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### Silylated Cellulose Materials in Design of Supramolecular Structures of Ultrathin Cellulose Films

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## SILYLATED CELLULOSE MATERIALS IN DESIGN OF SUPRAMOLECULAR STRUCTURES OF ULTRATHIN CELLULOSE FILMS

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### ABSTRACT

To use the structure-forming potential and the biodegradability of cellulose and nonionic cellulose ethers, we developed synthesis pathways for soluble and regenerable silyl celluloses suitable for the design of advanced materials. A 6-*O*-silylation of cellulose takes place in a heterogeneous phase reaction in the presence of ammonia-saturated polar aprotic solvents at  $-15^{\circ}\text{C}$  with hexyldimethylchlorosilane. After 2,3-di-*O*-methylation, this type of regioselectively-substituted cellulose derivatives yields sensor matrices for the detection of halohydrocarbons in air. On the other hand, hexyldimethylsilyl celluloses and trimethylsilyl celluloses with degrees of substitution in the 2.6 to 3.0 range form mono- and multilayered supramolecular structures by applying the Langmuir-Blodgett technique and, after desilylation, oriented ultrathin cellulose films.

## EXPERIMENTAL

### Synthesis of Trimethylsilyl Celluloses

Starting from different types of cellulose, trimethylsilyl celluloses were prepared by silylation with an excess of hexamethyldisilazane at 80°C after dissolution in dimethylacetamide/LiCl [1]. Their characteristics are listed in Table 1.

### Synthesis of 6-O-Theyldimethylsilyl-2,3-di-O-methylcellulose

Avicel (2.0 g) was dried at 105°C in vacuum and added to ammonia-saturated DMF at -15°C. After stirring for 1 hour at -15°C, theyldimethylchlorosilane (1.5 mol/mol repeating unit) was added dropwise, stirring was continued for 1 hour at this temperature, and for an additional 6 hours up to 60°C. The silylated polymer was precipitated in water at 20°C, collected, and dried. Yield: 96%, DS<sub>Si</sub> 0.99, DP<sub>w</sub> 200. Methyl ether formation was carried out by conversion with iodomethane in the presence of sodium hydride in THF at room temperature [3].

### Measurements

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded with a Bruker-WP 400 spectrometer in toluene-*d*<sub>3</sub> at 80°C. IR spectra were run on an FT-IR spectrometer 60 SK (Nicolet).

### Formation of Films of Silylated Celluloses

Mono- and multilayers of trimethylsilyl celluloses were formed by a Langmuir-Blodgett technique described in Ref. 4. Sensor films of the silylated celluloses were spin coated on Al<sub>2</sub>O<sub>3</sub> substrates in contact with Pt electrodes (Inter-Digital-Resistor) for determination of conductivity in the presence of halohydrocarbons in air [5].

TABLE 1. Characteristics of Trimethylsilyl Celluloses

Cellulose Type	Trimethylsilyl cellulose				
	DP <sup>a</sup>	DP <sub>n</sub> <sup>b</sup>	DP <sub>w</sub> <sup>b</sup>	Si/% <sup>c</sup>	DS <sup>d</sup>
Avicel PH 101 (Fluka)	200	80	220	21.98	2.9 (2.86) <sup>e</sup>
Spruce sulfite pulp	600	160	1100	21.83	2.9
Cotton linters	1400	420	3100	21.20	2.7

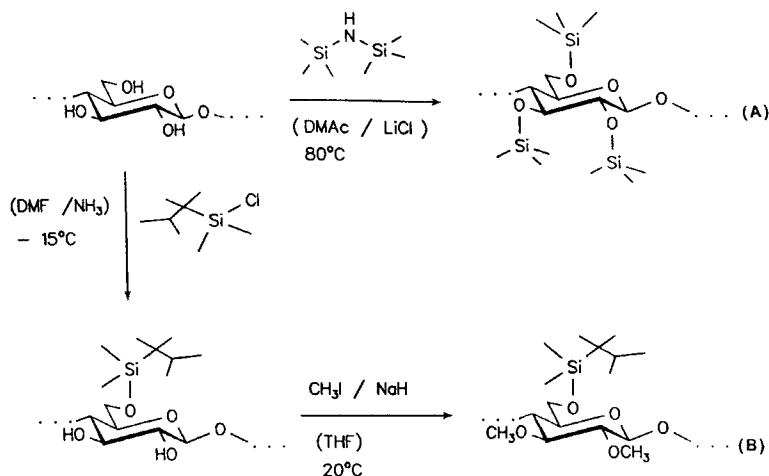
<sup>a</sup>Degree of polymerization, in cuoxam by viscosimetry.

