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Studies on the Film Formation of Polysaccharide Based Furan-2-Carboxylic Acid Esters

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Summary: Furan-2-carboxylic acid esters of xylan, cellulose, curdlan, dextran, and starch were synthesized and studied regarding their film formation abilities. The polysaccharide esters were utilized to prepare films of different appearance. To investigate supermolecular structures of the biopolymer derivatives, atomic force- and scanning electron microscopy were applied. The surface roughness and the macro-pore size and -distribution of the polysaccharide ester films were characterized. Starch furan-2-carboxylic acid ester (starch furoate) did not show film formation. In contrast, dextran furoates are very well suitable for the surface coating of inorganic compounds while the xylan-, cellulose-, and curdlan derivatives yield self-supporting films with different surface characteristics.

Keywords: atomic force microscopy (AFM); ester; nanostructures; polysaccharide; scanning electron microscopy (SEM)

Introduction

Polysaccharides represent a major class of biological macromolecules that occur throughout nature providing structural support in plant and animal cells, serve as energy reservoirs, encapsulate bacteria and are implicated in biofilm- and dental plaque formation, or microbial-induced metal corrosion.[1–3] They are also involved in cellular immunochemistry and cancer pathology.[4–8] It is obvious that the elucidation of their structure-function relationships is critical for the development of new materials. Both, native and artificial supermolecular structures of polysaccharides may influence the overall properties of these biopolymers significantly.[9,10] Moreover, the chemical modification of polysaccharides remains to be the most important approach to design novel structures and properties.[11] A wide range of applications of polysaccharide derivatives comprised their use as separation- and carrier materials. For instance, cellulose carbamates are studied as chromatographic column material for chiral systems.[12–15] Cellulose acetates are processed to asymmetric membranes that are used in ultrafiltration, nanofiltration, and reverse osmosis.[16] In general, studies about the film- and membrane formation of polysaccharide esters in addition to cellulosic materials are very few, but the conformational properties of these polysaccharides have been extensively studied by a combination of both analytical and scanning techniques characterizing the physiochemical properties of the specimen. Here, the structure formation on the nanometer scale is a rapidly growing field of research. Motivated by the atomic force microscope's (AFM) ability to measure distances on the Angstrom scale and forces on the pico-Newton scale with high resolution[17], properties of particulate molecules were studied applying this knowledge. Recent advances in AFM allow the conformation and structure of polysaccharides to be probed with increased resolution operating under conditions that closely mimic their natural environments. A broad diversity of molecular architecture was

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revealed.[18–20] Thus, we intended to use the different potential of the polymer backbones towards the formation of superstructures for the preparation of membrane materials with a variety of features.

In this work, AFM and scanning electron microscopy (SEM) were used to elucidate superstructural features, in particular macro-pore distributions and surface roughnesses of films of unconventional polysaccharide furan-2-carboxylic acid esters. The polysaccharides studied are cellulose, curdlan, dextran, starch, and xylan.

Experimental

Materials

Cellulose (**1**, Avicel® PH 101, M_W 45,444 g/mol) obtained from Fluka was treated in vacuum at 105 °C for 2 h prior to use. Curdlan from *Alcaligenes faecalis* (**2**, M_W 129,700 g/mol) obtained from Sigma, dextran from *Leuconostoc mesenteroides* strain no. NRRL B-512F (**3**, M_W 54,800 g/mol) purchased from Fluka, and potato starch (**4**, amylose content 31%, M_W 40,000,000 g/mol) obtained from National Starch & Chemical GmbH, Neustadt, Germany were used without further treatment. Xylan from birch wood (**5**, M_W 13,000 g/mol) was purchased from Roth, bleached with ClO_2, and washed with methanol and ethanol. All other chemicals were used without further purification. The furan-2-carboxylic acid, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N,N′*-carbonyldiimidazole (CDI), and LiCl were obtained from Fluka.

