-link

The high-levels of Agent (I) applied causes excess cross-linking of the treated fibre. Such excessive cross-linking leads to rigidly cross-linked fibre. Due to the afore-mentioned reasons, the tensile strength could be adversely affected. Consequently, relatively low-level of Agent (I) (e.g. 10 g/l) applied gave the best tensile strength for the treated lyocell fabric.

Table 8.18

Tensile strength of dyed lyocell samples subjected to a blank process

Blank Process	60 g/l DMDHEU	60 g/l Agent(I)	6% omf Agent(I)
Tensile Strength (kN/m)	10.2	10.4	10.5

(Tensile strength of untreated woven lyocell fabric: 10.5 kN/m)

Table 8.18 shows the tensile strength values of samples obtained using blank processes. With regard to the blank process for applying Agent (I), the results indicate that the tensile strength of the sample was similar to that of untreated fabric. Therefore, the blank process used for the application of Agent (I) does not have any influence on the tensile strength. However, with respect to the blank process corresponding to the application of a DMDHEU resin, the tensile strength of the samples decreased slightly, probably due to the acid-catalyzed depolymerisation of cellulose.

8.3.6 Repeated laundering of dyed woven lyocell

8.3.6.1 Stability of lyocell-O-Agent (I) bonding as an indication of fibrillation protection

To predict the stability of Agent (I)-treated dyed woven lyocell to repeated laundering, Agent (I) was converted to its methyl ether derivative, i.e. a model ether, to simulate attachment of lyocell to the agent as previously described in Chapter 4, Section 4.3.2.1.

This model compound was dissolved in the 1993 AATCC detergent solution and the mixture heated to 60 °C for 60 and 120 mins. The reaction mixture was analysed by HPLC at the start and end of the 60 & 120 mins treatments. HPLC showed only a single peak, corresponding to the starting

material. Hence one might expect dyed lyocell, post-treated with Agent (I) to be stable to a small number of repeat launderings.

8.3.6.2 Evaluation of Smoothness appearance and protection against fibrillation

This physical testing was described in Chapter 3. All samples, after repeated laundering, were compared to AATCC 3-D Smoothness Appearance (SA) replicas. The SA grades are described in Table 8.19.

Table 8.19

AATCC Fabric Smoothness Appearance (SA) Grades

Grade	Description
SA-5	Very smooth, pressed, finished appearance.
SA-4	Smooth, finished appearance.
SA-3.5	Fairly smooth but non-pressed appearance.
SA-3	Mussed, non-pressed appearance.
SA-2	Disordered, obviously wrinkled appearance.
SA-1	Crumpled, creased and severely wrinkled appearance.

Table 8.20 shows the smoothness and fibrillation (hairyness) of various fabric samples, examined visually, after 1, 5, 10 and 15 laundering cycles. After one laundering cycle, it was evident that the smoothness of the surface was greater for woven lyocell fabrics treated with either Fixapret CP, Fixapret ECO (DMDHEU) or Agent (I) than for untreated dyed ones. Although the untreated lyocell fabric appeared rough, the treated ones were smooth, with no fibrillation being observed on the surface of any of the samples.

Table 8.20 Smoothness Appearance (SA) grade and fibrillation protection after repeated laundering test

Agent		Untreated fabric	60g/l Fixapret CP	60g/l Fixapret ECO	Conc. of Agent I (g/l)				Agent I applied (omf)			
					10	20	40	60	1%	2%	4%	6%
1 laundering cycle	SA Grade	3	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Fibrillation	No	No	No	No	No	No	No	No	No	No	No
5 laundering cycles	SA Grade	2-3	4	4	3.5	4	4	4	3.5	4	4	4
	Fibrillation	Very little	No	No	Very little	No	No	No	Very little	No	No	No
10 laundering cycles	SA Grade	1-2	3.5-4	3.5-4	3	3	3	3.5-4	3	3	3	3
	Fibrillation	much	Very little	Very little	Little	little	Little	Very little	Little	little	little	little
15 laundering cycles	SA Grade	1	3	3	2	2	2	3	2	2	2	2
	Fibrillation	Very much	Little	Little	Much	Much	Much	Little	Much	Much	Much	Much

After 5 laundering (washing and drying) cycles, the untreated dyed fabric appeared disordered, obviously wrinkled. However, the surface was fairly smooth for fabrics treated with 10 g/l Agent (I) applied by the Pad-Dry-Bake process and 1% omf Agent (I), applied by an exhaustion process. Furthermore, the surface of fabrics finished with Fixapret CP resin was smoother than that of the fabrics treated with either 10 g/l Agent (I) (Pad-Dry-Bake process) or 1% omf Agent (I) (exhaustion process). However, when a higher amount of Agent (I) was applied to lyocell fabrics, the smoothness of the treated fabrics after five laundering cycles was similar to that of Fixapret CP and ECO finished fabric.

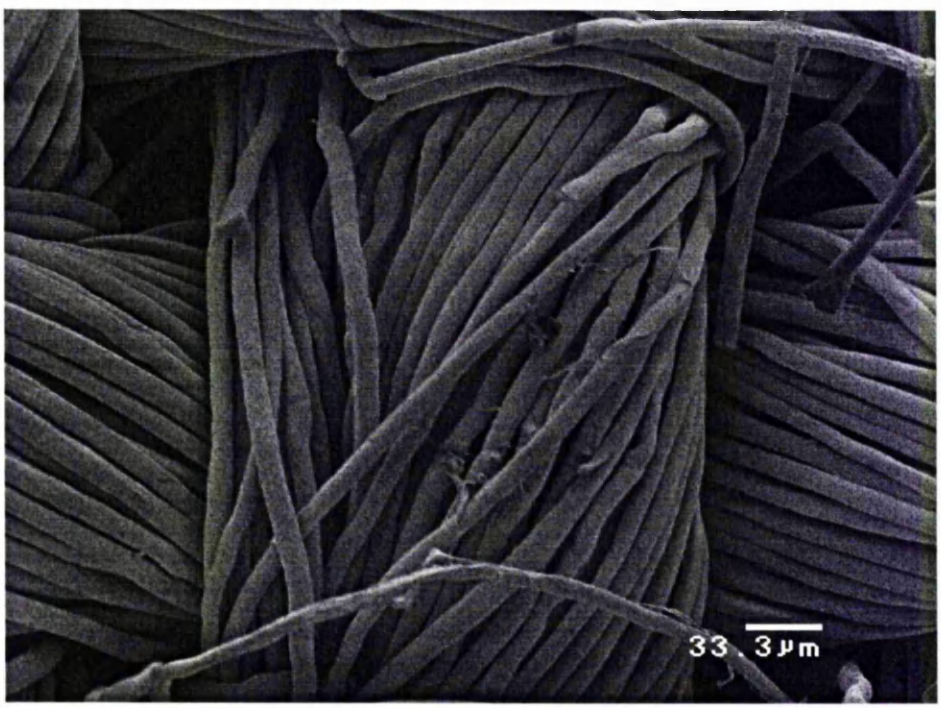
After 5 washing and drying cycles, slight fibrillation was observed (visually) on the surface of the untreated sample as well as fabrics treated with 10 g/l Agent (I) (applied by Pad-Dry-Bake process) and 1% omf Agent (I) (applied by an exhaustion process). However, visual fibrillation still could not be observed on other fabric surfaces. Therefore, it was apparent that low-levels of Agent (I) cannot protect lyocell sufficiently against fibrillation. However, in the case of lyocell fabrics, treated with 20 g/l Agent (I) or greater, by a continuous process, and those treated with 2% omf Agent (I) or greater by an exhaustion process, comparable results were obtained to fabrics finished with 60 g/l Fixapret CP and Fixapret ECO, both in terms of smoothness of appearance and protection against fibrillation.

After 10 or 15 laundering cycles, the untreated dyed lyocell fabric appeared crumpled, creased and severely wrinkled. The smoothness of fabrics treated with either Fixapret CP or Fixapret ECO or various concentrations of Agent (I) was much greater than that of the untreated sample. Among all the treated, dyed lyocell fabrics after ten and fifteen laundering cycles, those samples treated with either 60 g/l Agent (I) or 60 g/l DMDHEU resins gave the smoothest fabric surfaces.

After 10 or 15 laundering cycles, large amounts of fibrillation were observed on the surface of the untreated sample and treated fabrics, except for lyocell fabrics treated with 60 g/l Agent (I), Fixapret CP and Fixapret ECO. To examine surface features, a scanning electron microscopy (SEM) was used. SEM images were captured to compare the degree of fibrillation (Pictures 8.1-8.8).

The results show that, after 10 and 15 washes, fibrillation can be equally prevented on dyed lyocell fabrics, treated with either 60 g/l Agent (I) or with 60 g/l Fixapret CP / Fixapret ECO resins.

Picture 8.1 Untreated fabric after 10 laundering cycles

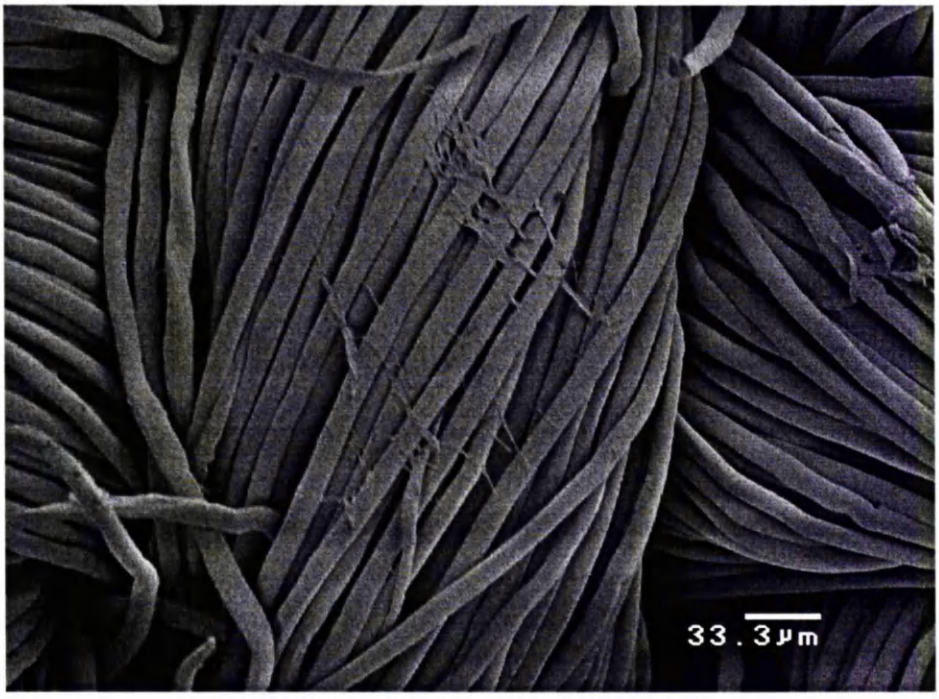


Picture 8.2 Fabric treated with 60 g/l Agent (I) after 10 laundering cycles

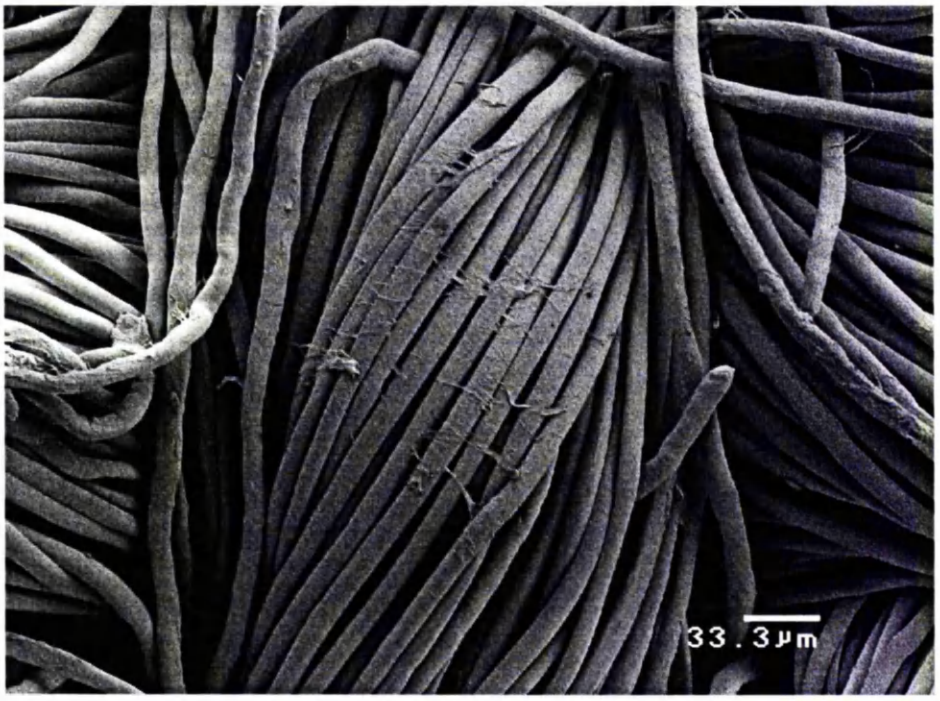
Picture 8.3 Fabric treated with 60 g/l Fixapret CP after 10 laundering cycles

Picture 8.4 Fabric treated with 60 g/l Fixapret ECO after 10 laundering cycles

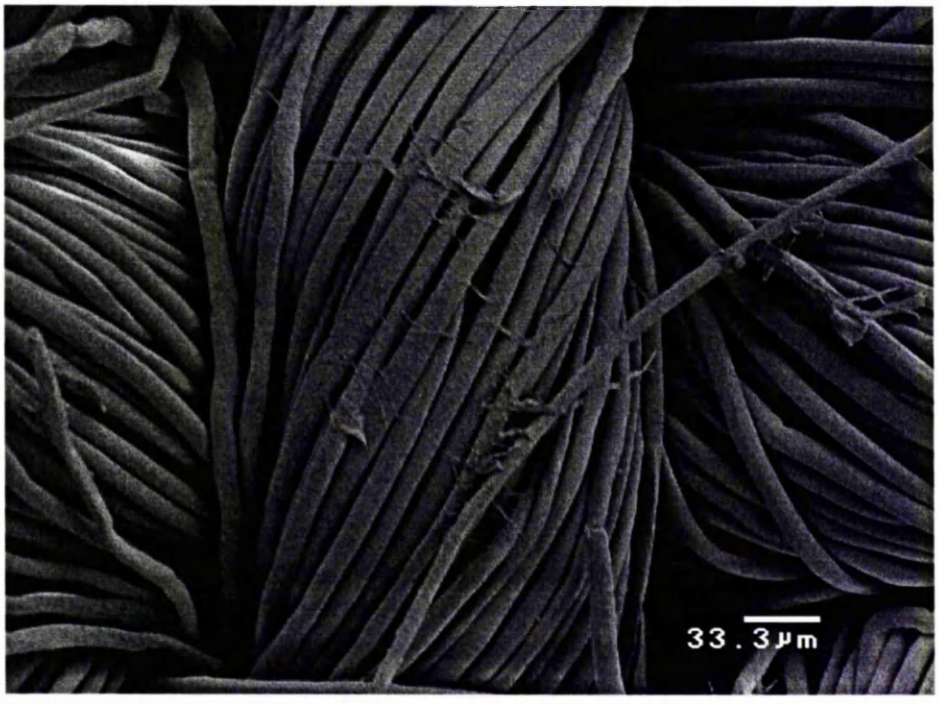
Picture 8.5 Untreated fabric after 15 laundering cycles



Picture 8.6 Fabric treated with 60 g/l Agent (I) after 15 laundering cycles



Picture 8.7 Fabric treated with 60 g/l Fixapret CP after 15 laundering cycles



Picture 8.8 Fabric treated with 60 g/l Fixapret ECO after 15 laundering cycles

8.3.7 Handle

The handle of woven dyed lyocell samples was assessed by touch. Table 8.21 shows that woven dyed lyocell fabric, treated with different concentrations of Agent (I), either by a continuous or by an exhaustion process, exhibited equal handle to the untreated sample and provided softer handle than those samples finished with Fixapret CP and Fixapret ECO. Fabrics finished with 60 g/l Fixapret CP exhibited the worst handle, compared with fabrics treated with various concentrations of Agent (I) or 60 g/l Fixapret ECO.

