NEW WATER SOLUBLE POLYSACCHARIDE CROSSLINKERS: 
SYNTHESIS, VISCOMETRIC STUDIES ABOUT THE CROSSLINKING 
REACTION AND CHARACTERIZATION OF CROSSLINKED PRODUCTS

B. Heublein, G. Kühne, U. Heinze, T. Heinze, D. Klemm,
A. Nechwatal, M. Nicolai, K.-P. Mieck

a Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University of Jena, Humboldtstrasse 10, D-07743 Jena, Germany
b TITK e.V., Breitscheidstrasse 97, D-07407 Rudolstadt-Schwarza, Germany

The synthesis of new crosslinking agents based on divinyl sulfone is described. The crosslinking efficiency was determined by rheological measurements starting from aqueous solutions of hydroxyethyl cellulose. Moreover, the new agents can be used to reduce the fibrillability of Lyocell fibers as a result of the crosslinking reaction.

Keywords: divinyl sulfone derivatives, crosslinking, rheology, Lyocell fibers

Introduction

Besides its growing impact on the chemical fiber market, the amine oxide process, employing a melt of N-methyl-morpholine-N-oxide (NMMNO) as solvent for cellulose, is both a stimulus to research in cellulose structure formation from solution and a catalyst in getting people from fundamental and applied research together for joint effort [1]. It is well known that cellulotic fibers of the ,,Lyocell“ type, i.e., fibers spun from cellulose-NMMNO solutions, are provided with extraordinary clothing-physiological properties. However, they may posses a high wet fibrillation tendency which is undesired for textiles with good wash and wear properties [2].

There are different approaches for reducing the fibrillation tendency. On one hand, the variation in the spinning technology and, on the other, chemical modifications of the cellulotic fibers by crosslinking may be appropriate to improve the fiber quality. Crosslinking agents reinforce among other things the linkage between the crystalline ranges and hence the dimensional stability, which can be result in a reduced wet abrasion tendency. Numerous crosslinking agents, as for instance triacryloyl-hexahydro-1,3,5-triazine and N,N'-methylene-bisacrylamide, have been used [3]. Moreover, polyfunctional reactive dyestuff can also influence the fibrillability of NMMNO fibers [4, 5].

In our studies water soluble precursors of divinyl sulfone (DVS) derivatives with various spacers between the reactive vinyl moieties were synthesized and the influence of the molecular structure of these crosslinkers on the wet abrasion tendency of the treated cellulose fibers using wet abrasion number was investigated [6]. For characterization of the crosslinking efficiency, hydroxyethyl cellulose (HEC) was used as a model compound and the crosslinking reaction was evaluated by means of small-amplitude oscillatory measurements [7].

Materials and methods

Syntheses of the crosslinkers [8]. 1,6-bis(2-hydroxyethyl sulfanyl)-hexane (typical example for preparation of a crosslinker with aliphatic spacer groups). A solution of 0.5 mol of 2-mercaptoethanol and 0.25 mol of 1,6-bis-bromohexane in 50 ml ethanol was refluxed
under inert conditions, and 0.5 mol of KOH in 200 ml ethanol/water (50:1) was added within one hour. After two hours reaction time with stirring and cooling down to room temperature, the potassium bromide was filtered off, the filtrate was concentrated, washed with chloroform and dried over sodium sulfate. Yield: 74%, Fp = 102-105 °C. \(^1\)H-NMR (DMSO-d<sub>6</sub>): δ 3.8-3.2 (hydroxyethyl), 3.1-1.4 (hexane).

1,2-bis(2-hydroxyethylsulfanyl)-benzene ("aromatic crosslinker"). To a stirred solution of 0.038 mol of benzene-1,2-dithiol in 25 ml of aqueous NaOH (10%, w/v) 0.078 mol of 2-chloroethanol was added and stirred under reflux for 3 h. After cooling to room temperature, 15 ml of acetic acid ethylester was added, the organic phase was separated and concentrated under vacuum. Fp = 84-86 °C. \(^1\)H-NMR (DMSO-d<sub>6</sub>): δ 7.4-7.2 (aromatics), 4.98-3.0 (hydroxyethyl). For details of the synthesis procedure see ref. [6].

The oxidation of sulfanyl functions to sulfonyl groups with H<sub>2</sub>O<sub>2</sub> and the sulfation of the hydroxyl groups with SO<sub>3</sub>-DMF complex was carried out as described in ref. [7] yielding the corresponding disodium bissulfatoethyl sulfonyl derivatives.

