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3-*O*-Propyl cellulose: cellulose ether with exceptionally low flocculation temperature

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Abstract The synthesis of 3-*O*-propyl cellulose with degree of substitution (DS) ranging from 0.19 to 1.02 was carried out via 2,6-di-*O*-thexyldimethylsilyl cellulose. The products were characterized by means of one- and two-dimensional NMR spectroscopy after peracetylation. The dissolution behavior of 3-mono-*O*-propyl cellulose in water was studied and compared with propyl cellulose derivatives having different degree of substitution and distribution of functional groups. Depending on the DS, exceptionally low flocculation temperatures between 15 and 23 °C were found for 3-*O*-propyl celluloses.

Keywords Regioselective synthesis · Structure–property-relationship · Cellulose ether · 3-*O*-Propyl celluloses · Reversible flocculation · NMR spectroscopy

Introduction

Because of their easy handling, low toxicity and properties like solubility in water or organic solvents, rheological and gelation behavior, and aggregation in solution etc., cellulose ethers are widely used for technical applications such as film formers, adhesives, stabilizers, detergents, thickeners for aqueous and organic solutions, as well as in the pharmaceutical, textile, and paper industries [1].

An important property of cellulose ethers is the ability to associate in aqueous solution upon heating reversibly, which is applied not only to purify the commercially produced products but also in food and pharmaceutical applications.

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This association is caused by different interactions and manifests in either gelling or flocculating [2, 3].

The cloud points of the different cellulose ethers differ from each other significantly. For instance, the flocculation temperature for methyl cellulose (MC) dissolved in water is in the range from 50 to 75 °C, for mixed ethers of MC such as hydroxyethylmethyl- and hydroxypropylmethyl cellulose between 60 and 90 °C [4].

The industrial production of cellulose ethers is carried out under heterogeneous conditions starting from alkali cellulose in a slurry process leading to products with a random distribution of the substituents both within the anhydroglucose unit and along the polymer chain. It has been recognized that not only the type of substituent, the degree of substitution (DS), the molar mass, and the polymer concentration but also the functionalization pattern within the anhydroglucose unit and along the polymer influence the cloud point temperature. Comparing the data for ethyl cellulose, there is a clear and amazing difference between the cloud points for 3-mono-*O*-ethyl cellulose (60 °C) and the randomly functionalized product (30 °C) [5]. In contrast, an aqueous solution of 3-mono-*O*-(2-methoxyethyl) cellulose does not show any flocculation at elevated temperature [6, 7]. On the contrary, 3-mono-*O*-butyl cellulose is insoluble in water. Thus, it was of interest to gain information about the interaction of the 3-*O*-propyl cellulose of different DS including the 3-mono-*O* derivative with water. Therefore, the synthesis and structure characterization of 3-*O*-propyl cellulose was carried out and the thermal behavior of aqueous solutions was investigated. The results will be compared with those of randomly functionalized propyl cellulose.

Experimental

Materials

Cellulose **1** (Avicel®, Fluka) and lithium chloride (Fluka) were dried for 3 h at 105 °C over potassium hydroxide in vacuum. 2,6-di-*O*-Thexyldimethylsilyl cellulose **2** was prepared according to reference [5]. Sodium hydride (Fluka) was used after washing of a 60% mineral oil suspension with dried *n*-hexane and *n*-pentane. *N,N*–Dimethyl acetamide (DMA, Fluka), tetrahydrofuran (THF, Aldrich) and pyridine (Fluka) were stored over molecular sieves. The phosphate buffer was prepared as described elsewhere [8]. All other chemicals were used as received.

