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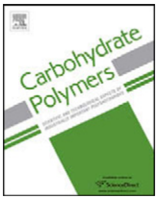

Review

Photoactive polysaccharides

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ABSTRACT

Light is a non-invasive stimulus or probe, which retains more and more attention in science and technology. In the present review the reader is informed about the important issue of the interactions of polysaccharides and light. Considering some aspects of polysaccharide structure and properties, topics such as absorption and fluorescence of polysaccharides, the structural analysis using light as a probe, and creation of new materials by combining chromophores and polysaccharides are discussed. Attention is also be given to polysaccharide derivatives, where absorption of light induces structural changes, including photocrosslinking and photochromism.

Contents

1. Introduction and scope

Polymer photoreactions were already applied 4000 years ago by the ancient Egyptians and Babylonians utilizing sunlight to photocrosslink linen during mummification and prepare waterproof papyrus boats via the photopolymerization of asphalt oil (Decker & Bendaikha, 1998).

Since the design of the first artificial photoreactive polymers by Minsk and co-workers in the 1950s (Minsk, Smithw, Deusen, & Wright, 1959), the development of different technical applications related to such polymers has become beneficial for daily life (Böttcher, Bendig, Fox, Hopf, & Timpe, 1991; Schnabel, 2007). To mention a few examples, photoresponsive polymers are used in photostructuring (Bendig & Timpe, 1991), as photoswitches (Feringa, 2001), and for optical information recording (Böttcher, 1991; Natansohn & Rochon, 1997; Schnabel, 2007, chap. 12). Moreover, fundamental light triggered biological processes, e.g., vision,

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Table 1
Structures of polysaccharides of different origin.

Polysaccharide	Source	Structure	Reference
Cellulose	Plants	β-(1 → 4)-D-Glucose	Klemm, Schmauder, and Heinze (2002)
Curdlan	Bacteria	β-(1 → 3)-D-Glucose	Nakata, Kawaguchi, Kodama, and Konno (1998)
Scleroglucan	Fungi	β-(1 → 3)-D-Glucose main chain, β-(1 → 6)-D-glucose branches	Giavasis, Harvey, and McNeil (2002)
Schizophyllan	Fungi	β-(1 → 3)-D-Glucose main chain, D-glucose branches	Rau (2002)
Dextran	Bacteria	α-(1 → 6)-D-Glucose main chain, D-glucose branches	Heinze, Liebert, Heublein, et al. (2006)
Pullulan	Fungi	α-(1 → 6) linked maltotriosyl units	Shingel (2004)
Starch	Plants		Tester and Karkals (2002)
Amylose		α-(1 → 4)-D-Glucose	
Amylopectin		α-(1 → 4) and α-(1 → 6)-D-Glucose	
Xylan	Plants	β-(1 → 4)-D-Xylose main chain, complex branches	Ebringerová and Heinze (2000)
Guar	Plants	β-(1 → 4)-D-Mannose main chain, D-galactose branches	Maier, Anderson, Karl, Magnuson, and Whistler (1993)
Inulin	Plants	β-(1 → 2)-Fructofuranose	Franck and DeLeenheer (2002)
Chitin	Animals	β-(1 → 4)-D-(N-acetyl)glucosamine	Uragami and Tokura (2006)
Chitosan	Animals	β-(1 → 4)-D-Glucosamine	
Alginate	Algae	α-(1 → 4)-L-Guluronic acid, β-(1 → 4)-D-mannuronic acid	Day (1998)

photosynthesis, photomorphogenesis, and photomovement at various biological levels, are of great academic and practical interest (Schnabel, 2007, chap. 8; Willner & Rubin, 1996).

The common feature of photoresponsive polymers is a chromophore incorporated in the macromolecular matrix. Therefore, light absorption and the involved electronic transitions can cause a series of transformations in the polymeric material. Some excellent review articles dealing with various aspects of polymers showing light-induced conformational changes, photostimulated variations of viscosity and solubility, photocontrol of membrane functions, and photomechanical effects are published (Barrett, ichi Mamiya, Yagerc, & Ikeda, 2007; Behl & Lendlein, 2007; Irie, 1990; Pieroni & Ciardelli, 1995; Pieroni, Fissi, & Opova, 1998; Viswanathan et al., 1999). However, research is mainly focused on synthetic polymers, polypeptides and proteins. Up to now there is no report summarizing the research results concerning photoresponsive polysaccharides, although polysaccharides are unique biopolymers with an enormous structural diversity and functional versatility. Huge amounts of polysaccharides are formed biosynthetically by many organisms. Polysaccharides can be used to tailor advanced materials, due to their extraordinary ability for structure formation by supramolecular interactions of variable types and the possibility to improve the given features by chemical modification.

This review is not intended to exhaustively cover the published literature. Instead, important examples of the research in the field of photoresponsive polysaccharides are highlighted from the polysaccharide chemist's point of view. Some aspects of polysaccharide structure and properties are discussed briefly in the review. Selected examples of light as a probe for the determination of structural features of polysaccharides and for special applications will be given. Moreover, processes including fluorescence and degradation of the polymer will be mentioned. Another issue of this review is to summarize some works dealing with the synthesis, properties, and application of photochromic polysaccharide derivatives.

As mentioned, there is a wide range of naturally occurring polysaccharides derived from plants, microorganisms, fungi, marine organisms, and animals as storage and structure forming macromolecules. The polysaccharides most commonly used for polymeranalogous reactions are summarized in Table 1. The common motifs are the polymer backbone, consisting of O-linked pyranose or furanose rings, and different functionalities, e.g., primary and secondary OH-groups, carboxylic acid moieties, and NH_2 groups, which are accessible to chemical modifications. Comprehensive reviews about important methods of modification, including esterification, etherification, and oxidation, are available (Bragd, van Bekkum, & Besemer, 2004; Heinze, 1998; Heinze, Liebert, Heublein, & Hornig, 2006; Heinze, Liebert, & Koschella, 2006; Klemm, Heublein, Fink, & Bohn, 2005; Philipp, Klemm, Heinze, Heinze, & Wagenknecht, 1998).

2. Light absorption and fluorescence

Although several books comprehensively dealing with the interactions of light with matter are available, some basic issues will be presented briefly, to introduce the reader to the field of photoresponsive polymers in general and polysaccharides in particular. Light absorption of a chromophore incorporated in the macromolecular matrix results in electronic transitions similar to those of low molecular weight compounds. These transitions involved in photoexcitation and relaxation of the excited states can be schematically summarized in a modified Jablonski diagram (Fig. 1). As a result of absorption (abs) of light, the chromophore reaches a higher energy state. The energy gained can be released either radiatively or non-radiatively. The non-radiative relaxation processes include internal conversion (ic), vibrational relaxation (vr), and intersystem crossing (isc). The relaxation processes including emission of light are fluorescence (fl) and phosphorescence (phos). While Fluorescence is a spin-allowed transition, taking place in picosecond-timescale, phosphorescence is a spin-forbidden transition, and thus a slow process taking place in milliseconds or even second-timescale. The energy of the excited molecule can also be released via interaction with other molecules by energy transfer, electron transfer or formation of excited complex. Absorption of light can also trigger photochemical reactions like isomerization, dissociation or crosslinking (react). However, some properties of polymers like relatively high rigidity, orderliness or anisotropy may

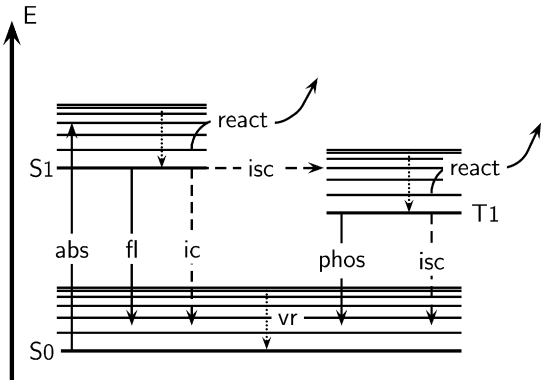


Fig. 1. Jablonski-type diagram. *Abbreviations*: abs, absorption; fl, fluorescence; phos, phosphorescence; ic, internal conversion; isc, intersystem crossing; vr, vibrational relaxation; react, other deactivation processes (see text).

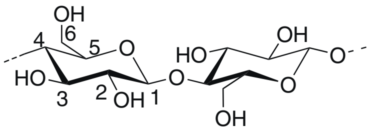


Fig. 2. Molecular structure of cellulose including numbering of C-atoms.

cause unusual spectroscopic properties and special effects within the deactivation processes.

While conventional UV/vis spectroscopy can be applied to analyze and identify polymers containing chromophors regarding their molecular constitution, sophisticated absorption methods provide powerful tools to study supramolecular structures as well. For example, circular dichroism (CD) spectroscopy allows the determination of different structural types as well as the detection of the alterations in the supramolecular structure of macromolecular systems. To mention a few examples, the secondary structure of proteins (α-helix, parallel and anti-parallel β-pleated sheets, and β-turns) can be designated in type and relative content, the thermal denaturation of superstructures such as those of DNA or collagen can be monitored, and the chirality of newly synthesized polymers can be characterized (Martin & Schilstra, 2008; Vekshin, 2002). The relevance of UV/vis spectroscopy and related spectroscopic methods for polysaccharide chemistry is discussed in the following section.

2.1. Light absorption in polysaccharides

Cellulose, the most abundant organic compound on earth, is a polydisperse linear homopolymer consisting of regio- and enantioselectively β-(1 → 4) linked D-glucose units (so-called anhydroglucose units) (Fig. 2). Beside the rather simple molecular structure, complex supramolecular structures can be formed, which have remarkable influence on both physical and chemical properties of the polymer (Lai, 1996; O'Sullivan, 1997). An important consequence of its supramolecular structure is the insolubility of the macromolecule in water and in common organic liquids, still stimulating the search for solvents appropriate for homogeneous phase reactions of cellulose (Heinze & Liebert, 2001; Liebert & Heinze, 2008; Swatloski, Rogers, & Holbrey, 2003). The carbon atoms of position 2, 3, and 6 possess hydroxyl groups, which are, in general, accessible to the typical conversions of primary and secondary –OH groups.

From the authors point of view cellulose is one of the most valuable starting materials for polymeranalogous chemical modification in order to design highly engineered products including products interacting with light. The polymer with its unique structure possesses properties like hydrophilicity, biocompatibility, stereoregularity, multichirality, polyfunctionality, and, last but not least, the ability to form supramolecular structures.

Chemically pure glucans, like bacterial cellulose are poor absorbers of UV and visible light on one hand. On the other, cellulosic pulps contain different chromophores that are formed from polysaccharides because of thermal-oxidative stress during pulping and bleaching. Pulping and bleaching are common process stages, when cellulosic materials free from non-cellulosic plant components, such as lignin and hemicellulose, are produced. Moreover, subsequent processing like fiber spinning and derivatization or even natural aging may lead to additional chromophores in products manufactured from cellulosic pulps.

