2
Substrates and their structure

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This chapter is divided into two major parts. The first part (2.1) is directed towards non-fibrous enzymatic substrates or, in other words, compounds that undergo reactions with enzymes. Included in this part are dyes, natural sizing and thickener materials, such as starches and cellulose derivatives, and so on. Also in this part is a description of compounds that might be present but are not true substrates for enzymes. Their presence, however, may interfere with enzymatic recognition or otherwise affect the reactivity of the enzymes. The second part (2.2) deals with textile fibers that function as substrates for enzymes.

2.1 Non-fibrous substrates and non-substrates

2.1.1 Colorants for textile materials

Colorants generally are divided into dyes and pigments. While dyes for textile materials have moderate to good solubility in the medium of application, allowing them to penetrate into the fiber, pigments are insoluble in the medium of use and have to be attached to the fiber surface by other means, such as binders. Polymeric dyes fall in-between these two categories. Dyes can be classified by chemical class or by application method. Details of dye structure, application and end-use performance are listed in the Colour Index (CI) (Colour Index, 1999). A practical guide for dyeing and for printing can be found in Rivlin (1992) and in Miles (1994), respectively. For more theoretical background, a good reference is Zollinger's Color Chemistry (Zollinger, 1991). Dyes for specific fibers are discussed in Lewis (1992) for wool and wool blends and in Shore (1990a, 1995) for cellulosic fibers.

Efforts have been made to decolorize and/or fragment the chromophore of colorants on textile materials for bleaching or fading purposes, such as indigo on denim with laccases (Campos *et al.*, 2001). Furthermore, research was performed on dyehouse effluent treatment of aqueous suspensions/
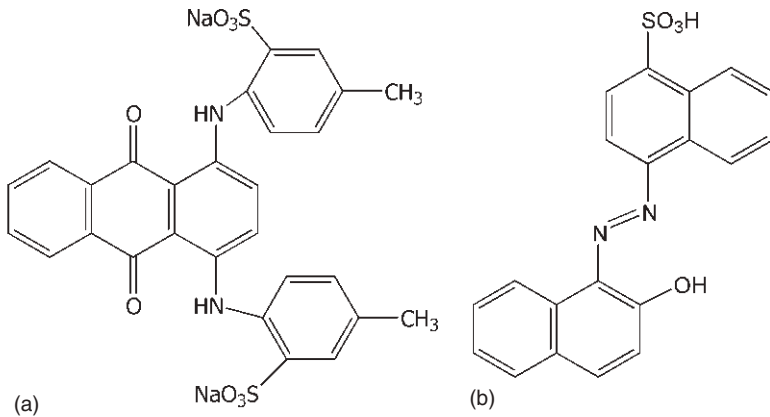
2.1 (a) CI Acid Green 25 and (b) CI Acid Red 88 as examples of acid dye structures.

solutions with peroxidases and laccases in the presence or absence of mediators (Call and Muecke, 1997; Tzanov *et al.*, 2000; Abadulla *et al.*, 2000).

In the following section, textile colorants as classified by their application method will be discussed briefly in alphabetical order of the dye class, followed by azoic and polymeric dyes as transition to pigments.

2.1.1.1 Acid dyes

Acid dyes are water-soluble dyes for polyamide fibers, wool and silk. The chromophore is often based on anthraquinone or one to several azo-groups and varies in molecular size (Fig. 2.1). Characteristic to all acid dyes are one or more sulfonic acid or carboxylic acid group(s), attached to the chromophore, which not only provide water solubility, but also form ionic bonds with the amino groups of the fiber polymer under acidic conditions. They show generally good washfastness and brilliant color shades.

1:1 and 1:2 metal complex dyes are a subcategory of acid dyes (Fig. 2.2). Their structural features allow for holding a transition metal ion via formation of a complex.

In 1:1 metal complex dyes, one dye molecule with two ortho-hydroxyl substitutions adjacent to the azo-group is coordinated with one metal ion, mostly chromium(III) or cobalt(III). When applied to the fiber, the three free coordinations of the metal ion interact with groups in the fiber, thus supporting dye–dye aggregation, the overall dye/fiber binding strength and ultimately the wash fastness. In 1:2 metal complex dyes, two dye molecules, which can be of the same or different type, form an octahedral arrangement with one transition metal ion in the center. In this case the metal ion is not available for additional bonds with the fiber since it is already fully coor-
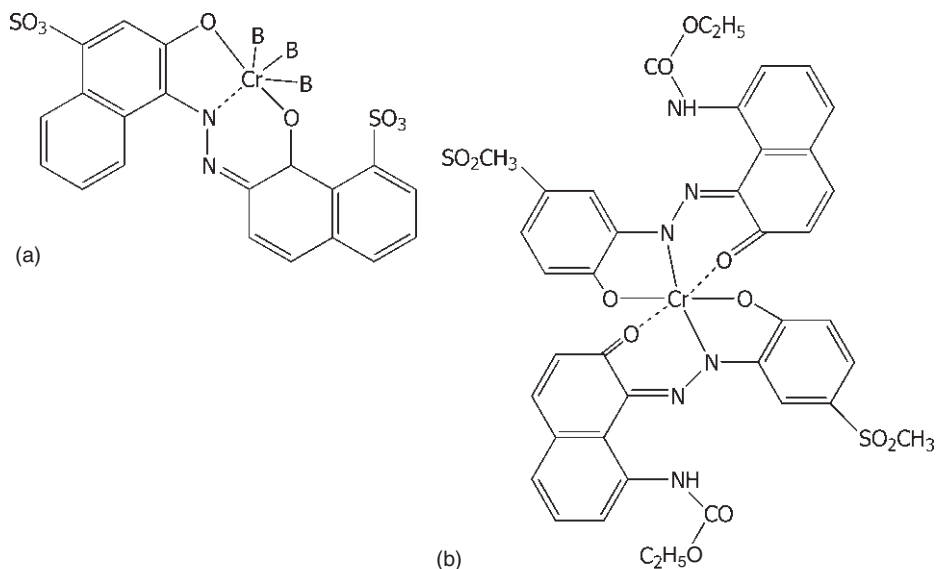
2.2 (a) CI Acid Blue 158 (B represents replaceable groups, such as water molecules) is an example of a 1:1 metal complex dye; (b) CI Acid Black 58 is an example of a 2:1 metal complex dye.

dinated. Dye/fiber binding in this case is improved through the dye molecular size and by hydrophobic interactions of these fairly large dye complexes with the fiber.

A similar subcategory comprises mordant dyes. Owing to environmental concerns as well as possible fiber damage, mordanting is no longer practiced commercially to any extent today. In mordant dyeing, a mordant solution is applied prior to acid dyeing to obtain various color shades. Popular mordants included salts of aluminum, iron and copper (Schweppe, 1993) and, dependent on the compound selected, a wide range of hues could be generated on wool, but also on linen and cotton. The most common mordant, however, was chromium applied in the form of sodium or potassium dichromate solution to wool in either a pre- or a post-treatment. The reduction of chromium(VI) to chromium(III) takes place in the fiber through cystine, by the way of hydrogen sulfide. Other groups in wool are possibly also involved in the reduction/oxidation process (Lewis, 1992).

2.1.1.2   Basic (cationic) dyes

Many naturally occurring dyes belong to the class of basic dyes. Examples are Crystal Violet (C.I. Basic Violet 3; Fig. 2.3a) and Malachite Green (C.I. Basic Green 4). The characteristic feature of basic dyes is a positively charged group within the molecule, either localized and fixed at a specific
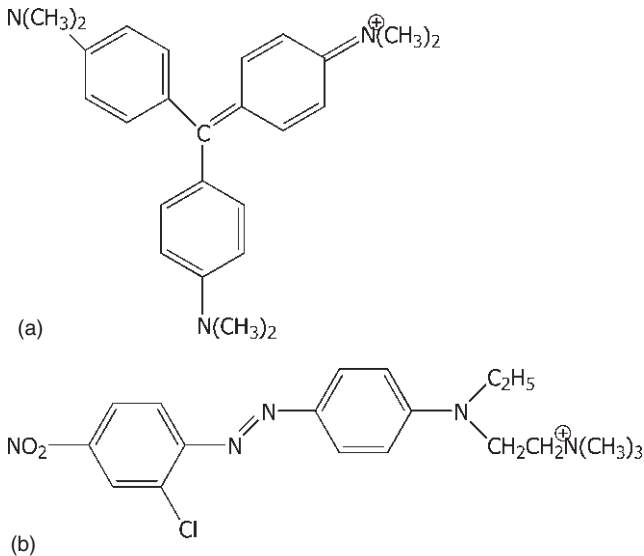
2.3 (a) Crystal Violet (CI Basic Violet 3) with delocalized positive charge and (b) CI Basic Red 18 with localized positive charge.

position (e.g. C.I. Basic Red 18; Fig. 2.3b) or delocalized over the entire structure (e.g. triarylmethane dyes). Historically used on silk, the major application of basic dyes today is focused on acrylic fibers and basic-dyeable polyester where strong ionic bonds with the acid groups incorporated in the fiber can be formed.

2.1.1.3 Direct dyes

Direct dyes are fairly high molecular weight, water-soluble, anionic dyes with substantivity for cotton and other cellulosic fibers. Direct dyeing is a simple exhaust process from neutral solution at boiling temperatures with the addition of an inorganic salt. Direct dyes are held inside the fiber through dye–dye aggregation, as well as by weak secondary forces formed by parallel alignment of dye molecules and cellulose chains. Owing to the size of their chromophores (Fig. 2.4), color shades are less brilliant and washfastness is limited. After treatments with cationic fixing agents, such as quaternary ammonium compounds, complex fatty acids and melamine derivatives, or crosslinking with amide–formaldehyde resins the wet performance of direct dyed goods can be improved.
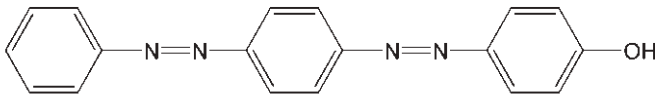
2.1.1.4 Disperse dyes

Disperse dyes consist of small chromophores with strong auxochromes (see Fig. 2.5 for examples) and show very low water solubility, hence their name.
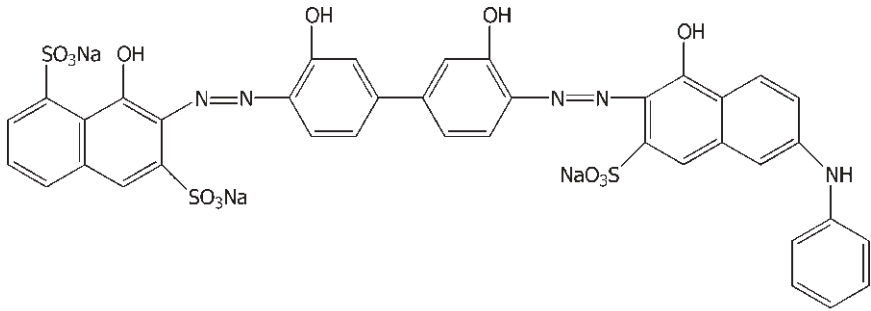
2.4 CI Direct Blue 98.
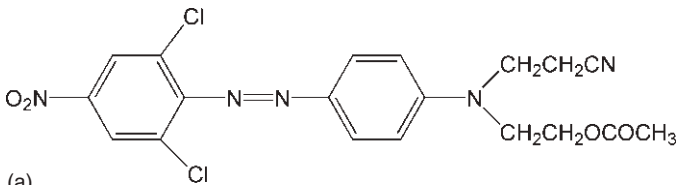
2.5 (a) CI Disperse Orange 30 and (b) CI Disperse Yellow 23.