Table 8.21

Comparison of handle touch (subjective testing by a panel of people)

Fabric Samples	Untreated	All concentrations of Agent (I)	60 g/l Fixapret CP	60 g/l Fixapret ECO
Handle	Soft	Soft	Very stiff	Harsh

8.4 Conclusions

Resin finishing with Fixapret CP and Fixapret ECO (DMDHEU) gave lyocell fabrics with good anti-fibrillation properties but with adversely affected mechanical properties. However, the results in this study showed that dyed woven lyocell fabric, treated with Agent (I), either by a continuous (Pad-Dry-Bake) or by an exhaustion process, exhibited both an improved abrasion resistance and tensile strength. Moreover, dyed woven lyocell fabric

treated with different concentrations of Agent (I) showed softer handle than when finished with 60 g/l Fixapret CP and 60 g/l Fixapret ECO.

With regard to dry crease recovery, dyed woven lyocell fabrics treated with at least 40 g/l Agent (I) by a continuous process and with at least 6% omf Agent (I) by an exhaustion process, achieved better crease recovery properties compared with fabrics finished with Fixapret CP and Fixapret ECO. The crease recovery of fabrics, treated with lower concentrations of Agent (I), was only slightly lower than that of fabrics finished with Fixapret CP and Fixapret ECO, but was significantly higher than that of untreated samples.

With respect to repeated laundering, after 5 washes, dyed lyocell fabrics treated with medium to high-levels of Agent (I) were able to achieve similar performances to those finished with 60 g/l Fixapret CP and Fixapret ECO, both in terms of the smoothness in appearance of the fabrics and protection against fibrillation. However, after 10-15 laundering cycles, only fabrics treated with 60 g/l Agent (I) showed comparable results, i.e. similar extent of smoothness and efficiency of fibrillation prevention, to fabrics finished with Fixapret CP and Fixapret ECO resins.

With the wet Martindale abrasion test, lyocell treated with Agent (I) showed lower fibrillation resistance than lyocell finished with either Fixapret CP or Fixapret ECO at the same applied concentration. However, Agent (I) gave better protection against fibrillation than untreated fabric.

Comprehensive physical testing, i.e. dry creasing resistance test, Martindale abrasion test, tensile strength test, repeated domestic laundering test and 'handle' test, showed that it is possible to apply 60 g/l Agent (I) to lyocell by a Pad-Dry-Bake process as an alternative to finishing lyocell with 60 g/l Fixapret CP and Fixapret ECO. The benefit is that treatment with Agent (I) can achieve most of the advantages of Fixapret CP and Fixapret ECO (DMDHEU finishing), such as fibrillation protection, good crease recovery and smooth fabric surface after repeated laundering, while at the same time being free of the short-comings of resin finishing, i.e. formaldehyde release, harsh handle, drop in tensile strength and poor abrasion resistance.

CHAPTER 9

CONCLUSIONS

9.1 2,4-Diacrylamidobenzenesulphonic acid as a pre-treatment for lyocell

1. This agent is a novel, colourless, water-soluble, anionic compound which can be applied to 'never-dried' lyocell fibres by a Pad-Steam method (as currently used in the production of Tencel LF and Tencel A100).
2. This agent furnished cross-linked lyocell fibres with good wet abrasion resistance (NSF) and stable lyocell-O-agent bonds to subsequent hot exhaust reactive dyeing conditions.
3. The fibre-agent bonds showed some instability to polyester dyeing conditions (130 ^{o}C, at pH 4.0). This is rationalised in terms of hydrolysis of the amide bond *ortho* to the sulphonic acid group *via* a neighbouring group participation mechanism.
4. Never-dried lyocell, treated with this agent, exhibited no 'resist effect', i.e. it gave similar colour yields to untreated lyocell following subsequent dyeing with a series of polysulphonated reactive dyes.

9.2 Stability of benzeneacrylamido compounds to high temperature acidic environments

A number of benzeneacrylamido compounds, each with at least one sulpho or

carboxyl group, have been synthesised, converted to their corresponding methyl ethers, and the derivatives subjected to high temperature polyester dyeing conditions for one hour. Derivatives with sulpho groups *meta* or *para* to the amide links proved to be hydrolytically stable to the HT treatment, whereas derivatives with either an *ortho* sulpho or an *ortho* carboxyl substituent underwent significant amide hydrolysis. This was consistent with previous findings and with a neighbouring group participation mechanism.

9.3 Effect of 4,4'-diacrylamidobiphenyl-2,2'-disulphonic acid and 3,5-diacrylamido-2,4,6-trimethylbenzene-sulphonic acid on lyocell

1. Both agents, devoid of a sulpho group *ortho* to the acrylamido group are novel, colourless compounds. They were applied to 'never-dried' lyocell fibres by a Pad-Steam method.
2. The corresponding model ethers of both compounds were synthesised to simulate the attachment of lyocell to agents. Both ethers proved to be hydrolytically stable, thus, by inference, showing the stability of the lyocell-O-agent bonding under high temperature polyester dyeing conditions.
3. Lyocell cross-linked with both agents showed unacceptably low wet abrasion resistance, presumably as a result of their low fixation to lyocell.

9.4 Effect of 4,4'-diacrylamido-2,2'-stilbenedisulphonic acid on lyocell

1. This agent devoid of a sulpho group *ortho* to the acrylamido group has been synthesized, however, further application to lyocell was not carried out due to its yellow colour.

2. Lyocell, crosslinked with this agent, was likely to be stable under high temperature treatment conditions, as verified by the same "model ether" experiment for the afore-mentioned agents.

9.5 2,4-Diacrylamidobenzenesulphonic acid as an after-treatment for lyocell

1. This agent has been applied to woven lyocell fabric by a Pad-Dry-Bake method after dyeing.
2. In terms of crease recovery properties, anti-fibrillation properties and fabric smoothness after repeated laundering, lyocell treated with 60 g/l of this agent gave similar results to lyocell finished with Fixapret CP and Fixapret ECO.
3. In terms of tensile strength and dry abrasion resistance, lyocell treated with various concentrations of this agent achieved better performance than that finished with Fixapret CP and Fixapret ECO.

4. In terms of wet abrasion resistance, lyocell treated with this agent exhibited lower fibrillation resistance than that finished with Fixapret CP and Fixapret ECO at the same application level.

5. In terms of handle, woven lyocell fabric treated with various concentrations of this agent showed softer handle than when finished with 60 g/l Fixapret CP and Fixapret ECO.

9.6 Overall conclusions

This research was centred on the synthesis, application and evaluation of novel cross-linking agents based on a series of readily available sulphonated aromatic amines.

As a pre-treatment, 2,4-diacrylamidobenzenesulphonic acid is an effective cross-linking agent for the protection of lyocell against fibrillation. Moreover, lyocell treated with this agent does not adversely affect subsequent dyeing properties. The lyocell-O-agent bonds so generated are stable to hot reactive dyeing but show some instability to high temperature (HT) polyester dyeing conditions. This has been rationalised in terms of acid catalysed hydrolysis of the amide bond *ortho* to the sulphonic acid group via a neighbouring group participation mechanism.

The feasibility of the above mechanism is further confirmed by checking a number of related benzeneacrylamido derivatives. Derivatives with sulpho

groups *meta* or *para* to the amide links proved to be hydrolytically stable to the HT treatment, whereas derivatives with either an *ortho* sulpho or an *ortho* carboxyl substituent undergo significant amide hydrolysis. Accordingly, benzeneacrylamido cross-linking agents, designed to be hydrolytically stable to a range of high temperature polyester dyeing conditions, should be devoid of *ortho* sulpho or *ortho* carboxyl substituents.

Hence, 3,5-diacrylamido-2,4,6-trimethylbenzenesulphonic acid, 4,4'-diacryl-amidobiphenyl-2,2'-disulphonic acid and 4,4'-diacrylamido-2,2'-stilbene-disulphonic acid, were synthesised to represent novel agents devoid of the *ortho* sulpho structure. Never-dried lyocell, cross-linked with these three agents, are predicted to be stable under high temperature treatment conditions, and this was supported by the stability of their corresponding "model ethers". However, lyocell treated with the first two agents exhibited poor wet abrasion resistance, whereas the last agent was inherently yellow. Therefore, these agents are of no value for the protection of lyocell against fibrillation.

As an after-treatment, It is possible to apply 60 g/l of 2,4-diacrylamido-benzenesulphonic acid to lyocell by a continuous process as an alternative to finishing lyocell with 60 g/l Fixpret CP and Fixapret ECO, with the benefit of:

- retaining most of the advantages of conventional resin finishing,
- providing improved tensile strength and dry abrasion resistance properties.

Overall, the novel cross-linking agent, 2,4-diacrylamidobenzenesulphonic acid, exhibits promising features as a potential, industrially-viable chemical for both pre-treatment and after-treatment of lyocell.

FUTURE WORK

1. To continue designing and synthesizing cross-linking agents, wherein the sulphonic acid group is not adjacent to the acrylamido reactive group.
2. To modify the application conditions for increasing the fixation level and fibrillation protection of 4,4'-diacrylamidobiphenyl-2,2'-disulphonic acid and 3,5-diacrylamido-2,4,6-trimethylbenzene- sulphonic acid to lyocell.
3. To maximise the technical performance of 2,4-diacrylamidobenzene-sulphonic acid as an after-treatment for woven lyocell fabrics.

REFERENCES

1. E. Ott, H. G. Tennent, *Cellulose and cellulose derivatives*, 2nd Edn, part 1, New York, Wiley-Interscience, (1954) 1.
2. E. R. Trotman, *Dyeing and Chemical Technology of Textile Fibres*, Edward Arnold (1993) 37.
3. J. Shore, *Cellulosics Dyeing*, Society of Dyers and Colourists, Bradford, (1995) 14.
4. http://www.encyclopedia.com/html/r/rayon.asp, "rayon."
5. P. White, *Regenerated Cellulosic Fibres*, Ed Calvin Woodings, Textile Institute, CRC Press, Woodhead Publishers Ltd., (2001) 65.
6. R. W. Moncriff, *Man-made fibres*, 6th Edn, Part 2, London: Newnes-Butterworth (1975)111.
7. A. D. Broadbent, *Basic Principles of Textile Coloration*, Society of Dyers and Colourists, Bradford, (2001) 93.
8. J. G. Cook, *Handbook of Textiles Fibres Man-made Fibres*, Merrow Publishing Co. Ltd., England, (1984) 25.
9. P White, *Regenerated Cellulosic Fibres*, Ed Calvin Woodings, Textile Institute, CRC Press, Woodhead Publishers Ltd., (2001) 62.
10. H. Firgo, M. Eibl, W. Kalt and G. Meister, *Lenzinger Berichte*, **9** (1994) 80
11. X. Colom, F. Carrillo, *European Polymer Journal*, **38**(2002) 2225-2230.
12. D. Eichinger, M. Eibl, *Lenzing lyocell- an interesting cellulose fibre for the textile industry*, Dornbin Man-made Fibres Conference (1995).
13. S.M. Burkinshaw, D. Katsarelias, *Dyes and Pigments*, **29** (2) (1995) 153.
14. W. Ingamells, *Colour for Textiles a User's Handbook*, the Society of Dyers and Colourists, Bradford, (1993) 88.
15. T. L. Vigo, *Textile Processing and Properties: Preparation, Dyeing, Finishing and Performance*, Elsevier, Amsterdam (1994) 119.
16. U. Baumgarte, *The Dyeing of Cellulosic Fibres*, Dyers' Co. Publications Trust, England, (1986) 224-232.
17. J. Shore, *Cellulosics Dyeing*, Society of Dyers and Colourists, Bradford, (1995) 562-564.
18. L. Tigler, S. Division, Dyeing Primer: Fundamentals of Dyeing, AATCC,

(1990) 17.

19. J. Shore, *Colorants and auxiliaries*, Vol. 2, Society of Dyers and Colourists, (1990) 549.
20. S. R.Cockett, K.A. Hilton, *Dyeing of Fibres and Related Processes*, (1961) 133.
21. C. Preston, *The Dyeing of Cellulosic Fibres*, Dyers' Co. Publications Trust, England, (1986) 290-292.
22. J. Shore, *Colorants and Auxiliaries: Organic Chemistry and Application Properties,* Society of Dyers and Colourists, Bradford, (1990) 520.
23. J . Shore, *Cellulosics Dyeing*, Society of Dyers and Colourists, Bradford, (1995) 322.
24. J. Rivlin, *The Dyeing of Textile Fibres Theory and Practice*, Philadephia, (1992)136.
25. A. Johnson, *The Theory of Coloration of Textiles, Society of Dyers and Colourists*, Bradford, (1989) 438.
26. J. Shore, *Cellulosics Dyeing*, Society of Dyers and Colourists: Bradford (1995) 192.
27. A. H. Renfrew, *Reactive Dyes for Textile Fibres*, Society of Dyers and Colourist, (1999) 12-18.
28. J. Rivlin, *The Dyeing of Textile Fibres Theory and Practice*, Philadephia, (1992) 139.
29. J. Shore, *Cellulosics Dyeing*, Society of Dyers and Colourists: Bradford (1995) 194-196.
30. G. W. Madaras, G.J. Parish, J. Shore, *Batchwise Dyeing of Woven Cellulosic Fabric*, Society of Dyers and Colourists (1993) 46.
31. A. Nechwatal, M. Nicolai, *Textile Chemist and Colorist*, **28** (5) (1996) 24.
32. R. Chemie, *Lyocell technology*, Company brochure (1998).
33. Lyocell by Lenzing at www. Austria. Eu.net/lyocell/
34. T. Hongu, G.O. Phillips, *New Fibers*, Woodhead Publishing Ltd., second edition, (1997)193.
35. J. Taylor, *J.S.D.C.*,**114** (1998) 191.
36. Manufacture of Lyocell Fibre at http://www.texguide.com/news_group/lyocell.htm, Nov. 1998.

37. Lyocell / Tencel: Facts behind the Fiber at http://www.lotusorganics.com/articles/lyocell.aspx
38. A. Slater, *Chemical Fibre International*, **1**(2006) 45.
39. P White, *Regenerated Cellulosic Fibres*, Ed Calvin Woodings, Textile Institute, CRC Press, Woodhead Publishers Ltd (2001) 69.
40. P White, *Regenerated Cellulosic Fibres*, Ed Calvin Woodings, Textile Institute, CRC Press, Woodhead Publishers Ltd, (2001) 76.
41. E. Miosda, *Melliand International*, **7-8** (1998) E148.
42. A Nechwatal, M Nicolai and K-P Mieck, *Textile Chemist and Colorist*, **28 (5)** (1996) 24.
43. J. Lenz, J. Schurz, and E Wrentschur, *Acta Polymer*, **43** (1992) 307.
44. J. Schurz, *Lenzinger Berichte*, **9** (1994) 37.
45. K Bredereck, F Schulz and A Otterbach, *Melliand Textilberichte*, **78(10)** (1997) 703.
46. J.M. Taylor, P. Mears, *J.S.D.C.*, **107** (1998) 64-69.
47. T. Hohberg and S Thumm, *Milliand International*, **2** (1998) 122.
48. Courtaulds *Tencel Information Sheets*, Nov. (1996).
49. Meeting Notes from Acordis, Spondon Nov. (1998).
50. Technical Tencel Information at www. Newfibres.com, Nov. (1998).
51. F. Brauneis and M. Eibl, *Melliand Textilberichte*, **79** (3), (1998), E38-E39.
52. R. Kampl and J. Leitner, *Melliand Textilberichte*, **81** (4), (2000), E67-E69.
53. Manufacture of Lyocell Fibre at www.texguide.com/news_group/lyocell.htm, Nov. (1998).
54. C. R. Woodings, *International Journal of Biological Macromolecules*, **17**(6) (1995) 305.
55. J.M. Taylor, *J.S.D.C.*, **115** (1999) 294-296
56. A. Slater, *Chemical Fibres International*, **1** (2006), 45.
57. P. Alwis, J. Taylor, *Melliand International*, **3** (2001), E54.
58. K.C. Schuster, C. Rohrer,D. Eichinger, J. Schmidtbauer, P. Aldred, and H. Firgo, *Natural Fibers, Plastics and Composites*, (2004) 123.
59. H. Firgo, M. Eibl, and D. Eichinger, *Lenzinger Berichte.*, **75** (1995) 47.