The chemical nature of the chromophores in cellulose has been studied utilizing reference model compounds since the 1960s (Beelik & Hamilton, 1961; Bos, 1972). The weak absorption bands in the 210–320 nm UV range were assigned to carbonyl and acetal groups as well as various impurities such as trace amounts of transition metal ions (Atalla & Nagel, 1972). So far, the reason for the visible yellowing effect of cellulosic fibers and derivatives was largely unclear, since the overall discoloration effect is caused by a large number of chromophores. In addition, the concentration of these chromophores is generally extremely low, mostly in the ppb range. By a chromophore release and identification procedure, which applies boron trifluoride–acetic acid complexes in combination with sodium sulfite, a number of hydroxybenzoquinone, hydroxyacetophenone, and naphthoquinone structures were isolated from different cellulosic materials (Fig. 3) (Rosenau, Potthast, Milacher, Hofinger, & Kosma, 2004; Rosenau, Potthast, Kosma, Suess, & Nimmerfroh, 2007). Some of these compounds, so called Theander products, arise from cellulose degradation starting from keto structures, e.g., oxidized spots in cellulose. They are formed mainly upon acidic, basic, and thermal treatment of polysaccharide fragments in the presence of air and thus their formation is largely independent of origin of the cellulosic material (Popoff & Theander, 1976a; Popoff & Theander, 1976b; Popoff, Theander, & Westerlund, 1978; Theander & Westerlund, 1980). Moreover secondary, mainly process-specific, chromophores are present in cellulose II products such as fibers, which are more prominent and color-intensive (Rosenau et al., 2007). Recent studies using UV-resonance Raman spectroscopy also demonstrate the formation of aromatic structures from the reducing end groups of polysaccharide chains (Vikkula, Valkama, & Vuorinen, 2006).

Due to the consumer notion, that only "really white" materials are clean, both the optical properties of cellulosic materials and the formation of chromophores are still a focus of research (Bikova & Treimanis, 2004; Forsskahl, Tylli, & Olkkonen, 2000). In particular, the role of aromatic structures in brightness reversion is studied applying sophisticated analytical tools including reflectance UV/vis spectroscopy, UV-resonance Raman spectroscopy, gel permeation chromatography, and chemical methods (Jääskelainen, Toikka, Lahdetie, Liitia, & Vuorinen, 2009; Krainz et al., 2009; Loureiro, Fernandes, Carvalho, & Evtuguin, 2010). A thorough knowledge about chemical structure of the chromophores and their origin

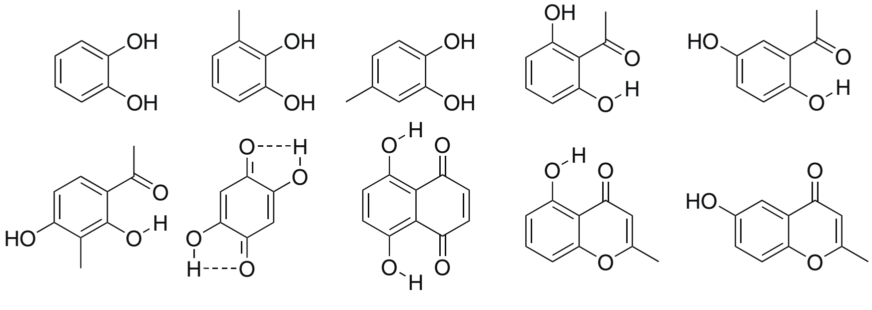


Fig. 3. Chromophores isolated from cellulosic materials by a chromophore release and identification procedure (Rosenau et al., 2004, 2007).

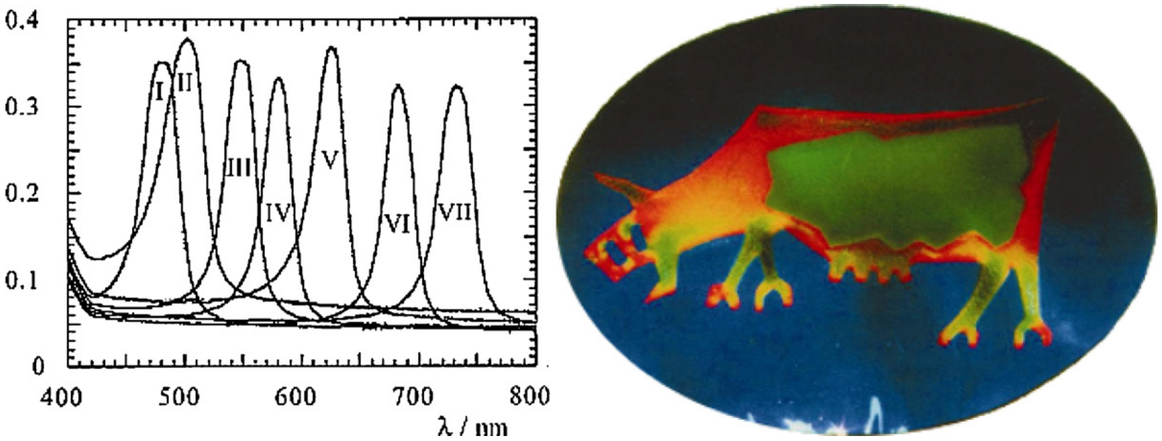


Fig. 4. Left: UV/vis spectra of a cholesteric mixture containing 3-(trifluoromethyl)phenyl urethane of cellulose (45 wt.%) and diethylene glycol dimethacrylate crosslinked at I: 20 °C, II: 25 °C, III: 30 °C, IV: 35 °C, V: 40 °C, VI: 45 °C, VII: 50 °C. Right: Picture of a film prepared from the cholesteric mixture photo-crosslinked at different temperatures (blue: 20 °C, green: 30 °C, orange: 45 °C).

Adapted from "Cholesteric phases and films from cellulose derivatives" (Müller & Zentel, 2000) with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

might help to develop strategies to reduce the formation of these impurities in the processes of the paper and textile industries from the outset, and for example, save bleaching costs.

Furthermore, absorption spectroscopy is a valuable tool especially for analytics of cellulose derivatives. First of all, the success of functionalization with a light absorbing moiety can allow the determination of the degree of substitution (DS) by utilizing a reference compound. Moreover, the elucidation of supramolecular structures is possible. For example, cellulose derivatives displaying lyotropic or thermotropic cholesteric phases can be characterized by means of absorption spectroscopy. By measuring the cholesteric reflection peaks, the pitch height of the helicoidal arrangement was determined for a series of cellulose derivatives (Bhadani & Gray, 1983; Hou, Reuning, Wendorff, & Greiner, 2000; Müller & Zentel, 2000; Rusig et al., 1994; Tseng, Valente, & Gray, 1981). Fig. 4 shows the UV/vis spectra of a lyotropic mixture of cellulose carbanilate with a –CF_3 moiety in *meta*-position and diethylene glycol dimethacrylate. After crosslinking the mixture at different temperatures, the cholesteric helix and thus their pitch were fixed. The spectra, subsequently recorded at room temperature, illustrate the selective reflection of the cholesteric sample and allow the determination of the pitch height according to DeVries (1951). Beside the selective reflection, the cholesteric state is optically uniaxial and therefore displays optical rotation dispersion and circular dichroism. These features could be used for the determination of further structural parameters, including handedness of the cholesteric helix. The combination of the optical effects sketched above, make lyotropic and thermotropic cellulose derivatives interesting materials for opto-electronic applications as well as for opalescent cholesteric films (Costa, Filip, Figueirinhas, & Godinho, 2007; Greiner et al., 2003; Müller & Zentel, 2000). Moreover, these issues reveal the potential of absorption spectroscopy for the understanding of supramolecular structures.

2.2. *Fluorescence of polysaccharides and polysaccharide derivatives*

The absorption of light results in an electronically excited state of the polymer itself or only the attached/incorporated chromophore. From the different deactivation processes which can occur, fluorescence is one of the most prominent pathways. For the basics of fluorescence the reader is referred to an excellent textbook (Lakowicz, 2006). The following section will give some examples that connect the phenomenon of fluorescence to the field of polysaccharide chemistry.

Fluorescence typically occurs from highly conjugated polycyclic aromatic molecules. For polysaccharides in general, and cellulosics in particular, different impurities like lignin appear to be the main contributors to fluorescence emission. Thus the fluorescences of lignocellulosics have been extensively studied and the nature of the fluorescent chromophores in lignin was investigated by means of lignin model molecules (Albinsson, Li, Lundquist, & Stomberg, 1999; Olmstead & Gray, 1997; Radotic et al., 2006). Coniferyl alcohol, biphenyl, stilbene, phenylcoumarone and structures similar to coniferyl aldehyde are widely considered to be the main structural elements responsible for the fluorescence emission of wood and lignin-rich pulps.

Nevertheless, fluorescence could still be observed in different cellulose samples, even when lignin was removed by pulping and bleaching (Castellan, Trichet, Pommier, Siohan, & Armagnacq, 1995). In view of their universal presence in all living organisms, proteins have been suggested as the source of fluorescence emission as well as residual lignin (Olmstead & Gray, 1997). However, Castellan, Ruggiero, Frollini, Ramos, and Chirat (2007) pointed out that the presence of contaminants (protein, tyrosine, etc.) in microcrystalline cellulose is very unlikely. Moreover, the lignification process for cotton linters is quite limited. Thus, it is puzzling that fluorescence could still be observed in both cases. Although phenolic and quinoid chromophores are proposed to be the source of fluorescence emission, the exact chemical structure of fluorophores in cellulosics remains unclear (Fig. 3). However, since fluorescence techniques are highly sensitive, they are suitable for detailed investigations of residual lignin in bleached pulps. Moreover, they are useful tools for the observation of bleaching and brightness reversion (Liukko, Tasapuro, & Liitia, 2007).