They are the major dye class for polyester and other hydrophobic fibers, such as acetate, and to a lesser extent nylon. Several routes can be taken for the coloration with disperse dyes. If applied from an aqueous dispersion in an exhaust process, dyeing proceeds very slowly. Pressure and/or heat or the addition of so-called carriers are necessary measures to increase the dyeing rate. Carriers are small organic compounds that both support the dispersion properties of the dye as well as improve the accessibility of the fiber for the dye. The use of carriers is minimized as much as possible though, owing to their toxicity, odor and other undesirable properties.

An alternative route for application of disperse dyes is by a pad-dry-cure process (thermosol process). After padding the fairly concentrated dye dispersion onto the fabric, the remaining water is removed and dry heat close to the glass transition temperature of the fiber causes the sublimation of these dyes into the fiber structure.

2.1.1.5   Reactive dyes

The main characteristic of this water-soluble dye class is their ability to form a covalent bond with the fiber via a chemical reaction. Most of these dyes

HO3SOH2CH2CO2S

SO2CH2CH2OSO3H

NH2   OH

HO3S

SO3H
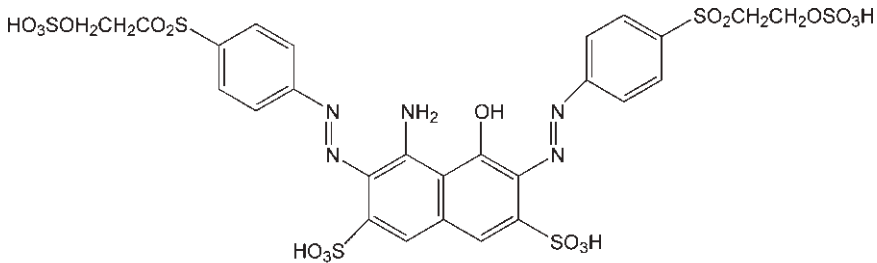
2.6 CI Reactive Black 5, bifunctional reactive dye.

OCH3   HO

N=N

H3C
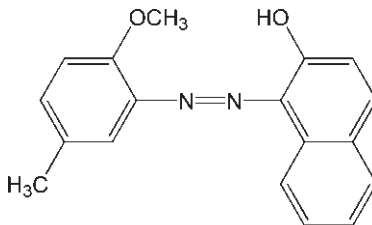
2.7 CI Solvent Red 17.

have been developed for cellulosics, but some special compounds also exist for the dyeing of wool (Lewis, 1992). In a reactive dye one or more reactive groups (same or different types) carrying a 'leaving' group are connected to the chromophore via a link (the different components of a reactive dye are shown in Fig. 2.6). The chromophore carries one or more water-solubilizing groups. The reaction with the fiber generally occurs by displacement of the leaving group (usually a halogeno substituent) at alkaline conditions via a nucleophilic substitution or elimination/addition mechanism depending on the type of reactive group. Under normal end-use conditions the stability of the formed covalent bond in cellulosics is good. Owing to the sensitivity to high pH, wool is dyed at neutral to slightly acidic conditions with especially developed reactive dyes. An alkaline aftertreatment with ammonia might be necessary.

2.1.1.6 Solvent dyes

Dyes in this class are water insoluble but can be dissolved in organic solvents, such as alcohols, ketones or hydrocarbons, for application. Their molecular weight is fairly low (Fig. 2.7) and their end-use properties (washfastness, etc.) vary considerably. Many solvent dyes find alternative uses in industries other than the textile industry.
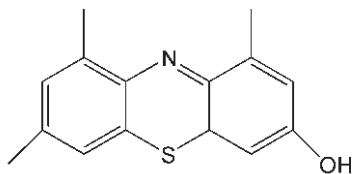
2.8 Example of a sulfur dye fragment.

2.1.1.7 Sulfur dyes

Sulfur dyes are water-insoluble polymeric dyes with sulfur as an integral part of the chromophore and sulfur in the form of polysulfide bridges within the dye structure, hence their name (see Fig. 2.8). The exact chemical structure and composition of most sulfur dyes is unknown. Under alkaline conditions internal S—S bridges can be split with a reducing agent, rendering the resulting dye fragments water soluble (*leuco* form of the dye) and with substantivity for cellulosic fibers:

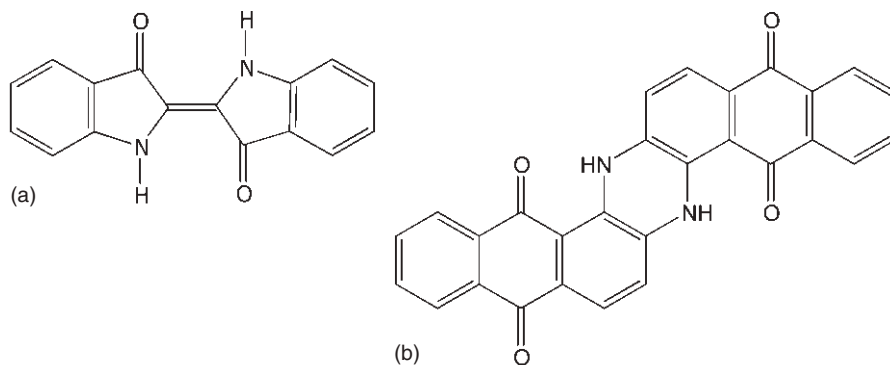$$\text{Chromophore-S-S-chromophore} + Na_2S \rightarrow {}^2\text{chromophore-S}^-Na^+$$
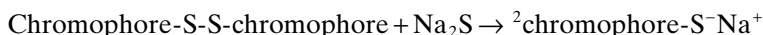
Once absorbed by the textile material, the dye fragments are reoxidized and combined to large network-like structures. Because of their insolubility and their molecular size they have good washfastness and thus are valuable in combined application with direct dyes, but their shades are dull and the color range obtainable is limited to browns, greens, blues and blacks.

Sulfur dyes are available in different forms on the market. Leuco sulfur dyes contain both the prereduced soluble *leuco* form of the dye and the reducing agent, such as sodium sulfide, and can be applied directly to the fiber. Solubilized sulfur dyes are thiosulfuric acid derivatives that can be converted to the alkali-soluble thiol form and exhausted onto the fiber. Condense sulfur dyes are S-alkyl- or S-arylthiosulfates which need sodium sulfide or polysulfide for reduction and solubilization.

2.1.1.8 Vat dyes

Application and manufacture of vat dyes have been known for centuries; indigo and Tyrian Purple (6,6′-dibromo indigo) are the most famous historic representatives of this dye class (Fig. 2.9). Similarly to sulfur dyes, vat dyes have to be made water soluble by reduction of the keto group in alkaline solution to the enolate form. Once in water-soluble form (leuco vat dye) they have sufficient substantivity for cellulosic fibers. Reoxidation with air or a mild oxidizing agent reforms the original water-insoluble dye molecule. Vat dyes show good washfastness and fairly brilliant colors. They can also be obtained in their prereduced salt form (sulfatoesters of vat dyes) for pH sensitive fiber materials (wool, blends) and easier application. However, the shelf life of these soluble vat dyes is limited.

2.9 (a) CI Vat Blue 1 (indigo) and (b) CI Vat Blue 4.
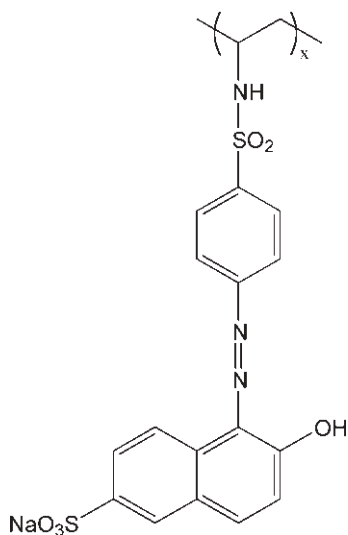
Poly S^{TM}-119

2.10 Structure of a commercial polymeric dye.

2.1.1.9 *Polymeric dyes*

In the case of polymeric dyes, the chromophore is attached to a polymer backbone, such as polyethylene glycol (Fig. 2.10). A review of polymeric dyes (i.e. polymers that contain chromophoric substituent groups or polymers which contain a chromophoric group as part of the polymeric backbone), emphasizing synthesis and characterization, can be found in Guthrie (1990).
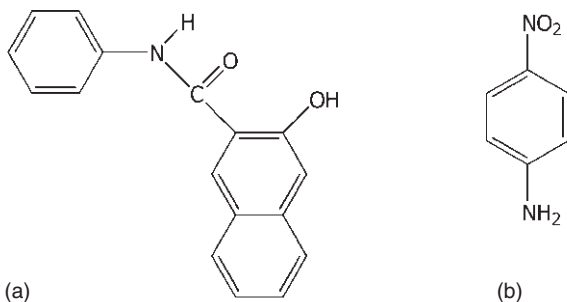
2.11 Structure of (a) CI Azoic Coupling Component 2 and (b) CI Azoic Diazo Component 37.

2.1.1.10 Azoic dyes

Azoic dyes are relatively small, mostly monoazo, compounds that are synthetized on the fiber by coupling a water-soluble diazo compound and a water-soluble coupling component (Fig. 2.11). Coupling components are substituted β-naphthols with affinity for cellulosic fibers which have been made water-soluble in alkaline solution (Colour Index terminology: Azoic Coupling Component). Diazo compounds (Azoic Diazo Component) are aromatic primary amines or stabilized diazonium compounds that are reacted to diazonium salts under acidic conditions before coupling in a separate bath. The naphthol is first applied to the textile material and, after removal of excess liquor, developed in diazonium salt solution. Although the application process is fairly complicated and time consuming, azoic dyes have some advantages over other dye classes. Color shades obtained are especially strong and brilliant in the red and orange area, but also in blue and black. The dye formed is water insoluble with high wash fastness. However, crock fastness is limited, the reason being that the dye formed on the surface resembles a pigment, lacking the binder to fix it properly. Surface dye particles are thus easily removed upon mechanical action. Today azoic dyes are mainly used for coloring cellulosic materials, but can also be applied to polyester and triacetate.

2.1.1.11 Pigments

Pigments are organic or inorganic colorants (see Fig. 2.12 for an example of an organic pigment) that are insoluble in the medium of application and thus remain in the particle state. If used on textile materials they are fixed to the surface with the help of binders or in the form of coatings or mixed into the spinning dope of synthetic fibers. Suitable adhesives often consist of resins that can be heat set, holding the pigments in place. Fastness to washing, dry cleaning and especially crocking (rubbing) of
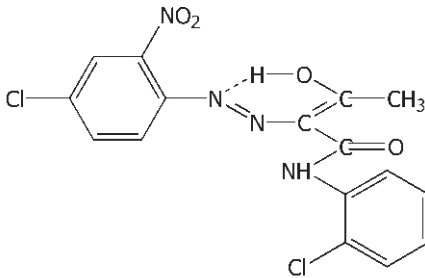
2.12 CI Pigment Yellow 3.

pigment prints are usually determined by the wear-and-tear properties of the binder used.

## 2.1.2 Natural auxiliaries for textile processing

The purpose of auxiliaries is to facilitate a textile process and/or increase its efficiency. They serve as sizing materials, lubricants, wetting agents, emulsifiers, agents accelerating or decelerating the dyeing rate, thickeners, binders, etc. often with considerable overlap in the functions and abilities of a specific chemical. Compounds used encompass many different chemical classes, some of which are affected by enzymes and thus can be regarded as substrates, and some of which remain unaffected. Owing to environmental and economical concerns, auxiliaries are used as sparingly as possible. Once the respective process is terminated they are to be removed completely from the treated material; however, traces could still be present and interfere negatively with subsequent processing steps.

2.1.2.1 *Natural sizing compounds, coating materials and thickeners*

Starch

Sizing compounds and lubricants are applied to yarns before fabric formation to protect the integrity of the yarns. While increasingly faster weaving processes demand more enduring sizes, such as acrylic-based compounds, natural sizes that can be decomposed by enzymes are still on the market. Such compounds comprise starch and starch derivatives, as well as soluble cellulose derivatives, with waxes often admixed. Desizing with amylases is one of the oldest enzymatic processes used in the textile industry. A comprehensive description of the process can be found in Uhlig (1998).

