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Efficient allylation of cellulose in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate

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Summary

The cellulose solvent dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) was successfully applied as reaction medium for the synthesis of allyl cellulose by conversion of the polymer with allyl chloride in the presence of solid NaOH. Samples with degree of substitution from 0.50 to 2.98 were accessible by varying the molar ratio anhydroglucose unit:allyl chloride:NaOH and reaction time. DMSO/TBAF was found to be an efficient reaction medium for the preparation of highly functionalized samples from spruce sulfite pulp with degree of polymerization of about 500 even in a scale of 50 g. The allyl cellulose samples were characterized by means of FTIR- and NMR spectroscopy. Size exclusion chromatography revealed negligible polymer degradation during synthesis and purification of the samples.

Introduction

Organo-soluble allyl cellulose is a promising biopolymer derivative that allows the design of novel products by various subsequent reactions of the double bonds. The heterogeneous allylation of mercerized cellulose with allyl bromide was described as early as 1929 [1]. Further studies on heterogeneous allylation lead to products with degree of substitution (DS) of up to 1.2 [2]. In a recent work, alkali cellulose was allowed to react with allyl chloride in isopropanol yielding allyl cellulose with DS 0.37 [3]. Alternatively, allyl cellulose of high DS could be obtained by treatment of cellulose acetate dissolved in dimethyl sulfoxide (DMSO) with sodium hydroxide powder and allyl chloride [4]. Tri-*O*-allyl cellulose was obtained after 4 h at 70°C applying 30 mol allyl chloride and sodium hydroxide per mole repeating unit, which is soluble in benzene, chloroform, tetrahydrofuran, and dichloromethane. The allylation of cellulose dissolved in the well-known solvent *N,N*-dimethylacetamide/LiCl was studied applying cellulose with a degree of polymerization (DP) of 172 and a large excess of 37 mol sodium hydroxide and 37 mol allyl chloride per mole repeating unit [5]. After a reaction time of 3 d at 50°C, highly functionalized allyl cellulose was obtained.

Recently, DMSO in combination with tetrabutylammonium fluoride trihydrate (TBAF) has proved to be an efficient cellulose solvent and reaction medium for the homogeneous acylation of the biopolymer [6]. Moreover, benzyl cellulose with DS as high as 1.27 was synthesized applying in DMSO/TBAF as reaction medium [7]. In the context of our own studies on the structure design of novel cellulose derivatives, DMSO/TBAF is applied for chemistry of the biopolymer starting from the dissolved state.

This paper reports about the efficient preparation of highly functionalized organo-soluble allyl cellulose starting from spruce sulfite pulp with comparably high DP of about 500 in DMSO/TBAF. The structure of the cellulose ether was studied in detail by NMR- and FTIR spectroscopy.

Experimental

Materials

Cellulose **1** (spruce sulfite pulp, degree of polymerization 504, 3.4% hemicellulose) was purchased from Fluka. Allyl chloride (Fluka), dimethyl sulfoxide (DMSO, Acros), and tetrabutylammonium fluoride trihydrate (TBAF, Fluka) were used as received.

Allylation of cellulose in DMSO/TBAF

Cellulose **1** (3.0 g, 0.019 mol) was slurried in 180 ml DMSO for 10 min at room temperature under argon. 36.0 g TBAF were added before increasing the temperature to 60°C. A pale yellow solution was obtained after stirring the mixture for 1 h. It was cooled to 50°C. 27.4 g (0.684 mol) NaOH were dispersed in 150 ml DMSO (Ultra Turrax) and added to the cellulose solution. 56.0 ml (0.684 mol) allyl chloride was added after 30 min under exclusion of light and stirring was continued for 3 d at 50°C. The polymer was precipitated in 400 ml water, filtered off, washed thrice with 400 ml aqueous $NaHCO_3$ solution (1%, w/v), and water until neutral reaction. After drying for 3 h at 50°C in vacuum, the product was Soxhlet-extracted with n-hexane for 16 h, dried in vacuum, approximately 50 mg hydroquinone was added, and stored at -20°C.
Yield: 4.53 g (93%, sample **2**).