Beside the continuing research regarding the nature of fluorescent chromophores in cellulosics themselves, fluorescence spectroscopy provides the possibility to analyze the molecular structure of the polymer backbone. For example, Fig. 5(a) shows different oxidized functionalities, which may occur in polysaccharides in general and in cellulosics in particular. Oxidized positions in cellulose are main reasons for strength loss and decreased performance parameters in textiles, paper, and other cellulosic materials. Moreover, they are responsible for general aging and are assumed to be the promoter of thermal and light induced yellowing processes (Duran, Gomez, & Mansilla, 1987; Lewin, 1997). The reliable and accurate determination of aldehyde-, keto-, and carboxyl groups in cellulose and other polysaccharides represented a largely unsolved problem in polysaccharide research. Recently, different methods to quantify small amounts of oxidized

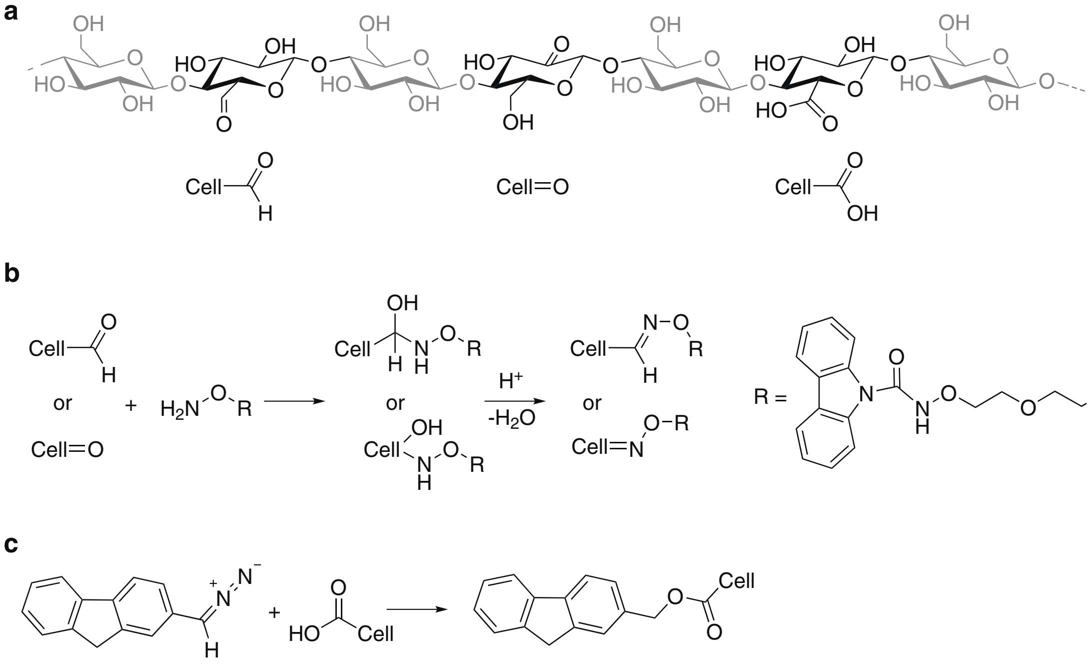


Fig. 5. (a) Schematic representation of oxidized functionalities in polysaccharides, including aldehyde-, keto-, and carboxyl groups (end groups not shown). (b) Reaction pathway for the determination of the carbonyl content in cellulosics by fluorescence labeling. (c) Reaction pathway for the determination of the carboxyl content in cellulosics by fluorescence labeling (Bohrn et al., 2005; Röhrling, Potthast, Rosenau, Lange, Borgards, et al., 2002).

structures via fluorescence spectroscopy in cellulosic pulps were developed.

As shown in Fig. 5(b), a carbazole fluorophore decorated with a spacer and an appropiate anchor group was used to label carbonyl groups selectively (Röhrling et al., 2001; Röhrling, Potthast, Rosenau, Lange, Borgards, et al., 2002). The derivatization presented proceeds completely over the whole molecular weight range in the "exotic" solvent N,N-dimethylacetamide/lithium chloride, which is one of a limited number of solvents dissolving high molecular polysaccharides. Moreover, the fluorophore does not interfere with the multi angle laser light scattering (MALLS) detection of chromatographic procedures and the spacer avoids any shift of the fluorescence emission, which might be caused by the spatial environment of the fluorophore. By implementing these method into gel permeation chromatography (GPC), it became possible to determine not only the carbonyl content as a sum parameter, but also with regard to the molecular weight distribution for the first time (Kostic, Potthast, Rosenau, Kosma, & Sixta, 2006; Potthast et al., 2003; Röhrling, Potthast, Rosenau, Lange, Ebner, et al., 2002). Moreover, a similar method for the determination of carboxyl content and carboxyl profile was developed applying 9*H*-fluoren-2-yl-diazomethane as selective fluorescence label (Fig. 5(c)) (Bohrn, Potthast, Rosenau, Sixta, & Kosma, 2005; Bohrn et al., 2006).

The combination of polysaccharides or polysaccharide derivatives with fluorescence methods also leads to promising applications in the biomedical field. Here dextran is of particular interest. Dextran, a family of neutral polysaccharides, finds widespread use in medicinal and pharmaceutical applications, e.g., as blood plasma substitute or coating material to prevent protein opsonization (DeBelder, 1996). The polymer, produced by numerous bacteria strains (*Leuconostoc* and *Streptococcus*), consists of a α-(1 → 6) linked D-glucose main chain with varying branches. The content of α-(1 → 6) linkages may vary from 97 to 50% of total glycosidic bonds. The number and type of branches, bound by α-(1 → 2), α-(1 → 3), and α-(1 → 4) glycosidic bonds, depend on the origin (Leathers, 2002).

The commercially applied bacteria strain *Leuconostoc mesenteroides* NRRL B-512(F) produces a dextran that is predominately α-(1 → 6) linked and contains a relatively low level (<5%) of randomly distributed α-(1 → 3) branched linkages (Fig. 6) (Hornig, Liebert, & Heinze, 2007). This dextran is generally soluble in water and organic solvents such as dimethylsulfoxide. It can be utilized for chemical conversion into unconventional derivatives, like dextran pyroglutamate or dextran furoate, which show formation of nano-scaled particles (Hornig & Heinze, 2007).

The exploration of chemical micro environments in organisms as well as on the cellular level can be realized with dextran based fluorescent nanoparticles. A sensor system for pH monitoring in living cells is based on nano-scaled particles prepared from dextran decorated with propionic acid, sulforhodamine B acid, and the pH indicator dye fluorescein (Fig. 7) (Hornig et al., 2008). The use of the natural polymer as a basis for such functionalized nanoparticles may overcome drawbacks like toxicity due to monomer and surfactant residues in synthetic polymers or the need of stimulating agents for cell uptake.

Fluorescence is one example of photoluminescence, but light emission can be also initiated by applying voltage. An application,

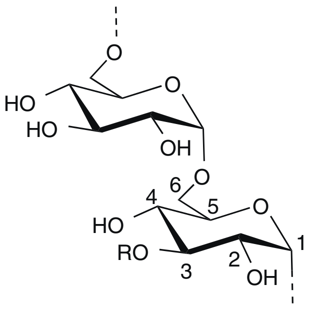


Fig. 6. Structure of dextran obtained from *Leuconostoc mesenteroides* NRRL B-512(F). R = predominately H and 5% glucose or α-(1 → 6) linked glucopyranosyl-α-D-glucopyranoside.

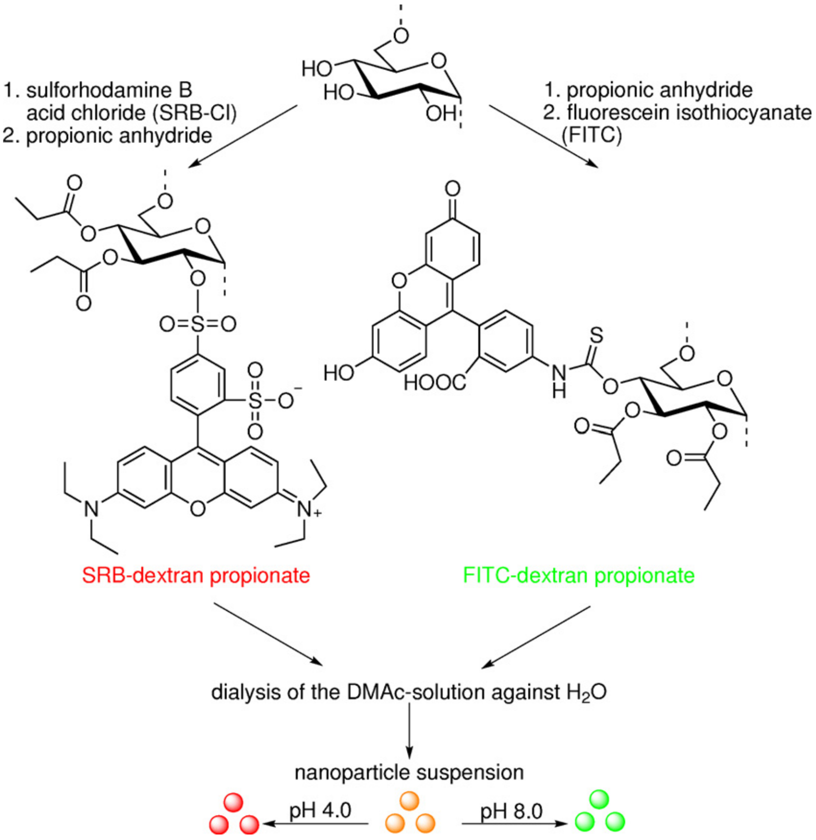


Fig. 7. Synthesis of sulforhodamin B and fluorescein labeled dextran propionate and the preparation of nano sized spheres for pH-sensoring; one anhydroglucose unit is schematically represented (Hornig et al., 2008).

taking advantage of electroluminescence, is devices like Organic Light Emitting Diodes (OLEDs). Cellulose and starch were mainly used as a supporting material in order to provide biocompatibility (Legnani et al., 2008), to improve mechanical properties (Okahisa, Yoshida, Miyaguchi, & Yano, 2009; Small & Johnston, 2008), or to enhance photoluminescence and electroluminescence efficiency of OLEDs (Frampton et al., 2008). However, the application of functionalized cellulose for both OLEDs and an organic memory device is reported as well (Karakawa, Chikamatsu, Vakamoto, et al., 2007; Karakawa, Chikamatsu, Yoshida, et al., 2007). Different regioselectively substituted derivatives were achieved using 9-(4-bromobutyl)-9*H*-carbazole and p-methoxytrityl cellulose. These fluorescent cellulose compounds show properties similar to poly(N-vinylcarbazole), widely used for OLEDs. However, the results indicate that the packing manner of the carbazole moieties as a consequence of the substitution pattern greatly affects optical properties like the emission intensity and spectrum or the luminance voltage.

Polysaccharide scaffolds also have been shown to be important in preparing solid structures of precisely organized chromophores. Thus the fluorescence properties can be preserved and at the same time a high concentration of chromophores is present. The preparation of chromophore films without scaffolding can lead to quenching of fluorescence due to aggregation, which reduces their performance as sensitizers or photocurrent generators. Typical examples are cellulose derivatives that are regioselectively functionalized in position 6 with porphyrin moieties (DS 0.6). The chirality and the stiff backbone of cellulose combined with the strictly defined regiochemistry lead to a helical arrangement of the cellulose-bound porphyrins as shown by CD spectroscopy. Moreover, porphyrin cellulose was studied by means of spectroelectrochemistry and picosecond laser fluorescence in context with the application as an optoelectronic material (Holzer, Penzkofer, Redl, Lutz, & Daub, 2002; Redl, Lutz, & Daub, 2001). Langmuir–Blodgett films of porphyrin–cellulose show improved photocurrent generation in electrochemical cells compared to porphyrin films, indicating the beneficial role of cellulose as a scaffold (Sakakibara, Ogawa, & Nakatsubo, 2007). The chromophores are spaced at a fixed distance using cellulose with its rigid structure and thus the photocurrent quantum yields for the LB films are increased (Sakakibara & Nakatsubo, 2008b). A further improvement of photocurrent performance was obtained by the incorporation of fullerene (C60) in porphyrin–cellulose films (Sakakibara & Nakatsubo, 2008a).