Rheological measurements. To a solution of divinyl sulfone derivatives (4 x 10<sup>-5</sup> mol/2 ml), dissolved in water at 50 °C for 30 minutes under stirring, 1.5 x 10<sup>-4</sup> mol of hydroxyethyl cellulose (HEC; medium viscous) was added and cooled to room temperature. After addition of 0.16 ml of 10% (w/v) aqueous sodium hydroxide, the solution was transferred to the cone-plate system of the rheometer.

The crosslinking reaction of hydroxyethyl cellulose with an appropriate divinyl sulfone derivative under alkaline conditions at 25 °C was monitored by determination of the storage (G') and the loss (G'') modulus as well as the complex viscosity (η*) at a fixed frequency of 2.15 Hz and a deformation of 0.02 as a function of time. The reaction time was monitored from lye addition for 30 minutes.

An accurate temperature control (within ± 0.1 °C) was achieved with a Haake F6-C25 thermostat. A Haake controlled-stress rheometer (Rheo Stress 150) with air bearing was used to perform small-amplitude oscillatory measurements, using a cone-plate geometry (C60/1 Ti).

The reaction of the crosslinkers with Lyocell fibers according to the Foulard procedure (so-called Kalt-Klotz-Verweil-Verfahren) and the characterization of the obtained fibers by loop, elongation and tenacity strength were carried out as described in detail in ref. [9,10] and according to standard methods (DIN 53816). The wet abrasion number z<sub>n</sub> was determined by stressing the fiber on a rotating hollow shaft until the fiber breaks.

The \(^1\)H and \(^13\)C NMR spectra of synthesized crosslinkers were recorded on AC 200 and WP 200 SY spectrometers (Bruker).

The sulfur content of the fibers was determined by an elemental analyzer CHNS-936 (LECO).

**Results and discussion**

Lyocell fibers are characterized by extraordinary textile properties but also by a special fibrillation propensity caused by reduced cohesion of the fibrils in the water swollen state. It is known that the crease recovery and wash and wear properties of cellulose fibers and fabrics can be improved by crosslinking with divinyl sulfone [11, 12].

**Synthesis of new crosslinkers containing divinyl sulfone moieties.** As shown in Figure 1, in our study new water soluble precursors of divinyl sulfone derivatives with aliphatic (-CH<sub>2</sub>-, -C<sub>2</sub>H<sub>4</sub>-, -C<sub>6</sub>H<sub>12</sub>-) and aromatic (ortho- and meta-substituted) spacers were synthesized. For improving the water solubility, the precursors were converted into the corresponding disodium bissulfatoethyl sulfonyl derivatives (Table 1).

Addition of alkali to an aqueous solution of the disodium bissulfatoethyl sulfonyl derivatives leads to the formation of vinyl sulfone groups which react according to the well known Michael addition with activated hydroxyl functions of cellulose, e.g., forming stable crosslinks (see Figure 2).

By means of rheological measurements using hydroxyethyl cellulose as a water-soluble polymer it was revealed that the change of the elastic and viscous behavior may be used to evaluate the crosslinking efficiency of the new vinyl sulfone derivatives. A typical curve for a gel-like polymer established by crosslinking of hydroxyethyl cellulose with compound I, II or...
demonstrating the evolution of the storage modulus (G') and the loss modulus (G'') at constant frequency as a function of time is shown in Figure 3. The beginning of the crosslinking process is dominated by a viscous behavior of the system (G'' > G'). After a short reaction time (80 s in case of derivative II) the elastic behavior dominates (G' >> G''). Both moduli increase as a result of the growing junction zones density. However, the increase of the storage modulus is more sharp. Moreover, the slope of G' in dependence on the reaction time is much higher for aliphatic spacer groups of the DVS derivatives with increasing chain length, i.e., hexyl > ethyl > methyl. Within a reaction time of up to 30 minutes, the values of G' have a great variation covering about two orders of magnitude, whereas that of G'' was distinctly lower than one order.

### Table 1. Characterization of divinyl sulfone derivatives with various spacers (X-CH$_2$-CH$_2$-SO$_2$-spacer-SO$_2$-CH$_2$-CH$_2$-X).

