European Polymer Journal 46 (2010) 1688–1695

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Synthetic photocrosslinkable polysaccharide sulfates

Holger Wondraczek, Annett Pfeifer, Thomas Heinze *

Center of Excellence for Polysaccharide Research, Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University of Jena, Humboldstraße 10, D-07743 Jena, Germany

ARTICLE INFO

Article history:
Received 9 April 2010
Received in revised form 7 June 2010
Accepted 18 June 2010
Available online 23 June 2010

Keywords:
Biopolymers
Dextran
Pullulan
Photoactivity
Polysaccharide
Water solubility

ABSTRACT

Photoactive derivatives of dextran and pullulan with high degree of substitution were prepared by an efficient and mild esterification of the biopolymers with [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetic acid via *in situ* activation of the carboxylic acid with *N,N′*- carbonyldiimidazole. Subsequently, sulfation was carried out with the gentle and easily manageable SO_3/DMF complex as reagent. Thus, water soluble polyelectrolytes decorated with high amounts of photochemically active moieties were obtained. The structures of the novel polysaccharide esters and the polyelectrolytes were evaluated by means of NMR and IR spectroscopy. Moreover, the photochemistry of both the carboxylic acid esters and their sulfated derivatives was studied by means of UV–Vis spectroscopy in the dissolved state. The changes observed may be used to control the properties and are thus of interest in the design of smart materials.

1. Introduction

Light sensitive polymers provide the basis for very special materials and are employed in various quite different technical applications [1]. Some excellent review articles are published, dealing with various aspects of polymers showing light-induced conformational changes, photostimulated variations of viscosity and solubility, photocontrol of membrane functions, and photomechanical effects [2–7]. Moreover, fundamental light triggered biological processes, e.g., vision, photosynthesis, photomorphogenesis, and photomovement at various biological levels, are of great academic and practical interest [8,9].

Polysaccharides are unique biopolymers with an enormous structural diversity and functional versatility. Huge amounts of polysaccharides are formed biosynthetically by many organisms. Due to their extraordinary ability for structure formation by supramolecular interactions of variable types polysaccharides can be used to tailor advanced materials.

However, in contrast to the enormous interest regarding photoresponsive synthetic polymers, polypeptides, and proteins, the synthesis and characterization of photosensitive polysaccharide derivatives is discussed in literature very scarcely [10,11]. Mostly, photosensitive polysaccharide derivatives are reported that are decorated only with minor amounts of photoactive substituents (degree of substitution, DS, below 0.1) or in case of higher DS values they are soluble only in organic solvents.

In the context of our work to design smart polymers by chemical modification of polysaccharides, including polysaccharide-based nanoparticles, and polysaccharide polyelectrolytes, our interest is focused on photoactive biopolymer derivatives [11–14]. In the present work we describe the homogeneous preparation of highly functionalized photosensitive esters of dextran and pullulan containing [(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetic acid and sulfuric acid half ester moieties. Thus, water soluble derivatives are obtained, which might allow the photocontrol of solution properties or may be applied for self assembly onto various surfaces. The structure of the novel derivatives is studied by means of NMR and IR

* Corresponding author. Tel.: +49 3641 9 48270; fax: +49 3641 9 48272.
E-mail address: thomas.heinze@uni-jena.de (T. Heinze).
URL: http://www.chemie.uni-jena.de/institute/oc/heinze/ (T. Heinze).

0014-3057/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2010.06.005

spectroscopic techniques. Investigations of the photochemical behavior of the dissolved derivatives were studied as well.

2. Experimental

2.1. Materials

Dextran (Fluka) produced by *Leuconostoc mesenteroides* strain no. NRRL B-512(F) possesses a $\overline{M}_w$ of 54,400 g/mol and a $\overline{M}_n$ of 34,960 g/mol. Pullulan (Sigma) produced by *Aureobasidium pullulans* possesses a $\overline{M}_w$ of 137,000 g/mol and a $\overline{M}_n$ of 71,600 g/mol. Other chemicals were purchased from Aldrich and were used without further treatment. The reactions were carried out in the dark to avoid undefined photoreactions. [(4-Methyl-2-oxo-2H-chromen-7-yl) oxy]acetic acid was obtained according to the procedure described by Chimichi et al. [15]. Methyl bromoacetate was used instead of ethyl bromoacetate.

2.2. Measurements

NMR spectra were acquired on a Bruker Avance 400 MHz and Avance 600 MHz spectrometer with 16 scans for ^{1}H NMR (room temperature) and up to 200,000 scans for ^{13}C NMR (70 °C) applying 25 mg sample per mL for ^{1}H NMR and 100 mg sample per mL for ^{13}C NMR studies. FTIR spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer with the KBr technique. Elemental analyses were performed by CHNS 932 Analyzer (Leco). For UV–Vis studies a PerkinElmer λ 10 UV–Vis Spectrometer and quartz glass cuvettes were used. The relative viscosities were determined with an automatic Lauda PVS 1/2 viscometer equipped with a dilution Ubbelohde viscometer (capillary No. Ic, Schott Instruments, Mainz, Germany) in a thermostated water bath (Lauda E 200, Lauda-Königshofen, Germany) at 20 °C.