2,6-di-*O*-Thexyldimethylsilyl-3-mono-*O*-propyl cellulose (**3a**)

Sodium hydride (4.58 g, 190.83 mmol, 5 mol/mol anhydroglucose unit, AGU) was carefully added to a solution of 17 g 2,6-di-*O*-thexyldimethylsilyl cellulose **2** (38.55 mmol) in 200 mL THF. After 30 min stirring at room temperature, 18.59 mL (191.38 mmol, 5 mol/mol AGU) 1-iodopropane were added dropwise under stirring. After conversion for 24 h at room temperature and 24 h at 50 °C, the same amount of both sodium hydride and 1-iodopropane (each 5 mol/mol AGU) were added. The mixture was allowed to react for additionally 3 days at 50 °C under stirring. After cooling to room temperature, 10 mL 2-propanol and additionally 10 mL water were added to destroy the excess of NaH. The reaction mixture was poured into 1 L phosphate buffer. The precipitate was separated, washed three times with water and twice with ethanol (each 500 mL) and dried in vacuum at 100 °C.

Yield: 14 g

IR (KBr, cm^{-1}): 2960, 2876 $\nu(C–H)_{saturated}$; 1466, 1377 $\delta(CH_3)$, $\delta(CH_2)$; 1253 ν(Si–C); 1116, 1087, 1039 $\nu(C–O–C_{AGU})$; 826, 779 ν(Si–C).

3-*O*-Propyl cellulose (**4a**)

13.6 g 2,6-di-*O*-thexyldimethylsilyl-3-mono-*O*-propyl cellulose **3a** (28.27 mmol) were dissolved in 150 mL THF. Tetra-*n*-butyl-ammoniumfluoride trihydrate (35.17 g, 111.47 mmol, 4 mol/mol AGU) were added. After stirring for 24 h at 50 °C, the reaction mixture was precipitated in 500 mL 2-propanol, the precipitate was filtered off and re-dissolved (non-dried) in 70 mL dimethyl sulfoxide (DMSO). After addition of 12 g tetra-*n*-butyl-ammoniumfluoride trihydrate (38.03 mmol), the mixture was treated for 24 h at 50 °C under stirring. After precipitation in 500 mL 2-propanol, the product was isolated and washed four times with 2-propanol and finally dried in vacuum at 100 °C.

Yield: 3.7 g

Degree of substitution, DS: 0.95 (determined by ^{1}H-NMR spectroscopy after peracetylation).

IR (KBr, cm^{-1}): 3439 ν(OH), 2965, 2933, 2880 ν(CH); 1627 $\nu(H_2O)$; 1461 $\delta(CH_2, CH_3)$; 1375 $\delta(CH_3)$; 1157, 1068 $\nu(C–O–C_{AGU})$.

2,6-di-*O*-Acetyl-3-mono-*O*-propyl cellulose (**5a**)

250 mg of 3-*O*-propyl cellulose **4a** were dissolved in 5 mL pyridine. After the addition of 5 mL acetic anhydride and a spatula tip of *N,N*-dimethylaminopyridine, the reaction mixture was allowed to react for 24 h at 80 °C under stirring. After cooling down, the product was precipitated in 50 mL ethanol, filtered off, washed five times with ethanol (each 30 mL) and dried in vacuum at 100 °C.

^{1}H-NMR ($CDCl_3$, ppm): 0.80 (CH_3 Propyl), 1.42 (CH_2 Propyl), 2.05 (CH_3 Acetate), 2.97–5.03 (AGU-Protons, CH_2 Propyl).

^{13}C-NMR ($CDCl_3$, ppm): 10.3, 10.7 (CH_3 Propyl); 20.7 (CH_3 Acetate); 23.1 (CH_2 Propyl); 62.4 (C-6 Acetate); 72.9, 73.1, 77.5, 80.7 (C-2 to C-5); 74.3, 74.7 (CH_2 Propyl); 100.8, 102.4 (C-1); 169.2, 170.3 (C=O).