Degree of substitution (DS): 2.50 (based on the elemental analysis after bromination of the double bonds).

FTIR (KBr, cm^{-1}): 3440 $\nu(OH)$, 3079 $\nu(=CH_2)$, 2908 $\nu(CH_2)$, 1458 $\delta(CH_2)$, 1357 $\delta(OH)$, 1647 $\nu(C=C)$, 995, 922 $\delta(C=C)$.

^1H NMR ($CDCl_3$, ppm): 4.43 (H-1), 3.11 (H-2), 3.23 (H-5), 3.32 (H-3), 3.83 (H-6, H-4), 3.70 (H-6), 4.02, 4.05, 4.20 (H-7), 5.91 (H-8), 5.24, 5.21, 5.10 (H-9).

^{13}C NMR ($CDCl_3$, ppm): 102.6 (C-1), 75.2 (C-5), 77.3 (C-4), 81.6 (C-2), 83.1 (C-3), 68.1 (C-6), 72.0, 74.0, 73.7 (C-7), 136.3, 135.4, 135.1 (C-8), 116.1, 115.9, 115.4 (C-9).

2 is soluble in chloroform and tetrahydrofuran.

Allylation of cellulose in DMSO/TBAF – scale up

A double-walled glass reactor equipped with a mechanical stirrer, reflux condenser, argon in- and outlet was covered with aluminium foil to exclude light. 50.0 g

(0.31 mol) cellulose **1** was dissolved in 750 ml DMSO and 150 g TBAF as described above. 247.0 g (6.17 mol) NaOH were dispersed in 500 ml DMSO and added to the cellulose solution at 50°C. After stirring the mixture for 30 min, 503.0 ml (6.17 mol) allyl chloride were added within 6 h. The reaction mixture was allowed to react for 2 d at 50°C under stirring. The polymer was precipitated with 2000 ml water, filtered off, washed thrice with 1000 ml aqueous $NaHCO_3$ (1%, w/v), four times with 1000 ml water, thrice with 800 ml methanol, and dried at 40°C in vacuum. It was stabilized with 200 mg hydroquinone and Soxhlet-extracted with n-hexane for 16 h, dried in vacuum, and stored at -20°C.
Yield: 78.5 g (94%, sample **16**)
DS: 2.7 (based on the elemental analysis after bromination of the double bonds).
^{1}H NMR spectrum ($CDCl_3$, ppm): 4.40 (H-1), 3.10 (H-2), 3.19 (H-5), 3.31 (H-3), 3.83 (H-4, H-6), 3.74 (H-6), 4.01, 4.18, 4.40 (H-7), 5.89 (H-8), 5.24, 5.17, 5.08 (H-9).
The product is soluble in chloroform and tetrahydrofuran.

Bromination of allyl cellulose, general procedure

300 mg of allyl cellulose were stirred in 10 ml chloroform for 24 h under exclusion of light. A freshly prepared solution of bromine in chloroform was added until a slight bromine excess remained in the mixture. After 2 h stirring at room temperature, the polymer was precipitated in 40 ml methanol. The collected product was washed twice with 40 ml aqueous sodium thiosulfate (10%, w/v), thrice with 40 ml water, thrice with methanol, and dried at 40°C in vacuum.

Measurements

FTIR spectra were acquired with a Nicolet Avatar 370 DTGS spectrometer using the KBr technique. NMR spectra were obtained with a Bruker Avance 400 NMR spectrometer collecting 16 scans for ^{1}H- and up to 65.000 scans for ^{13}C NMR spectra at temperatures of 25 and 60°C. Elemental analyses were performed on a Vario EL III device (Elementaranalysensysteme Hanau GmbH). The bromine content was determined after combustion and potentiometric titration according to [8]. A SEC-system from JASCO consisting of a pump 980, UV detector 975 working at $\lambda = 254$ nm, refractometer 930, polystyrene columns with the pore size 10^{-7}, 10^{-6}, and 10^{-4} m (Polymer Standards Service GmbH, Mainz, Germany) operating at 30°C with 0.1 ml/min THF as eluent was used.