2.3. Photo irradiation

Irradiation was carried out using a HBO 200 mercury lamp with a metal interference filter (Zeiss 333 nm) for UV light with wavelength 350–310 nm and with a color filter (Zeiss UB-4) for visible light $\lambda > 400$ nm.

2.4. Synthesis

2.4.1. [(4-Methyl-2-oxo-2H-chromen-7-yl)oxy] acetates of dextran (**4a**–**f**) and pullulan (**4g**–**l**)

Dextran (**1**) and pullulan (**2**) were allowed to react with [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetic acid (**3**) according to the procedure described previously [11]. The synthesis were carried out applying different molar ratio of carboxylic acid and *N*,*N*-carbonyldiimidazole (CDI) to control the DS (Table 1). Analytical values for typical sample **4c**: IR (KBr): 3600–2900 (s, OH), 1721 (vs, C=O), 1615 (vs, C=O), 1100 (vs, C—O); ^{1}H NMR (250 MHz, DMSO-d6): δ = 7.39, 6.76 (CH arom), 6.00 (CH lacton), 4.79 (CH2 linkage), 2.16 (CH3); 5.6–3.5 (CH AGU and OH).

Table 1
Conditions and results of the esterification of dextran and pullulan with [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetic acid (**3**) via activation with *N*,*N*-carbonyldiimidazole (CDI) in dimethyl sulfoxide.

No.	Polysaccharide	Molar ratio			DS	
		AGU[a]	CDI	**3**	UV[b]	NMR[c]
4a	Dextran	1	0.125	0.125	0.12	0.11
4b	Dextran	1	0.250	0.250	0.25	0.25
4c	Dextran	1	0.375	0.375	0.38	0.38
4d	Dextran	1	0.500	0.500	0.47	0.48
4e	Dextran	1	0.750	0.750	0.71	0.69
4f	Dextran	1	1.000	1.000	0.90	0.93
4g	Pullulan	1	0.125	0.125	0.12	0.11
4h	Pullulan	1	0.250	0.250	0.19	0.21
4i	Pullulan	1	0.375	0.375	0.24	0.25
4j	Pullulan	1	0.500	0.500	0.37	0.37
4k	Pullulan	1	0.750	0.750	0.57	0.51
4l	Pullulan	1	1.000	1.000	0.74	0.76

[a] Anhydroglucose unit.
[b] Determined by means of ^{1}H NMR spectroscopy after perpropionylation.
[c] Determined by means of UV–Vis spectroscopy after perpropionylation.

2.4.2. Perpropionylation, general procedure

To determine the DS of the polysaccharide esters by means of ^{1}H NMR spectroscopy and to improve the solubility in typical UV–Vis-solvents, perpropionylation with propionic anhydride was carried out. IR (KBr): no ν (OH).

2.4.3. Sulfation of [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetates of dextran (**5a**–**f**) and pullulan (**5g**–**l**)

The polysaccharide esters (**4**) were dissolved in *N*,*N*-dimethylformamide (0.05 g/mL). After adding 2-methyl-2-butene as a proton scavenger and SO_3/DMF complex, the solution was allowed to react for 2 h at 30 °C under stirring. The reaction mixture was neutralized with a saturated aqueous $NaHCO_3$ solution and subsequently precipitated in ethanol. The product was purified via dialysis against water through a cellulose membrane (Spectra/Por®; MWCO = 3500 g/mol) and isolated by lyophilization.

3. Results and discussion

Dextran is a family of neutral, water soluble polysaccharides consisting of a α-(1 → 6) linked D-glucose main chain with varying branches. The content and type of branches depend on the origin and ranges from 3% to 50% [16]. In general branches may arise from α-(1 → 2), α-(1 → 3), and α-(1 → 4) glycosidic bonds [17]. The dextran (**1**) used in our studies originates from the most frequently used bacterial strain *Leuconostoc mesenteroides* NRRL B-512F. The α-(1 → 6) linked glucose main chain contains about 5% of randomly distributed α-(1 → 3) branches (Fig. 1). A detailed structure analysis of the dextran sample **1** was published recently [18,19].

Pullulan is also a neutral, water soluble polysaccharide produced extracellularly by certain strains of the polymorphic fungus *Aureobasidium pullulans* via the fermentation of sugars like maltose, xylose, arabinose, glucose, and sucrose. It is a non-branched glucan consisting of α-(1 → 6) linked maltotriosyl repeating units [20,21]. In the repeating unit three D-glucose moieties are joined by α-(1 → 4) linkages (Fig. 1).