IR (KBr, cm^{-1}): 2968, 2940, 2879 $\nu(C–H)_{saturated}$; 1751 ν(C=O); 1463, 1435, 1375 $\delta(CH_3)$, $\delta(CH_2)$; 1231, 1043 $\nu(C–O–C_{AGU})$

Propyl cellulose (**6b**, according to [9])

Microcrystalline cellulose (2.1 g, 12.95 mmol, Avicel®) was suspended in 60 mL DMA and stirred for 2 h at 120 °C. After cooling to ca. 80 °C, 3.6 g dried LiCl were added and the mixture was allowed to cool to room temperature (r.t.) under stirring over night. Freshly ground NaOH powder (6.17 g, 154.26 mmol, 12.5 mol/mol AGU) was dispersed in the clear cellulose solution under argon atmosphere and stirred for 1 h at r.t. The addition of the 1-iodopropane (total amount 12.05 mL, 124.05 mmol, 10 mol/mol AGU) was carried out in four portions. At first, 2/3 of the total amount of 1-iodopropane were added. After 2 h stirring at r.t., 1/9 of the total amount of 1-iodopropane were added. The following two portions of the alkylating agent (1/9 of the total amount each) were added after 1 and 2 h. The temperature was subsequently increased to 70 °C and maintained for 18 h under stirring. The product was precipitated in a methanol/water mixture (80/20, v/v), neutralized with acetic acid, filtered off, washed four times with methanol, and dried in vacuum.

Yield: 1.81 g

NMR data after peracetylation of **6b** (compound **7b**):

^{1}H-NMR ($CDCl_3$, ppm): 0.87 (CH_3 Propyl), 1.54 (CH_2 Propyl), 1.93–2.11 (CH_3 Acetate), 2.96–5.05 (AGU-Protons, CH_2 Propyl).

^{13}C-NMR ($CDCl_3$, ppm): 10.5, 10.8 (CH_3 Propyl); 20.4, 20.6 (CH_3 Acetate); 22.9, 23.1, 23.4 (CH_2 Propyl); 62.1 (C-6 Acetate); 67.6 (C-6 s); 72, 72.6, 72.9, 76.4 (C-2 to C-5); 75.3 (CH_2 Propyl); 100.4, 102.5 (C-1); 169.2, 169.6, 170.1 (C=O).

Measurements

NMR spectra were acquired with Bruker Avance 250 (250 MHz) and Avance 400 (400 MHz) spectrometers in $CDCl_3$ (sample concentration 2–8%) using standard pulse sequences for one- (^{1}H, ^{13}C) and two-dimensional (COSY) NMR spectra.

FTIR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer using the KBr technique.

Temperature-dependent phase separation measurements were conducted with a turbidimetric photometer TEPPER Analytik (Germany, $\lambda = 670$ nm) by heating the aqueous solutions of propyl cellulose (1%, w/w) from 5 to 49 °C and cooling to 5 °C with a temperature ramp of 1 °C/min. The transmittance at the initial temperature was set to 100%. The flocculation temperature was estimated by applying the tangents to the turbidity curves of the samples (heating curves) and determination of the temperature at the intersection point.

The DS_{Propyl} was calculated from the ^{1}H-NMR spectra of the peracetylated propyl celluloses (Eq. 1).

$$DS_{Propyl} = 3 - \frac{13}{\frac{I_{AGU}}{I_{Ac}} \cdot 3 + 2} \qquad (1)$$

I_{AGU} Integral of the anhydroglucose unit signals from 2.97 to 5.03 ppm
I_{Ac} Integral of the acetyl signal at 2.05 ppm

A JASCO SEC system was applied consisting of a degasser DG 980-50, pump PU 980, UV detector 975 (λ 354 nm), refractive index detector 930, column oven, and guard column. Chloroform with a flow rate of 1 mL/min was chosen as eluent. Separation was carried out using three SDV-Gel columns (10^6, 10^4, and 10^3 A, Polymer Standards Service, Mainz, Germany) at 30 °C.