60. D. Eichinger, H. Firgo and Ch. Rohrer, *Materials Research Society Symposium Proceedings*, **702** (2002) 43-54.
61. F. Brauneis and M. Eibl, *Melliand Textilberichte*, **79** (3) (1998) E38-E39.
62. R. Kampl and J. Leitner, *Melliand Textilberichte*, **81** (4) (2000) E67-E69
63. U. Sayed, M. R. Pratap, A. S. Singh, Y. N. Rane, and A. L. Pawar, *Colourage*, **49**(10) (2002) 33.
64. V. Agarwal, *Man-Made Textiles in India*, **44**(6) (2001) 215.
65. H. Harms, *Materialwissenschaft und Werkstofftechnik*, **34**(3) (2003) 267.
66. W. Zhang, S Okubayashi and T Bechtold, *Carbohydrate Polym.*, **59**(2) (2005) 173.
67. K. Fang, L. Hao, X. Hu, and H. Shao, *Text. Res. J.*, **73**(11) (2003) 1013.
68. D. Eichinger, M. Eibl, *Lenzinger Berichte*, **75** (1996) 41.
69. D.Eichinger, *Lenzinger Berichte*, **75** (1996) 69.
70. I. Marini, *Textilveredlung*, **9/10** (1996) 194.
71. H. P. Fink, P. Weigel, H. J. Purz and J. Ganster, *Prog. Polym. Sci.*, **26** (9) (2001) 1473.
72. A. Nechwatal, M. Nicolai and K-P Mieck, *Textile Chemist and Colorist*, **28** (5) (1996) 24.
73. R.Kampl, W.Schaumann, *Lenzinger Berichte*, **75** (1996) 91.
74. Bredereck et al., *"The pore system of cellulose fibres and their significance for fibre properties"*, 7th IFVTCC Congress, Vienna, 1996.
75. J. Schurz, *Lenzinger Berichte*, **74** (1994) 37.
76. S. Davies, *Textile Outlook International*, **4** (1992) 8.
77. P I Patterson, *WO 9805815* (1998).
78. European Patent, *WO 9940251* (Akzo Nobel Uk Limited;1999) .
79. Tencel, *Dyeing/Finishing Manual*, Section 6, **3** (1993).
80. P White, *Regenerated Cellulosic Fibres*, Ed Calvin Woodings, Textile Institute, CRC Press, Woodhead Publishers Ltd, (2001) 81.
81. K.Gandhi, S. M. Burkinshaw, G. W. Collins and J. M.Taylor, *Book of Papers - International Conference & Exhibition,* AATCC (1999), 160.

82. K. Gandhi, S. M. Burkinshaw, J. M. Taylor, *AATCC Review*, **2**(4) (2002) 48.
83. Japanese Patent, *JP11117182* (Honda, Mariko Unitika Ltd.; 1999).
84. Ch. Rohrer, P. Retzl and H. Firgo, *Man-made Fibre Year Book*, **8** (2001) 26.
85. Austrian Patent, *WO 99/19555* (Lenzing AG; 1997).
86. Ch. Rohrer, P. Retzl and H. Firgo, *Chemical Fibers International*, **50** (6) (2000) 552,554-555.
87. H. Firgo, Ch. Rohrer and P. Retzl, *Lenzinger Berichte*, **80** (2001) 75.
88. L. Maosong, Y. Zhigan and Z. Zhou, *Fangzhi Xuebao*, **24**(6) (2003)25.
89. H. Firgo, M. Eibl, W. Kalt, and G. Meister, *Lenzinger Berichte*, **9** (1994) 80.
90. T. Eynon, *Japanese Business News*, **12** (1998) 1.
91. P. Alwis, J. Taylor, *Melliand Textilberichte*, **82**(3) (2001) E54, E56, 196-199.
92. European Patent *882836* (Ciba Specialty Chemicals; 1998).
93. European Patent *538977* (Courtaulds Fibres ; 1992).
94. Austrian Patent 002,527 (Lenzing AG ; 1998).
95. A H M Renfrew, D A S Phillips, *Coloration Technology*, **119** (2003) 116.
96. European Patent *950,751* (Ciba Specialty Chemicals; 1999).
97. European Patent *903,434* (Ciba Specialty Chemicals; 1998).
98. Japanese Patent *08-025888* (Sumitomo;1996).
99. *WO 9735848* (BASF; 1996).
100. European Patent *950,750* (Ciba Specialty Chemicals; 1998).
101. A. Nechwatal, M. Nicolai, K-P Mieck, B. Heublein, G. Kühne and D. Klemn, *Angew. Makromol. Chem.*, **271** (1999) 84.
102. P. Rhone, French Patent 2,273,091 (1974).
103. M. Karypidis, M.A. Wilding, C.M. Carr and D.M. Lewis, *AATCC Review*, **1**(8) (2001) 40.
104. S M Burkinshaw and K Gandhi, *International Conference and Exhibitions,* AATCC, (1997) 476.
105. K. Bredereck, F. Schulz and A. Otterbach, Melliand Textilberichte, **78**(10) (1997), 703-704,707-708,710-711,E155-E158.
106. M. Nicolai, A. Nechwatal and K.P. Mieck, *Textile Res J*, **66** (9) (1996)

575.

107. J. Taylor; G.W. Collins, *WO 02103104* (Tencel Ltd.; 2002).

108. E. Miosga, *Melliand Textilberichte*, **79** (7/8) (1998), 532-534, E148-E149.

109. BASF, *Manual Textile Finishing*, 1978(22).

110. E. Agster, *Melliand International*, **3** (1997)152, 154, 156.

111. S. B. Sello, *J.S.D.C.*, 101(3) (1985) 99.

112. USA Patent, *WO 2001073186* (Procter & Gamble Company, 2001).

113. S.B. Sello, J.P Stevens, *Textile Chemist and Colorist*, **14** (11) (1982) 222.

114. USA Patent, *WO 89-US2628* (United States Dept. of Commerce; (1989).

115. USA Patent, *US 88-207461* (United States Dept. of Health and Human Services; 1988).

116. F. Reinert, *Environmentally Acceptable Resin*, 17th IFVTCC Congress, Vienna, June (1996) 39-43.

117. I. Holme, *Challenge and Change in Functional Finishes for Cotton*, Cotton-Europe Conference, (1996) 17-24.

118. European Patent, *WO 9500697*, (Courtaulds Fibres; 1993).

119. European Patent *691,426* (Courtaulds Fibres ; 1994).

120. *WO 9607780* (BASF; 1994).

121. European Patent *783,602* (Lenzing AG; 1995), *796358* (Lenzing AG; 995).

122. *WO 96/20302* (Akzo Nobel N.V.; 1996).

123. European Patent *978,585* (Ipposha Oil Industries Co. Ltd., 1998).

124. A. Necheatal, K. P, Mieck, T. Reussmann and M. Nicolai, *Melliand Textilber.*, **81**(3) (2000) E46.

125. J. M. Taylor, P. Alwis, L. Harrington and M. Geubtner, *Melliand Textilber.*, **83**(3) (2002) E37.

126. J. Schurz, Lenzinger Berichte, **74** (1994) 37.

127. H. Firgo, M. Eibl, W. Kalt and G. Meister, *Lenzing Berichte*, **74** (1994) 81.

128. J. M. Taylor, *WO 92/124, WO 92/14871* (1992).

129. P. Weigel, J. Gensrich and H. P. Fink, *Lenzing Berichte*, **74** (1994)

31.

130. German patent, *DE 19753190* (Ger. Offen.1999).

131. European Patent, *WO 9723669* (Courtaulds Fibres; 1997).

132. European Patent, *WO 9621758* (Courtaulds Fibres; 1996).

133. European Patent, *WO 9713893* (Lenzing AG; 1997).

134. R. Breier, *Lenzinger Berichte*, **77** (1997) 35.

135. T. Hohberg, and S. Thumm, *Melliand Textilber*, **79** (6) (1998) E124.

136. R. Breier, *Lenzinger Berichte*, **74** (1994) 99.

137. P. Lo Nostro, D. Corrieri, M. Ceccato and P. Baglioni, *J. Colloid Interface Sci.*, **236** (2) (2001) 270.

138. A. Kumar, A. Harnden, *Textile Chemist and Colorist*, **1**(1) (1999) 37.

139. E. Prichard, *Practical Laboratory Skills Training Guides High Performance Liquid Chromatography*, (2003) 2.

140. R. Kellner, J. Mernet, M. Otio, H.M. Widmer, *Analytical Chemistry*; Chichester: Wiley-VCH, (1998) 394.

141. T.W. Graham Solomons, C. B. Fryhle, *Organic Chemistry*, Wiley New York , (1998) 586.

142. J. Shore, *Cellulosics dyeing*, Society of Dyers and Colourists, Bradford, (1995) 204.

143. R. McDonald, *Colour Physics for the Industry*, **2** (1988)103.

144. J.H. Nobbs, *Kubelka-Monk theory and prediction of reflectance*, Rev. Prog. Color Rel. Topics 15 (1985) 66-75.

145. J.I. Goldstein, H. Yakowitz, *Practical Scanning Electron Microscopy*, Plenum Press, London, (1976) 2-3.

146. J. March, *Advances in Organic Chemistry*, John Wiley & Sons, New York Chichester Brisbane Toronto Singapore, 4th Ed., (1992), 311.

147. C.L. Perrin, *Acc. Chem. Res.* **22** (1989) 268.

148. I. Bates, E. maudru, D.A.S. Phillips, A.H.M. Refrew, Y. Su and J. Xu, *Coloration Technology*, **120**(2004)294.

149. E. Anelise, B. Thomas, *Lenzinger Berichte*, **84**(2005)116-122.

150. Y. Shin, K. Yeh, *Textile Research Journal*, **11**(1989) 635.

151. W.E. Morton, J.W.S. Hearle, *Physical Properties of Textile Fibres*, The Textile Institute, Manchester, (1993) 453.

PUBLICATIONS

1. **Crosslinking agents for protection of lyocell against fibrillation: Synthesis, application and technical assessment of 2,4-diacrylamidobenzenesulfonic acid.**

Bates, I.; Maudru, E.; Phillips, D. A. S.; Renfrew, A. H. M.; **Su, Y.**; Xu, J. Christian Doppler Laboratory for Cellulosic Fibre and Textile Chemistry, UMIST, Manchester, UK. Coloration Technology (2004), 120(6), 293-300. Publisher: Society of Dyers and Colourists.

2. **Cross-linking agents for the protection of lyocell against fibrillation: Stability of benzeneacrylamido compounds to high temperature acidic environments.**

Su, Y.; Renfrew, A. H. M.; Phillips, D. A. S.; Maudru, E. Christian Doppler Laboratory for Cellulosic Fibre and Textile Chemistry, Textiles and Paper Group, School of Materials, University of Manchester, Manchester, UK. ColorationTechnology (2005), 121(4), 203-208. Publisher: Society of Dyers and Colourists.

Cross-linking agents for the protection of lyocell against fibrillation: synthesis, application and technical assessment of 2,4-diacrylamidobenzenesulphonic acid

Coloration Technology

Society of Dyers and Colourists

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A novel, colourless, water soluble, anionic cross-linking agent, 2,4-diacrylamidobenzenesulphonic acid, has been synthesised, applied to lyocell by a pad–steam method and the wet abrasion resistance measured. The agent furnished cross-linked lyocell fibres with good wet abrasion resistance and stable lyocell–agent bonds to subsequent hot exhaust reactive dyeing conditions. Surprisingly, the fibre–agent bonds showed some instability to polyester dyeing conditions at pH 4.5 and 5.0. This is rationalised in terms of hydrolysis of the amide bond *ortho* to the sulphonic acid group via a neighbouring group participation mechanism.

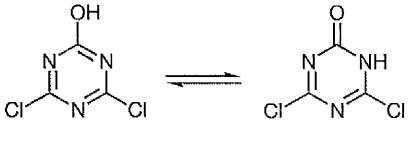
Introduction

Lyocell is a solvent-spun cellulosic fibre manufactured by a 'closed-loop' method which enables almost complete recovery of the organic solvent [1,2]. The process involves dissolving wood cellulose in a solution of *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate and extruding the filaments into an aqueous NMMO spinning bath solution followed by washing and cutting.

The resultant lyocell fibres are structurally different from conventional viscose and display superior dry, wet and loop strength and low shrinkage [3] compared to the latter fibre. This marked improvement in the mechanical properties of lyocell [4,5] compared to viscose, is a direct consequence of the solvent spinning technique used in the lyocell process [6] and results in longer crystallites and shorter and better orientated amorphous regions [4]. Moreover, lyocell is also noted for its bulkiness, ability to drape and softness to handle. However, lyocell is more technically challenging to process compared to viscose or modal, in fabric and garment form, due to fibrillation. Fibrillation is the abrading of small fibrillar hairs from the fibre surface of wet swollen lyocell when the fibre is subjected to any kind of mechanical stress [6]. The fibrils split lengthwise along the fibre axis and this change is brought about by an expansion of the less ordered interfibrillar zones, or voids, on swelling and a reduction in the cohesive forces between the fibrils [3–6]. The shape of the voids is important. Lyocell is characterised by anisotropic, elongated voids which are absent in normal viscose and modal [4–6].

Fibrillation has a positive side. If properly controlled during wet processing, deliberate (secondary) fibrillation can furnish fabrics with unusual sensory character, e.g. the production of microfibres on a lyocell fabric surface gives rise to the so-called 'peach-skin' effect. While fibrillation can be a useful property, for many outlets it is undesirable and restricts wider use of lyocell. In particular, fabric dyed in dark hues, to medium/heavy depths, can develop a 'frosty' appearance caused by fibrils so fine as to be virtually transparent, becoming detached from the fibre surface. In principle, the production of low-fibrillation lyocell fibres, i.e. fibre made up of fibrils with better cohesion, through variations of the spinning solution and process should be possible [6], but to date this objective has not been achieved.

It has been known for three decades that interfibrillar cross-linking of regenerated cellulose fibres with polyelectrophilic agents reduces fibrillation [7]. Consequently, Lenzing currently employs an 'in-line' cross-linking after-treatment of their 'never dried' fibres to minimise the fibre's propensity to fibrillate. Lyocell LF [8] uses dichlorohydroxytriazine (**1**) and Tencel A100 [2] uses 1,3,5-triacryloylhexahydrotriazine (**2**). However, neither cross-linking agent is ideal. Dichlorohydroxytriazine produces cross-links which are stable to strong alkali but show some instability to acidic environments. For the hexahydrotriazine agent the reverse is true, giving cross-links which are stable to acid but less so to strong alkali.



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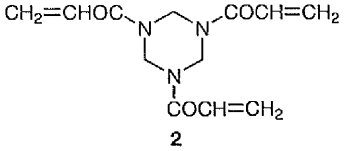


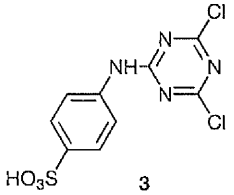
2

A number of low and zero formaldehyde resins to facilitate wet and dry cross-linking have been described as alternative approaches to minimising the wet abrasion of lyocell [3,9], i.e. *N*-methylol resins [10], dialdehydes [11], reactive sulphonium salts [12], functionally modified self-cross-linking siloxanes [13] and aliphatic ethers containing two to six chlorohydrin groups [14]. Moreover, reactive dyes carrying up to three reactive groups [6,15], optionally in combination with conventional wash and wear cross-linking agents [16], have also been studied in the context of minimising fibrillation. Mono functional reactive dyes showed little effect and not all bi- and tri-functional reactive dyes proved satisfactory. It has been shown that chromophore, dye concentration and general dyeing conditions influence the efficacy of such products [6,15].

Much interest has also been shown in colourless agents carrying conventional fibre-reactive groups for cellulose as potential anti-fibrillating agents, e.g. dichlorotriazines (DCT) [17–20], e.g. Sandospace R (**3**) [21] and Cibatex AE 4425 (**4**) [20]. In addition to the more familiar combination of halotriazine and vinyl sulphone reactive groups [17,20, 22,23], the use of halotriazine and acrylamido groups [24] have also been claimed in patents. Logically, an argument can be made for the use of colourless bi- and tri-functional agents with the same reactive group or with groups of similar reactivity [2,6,8]. The initial success of Cibatex AE 4425 (**4**) (now withdrawn) was probably due to the molecule containing, at application pH 12, a deactivated DCT group in conjunction with a vinyl sulphone group generated from the sulphatoethyl-sulphone group present in the parent molecule [25].