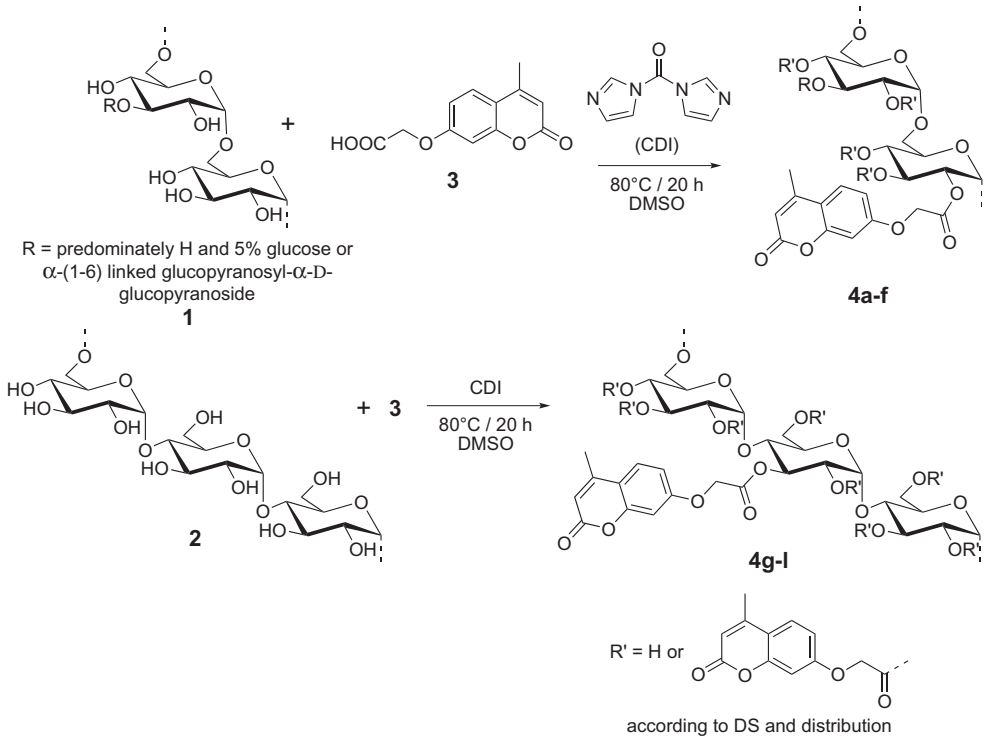

Fig. 1. Synthesis of dextran- and pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetates via *in situ* activation of the carboxylic acid with *N,N*-carbonyldiimidazole (CDI) in dimethyl sulfoxide (DMSO).

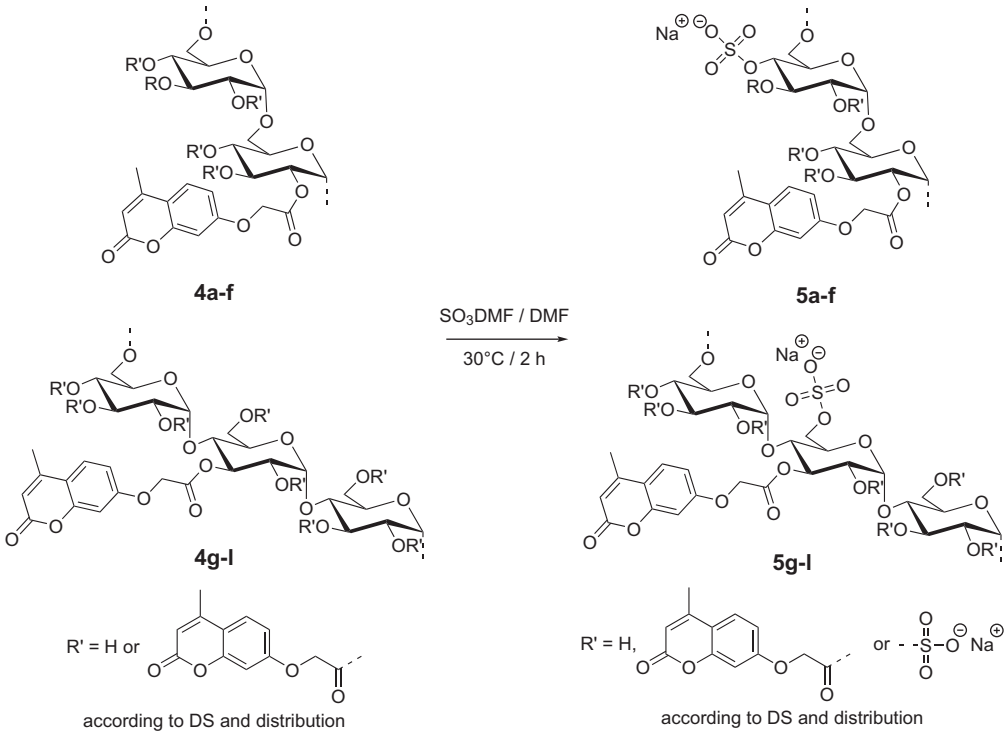

Fig. 2. Sulfation of pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetates with SO_3/DMF complex in *N,N*-dimethylformamide (DMF).