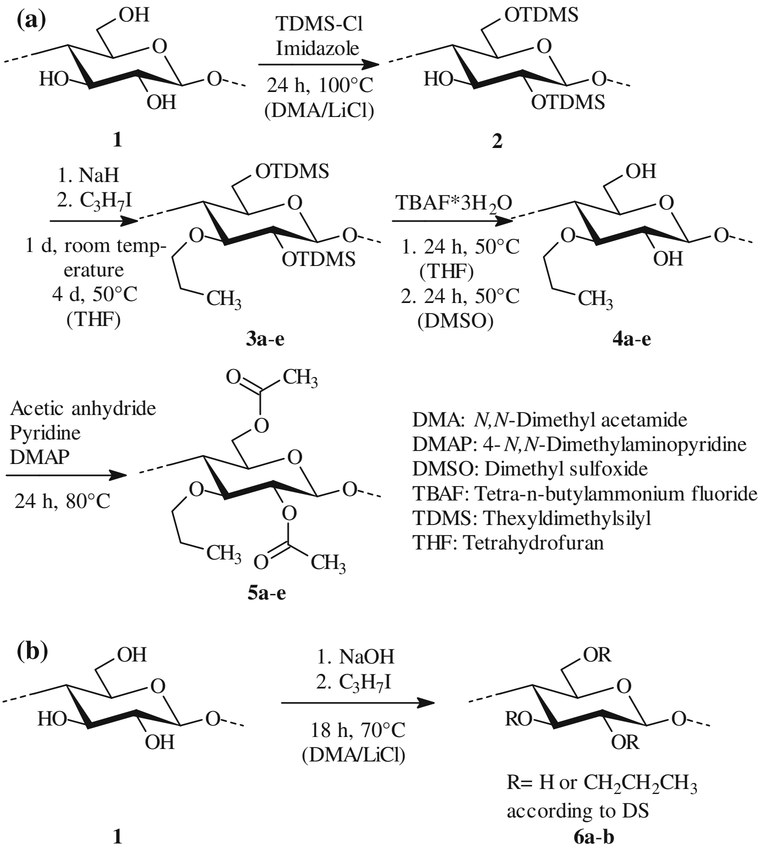
Results and discussion

3-*O*-propyl cellulose **4a**–**4e** was prepared via 2,6-di-*O*-thexyldimethylsilyl (TDMS) cellulose (sample **2**, degree of substitution of TDMS groups, DS_{Si} 1.95) by alkylation of position 3 with 1-iodopropane in the presence of sodium hydride and subsequent desilylation (Scheme 1a). The conditions of the alkylation were varied to facilitate different DS values (Table 1). Due to the hydroxyl groups at position 2 and 6 leading to both intra- and intermolecular interactions, the resolution of the NMR spectra is reduced as usually found for cellulose derivatives with a DS $<$ 3. In order to improve the resolution of the NMR spectra, the products were peracetylated.

The ^{1}H/^{1}H-COSY-NMR spectrum of sample **5a** shows all signals corresponding to a 2,6-di-*O*-acetyl-3-mono-*O*-propyl cellulose (Fig. 1, numbering 1–6). Moreover, signals of substructures can be found in very small amounts that cannot be quantified. However, the substructures can be interpreted by considering the individual reaction steps. The DS_{Si} value after the conversion of cellulose with TDMS-Cl was determined to be 1.95 (sample **2**). Hence, some repeating units bearing a TDMS group only at position 6 were present in the polymer chain and alkylated afterwards at positions 2 and 3 (Fig. 1; 6-*O*-acetyl-2,3-di-*O*-propyl cellulose, numbering 1*–6*). Still, most of the repeating units were silylated at positions 2 and 6 as intended. Some of the modified anhydroglucose units (AGUs) were not alkylated at position 3 during the conversion with 1-iodopropane, which was also confirmed by FTIR analysis of sample **3a** (Fig. 2). After desilylation and peracetylation of three OH groups, triacetylated AGUs were obtained (Fig. 1; 2,3,6-tri-*O*-acetyl cellulose, numbering 1′–6′). As described above, repeating units silylated only at position 6 were present and some did not react completely under the alkylation conditions leading to repeating units bearing a propyl moiety only at position 2 (Fig. 1; 3,6-di-*O*-acetyl-2-*O*-propyl cellulose, numbering 1″–6″).

The DS_{Propyl} of 0.95, which was calculated from the ^{1}H-NMR spectrum of the peracetylated 3-*O*-propyl cellulose **5a**, confirms the substructures mentioned above.