Starch has also been very useful as a thickener in printing pastes and as a component of adhesives. In printing processes, starches are applied to
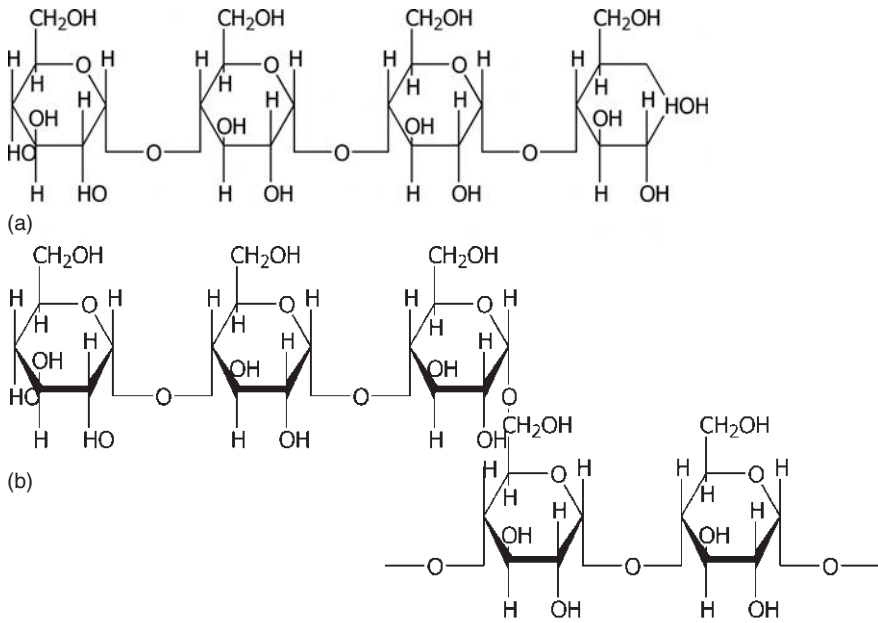
2.13 (a) Amylose and (b) amylopectin, the two components of starch.

guarantee a defined design and to avoid spreading of the printing paste. In the paper industry, starches increase sheet strength and, as coatings, improve the writing and printing properties of high quality paper.

Native starch contains two components, amylose and amylopectin (see Fig. 2.13), bound together by hydrogen bonding. Degrees of polymerization and cross-linking vary, yielding a large variety of starches with differing characteristics, including swelling and gelatinization properties. Amylose is a polymer of linear unbranched α-1,4-glucan, while amylopectin, also a α-1,4-glucan, is additionally highly branched at the C-6-position. The ratio of amylose and amylopectin depends on the source and processing of the respective starch.

Enzymes capable of hydrolyzing starch include α- and β-amylase, amyloglucosidase (glucoamylase) and isoamylase (Uhlig, 1998). Both α- and β-amylases attack the α-1,4-linkage, but are unable to break the 1,6-branched linkages. They predominantly produce maltose and dextrins as end products. Glucoamylase liberates glucose from non-reducing ends at α-1,4 and 1,6-linkages and generates glucose. Isoamylase is a debranching enzyme, producing mainly maltose.

Modified starches

The hydroxyl groups in starch can be functionalized to form acetates, ethers or esters to various degrees of substitution. Such modifications have an

impact on the gelation and swelling behavior and are useful for printing applications as well as in the food and pharmaceutical industry. Among others, hydroxyethyl-, methyl- and carboxymethyl-starches are important as thickeners. Corresponding water-soluble cellulose derivatives can also be produced for application in thickener formulations (see below).

Gums

Dry roasting of starches at 135–190°C yields British gums. Such starch derivatives are crosslinked in the 1,6 position with decreased degree of polymerization (DP). Other gums that are important for thickening purposes are alginate based (from seaweed) or obtained from other natural polysaccharides (gum arabic, xanthate gum, gum tragacanth, etc.; Miles, 1994). Some of these compounds can also economically be grown by microorganisms. Dextrins (see below) are produced by pyroconversion with very small amounts of acid in the form of a fine spray. Gums and dextrins play an important role as adhesives and binders in the coating industry and as encapsulating compounds.

Xanthan

Xanthan gum consists of a β-1,4 linked glucan main chain with a negatively charged trisaccharide (two mannose units and one glucuronic acid residue) side chain at alternating C3 atoms. Because of these substitutions, xanthan is a highly charged polyanion, giving it a rigid-rod structure in solution as a result of repulsion effects. Considering its structure and its high molecular weight, it is not surprising that its solution is highly viscous. Low concentrations are sufficient to prepare an excellent thickening agent for printing (Miles, 1994) and other purposes.

Alginates

Alginates are polyanionic block copolymers of high molecular weight of α-D-guluronic acid and β-L-mannuronic acid (De Baets *et al.*, 2002). Commercial alginates are obtained from seaweed. With the help of enzymes or by chemical means the ratio of guluronic acid and mannuronic acid can be modified and thus their gelation properties tailored to specific applications. The high viscosity of their solutions and their chemical inertness towards dyes makes them valuable textile printing thickeners.

Dextrin and cyclodextrin

Dextrins are α-1,6-D-glucopyranosyl polymers, branched through (1,2), (1,3) or (1,4) linkages, while cyclodextrins are cyclic molecules formed by
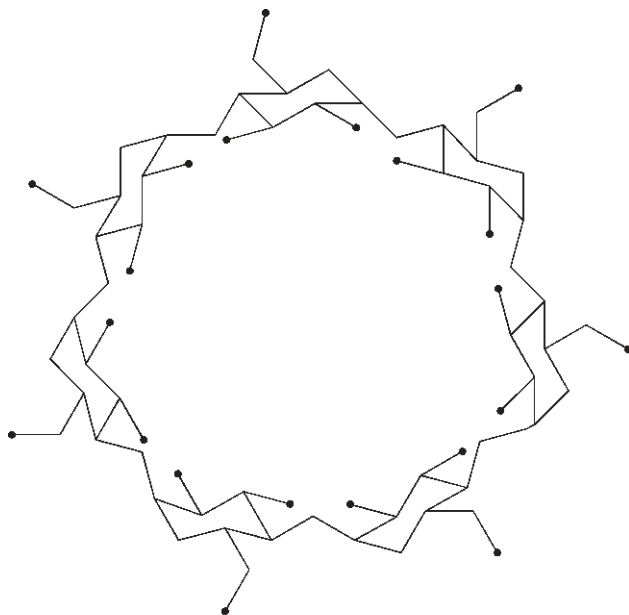
2.14 Structure of cyclodextrin, made from seven glucopyranose
residues.

six, seven, eight or, less commonly, nine α-D-(1,4)-linked glucopyranose
residues (see Fig. 2.14). Cyclodextrins form water-soluble ring structures
with numerous hydroxyl groups at the outside. The interior cavity on the
other hand is fairly hydrophobic and capable of holding small molecules.
Besides sequestering small molecules, cyclodextrins can serve as amylase
inhibitors.

Cellulose derivatives

Water-soluble cellulose ethers (Fig. 2.15) are versatile auxiliaries owing to
their availability and low toxicity. Carboxymethyl cellulose, and methyl
(MC) and hydroxyethyl celluloses (HEC) are commercially important
thickeners, film formers, adhesives and water-retaining agents for the
textile, pulp and paper industries (Heinze, 1998). Organic and inorganic cel-
lulose esters are used in coatings, thermoplastic films and resins (e.g. cellu-
lose acetobutyrate) and for textile finishing (e.g. cellulose phosphate for
flame retardancy for cotton). Cellulose acetate can also be produced in
textile fiber form and is discussed in Section 2.2.1.

Cellulases are suitable enzymes for the decomposition of cellulose deriv-
atives on condition that the derivatization of the cellulose backbone does
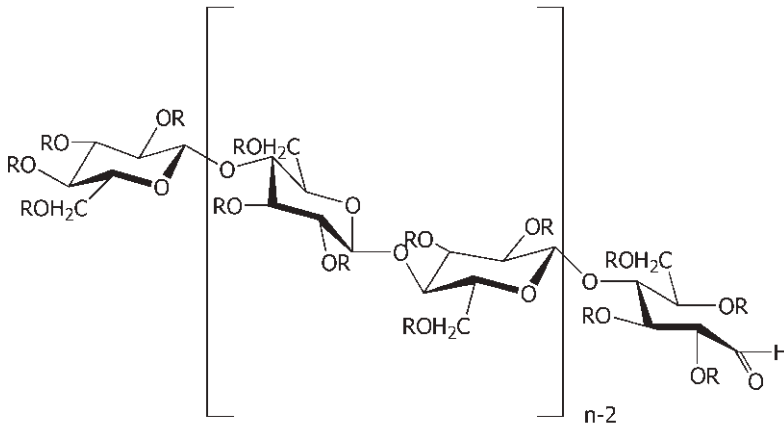
Cellulose derivatives (some R = H, some R = ester-, ether-, etc. forming groups)

2.15 Modified celluloses (some rest groups R=H, some or all R=CH₃, C₂H₅, COCH₃, etc.).
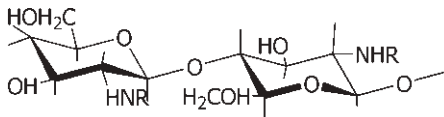
2.16 Chitosan (R=H) and chitin (R = acetate).

not have a significant impact on enzyme recognition (Philipp and Stscherbina, 1992; Glasser *et al.*, 1994). Whole cellulases, composed of cellobiohydrolases, endocellulases and β-glucosidases, can be applied either individually or in combination with enzymes that focus on other compounds in the thickener or sizing material, such as amylases (starch degradation) or lipases (fat hydrolysis). In enzyme mixtures the requirements for active pH and temperature of all components must be considered for the system to be effective.

Chitosan

Chitosan (copolymer of *N*-acetylglucosamine and glucosamine, Fig. 2.16; De Baets *et al.*, 2002) is produced from chitin (β-1,4-linked *N*-acetylglucosamine) by deprotonization, demineralization and partial deacetylation to a product soluble in 1% acetic acid. Chitosan can be used as a viscosity controlling compound in mixtures with other swelling agents. Further, as a

polycation, chitosan binds to polyanions such as anionic dyes, and can improve dyeability if applied as a coating or film forming agent. It is possible to manipulate film stabilities by crosslinking. Chitosan oligomers of DP >30 have antimicrobial properties and thus are useful as wound dressings as well as in finishing of apparel and household goods (Kumar, 2000). As a paper coating or mixed into pulp, paper sheet strength can be improved.

Chitinases (poly-β-glucosaminidases) hydrolyze 1,4-β-linkages of N-acetyl-D-glucosamine polymers of chitin. They are produced by microorganisms and by plants, such as soybeans and tomatoes, and consist of three types of enzymes, endo- and exochitinases and chitobiase. These enzymes catalyze the breakdown of cell walls of organisms with glucosamine polymeric structures. Chitosanases cause endohydrolysis of 1,4-β-linkages only in polymers with 30–60% acetylation (Fukamizo, 2000).

2.1.2.2   *Spin finishes, natural lubricants, oils, waxes*

Spin finishes fulfill either the task of increasing fiber friction in the form of cohesive agents or of decreasing fiber friction and softening. Natural sources of lubricants are fatty acids obtained by saponification of fats and waxes, such as coconut, cotton seed, peanut, corn or palm oil, butter fat, lard or beef tallow. Commercial products for fiber lubrication usually contain mixtures of various natural and/or synthetic compounds (Slate, 1998). Oils and fats can be hydrolyzed by superheated pressurized steam. Alternatively, enzymatic hydrolysis with lipases partially or fully achieves the degradation of fats and oils to free fatty acids and glycerol (Uhlig, 1998).