<sup>b</sup>Estimated by GPC in THF.

<sup>c</sup>Determined gravimetrically (SiO<sub>2</sub>) [2].

<sup>d</sup>Degree of substitution, from Si/%.

<sup>e</sup>Calculated from <sup>1</sup>H-NMR spectra.



SCHEME 1.

## RESULTS AND DISCUSSION

One aim of our present work consists of an investigation of cellulose derivatives with regular molecular structures suitable for building-up supramolecular architectures in biodegradable advanced materials.

Starting from different cellulose samples (see Table 1), trimethylsilyl celluloses were prepared by complete silylation in homogeneous cellulose solutions in dimethylacetamide/lithium chloride (Scheme 1, top). A regioselective 6-*O*-thexyldi-

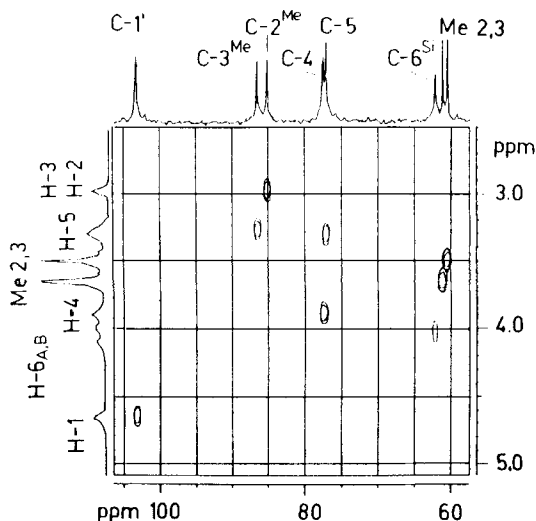


FIG. 1. The  $^{13}\text{C}[^1\text{H}]$ -NMR spectra of 6-*O*-thexyldimethylsilyl-2,3-di-*O*-methylcellulose in deuterotoluene.

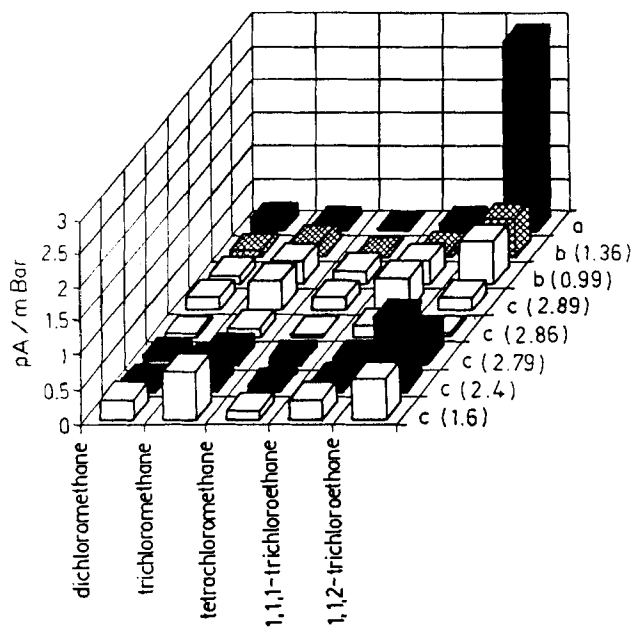


FIG. 2. Sensor sensibility (pA/mBar) for 6-*O*-hexyldimethylsilyl-2,3-di-*O*-methylcellulose (a), hexyldimethylsilyl cellulose (b), and trimethylsilyl cellulose (c) [5]. In parentheses: degree of substitution of silyl groups.