Results and discussion

The conversion of cellulose dissolved in *N,N*-dimethylacetamide (DMA)/LiCl with 37 mol allyl chloride and sodium hydroxide per mole anhydroglucose unit (AGU) for 3 d at 50°C yields allyl cellulose with degree of substitution (DS) of about 3 [5]. Although DMA/LiCl is widely used in the homogeneous phase chemistry of cellulose, the dissolution process is time-consuming. The components (cellulose, DMA, LiCl) must be water-free and an activation of the cellulose is required. A novel non-derivatizing solvent, dimethyl sulfoxide (DMSO) in combination with tetrabutylammonium fluoride trihydrate (TBAF) is capable of dissolving cellulose without any pre-treatment within a short time. Moreover, the solution complex formed may influence the reactivity of the cellulose.

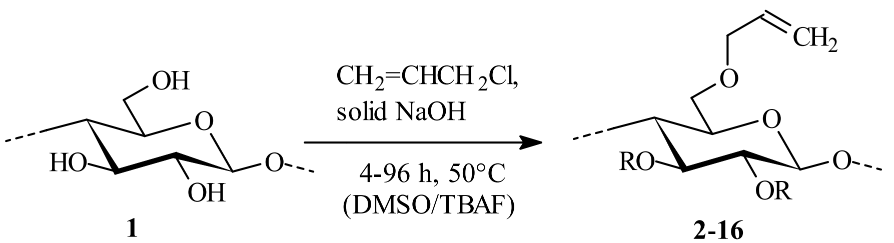
The cellulose (spruce sulfite pulp, degree of polymerization, DP, 504) could be dissolved in DMSO/TBAF at concentrations of 2 and 7% by adding TBAF (20%, w/v, related to DMSO) to a slurry of cellulose in DMSO followed by stirring for 1 h at 60°C. The addition of sodium hydroxide dispersed in DMSO causes a gelation of the mixture, which was allowed to react with allyl chloride at 50°C at different times (Figure 1). The polymer was isolated by a usual work-up procedure (precipitation in water, washing of the polymer with sodium hydrogencarbonate, water, and drying). Soxhlet extraction with n-hexane was applied to remove diallyl ether and other by-products. The products were stabilized with hydroquinone and stored at -20°C under argon.

The conversion of a 2% solution of cellulose with 19 mol allyl chloride in the presence of 22 mol NaOH yielded allyl cellulose with DS 2.50 after 72 h at 50°C (sample **3**). The increase of the molar ratio (AGU:allyl chloride:sodium hydroxide 1:37:37) did not changed the DS (DS 2.50, **2**), however, a soluble product is obtained. The increase of the sodium hydroxide amount (molar ratio 1:37:45) led to an insoluble product with increased DS of 2.80 (**4**).

Further etherification reactions were carried out starting with a 7% (w/v) solution of cellulose in DMSO/TBAF. The variation of the molar ratio AGU:allyl chloride:sodium hydroxide showed a distinct influence on the DS after 24 h reaction time (Table 1). The conversion of cellulose with 5 mol reagent per mole AGU yielded sample **5** with DS 0.50. Increase of the molar ratio to 1:10:10 resulted already in a significant higher DS of 2.84 (sample **6**). A further increase of DS was observed applying a molar ratio of 1:19:19 (DS 2.92, **7**) and 1:38:38 (2.96, **13**).