A further indication of the ability of polysaccharides to act as an efficient scaffold can be concluded from studies of anthracene molecules attached to dextran (Nowakowska, Zapotoczny, Sterzel, & Kot, 2004). The polymers are water soluble at low DS of anthracene. Quenching of fluorescence after addition of suitable energy or electron acceptors in the water solution is observed, indicating photoinduced energy or electron transfer. Thus, these are promising polymers for photosensitation of reactions of organic compounds in aqueous solutions (Nowakowska, Sterzel, Zapotoczny, & Kot, 2005).

3. Photoreactions

Like in the case of light absorption or fluorescence, photoreactions of polymer based systems, in particular polysaccharides, must be considered from different aspects: that of the polysaccharide itself, that of low molecular weight compounds hosted by the polysaccharide matrix, and that of chromophores covalently attached to the polymer backbone. These aspects cannot be strictly separated from each other at any time and the following section will give an overview about photochemical processes such as photodegradation, photocrosslinking, and photochromic effects.

The absorption of light can cause photolysis in cellulose and their derivatives (Duran et al., 1987). In general, a decrease of the degree of polymerization and an increase of the copper number as well as an increase of alkali solubility can be observed. Moreover, the light induced degradation is accompanied by yellowing and the formation of carbonyl- and carboxyl groups along the polymer chain. Carbon monoxide, carbon dioxide, and hydrogen are the main gaseous products formed during photolysis of polysaccharides. Since society invests considerable resources in the preservation of cultural heritage a detailed understanding of photoinduced degradation of polysaccharides in general and in particular cellulose is of major interest. (Bertolini et al., 2001; de la Orden & Urreaga, 2006; Malesic et al., 2005; Tylli, Forsskahl, & Olkkonen, 1993; Wach, Kudoh, Zhai, Muroya, & Katsumura, 2005). Moreover, light stability is of growing importance in material sciences, where a wide revival of interest by researchers and industrialists for polysaccharides recently occurred. The destructive nature of UV and visible light, in particular in case of high intensity or long exposure time, must be kept in mind for the discussion of photoreactions that follows.

3.1. *Photocrosslinking*

In polysaccharide chemistry light induced crosslinking is applied for the improvement of material properties (Klemm, Schnabelrauch, & Stein, 1990), the stabilization of supramolecular structures (Esker, Grül, Wegner, Satija, & Han, 2001), and the immobilization of biomolecules (Bora, Sharma, Kannan, & Nahar, 2006). Some aspects of these fields will be pointed out.

Polysaccharides in general and starch in particular were investigated as promising raw materials in order to replace synthetic polymers and thus reduce environmental impact of plastic wastes especially from packing. For example, thermoplastic starch mixtures have found application in the polymer market as loose filler materials. Nevertheless, the hydrophilic nature of thermoplastic starch seriously limits its wider applications. Thermoplastic starch is sensitive to water and since the water content of the materials changes with environmental humidity, mechanical properties change during use and storage. Photocrosslinking is one interesting attempt to overcome these disadvantages. A solid state crosslinking procedure of sensitized starch films using UV irradiation and sodium benzoate as water-soluble photo additive was described (Delville, Joly, Dole, & Bliard, 2002). In contrast to conventional crosslinking procedures, there was no need of organic solvents and toxic crosslinking agents like epichlorohydrine or phosphoryl chloride. The crosslinking kinetics was established by the determination of swelling degree and gel fraction, in order to characterize the created network. The results indicated that mechanical properties like Young's moduli and ultimate strength could be improved via UV treatment. Additional investigations described the influence of photocrosslinking on the retrogradation of starch based materials (Delville, Joly, Dole, & Bliard, 2003). It was shown that the crosslinking treatment partially inhibited retrogradation of starch films by limiting crystallization and thus partially prevented aging and decreased the ultimate mechanical properties (elongation and stress at break, Young's moduli). Sodium benzoate was also used as sensitizer for surface modifications of starch sheets, in order to improve the surface properties without changing the bulk composition and characteristics (Zhou, Zhang, Ma, & Tong, 2008; Zhou, Ma, Zhang, & Tong, 2009). Compared with the bulk photocrosslinking, the required amount of sensitizer was significantly lower and the crosslinking reaction occurred much easier in the surface layer. One primary result of these investigations was a significant increase of the surface water contact angle indicating an enhancement of hydrophobic character of the surface and a lower value for the polar component of the surface energy. Moreover, the surface modification led to notably lower moisture uptake and an overall improvement of water resistance.

The preparation of composite materials by means of photochemical methods is also an approach to enhance existing properties or impart new properties in polysaccharide based polymers. UV irradiation and sodium benzoate as a photo sensitizer were used in order to crosslink films of cellulose reinforced starch and the obtained biocomposites showing remarkably improved physical and mechanical properties(Kumar & Singh, 2008). Moreover, the synthesis of interpenetrating polymer networks and polysaccharide based copolymers is a valuable tool to gain new materials with promising properties. In this sense, photocrosslinking was applied to graft synthetic polymers to polysaccharides (AbdelRazik, 1997; Li, Wang, & Huang, 2007), or to preserve the structures possessed by the polysaccharide during the preparation of the composite material (Kamath, Kincaid, & Mandal, 1996). Cinnamoylisopentylcellulose is one interesting hairy-rod-like polysaccharide (HRP) derivative that can be utilized to create Langmuir–Blodgett (LB) assemblies of defined thickness on the nanometer scale. By crosslinking the cinnamoyl groups, stable LB films with properties such as isotopic selectivity or a certain swelling degree are obtained (Esker et al., 2001). As shown in Fig. 8 such LB assemblies were used as a primer for surface modification by polymerization (Woo, Schiewe, & Wegener, 2006). The incorporation of methyl methacrylate as typical monomer (Fig. 8(a)) and a subsequent polymerization led to homogeneous nano-scaled composite films (Fig. 8(b)).

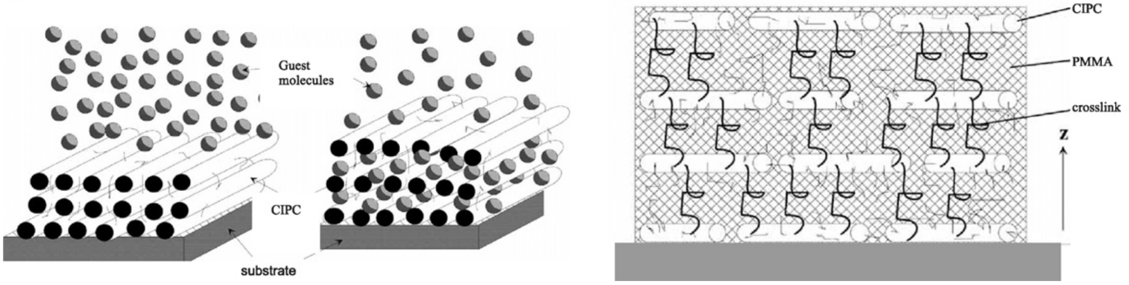
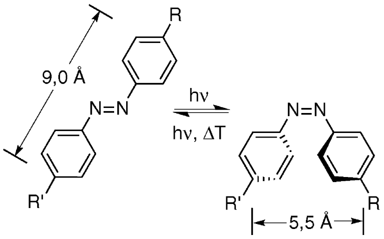
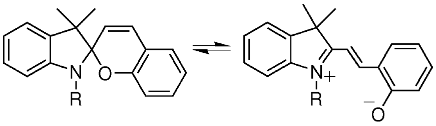
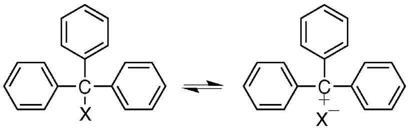
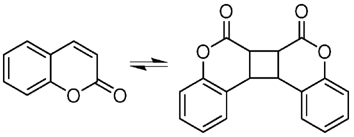


Fig. 8. (a) Schematic model of of a swellable LB film of photocrosslinked cinnamoylisopentylcellulose (CIPC). Guest molecules can be solvent, dye molecules or monomers. (b) Schematic picture of the composite multilayered CIPC and poly methyl methacrylate (PMMA) incorporated via vapor phase photopolymerization. The scale of the CIPC hairy-rods and periodic spacing is only schematically represented.
Adapted from "Multilayered assembly of cellulose derivatives as primer for surface modification by polymerization" (Woo et al., 2006) with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

Table 2
Typical photoisomerizations.

Reaction type	Example
(a) Trans–cis isomerization of double bonds	
(b) Zwitter ion formation	
(c) Ionic dissociation	
(d) Ring formation and ring cleavage	

3.2. Photochromic polysaccharide derivatives

Photochromic compounds undergo reversible change of color upon illumination. As the compound is interconverted between two states by means of irradiation or a thermal stimulus, the absorption spectrum and physical properties of the compound change. The interconversion between two forms can schematically be expressed as:

$$A \underset{h\cdot\nu' \text{ or } \Delta}{\overset{h\cdot\nu}{\rightleftharpoons}} B$$

Typical examples of chromophores, which show photochromic behaviour upon irradiation with light of an appropriate wavelength, are summarized in Table 2. In the following subsections some photochromic polysaccharide derivatives are discussed.

3.2.1. Polysaccharides containing trans–cis isomerizable chromophores

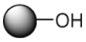
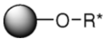
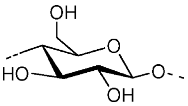
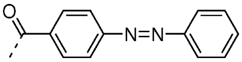
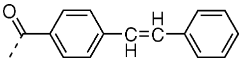
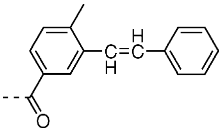
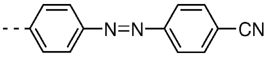
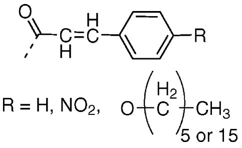
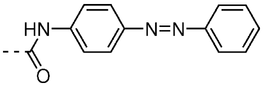
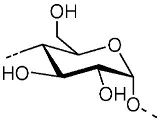
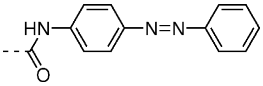
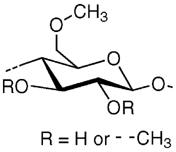
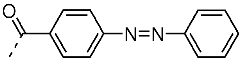
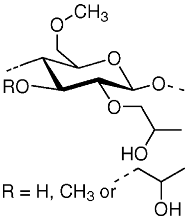
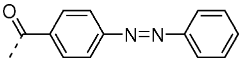
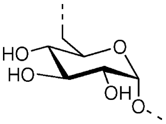
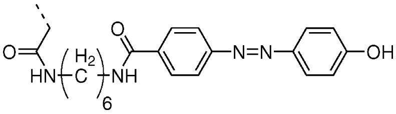
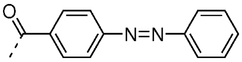
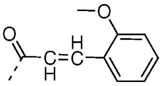
The introduction of photoisomerizable compounds (Table 2(a)) in polymers may yield a photoinduced conformational change of the polymer chain induced by the conformational change of the chromophore. Azobenzene compounds (azos), characterized by an azo linkage (–N=N–) joining two phenyl rings, are the most prominent photoisomerizable molecules. The azobenzene photochemistry gives rise to numerous photoswitching and photostructuring applications due to the fact that azobenzene chromophores undergo a large change both in structure and dipole moment during the isomerization. Moreover, a photoinduced orientation of the azobenzene chromophores in polymers and, therefore, a mass transport process is possible when irradiating with polarized light. Additionally, azos are chemically robust molecules and can easily be incorporated into a polymer matrix or even covalently attached (Griffiths, 1972; Yager & Barrett, 2006).