The 3-mono-*O*-propyl cellulose **4a** is soluble in *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). If the solubility test was conducted in water at room temperature, **4a** appeared to be insoluble. Very interestingly, between 0 and 5 °C almost clear solution was formed (Fig. 3). A cloudy mixture was formed upon heating to room temperature that re-dissolved upon cooling.



DMA: *N,N*-Dimethyl acetamide
DMAP: 4-*N,N*-Dimethylaminopyridine
DMSO: Dimethyl sulfoxide
TBAF: Tetra-n-butylammonium fluoride
TDMS: Thexyldimethylsilyl
THF: Tetrahydrofuran

Scheme 1 Preparation of: **a** 3-*O*-propyl cellulose **4a**–**4e** using protective group technique and **b** propyl cellulose with random distribution of the substituents

The water-soluble samples were subjected to temperature-dependent photometric analyses to gain information on the cloud point temperature (Fig. 4). A cloud point temperature of 15.7 °C was determined for sample **4a** (DS 0.95).

It was interesting to study the water solubility of 3-*O*-propyl celluloses depending on the DS_{Propyl}. To obtain samples of lower DS_{Propyl}, the molar ratio AGU:1-iodopropane:NaH was decreased while keeping both reaction time and temperature constant. At a molar ratio of 1:3:3 (AGU:1-iodopropane:NaH), a DS_{Propyl} of 0.19 was realized (Table 1, sample **4c**). An increase in the molar ratio up to 1:4:4 led to a product with DS_{Propyl} of 0.34 under the same conditions (Table 1, sample **4d**). Both samples **4c** and **4d** are insoluble in water, even after storing the mixtures in the refrigerator. Increasing the molar ratio to 1:8:8, a water-soluble propyl cellulose with DS_{Propyl} 0.71 (sample **4e**, Table 1) was obtained that is soluble in DMSO, DMF, and after cooling the solution also in water. Sample **4e** precipitates from the water solution upon heating.

Table 1 Conditions for and results of the preparation of 3-*O*-propyl cellulose

Conditions						Results			
TDMSC[a]	Molar ratio			Reaction time at		Sample	DS[d]	DP_n^e	DP_w^e
	AGU[b]	C_3H_7I	NaH	r.t.[c]	50 °C (day)				
2	1	5	5	1 day	4.0	**4a**	0.95	191	262
2	1	5	5	1 day	4.0	**4b**	1.02	171	265
2	1	3	3	3 h	3.0	**4c**	0.19	45	98
2	1	4	4	3 h	3.0	**4d**	0.34	63	147
2	1	8	8	3 h	1.5	**4e**	0.71	148	262

[a] Thexyldimethylsilyl cellulose, TDMSC, degree of substitution 1.95

[b] Modified anhydroglucose unit

[c] Room temperature

[d] Degree of substitution

[e] Degree of polymerization, number average (DP_n) and weight average (DP_w) determined by SEC of the peracetylated compounds

Figure 4 depicts a comparison of the turbidity analysis of sample **4e** (DS_{Propyl} 0.71) to those of samples **4a** (DS_{Propyl} 0.95) and **4b** (DS_{Propyl} 1.02). It was found that the cloud point temperature is influenced by the DS. Thus, sample **4b** (DS 1.02) becomes insoluble at a slightly decreased temperature of 15.2 °C. A 3-*O*-propyl cellulose with lower DS of 0.71 (sample **4e**) flocculated at 23.5 °C. The cloud point temperature of samples **4a** and **4b** having almost ideal structure of 3-mono-*O*-propyl cellulose was nearly identical. However, a sample with lower DS at position 3 showed a slightly higher cloud point temperature. Hence, the flocculation temperature can be controlled by varying the DS value.