In our studies well defined dextran and pullulan (see 2.1) were used, due to the fact that the properties of polysaccharide derivatives are not only influenced by the functional group but also by the molar mass and molar mass distribution.

3.1. Esterification of dextran and pullulan with photoactive coumarin derivatives

Conventional esterification employs acyl chlorides and acid anhydrides. Novel acylation systems applying the carboxylic acid are required in order to overcome disadvantages like the poor solubility of the acyl chlorides in appropriate organic reaction media, the limited availability of the carboxylic acid anhydrides, and the formation of acidic by-products. The *in situ* activation of carboxylic acids by the coupling reagents known from peptide chemistry provides a valuable tool especially for the synthesis of unconventional polysaccharide derivatives with sensitive functional groups. In particular, *N*,*N*-carbonyldiimidazole (CDI) was found to be an efficient activating agent for acylation of polysaccharides in non-aqueous systems [24].

Different dextran- and pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetates **4** were prepared in a homogeneous one pot reaction using *in situ* activation of the photochemically active carboxylic acid **3** with CDI (Fig. 1). The functionalization of the hydroxyl groups of dextran and pullulan provides a hydrophobic material that could be easily dissolved in organic media. The DS can easily be adjusted by the molar ratio of the carboxylic acid/CDI to the anhydroglucose units (AGU, Table 1). The reaction of the dissolved polysaccharides **1** and **2** with [(4-methyl-2-oxo-2H-chromen-7-yl)oxy]acetic acid (**3**) in the presence of an equimolar amount of CDI yields the corresponding esters with DS values in the range from 0.11 to 0.90 (dextran) and from 0.11 to 0.75 (pullulan). The DS values indicate a different reactivity for dextran and pullulan. In case of the lowest molar ratio of AGU:CDI:**3** of 1:0.125:0.125 (sample **4a** and **g**), the carboxylic acid is converted quantitatively into the corresponding ester. With increasing molar ratio, the efficiency of conversion to the ester decreases to 90% for dextran and 75% for pullulan. These differences might be a result of both different molecular structures of the polymers and their different molar masses. However, in both cases the reaction yield achieved is very high for polymeranalogous conversions of polysaccharides.

The DS values were determined by ^{1}H NMR- and UV–Vis spectroscopy after perpropionylation of the polysaccharide ester. It is important to note that the DS values calculated based on the different methods agree very well. The novel polysaccharide esters are well soluble in DMSO, DMAc, and DMF. After perpropionylation (no *v*OH signal appears in the IR spectra), solubility in chloroform and acetonitrile appears additionally.

3.2. Sulfation of photoactive dextran- and pullulan esters

Several homogeneous and heterogeneous synthesis pathways for sulfation of polysaccharides have been developed [18]. The strongly acidic H^+ form of the sulfuric acid half ester must be converted to its sodium salt, to avoid the auto-catalytic hydrolysis of the ester moieties and chain degradation. A gentle method in order to produce well-defined polysaccharide sulfuric acid half esters is the application of SO_3 complexes of organic bases (e.g., pyridine) or aprotic dipolar solvents like DMF [13,22].

In the present work the easily manageable SO_3/DMF complex was applied as reagent and DMF as reaction media, which completely dissolves the polymer esters (Fig. 2). Moreover, 2-methyl-2-butene was added as a proton scavenger in order to prevent undesired polymer degradation. The DS was adjusted by varying the molar ratio of modified AGU to sulfating agent and thus the hydrophilic/hydrophobic balance of the polysaccharide esters was controlled (Table 2). Water soluble products were in the center of interest.

Table 2
Conditions and results of the sulfation of the [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetates (**4**) of dextran and pullulan with SO_3/DMF complex in *N*,*N*-dimethylformamide.

No.	Polysaccharide	Molar ratio		DS	
		4	SO_3/DMF	Coumarin[a]	SO_3Na[b]
5a1	Dextran	1	1	0.12	0.24
5a2	Dextran	1	2	0.12	0.53
5a3	Dextran	1	3	0.12	0.77
5b1	Dextran	1	1	0.25	0.47
5b2	Dextran	1	2	0.25	1.06
5b3	Dextran	1	3	0.25	1.20
5c1	Dextran	1	1	0.38	0.68
5c2	Dextran	1	2	0.38	0.87
5c3	Dextran	1	3	0.38	1.06
5d1	Dextran	1	1	0.47	0.29
5d2	Dextran	1	2	0.47	0.79
5d3	Dextran	1	3	0.47	0.82
5e1	Dextran	1	1	0.71	0.41
5e2	Dextran	1	2	0.71	0.54
5e3	Dextran	1	3	0.71	0.75
5f1	Dextran	1	1	0.91	0.69
5f2	Dextran	1	2	0.91	1.04
5f3	Dextran	1	3	0.91	1.11
5g1	Pullulan	1	1	0.12	0.50
5g2	Pullulan	1	2	0.12	1.00
5g3	Pullulan	1	3	0.12	1.40
5h1	Pullulan	1	1	0.20	0.42
5h2	Pullulan	1	2	0.20	0.84
5h3	Pullulan	1	3	0.20	1.37
5i1	Pullulan	1	1	0.25	0.59
5i2	Pullulan	1	2	0.25	1.15
5i3	Pullulan	1	3	0.25	1.27
5j1	Pullulan	1	1	0.37	0.45
5j2	Pullulan	1	2	0.37	1.11
5j3	Pullulan	1	3	0.37	1.38
5k1	Pullulan	1	1	0.54	0.44
5k2	Pullulan	1	2	0.54	1.02
5k3	Pullulan	1	3	0.54	1.35
5l1	Pullulan	1	1	0.75	0.39
5l2	Pullulan	1	2	0.75	1.55
5l3	Pullulan	1	3	0.75	1.34