<table>
<thead>
<tr>
<th>No.</th>
<th>Spacer</th>
<th>X = OH m. p. (°C)</th>
<th>X = SO$_2$Na MW (g/mol)</th>
<th>WS</th>
<th>-SO$_2$CH=CH$_2$ MW (g/mol)</th>
<th>distance $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CH$_2$</td>
<td>83</td>
<td>436</td>
<td>++</td>
<td>196</td>
<td>C(1)...C(7)</td>
</tr>
<tr>
<td>II</td>
<td>(CH$_2$)$_2$</td>
<td>114-115</td>
<td>450</td>
<td>+</td>
<td>210</td>
<td>C(1)...C(8)</td>
</tr>
<tr>
<td>III</td>
<td>CH$_2$</td>
<td>102 105</td>
<td>506</td>
<td>++</td>
<td>226</td>
<td>C(1)...C(12)</td>
</tr>
<tr>
<td>IV</td>
<td>meta-C$_6$H$_5$</td>
<td>106-108</td>
<td>498</td>
<td>++</td>
<td>258</td>
<td>C(1)...C(8)</td>
</tr>
<tr>
<td>V</td>
<td>meta-C$_6$H$_5$</td>
<td>108-110</td>
<td>498</td>
<td>++</td>
<td>258</td>
<td>C(1)...C(9)</td>
</tr>
</tbody>
</table>

$^a$ Water solubility: soluble in + hot and ++ cold water  
$^b$ Distance in nm between the divinyl sulfone moieties calculated by Cosmos [13]; divinyl sulfone C(1)...C(5), 0.373 nm

In contrast to these findings, in case of DVS derivatives with aromatic spacer groups (IV and V, Table 1) a significantly steeper rise of the storage modulus can be observed (Figure 4). Besides this, no G'-G'' cross-over is measurable because of an extremely fast crosslinking reaction as compared to the samples described above. That means that the very short period of viscous behavior is due to the described preparation conditions and cannot be detected further by oscillatory measurements. After a rapid increase of G' up to about 300 Pas the storage modulus keeps increasing slightly. It can be assumed that mainly within 150 s the formation of crosslinks takes place. In dependence on a drop of accessibility of reaction sites of HEC the crosslinking with the aromatic divinyl sulfone derivatives occurs then significantly slower. The graphical course of the complex viscosity ($\eta^*$) is similar to that of G' (Figure 5). This result can be traced back to the significant differences of G' and G'' values (G' >> G''). Because of that, the complex viscosity ($\eta^* = G''/(\omega^{1/2})$) is predominantly influenced by elastic behavior of the crosslinked polymers. However, no significant deviation in the crosslinking efficiency between the two DVS derivatives with aromatic spacer groups could be observed. The elastic behavior is independent of the position of the vinyl sulfone groups within the aromatic ring (ortho or meta). The reaction of the crosslinkers with Lyocell fibers using the Foulard procedure leads to fibers of a reduced fibrillability as indicated by a high wet abrasion number ($z_9$). Besides this reduction of fibrillability, other fiber properties like tenacity, loop and elongation strength decrease in
dependence on the concentration of DVS. The textile-physical parameters of Lyocell fibers crosslinked with DVS and with different bissulfatoethyl sulfonyl derivatives are summarized in Table 2. It is worth to mention that the crosslinkers with aromatic spacer groups exert a slightly stronger influence onto \( z_n \) than aliphatic ones. In comparison to the very significant differences in elastic behavior of HEC crosslinked starting from a homogeneous solution, the results of crosslinking Lyocell fibers under heterogeneous conditions indicate that the degree of crosslinking depends, besides structural and solubility reasons, also on the affinity of the crosslinking agent to the fibers.

**Figure 4.** Storage (\( G' \)) and loss (\( G'' \)) moduli of hydroxyethyl cellulose crosslinked with disodium bissulfatoethyl sulfonyl derivative with a \( m \)-phenylene spacer group in dependence on crosslinking time.

**Figure 5.** Storage modulus (\( G' \)) of hydroxyethyl cellulose crosslinked with divinyl sulfone derivatives I-V (see Table 1) as a function of reaction time.

**Table 2.** Fiber parameters of Lyocell crosslinked with divinyl sulfone (DVS) and different bissulfatoethyl sulfonoyl derivatives (crosslinker 20 g/l; 2 ml 4 % (w/v) aq. NaOH; 40 g/l \( Na_2SO_4 \); duration time 18 h at 22 °C).