2.1.3   Synthetic auxiliaries for dyeing and finishing

2.1.3.1   *General*

The function of auxiliaries in Section 2.1.2 including compounds that are affected or degraded by enzymes was discussed. Surface active substances, salts, oxidizing and reducing agents, and acids and bases also belong to the category of auxiliaries; however, they are not considered enzymatic substrates although they might influence the effectiveness or mode of action of enzymes.

2.1.3.2   *Electrolytic compounds and pH control substances*

For all textile processing steps, water quality and softness, pH and electrolyte content are important considerations. Water hardness is caused by calcium and magnesium sulfates, chlorides (permanent hardness) and carbonates (temporary hardness). These salts not only contribute to deposits

on equipment, but also interfere with preparation, dyeing and finishing. Various techniques are available to soften water on an industrial level, most commonly via ion exchange. A more direct and more expensive approach is the addition of sequestering agents to process water where water softness is crucial. Sequestering agents have functionalities that allow complexing (chelating) of metal ions. Examples for such chelators are poly-carboxylic acids (e.g. oxalic acid), aminopolycarboxylic acids (EDTA, eth-ylenediaminetetra-acetic   acid),   sodium   polyphosphates   (sodium hexametaphosphate, Calgon®), and others.

Besides water softness, the pH of the treatment bath in preparation, dyeing and finishing plays an important role owing to the sensitivity of the textile material to acid or basic conditions on the one hand and the reac-tivity of dyes and finishing compounds on the other hand. Many processes even require the stabilization of the pH with the help of a buffer system. Buffer systems consist of an acid and the corresponding salt, for example, acetic acid and sodium acetate for pH 4–5, or a base and the correspond-ing salt. Buffer systems for any type of pH range can be found in general laboratory reference books (e.g. Shugar and Ballinger, 1990). Common acids are inorganic acids (e.g. sulfuric acid, hydrochloric acid, pH below 2), organic acids (acetic acid, citric acid, pH 4.5–3.5), acidic inorganic salts (ammonium sulfate, etc. for pH 6.5–5.5) and mixtures thereof. Alkaline pH ranges are adjusted with common bases (sodium or potassium hydroxide, pH 11 or higher) or basic salts (e.g. carbonates, borax). Great care has to be exercised to make sure that adequate rinsing takes place after each treat-ment step and that sufficient time is allowed for internal exchange processes within the fiber. Because of adsorption processes, the release of acids, bases or salts can be fairly slow, and the pH of the rinse bath might not represent the realistic pH situation inside the fiber pores.

A large number of dyeing processes afford the addition of common salts, such as sodium chloride or sodium sulfate to enhance dye adsorption and fixation. The amount of these salts can be quite considerable, often 10% of the weight of fiber or more. The function of these salts is first to help alle-viate negative fiber surface charges, thus reducing repulsion between neg-atively charged dye molecules and the fiber wall. Second, they support the aggregation of dye molecules inside the fiber pores by making the dye less ionic (for example, in direct dyeing of cellulosics). In some cases, an example being acid dyeing of wool, salts act as retarders. The smaller salt ions temporarily take the place of the dye at the fiber dye-site. They are then replaced by the larger and slower moving dye molecules, yielding much more uniform dyeing results. Thorough rinsing has to follow any dyeing process, not only to remove unbound and loosely attached surface dye, but also to eliminate any auxiliaries. Even minute amounts of remaining salts can show up as white deposits on dyed goods.

2.1.4 Compounds with whitening effect

High levels of whiteness are desirable for textile materials as well as fundamental for reproducible color shades. Thus, whitening is usually carried out prior to dyeing and finishing. Most commonly this is achieved by the use of oxidizing agents that destroy chromophoric substances. Additionally, fluorescent brightening agents are added that mask yellowing compounds. Natural cellulosics are in most need of bleaching. Most synthetics are already fairly white; however, if necessary, fluorescent brighteners can be included in the spinning dope. Wool and silk are not routinely bleached.

Common bleaching agents include hydrogen peroxide and chlorine-containing compounds (Trotman, 1984; Shore, 1990b). Hydrogen peroxide is preferred over other bleaching agents as it decomposes into oxygen and water without impact on the environment. Bleaching is performed at pH 10.5–11 at boiling temperatures in the presence of stabilizers, sequestrants to control water softness and metal content, and surfactants with detergency. Stabilizers often consist of polysilicates, acrylates or magnesium salts.

The mechanism of bleaching most likely follows a radical route (Zeronian and Inglesby, 1995). In the presence of metal ions that act as peroxide activators, fiber damage is possible as radicals can attack the fiber polymer instead of the chromophore of the colorant. Small amounts of hydrogen peroxide that might still be held back by the fiber after bleaching have to be removed to avoid interference later on with dyes or finishes. Besides by chemical means, this step can also be performed enzymatically with catalase, an oxidoreductase that catalyzes the breakdown of hydrogen peroxide to water (Tzanov *et al.*, 2002).

The bleaching effect of sodium chlorite strongly depends on the pH value. The reaction occurs most rapidly at low pH and higher temperatures. In commercial operations bleaching is performed at pH 3.5–6 for cotton and temperatures around 80°C. Toxic chlorine dioxide is produced at lower pH; above pH 9 the bleaching effect is insignificant.

Sodium hypochlorite bleaches at pH values above 11 in a buffered system. The active chlorine content should be determined before use. Severe oxidative fiber damage can be expected if the pH falls below 9 with formation of hydrochloric acid, which will reduce the pH despite the buffer system. Further, hypochlorite decomposes upon storage or exposure to light, and an antichlor after-treatment with reducing agents following treatment with chlorite and hypochlorite might be necessary to remove chlorine traces from the fiber. Owing to the possible encounter of significant problems with hypochlorite and chlorite, hydrogen peroxide has advanced to the favored bleaching agent in commercial wet-processing operations nowadays. Still, chlorine-containing agents are sometimes applied to bleach bast fibers, such as flax or jute.
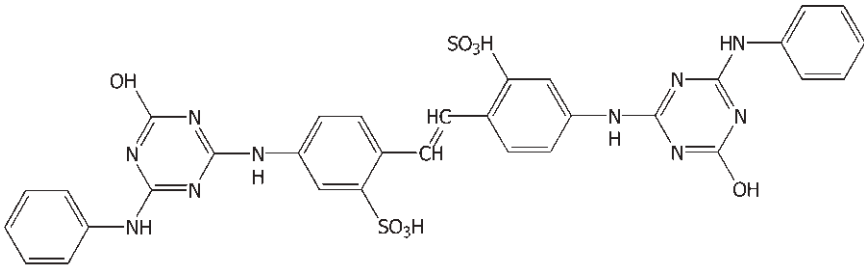
2.17 CI Fluorescent Brightener 32 for cotton.

Fluorescent brighteners (optical whiteners) for cellulosics are essentially colorless direct dyes (Fig. 2.17) and colorless acid dyes are used for wool. These compounds mask yellowness in fibers by absorbing light in the ultraviolet (UV)-range and emitting it in the violet or blue region of the visible light, thus compensating for minor yellowness of the textile substrate. Fluorescent brighteners and bleaches are often applied together. Many of these 'dyes' are not ultimately washfast on natural fibers and are reapplied with the laundry detergent at each domestic wash. Fluorescent brighteners for synthetic fibers can be incorporated in the spinning dope and, in this case, are permanent. Photoyellowing of textile material can occur faster if fluorescent brighteners are present as a consequence of the breakdown or photomodification of its chromophoric system. These light-induced processes can then turn the fluorescent brightener into a regular dye.

2.1.5 Compounds intended to affect interfacial properties

2.1.5.1 Surfactants

Surface-affecting substances (surfactants) are a very important group of textile auxiliaries. They find use as wetting agents, softeners, detergents, emulsifiers and defoaming agents, to name just a few applications. Commercial products rarely contain a pure compound, but rather mixtures of a range of surfactants to tailor their properties to the tasks in demand (Flick, 1993).

Surfactants generally consist of a hydrophilic part, providing water solubility, and a hydrophobic part, creating a link to non-aqueous media. Based on the nature of the hydrophilic portion of the molecule they are classified as follows (Broze, 1999):

• Anionic surfactants: negatively charged groups (e.g. sulfates, carboxylates, phosphates or sulfonates) are associated with the hydrophobic part of the molecule. These surfactants are important wetting agents and detergents. Owing to the fact that many substrates are also negatively

charged, anionic surfactants do not firmly adhere to such surfaces and impede redeposition of soil.

- Non-ionic surfactants: polar but without actual charge, solubilization properties in non-ionic surfactants are usually provided by incorporation of ethoxy units into their structure (alcohols, ethers, esters, etc.). Non-ionic surfactants can be mixed with any other group of surfactants and are fairly insensitive to water hardness. Most commonly, they are blended with anionic surfactants for increased detergency or used alone as emulsifiers.
- Cationic surfactants: these surfactants carry a positively charged group, commonly a quaternary ammonium group, associated with the hydrophobic portion of the molecule. Often, these compounds are additionally ethoxylated. Being positively charged, cationic surfactants adsorb more firmly to negatively charged substrates. Their major application is in softeners and emulsifiers.
- Amphoteric (zwitterionic) surfactants: these surfactants contain both anionic and cationic groups in their structure and thus behave as cationic or anionic compounds dependent on the respective pH. Common structures are betaines, amino acid derivatives and imidazoline derivatives. Their isoelectric point does not necessarily lie at pH 7. Although they seem to have a great application potential, they are the least important commercially.

The hydrophobic portion in all four types of surfactant consists of fairly long-chained linear saturated or unsaturated alkanes, derived from fats or oils. The chain length lies between 8 to 18 carbon atoms (e.g. stearate, palmitate, oleate, linoleate). Aromatic moieties and/or alkyl-substituted groups are also common.

Surfactants added in increasing amounts to water orient themselves at the interface of water/air with their hydrophilic parts towards the water and the hydrophobic parts pointing into the air. At a specific concentration (critical micelle concentration), when the entire water surface is covered by surfactant molecules, more or less ordered aggregations of surfactant molecules form in the bulk of the solution (micelles). In a micelle the polar hydrophilic parts of the surfactant molecules are oriented towards the water, the hydrophobic parts towards the interior of the micelle (in oil instead of water, their orientation is reversed). The hydrophobic center of the micelle can thus interact with hydrophobic compounds of the system, such as insoluble dyes, finishes, oils, etc., fulfilling solubilizing, emulsifying and dispersing tasks (Datyner, 1993).

Enzyme reactions on textile materials have been performed in the presence of the various types of surfactants and their effect studied. The reports, however, often provide controversial results (Helle *et al.*, 1993; Kaya *et al.*, 1995; Ueda *et al.*, 1994).

2.1.5.2   Foam control substances

Foam control is a very important issue for various textile processes, such as scouring, dyeing and printing, and wet processing with the goal of economic, low water pick-up. For a foaming system to be effective both foam and anti-foam agents are necessary to control the liquid drainage rate from the film walls. The interfacial tension between the foaming and defoaming compound needs to be manipulated. Anionic and non-polar surfactants can function as both types; however, fats, waxes, fatty acids and oils, long-chaine alcohols and polyglycols, polyalkylsiloxanes and their block copolymers with poly(oxyethylene) are more efficient as defoamers.

Foam application with controlled foam stabilization and collapse can be created with a blend of anionic and non-ionic surfactants and foam stabilizers, such as poly(vinyl alcohol), poly(acrylic acids), polysaccharides and cellulose derivatives.

Foam breakers are compounds that destroy foam, while foam inhibitors are made to prevent foam from being formed. Foam breakers quickly drain liquid and drastically reduce the surface tension at interfaces. They often consist of metal carboxylates in oil dispersion. Common formulations for effective foam inhibitors are water-soluble silicone glycol chemicals (see below), silica dispersed in water, or fluorinated alcohols and acids. Such compounds replace the elastic surface film by a more brittle film, so that the increase in surface tension caused by expansion is counterbalanced (Slate, 1998).