The peracetylated samples were subjected to SEC analysis to calculate the number average degree of polymerization (DP_n) and weight average degree of polymerization (DP_w, see Table 1). Interestingly, the insoluble samples of low DS (**4c** and **4d**) possess comparable low DP_n (45 and 63) and DP_w (98 and 147). The DP_w value of the water-soluble samples is almost identical in the range of 262–265. However, the samples differ in DP_n. While values of samples with a DS of ≈ 1 (DP_n 191, **4a**) and (DP_n 171, **4b**) possess a comparable value, sample **4e** (DS 0.71) exhibited a remarkably lower DP_n of 148. Surprisingly, the samples of low DS possess low DP values as well that cannot be discussed based on the present results.

In order to compare the properties of regioselectively functionalized 3-*O*-propyl cellulose with those of randomly functionalized cellulose ethers, the synthesis of propyl cellulose according to Kondo and Gray [9] was carried out in *N,N*-dimethyl acetamide/LiCl using NaOH and 1-iodopropane (Scheme 1b, Table 2). The propyl cellulose samples **6a** and **6b** showed distinct different solubilities at comparable DS_{Propyl} values. For instance, regioselectively synthesized 3-*O*-propyl cellulose samples with a DS_{Propyl} 0.71 and 1.02 are soluble in DMSO, DMF, and water. The randomly functionalized samples having a DS_{Propyl} of 0.64 (sample **6a**) and 0.93 (sample **6b**) are insoluble in DMSO, DMF and water.

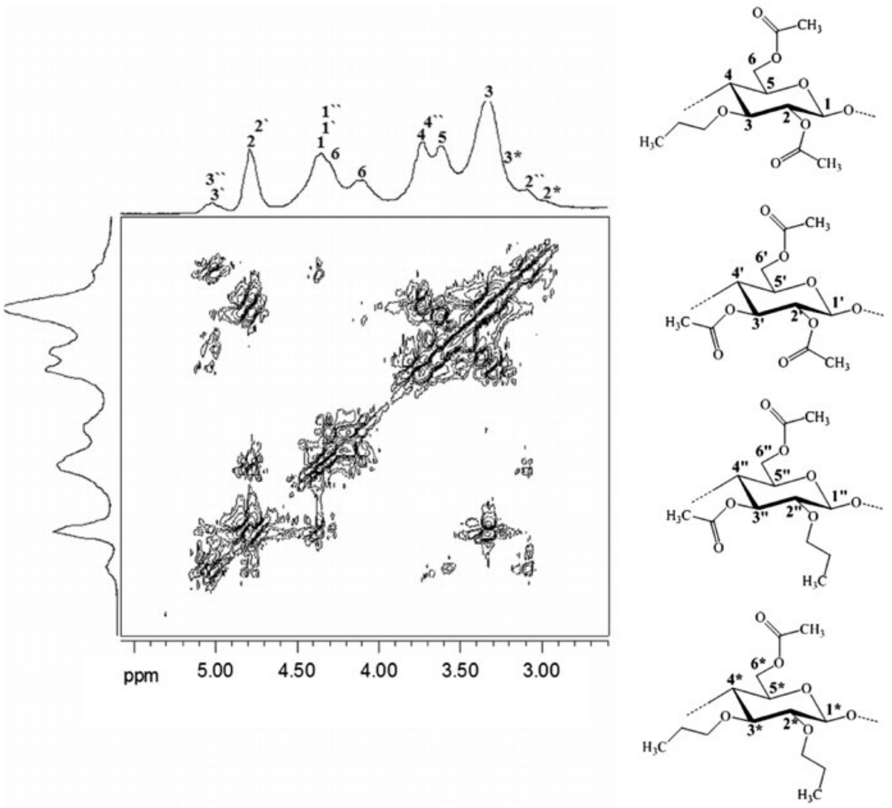


Fig. 1 ^{1}H/^{1}H-COSY-NMR spectrum of 2,6-di-*O*-acetyl-3-mono-*O*-propyl cellulose **5a** (degree of substitution of propyl groups 0.95) in $CDCl_3$