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Wet abrasion no. ( z_n )</th>
<th>Tensile strength (cN/tex)</th>
<th>Loop strength (cN/tex)</th>
<th>Elong. strength (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>20</td>
<td>40</td>
<td>14</td>
<td>12 14</td>
</tr>
<tr>
<td>DVS ( a )</td>
<td>408</td>
<td>35.1</td>
<td>10.6</td>
<td>10.0</td>
</tr>
<tr>
<td>I</td>
<td>107</td>
<td>35.2</td>
<td>10.7</td>
<td>11.6</td>
</tr>
<tr>
<td>II</td>
<td>159</td>
<td>37.7</td>
<td>13.1</td>
<td>14.2</td>
</tr>
<tr>
<td>III</td>
<td>84</td>
<td>35.8</td>
<td>12.4</td>
<td>12.3</td>
</tr>
<tr>
<td>IV</td>
<td>240</td>
<td>34.1</td>
<td>11.5</td>
<td>10.5</td>
</tr>
<tr>
<td>V (1,3)</td>
<td>&gt; 386</td>
<td>31.1</td>
<td>8.7</td>
<td>9.2</td>
</tr>
</tbody>
</table>

\( a \) Concentration 10 g/l

**Conclusions**

New water soluble disodium bissulfatoethylsulfonyl derivatives with aliphatic (-\( CH_2 - \), -\( C_2H_4 - \), -\( C_6H_{12} - \)) and aromatic (\( ortho- \) and \( meta \)-substituted) spacers were synthesized which crosslink hydroxyl groups containing polymers (e.g., hydroxyethyl cellulose and cellulose fibers) under alkaline conditions via formation of the corresponding reactive divinyl sulfone derivatives. The influence of the molecular structure of the crosslinker on the efficiency of crosslinking reaction was investigated by means of small-amplitude oscillatory measurements. The slope of storage modulus (\( G' \)) of hydroxyethyl cellulose crosslinked with aliphatic disodium bissulfatoethylsulfonyl derivatives increased dependent on the chain length of the spacer (methyl < ethyl < hexyl). In case of aromatic spacer moieties a significant steeper rise of storage modulus and no \( G' - G'' \) cross-over can be observed. It is likely that this behavior is caused preferably by electronic factors, since only minor differences exist between aliphatic and aromatic spacer group distances.

The textile-physical properties of Lyocell fibers are improved by the treatment with the disodium bissulfatoethyl sulfonoyl derivatives. The fibrillability is reduced while other fiber properties remain almost unchanged.
aliphatic spacers ($n = 1, 2, 6$)

$$
2\text{HO-CH}_2\text{-CH}_2\text{-SH} + \text{Br-(CH}_2)_n\text{-Br} \xrightarrow{\text{NaOIl}} \text{HO-CH}_2\text{-CH}_2\text{-S-(CH}_2)_n\text{-S-CH}_2\text{-CH}_2\text{-OH}
$$

aromatic spacers (ortho-, meta-)

$$
2\text{HO-CH}_2\text{-CH}_2\text{-Cl} + \text{NaOH} \xrightarrow{} \text{HO-CH}_2\text{-CH}_2\text{-S-(spacer)-S-C}_2\text{H}_4\text{-OH}
$$

$$\text{H}_2\text{O}_2 \rightarrow \text{HO-C}_2\text{H}_4\text{-S-(spacer)-S-C}_2\text{H}_4\text{-OH}$$

1. $\text{SO}_2\text{-DMF}$
2. $\text{NaOH} \rightarrow \text{Na}_2\text{SO-C}_2\text{H}_4\text{-S-(spacer)-S-C}_2\text{H}_4\text{-OSO}_2\text{Na}$

Figure 1. Synthesis of water soluble precursors of divinyl sulfone derivatives.

$$\text{Na}_2\text{SO-C}_2\text{H}_4\text{-S-(spacer)-S-C}_2\text{H}_4\text{-OSO}_2\text{Na} \xrightarrow{\text{NaOH}} \text{CH}_2=\text{CH-S-(spacer)-S-CH=CH}_2$$

1. Cell-OR$\rightarrow$ Cell-O-H-O-C$_2$H$_4$-S-(spacer)-S-C$_2$H$_4$-O-R-O-Cell

Cell-OR =

R = H or C$_2$H$_6$OH

Figure 2. Reaction of vinyl sulfone derivatives with cellulose.

References