The influence of the reaction time was studied applying a molar ratio AGU:allyl chloride:sodium hydroxide of 1:38:38 at 50°C within a period from 4 to 96 h. The time course showed an increase of the DS from 0.50 after 4 h (**10**) to 2.20 after 16 h (**12**). The maximum DS (DS 2.96, sample **13**) was reached after a reaction time of 24 h. Compare also samples **8**, **14**, and **15** (Table 1). The slight decrease of the DS to 2.90 after 96 h reaction time (**15**) may be caused by side-reactions, e.g., cross-linking. Cross-linked moieties will not be included in the DS determination and, hence, a lower DS is calculated.

The solubility of the allyl celluloses was tested in tetrahydrofuran (THF) and chloroform (Table 2). Samples of comparably low DS were insoluble in both solvents. Samples with DS of 2.50 (**2**) dissolve in chloroform.



1

2-16

R = H or $CH_2CH=CH_2$
according to degree of
substitution

Figure 1. Allylation of cellulose dissolved in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF).

Prolongation of the reaction time is connected with increasing cross-linking and, hence, renders the polymers insoluble (**15**, DS 2.90, reaction time of 96 h). Not only the reaction time but also other conditions may lead to cross-linking and, hence, to insoluble products that appears in the case of sample **2** and **3**. Here, an excess of NaOH seems to be reasonable for forming an insoluble sample. This holds true for sample **4** and **8** as well while this effect is diminished starting with a high amount of cellulose (20 g versus 2-9 g). It can be concluded that the best conditions for the preparation of highly functionalized and soluble allyl cellulose in DMSO/TBAF is a molar ratio of AGU:allyl chloride:sodium hydroxide in the range from 1:19:19 (sample **7**, DS 2.92), 1:20:20 (sample **16**, DS 2.70) to 1:38:38 (sample **14**, DS 2.98) at a reaction time of 24-48 h.

The structure of the allyl cellulose was confirmed by means of FTIR- and NMR spectroscopy. The FTIR spectra of the allyl cellulose samples showed the typical absorption bands of the polymer backbone at 2908 cm^{-1} (ν CH), 1458 cm^{-1} (δ CH), 1092 cm^{-1} (ν C-O-C) (Figure 2). Moreover, the vibrations of the allyl group were detected at 3079 cm^{-1} (ν =C-H), 1647 cm^{-1} (ν C=C), as well as at 995 and 922 cm^{-1} (δ C=C).

The structure of the allyl cellulose was characterized by means of NMR spectroscopy including one- and two-dimensional methods. It must be pointed out that the complete peak assignment was possible even for samples with comparable high DP. The COSY- and HSQC/DEPT NMR spectra of sample **2** (DS 2.50) are shown in Figures 3 and 4.

Table 1. Conditions for and results of the conversion of cellulose dissolved in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate with allyl chloride in the presence of solid sodium hydroxide at 50°C.

Cellulose		Molar ratio[a]		Time (h)	Product		
Amout (g)	Concentration (%, w/v)	Allyl Cl	NaOH		Sample	Yield (%)	DS[b]
3.0	2	37	37	72	**2**	93	2.50
2.4	2	19	22	72	**3**	78	2.50
9.0	2	37	45	72	**4**	90	2.80
2.0	7	5	5	24	**5**	71	0.50
2.0	7	10	10	24	**6**	85	2.84
2.0	7	19	19	24	**7**	99	2.92
9.0	7	38	45	72	**8**	80	2.90
20.0	7	37	45	72	**9**	87	2.90
2.0	7	38	38	4	**10**	76	0.50
2.0	7	38	38	8	**11**	80	1.30
2.0	7	38	38	16	**12**	81	2.20
2.0	7	38	38	24	**13**	95	2.96
2.0	7	38	38	48	**14**	83	2.98
2.0	7	38	38	96	**15**	75	2.90
50.0	7	20	20	48	**16**	94	2.70

[a] Mol per mole anhydroglucose unit.

[b] Degree of substitution, DS, calculated from the halogen content after bromination of the allyl moieties.

Table 2. Solubility of allyl cellulose.