In Table 3, a series of polysaccharide derivatives decorated with trans–cis isomerizable moieties are summarized. Beside azobenzene chromophores (Table 3 entry 1, 4, and 6–11), stilbene (Table 3 entry 2 and 3) and cinnamic acid (Table 3 entry 5 and 12) were linked to the polymer backbone. Cellulose was the most common starting polymer at the beginning of the research on modification of polysaccharides with isomerizable substituents (Table 3 entry 1–6). Recently, other polysaccharides in particular dextran and starch (Table 3 entry 7 and 10–12) came into focus as well as commercial polysaccharide derivatives like methylcellulose or hydroxypropyl methylcellulose (Table 3 entry 8 and 9). The linkage between the polymer backbone and the photoresponsive moieties was realized in different ways. For example, esterification (Arai & Kawabata, 1995a; Arai & Sano, 1994; Arai, Sano, & Satoh, 1992; Arai & Udagawa, 1988; Hu et al., 2004; Klemm et al., 1990; Wang & Wang, 2007; Wondraczek & Heinze, 2008; Zheng et al., 2004), etherification (Yang, Jacob, et al., 2001; Yang et al., 2002), and the formation of carbamates were applied (Yashima, Noguchi, & Okamoto, 1995). However, esterification was the most important path for introducing photoactive functionalities up to now. In general, a conventional esterification procedure was employed, using the acyl chloride either heterogeneously or homogeneously. Recently, we have studied N,N-carbonyldiimidazole as an efficient activating agent for the homogeneous acylation of polysaccharides in non-aqueous systems for substituents like azobenzene- and cinnamic acid (Wondraczek & Heinze, 2008).

Cellulose derivatives containing azobenzene groups (azocellulose) were prepared for the first time heterogeneously by the reaction of microcrystalline cellulose with 4-phenylazobenzoyl chloride in pyridine (Arai & Udagawa, 1988). Similar cellulose stilbene derivatives were synthesized using stilbene-4-carbonyl chloride (Arai et al., 1992). Using these derivatives as the adsorbent in thin layer chromatography, the photoregulation of the rate of flow of different compounds was possible.

Since these first attempts to control the special properties of polysaccharides by means of trans–cis isomerizable substituents, a series of other approaches were developed. The photocontrolled enantioselective adsorption of several neutral racemates

Table 3
Polysaccharides forming ionic structures upon irradiation.

No.	Starting polymer 	Photoresponsive moiety[a] 	Reference
1			Arai and Udagawa (1988)
2			Arai et al. (1992)
3			Arai and Sano (1994)
4			Yang, Jacob, et al. (2001, 2002)
5			Klemm et al. (1990)
6			Yashima et al. (1995)
7			Yashima et al. (1995)
8			Arai and Kawabata (1995a)
9			Zheng et al. (2004)
10			Hu et al. (2004) Wang and Wang (2007) Patnaik, Sharma, Garg, Gandhi, and Gupta (2007)
11			Wondraczek and Heinze (2008)
12			Wondraczek and Heinze (2008)

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[a] Including linkage to the polymer backbone.

on solid [4-(phenylazo)phenyl]carbamoylated cellulose and amylose membranes was reported (Yashima et al., 1995). Moreover, liquid crystalline phase formation and the sol–gel transformation behaviour of different cellulose derivatives were regulated by light induced trans–cis isomerization (Arai & Kawabata, 1995a; Arai & Satoh, 1992). The sol–gel transformation could be influenced not only by the conversion of the photochromic group but also by additives like α-cyclodextrin (Hu et al., 2004; Wang & Wang, 2007; Zheng et al., 2004). Fig. 9 shows the thermoreversible sol–gel transition of an aqueous solution of azobenzene functionalized

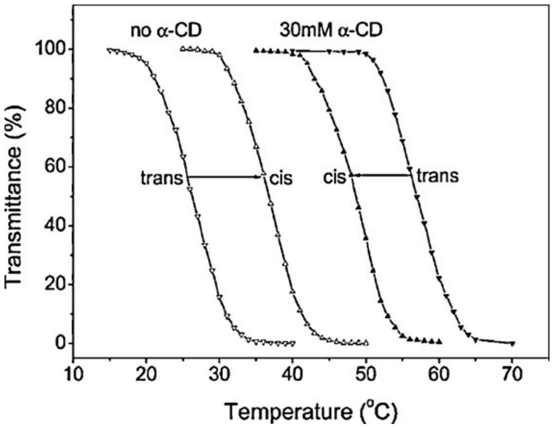


Fig. 9. Sol–gel transition behaviour of azobenzene functionalized hydroxypropyl methylcellulose in the absence and presence of α-cyclodextrin (α-CD); trans: sample irradiated with visible light; cis: sample irradiated with UV light.
Adapted from "Photoregulated sol–gel transition of novel azobenzene-functionalized hydroxypropyl methylcellulose and its alpha-cyclodextrin complexes" (Zheng et al., 2004) with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

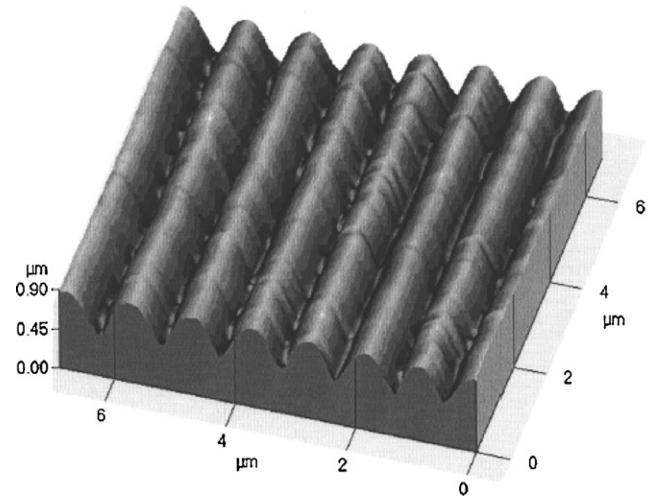


Fig. 10. Three-dimensional view of a photoinduced surface relief grating on an azo-cellulose film.
Adapted from "Photoinduced surface relief gratings on azocellulose films" (Yang, Li, et al., 2001) with permission from Taylor & Francis.

hydroxypropyl methylcellulose monitored by turbidity measurements. Thus, isothermal and reversible regulation of the sol–gel transition of the azo-cellulose polymer can be realized by photoirradiation. The difference in gelation temperature between the trans- and cis isomers can also be influenced by addition of α-cyclodextrin, which selectively forms inclusion complexes with the trans azobenzene (Murakami, Kawabuchi, Kotoo, Kunitake, & Nakashima, 1997).

Another approach, impressively demonstrating the enormous potential of polysaccharides decorated with trans–cis isomerizable moieties, was reported by Yang and co workers (Yang, Jacob, et al., 2001; Yang et al., 2002; Yang, Li, Cholli, Kumar, & Tripathy, 2001). Applying a Mitsunobu type ether formation, 4-cyanophenylazophenol was linked to cellulose with ultrahigh molecular weight. The irradiation with linearly polarized light led to the trans–cis–trans isomerization accompanied by reorientation. The orientation redistribution of the azobenzene chromophores finally drives the cis-isomer predominantly oriented perpendicular to the polarization of the irradiating light. This procedure results in a net dichroism and birefringence of the material. Moreover, holographic gratings can be developed by irradiating the photoanisotropic films by two polarized interfering beams (Fig. 10). The experiments reported clearly demonstrated how to inscribe volume gratings to a ultrahigh molecular weight polymer exhibiting no glass transition temperature even up to the temperature of decomposition.

3.2.2. *Polysaccharide derivatives forming ionic structures upon irradiation*

The light induced formation of a zwitterion (Table 2b) provides the possibility of creating strong dipoles. Thus, a change of the polymer conformation and properties can be obtained photochemically, by introducing compounds like spiro benzopyran. The spiro benzopyran chromophores as well as the closely related spiro benzoxazines and spiro naphthoxazines are well known for the formation of a merocyanine zwitterion, by a ring-opening reaction (Bertelson, 1971; Bertelson, 1999; Guglielmetti, 2003). Upon irradiation with UV light, the rupture of the C–O linkage takes place, according to the mechanism shown in Fig. 11. This reaction can be reversed either thermally or photochemically. The second way to form ionic structures under UV irradiation is the dissociation to ions as known for triphenylcarbinol or related compounds Table 2(b).

In Table 4 different polysaccharides bearing moieties with a photochromic character similar to triphenylcarbinol (entry 1 and 2) and spiro benzopyran (entry 3–6) are summarized. Cellulose (Table 4 entry 1 and 2), methylcellulose (entry 3 and 4), cellulose acetate (entry 5), and dextran (entry 6) were applied as starting polymer for the modification with these chromophores. The linkage between polymer backbone and the chromophoric group was realized by etherification (Table 4 entry 1, 2, and 5) or esterification (entry 3, 4, and 6). All products were obtained under homogeneous reaction conditions.

The control of material properties like degree of swelling and contact angle was the main ambition of linking photochromic substituents, displaying formation of ionic structures, to polysaccharides in the beginning of research (Arai & Kawabata, 1995b; Arai, Ohyama, & Shitara, 1997; Arai, Shitara, & Ohyama, 1996). Photoconductive cellulosic films were also prepared applying cellulose decorated with 4,4′-bis(dimethylamino) diphenylmethyl groups (Heinze et al., 1995). Edahiro et al. developed a system, which exists in a uniform single phase at room temperature in the dark, and separates into two aqueous phases through blue light irradiation (Edahiro, Sumaru, Takagi, Shinbo, & Kanamori, 2006). The system was composed of an aqueous solution of photochromic 6-nitrospiropyran modified dextran and polyethylene glycol, which are the first studies about the control of the affinity of photoresponsive and non-photoresponsive polymers in aqueous solution.