A paper by Nechwatal *et al.* describes the synthesis and application of bis-sulphatoethyl sulphones (masked vinyl sulphones) attached to bridging groups of different size [24]. All of the cross-linking agents studied were successful in reducing the wet abrasion of lyocell and if the concentration of cross-linking agent on the fibre was used as the basis of comparison, the different structures had a similar effect. Accordingly, for swollen lyocell the molecular dimensions of a vinyl sulphone cross-linking agent do not appear to be a critical factor.

This paper describes the synthesis, application and technical properties of the novel diacrylamido cross-linking agent (**5**) [26]. Agent **5** employs acrylamido reactive groups similar to those used to produce Tencel A100. However, in this case the agent carries a permanent anionic group, increasing water solubility, lowering vapour pressure and favouring safer handling.



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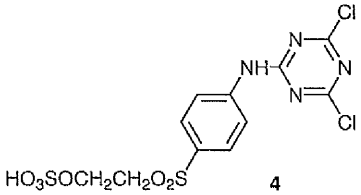

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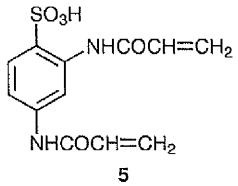

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Experimental

Wet abrasion resistance

The propensity to fibrillate was determined and the wet abrasion numbers (NSF; Nass-Scheuer-Festigkeit) calculated using an instrument (Delta 100) manufactured by Lenzing AG. The instrument consists of a 10 mm diameter shaft with a sandblasted surface which can rotate at 100–500 rpm. The shaft is horizontally mounted and sits in a small trough of deionised water, which is constantly being replenished. This trough ensures that the shaft has a constant film of water over its surface. In addition the shaft can oscillate 10 mm/min along the axis of rotation. This ensures that a fibre sample is subjected to a more even abrasion from the shaft.

The fibres being tested are held in contact with the bar and their contact angle can be adjusted from 0–100°. To apply a degree of tension, weights in the form of clips are attached to the lower end of each fibre. During the testing process as each individual fibre breaks, the respective clip falls into a channel below, which guides the clip to a detector. Up to 20 samples are measured at any one time. The usual settings are 50 mg weight, 40° contact angle, 500 rpm and with the shaft oscillation operating. The whole process of instrument control and data processing is achieved by use of a personal computer.

Chromatography

High performance liquid chromatography (HPLC) was carried out with a Hewlett Packard 1100 series fitted with a quaternary pump. The column was a Purosphere RP-18E 5 µm 125*4 mm and a LiChrocart 125-4 HPLC column cartridge; solvent A, acetonitrile; solvent B, water with 0.25% dicyclohexylammonium phosphate; flow rate, 2 ml/min; temperature, 40 °C; injection volume, 5 µl; samples were analysed using a diode array detector. The gradient programmes shown in Table 1 were used in this study. Retention times (t_R) were measured in minutes.

Table 1 HPLC gradient programmes

			Solvent (%)	
Programme	Flow rate (ml/min)	Time[a]	A	B
1	2	0	30	70
		5	50	50
		6	40	60
		7	30	70
2	2	0	15	85
		8	50	50
		10	15	85
3	1	0	75	25
		9	85	15
		12	90	10
		12.5	75	25
		14	75	25

a Stop times for programmes 1, 2 and 3 = 7, 10 and 14 min, respectively

Mass spectrometry

Method A

Mass spectra were recorded with a Micromass Instrument LCT orthogonal time-of-flight mass spectrometer fitted with a Z-spray electrospray ion source operating in negative mode at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data was stored in the continuum mode on a Micromass Instruments MassLynx data station utilising Version 3.5 software pack. Infusion was at a rate of 20 µl/min with a Harvard Instruments syringe pump utilised for sample introduction.

Method B

Fast-atom bombardment (FAB) mass spectra were recorded with a VG 70-70 EG high resolution mass spectrometer run in positive ion mode using *m*-nitrobenzylalcohol as FAB matrix. The instrument was run as a double focusing instrument and calibrated with cesium iodide over the desired mass range.

NMR spectroscopy

Nuclear magnetic resonance (NMR) data were recorded on a Bruker Avance at 300 MHz for ^{1}H NMR and at 75.47 MHz for ^{13}C NMR in D_2O unless otherwise stated. Chemical shifts (δ) were measured in ppm from the internal standard and coupling constants (J) in Hz.

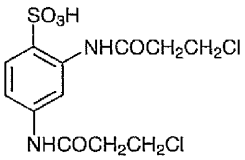
Syntheses

2,4-Diacrylamidobenzenesulphonic acid (5) (route 1)

To a solution of *m*-phenylenediaminesulphonic acid (98% strength; 9.6 g; 0.05 mol) in water (150 ml) was added caustic soda to give a clear solution and pH 5.5. The solution was cooled to 2 °C and acryloyl chloride (96% strength; 19 ml; 0.23 mol) was added dropwise, with stirring, while maintaining a pH of 3.0–4.0 with a sodium carbonate solution. The reaction mixture was filtered to remove a small quantity of white solid and sodium chloride (20% w/v) was added to the filtrate. The precipitate so formed was filtered off, washed with 20% brine (20 ml), pulled down and oven-dried to give the product (11 g). A small portion was lixiviated in ice cold water, filtered and dried. Elemental analysis: found C, 42.2; H, 3.1; N, 8.0; S, 8.7. $C_{12}H_{11}N_2O_5SNa$ (93% pure) requires C, 42.2; H, 3.2; N, 8.5; S, 9.4%. HPLC showed a single peak at t_R = 0.97; mass spectral analysis (method B) gave a molecular ion at *m/z* 319 [$(M + H)^+$, 35%]; ^{1}H (300 MHz,): δ(ppm) 5.69–5.73 (1H, t, *J* 5.6, –CH=), 5.79–5.83 (1H, dd, *J* 2.6 and 8.3, –CH=), 6.16 (2H, d, *J* 5.6, CH_2=), 6.21 (2H, m, CH_2=), 7.17–7.21 (1H, dd, *J* 1.5 and 8.7, ^{Ar}H), 7.59 (1H, d, *J* 8.7, ^{Ar}H), 8.09 (1H, s, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 114.6, 116.5, 128.5, 128.8, 129.2, 129.3, 130.6, 131.3, 134.5 and 140.8 (10 C, ^{Ar}C and 2 × –*C*H= and 2 × =*C*H_2), 166.4 and 166.6 (2 C, C=O).

2,4-Diacrylamidobenzenesulphonic acid (5) (route 2)

Initially, 2,4-bis(γ-chloropropionylamino)benzenesulphonic acid (**6**) was prepared according to the following route. To *m*-phenylenediaminesulphonic acid (98% strength; 77.6 g; 0.4 mol) in ice water (500 ml) was added calsolene oil (5 drops) and caustic soda to give a clear solution and pH 6.5. The resultant solution was cooled to 8 °C and 3-chloropropionyl chloride (98% strength; 108.8 g; 0.84 mol) was added dropwise, at 5–10 °C, with stirring,



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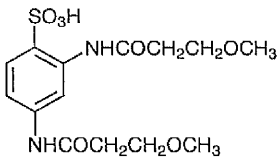
while maintaining a pH of 3.4–4.3 with sodium carbonate solution. A final volume of 1300 ml was given at 8 °C and pH 4.1. Sodium chloride (170 g) was added portionwise to give a precipitate which was filtered off, washed with brine (20%) and oven-dried at 60 °C to give a pale grey solid (287.8 g). HPLC showed a major peak (91%) at t_R = 1.63 and mass spectral analysis (method B) gave a molecular ion at *m/z* 391 [$(M + H)^+$, 23%]. Analysis showed the product to contain sodium chloride (18%), moisture (29.8 %) and total organic content (150.2 g; 96% yield); ^{1}H (300 MHz): δ(ppm) 2.77–2.91 (4H, dt, *J* 6.0 and 29.1, 2 × CH_2C=O), 3.76–3.85 (4H, dt, *J* 6.0 and 12.4, 3 × CH_2Cl), 7.25–7.28 (1H, dd, *J* 1.9 and 8.7, ^{Ar}H), 7.71 (1H, d, *J* 8.7, ^{Ar}H) and 8.01 (1H, s, ^{Ar}H); ^{13}C (75.5 MHz, D_2O): δ(ppm) 39.7, 40.3, 40.4 and 40.5 (4 C, 4 × –*C*H_2), 115.9, 117.2, 128.7, 129.8, 134.4 and 140.7 (6 C, ^{Ar}C), 171.7 and 172.0 (2 C, 2 × C=O).

The benzenesulphonic acid **6** (357 g; 0.97 mol) was then suspended in water (500 ml) and stirring and heating commenced. At 37 °C, caustic soda solution (30% w/v) was added to give and maintain a pH in the range 11.0–11.5 and the temperature raised to 50 °C. After 25 min the solution had a steady pH of 11.1. The reaction was continued for a further 0.75 h. HPLC showed 95% conversion to the desired product which started to precipitate out. The pH was adjusted to 7.0, sodium chloride (10% w/v) added and stirring continued for a further 0.5 h. After 7 days, the grey solid so formed was isolated by filtration and dried to give the product (**5**) (104 g) which was 100% organically pure by HPLC and identical to the product prepared from acryloyl chloride (route 1).

2,4-Bis(γ-methoxypropionamido)benzenesulphonic acid (7)

To the acid **5** (77.9% strength; 10 g) was added methanol (60 ml), water (60 ml) and sodium carbonate (2 g) and the reaction mixture heated under reflux for 48 h. The solvent was removed under vacuum with a rotary evaporator to give an off-white solid (8.2 g) which was lixiviated with acetone (100 ml), filtered and oven-dried at 40 °C. HPLC showed a single peak at t_R = 0.87 and mass spectral analysis (method A) gave ions at *m/z* 359 [$(M - H)^-$, 100%], 327 [$(M - H - CH_3OH)^-$, 42%]; ^{1}H (300 MHz): δ(ppm) 2.51 (2H, t, *J* 5.6, –*C*H_2C=O), 2.58 (2H, t, *J* 5.6, –*C*H_2C=O), 3.19 (3H, s, OCH_3), 3.22 (3H, s, OCH_3), 3.58–3.64 (4H, m, 2 × CH_2O), 7.20 (1H, d, *J* 8.7, ^{Ar}H), 7.62 (1H, d, *J* 8.7, ^{Ar}H) and 7.94 (1H, s, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 37.1 and 37.5 (2C, 2 × OCH_3), 58.5 (2C, 2 × –*C*H_2), 68.1 and 68.4 (2C, 2 × –*C*H_2O), 115.9, 117.1, 128.5, 129.6, 134.5 and 140.7 (6C, ^{Ar}C), 168.3 and 172.8 (2C, 2 × C=O).



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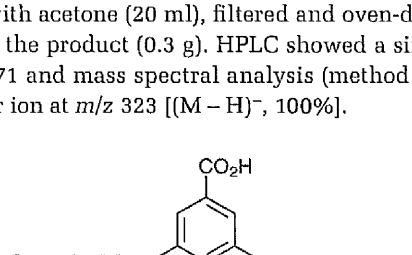
3,5-Diacrylamidobenzoic acid (8)

To a solution of 3,5-diaminobenzoic acid (43.5 g; 0.29 mol) in water (600 ml) was added hydrochloric acid (32% w/v; 50 ml) and the suspension stirred for 1 h. The solution at pH 2.5 was filtered to remove a small quantity of undissolved solid and the pH raised to 3.1 with sodium hydroxide solution. The solution was cooled to 10 °C and acryloyl chloride (96% strength; 60 ml; 0.7 mol) was added dropwise, with stirring, over 1 h, while maintaining a pH of 3.0–4.0 with sodium carbonate solution, to give a grey solid. The solid, which gave a positive Ehrlich's test, was filtered off, redissolved in water (500 ml) and the pH raised to 10 with sodium carbonate solution. Further acryloyl chloride (96% strength; 12 ml; 0.15 mol) was added and the pH allowed to fall. Sodium carbonate solution was added to raise the pH to 10.7 and sodium chloride (10% w/v) added to give a grey solid. The solid was filtered off, washed with brine (20% w/v; 400 ml), pulled down and oven-dried to give the product (51 g). HPLC showed a single peak at t_R = 0.84 and mass spectral analysis (method B) gave a ions at *m/z* 305 [$(M + Na)^+$, 92%], 283 [$(M + H)^+$, 78%]. There was also a sodiumated dimer ion at *m/z* 587 [$(2M + Na)^+$, 15%]; ^{1}H (300 MHz, NaOD): δ(ppm) 5.50–5.54 (2H, t, *J* 6.0, 2 × CH=), 5.97 (4H, d, *J* 5.6, 2 × CH_2), 7.33 (2H, s, ^{Ar}H) and 7.48 (1H, s, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 115.1, 117.5, 128.5, 130.6, 137.9 and 138.0 (10C, ^{Ar}C, –*C*H= and –*C*H_2=), 166.4 (2C, C=O) and 171.1 (1C, *C*OOH).

3,5-Bis-(γ-methoxypropionamido)benzoic acid (9)

To 3,5-diacrylamidobenzoic acid **8** (93.1% strength; 0.7 g) and sodium carbonate (0.6 g) was added a mixture of methanol (24 ml) and water (12 ml) and the reaction mixture refluxed for 48 h. The solvent was removed on a rotary evaporator to give an off-white solid which was washed with acetone (20 ml), filtered and oven-dried at 40 °C to give the product (0.3 g). HPLC showed a single peak at t_R = 0.71 and mass spectral analysis (method A) gave a molecular ion at *m/z* 323 [$(M - H)^-$, 100%].



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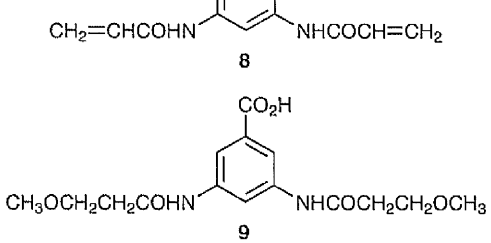

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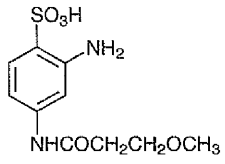
2-Amino-4-(γ-methoxypropionamido)benzenesulphonic acid (10)

Initially, 2-amino-4-acrylamidobenzenesulphonic acid (**11**) was prepared as follows. To water (200 ml) was added *m*-phenylenediaminesulphonic acid (94 g; 0.5 mol) and the pH was adjusted to 6.5. Acryloyl chloride (96% strength; 44 ml; 0.51 mol) was added dropwise, at 0–3 °C, while maintaining the pH at 4.7–5.6 with sodium carbonate solution (2 M). The reaction was stirred for 2 h, and salt (30% w/v) added and stirring continued for a further 1 h. The precipitate which formed was isolated by filtration,



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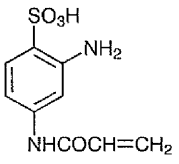


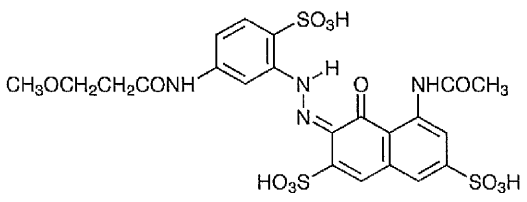
11

washed with saturated brine and dried at 40 °C to give the product (74.3 g). HPLC showed a single peak at t_R = 0.74 and mass spectral analysis (method A) gave a molecular ion at *m/z* 241 [$(M - H)^-$, 94%]; ^{1}H (300 MHz): δ(ppm) 5.88–5.91 (1H, dd, *J* 1.9 and 9.8, C*H*=), 6.31–6.37 (1H, dd, *J* 1.5 and 16.9, C*H*H=), 6.40–6.48 (1H, dd, *J* 9.8 and 16.9, CH*H*=), 6.92–6.96 (1H, dd, *J* 1.9 and 8.7, ^{Ar}H), 7.17 (1H, d, *J* 1.9, ^{Ar}H) and 7.62 (1H, d, *J* 8.7, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 109.4, 110.6, 119.4, 128.7, 129.1, 130.6, 141.0 and 145.0 (8C, ^{Ar}C, –*C*H= and –*C*H_2=) and 167.1 (1C, C=O).