[a] Determined by means of ^{1}H NMR and UV–Vis spectroscopy after perpropionylation (Table 1).
[b] Determined by means of elemental analysis.

3.3. Structure characterization of carboxylic acid esters and mixed carboxylic acid–sulfuric acid half esters of dextran and pullulan

The structure of the polysaccharide esters was studied by ^{1}H- and ^{13}C NMR spectroscopy. To eliminate intra-

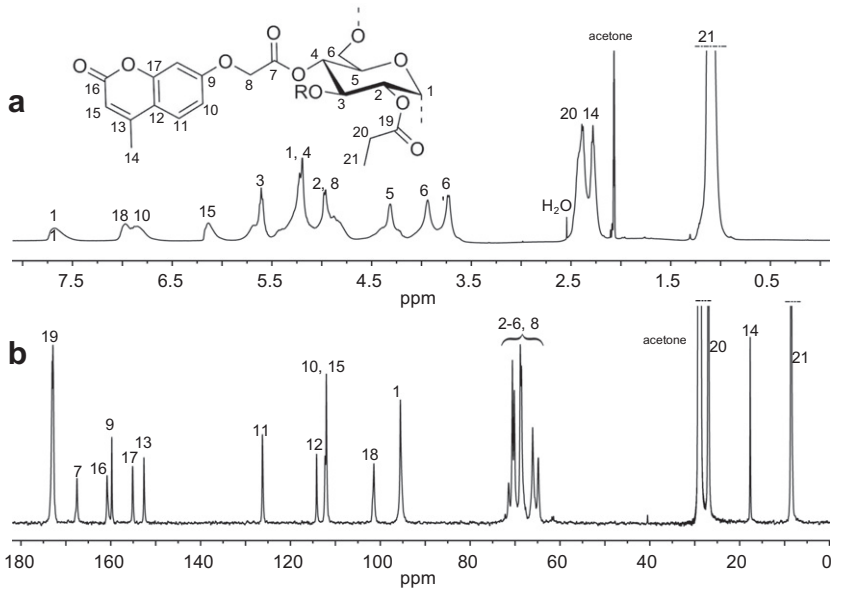

Fig. 3. ^{1}H NMR (a) and ^{13}C (b) NMR spectra of perpropionylated dextran [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**4c**, DS 0.38) both acquired in aceton-d6.

and intermolecular interactions of the polymer chains by hydrogen bonds and any overlap of the signals of the protons of the AGU and the hydroxyl groups, the remaining OH groups were perpropionylated. Thus, the completely modified polysaccharide esters were used for NMR studies in case of the samples **4a**–**l** that gave well resolved spectra.

Typical NMR spectra of perpropionylated dextran [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate are shown in Fig. 3. For sample **4c**, the proton resonances of the substituents appear at 7.6 (H11), 6.9 (H18), 6.8 (H10), 6.1 (H15), and 4.8 ppm (H8). The signal of the methyl group (H14) overlaps with the resonance of the methylene protons of the propionate moiety. Furthermore, the proton signals of the AGU are visible in the range from 3.7 to 5.7 ppm (Fig. 3a). The well resolved ^{13}C NMR spectrum (Fig. 3b) allows the assignment of the carbon atoms by comparison with spectra of both **3** and dextran propionate reported (spectra not shown). The NMR spectra prove the success of functionalization with the photoactive moiety. Moreover, the DS value could be calculated from the ^{1}H NMR spectrum out of the relation of the spectral integrals of the protons of the aromatic system (5.9–7.9 ppm) versus the CH_3 protons of the propionate moiety (1.0 ppm):

$$\mathrm{DS} = \frac{3 \cdot I_{\mathrm{H},10+11+15+18}}{4 \cdot \left(\frac{I_{\mathrm{H},10+11+15+18}}{4} + \frac{I_{\mathrm{H},21}}{3} \right)}$$

Fig. 4 shows the ^{13}C NMR spectra of pullulan (Fig. 4a), pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (Fig. 4b), and sulfated pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (Fig. 4c). Due to presence of 3 different AGU's of the repeating unit, the spectra show much more signals as those of the dextran samples. For a more detailed assignment of each signal of the pullulan spectrum, the reader is referred to literature [23]. However, the spectra reveal the success of both, the esterification with the photoactive moiety and the sulfation with the SO_3/DMF complex. In both spectra (Fig. 4b and c) the typical signals of the [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate moiety are visible indicating the covalent attachment via *in situ* activation with CDI and the stability of these ester moieties during sulfation. The sulfation is proved by the typical shift of the position 1 signals resulting from sulfation in position 2 [13]. Moreover, a larger line width could be noticed resulting from short lifetime of longitudinal and transversal magnetization; a typical phenomenon observed in polyelectrolytes caused by the electrostatic repulsion forces and thus a decrease in flexibility.