Sample	DS[a]	Solubility[b]	
		$CHCl_3$	Tetrahydrofuran
2	2.50	+	+
3	2.50	-	-
4	2.80	-	-
5	0.50	-	-
6	2.84	-	S
7	2.92	+	S
8	2.90	S	S
9	2.90	+	+
10	0.50	-	-
11	1.30	-	-
12	2.20	-	S
13	2.96	+	+
14	2.98	+	S
15	2.90	-	-
16	2.70	+	+

[a] See Table 1.
[b] Soluble (+), insoluble (-), swells (S).

The chemical shift of the methylene protons of the allyl moiety (position 7) is position sensitive, i.e., separate peaks are detected for allyl groups at position 6 and at position 2/3. However, an unambiguous assignment of position 2 and 3 is not possible due to overlapping of the corresponding peaks. Thus, cross-peaks assigned to position 7 appear in the chemical shift range from 4.0 to 4.5 ppm. At 4.4 ppm, the signal of the protons at position 1 and the methylene group of the allyl moiety (position 7) bound to the secondary OH groups are overlapped. The peak assignment for the ^{1}H- and ^{13}C NMR spectra of sample **2** is listed in Table 3. The ^{1}H- and ^{13}C NMR spectra of almost fully functionalized allyl cellulose with DS 2.92 (sample **7**) are shown in Figure 5.

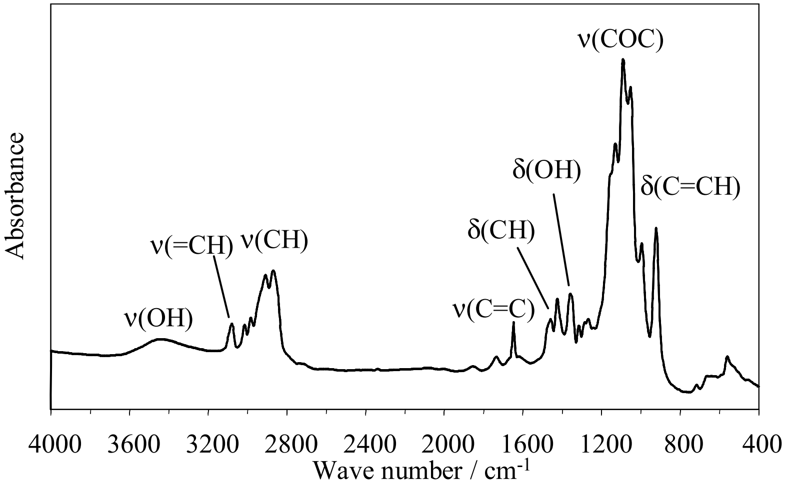


Figure 2. FTIR spectrum of allyl cellulose **2** (degree of substitution 2.50).