2.1.5.3   Softening agents

Besides cationic surfactants, often mixed with non-ionic surfactants, polysiloxanes are frequently used for fabric softening. Siloxanes are usually non-durable, but can be made durable by modification and addition of functional groups, followed by crosslinking. Other permanent types include reactive N-methylol derivatives of fatty acids and chlorotriazines, similar to reactive groups in fiber-reactive dyes. Some of these softeners are commonly applied together with easy-care finishes. Finishing compounds that render the textile material less hydrophilic by either coating the fiber surface and/or crosslinking and thus closing up the amorphous areas can present a barrier for enzymatic access.

2.1.6   Silicones and fluorochemicals

Silicones (Fig. 2.18) are compounds that can act as defoamers, soil repellants or lubricants. Fluorochemicals are especially useful as water- and stain-repellants. Both chemical classes encompass a wide range of compounds and are valuable for various purposes. Depending on the chemical
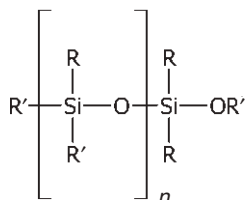
Silicone (R, R' = H, OH, CH$_3$, etc)

2.18 Silicone backbone.

composition, their viscosity and hydrophobicity differ. Most common are poly(dimethyl siloxane), poly(dimethylmethyl:phenyl siloxane) and poly(glycol/silicone copolymers). Such compounds are hydrophobic and add water repellency to cotton. However, they can increase the propensity for soiling. Modification with fluoroalkoxyalkyl groups gives compounds that yield water-, oil- and stain-resistant properties on textile materials. Besides modified silicone-based water- and stain-repellent compounds, effective fluorinated carbamates, fluorocarbon urethanes, polyfluorourea resins as well as fluoroalkyls combined with phosphates have been developed for cotton, wool and carpet fibers (Slate, 1998). Many of these compounds are proprietary.

2.1.7 Synthetic sizes and thickeners

A large group of synthetic sizes and thickening agents are acrylic-based polymers, either linear or crosslinked in structure. If used for sizing, they often remain on the fabric to add to the hand properties and softness of the textile material. Besides, complete desizing is often problematic (Lewin and Sello, 1983a; Lewin and Pearce, 1998).

Poly(vinyl alcohol) used as a synthetic size or thickener has the advantage of being easily recyclable and reusable as it can be removed by dissolving in hot water (Reife and Freeman, 1996). Polyacrylates swell in hot water and need sufficient mechanical impact to be completely removed from the fabric. Polyester-based sizes are broken down by hot alkaline solutions; however, insoluble oligomers may remain on the fabric (Shore, 1990b).

Copolymers of methyl methacrylate are soluble in organic solvents. Their application and removal occurs in non-aqueous media. If completed in a closed system, they are valued as environmentally benign; however, the machinery necessary needs modification from standard equipment to accommodate the process with solvents other than water.

2.1.8 Crosslinking resins

A large number of cellulosic fabrics, especially cotton and cotton in blends with polyester, are finished with easy-care or wrinkle-resistant finishes. Compounds used for this process form crosslinked networks involving the cellulosic hydroxyl functional groups on the fiber surface as well as in the accessible fiber interior, thus providing dimensional stability by fixing the structure in a specific state. Coloration of the textile material has to be performed prior to crosslinking because otherwise the amorphous areas become partially or completely inaccessible. If carried out on dyed material, crosslinking leads to improved wet fastness, locking the dye molecules in place.

Crosslinking resins are usually applied in monomeric or prepolymerized form together with a catalyst, and dried and cured for short times at fairly high temperatures (Vigo, 1994; Lewin and Sello, 1983b). As a general rule, the length of the crosslinks is determined by the moisture content and thus by the amount of swelling of the fiber. Therefore, in wet fibers the crosslinks are the longest, which may create some slack in the dried fiber. Wrinkle resistance is moderate to good and loss in tensile strength is limited. Crosslinking of dry fibers, on the other hand, yields short bridges, provides excellent wrinkle recovery and fairly high tensile strength losses. Hand builders are often added to improve the harsh feel of these finished goods.

The selection of compounds explored for this process is very large and is documented in thousands of publications and patents. A major group of crosslinking resins is based on urea and melamine–formaldehyde precondensates. Examples of common resins are dimethyloldihydroxyethylene urea (DMDHEU, Fig. 2.19), dimethylolethylene urea (DMEU) and dimethylolpropylene urea (DMPU). Newer compounds include polyfunctional carbamates, 4-alkoxypropylene ureas and *N*-methylolacrylamide derivatives (Vigo, 1994). Catalysts for these finishes are most often inorganic acids or salts, which can cause a drop in DP of the fiber polymer owing to the sensitivity of cellulosics to acidic conditions. Formaldehyde-free compounds include multifunctional carboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA, Fig. 2.19), citric acid and maleic acid (Raheel, 1998). Their finishing effect is somewhat less in most cases.

2.1.9 Flame-retardant finishes

Flammability of textile materials has always been a major problem and numerous attempts have been made to develop effective finishes to improve flame retardancy for all types of textile fibers (Lewin and Pearce, 1998). The approach taken involves delaying ignition, reducing the amount of flammable gases during a fire, increasing the amount of charred mater-
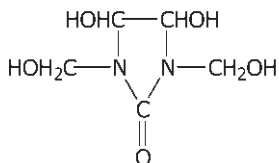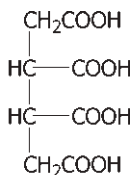
2.19 Structures of DMDHEU and BTCA as examples of formaldehyde-
containing and formaldehyde-free crosslinking agents,
respectively.

ial formed, and enhancing the capability of a material to withdraw from the
source of combustion (thermoplastic fibers). Depending on the fiber type,
flame-retardant compounds can be applied as topical finishes, grafted onto
the fiber, copolymerized during fiber formation, or incorporated into the
spinning dope of synthetic fibers. The durability and effectiveness of these
finishes vary. Commercially available compounds are based on a variety of
inorganic metal salts (e.g. antimony, titanium, zirconium), on boric acid and
its salts, phosphoric acid and its salts, organophosphates and halogen-
containing compounds. Combinations of different compounds are found to
have a synergistic effect (Lin and Zheng, 2002).

2.2   Textile fibers as substrates for enzymes

Classic textile substrates for enzymes are natural fibers, but a few synthetic
fibers have also been subjected to enzymatic treatments. The major goal of
most enzyme treatments is the modification of the fiber surface to enhance
the hand and appearance of the fiber. Examples for such fiber modifications
are the treatment of cotton denim with cellulases to achieve a soft jeans
material with a washed-and-worn look, or biopolishing of cotton to brighten
the colors and enhance the comfort. Other goals are to remove undesirable
byproducts, such as pectins or fats, from the unscoured fiber or to soften
woody material during retting with the help of suitable enzymes. The use
of enzymes has also been explored in connection with shrink-proofing of
wool and degumming of silk. In either case the enzymes of choice belong
to the class of hydrolases and usually consist of multicomponent systems
with a synergistic mode of action rather than of individual enzymes. Enzy-
matic processes offer major advantages over conventional treatments,
including savings in chemicals and energy, and less or no impact on the envi-
ronment. Additionally, if carefully controlled, they do not cause any fiber
damage.
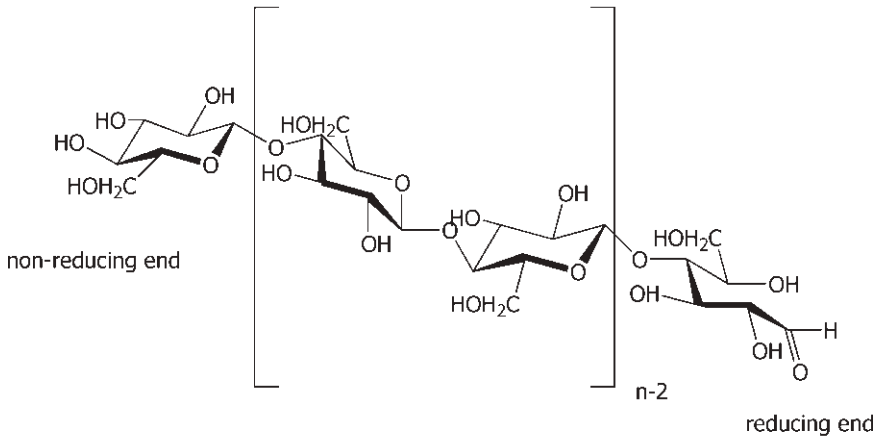
2.20 Structure of cellulose.

2.2.1 Cellulosic fibers

Cellulose is the most abundant renewable polymer today. In fairly pure form, cellulose occurs in the seed hairs of cotton plants, and is less pure in grasses and other plant material. Most cellulose, however, is found in the cell walls of woody plants together with lignin, hemicelluloses and other compounds as byproducts.

Cellulose is a linear 1,4-linked β-D-glucan homopolymer (Fig. 2.20) and constitutes the major component of higher plant cell walls. The monomeric unit is represented by cellobiose. The DP varies strongly dependent on the cellulose source and processing stage of the cellulosic material. Three free hydroxyl groups in C2, C3 and C6 per anhydroglucose unit (AGU) are available for formation of strong inter- and intramolecular hydrogen bonds as well as bonds/interactions with introduced compounds such as dyes and finishing agents. Further, all three or part of the primary and secondary hydroxyl groups can be chemically transformed into cellulose derivatives.

For textile materials, cellulosic fibers can either be obtained from the respective plants, e.g. cotton, flax, ramie, jute, or by dissolution and regeneration of cellulosic material and left unmodified (regenerated cellulosics, such as viscose rayon, Tencel, etc.) or derivatized to result in modified regenerated cellulosic fibers such as cellulose acetate. The approximate chemical composition (without coloring matter, water solubles and moisture) of some important cellulosic fibers is listed in Table 2.1. For regenerated cellulosic fibers inexpensive sources for cellulose are identified. Examples include wood chips, cellulosic fibers too short for spinning, linters and others.

Table 2.1 Approximate chemical composition (%) of cellulosic fibers (Kraessig *et al.,* 1996; Lewin and Pearce, 1998)

Fiber	Cellulose	Hemicelluloses	Pectin	Lignin	Fat/wax
Seed hair fibers					
Cotton	92–95	5.7	1.2	0	0.6
Bast fibers					
Flax	62–71	16–18	1.8–2.0	2.0–2.5	1.5
Hemp	67–75	16–18	0.8	2.9–3.3	0.7
Ramie	68–76	13–14	1.9–2.1	0.6–0.7	0.3
Jute	59–71	12–13	0.2–4.4	11.8–12.9	0.5
Leaf fibers					
Sisal	66–73	12–13	0.8	9.9	0.3
Abaca	63–68	19–20	0.5	5.1–5.5	0.2
Nut husk fibers					
Coir	36–43	0.2	3–4	41–45	

Short-chain polymers of plant sugars are termed hemicellulose. They mainly consist of xylans, arabinogalactans and mannans (Gregory and Bolwell, 1999; Dey and Harborne, 1997). Pectinic substances are mainly calcium, magnesium and iron salts of polygalacturonic acid and the respective esters with a certain degree of branching (Dey and Harborne, 1997). Depending on the degree of esterification, they are insoluble in water, but can be removed by aqueous alkali or with the help of suitable enzyme systems. All natural cellulosic fibers, except for cotton, contain a certain portion of lignin, a complex polyphenolic network made of derivatives of phenylpropane. A detailed overview of the chemistry of lignin can be found in Hon and Shiraishi (2001).