Fig. 5 shows the IR spectra of pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**4j**, DS 0.37, black) and its sulfated derivative (**5j3**, DS 0.37, DS_{SO_3Na} 1.38, gray). In both spectra the typical $\nu_{C=O}$ stretching is visible at about 1720 and 1610 cm^{-1}. The signal at 1720 cm^{-1} arise from the carbonyl group of the ester linkage of coumarin chromophore (C7 according to Fig. 3). The carbonyl group of the lactone like structure of the substituent (C16 according to Fig. 3) gives rise to the signal at 1610 cm^{-1}. These signals prove the presence of [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate moieties, which are covalently linked to the polymer backbone. A very strong signal is visible at about 1260 cm^{-1} in the spectrum of the sulfated derivative. This signal typically arises from the $\nu_{S=O}$ stretching of sulfate groups linked to polysaccharides [13].

3.4. Photochemical behavior of carboxylic acid esters and mixed carboxylic acid–sulfuric acid half esters of dextran and pullulan

The ultraviolet light-triggered photodimerization of coumarins has been studied since 1903 [25]. The reaction proceeds by a [2 + 2] cycloaddition of the ethylenic groups

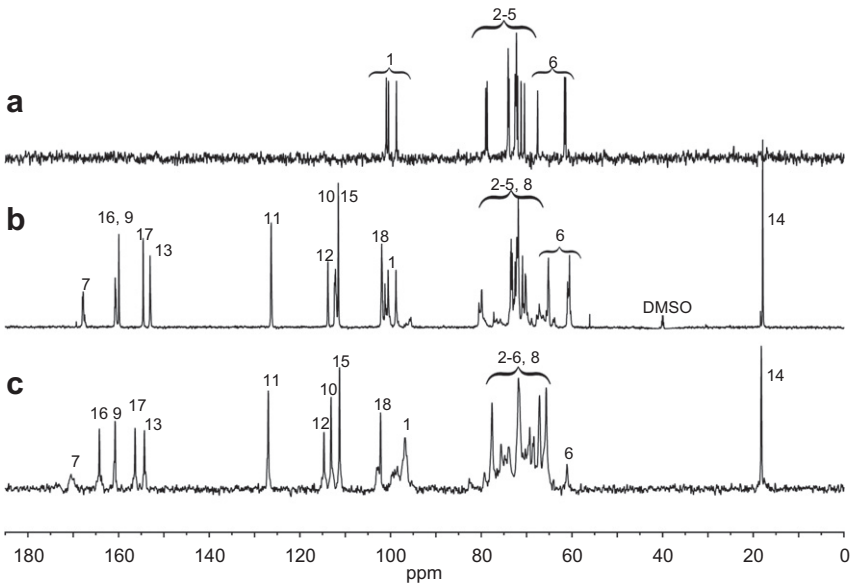

Fig. 4. ^{13}C NMR spectra of: (a) pullulan in D_2O, (b) pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**4j**, DS 0.37) in DMSO-d6, (c) sulfated pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**5j3**, DS 0.37, DS_{SO_3Na} 1.38) in deuterated water; numbering according to Fig. 3.

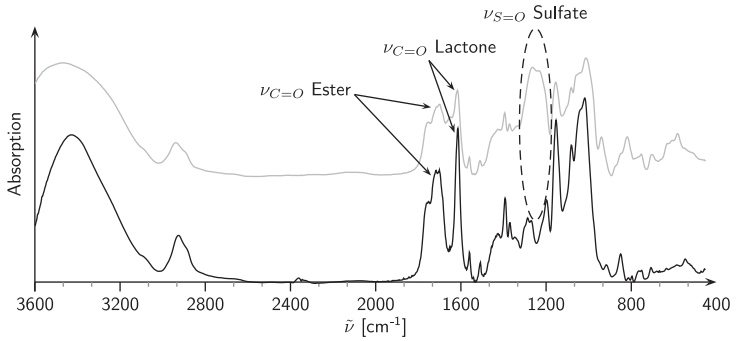

Fig. 5. IR spectra of pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**4j**, DS 0.37, dashed) and sulfated pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**5j3**, DS 0.37, DS_{SO_3Na} 1.38, solid).