To methanol (50 ml) and water (50 ml) was added, with stirring, compound **11** (7 g) and sodium carbonate (1.8 g). The reaction mixture was heated under reflux for 48 h and the solvent (50 ml) removed on a rotary evaporator. Salt (20% w/v) was added to the remaining solution and the resulting precipitate isolated by filtration. The solid was dried at 40 °C to give the product (**10**) (5.23 g). HPLC showed a single peak at t_R = 0.71 and mass spectral analysis (method A) gave a molecular ion at *m/z* 273 [$(M - H)^-$, 100%]; ^{1}H (300 MHz): δ (ppm) 2.49 (2H, t, *J* 5.6, *C*H_2C=O), 3.21 (3H, s, OCH_3), 3.60 (2H, t, *J* 5.6, CH_2O), 6.67 (1H, d, *J* 8.3, ^{Ar}H), 6.92 (1H, s, ^{Ar}H) and 7.43 (1H, d, *J* 8.3, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 37.2 (1C, OCH_3), 58.6 (1C, CH_2), 68.6 (1C, CH_2O), 109.6, 110.8, 127.2, 128.8, 141.2 and 145.3 (6C, ^{Ar}C) and 165.1 (1C, C=O).

8-Acetylamino-2-[5'(3"-methoxy)propionamido-2'-sulpho]phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (12)

To water (20 ml) was added 2-amino-4-(γ-methoxypropionamido)benzenesulphonic acid (**10**) (50.3% strength; 4 g; 7.6 mmol) and the solution cooled to 0–5 °C in an ice bath. Concentrated hydrochloric acid (4 ml) was added dropwise and pH dropped from 10.4 to 1.0, followed by sodium nitrite solution (6.8 ml; 1 M) while maintaining a temperature of 0–5 °C. After 30 min the reaction mixture was added to a solution of acetyl H-acid (2.75 g; 7 mmol) dissolved water (20 ml), at 0–5 °C, and the pH was adjusted to 6.5 with a sodium carbonate solution (2 M). Potassium chloride (15% w/v) was added and the reaction mixture stirred for a further 1 h. The solid so formed was isolated by filtration and air-dried to give a red solid (1.9 g). HPLC showed a single peak at t_R = 1.63, and mass spectral analysis (method A) gave ions at *m/z* 699 [$(MNa_2 - H)^-$, 6%], 683 [$(MK - H)^-$, 15%], 667 [$(MNa - H)^-$, 48%] and 645 [$(M - H)^-$, 85%]; ^{1}H (300 MHz): δ(ppm) 2.37 (3H, s, CH_3C=O), 2.66 (2H, s, CH_2C=O), 3.34 (3H, s, OCH_3), 3.74 (2H, s, OCH_2), 7.42–7.68 (5H, m, ^{Ar}H) and 8.82 (1H, s, ^{Ar}H).



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Diazotisation and coupling of the reaction mixture obtained after subjecting compound 7 to high temperature

Compound **7** (79.6% strength; 0.5 g; 1 mmol) in pH 4.5 buffer solution (15 ml) was heated to 130 °C for 1 h and the resultant solution cooled to 0–5 °C in an ice bath. Concentrated hydrochloric acid (4 ml) was added dropwise and the mixture titrated with standard 0.1 M sodium nitrite solution (2.8 ml). Excess nitrous acid was destroyed with sulphamic acid. The diazotisation solution was added to a suspension of acetyl H-acid (0.11 g, 0.3 mmol) at 0–5 °C and the pH raised to 6.5 with a sodium carbonate solution (2 M) to give a red dye. HPLC (programmes 1, 2 and 3) showed the dye to be identical to compound **12**.

Volumetric analysis of the reaction mixture obtained by high temperature treatment of compound 7

Compound **7** (0.5 g) and pH 4.5 buffer solution (15 ml) were heated to 130 °C for 1 h then cooled to 0–5 °C. Concentrated hydrochloric acid (2 ml) was added and the solution titrated with a standard sodium nitrite solution (0.1 M) to a sulphone indicator end point. This process was to determine the concentration of primary amine present.

Application of cross-linking agents to lyocell

All experiments were performed with 'never-dried' lyocell fibres (1.3 dtex; 40mm staple) provided by Lenzing.

Pad–steam method

Padding solutions comprising, cross-linking agent (*X* g/l, at 100% strength), sodium hydroxide (4 g/l) and sodium sulphate (100 g/l) were prepared using distilled water. The solutions were applied in turn to lyocell fibre using the following conditions: impregnate, 5 min at room temperature; squeeze at 3 bar, padding speed 2.0 ml/min with monitoring of wet pick-up; steam at 100 °C with saturated steam for 5 min; air dry overnight; wash-off (cold rinse for 5 min, soap at the boil for 10 min, cold rinse for 5 min; air dry.

High temperature treatment of cross-linked lyocell

Cross-linked lyocell was treated in the following manner: (a) at 80 °C and pH 11 for 60 min (to simulate hot reactive dyeing) (Figure 1); and (b) at 130 °C in buffer solutions of pH 4.5, 5.0, 6.0 and 7.5 for 60 min (to simulate high temperature dyeing of the polyester component of a polyester/lyocell blend) (Figure 2). The treatments were performed in sealed stainless steel dye pots housed in a Mathis Labomat BFA 12 dyeing machine.

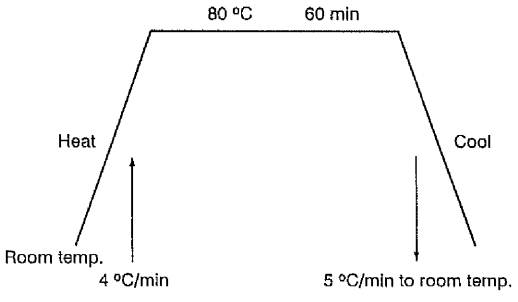


Figure 1 Hot reactive lyocell dyeing profile at pH 11

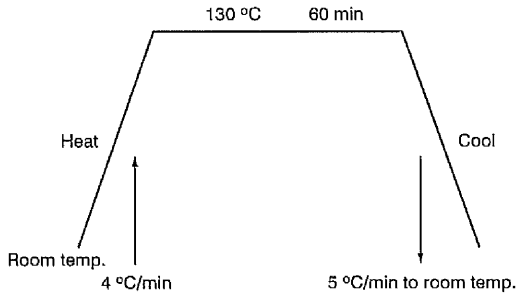


Figure 2 High temperature polyester dyeing profile

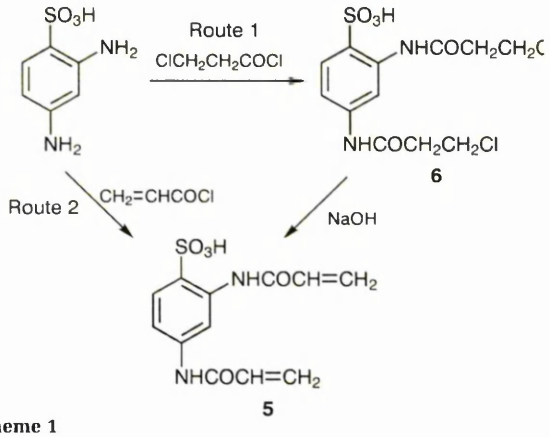
Results and Discussion

An ideal cross-linking agent for lyocell needs to satisfy many applications, technical and environmental criteria as well as being cost effective for the fibre manufacturer or the dyer and finisher. Some of the important technical/commercial features of an ideal cross-linking agent for lyocell include:

- good water solubility,
- colourless on fibre,
- substantive,
- reactive yet stable to handling/storage,
- reactive groups of equal reactivity,
- easy/versatile application,
- high wet abrasion resistance properties,
- stable agent–lyocell bonding,
- no yellowing in UV light,
- no change to the fibre's mechanical properties,
- low vapour pressure,
- non-toxic,
- biogradable,
- low cost.

To design such a cross-linking agent, the presence of an anionic group was considered essential to satisfy the criteria of good water solubility, low vapour pressure and low toxicity. Acrylamido reactive groups were selected for the cross-linking reaction. Although the Michael addition products are susceptible to base catalysed β-elimination they are more robust than the related vinyl sulphone products. Triazine chemistry was ruled out on the basis of the sensitivity of alkyl triazinyl ethers to hot acid environments. 2,4-Diaminobenzenesulphonic acid was selected as the starting material being a low cost industrial scale intermediate. Acryloylation of this intermediate furnishes the novel cross-linking agent, 2,4-diacrylamidobenzenesulphonic acid (**5**) (Scheme 1).

The cross-linking agent **5** can be prepared directly with acryloyl chloride as acylating agent (route 1), or indirectly with 3-chloropropionyl chloride followed by base catalysed β-elimination (route 2). All reactions were performed in water as solvent. Agent **5** is colourless with good water solubility and was applied to lyocell by a pad–steam method. Wet abrasion numbers (NSF) were determinde as such numbers are a good indicator of fibre cross-linking [3,16]. The NSF values of untreated lyocell cross-linked with different concentrations of **5** are given in Figure 3. The results show that this compound proved to be a good cross-linking agent, giving NSF values comparable to those



Scheme 1

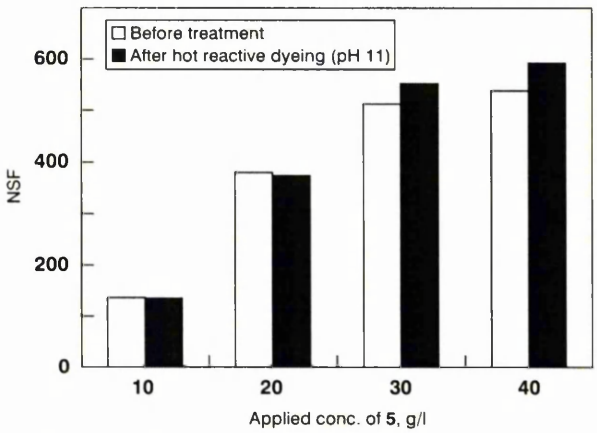


Figure 3 Wet abrasion resistance (NSF) of lyocell cross-linked with agent **5** before and after hot reactive dyeing conditions

produced using commercial agents **1** and **2**. To evaluate the stability of the lyocell–agent bonding the cross-linked fibre was subjected to hot reactive dyeing conditions (1 h at 80 °C and pH 11) and the results are also shown in Figure 3. It is clear that the bonds are stable to such conditions, with the slight increase in NSF values at the higher concentrations possibly being attributed to some mono-attached agent undergoing cross-linking.

The stability of the lyocell–agent **5** bonding was also evaluated under high temperature (HT) polyester dyeing conditions (1 h at 130 °C and over a range of pH values). The NSF values in Figure 4 indicate significant instability of the lyocell–agent bonds to HT polyester dyeing conditions at pH 4.5 and 5.0. This was particularly so at pH 4.5 and 40 g/l applied agent where approximately 50% reduction in NSF value was found. This was unexpected as the structurally-related 1,3,5-triacryloylhexahydrotriazine (**2**) gives stable lyocell–agent bonding to HT polyester dyeing conditions. Nitrogen analysis of the lyocell fibre, cross-linked with agent **5**, before and after HT polyester dyeing conditions was unchanged, indicating that despite the fall in NSF values the cross-linking agent was still attached to the fibre.

To investigate what may have occurred, a model ether **7** was synthesised from **5** (Scheme 2) (to simulate attachment of lyocell to agent **5**) and then the model compound was subjected to high temperature treatment over a range of acid pH values.

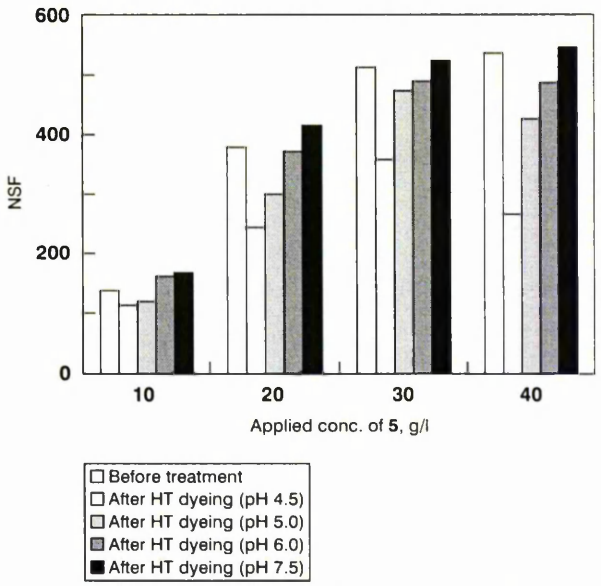
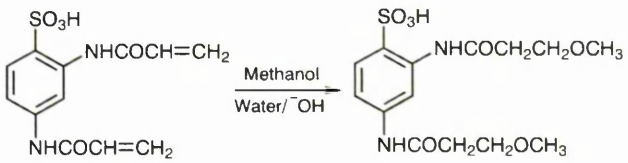


Figure 4 Wet abrasion resistance (NSF) of cross-linked lyocell with agent **5** under high temperature (HT) polyester dyeing conditions



Scheme 2

At pH 4.5 and 5.0 the appearance of a small new peak at t_R 0.65 was observed by HPLC (for compound **7**, t_R 0.87). Moreover, subjecting agent **5** to a similar treatment also brought about a chemical change and a lower retention time product was also detected by HPLC. At this stage it was suspected that the presence of the sulphonic acid group was exerting a neighbouring group influence on the stability of compounds **5** and **7**. Accordingly, compound **9** was synthesised (via **8**) and subjected to high temperature treatment as before.

For compound **9** at pH 4.5, 5.0 and 6.0 no chemical change was observed after 1 h at 130 °C supporting the view that degradation of compounds **5** and **7** was related to the presence of the *ortho* sulphonic acid group. Further support was given by the application of cross-linking agent **8** to lyocell followed by treatment of the cross-linked fibres under HT polyester dyeing conditions. No significant decrease in NSF values was found (Figure 5).

Initial findings suggested that under HT polyester dyeing conditions hydrolysis of the amide link *ortho* to the sulphonic acid group may be taking place. The sterically favourable position of the SO_3^- group can furnish a six-membered intermediate on protonation of the amide group (Scheme 3). It is known that the neighbouring group mechanism operates effectively only for certain ring sizes with the most rapid reactions occurring for 3, 5 and 6 membered rings [27]. Anchimeric assistance by sulphonic acid groups has not been recorded previously. Scheme 3 shows protonation of the amide group on the carbonyl oxygen atom, although some amides can protonate on nitrogen [28].

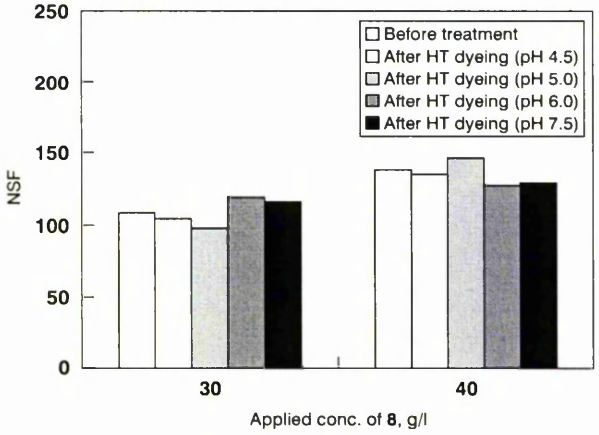
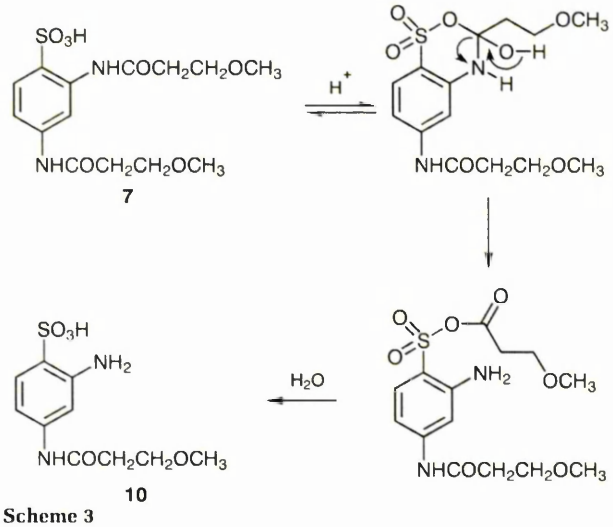


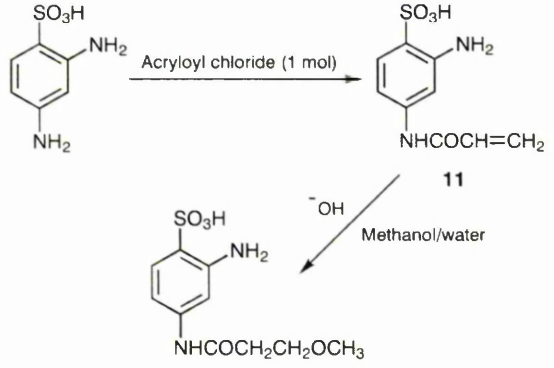
Figure 5 Wet Abrasion resistance (NSF) of cross-linked lyocell with agent **8** under high temperature (HT) polyester dyeing



Scheme 3

To further investigate the anchimeric assistance hypothesis, 2-amino-4-(γ-methoxy-propionamido)benzene-sulphonic acid (**10**) was synthesised (Scheme 4) and the product shown to be identical, by HPLC, to the hydrolysis product formed by subjecting compound **7** to HT polyester dyeing conditions at pH 4.5. However, formation of the other isomer of **10** could not be ruled out.