Cellulose chains are bound by strong hydrogen bonds to form areas of high order (crystallinity) alternating with areas of less order. Strong sodium hydroxide and a few solvent systems are able to penetrate the crystalline areas; however water and most treatment solutions are only able to access the areas of low organization, resulting in swelling of the fiber. The moisture uptake of the fibers varies with the fiber type from approximately 6–7% (cotton, ramie) to 10–11% (jute, sisal; Lewin and Pearce, 1998) at standard conditions of 21°C and 65% relative humidity and can be modified to a certain extent by preparation treatments (mercerized cotton has a moisture regain of 8–12%).

Their ability to absorb water and swell has enabled dyeing and finishing of cellulosic fibers from aqueous solutions by exhaust procedures. Water-filled pores act as transportation ways for dyes, auxiliaries and other compounds to accessible functional groups in the interior of the cellulosic fiber.
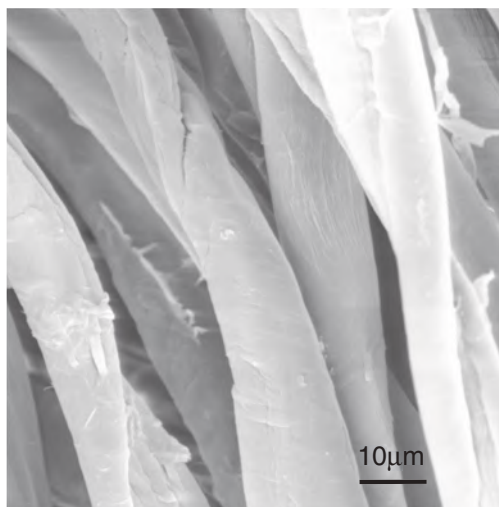
2.21 Scanning electron microscopic picture of raw cotton fibers.

Increased temperature supports the process by accelerating the reaction rate; however, swelling already occurs at room temperature.

2.2.1.1 Natural cellulosics

Cotton

By far the most important textile cellulosic fiber is cotton. Cotton grows as unicellular fiber on seeds (seed hair fiber). A thin cuticle that mainly consists of waxes and pectins protects the outside of the fiber. The primary wall in mature fibers is only 0.5–1 µm thick and contains about 50% cellulose. Non-cellulosic impurities consist of pectins, fats and waxes, proteins and natural colorants. The secondary wall, containing approximately 92–95% cellulose, is built of concentric layers with alternating S- and Z-shaped twists. The layers consist of densely packed elementary fibrils, organized into microfibrils and macrofibrils. Bundles of fibrils, as well as individual arrangements of cellulose polymeric chains, are held together by strong hydrogen bonds. A hollow channel, the lumen, forms the center of the fiber. During plant growth it was filled with protoplasma. After maturing and harvest of the cotton fiber it dries and collapses giving the fiber a ribbon-like appearance with a kidney-shaped cross-section (Fig. 2.21).

2.2.1.2   Bast fibers

Flax

Besides cotton, fibers from flax (the term 'linen' generally describes fabric from flax fibers) are probably the second most important cellulosic fibers for apparel and household textiles. Suitable fibers are isolated from fibrous bast components by several steps. First, leaves and seeds are mechanically removed from the stalks (rippling), followed by the stripping of the bark (decortication). Subsequently attached woody compounds are chemically or enzymatically decomposed by retting. Scutching frees the coarse fiber bundles and during hackling the coarse bundles are separated into finer bundles. Flax fibers are usually not completely divided into single fibers but kept in small arrays of several individual fibers held together by gummy substances. In opposition to cotton, flax and all other bast fibers are multicellular, the cells being called ultimate cells or ultimates. Their cross-section is hexagonal with a lumen in the center. Along the fibers, characteristic cross markings, so-called nodes, are visible at the microscopic level. Purified flax fibers are approximately 70% crystalline. Owing to the presence of lignin and hemicelluloses, bast fibers have a higher moisture regain than cotton because these compounds add to the non-crystalline content of the fiber.

Ramie

Ramie is often blended with cotton for apparel because of its attractive luster. Fiber isolation from the plant follows similar procedures to those described for flax; however, ramie is embedded in a highly gummy pectinous bark and is hard to isolate by conventional retting processes. Enzymatic degumming using pectate lyase and xylanase has been explored (Bruhlmann *et al.*, 2000). Ramie is longer and coarser than flax. The cross-section of the fiber is multilobal with/without lumen. The crystallinity of ramie has been reported to be approximately 61% (Lewin and Pearce, 1998).

Hemp and jute

In many ways hemp fibers resemble flax and cotton fibers, but are less fine than flax. Their cross-section is uneven polygonal with rounded edges. Like flax and ramie, the lignin content is fairly low. The ratio of crystalline and less ordered regions in hemp is similar to that of flax.

   The lignin content in jute is very high compared to the other bast fibers (see Table 2.1). The fiber has lower crystallinity, is hard to bleach to an acceptable whiteness and has a harsh hand. Retting of jute gives only a

relatively small yield. Thus, the economic importance of jute for high quality textile materials has increasingly diminished over the years with synthetic fibers taking its place.

Leaf and nut husk fibers

Sisal, abaca (banana) and pina (pineapple) fibers are examples of leaf fibers; coir (coconut) belongs to nut husk or seed fibers. They are mostly used for cordage or industrial uses, in rare cases for decorative purposes (pina) and are not discussed here. Details on these fibers can be found in Lewin and Pearce (1998).

2.2.1.3   Common finishes for cellulosic fibers

Preparation finishing for natural cellulosic fibers includes desizing, scouring and bleaching (Trotman, 1984). Preparation can be performed in series or in a manner that combines two or all three steps. The purpose of scouring is to remove non-cellulosic impurities, oils and dirt, and the chemicals used for the process are hot aqueous alkali solution, often supported by detergents. Desizing can be achieved by hot water, acid or enzymatic hydrolysis, depending on the sizing compound used. For bleaching, oxidizing agents such as peroxides or chlorine-containing compounds are applied (see Section 2.1.2). Owing to the higher pectin content and the presence of lignin, bast fibers require stronger bleaching conditions. A scoured, desized and bleached fiber possesses excellent water absorbency and a high level of whiteness (exception: jute). Owing to the concerns outlined earlier, it is not surprising that milder processing alternatives are sought by the use of suitable enzyme systems.

   Additionally, for high quality cotton goods mercerization is included in the preparation. Mercerization consists of a swelling process in 20–25% sodium hydroxide (Trotman, 1984). Sodium hydroxide in high concentration is capable of penetrating into the crystalline areas of the fiber and altering the cellulose I crystal lattice of native cotton to cellulose II, simultaneously affecting its pore structure and accessibility. If performed under tension of the textile material, the fibers obtain high luster owing to a rounder cross-sectional shape, increased tensile strength and dye uptake; if performed under slack conditions, enhanced water absorbency can be achieved.

   Performance finishes and finishes adding functionality are optional. Generally, cellulosics show excellent comfort properties which are related to their moisture and heat transport capabilities. Their shortcomings are found in low wrinkle recovery, high shrinkage and high flammability. Finishes (Vigo, 1994) can be applied to address these properties to keep cellulosic

fibers competitive with synthetics, such as polyester. The mechanism of crosslinking the structure of cellulosics and common chemicals used for easy-care properties are briefly outlined in Section 2.1.8; fluorochemicals to impart water- and stain-repellency are discussed in Section 2.1.6 and flame-retardant finishes are found in Section 2.1.9.

### 2.2.1.4   Regenerated cellulosic fibers

Viscose rayon

The process of regenerating cellulosic fibers in filament form from in-expensive cellulose sources has been modified many times over the past decades (Lewin and Pearce, 1998). In the viscose process, starting materials, such as wood chips, pulp or linters, are steeped in sodium hydroxide to form alkali cellulose, and allowed to age. During this process step considerable depolymerization takes place. The next processing stage involves the addition of carbon disulfide to form xanthate which is dissolved in dilute sodium hydroxide. After maturing, the viscose dope is filtered and extruded through spinnerets into an acidic regeneration bath where the fiber coagulates. Spinning speed, draw ratio, chemical auxiliaries and the composition of baths determine the properties of the resulting fiber (Kraessig *et al.*, 1996). Depending on the regeneration conditions the fibers show clearly defined skin–core structures. Skin and core exhibit different properties regarding, for example, crystallinity, accessibility and swelling.

   The degree of crystallinity and orientation of regenerated cellulosic fibers strongly depend on the coagulation conditions and the applied draw ratio and are generally lower than those of natural cellulosic fibers. The basic structural unit of the regenerated fiber is the anhydroglucose unit (AGU), identical to that of natural cellulose. However, the DP amounts to approximately 400–600 only. The crystal lattice has been fully converted to cellulose II. Moisture uptake and water retention are typically higher than that of cotton. Dyes suitable for natural cellulosics can also be applied to regenerated cellulosics; however, care has to be taken because of the higher alkali sensitivity and the lower wet strength of some types of viscose rayon fibers.

Solvent-spun regenerated cellulosic fibers

The so-called solvent-spun fibers entered the market in the 1990s and the patent literature is vast, covering every step from dissolution and equipment to fiber modification (see Mulleder *et al.*, 1998, for example). The production of these fibers is based on the dissolution of cellulose in cyclic amines, such as *N*-methylmorpholine *N*-oxide/water ($NMMO/H_2O$), followed by a dry-jet–wet-spinning process (Marini and Brauneis, 1996).
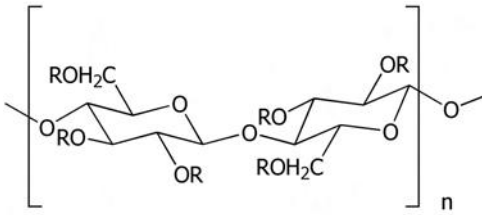
Cellulose triacetate (all R = COCH$_3$) and
cellulose acetate (2/3 R = COCH$_3$, 1/3 R = H)

2.22 Structure of cellulose acetate and triacetate.

Lyocell fibers, produced by Courtaulds under the trade name Tencel since 1993, have also been produced in European countries since mid-1997. Fibrillation of these fibers, although useful for fiber entanglement in nonwovens, has been a problem in other fabric forms, but is currently controlled by enzyme treatments or resin finishing (Bredereck *et al.*, 1997). NewCell (Krueger, 1994) and ALCERU fibers (Alternative Cellulosics Rudolphstadt), also obtained through dissolution of the raw materials in NMMO, are variations of Lyocell with slightly different fibrillation properties and as a result, slightly different finishing procedures. Because of the high recycle rate of the solvent NMMO and the fact that the substrate is complexed in the solution without chemical reaction, the production of these fibers is considered to be environmentally friendly.

A 'peach-skin effect' can be produced on solvent-spun fibers by mechanical fibrillation, followed by secondary fibrillation/defibrillation through enzymatic hydrolysis with fairly aggressive cellulases (Gandhi *et al.*, 2002). The result is a very fine fibrillic pile with soft, silk-like hand, and improved volume and appearance. This treatment is often accompanied by a silicone softener treatment (Breier, 1994).

2.2.1.5 Cellulose esters – acetate and triacetate

Three hydroxyl groups per AGU are available in cellulose that can be acetylated to 83–98.7% (Hatch, 1993) to form cellulose esters. Cellulose acetate consists of heterogeneous cellulose chains with 2.5 hydroxyl groups substituted by acetate groups on the average (Fig. 2.22). The DP of this fiber (250–300) is lower than that of viscose rayon, and the degree of orientation and crystallization is very low with fewer intermolecular hydrogen bonds. While acetate fibers are still fairly hydrophilic with a moisture regain quite close to that of cotton, triacetate exhibits the properties of a hydrophobic

fiber. To increase its low crystallinity after extrusion, triacetate has to be heat-set, a process routinely applied to most synthetic fibers. During the heat-setting process, the polymeric chains are arranged in closely packed arrays to form a highly crystalline structure. Acetate, on the other hand, cannot be heat-set. As with non-modified regenerated cellulosics, various cellulose acetate and triacetate types and manufacturing methods exist, resulting in fibers with a wide range of properties (Lewin and Pearce, 1998).