[26]. Additionally to the photodimerization, a light induced photocleavage allows some dimers to revert to their original structure [27]. The application of these processes were intensively studied in the fields of polymer photochemistry [28]. The photochemical response of the polysaccharide esters **4a**–**l** and their sulfated derivatives **5a**–**l** was studied by means of UV–Vis spectroscopy. In case of **4a**–**l** the perpropionylated derivatives were used because of the limited solubility of the esters in solvents appropriate to photochemistry and UV–Vis spectroscopy at all relevant wavelengths (acetonitrile). In case of **5a**–**l** water was used as solvent. The photochemical behavior of one representative sample will be discussed in the following.

Fig. 6a shows the UV–Vis spectra of sample **4e** without (0 s) and after irradiation (10, 35, 70, 120 and 200 s). An intense absorption is visible in all spectra from 260 to 350 nm, which is assigned to the $\pi\pi^*$-transition of the coumarin chromophore. The excitation with UV light (333 nm) leads to the dimerization of the coumarin chromophores and thus a decrease of the absorption. After 4 min, a stationary state is reached and no further decrease could be observed. At 256 nm an isosbestic point appears indicating the uniformity of the reaction. The kinetics of the photoreaction were studied by analyzing the change of the absorption maximum at 316 nm. The graphical plot according to $k \cdot t = \frac{1}{A} - \frac{1}{A_0}$ (Fig. 6b) proves a second-order reaction kinetic as expected for a bimolecular dimerization. The dimers formed are thermally stable. However, irradiation at 254 nm leads to the photocleavage that is clearly indicated by the reverse effects in the UV–Vis spectra. Even the isosbestic point appears at 256 nm. The aqueous solution of the sulfated derivatives show the same absorption behavior and the same photochemical response.

Moreover, preliminary experiments about photocontrol of solution properties were carried out. The relative viscosity of a solution of sulfated pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**5j3**, DS 0.37, DS_{SO_3Na} 1.38, c = 1.5 mg/mL) in water was measured. Subsequently, the solution was irradiated with UV light (333 nm) for 10 min and the relative viscosity was

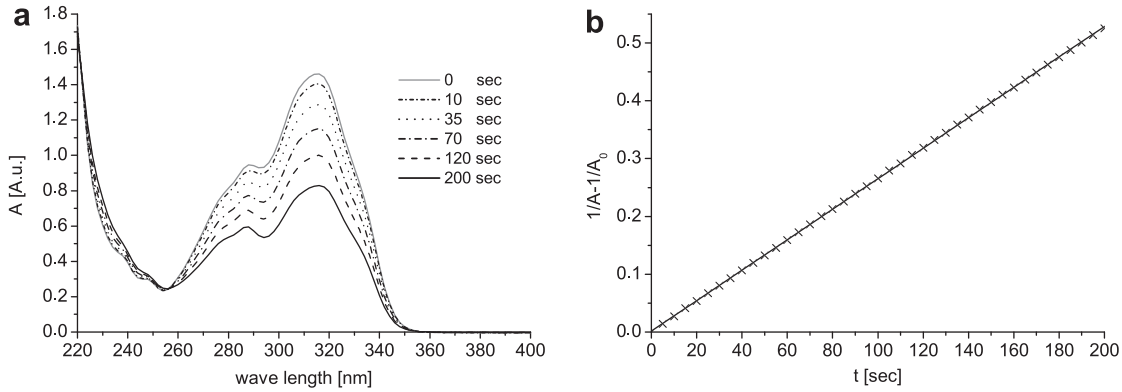

Fig. 6. (a) UV–Vis spectra of perpropionylated dextran [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate (**4e**, degree of substitution 0.70) recorded during the irradiation at 333 nm in acetonitrile. (b) UV–Vis spectroscopic analysis of the kinetics of the photoreaction; graphical analysis according to second-order reaction kinetics.

determined again. Interestingly, the relative viscosity decreases from 619 to 520 mL/g. Up to now it is difficult to give a definitive interpretation. We suppose that the crosslinking of the [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate moieties takes place within one polymer chain predominantly at this concentration. This may cause to a more compact polymer coil and thus a decrease of relative viscosity. However, the photocontrol of viscosity, including the dependency on concentration and the DS of both [(4-methyl-2-oxo-2H-chromen-7-yl)oxy] acetate- and sulfate moieties, is under investigation and will be reported elsewhere.

4. Conclusion

The preparation of water soluble photocrosslinkable dextran and pullulan derivatives was carried out efficiently by introduction of [(4-methyl-2-oxo-2Hchromen-7-yl)oxy] acetic acid via *in situ* activation with CDI homogeneously in DMSO and subsequent conversion with the easily manageable SO_3/DMF complex, as mild reagent for the sulfation. The structure of the novel biopolymer derivatives could be clearly described based on the NMR and IR spectra.