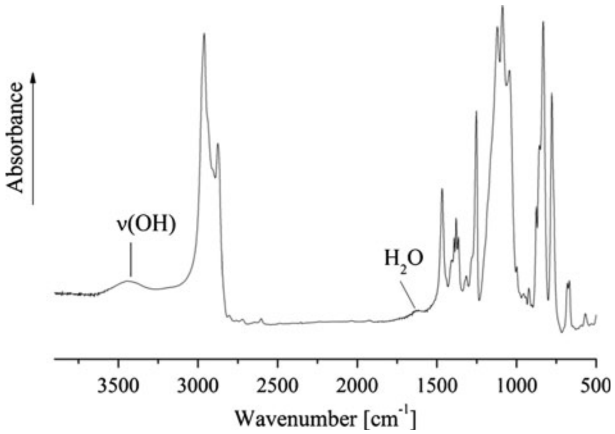


Fig. 2 FTIR spectrum of 2,6-di-*O*-thexyldimethylsilyl-3-mono-*O*-propyl cellulose **3a**

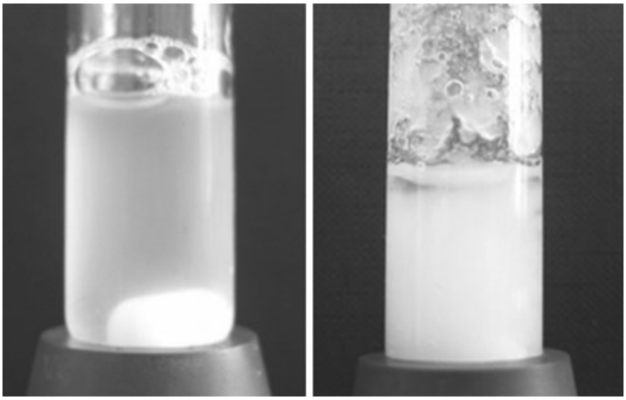


Fig. 3 Dissolution behavior of 3-mono-*O*-propyl cellulose **4a** (degree of substitution 0.95) in water at 0 °C (*left*) and at room temperature (*right*)

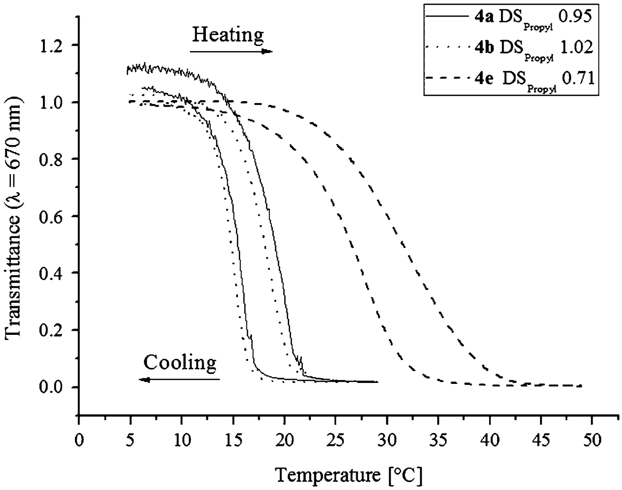


Fig. 4 Temperature dependent transmittance of aqueous propyl cellulose solutions with varying degree of substitution of 3-*O*-propyl groups (DS_{Propyl})

Table 2 Synthesis of randomly functionalized propyl cellulose by conversion of cellulose in *N*,*N*-dimethyl acetamide/LiCl applying powdered sodium hydroxide and 1-iodopropane for 18 h at 70 °C

Molar ratio			Results		
AGU	C_3H_7I	NaOH	Sample	DS	Sample after peracetylation
1	10	12.50	**6a***	0.64	**7a**
1	10	12.50	**6b**	0.93	**7b**

* Addition of water

Conversions of cellulose using aqueous NaOH and 1-iodopropane in isopropanol or dimethoxyethane slurry as well as the conversion of cellulose dissolved in DMSO/tetra-*n*-butyl-ammoniumfluoride trihydrate were not feasible; products with very low DS_{Propyl} values were synthesized.