2.2.1.6   Possibilities for enzyme applications for cellulosic substrates

Published research on enzymatic hydrolysis of cellulosic materials is very extensive. Suitable enzymes for cellulosic substrate surface finishing are cellulases which are commercially available with various pH and temperature activity profiles. Their properties and modes of action are covered elsewhere in this book. Mild treatments lead to surface polishing by removing small fiber fibrils on the surface, rendering the textile material softer and improving color brilliance. Harsher conditions can lead to higher weight and tensile strength losses and eventually to the complete fiber breakdown. Enzymatic finishing processes may be performed before or after coloration as well as before or after selected chemical finishing procedures.

Commonplace in denim finishing today is the biostoning process to give jeans a worn and washed appearance, replacing the pumice stones that were traditionally used. Various approaches have been taken, including cellulases with or without a reduced quantity of pumice stones (Klahorst *et al.*, 1994), mixtures of amylases and cellulases (Uhlig, 1998) and laccases (Mueller and Shi, 2001).

Enzymatic scouring has generated a great deal of interest in the light of cost savings and growing environmental concerns. Pectinases, cellulases, proteases and lipases have all been investigated with respect to their effectiveness in removing non-cellulosic impurities and increasing the wettability of the textile material (Roessner, 1995; Buschle-Diller *et al.*, 1998; Takagishi *et al.*, 2001; Traore and Buschle-Diller, 2000; Waddell, 2002). More recently, efforts to include enzymatic bleaching with glucose oxidases and peroxidases have also been reported (Buschle-Diller *et al.*, 2001; Tzanov *et al.*, 2002) with the glucose oxidase in free form or immobilized on a support material.

2.2.2   Protein fibers

Protein fibers for textile uses can be divided into animal hair fibers, such as wool (defined as fibers from various breeds of domesticated sheep) and speciality hair (all other animal hair fibers, such as mohair, cashmere, alpaca, angora, etc.), and animal secretion fibers (silk).

2.2.2.1 Wool and animal hair fibers

Fibers obtained from sheep and other animals vary significantly in length and fiber fineness, shape, pigmentation, crimp and surface properties. Within one breed, variations occur that depend on the age and the nutritional condition of the animal and on the part of the body from which the fibers were acquired.

All animal hair fibers have some common features. The exterior of wool and other animal fibers consists of flat overlapping cuticle cells ('scales') that protect long spindle-shaped cortex cells in the interior. The cortical cells surround the innermost cells with vacuoles, the medulla, which might be missing in some types of finer animal hair fibers. Each cuticle cell is made up of three layers, epicuticle, exocuticle and endocuticle. Cortex cells consist of ortho, para and meso cells. Each layer of the cuticle and the cortex cells differ in cystine and isodipeptide content. The cell membrane complex, which is made of proteins with low crosslink density and lipids, fuses the different layers of the fiber together.

Keratin, the wool protein, is built up from a total of 24 major amino acids with different functionalities (Fig. 2.23). Amino acids with acidic character include aspartic acid, glutamic acid, asparagine and glutamine; basic character is introduced by arginine and lysine, histidine and tryptophan. The wool fiber is thus amphoteric and internal salt bridges can be formed. At the isoelectric point (pH 4.8–4.9), the number of anionic groups equals the number of cationic groups and the fiber is in its most stable form. Besides ionic interactions, amino acids containing hydroxyl groups (serine, threonine and tyrosine) are capable of forming intramolecular hydrogen bonds to add stability to the wool fiber. Additionally, unlike other proteins, several amino acids carry sulfur-containing side chains – cysteine, cystine, cysteic acid, methionine, thiocysteine and lanthionine – with cystine accounting for the highest weight percentage of sulfur in the form of disulfide bridges. These disulfide bridges which are formed between two polypeptide chains significantly influence fiber stability. The remaining amino acids do not have any specific reactivity. They include glycine, leucine, proline, valine, alanine, isoleucine and phenylalanine. In summary, stability of the wool fiber is thus achieved not only through the formation of salt bridges and hydrogen bonds, but also via disulfide bridges between two cystine residues, covalent bonding between glutamic acid and lysine residues, and hydrophobic interactions between non-polar amino acid side groups (Zahn and Hoffmann, 1996).

Each polypeptide is twisted in the form of an α-helix (right-handed screw). Two such helices are joined together to form a left-handed coiled assembly. With the hydrophobic side chains pointing to the outside, the chains are held together tightly through intramolecular hydrogen bonds. By
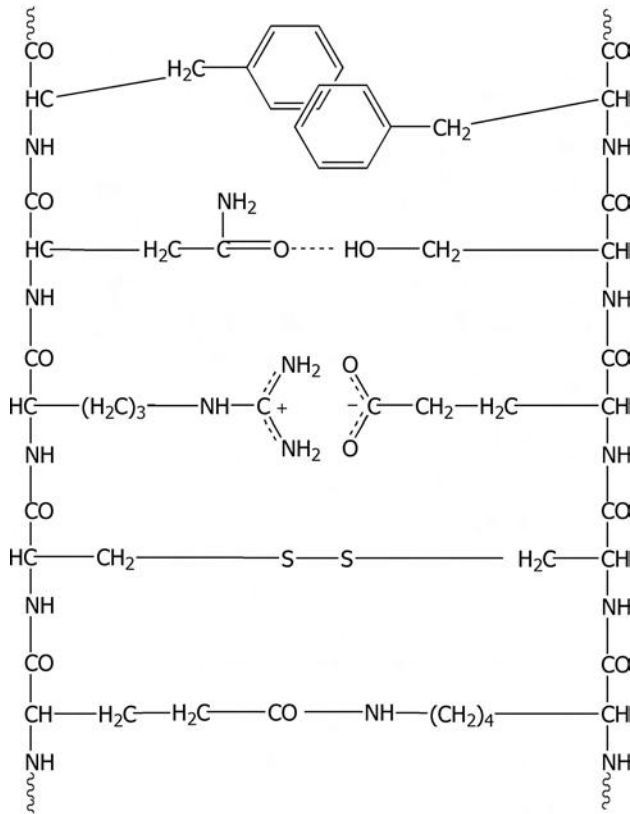
2.23 Wool keratin.

coming close enough, crystalline areas that alternate with amorphous regions are formed.

Fatty acids (2%) and proteinaceous compounds are found in the cuticle surface and the cell membrane complex that holds cuticle and cortex cells together. These fatty acids include palmitic, stearic and oleic acid as free fatty acids, 18-methyleicosanoic acid bound to proteins, cholesterol and cholesterol sulfate, as well as polar lipids, such as ceramides and cerebrosides.

The fatty acids provide a hydrophobic barrier at the fiber surface while the interior of the fiber is hydrophilic. The moisture regain at 65% relative humidity and 21°C is approximately 12–15%. The uptake of liquid water is accompanied by considerable radial swelling, especially above and below the isoionic point. With excessive positive or negative charge the polypeptide chains electrostatically repel each other, thus allowing for increased swelling accompanied by decreased mechanical stability. In case friction or agitation is present during the wetting process, the scales interlock and form a felted structure (felting shrinkage, see below).

Owing to their complex composition, protein fibers can undergo reactions occurring at covalent bonds including the polypeptide backbone, and within the side chains. Chemical degradation occurs with moist heat, under alkaline conditions and with strong mineral acids by hydrolysis of polypeptide bonds as well as degradation of some of the side chains, liberating hydrogen sulfide, ammonia and other decomposition products. Oxidizing and reducing agents predominately attack the disulfide bridges. Splitting and reformation of disulfide bridges under controlled conditions, however, allows for setting of wool for stabilization reasons. Amino groups of the side chains are major dye sites for acid dyes, while anionic groups can form covalent bonds with specifically developed reactive dyes (for more details on wool dyeing see, for example, Bearpak *et al.*, 1986 and Lewis, 1992).

2.2.2.2   Common chemical finishes for protein fibers

Raw animal fibers contain high amounts of grease, suint and vegetable matter with the average amounts varying with animal rearing conditions. Although wool grease is easily solubilized in organic solvents, hot water or aqueous alcohol is usually the scouring method of choice to remove suint and soil impurities simultaneously (Zahn and Hoffmann, 1996). Great care has to be taken not to cause felting shrinkage through mechanical movement of the fibers in the scouring bath. The scoured fibers are treated in a way so as to retain a minor amount of grease (about 0.5%). If unacceptable quantities of cellulosic matter contaminate the fibers, an addition carbonization treatment can be performed which constitutes short exposure to sulfuric acid with heating or treatment with cellulases.

As mentioned, a disadvantage of animal fibers is their tendency to cause felting shrinkage, caused by the scale structure of the cuticle. Anti-felting finishes are targeted to reduce the rough surface, either by partial removal of the scales by chemical treatment, by coating the scales with a polymer, or by preventing their contact through spot welding by deposition of polymer aggregates that keep the fibers at a fixed distance from each other (Vigo, 1994). Chemical treatments involve reducing agents, solvents or oxidizing reagents, such as chlorine, peroxysulfuric acid or permanganate. Because the conditions of this treatment are fairly harsh and might lead to fiber damage, a later development combines a milder chlorination treatment with hypochlorite and a polyamide coating (Hercosett®). Such anti-felting finishes produce washable wool, although they affect the dyeing behavior, hand and other properties. Newer developments focus on the application of plasma (Hoecker, 1997) and enzymatic processes for wool fibers (El-Sayed *et al.*, 2002).

Enzymes have been used to support the descaling process with the goal of improving shrink resistance and hand of wool (Heine and Hoecker, 1995; Heine *et al.*, 1998; Galante *et al.*, 1998; Breier, 2000) and for bleaching and

scouring purposes (Levene, 1997; Brahimi-Horn *et al.*, 1990). Most research work on softening and diminishing the cuticle scale structure has been concerned with finding suitable proteases that would not significantly weaken the fiber otherwise. Proteases of plant origin, such as papain, as well as from other sources, have been explored, either in combination with a chemical treatment, e.g. chlorination, or by themselves. For scouring, various lipases and esterases have been studied.
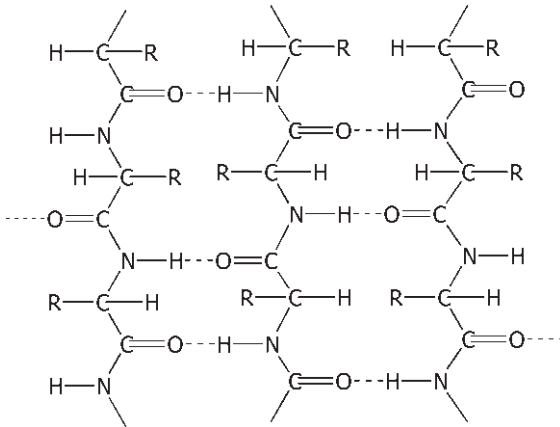
2.2.2.3   Silk fibers

Silk as a useful animal secretion fiber is obtained from the domesticated moth (*Bombyx mori*) feeding solely on mulberry leaves, and from the wild tussah varieties (*Antheraea pernyi* and *A. mylitta*), feeding on oak or castor leaves. Spider silks of the Arachnida family have been explored, so far mostly for research purposes. Silk is extruded from the silk-producing glands of the larvae as a double filament, made of fibroin, held together by a cementing layer of sericin and solidified in air. The cross-section of cultivated silk is irregular trilobal with rounded edges, while wild silk is flatter, wedge-shaped with less sericin.

Silk consists of 18 amino acids with glycine, alanine, serine, and to a minor extent, tyrosine, making up more than 90 mol% of the fibroin (Zahn, 1993). In cultivated silk, glycine amounts to almost 45%, while in wild silk alanine predominates. The amount of cystine is very small in both types. Overall, the total number of acidic groups is two to three times that of basic groups (isoelectric range pH 4–5). The fibers are highly oriented. Owing to the small quantity of bulky side groups, the polypetide chains permit the formation of a β-pleated sheet structure instead of a helix as is the case for wool (Fig. 2.24). The sheets can stack and form crystalline regions with intramolecular hydrogen bonding between the sheets.