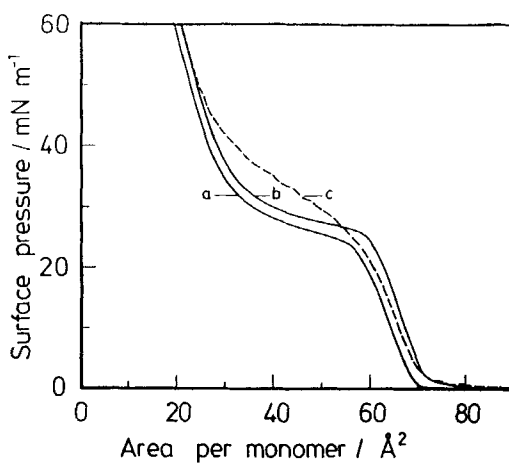
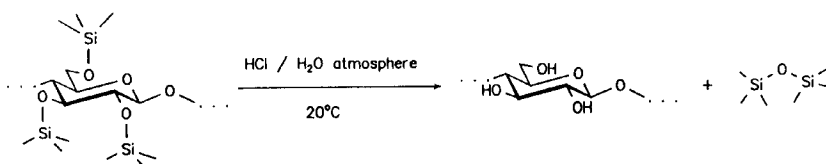


FIG. 3. The surface pressure area isotherms recorded at 20°C on air-water interfaces for trimethylsilyl celluloses; DP 200, DS 2.9, spread from chloroform (a); DP 1400, DS 2.7, from chloroform (b); DP 1400, DS 2.7, from *n*-hexane (c).



SCHEME 2.

methylsilylation was carried out in ammonia-saturated polar aprotic solvents followed by 2,3-*O*-methylation (Scheme 1, bottom).

The regular molecular structure of the methylated hexyldimethylsilyl cellulose has been confirmed by  $^{13}\text{C}$ [ $^1\text{H}$ ]-NMR spectra (see Fig. 1).

In the course of studies on polymers as sensor materials for the detection of halohydrocarbons in air, the synthesized celluloses have been investigated. As seen from Fig. 2, spin-coated sensor films of hexyldimethylsilylated methyl cellulose on Inter-Digital-Resistors (see Experimental Section) show a significant sensitivity toward 1,1,2-trichloroethane compared with the other silylcelluloses [5].

On the other hand, 6-*O*-hexyldimethylsilyl cellulose and trimethylsilyl celluloses (degree of substitution 2.6–2.9) have been used as soluble intermediates for building up well-defined mono- and multilayered ultrathin films of regenerated cellulose. Spreading of the silylcelluloses from chloroform or *n*-hexane solutions and compressing the polymer molecules on an air–water interface by the Langmuir–Blodgett technique [4] form monolayers up to a surface pressure of 24 mN/m (see Fig. 3). At higher surface pressures a plateau region is reached and the monofilm collapses. After transfer of the layer onto hydrophobized glass slides, silicon wafers, or gold surfaces and subsequent in-situ desilylation, mono- and multilayers of cellulose resulted [4]. The desilylation (Scheme 2) can be carried out in a simple way with gaseous HCl with 30 seconds.

In the case of *n*-octyldimethylsilyl cellulose, a comparable formation of monolayers on the air–water interface can be observed, but the low surface pressure of 10 mN/m does not allow the transfer of these layers onto a substrate. On the other hand, trimethylsilyl celluloses with degrees of substitution lower than 2.5 and 6-*O*-hexyldimethylsilyl cellulose (without methylation of the secondary OH groups) are unsuitable for preparing monolayers because of molecular aggregation in the solvents used.

## CONCLUSIONS

Silylated celluloses are suitably soluble and regenerable polymers to design supramolecular structures in Langmuir–Blodgett and spin-coated films. Trimethylsilyl celluloses with degrees of substitution higher than 2.5 form well-defined mono- and multilayered architectures. In-situ desilylation of these films represents a convenient method to generate oriented thin hydrophilic and biodegradable cellulose films.

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