The reaction mixture obtained by subjecting a solution of the model bis-methyl ether **7** to HT polyester dyeing conditions at pH 4.5 was titrated with sodium nitrite



Scheme 4

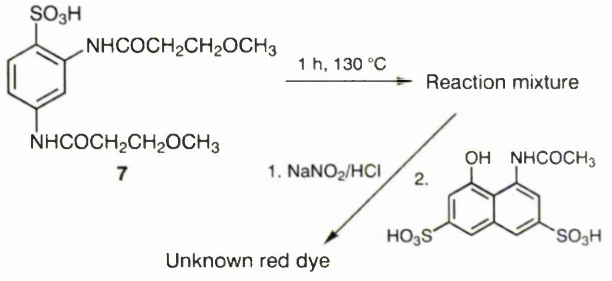
Table 2 Titration of the reaction mixture obtained from high temperature treatment of compound **7**[a]

Sample	Titre[b] (ml)	Primary amine present (%)
1	2.60	27.2
2	2.75	28.8

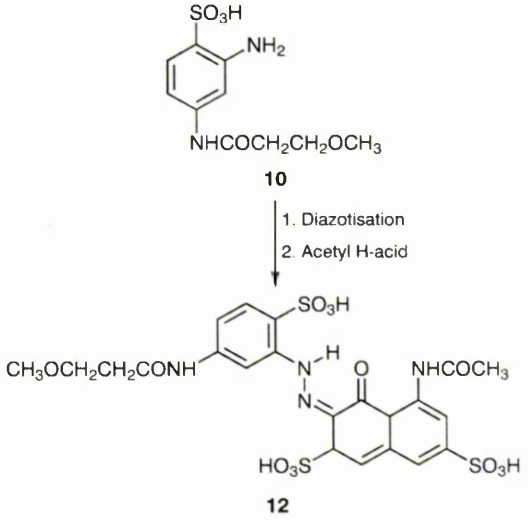
a Weight of compound = 0.5 g (73.0% strength)

solution to determine the concentration of primary amine present. The results are shown in Table 2 and it is clear that this treatment resulted in approximately 28% amide hydrolysis. Consequently, if a similar hydrolysis took place for lyocell, cross-linked with the bis-acrylamido agent **5**, a significant reduction in NSF would be expected.

To further investigate the product of the bond cleavage reaction, the diazo solutions from the sodium nitrite titrations were coupled with acetyl H-acid (8-acetylamino-1-naphthol-3,6-disulphonic acid) to give an unknown red dye (Scheme 5). The anticipated product formed in Scheme 5 was unambiguously synthesised as shown in Scheme 6. Dye **12** and the unknown dye (Scheme 5) were analysed individually and in admixture using three different HPLC programmes and the results shown in Table 3. HPLC analyses of the mixture resulted in a single peak for the three methods used. Virtually identical retention times for



Scheme 5



Scheme 6

Table 3 HPLC retention times (t_R) for each of the three HPLC programmes

	t_R (min)		
Programme	Dye **12**	Unknown dye	Mixture
1	0.77	0.77	0.82
2	4.97	4.99	4.98
3	1.62	1.60	1.71

the individual analyses and the appearance only of a single peak for the mixtures strongly supported the hypothesis that the unknown dye (Scheme 5) and dye **12** (Scheme 6) were identical. Virtually superimposible visible spectral curves for dye **12** (λ_{max} 503 nm) and for a solution of the unknown red dye (λ_{max} 505 nm) provided additional support.

Conclusions

2,4-Diacrylamidobenzenesulphonic acid (**5**), applied by a pad–steam process, is an effective cross-linking agent for lyocell. The lyocell–agent bonds so generated are stable to hot reactive dyeing but show some instability to HT polyester dyeing conditions particularly at pH 4.5. This has been rationalised in terms of acid catalysed hydrolysis of the amide bond *ortho* to the sulphonic acid group via a neighbouring group participation mechanism.

References

1. P White, *Regenerated Cellulosic Fibres*, Ed. Calvin Woodings (Manchester: Textile Institute, 2001) 62.
2. H Firgo, M Eibl, W Kalt and G Meister, *Lenzinger Ber.*, **9** (1994) 80.
3. A Nechwatal, M Nicolai and K-P Mieck, *Text. Chem. Colorist*, **28** (5) (1996) 24.
4. J Lenz, J Schurz and E Wrentschur, *Acta Polym.*, **43** (1992) 307.
5. J Schurz, *Lenzinger Ber.*, **9** (1994) 37.
6. K Bredereck, F Schulz and A Otterbach, *Melliand Textilber.*, **78** (10) (1997) 703.
7. *FP2273091* (Rhone Poulenc; 1975).
8. P Bartsch, B Koell and E Muelleder, *WO9919555* (Lenzing AG; 1999).
9. L Pearson and J M Taylor, *WO9500697* (Courtaulds Plc; 1995).
10. P G Urben, *EP691426* (Courtaulds Plc; 1996).
11. W Badura and W Schrott, *WO9607780* (BASF; 1996).
12. H Firgo and S Seidl, *EP783602* and *EP796358* (Lenzing AG; 1997).
13. A Hashemzadeh, *WO9620302* (Akzo Nobel NV; 1996).
14. K Tsuji, S Fujita and S Nishikawa, *EP978585* (Ipposha Oil Industries Co. Ltd; 2000).
15. M Nicolai, A Nechwatal and K-P Mieck, *Angew. Makromol. Chem.*, **256** (1998) 21.
16. M Nicolai, A Nechwatal and K-P Mieck, *Text. Res. J.*, **66** (9) (1996) 575.
17. P Aeschlimann and P Scheibli, *EP882836* (Ciba Geigy AG; 1998).
18. P Aeschlimann, *EP903434* (Ciba Geigy AG; 1999).
19. P Aeschlimann and B Mueller, *EP950750* (Ciba Geigy AG; 1999).
20. P Aeschlimann, *EP950751* (Ciba Geigy AG; 1999).
21. J M Taylor, *EP538977* (Courtaulds Plc; 1993).
22. *Japanese Patent 08-025888* (Sumitomo; 1996 application).
23. T Groesser, M Patsch, R Krallmann and W Reuther, *WO9735848* (BASF; 1997).
24. A Nechwatal, M Nicolai, K-P Mieck, B Heublein, G Kühne and D Klemn, *Angew. Makromol. Chem.*, **271** (1999) 84.
25. A H M Renfrew and D A S Phillips, *Color. Technol.*, **119** (2003) 116.
26. A H M Renfrew, *WO03038164* (Chemiefaser Lenzing AG; 2003).
27. J March, *Advances in Organic Chemistry*, 4th Edn (London: John Wiley & Sons, 1992) 311.
28. C L Perrin, *Acc. Chem. Res.*, **22** (1989) 268.

Cross-linking agents for the protection of lyocell against fibrillation: stability of benzeneacrylamido compounds to high temperature acidic environments

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A number of benzeneacrylamido compounds, each with at least one sulphonic acid or carboxylic acid group, have been synthesised and converted to the corresponding methyl ethers. The derivatives were then subjected to high temperature polyester dyeing conditions (130 °C) in pH 4.0 buffer solution for 1 h. Derivatives with sulphonic acid groups *meta* or *para* to the amide links proved to be hydrolytically stable to the high temperature treatment, whereas derivatives with either an *ortho* sulphonic acid or carboxylic acid substituent underwent significant amide hydrolysis. This is consistent with previous findings and with a neighbouring group participation mechanism. Accordingly, benzeneacrylamido cross-linking agents for lyocell fibres, designed to be hydrolytically stable to a range of high temperature polyester dyeing conditions appropriate for polyester/lyocell blends, should be devoid of *ortho* sulphonic acid or carboxylic acid substituents.

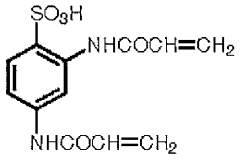
Introduction

Lyocell is the first solvent-spun cellulosic fibre to be available on a commercial scale [1–3]. The solvent used for pulp dissolution is *N*-methylmorpholine-*N*-oxide (NMMO) and while there are some hazards associated with the use of this compound [4], this approach results in two major benefits over the established xanthate route for viscose rayon. The first is a dramatically improved environmental outcome, with almost complete recovery of the organic solvent, and the second is the production of a fibre with superior wet and dry tenacity compared with traditional regenerated cellulosic fibres.

Lyocell and viscose/modal fibres have identical empirical formulae but have different supermolecular structures [5,6], resulting in different technical properties. One of the marked differences of lyocell is that it shows a greater propensity to fibrillate compared with viscose and modal [7]. Fibrillation is the formation of micro-fibrils on the fibre surface as a result of mechanical abrasion particularly in the wet state. A combination of factors associated with the supermolecular structure of lyocell contribute to this problem, e.g. high wet swelling, elongated pores or voids and weak lateral links between the fibrils.

It is known that interfibrillar cross-linking of regenerated cellulose fibres, with bi- or tri-functional electrophilic agents, reduces fibrillation (wet abrasion) [8] and, currently, cross-linking agents are applied to 'never dried' lyocell fibres to produce grades of fibre with superior wet abrasion resistance, e.g. Tencel LF and Tencel A 100. Certain bifunctional cellulose reactive dyes also offer some protection against wet abrasion [9–12].

Cross-linking agents have also been used commercially to pre-treat dried lyocell fabric prior to dyeing [7] and a number of cross-linking agents have been patented as approaches to reduce wet abrasion [13–24]. One recent study by this group examined the synthesis, application and technical properties of 2,4-diacrylamidobenzene-sulphonic acid (**1**) [7]. This agent furnished cross-linked lyocell fibres with good wet abrasion resistance (high NSF values; Nass Scheuer Faestigheit) and stable lyocell–agent bonds to both warm and hot exhaust reactive dyeing conditions.



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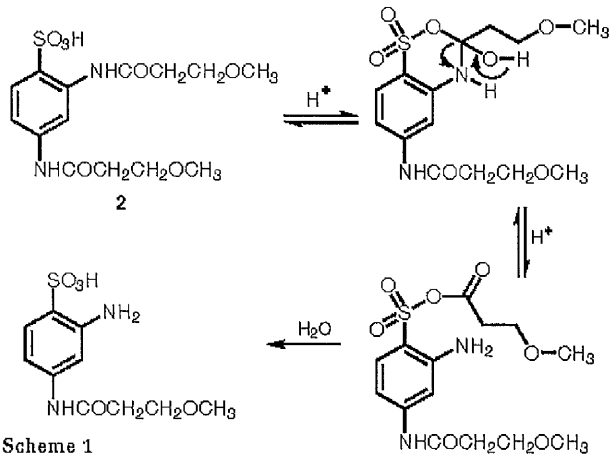
However, the fibre–agent bonds showed some instability to high temperature (HT) polyester dyeing conditions at pH 4.5 and 5.0 and this was rationalised in terms of hydrolysis of the amide bond *ortho* to the sulphonic acid group via a neighbouring group participation mechanism. Simulation of the agent–lyocell bonding with a model bis-methylether (**2**) has furnished some support for this mechanism (Scheme 1) [7].

Further work on benzeneacrylamido derivatives was undertaken, both to test the validity of the neighbouring group hypothesis and to aid the development of new agents with improved stability to HT polyester dyeing conditions.



Scheme 1

Experimental

Chromatography

High performance liquid chromatography (HPLC) was carried out with a Hewlett Packard 1100 series fitted with a quaternary pump. The column was a Purosphere RP-18E 5μm 125*4 mm and a LiChrocart 125-4 HPLC column cartridge; solvent A, acetonitrile; solvent B, water with 0.25% dicyclohexylammonium phosphate; flow rate, 2 ml/min; temperature, 40 °C; injection volume, 5 μl; samples were analysed using a diode array detector. The gradient programmes shown in Table 1 were used. Retention times recorded for the synthesised compounds used programme 1. Retention times (t_R) were measured in min.

Table 1 HPLC gradient programmes

			Solvent (%)	
Programme	Flow rate (ml/min)	Time[a]	A	B
1	2	0	30	70
		5	50	50
		6	40	60
		7	30	70
2	2	0	15	85
		8	50	50
		10	15	85
3	1	0	75	25
		9	85	15
		12	90	10
		12.5	75	25
		14	75	25

a Stop times for programmes 1, 2 and 3 = 7, 10 and 14 min, respectively

Mass spectrometry

Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-flight mass spectrometer fitted with a Z-Spray electrospray ion source operating in negative mode at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data was stored in the continuum mode on a Micromass Instruments MassLynx data station utilising Version 3.5 software pack. Infusion was at a rate of 20 μl/min and a Harvard Instruments syringe pump was used to introduce the sample.

NMR spectroscopy

Nuclear magnetic resonance (NMR) data were recorded on a Bruker Avance at 300 MHz for ^{1}H NMR and at 75.47 MHz for ^{13}C NMR in D_2O unless otherwise stated. Chemical shifts (δ) were measured in ppm from the internal standard and coupling constants (J) in Hz.

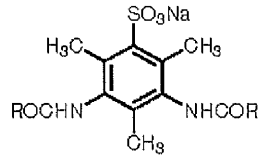
Syntheses

3,5-Diacrylamido-2,4,6-trimethylbenzenesulphonic acid (3; R = CH=CH$_2$)

To 3,5-diamino-2,4,6-trimethylbenzenesulphonic acid (9.2 g; strength 96%; 0.04 mol) in water (50 ml) was added sodium carbonate solution (2 M) to give a clear solution and pH 9.0. The solution was cooled to 0–5 °C and acryloyl chloride (8.46 ml; strength 96%; 0.1 mol) added dropwise, with stirring, while maintaining a pH of 4.5–5.5 with a sodium carbonate solution (2 M). The reaction was left to stir for 24 h. The resultant solution was evaporated on a rotary evaporator to give a solid which was washed with acetone (80 ml), filtered off and oven dried (40 °C) to give the product **3** (R = CH=CH$_2$) as a yellow solid (12.5 g). HPLC showed a single peak at t_R = 0.78; mass spectral analysis gave a molecular ion at m/z 337 [(M – H)$^-$, 100%]; ^{1}H (300 MHz, NaOD): δ(ppm) 2.08 (3 H, s, CH$_3$-p-SO$_3$Na), 2.39 (6 H, s, 2 × CH$_3$-o-SO$_3$Na), 5.68–5.72 (2 H, dd, J 1.9 and 10.2, 2 × C*H*H=), 6.16–6.22 (2 H, dd, J 1.9 and 16.9, 2 × CH*H*=), 6.45–6.54 (2 H, dd, J 10.2 and 16.9, CH=); ^{13}C (75.5 MHz, NaOD): δ(ppm) 13.8 (1 C, CH$_3$-p-SO$_3$Na), 17.2 (2 C, 2 × CH$_3$-o-SO$_3$Na), 122.0 and 126.4 (2 C, 2 × CH=CH$_2$), 131.8, 133.1 and 133.5 (6 C, 6 × ^{Ar}C) and 167.2 (2 C, 2 × C=O).