UV–Vis studies gave information about the photochemistry of dextran- and pullulan [(4-methyl-2-oxo-2H-chromen-7-yl)-oxy] acetates and their sulfated derivatives, indicating that the photoreaction typical for the low molecular weight chromophore appear with the polymer-bound chromophore as well. A detailed study about photocontrol of solution properties and the application of the sulfated derivatives for self assembly onto different surfaces is under investigation and will be reported elsewhere.

Acknowledgments

The financial support of the German Science Foundation (DFG, project HE 2054/11-1) is gratefully acknowledged. Th. H. thanks the "Fonds der Chemischen Industrie", Germany for general financial support.

References

[1] Schnabel W. Polymers and light. Weinheim: Wiley-VCH; 2007.
[2] Irie M. Photoresponsive polymers. Adv Polym Sci 1990;94:27–67.
[3] Pieroni O, Ciardelli F. Photoresponsive polymeric materials. Trends Polym Sci 1995;3:282–7.
[4] Pieroni O, Fissi A, Opova G. Photochromic polypeptides. Prog Polym Sci 1998;23:81–121.
[5] Viswanathan NK, Kim DY, Bian S, Williams J, Liu W, Li L, et al. Surface relief structures on azo polymer films. J Mater Chem 1999;9:1941–55.
[6] Behl M, Lendlein A. Actively moving polymers. Soft Matter 2007;3:58–67.
[7] Barrett CJ, ichi Mamiya J, Yagerc KG, Ikeda T. Photo-mechanical effects in azobenzene-coating soft materials. Soft Matter 2007;3:1249–61.
[8] Willner I, Rubin S. Control of the structure and functions of biomaterials by light. Angew Chem Int Ed 1996;35:367–85.
[9] Ercole F, Davis TP, Evans RA. Photo-responsive systems and biomaterials: photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond. Polym Chem 2010;1:37–54.
[10] Wondraczek H, Heinze T. Polysaccharides and Light. Carbohydr Polym, submitted for publication.
[11] Wondraczek H, Heinze T. Efficient synthesis and characterization of new photoactive dextran esters showing nanosphere formation. Macromol Biosci 2008;8:606–14.
[12] Heinze T. Hot topics in polysaccharide chemistry – selected examples. Macromol Symp 2009;280:15–27.
[13] Daus S, Heinze T. Xylan-based nanoparticles: Prodrugs for ibuprofen release. Macromol Biosci 2010;10:211–20.
[14] Gericke M, Liebert T, Heinze T. Polyelectrolyte synthesis and in situ complex formation in ionic liquids. J Am Chem Soc 2009;131:13220–1.
[15] Chimichi S, Boccalini M, Cosimelli B. A new concenient route to 2-oxoethoxycoumarins: key intermediates in the synthesis of natural products. Tetrahedron 2002;58:4851–8.
[16] DeBelder AN. In: Whistler RL, BeMiller JN, editors. Industrial Gums, Polysaccharides and their derivatives. San Diego: Academic Press; 1993. p. 399–425.
[17] Taylor C, Cheetham NWH, Walker GJ. Application of high-performance liquid-chromatography to a study of branching in dextrans. Carbohydr Res 1985;137:1–12.
[18] Heinze T, Liebert T, Heublein B, Hornig S. Functional polymers based on dextran. Adv Polym Sci 2006;205:199–291.
[19] Hornig S, Liebert T, Heinze T. Structure design of multifunctional furoate and pyroglutamate esters of dextran by polymer-analogous reactions. Macromol Biosci 2007;7:297–306.
[20] Leathers TD. In: Vandamme EJ, DeBaets SAS, editors. Biopolymers – Polysaccharides II, vol. 6. Weinheim: Wiley-VCH; 2002. p. 1–35.
[21] Spiridon I, Popa VI. In: Dumitriu S, editor. Polysaccharides structural diversity and functional versatility. New York: Marcel Dekker; 2005. p. 459.

[22] Gericke M, Liebert T, Heinze T. Interaction of ionic liquids with polysaccharides 8 – synthesis of cellulose sulfates suitable for polyelectrolyte complex formation. Macromol Biosci 2009;9:343–53.
[23] McLntyre DD, Vogel HJ. Structural studies of pullulan by magnetic resonance spectroscopy. Starch/Stärke 1993;45:406–10.
[24] Heinze T, Liebert T, Koschella A. Esterification of Polysaccharides. Heidelberg: Springer-Verlag; 2006.
[25] Ciamician G, Silber P. Chemische Lichtwirkungen. Ber Dtsch Chem Ges Berlin 1903;36:4266–72.
[26] Hoffman R, Wells P, Morrison H. Organic photochemistry 12: Further studies on mechanism of coumarin photodimerization – observation of an unusual heavy atom effect. J Org Chem 1971;36:102–8.
[27] Krauch CH, Farid S, Schenck GO. Photo-c4-cyclodimerisation von Cumarin. Chem Ber 1966;99:625–33.
[28] Trenor SR, Shultz AR, Love BJ, Long TE. Coumarins in polymers: From light harvesting to photo-cross-linkable tissue scaffolds. Chem Rev 2004;104:3059–78.