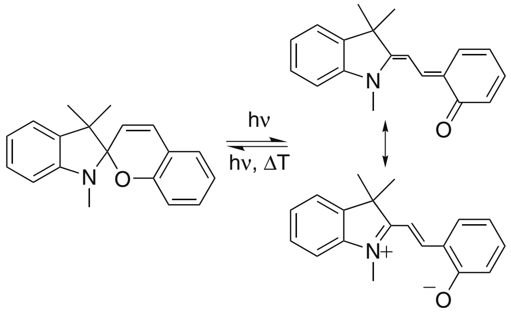
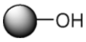
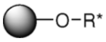
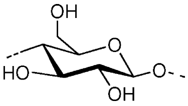
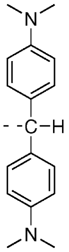
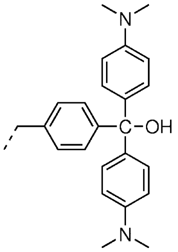
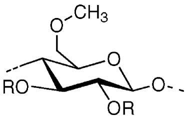
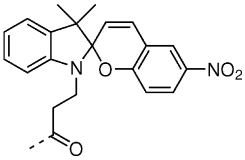
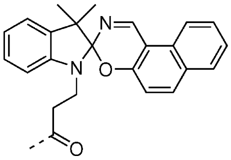
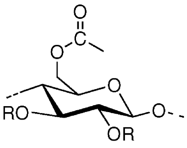
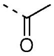
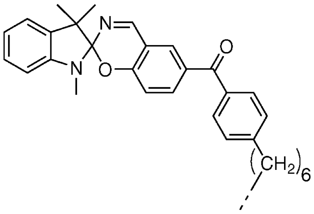
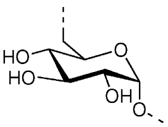
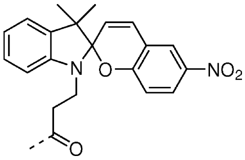


Fig. 11. Photochromic transformation of spiro benzopyran to a resonance hybrid of a quinoid and a bipolar structure.

Table 4
Polysaccharides forming ionic structures upon irradiation.

	Starting polymer 	Photoresponsive moiety[a] 	Reference
1			Heinze et al. (1995)
2			Arai and Kawabata (1995b)
3	 R = H or - -CH_3		Arai et al. (1996)
4			Arai et al. (1997)
5	 R = H or 		Lee, Li, and Kim (2000)
6			Edahiro et al. (2006)

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[a] Including linkage to the polymer backbone.

4. Conclusion

From the authors point of view the synthesis of photoresponsive polysaccharide derivatives is a promising area of polysaccharide research to design novel functional polymers. Light is a valuable tool for probing polysaccharide materials and for determination of properties of technical, commercial, and scientific interest. Moreover, polysaccharides do not only afford a renewable alternative to synthetic polymers to a certain extent but also provide unique features like polyfunctionality and biocompatibility, making them valuable starting materials for highly engineered products. The potential arising from the chemical and physical characteristics of polysaccharides is far from being exhausted. For example, the influence of regioselectivity of photoresponsive polysaccharide derivatives on their properties has only been touched on in the literature. Moreover, only a very few investigations are reported studying photochemistry of polysaccharides with regard to the broad structural diversity, i.e. there is no information about the influence of the polysaccharide backbone on the photochemistry of a functional group. On the other hand, the results summarized in this review may provide a basis for further studies in the field of photoactive polysaccharides.

Acknowledgements

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References

AbdelRazik, E. A. (1997). Photoinduced graft copolymerization of ethyl acrylate, methyl methacrylate and methyl acrylate onto ethyl cellulose in homogeneous media. *Journal of Photochemistry and Photobiology A: Chemistry*, *107*, 271–274.

Albinsson, B., Li, S. M., Lundquist, K., & Stomberg, R. (1999). The origin of lignin fluorescence. *Journal of Molecular Structure*, *508*, 19–27.

Arai, K., & Kawabata, Y. (1995a). Changes in the sol–gel transformation behaviour ofazobenzene moiety-containing methylcellulose irradiated with UV light. *Macromolecular Rapid Communications*, *16*, 875–880.

Arai, K., & Kawabata, Y. (1995b). Preparation of triphenylcarbinol moiety-containing cellulose derivative and its properties. *Macromolecular Chemistry and Physics*, *196*, 2139–2147.

Arai, K., Ohyama, T., & Shitara, Y. (1997). Preparation of a spironaphthoxazine moiety-containing methyl cellulose and photoregulation of its properties. *Polymer Journal*, *29*, 780–783.

Arai, K., & Sano, S. (1994). Preparation of cellulose 2-methylstilbene-5-carboxylate and photoregulation of its properties. *Journal of Materials Chemistry*, *4*, 275–278.

Arai, K., Sano, S., & Satoh, H. (1992). Preparation of cellulose stilbene-4-carboxylate and its application to thin-layer chromatography. *Journal of Materials Chemistry*, *2*, 1257–1260.

Arai, K., & Satoh, H. (1992). Liquid crystalline phase-formation behavior of cellulose cinnamate. *Journal of Applied Polymer Science*, *45*, 387–390.

Arai, K., Shitara, Y., & Ohyama, T. (1996). Preparation of photochromic spiropyrans linked to methyl cellulose and photoregulation of their properties. *Journal of Materials Chemistry*, *6*, 11–14.

Arai, K., & Udagawa, H. (1988). Application of photoresponsive groups-containing cellulose as an adsorbent for thin layer chromatography. *Macromolecular Rapid Communications*, *9*, 797–800.

Atalla, R. H., & Nagel, S. C. (1972). Laser-induced fluorescence in cellulose. *Chemical Communications*, *19*, 1049–1050.

Barrett, C. J., ichi Mamiya, J., Yagerc, K. G., & Ikeda, T. (2007). Photo-mechanical effects in azobenzene-containing soft materials. *Soft Matter*, *3*, 1249–1261.

Beelik, A., & Hamilton, J. K. (1961). Ultraviolet irradiation of model compounds related to cellulose. *Journal of Organic Chemistry*, *26*, 5074–5080.

Behl, M., & Lendlein, A. (2007). Actively moving polymers. *Soft Matter*, *3*, 58–67.

Bendig, J., & Timpe, H.-J. (1991). Photostructuring. In H. Böttcher (Ed.), *Technical applications of photochemistry* (pp. 172–252). Leipzig: Deutscher Verlag für Grundstoffindustrie.

Bertelson, R. C. (1971). Photochromic processes involving heterocyclic cleavage. In G. H. Brown (Ed.), *Photochromism* (pp. 45–431). New York: Wiley-Interscience.

Bertelson, R. C. (1999). Spiropyrans. In J. C. Crano, & R. J. Guglielmetti (Eds.), *Organic photochromic and thermochromic compounds* (pp. 11–84). New York/London: Plenum Press.

Bertolini, A. C., Mestres, C., Raffi, J., Buleon, A., Lerner, D., & Colonna, P. (2001). Photodegradation of cassava and corn starches. *Journal of Agricultural and Food Chemistry*, *49*, 675–682.

Bhadani, S. N., & Gray, D. G. (1983). Cellulose-based liquid-crystalline polymers – esters of (hydroxypropyl) cellulose. *Molecular Crystals and Liquid Crystals*, *99*, 29–38.

Bikova, T., & Treimanis, A. (2004). UV-absorbance of oxidized xylan and monocarboxyl cellulose in alkaline solutions. *Carbohydrate Polymers*, *55*, 315–322.

Böttcher, H. (1991). Optical information recording. In H. Böttcher (Ed.), *Technical applications of photochemistry* (pp. 118–171). Leipzig: Deutscher Verlag für Grundstoffindustrie.

Böttcher, H., Bendig, J., Fox, M. A., Hopf, G., & Timpe, H.-J. (1991). *Technical applications of photochemistry*. Leipzig: Deutscher Verlag für Grundstoffindustrie.

Bohrn, R., Potthast, A., Rosenau, T., Sixta, H., & Kosma, P. (2005). Synthesis and testing of a novel fluorescence label for carboxyls in carbohydrates and cellulosics. *Synlett*, *20*, 3087–3090.

Bohrn, R., Potthast, A., Schiehser, S., Rosenau, T., Sixta, H., & Kosma, P. (2006). The FDAM method: Determination of carboxyl profiles in cellulosic materials by combining group-selective fluorescence labeling with GPC. *Biomacromolecules*, *7*, 1743–1750.

Bora, U., Sharma, P., Kannan, K., & Nahar, P. (2006). Photoreactive cellulose membrane – a novel matrix for covalent immobilization of biomolecules. *Journal of Biotechnology*, *126*, 220–229.

Bos, A. (1972). UV spectra of cellulose and some model compounds. *Journal of Applied Polymer Science*, *16*, 2567–2576.

Bragd, P. L., van Bekkum, H., & Besemer, A. C. (2004). Tempo-mediated oxidation of polysaccharides: Survey of methods and applications. *Topics in Catalysis*, *27*, 49–66.

Castellan, A., Ruggiero, R., Frollini, E., Ramos, L. A., & Chirat, C. (2007). Studies on fluorescence of cellulosics. *Holzforschung*, *61*, 504–508.

Castellan, A., Trichet, V., Pommier, J. C., Siohan, A., & Armagnacq, S. (1995). Photo and thermal-stability of totally chlorine-free softwood pulps studied by UV/vis diffuse-reflectance and fluorescence spectroscopy. *Journal of Pulp and Paper Science*, *21*, J291–J296.

Costa, I., Filip, D., Figueirinhas, J. L., & Godinho, M. H. (2007). New cellulose derivatives composites for electro-optical sensors. *Carbohydrate Polymers*, *68*, 159–165.

Day, D. F. (1998). Alginates. In D. L. Kaplan (Ed.), *Biopolymers from renewable resources* (pp. 119–143). Berlin: Springer.

de la Orden, M. U., & Urreaga, J. M. (2006). Photooxidation of cellulose treated with amino compounds. *Polymer Degradation and Stability*, *91*, 2053–2060.

DeBelder, A. N. (1996). Medical applications of dextran and its derivatives. In S. Dumitriu (Ed.), *Polysaccharides in medicinal applications* (pp. 505–524). New York: Marcel Dekker.

Decker, C., & Bendaikha, T. (1998). Interpenetrating polymer networks. ii. Sunlight-induced polymerization of multifunctional acrylates. *Journal of Applied Polymer Science*, *70*, 2269–2282.

Delville, J., Joly, C., Dole, P., & Bliard, C. (2002). Solid state photocrosslinked starch based films: A new family of homogeneous modified starches. *Carbohydrate Polymers*, *49*, 71–81.

Delville, J., Joly, C., Dole, P., & Bliard, C. (2003). Influence of photocrosslinking on the retrogradation of wheat starch based films. *Carbohydrate Polymers*, *53*, 373–381.