3,5-(γ-Methoxy)propionamido-2,4,6-trimethylbenzenesulphonic acid (3; R = CH$_2$CH$_2$OCH$_3$)

To methanol (70 ml) and water (35 ml) was added, with stirring, 3,5-diacrylamido-2,4,6-trimethylbenzenesulphonic acid (5.0 g) and sodium carbonate (1.0 g). The reaction mixture was heated under reflux for 48 h and then the solvent removed on a rotary evaporator to give a solid. The solid was lixiviated with acetone (80 ml), filtered off and dried in an electric oven (40 °C) to give the product **3** (R = CH$_2$CH$_2$OCH$_3$) (5.1 g). HPLC showed a single peak at t_R = 0.73 and mass spectral analysis gave ions at m/z 401 [(M – H)$^-$, 100%] and 369 [(M – H –CH$_3$OH)$^-$, 52%]; ^{1}H (300 MHz): δ(ppm) 1.97 (3 H, s, CH$_3$-p-SO$_3$Na), 2.37 (6 H, s, 2 × CH$_3$-o-SO$_3$Na), 3.69 (4 H, t, J 6.0, 2 × CH$_2$CO), 3.32 (6 H, s, 2 × OCH$_3$), 3.73 (4 H, t, J 6.0, 2 × CH$_2$O); ^{13}C (75.5 MHz): δ(ppm) 13.8 (1 C, CH$_3$-p-SO$_3$Na), 16.8 (2 C, 2 × CH$_3$-o-SO$_3$Na), 36.1 (2 C, 2 × OCH$_3$), 58.4 (2 C, 2 × CH$_2$C=O), 68.6 (2 C, 2 × CH$_2$O), 127.0, 133.4, 135.7 (6 C, 6 × ^{Ar}C) and 167.9 (2 C, 2 × C=O).



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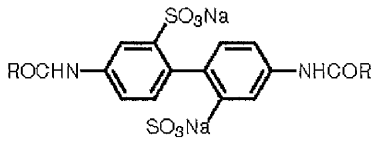

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4,4′-Diacrylamidobiphenyl-2,2′-disulphonic acid (4; R = CH=CH$_2$)

To 4,4′-diaminobiphenyl-2,2′-disulphonic acid (15.8 g; strength 96%; 0.05 mol) in water (50 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0–5 °C and acryloyl chloride (11.8 ml; strength 96%; 0.07 mol) added dropwise, with stirring, while maintaining a pH of 4.5–5.5 with sodium carbonate solution (2 M). The reaction was continued for 48 h and HPLC showed 98% conversion to a new product t_R = 1.02 (4,4′-diaminobiphenyl-2,2′-disulphonic acid compound, t_R = 0.61). Sodium chloride (20 g; 10% w/v) was added portionwise to give a precipitate which was filtered off and oven dried at 40 °C to give a white solid of the product **4** (R = CH=CH$_2$) (22.6 g). HPLC showed a single peak at t_R = 1.09 and mass spectral analysis gave ions at *m/z* 473 [(M – 2H + Na)$^-$, 68%] and 451 [(M – H)$^-$, 75%]; ^{1}H (300 MHz): δ(ppm) 5.75–5.79 (2 H, dd, *J* 2.3 and 9.0, 2 × CH=), 6.20–6.36 (4 H, m, 2 × CH$_2$=), 7.11 (2 H, d, *J* 8.3, 2 × H-*m*-ArSO$_3$Na), 7.42 (2 H, dd, *J* 1.9 and 8.3, 2 × H-*p*-ArSO$_3$NaAr), 8.05 (2 H, d, *J* 1.9, 2 × H-*o*-ArSO$_3$NaAr); ^{13}C (75.5 MHz): δ(ppm) 119.9 and 122.6 (4 C, 2 × CH$_2$= and 2 × CH=), 129.1, 130.7, 133.2, 134.1, 136.9 and 141.6 (12 C, 12 × ^{Ar}C), 167.1 (2 C, 2 × C=O).

4,4′-(γ-Dimethoxy)propionamidobiphenyl-2,2′-disulphonic acid (4; R = CH$_2$CH$_2$OCH$_3$)

To methanol (50 ml) and water (25 ml) was added, with stirring, 4,4′-diacrylamidobiphenyl-2,2′-disulphonic acid (4 g) and sodium carbonate (0.8 g) and the reaction mixture heated under reflux for 48 h. The solution so-formed was evaporated to dryness on a rotary evaporator to give an off-white solid. The product was lixiviated in acetone, filtered off and oven-dried at 40 °C to give the product **4** (R = CH$_2$CH$_2$OCH$_3$) (2.1 g). HPLC showed a single peak at t_R = 1.09 and mass spectral analysis gave ions at *m/z* 515 [(M – H)$^-$, 100%] and 483 [(M – H – CH$_3$OH)$^-$, 35%]; ^{1}H (300 MHz): δ(ppm) 2.60 (4 H, t, *J* 6.0, 2 × CH$_2$C=O), 3.27 (6 H, s, 2 × OCH$_3$), 3.69 (4 H, t, *J* 6.0, 2 × CH$_2$O), 7.18–7.22 (2 H, dd, *J* 3.4 and 8.3, 2 × H-*m*-ArSO$_3$Na), 7.44–7.47 (2 H, dd, *J* 1.9 and 8.3, 2 × H-*p*-ArSO$_3$NaAr), 7.92 (2 H, d, *J* 1.9, 2 × H-*o*-ArSO$_3$NaAr); ^{13}C (75.5 MHz): δ(ppm) 37.0 (2 C, 2 × OCH$_3$), 58.5 (2 C, 2 × CH$_2$C=O), 68.5 (2 C, 2 × CH$_2$O), 120.3, 123.1, 133.0, 134.2, 136.9 and 141.7 (12 C, 12 × ^{Ar}C), 167.8 (2 C, 2 × C=O).

2-Acrylamidobenzoic acid (5; R = CH=CH$_2$)

To anthranilic acid (14 g; strength 98 %; 0.1 mol) in deionised water (60 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0–5 °C and acryloyl chloride (10.46 ml; strength 98%; 0.124 mol) added dropwise, with stirring, while maintaining a pH of 4.5–5.5 with sodium carbonate solution (2 M). The reaction was continued for 35 h to give a white precipitate. HPLC of the reaction mixture showed 85% conversion to a new product, t_R = 1.65 (starting material, t_R = 1.22). The precipitate was filtered off, washed with 10% brine and air dried to give the product **5** (R = CH=CH$_2$) as a white solid (18.9 g). HPLC showed a single peak at t_R = 1.59, mass spectral analysis gave ions at *m/z* 190 [(M – H)$^-$, 88%] and 146 [(M – H – CO$_2$)$^-$, 100%]; ^{1}H (300 MHz, D$_2$O and NaOD): δ(ppm) 5.55–5.58 (1 H, dd, *J* 2.3 and 9.0, CH=), 6.93–6.09 (2 H, m, CH$_2$=), 6.84–6.89 (1 H, td, *J* 0.8 and 7.5, ^{Ar}H), 7.11–7.16 (1 H, tt, *J* 0.8 and 7.5, ^{Ar}H), 7.56–7.59 (1 H, dd, *J* 1.5 and 7.9, ^{Ar}H) and 7.84 (1 H, d, *J* 8.3, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 120.8, 124.1, 124.9, 127.8, 131.0, 132.0, 132.2 and 138.4 (8 C, 6 × ^{Ar}C, CH= and CH$_2$=), 174.7 and 166.4 (2 C, C=O and COONa).

2-(γ-Methoxy)propionamidobenzoic acid (5; R = CH$_2$CH$_2$OCH$_3$)

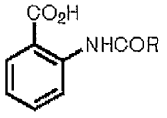
To methanol (100 ml) and water (50 ml) was added, with stirring, 2-acrylamidobenzoic acid (8.0 g) and sodium carbonate (1.6 g) and the reaction mixture heated under reflux for 40 h. The solvent was removed on a rotary evaporator to give a solid which was lixiviated in acetone (100 ml), filtered off and oven dried at 40 °C to give the product **5** (R = CH$_2$CH$_2$OCH$_3$) (8.1 g). HPLC showed a single peak at t_R = 1.68 and mass spectral analysis gave ions at *m/z* 244 [(M – 2H + Na)$^-$, 5%] and 222 [(M – H)$^-$, 100%]; ^{1}H (300 MHz): δ(ppm) 2.57 (2 H, t, *J* 6.0, CH$_2$C=O), 3.25 (3 H, s, OCH$_3$), 3.65 (2 H, t, *J* 6.0, CH$_2$O), 7.04–7.1 (1 H, td, *J* 1.1 and 7.9, ^{Ar}H), 7.31–7.37 (1 H, td, *J* 1.5 and 7.2, ^{Ar}H), 7.70 (1 H, dd, *J* 1.5 and 7.5, ^{Ar}H) and 7.97 (1 H, d, *J* 7.9, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 38.0 (1 C, OCH$_3$), 58.5 (1 C, CH$_2$C=O), 68.4 (1 C, CH$_2$O), 121.4 and 124.5 (2 C, 2 × ^{Ar}C), 125.0 (1 C, ^{qAr}C), 130.8 and 131.9 (2 C, 2 × ^{Ar}C), 136.0 (1 C, ^{qAr}C), 167.9 and 175.0 (2 C, C=O and COOH).

3-Acrylamidobenzenesulphonic acid (6; R = m-NHCOCH=CH$_2$)

To *m*-aminobenzenesulphonic acid (17.3 g; strength 98%; 0.1 mol) in deionised water (50 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0–5 °C and acryloyl chloride (8.5 ml; strength 98%; 0.1 mol) added dropwise, with stirring, while maintaining a pH of 4.5–5.5 with sodium carbonate solution (2 M). The reaction was continued for 24 h and HPLC showed 94% conversion to a new product, t_R = 0.86 (starting material, t_R = 0.66). Sodium chloride (82.5 g; 25% w/v) was added portionwise, with stirring, to give a precipitate which was filtered off and oven dried at 40 °C to give **6** (R = *m*-NHCOCH=CH$_2$) as a white solid (8.1 g). HPLC showed a single peak at t_R = 0.88 and mass spectral analysis gave a molecular ion at *m/z* 226 [(M – H)$^-$, 100%]; ^{1}H (300 MHz): δ(ppm) 5.70–5.74 (1 H, dd, *J* 3.3 and 8.3, CH=), 6.14–6.28 (2 H, m, CH$_2$=), 7.34 (1 H, t, *J* 7.9, ^{Ar}H), 7.45 (2 H, t, *J* 7.9, ^{Ar}H) and 7.86 (1 H, s, ^{Ar}H); ^{13}C (75.5 MHz, D$_2$O): δ(ppm) 118.3, 122.4, 124.2, 129.1, 130.2, 130.5 (6 C, 6 × ^{Ar}C), 137.8 and 143.5 (2 C, 2 × ^{qAr}C) and 167.1 (1 C, C=O).

3-(γ-Methoxy)propionamidobenzenesulphonic acid (6; R = m-NHCOCH$_2$CH$_2$OCH$_3$)

To methanol (60 ml) and water (30 ml) was added, with stirring, 3-acrylamidobenzenesulphonic acid (2.5 g) and sodium carbonate (0.5 g) and the reaction mixture heated under reflux for 40 h. The solvent was removed on



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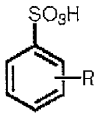


6

a rotary evaporator to give a solid which was lixiviated in acetone (80 ml), filtered off and oven dried at 40 °C to give the product **6** (R = *m*-NHCOCH$_2$CH$_2$OCH$_3$) (1.28 g). HPLC showed a single peak at t_R = 0.92 and mass spectral analysis gave a molecular ion at *m/z* 258 [(M – H)$^-$, 100%] and 226 [(M – H – CH$_3$OH)$^-$, 75%]; ^{1}H (300 MHz): δ(ppm) 2.56 (2 H, t, *J* 6.0, CH$_2$C=O), 3.25 (3 H, s, OCH$_3$), 3.65 (2 H, t, *J* 6.0, CH$_2$O), 7.38 (1 H, t, *J* 7.9, ^{Ar}H), 7.45–7.49 (2 H, m, ^{Ar}H) and 7.78 (1 H, s, 2-^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 36.9 (1 C, OCH$_3$), 58.4 (1 C, CH$_2$C=O), 68.4 (1 C, CH$_2$O), 118.6, 122.4, 124.6 and 130.2 (4 C, 4 × ^{Ar}C), 137.7 and 143.5 (2 C, 2 × ^{qAr}C), 168.1 (1 C, C=O).

*2-Acrylamidobenzenesulphonic acid (**6**; R = o-NHCOCH=CH$_2$)*

To orthanilic acid (14.3 g; strength 80.6%; 0.067 mol) in deionised water (60 ml) was added sodium hydroxide solution (2 M) to give a clear solution and pH 6.5. The solution was cooled to 0–5 °C and acryloyl chloride (10.5 ml; strength 98%; 0.127 mol) added dropwise, with stirring, while maintaining a pH of 4.5–5.5 with sodium carbonate solution (2 M). The reaction was continued for 35 h and HPLC showed 81% conversion to a new product, t_R = 0.99 (orthanilic acid, t_R = 0.76). Salt (15% w/v) was added and the reaction mixture stirred for a further 30 min. The precipitate was filtered off, washed with 20% brine and air dried to give **6** (R = *o*-NHCOCH=CH$_2$) as a white solid (18.9 g). HPLC showed a single peak at t_R = 0.98 and mass spectral analysis gave a molecular ion at *m/z* 226 [(M – H)$^-$, 100%]; ^{1}H (300 MHz): δ(ppm) 5.84 (1 H, m, CH=), 6.23–6.41 (2 H, m, CH$_2$=), 7.28 (1 H, t, *J* 7.5, ^{Ar}H), 7.48–7.53 (1 H, td, *J* 0.8 and 7.5, ^{Ar}H), 7.80 (2 H, d, *J* 7.9, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 125.4, 126.4, 127.8, 129.2, 131.0, 132.7, 133.5 and 134.6 (8 C, 6 × ^{Ar}C, CH= and CH$_2$=) and 167.3 (1 C, C=O).

*2-(γ-Methoxy)propionamidobenzenesulphonic acid (**6**; R = o-NHCOCH$_2$CH$_2$OCH$_3$)*

To methanol (110 ml) and water (50 ml) was added, with stirring, 2-acrylamidobenzenesulphonic acid (12 g) and sodium carbonate (1.8 g). The reaction mixture was heated under reflux for 40 h and then the solvent removed on a rotary evaporator to give a white solid. The solid was lixiviated in acetone (100 ml), filtered off and oven dried at 40 °C to give the product **6** (R = *o*-NHCOCH$_2$CH$_2$OCH$_3$) (14.8 g). HPLC showed a single peak at t_R = 0.92 and mass spectral analysis gave ions at *m/z* 258 [(M – H)$^-$, 56%] and 226 [(M – H – CH$_3$OH)$^-$, 9%]; ^{1}H (300 MHz): δ(ppm) 2.65 (2 H, t, *J* 5.7, CH$_2$C=O), 3.31 (3 H, s, OCH$_3$), 3.70 (2 H, t, *J* 5.8, CH$_2$O), 7.26 (1 H, t, *J* 7.5, ^{Ar}H), 7.45–7.51 (1 H, td, *J* 1.1 and 7.9, ^{Ar}H), 7.74–7.80 (2 H, td, *J* 1.1 and 7.9, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 37.3 (1 C, OCH$_3$), 58.5 (1 C, CH$_2$C=O), 68.2 (1 C, CH$_2$O), 125.7, 126.3, 127.7 and 132.6 (4 C, 4 × ^{Ar}C), 133.5 and 134.6 (2 C, 2 × ^{qAr}C), 173.3 (1 C, C=O).

*4-Acrylamidobenzenesulphonic acid (**6**; R = p-NHCOCH=CH$_2$)*

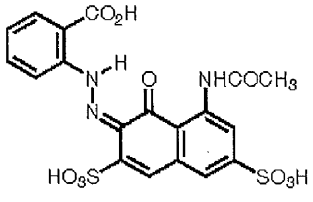
To sulphanilic acid (14.58 g; strength 99%; 0.083 mol) in deionised water (50 ml) was added sodium hydroxide solution (2 M) to give a clear solution at pH 6.5. The solution was cooled to 0–5 °C and acryloyl chloride (20.5 ml; strength 96%; 0.24 mol) added dropwise, with stirring, while maintaining a pH of 4.5–5.5 with a sodium carbonate solution (2 M). The reaction was continued for 24 h and HPLC showed 93% conversion to a new product, t_R = 0.77 (starting material, t_R = 0.98). Salt (18% w/v) was added and the reaction mixture stirred for a further 30 min. The precipitate was filtered off and then air dried to give **6** (R = *p*-NHCOCH=CH$_2$) as a white solid (8.26 g). HPLC showed a single peak at t_R = 0.78 and mass spectral analysis gave a molecular ion at *m/z* 226 [(M – H)$^-$, 100%]; ^{1}H (300 MHz): δ(ppm) 5.77–5.81 (1 H, dd, *J* 2.6 and 9.0, CH=), 6.20–6.35 (2 H, m, CH$_2$=), 7.54 (2 H, d, *J* 8.7, ^{Ar}H), 7.67–7.72 (2 H, dt, *J* 1.9 and 8.7, ^{Ar}H); ^{13}C (75.5 MHz, D$_2$O): δ(ppm) 121.4 and 126.9 (4 C, 4 × ^{Ar}C), 129.4 and 130.6 (2 C, 2 × C=C), 138.71 and 140.2 (2 C, 2 × ^{qAr}C), 167.2 (1 C, C=O).