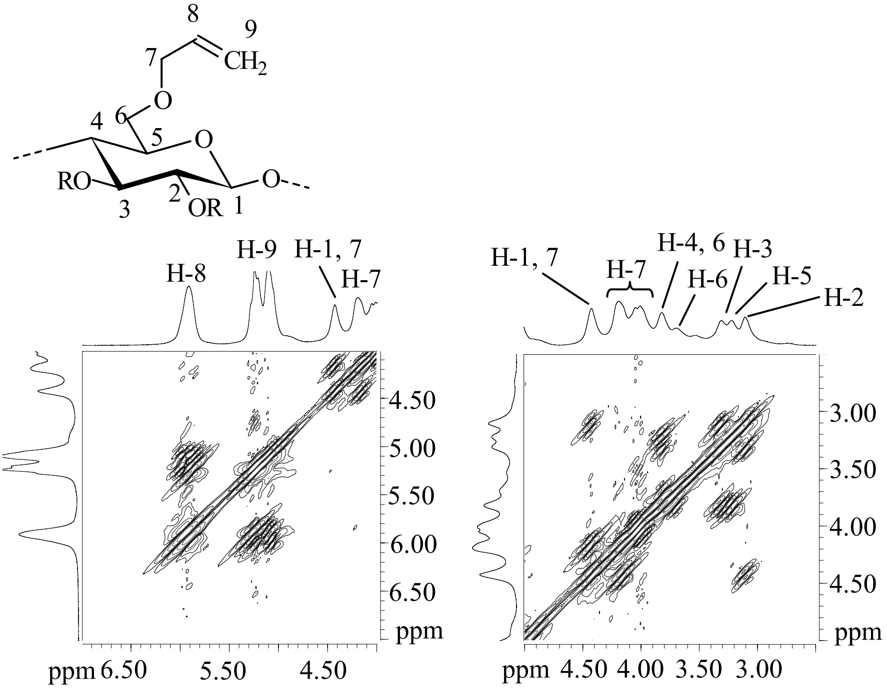


Figure 3. COSY NMR spectrum of allyl cellulose **2** (degree of substitution 2.50) recorded in $CDCl_3$.

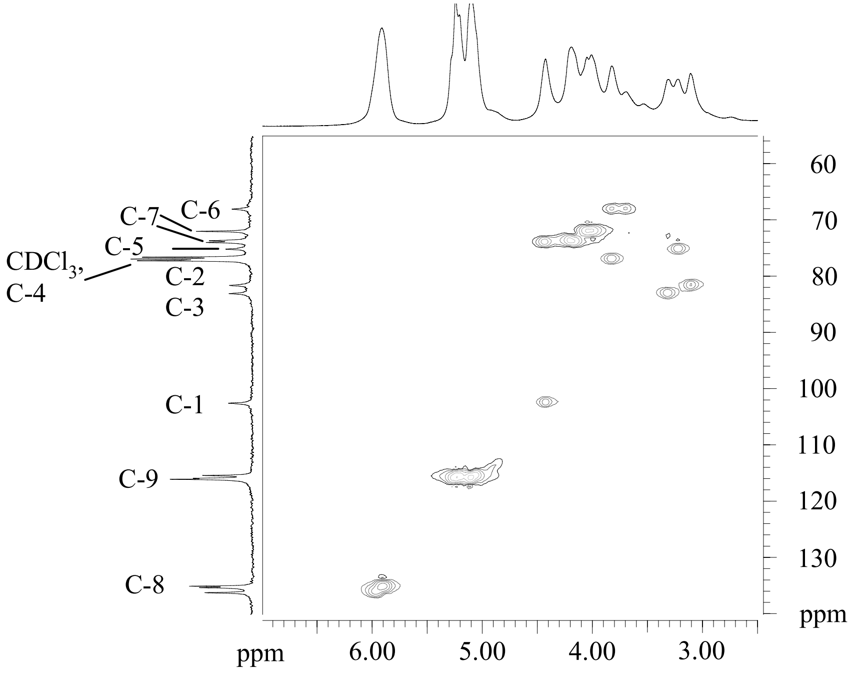
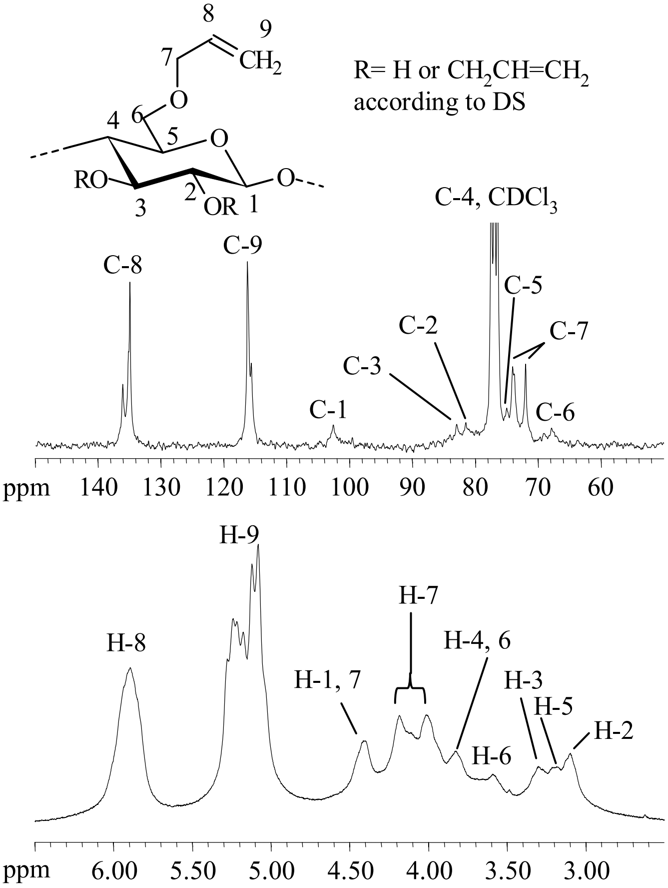