Sericin, which makes up 17–25% of the fiber weight, significantly differs from fibroin. Its major amino acids are glycine, serine and aspartic acid in cultivated silk, and glycine, serine, threonine and aspartic acid in wild silk with serine occurring in the greatest amount in both silk types. The ratio of non-polar to polar amino acid residues is 1:3, with approximately 60% hydroxyl groups, 30% acidic and 10% basic groups (isoelectric point at pH 4.0). The cystine content is slightly higher than in fibroin. Sericin also contains about 1.5% fats and waxes and about 1% mineral compounds.

The virtual absence of disulfide bridges renders the silk fiber more sensitive to acids but less sensitive to alkalis than wool fibers. Large amounts of polar amino acids account for the hydrophilicity of the fiber. Under standard conditions of 65% relative humidity and 21°C, the moisture regain of silk is approximately 10–11%. Silk can absorb considerable quantities of salt solutions, a property that is used in the process of weighting of silk to

2.24 Chemical structure of silk (for R see text).

correct for the weight lost during degumming (see below). Acid dyes are the dyes of choice for silk fibers today, because the basic dyes as used in earlier years proved to have rather limited light fastness. Tussah silk is more resistant against chemicals and can also be dyed with reactive dyes under alkaline conditions. Washable silk usually refers to silk coated with a protective polymer (Tsukada *et al.*, 2001).

The separation of the silk double filaments (degumming) by removal of sericin has conventionally been achieved by immersion of the fibers in alkaline solution and soap. This process results in considerable weight loss (up to 20%). Enzymatic degumming with bacterial or fungal proteases leads to improved dyeing and hand properties with slightly lower weight loss (Uhlig, 1998; Gulrajani *et al.*, 1996).

2.2.3 Synthetic fibers

Generally, natural fibers are true substrates in enzymatic processes. Synthetic fibers have been explored in the context with their support properties for enzyme immobilization and for special applications such as biosensors or membranes. A few selected synthetic fibers have also been subjected to enzymatic modifications in the form of textile substrates, the most frequently studied probably being polyester (Yoon *et al.*, 2002). Therefore only major synthetic fibers will be briefly discussed below. If more detailed information is needed, the reader is referred to a general fiber science book, such as Lewin and Pearce (1998).

All synthetic fibers are petroleum derivatives. They are designed in the chemical laboratory and created to achieve the most favorable properties at reasonable cost. Production conditions determine the composition, DP,
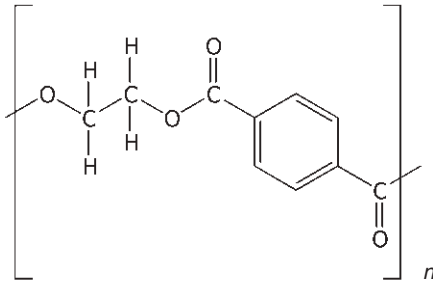
2.25 Structure of PET.

fiber diameter and shape, mechanical properties, etc. of the final fiber. Synthetic fibers are generally formed as continuous strands of filaments, which may be cut into staple lengths if necessary. With advances in polymer synthesis, engineering and fiber formation methods, more and more custom-made fibers are entering the market place.

2.2.3.1   Polyester (poly(ethylene terephthalate))

By a generic definition, fibers composed of at least 85% by weight of an ester of a substituted aromatic (or aliphatic) carboxylic acid are termed polyesters (Hatch, 1993). Polyesters with a sufficient DP are generally made by reaction of diols with dicarboxylic acids. The most important representative of this category is poly(ethylene terephthalate) or PET (Fig. 2.25).

The draw ratio and processing history determine the degree of orientation and also influence the crystallinity of the fiber. Usually, highly crystalline areas alternate with regions of low crystallinity. Tensile strength, extension at break and initial modulus are directly related to the ratio of ordered to less ordered regions and the degree of orientation. In comparison with other synthetic fibers, PET belongs to the stronger (in the range of nylon and polypropylene) and stiffer fibers, although the different PET types vary according to their manufacturing conditions. Owing to the high tensile strength of PET, pilling – the formation of small fiber pills on the surface of a polyester fabric – presents a problem, especially when PET is blended with other, less strong fibers.

Polyester can be hydrolyzed under alkaline conditions. The rate of hydrolysis is very low without a catalyst and occurs only at the surface. This process that can be used to etch the surface increases the hydrophilicity of the fiber and alters its hand properties. Inorganic acids with catalysts that have sufficient diffusive capabilities, organic acids (e.g. dichloroacetic acid), amino compounds, such as ammonia, primary and secondary amines, also hydrolyze polyester.
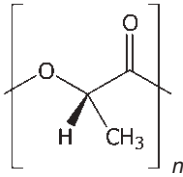
2.26 L-Poly(lactic acid), PLA.

PET is a hydrophobic fiber with maximum moisture regain of only 1% at 100% relative humidity. Until the development of disperse dyes, dyeing of polyester was difficult. Disperse dyes with very low water solubility can sublime into the fiber by heat (thermosol process, thermofixation), be applied with heat/pressure or with the help of carriers by an exhaust process (see Section 2.1.1). Basic-dyeable modified polyesters, copolymerized with units containing sulfonate groups, are also commercially available.

2.2.3.2 *Biopolyesters*

A newly emerging field comprises biopolyesters, encompassing polyesters produced by biocatalytic means, such as enzyme-catalyzed polymerizations, as well as polymers from biological origins or from renewable resources (Scholz and Gross, 2000). Poly(hydroxyalkanoates), PHAs, are the only biopolymers that are completely synthetized by microorganisms. They present energy and nutrient storage for the microorganisms in case the environment changes triggering the enzymatic breakdown of the biopolyesters.

The most important examples of compounds generated by biocatalytic routes are poly(lactic acid), PLA, and poly(glycolic acid), PGA, as well as their copolymers (Fig. 2.26). These polyesters exhibit high tensile strength and are non-toxic. Crystallinity, orientation and moisture sorption capabilities of the fibers are controlled by the production conditions. Such compounds are fully biodegradable and can be subjected to enzymatic modification.

2.2.3.3 *Polyamides*

In polyamides, the structural units are connected by amide groups. In generic terms, aliphatic polyamides are called nylons, aromatic polyamides are called aramids. Aramids will not be discussed here. Polyamides are formed either by condensation of diamines and diacids or by ring-opening polymerization of lactams. In aliphatic polyamides, nylons are named as (A,B), where the numbers signify the number of carbon atoms of the diamine and the diacid linked together (for example, nylon 6,10). If a single

(a)

(b)
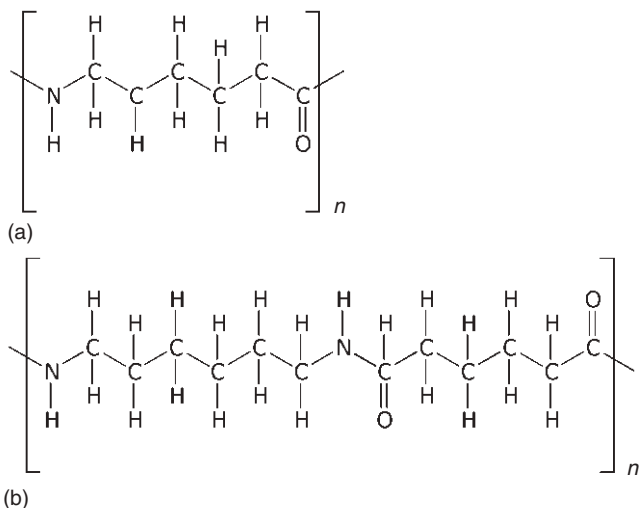
2.27 (a) Nylon 6 and (b) nylon 6,6.

number is given, it refers to the number of carbon atoms of a nylon pro-
duced by ring-opening polymerization (e.g. nylon 6 from ε-caprolactam). A
large array of products is available, including various copolymers; however,
the aliphatic polyamides of most economic significance are nylon 6, nylon
6,6 and nylon 6,10 (Fig. 2.27).

In general, both polymerization methods lead to a mixture of polymers
with various molecular weights. Apart from the DP and the molecular weight
distribution, the nature and number of end groups is important for chemical
reactivity and dyeing purposes. Nylons can be produced with approximately
equal numbers of acidic and amino end groups (regular type), mostly acidic
(acid-dye resistant nylon) or mostly amino end groups (deep dyeing nylons).
Zigzagging carbon segments line up closely between the end groups. They
are held together by van der Waals forces and intramolecular hydrogen
bonding through amide links to form sheet-like arrangements. By tight stack-
ing of these sheets, crystalline regions are created alternating with less
organized areas that do not have distinct boundaries. Drawing may cause
the development of crystalline areas in those less ordered regions. The
particular molecular arrangement in nylons results in high tensile strength,
elongation and elastic recovery upon application of stress.

Nylons are dyeable with disperse dyes (shade range is limited) or with
acid dyes under mild acidic conditions. Aqueous acids (below pH 3) as well
as bases cause the rupture of the polymer backbone. In the case of acid
dyeing, dye molecules only attach to available amino end groups, thus shade
depth is determined by the ratio of negatively charged groups of the dye
molecule to positively charged end groups in the fiber. Besides hydrolysis
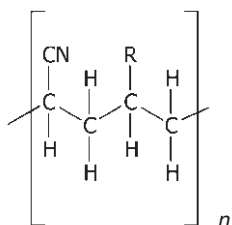
2.28 Polyacrylonitrile (homopolymer, R=CN and copolymer, R=COOH, SO_3H, etc.).

by chemical means, nylons are fairly susceptible to heat and light, manifested by decreased tensile strength and a yellowed appearance of the fiber. Commercially available fibers may thus contain antioxidants to reduce light sensitivity or copper(I) salts to improve thermal resistance.

2.2.3.4 Polyacrylonitriles

Commercial acrylic fibers contain at least 85% acrylonitrile copolymer (modacrylic fibers between 35 and 85%) combined with one or more other monomers (Fig. 2.28). The homopolymer (100% acrylonitrile) is difficult to process and dye, and thus is only made for industrial applications. The comonomers in acrylic fibers are selected with the purpose of giving the fiber specific properties, such as dyeability (sodium methallyl sulfonate, sodium sulfophenyl methallyl ether, etc.), modified fiber morphology (vinyl acetate, methyl acrylate, etc.) or flame retardancy (vinyl bromide, vinyl chloride, etc.). Copolymerization with different comonomers has opened up a venue to innumerable speciality products. Bicomponent fibers from acrylics of different composition with distinct properties add to these possibilities. For example, side-by-side bicomponent fibers exhibiting different shrinkage ratios impart crimp upon exposure to heat or wet conditions.

Commercial acrylic fibers are produced by free radical processes which make stereoregularity and thus crystallinity problematic. Nevertheless, with the help of spectroscopic methods it can be shown that acrylic fibers contain crystalline and less ordered areas with strong connections between the two phases. Intermolecular dipolar bonding accounts for relative stiffness in the lower ordered regions. The introduction of a comonomer generally reduces the crystallinity and the melting point. Thus, tensile strength and breaking elongation are lower compared with other synthetic fibers, such as polyester or nylon. Moisture regain is fairly low, depending to a certain extent on the nature of the comonomer.

Acrylic fibers with introduced negative groups can be dyed with basic (cationic) dyes under carefully controlled conditions. Dyeing is usually per-

formed in the presence of a retarder to decrease the rate of the dyeing process for uniform shade reproduction. Finishing processes for poly-acrylonitrile are limited since desirable properties can be more easily incorporated by copolymerization or by modification on the fiber level. For example, highly absorbent fibers are made by inclusion of a hydrophilic comonomer which is subsequently removed by hydrolysis.

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