DeVries, H. (1951). Rotatory power and other optical properties of certain liquid crystals. *Acta Crystallographica*, *4*, 219–226.

Duran, N., Gomez, E., & Mansilla, H. (1987). Biomass photo-chemistry. A review and prospects. *Polymer Degradation and Stability*, *17*, 131–141.

Ebringerová, A., & Heinze, T. (2000). Xylan and xylan derivatives – biopolymers with valuable properties. 1. Naturally occurring xylans: Structures, isolation, procedure and properties. *Macromolecular Rapid Communications*, *21*, 542–556.

Edahiro, J. I., Sumaru, K., Takagi, T., Shinbo, T., & Kanamori, T. (2006). Photoresponse of an aqueous two-phase system composed of photochromic dextran. *Langmuir*, *22*, 5224–5226.

Esker, A. R., Grül, H., Wegner, G., Satija, S. K., & Han, C. C. (2001). Isotopic selectivity in ultrathin Langmuir–Blodgett membranes of a cross-linked cellulose derivative. *Langmuir*, *17*, 4688–4692.

Feringa, B. L. (2001). *Molecular switches*. Weinheim, Germany: Wiley-VCH.

Forsskahl, I., Tylli, H., & Olkkonen, C. (2000). Participation of carbohydrate-derived chromophores in the yellowing of high-yield and TCF pulps. *Journal of Pulp and Paper Science*, *26*, 245–249.

Frampton, M. J., Claridge, T. D. W., Latini, G., Brovelli, S., Cacialli, F., & Anderson, H. L. (2008). Amylose-wrapped luminescent conjugated polymers. *Chemical Communications*, *24*, 2797–2799.

Franck, A., & DeLeenheer, L. (2002). Inulin. In S. DeBaets, A. Steinbüchel, & E. J. Vandamme (Eds.), *Biopolymers–polysaccharides II* (pp. 439–480). Weinheim: Wiley.

Giavasis, I., Harvey, L. M., & McNeil, B. (2002). Scleroglucan. In S. DeBaets, A. Steinbüchel, & E. J. Vandamme (Eds.), *Biopolymers–polysaccharides II* (pp. 37–60). Weinheim: Wiley.

Greiner, A., Hou, H., Reuning, A., Thomas, A., Wendorff, J. H., & Zimmermann, S. (2003). Synthesis and opto-electronic properties of cholesteric cellulose esters. *Cellulose*, *10*, 37–52.

Griffiths, J. (1972). Photochemistry of azobenzene and its derivatives. *Chemical Society Reviews*, *1*, 481–493.

Guglielmetti, R. (2003). $4n+2$ systems: Spiropyrans. In H. Dürr, & H. Bouas-Laurent (Eds.), *Photochromism: Molecules and systems* (pp. 314–466). Amsterdam: Elsevier Science & Technology.

Heinze, T. (1998). New ionic polymers by cellulose functionalization. *Macromolecular Chemistry and Physics*, *199*, 2341–2364.

Heinze, T., Erler, U., Heinze, U., Camacho, J., Grummt, U.-W., & Klemm, D. (1995). Synthesis and characterization of photosensitive 4,4′-bis(dimethylamino)diphenyimethyl ethers of cellulose. *Macromolecular Chemistry and Physics*, *196*, 1937–1944.

Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, *26*, 1689–1762.

Heinze, T., Liebert, T., Heublein, B., & Hornig, S. (2006). Functional polymers based on dextran. *Advances in Polymer Science*, *205*, 199–291.

Heinze, T., Liebert, T., & Koschella, A. (2006). *Esterification of polysaccharides*. Heidelberg: Springer Verlag.

Holzer, W., Penzkofer, A., Redl, F., Lutz, M., & Daub, J. (2002). Excitation energy density dependent fluorescence behaviour of a regioselectively functionalized tetraphenylporphyrin–cellulose conjugate. *Chemical Physics*, *282*, 89–99.

Hornig, S., Biskup, C., Grafe, A., Wotschadlo, J., Liebert, T., Mohr, G. J., et al. (2008). Biocompatible fluorescent nanoparticles for pH-sensoring. *Soft Matter*, *4*, 1169–1172.

Hornig, S., & Heinze, T. (2007). Nanoscale structures of dextran esters. *Carbohydrate Polymers*, *68*, 280–286.

Hornig, S., Liebert, T., & Heinze, T. (2007). Structure design of multifunctional furoate and pyroglutamate esters of dextran by polymer-analogous reactions. *Macromolecular Bioscience*, *7*, 297–306.

Hou, H. Q., Reuning, A., Wendorff, J. H., & Greiner, A. (2000). Tuning of the pitch height of thermotropic cellulose esters. *Macromolecular Chemistry and Physics*, *201*, 2050–2054.

Hu, X., Zheng, P., Zhao, X., Li, L., Tam, K., & Gan, L. (2004). Preparation, characterization and novel photoregulated rheological properties of azobenzene functionalized cellulose derivatives and their α-CD complexes. *Polymer*, *45*, 6219–6225.

Irie, M. (1990). Photoresponsive polymers. *Advances in Polymer Science*, *94*, 27–67.

Jääskelainen, A. S., Toikka, K., Lahdetie, A., Liitia, T., & Vuorinen, T. (2009). Reactions of aromatic structures in brightness reversion of fully-bleached eucalyptus kraft pulps. *Holzforschung*, *63*, 278–281.

Kamath, M., Kincaid, J., & Mandal, B. K. (1996). Interpenetrating polymer networks of photocrosslinkable cellulose derivatives. *Journal of Applied Polymer Science*, *59*, 45–50.

Karakawa, M., Chikamatsu, M., Vakamoto, C., Maeda, Y., Kubota, S., & Yase, K. (2007). Organic light-emitting diode application of fluorescent cellulose as a natural polymer. *Macromolecular Chemistry and Physics*, *208*, 2000–2006.

Karakawa, M., Chikamatsu, M., Yoshida, Y., Azumi, R., Yase, K., & Nakamoto, C. (2007). Organic memory device based on carbazole-substituted cellulose. *Macromolecular Rapid Communications*, *28*, 1479–1484.

Klemm, D., Heublein, B., Fink, H.-P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie, International Edition*, *44*, 3358–3393.

Klemm, D., Schmauder, H.-P., & Heinze, T. (2002). Cellulose. In S. DeBaets, A. Steinbüchel, & E. J. Vandamme (Eds.), *Biopolymers–polysaccharides II* (pp. 275–320). Weinheim: Wiley.

Klemm, D., Schnabelrauch, M., & Stein, A. (1990). Modification of o-trialkylsilylcellulose with cinnamic acid-containing side chains. *Macromolecular Chemistry*, *191*, 2985–2991.

Kostic, M., Potthast, A., Rosenau, T., Kosma, P., & Sixta, H. (2006). A novel approach to determination of carbonyl groups in DMAc/LiCl-insoluble pulps by fluorescence labeling. *Cellulose*, *13*, 429–435.

Krainz, K., Potthast, A., Suess, U., Dietz, T., Nimmerfroh, N., & Rosenau, T. (2009). Effects of selected key chromophores on cellulose integrity upon bleaching 10(th) EWLP, Stockholm, Sweden, August 25–28, 2008. *Holzforschung*, *63*, 647–655.

Kumar, A. P., & Singh, R. P. (2008). Biocomposites of cellulose reinforced starch: Improvement of properties by photo-induced crosslinking. *Bioresource Technology*, *99*, 8803–8809.

Lai, Y.-Z. (1996). Reactivity and accessibility of cellulose, hemicelluloses, and lignins. In D. N.-S. Hon (Ed.), *Chemical modification of lignocellulosic materials* (pp. 35–96). New York: Marcel Dekker.

Lakowicz, J. R. (2006). *Principles of fluorescence spectroscopy*. Springer Science+Business Media, LLC.

Leathers, T. D. (2002). Dextran. In S. DeBaets, A. Steinbüchel, & E. J. Vandamme (Eds.), *Biopolymers–polysaccharides I* (pp. 299–346). Weinheim: Wiley.

Lee, M. H., Li, X. D., & Kim, E. (2000). Preparation of photochromic cellulose derivatives containing spirobenzopyran. *Molecular Crystals and Liquid Crystals*, *349*, 51–54.

Legnani, C., Vilani, C., Calil, V. L., Barud, H. S., Quirino, W. G., Achete, C. A., et al. (2008). Bacterial cellulose membrane as flexible substrate for organic light emitting devices. *Thin Solid Films*, *517*, 1016–1020.

Lewin, M. (1997). Oxidation and aging of cellulose. *Macromolecular Symposia*, *118*, 715–724.

Li, Z. X., Wang, L. G., & Huang, Y. (2007). Photoinduced graft copolymerization of polymer surfactants based on hydroxyethyl cellulose. *Journal of Photochemistry and Photobiology A: Chemistry*, *190*, 9–14.

Liebert, T., & Heinze, T. (2008). Interactions of ionic liquids with polysaccharides. 5. Solvents and reaction media for the modification of cellulose. *BioResources*, *3*, 576–601.

Liukko, S., Tasapuro, V., & Liitia, T. (2007). Fluorescence spectroscopy for chromophore studies on bleached kraft pulps. *Holzforschung*, *61*, 509–515.

Loureiro, P. E. G., Fernandes, A. J. S., Carvalho, M. G. V. S., & Evtuguin, D. V. (2010). The assessment of chromophores in bleached cellulosic pulps employing UV-Raman spectroscopy. *Carbohydrate Research*, *345*, 1442–1451.

Maier, H., Anderson, M., Karl, C., Magnuson, K., & Whistler, R. L. (1993). Guar, locust bean, tara, and fenugreek gums. In J. N. BeMiller, & R. L. Whistler (Eds.), *Industrial gums: Polysaccharides and their derivatives* (pp. 181–205). Academic Pr. Inc.

Malesic, J., Kolar, J., Strlic, M., Kocar, D., Fromageot, D., Lemaire, J., et al. (2005). Photo-induced degradation of cellulose. *Polymer Degradation and Stability*, *89*, 64–69.

Martin, S. R., & Schilstra, M. J. (2008). Circular dichroism and its application to the study of biomolecules: Vol. 1 In vitro techniques. *Biophysical Tools For Biologists*, *84*, 263–293.

Minsk, L. M., Smithw, J. G., Deusen, P. V., & Wright, J. F. (1959). Photosensitive polymers. i. Cinnamate esters of poly(viny1 alcohol) and cellulose. *Journal of Applied Polymer Science*, *2*, 302–307.

Müller, M., & Zentel, R. (2000). Cholesteric phases and films from cellulose derivatives. *Macromolecular Chemistry and Physics*, *201*, 2055–2063.

Murakami, H., Kawabuchi, A., Kotoo, K., Kunitake, M., & Nakashima, N. (1997). A light-driven molecular shuttle based on a rotaxane. *Journal of the American Chemical Society*, *119*, 7605–7606.