Figure 4. HSQC/DEPT NMR spectrum of allyl cellulose **2** (degree of substitution 2.50).

Table 3. Chemical shift of the NMR signals of allyl cellulose **2** (degree of substitution 2.50) measured in $CDCl_3$.

Signal of position*	Chemical shift (ppm)	
	^{1}H	^{13}C
1	4.4	103
2	3.05	82
3	3.3	83
4	3.8	77
5	3.2	75
6_α	3.7	68
6_β	3.8	68
7 (Position 2, 3)	4.4	74
7 (Position 2, 3)	4.2	74
7 (Position 6)	4.0	72
8	5.9	135
9	4.95-5.35	115-117

*Numbering of position see Figures 3 and 5.



R= H or $CH_2CH{=}CH_2$ according to DS

Figure 5. ^{1}H- (bottom) and ^{13}C NMR spectra (top) of allyl cellulose **7** (degree of substitution, DS, 2.92) recorded in $CDCl_3$.

Figure 6 shows the size exclusion chromatogram of allyl cellulose samples. The number average molar mass (M_n) of sample **2** of 1.0816 10^5 g/mol corresponds to a number average DP of 413. With respect to the initial DP of 504 of the starting cellulose, the polymer degradation during etherification and purification is comparatively low. A tendency of polymer aggregation could not be detected. The SEC of sample **7** was recorded after a storage time of 1 year in the dark and yielded a M_n of 3.743.600 g/mol indicating that remarkable aggregation occurred.

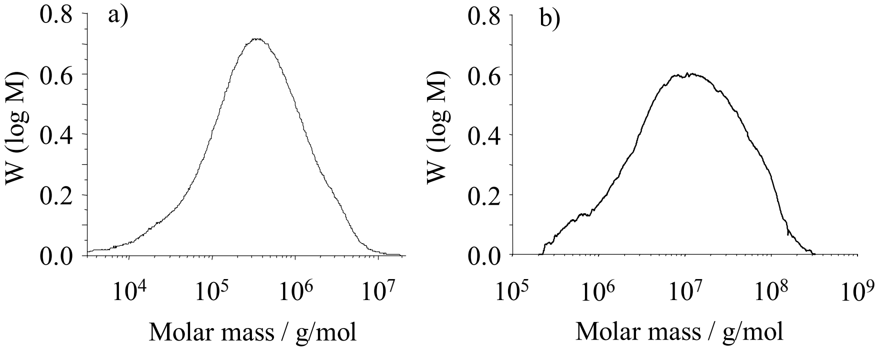


Figure 6. Size exclusion chromatogram of a) allyl cellulose **2** (degree of substitution, DS, 2.50) and b) sample **7** (DS 2.92) measured in $CHCl_3$.

Conclusions

Allyl cellulose of high DS could be efficiently synthesized starting from cellulose of high DP dissolved in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate. Optimized synthesis conditions enabled the preparation of organo-soluble allyl celluloses even in large scale of 50 g cellulose. The polymer degradation is rather low. The allyl cellulose will be included in studies to synthesize unconventional cellulose derivatives by the conversion of the double bonds.

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