In order to explain the difference of the solubilities between the regioselectively and randomly functionalized cellulose ethers, the ^{1}H- and ^{13}C-NMR spectra of the peracetylated compounds were compared (Figs. 5, 6). It is known that the chemical shift of the methyl group of the acetyl moiety depends on its position within the repeating unit. In the ^{1}H-NMR spectrum of sample **7b** (Fig. 5), this signal appeared as a multiplet in the range from 1.93 to 2.11 ppm indicating an uniform distribution of both the propyl and the acetyl groups at positions 2, 3, and 6. The signal of H-3 can be observed at 5 ppm, when an acetyl group is present at position 3 of the AGU.

This signal is much stronger for sample **7b**, allocating a lower amount of propyl moieties at position 3. Figure 6 shows the corresponding ^{13}C-NMR spectra of samples **5a** and **7b**. Again, the acetate signals at 20.4 and 20.6 ppm (CH_3) and from 169.2 to 170.1 ppm (C=O) as well as the propyl signals at 10.5 and 10.8 ppm (CH_3) in sample **7b** show distinct splitting, indicating the presence of the propyl moieties at position 2, 3, and 6 of the modified AGU.

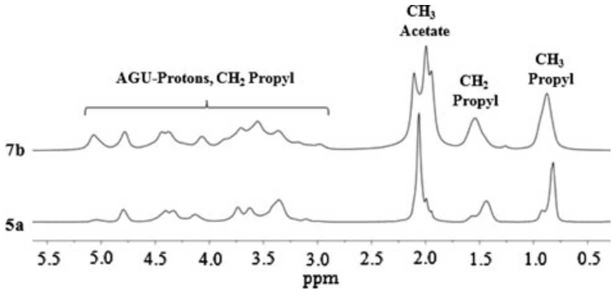


Fig. 5 ^{1}H-NMR spectra of peracetylated 3-mono-*O*-propyl cellulose (sample **5a**, degree of substitution of propyl groups, DS_{Propyl} 0.95) and randomly functionalized propyl cellulose (sample **7b** DS_{Propyl} 0.93) recorded in $CDCl_3$

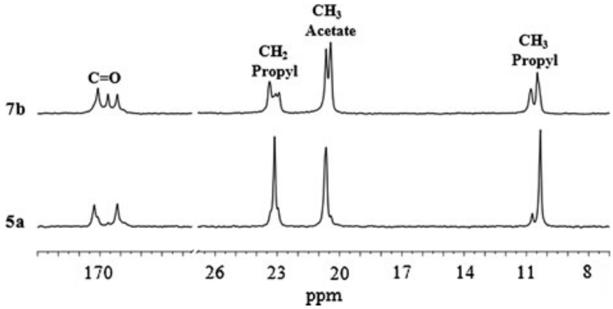


Fig. 6 ^{13}C-NMR spectra of peracetylated 3-mono-*O*-propyl cellulose (sample **5a**, degree of substitution of propyl groups, DS_{Propyl} 0.95) and randomly functionalized propyl cellulose (sample **7b** DS_{Propyl} 0.93) recorded in $CDCl_3$

Conclusion

The synthesis, structural characterization, and solubility of 3-*O*-propyl cellulose were investigated. The structure of the products was confirmed by spectroscopic techniques. In particular, two-dimensional NMR spectroscopic measurements of the peracetylated samples indicated the presence of substructures to a low extent. 3-*O*-propyl cellulose was soluble in *N,N*-dimethyl formamide, dimethyl sulfoxide, and water. It showed thermoreversible flocculation in water at low temperature (flocculation occurs between 15.2 and 23.5 °C) compared to 3-*O*-ethyl cellulose having only one CH_2 group less in the substituent (flocculation point 60 °C). Moreover, the flocculation temperature depends on the DS_{Propyl}. Furthermore, a comparison between the solubility of regioselectively and randomly synthesized propyl cellulose demonstrated that only the regioselectively modified compounds were soluble in water at comparable DS. These interesting results give rise to further investigations of the intra- and intermolecular interactions.

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