Nakata, M., Kawaguchi, T., Kodama, Y., & Konno, A. (1998). Characterization of curdlan in aqueous sodium hydroxide. *Polymer*, *39*, 1475–1481.

Natansohn, A., & Rochon, P. (1997). Azobenzene-containing polymers: Digital and holographic storage. *Photonic and Optoelectronic Polymers*, *672*, 236–250.

Nowakowska, M., Sterzel, M., Zapotoczny, S., & Kot, E. (2005). Photosensitized degradation of ethyl parathion pesticide in aqueous solution of anthracene modified photoactive dextran. *Applied Catalysis B: Environmental*, *57*, 1–8.

Nowakowska, M., Zapotoczny, S., Sterzel, M., & Kot, E. (2004). Novel water-soluble photosensitizers from dextrans. *Biomacromolecules*, *5*, 1009–1014.

Okahisa, Y., Yoshida, A., Miyaguchi, S., & Yano, H. (2009). Optically transparent wood-cellulose nanocomposite as a base substrate for flexible organic light-emitting diode displays. *Composites Science and Technology*, *69*, 1958–1961.

Olmstead, J. A., & Gray, D. G. (1997). Fluorescence spectroscopy of cellulose lignin and mechanical pulp: A review. *Journal of Pulp and Paper Science*, *23*, J571–J581.

O'Sullivan, A. C. (1997). Cellulose—The structure slowly unravels. *Cellulose*, *4*, 173–207.

Patnaik, S., Sharma, A. K., Garg, B. S., Gandhi, R. P., & Gupta, K. C. (2007). Photoregulation of drug release in azo-dextran nanogels. *International Journal of Pharmaceutics*, *342*, 184–193.

Philipp, B., Klemm, D., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). *Comprehensive cellulose chemistry* Weinheim: WILEY-VCH.

Pieroni, O., & Ciardelli, F. (1995). Photoresponsive polymeric materials. *Trends in Polymer Science*, *3*, 282–287.

Pieroni, O., Fissi, A., & Opova, G. (1998). Photochromic polypeptides. *Progress in Polymer Science*, *23*, 81–121.

Popoff, T., & Theander, O. (1976a). Formation of aromatic-compounds from carbohydrates. 3. Reaction of D-glucose and D-fructose in slightly acidic, aqueous-solution. *Acta Chemica Scandinavica B*, *30*, 397–402.

Popoff, T., & Theander, O. (1976b). Formation of aromatic-compounds from carbohydrates. 4. Chromosomes from reaction of hexuronic acids in slightly acidic, aqueous-solution. *Acta Chemica Scandinavica B*, *30*, 705–710.

Popoff, T., Theander, O., & Westerlund, E. (1978). Formation of aromatic-compounds from carbohydrates.6. Reaction of dihydroxyacetone in slightly acidic, aqueous-solution. *Acta Chemica Scandinavica B*, *32*, 1–7.

Potthast, A., Röhrling, A., Rosenau, T., Borgards, A., Sixta, H., & Kosma, P. (2003). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 3. Monitoring oxidative processes. *Biomacromolecules*, *4*, 743–749.

Radotic, K., Kalauzi, A., Djikanovic, D., Jeremic, M., Leblanc, R. M., & Cerovic, Z. G. (2006). Component analysis of the fluorescence spectra of a lignin model compound. *Journal of Photochemistry and Photobiology B*, *83*, 1–10.

Rau, U. (2002). Schizophyllan. In S. DeBaets, A. Steinbüchel, & E. J. Vandamme (Eds.), *Biopolymers–polysaccharides II, Vol. 6* (pp. 61–92). Weinheim: Wiley.

Redl, F. X., Lutz, M., & Daub, J. (2001). Chemistry of porphyrin-appended cellulose strands with a helical structure: Spectroscopy, electrochemistry, and in situ circular dichroism spectroelectrochemistry. *Chemistry-A European Journal*, *7*, 5350–5358.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Borgards, A., Sixta, H., et al. (2001). Synthesis and testing of a novel fluorescence label for carbonyls in carbohydrates and cellulosics. *Synlett*, 682–684.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Borgards, A., Sixta, H., et al. (2002). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 2. Validation and applications. *Biomacromolecules*, *3*, 969–975.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Ebner, G., Sixta, H., et al. (2002). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 1. Method development. *Biomacromolecules*, *3*, 959–968.

Rosenau, T., Potthast, A., Kosma, P., Suess, H. U., & Nimmerfroh, N. (2007). Isolation and identification of residual chromophores from aged bleached pulp samples. *Holzforschung*, *61*, 656–661.

Rosenau, T., Potthast, A., Milacher, W., Hofinger, A., & Kosma, P. (2004). Isolation and identification of residual chromophores in cellulosic materials. *Polymer*, *45*, 6437–6443.

Rusig, I., Godinho, M. H., Varichon, L., Sixou, P., Dedier, J., Filliatre, C., et al. (1994). Optical-properties of cholesteric (2-hydroxylpropyl) cellulose (HPC) esters. *Journal of Polymer Science Part B: Polymer Physics*, *32*, 1907–1914.

Sakakibara, K., & Nakatsubo, F. (2008a). Effect of fullerene on photocurrent performance of 6-o-porphyrin-2,3-di-o-stearoylcellulose Langmuir–Blodgett films. *Macromolecular Chemistry and Physics*, *209*, 1274–1281.

Sakakibara, K., & Nakatsubo, F. (2008b). Fabrication of anodic photocurrent generation systems by use of 6-o-dihydrophytylcellulose as a matrix or a scaffold of porphyrins. *Cellulose*, *15*, 825–835.

Sakakibara, K., Ogawa, Y., & Nakatsubo, F. (2007). First cellulose Langmuir–Blodgett films towards photocurrent generation systems. *Macromolecular Rapid Communications*, *28*, 1270–1275.

Schnabel, W. (2007). *Polymers and light*. Weinheim: Wiley-VCH.

Shingel, K. I. (2004). Current knowledge on biosynthesis, biological activity, and chemical modification of the exopolysaccharide, pullulan. *Carbohydrate Research*, *339*, 447–460.

Small, A. C., & Johnston, J. H. (2008). Novel hybrid materials of cellulose fibres and doped ZnS nanocrystals. *Current Applied Physics*, *8*, 512–515.

Swatloski, R. P., Rogers, R. D., & Holbrey, J. D., April 2003. Dissolution and processing of cellulose using ionic liquids WO 03/029329 a3, patent.

Tester, R. F., & Karkals, J. (2002). Starch. In S. DeBaets, A. Steinbüchel, & E. J. Vandamme (Eds.), *Biopolymers–polysaccharides II, Vol. 6* (pp. 381–438). Weinheim: Wiley.

Theander, O., & Westerlund, E. (1980). Formation of aromatic-compounds from carbohydrates. 8. Reaction of D-erythrose in slightly acidic, aqueous-solution. *Acta Chemica Scandinavica B*, *34*, 701–705.

Tseng, S. L., Valente, A., & Gray, D. G. (1981). Cholesteric liquid-crystalline phases based on (acetoxypropyl)cellulose. *Macromolecules*, *14*, 715–719.

Tylli, H., Forsskahl, I., & Olkkonen, C. (1993). A spectroscopic study of photoirradiated cellulose. *Journal of Photochemistry and Photobiology A: Chemistry*, *76*, 143–149.

Uragami, T., & Tokura, S. (2006). *Material science of chitin and chitosan*. Berlin: Springer.

Vekshin, N. (2002). *Photonics of biopolymers*. Berlin, Heidelberg: Springer Verlag.

Vikkula, A., Valkama, J., & Vuorinen, T. (2006). Formation of aromatic and other unsaturated end groups in carboxymethyl cellulose during hot alkaline treatment. *Cellulose*, *13*, 593–600.

Viswanathan, N. K., Kim, D. Y., Bian, S., Williams, J., Liu, W., Li, L., et al. (1999). Surface relief structures on azo polymer films. *Journal of Materials Chemistry*, *9*, 1941–1955.

Wach, R. A., Kudoh, H., Zhai, M. L., Muroya, Y., & Katsumura, Y. (2005). Laser flash photolysis of carboxymethylcellulose in an aqueous solution. *Journal of Polymer Science Part A: Polymer Chemistry*, *43*, 505–518.

Wang, W., & Wang, M.-Z. (2007). Effect of cyclodextrin on the photoisomerization of azobenzene functionalized hydroxypropyl methylcellulose in aqueous solution. *Polymer Bulletin*, *59*, 537–544.

Willner, I., & Rubin, S. (1996). Control of the structure and functions of biomaterials by light. *Angewandte Chemie, International Edition*, *35*, 367–385.

Wondraczek, H., & Heinze, T. (2008). Efficient synthesis and characterization of new photoactive dextran esters showing nanosphere formation. *Macromolecular Bioscience*, *8*, 606–614.

Woo, C. K., Schiewe, B., & Wegener, G. (2006). Multilayered assembly of cellulose derivatives as primer for surface modification by polymerization. *Macromolecular Chemistry and Physics*, *207*, 148–159.

Yager, K. G., & Barrett, C. J. (2006). Novel photo-switching using azobenzene functional materials. *Journal of Photochemistry and Photobiology A: Chemistry*, *182*, 250–261.

Yang, S., Jacob, M. M., Li, L., Cholli, A. L., Kumar, J., & Tripathy, S. K. (2001). Synthesis and characterization of novel azobezene-modified polymers: Azocellulose. *Macromolecules*, *34*, 9193–9196.

Yang, S., Jacob, M. M., Li, L., Yang, K., Cholli, A. L., Kumar, J., et al. (2002). Azobenzene modified cellulose. *Polymer News*, *27*, 368–372.

Yang, S. Z., Li, L., Cholli, A. L., Kumar, J., & Tripathy, S. K. (2001). Photoinduced surface relief gratings on azocellulose films. *Journal of Macromolecular Science Part A: Pure and Applied Chemistry*, *38*, 1345–1354.

Yashima, E., Noguchi, J., & Okamoto, Y. (1995). Photocontrolled chiral recognition by [4-(phenylazo)phenyl]carbamoylated cellulose and amylose membranes. *Macromolecules*, *28*, 8368–8374.

Zheng, P., Hu, X., Zhao, X., Li, L., Tam, K. C., & Gan, L. H. (2004). Photoregulated sol–gel transition of novel azobenzene-functionalized hydroxypropyl methylcellulose and its a-cyclodextrin complexes. *Macromolecular Rapid Communications*, *25*, 678–682.

Zhou, J., Ma, Y. H., Zhang, J., & Tong, J. (2009). Influence of surface photocrosslinking on properties of thermoplastic starch sheets. *Journal of Applied Polymer Science*, *112*, 99–106.

Zhou, J., Zhang, J., Ma, Y. H., & Tong, J. (2008). Surface photo-crosslinking of corn starch sheets. *Carbohydrate Polymers*, *74*, 405–410.