*4-(γ-Methoxy)propionamidobenzenesulphonic acid (**6**; R = p-NHCOCH$_2$CH$_2$OCH$_3$)*

To methanol (80 ml) and water (40 ml) was added, with stirring, 4-acrylamidobenzenesulphonic acid (5.3 g) and sodium carbonate (1.45 g) and the reaction mixture heated under reflux for 35 h. The solvent was removed on a rotary evaporator to give a solid which was lixiviated in acetone (80 ml), filtered off and oven dried at 40 °C to give the product **6** (R = *p*-NHCOCH$_2$CH$_2$OCH$_3$) (6.7 g). HPLC showed a single peak at t_R = 0.85 and mass spectral analysis gave a molecular ion at *m/z* 258 [(M – H)$^-$, 100%] and 226 [(M – H – CH$_3$OH)$^-$, 38%]; ^{1}H (300 MHz): δ(ppm) 2.64 (2 H, t, *J* 6.0, CH$_2$C=O), 3.29 (3 H, s, OCH$_3$), 3.70 (2 H, t, *J* 6.0, CH$_2$O), 7.51 (2 H, d, *J* 8.7, ^{Ar}H), 7.70 (2 H, d, *J* 8.7, ^{Ar}H); ^{13}C (75.5 MHz): δ(ppm) 37.1 (1 C, OCH$_3$), 58.5 (1 C, CH$_2$C=O), 68.5 (1 C, CH$_2$O), 121.6 and 126.9 (4 C, 4 × ^{Ar}C), 138.71 and 140.02 (2 C, 2 × ^{qAr}C), 167.42 (1 C, C=O).

8-Acetylamino-2-(2'-carboxy)phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (**7**)

To water (30 ml) was added anthranilic acid (0.98 g; strength 98%; 7 mmol) and the solution cooled to 0–5 °C in an ice bath. Concentrated hydrochloric acid (4 ml) was added dropwise followed by sodium nitrite solution (7 ml; 1 M), with stirring, while maintaining a temperature of 0–5 °C. After 25 min the reaction mixture was added to a solution of acetyl H-acid (2.82 g; 7 mmol) dissolved in water (15 ml) at 0–5 °C and the pH was adjusted to 6.5 with a sodium carbonate solution (2 M). Potassium chloride (17% w/v) was added and the reaction mixture stirred for a further 1 h. The solid so-formed was isolated by filtration and air dried to give the product **7** as a red solid (1.42 g). HPLC showed a single peak at t_R = 1.62 and mass spectral analysis gave a ions at *m/z* 508 [(M – H)$^-$, 100%] and 530 [(M – 2H + Na)$^-$, 30%]; ^{1}H (300 MHz): δ(ppm) 2.05 (3 H, s, CH$_3$), 6.89–6.95 (1 H, t, *J* 7.9, ^{Ar}H), 7.15 (1 H, d, *J* 7.9, ^{Ar}H), 7.38–7.43 (1 H, t, *J* 7.5, ^{Ar}H), 7.54 (2 H, d, *J* 5.3, ^{Ar}H), 8.06 (1 H, d, *J* 5.3, ^{Ar}H) and 8.30 (1 H, s, ^{Ar}H).



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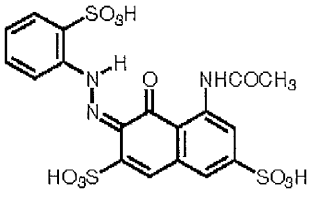

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8-Acetylamino-2-(2'-sulpho)phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (**8**)
To water (35 ml) was added orthanilic acid (2 g; strength 95%; 11 mmol) and the solution cooled to 0–5 °C in an ice bath. Concentrated hydrochloric acid (5 ml) was added dropwise followed by sodium nitrite solution (11 ml; 1 M), with stirring, while maintaining a temperature of 0–5 °C. After 30 min the reaction mixture was added to a solution of acetyl H-acid (4.5 g; 11 mmol) dissolved in water (20 ml) at 0–5 °C, the pH adjusted to 6.5 with sodium carbonate solution (2 M) and stirring continued for 3 h. Potassium chloride (18% w/v) was added and the reaction mixture stirred for a further 1 h. The solid so-formed was isolated by filtration and air dried to give a red solid (**8**) (2.1 g). HPLC showed a single peak at t_R = 1.65 and mass spectral analysis gave ions at *m/z* 566 [$(M - 2H + Na)^-$, 10%] and 544 [$(M - H)^-$, 100%]; ^1H (300 MHz): δ(ppm) 2.31 (3 H, s, CH_3), 7.21 (1 H, t, *J* 7.5, ^{Ar}H), 7.52 (1 H, t, *J* 7.9, ^{Ar}H), 7.62–7.74 (3 H, m, ^{Ar}H), 8.01 (1 H, d, *J* 8.3, ^{Ar}H), 8.77 (1 H, s, ^{Ar}H).

Diazotisation and coupling of the reaction mixture obtained after subjecting compounds **5** *(R = $CH_2CH_2OCH_3$) and* **6** *(R = o-$NHCOCH_2CH_2OCH_3$) to high temperature*
Compound (0.5 g) in pH 4.0 buffer solution (20 ml) was heated to 130 °C for 1 h and the resultant solution cooled to 0–5 °C in an ice bath. Concentrated hydrochloric acid (2 ml) was added dropwise and the mixture titrated with standard 0.1 M sodium nitrite solution to a positive 15 min sulphone indicator end-point. Where significant titrations were given, excess nitrous acid was destroyed with sulphamic acid. The diazotisation solution was then added to a suspension of acetyl H-acid (0.093 g) at 0–5 °C and the pH raised to 6.5 with a sodium carbonate solution (2 M) to give a red dye (see Scheme 2).

High temperature treatment
Each γ-methoxypropionamido compound (0.5 g), in pH 4.0 buffer solution (20 ml), was heated at 130 °C for 60 min, in a sealed stainless steel dye pot housed in a Mathis Labomat BFA 12 dyeing machine using the profile shown in Figure 1. The solutions were cooled and analysed by HPLC and by titration with sodium nitrite solution.

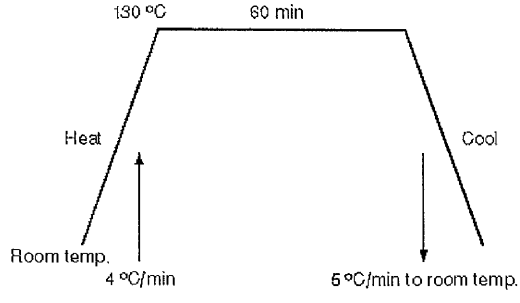


Figure 1 High temperature dyeing profile used in this study

Sodium nitrite titration
Each solution from the HT treatment above was titrated with 0.1 M standard sodium nitrite solution. A blank titration was performed on each starting material. Only compounds **5** (R = $CH_2CH_2OCH_3$) and **6** (R = o-$NHCOCH_2CH_2OCH_3$) gave significant titrations. For the other compounds tested one or two drops of sodium nitrite solution were needed only to reach the end point indicating that only a trace of primary amine was formed during HT treatment in an acidic environment.

HPLC results
Following HT treatment, each γ-methoxypropionamido compound listed above was analysed by HPLC. Only compounds compounds **5** (R = $CH_2CH_2OCH_3$) and **6** (R = o-$NHCOCH_2CH_2OCH_3$) showed the presence of a new peak. Before HT treatment, compound **5** (R = $CH_2CH_2OCH_3$) gave a peak at t_R = 1.68 and after HT treatment a new peak appeared at t_R = 1.09. For compound **6** (R = o-$NHCOCH_2CH_2OCH_3$); t_R = 0.92), a second peak at t_R = 0.84 was formed.

Results and Discussion

Previous studies showed that lyocell fibre pre-treated with cross-linker **1** underwent a loss of wet abrasion resistance after HT treatment, under acidic conditions. Wet abrasion resistance values have been shown to be a good measure of fibre cross-linking [5,12]. As elemental analysis of the fibre showed no loss of nitrogen, it was suggested that the sulphonic acid group *ortho* to one of the amide links was responsible for the observed hydrolytic instability of the cross-linking agent. Subjecting model compound **2** to similar conditions resulted in partial amide hydrolysis [7].

Accordingly, to further test the validity and to explore the generality of this hypothesis, a series of mono- and bis-acrylamido compounds was synthesised, converted to the corresponding methyl ethers and the latter compounds subjected to HT polyester dyeing conditions. A pH value of 4.0 was chosen for the HT treatment in order to subject the agents to the severe acid conditions encountered during polyester dyeing.

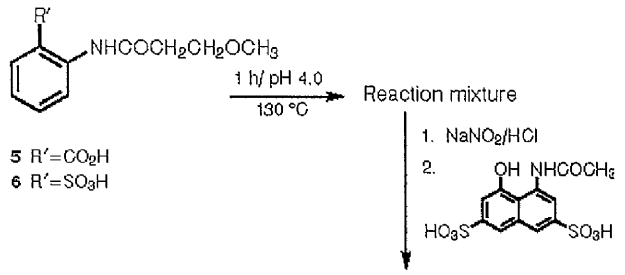
Compounds **3**, **4** (R = $CH_2CH_2OCH_3$) and **6** (R = *m*- and *p*-$NHCOCH_2CH_2OCH_3$), with sulphonic acid groups *meta* or *para* to the amide bond, are unable to participate in a neighbouring group hydrolysis mechanism. Each compound in this series was dissolved, in turn, in the buffer solution and subjected to the HT dyeing conditions. No new band was detected by HPLC and titration with sodium nitrite solution revealed only a trace of aromatic amine had been produced. Hence, the γ-methoxypropionamido compounds (**3**, **4** and **6**; R = *meta* and *para* isomers) proved to be, for all practical purposes, stable to HT polyester dyeing conditions.

Treatment of compounds **5** (R = $CH_2CH_2OCH_3$) and **6** (R = o-$NHCOCH_2CH_2OCH_3$), which contain either a carboxylic or a sulphonic acid group positioned *ortho* to the amide group, i.e. in a similar situation to that found in **1**, produced a different outcome. In the case of compound **5** (t_R = 1.68), with an *ortho* carboxylic group, HPLC chromatography following HT treatment showed the presence of a new HPLC peak at t_R = 1.09 and volumetric analysis with sodium nitrite solution showed 18.2% hydrolysis had occurred. Similarly, compound **6** (R = o-$NHCOCH_2CH_2OCH_3$; t_R = 0.92) showed the presence of a new peak at t_R = 0.84 and titration with sodium nitrite solution determined that 23.8% hydrolysis had occurred.

The above experimental results are fully consistent with a neighbouring group participation mechanism of the type shown in Scheme 1.

To further investigate the products of hydrolysis, the diazo solutions from the sodium nitrite titrations of γ-methoxypropionamido derivatives **5** (R = $CH_2CH_2OCH_3$) and **6** (R = *o*-$NHCOCH_2CH_2OCH_3$) were coupled, in turn, with acetyl H-acid (8-acetylamino-1-naphthol-3,6-disulphonic acid) to give an unknown red dye (Scheme 2).

The anticipated products that would be expected to be formed in Scheme 2 (i.e. structures **7** and **8**) were unambiguously synthesised, their HPLC retention times compared with those of the unknown products and the results listed in Tables 2 and 3.



Scheme 2

Table 2 HPLC retention times t_R corresponding to dye **7** for each of the three programmes

	t_R		
Programme	Dye **7**	Unknown dye	Mixture
1	1.49	1.42	1.47
2	4.71	4.70	4.70
3	0.79	0.79	0.79

Table 3 HPLC retention times t_R corresponding to dye **8** for each of the three programmes

	t_R		
Programme	Dye **8**	Unknown dye	Mixture
1	0.79	0.79	0.79
2	4.89	4.92	4.90
3	1.65	1.61	1.69

Virtually identical retention times for the individual analyses and the appearance of only a single peak for the mixtures, strongly supported structural assignments of **7** and **8** for the unknown dyes. Additional support was provided by comparing the visible spectral curves of the unknown dyes (Scheme 2) where R' = CO_2H (λ_{max} 533 nm) and R' = SO_3H (λ_{max} 503 nm) with those of dye **7** (λ_{max} 534 nm) and dye **8** (λ_{max} 505 nm).

Conclusions

The methyl ethers of a number of benzeneacrylamido compounds, with sulphonic acid groups *meta* and *para* to the amide links proved to be hydrolytically stable to the HT polyester dyeing conditions (60 min at 130 °C, pH 4.0). Two other derivatives, one with an *ortho* sulphonic acid substituent and the other with an *ortho* carboxylic acid group, underwent significant amide hydrolysis during the HT treatment. This is consistent with a neighbouring group participation mechanism and confirms previous findings [7]. Accordingly, benzeneacrylamido cross-linking agents, for lyocell fibres, must be devoid of *ortho* sulphonic acid or *ortho* carboxylic acid groups, in order to furnish cross-linked lyocell fibres with good hydrolytic stability to a range of HT polyester dyeing conditions.

References

1. P White, *Regenerated Cellulosic Fibres*, Ed. Calvin Woodings (Manchester: Textile Institute, 2001) 62.
2. H Firgo, M Eibl, W Kalt and G Meister, *Lenzinger Ber.*, **74** (1994) 81.
3. T Eynon, *Japanese Business News* (Dec 1998) 1.
4. T Rosenau, A Potthast, H Sixta and P Kosmo, *Prog. Polym. Sci.*, **26** (9) (2001) 1763-1837.
5. A Nechwatal, M Nicolai and K-P Mieck, *Text. Chem. Colorist*, **28** (5) (1996) 24.
6. T Kreze, S Jeler and S Strnad, *Mater. Res. Innovations*, **5** (2002) 277.
7. I Bates, E Maudru, D A S Phillips, A H M Renfrew, Y Su and J Xu, *Color. Technol.*, **120** (2004) 293.
8. Y Girel and H Rodier, *FR2273091* (Rhone Poulenc; 1975).
9. K Bredereck, F Schulz and A Otterbach, *Melliand Textilber.*, **78** (10) (1997) 703.
10. M Nicolai, A Nechwatal and K-P Mieck, *Angew. Makromol. Chem.*, **256** (1998) 21.
11. A Nechwatal, M Nicolai, K-P Mieck, B Heublein, G Kühne and D Klemn, *Angew. Makromol. Chem.*, **271** (1999) 84.
12. A Nechwatal, M Nicolai and K-P Mieck, *Text. Res. J.*, **66** (9) (1996) 575.
13. L Pearson and J M Taylor, *WO9500697* (Courtaulds; 1995).
14. P G Urben, *EP691426* (Courtaulds; 1996).
15. W Schrott and W Badura, *WO9607780* (BASF; 1995).
16. M Patsch, R Krallmann, W Reuther and T Groesser, *WO9735848* (BASF; 1997).
17. H Firgo, S Seidl, P Bartsch, B Koell and E Muelleder, *EP783601* (Lenzing; 1997)
18. S Seidl and H Firgo, *EP783602* (Lenzig; 1997).
19. H Firgo, E Muelleder and S Seidl, *EP796358* (Lenzig; 1997).
20. B Koell, P Bartsch and E Muelleder, *WO9919555* (Lenzig; 1999).
21. *AT2527U* (Lenzig; 1998).
22. A Hashemzadeh, *WO9620302* (Akzo Nobel; 1996).
23. S Nishikawa, S Fujita and K Tsuji, *EP978585* (Ipposha Oil Ind. Co. Ltd; 2000).
24. *Japanese Patent 08-025888* (Sumitomo; 1996 application).