Dissolution of Cellulose in DMAc/LiCl

To enable the dissolution of cellulose (**1**), 1.0 g (6.2 mmol) of dried cellulose and 40 mL DMAc was kept at 130 °C for 2 h under stirring. After the slurry has been allowed to cool down to 100 °C, 2.4 g of anhydrous LiCl were added. By cooling down to room temperature under stirring, the cellulose dissolved completely.

Esterification of Polysaccharides with Furan-2-Carboxylic Acid

Cellulose (1)

A solution of 5 g (31.0 mmol) *N,N′*-carbonyldiimidazole (CDI) was added to a solution of 3.46 g (31.0 mmol) furan-2-carboxylic acid in 20 mL DMAc. The clear solution was stirred at 40 °C for 24 h and was then added to the solution of 1.0 g (6.2 mmol) cellulose (**1**) dissolved in DMAc/LiCl. The homogeneous reaction mixture was stirred for 24 h at 60 °C. Product was isolated by precipitation into 300 mL ethanol and filtration. After washing three times with 100 mL ethanol, the polymer (**6**) was dried at 60 °C under vacuum.

DS (determined by ^{1}H-NMR after peracetylation): 1.81; ^{1}H NMR (of the peracetate dissolved in $CDCl_3$): δ (ppm) = 5.08 (H-3), 4.92 (H-2), 4.50 and 4.08 (H-6), 3.79, 3.68 (H-4, 5), 6.50 (H-10), 7.19 (H-9), 7.54 (H-11); ^{13}C NMR (DMSO-d_6): δ (ppm) = 157.6 (CO), 100.4 (C-1′), 71.8 (C-2), 72.7 (C-3), 77.3 (C-4), 75.6 (C-5), 62.0 (C-6), 143.6 (C-8), 119.2 (C-9), 112.2 (C-10), 147.2 (C-11), 20.2 (CH_3-acetate), 169.6 (CO-acetate).

Curdlan (2)

At room temperature, 15 g (93 mmol) CDI was added to a solution of 10.37 g (93 mmol) furan-2-carboxylic acid dissolved in 100 mL DMSO. After heating the solution to 60 °C under stirring, 5 g (31 mmol) curdlan (II) was added. The homogeneous reaction mixture was stirred for 6 h at 80 °C, cooled down, and again stirred for 20 h at room temperature. The polymer (**7**, DS_{fur} 1.59) was precipitated in 500 mL isopropyl alcohol, washed 3 times with isopropanol, and dried at 60 °C under vacuum.

Dextran (3)

The preparation of the furan-2-carboxylic acid ester based on dextran (III) was performed and the polymer (**8**, DS_{fur} 1.93) was isolated comparable to **7**. However, the polymer solution was not heated to 80 °C, but stirred for 6 h at 60 °C before cooling down and stirring the mixture at room temperature for 24 h.

*Starch (**4**)*

The preparation of the furan-2-carboxylic acid ester based on starch (IV) was performed comparable to **7**. The polymer (**9**, DS_{fur} 0.98) was isolated by precipitation into ethanol.

*Xylan (**5**)*

For a typical synthesis, dried xylan (1 g, 7.5 mmol) was dissolved in 20 ml DMSO at 100 °C for 10 min. Separately, 0.62 g CDI (3.8 mmol) were dissolved in 36 ml DMSO and 0.42 g (3.8 mmol) furan-2-carboxylic acid were added and stirred overnight. This mixture was slowly added to the xylan solution and stirred at 80 °C for 24 h. The polymers (**10**) were precipitated into 300 mL ethanol, washed 4 times with ethanol, and dried at 60 °C under vacuum, cf. Table 2.

Film Preparation

To produce self-supporting films, a droplet of a viscous polymer solution, e.g., 8.7 g cellulose furoate in 50 mL DMSO (14.8%, w/w), was cast with a doctor on a glass plate with a constant velocity, or was spin coated on a glass plate at 2,000 rpm for half a minute (DELTA 10 TT, SÜSS MicroTec Lithography GmbH, Germany). Films of 120 μm thicknesses were obtained, which were immediately treated with ethanol for 2 min, removed from the glass plate, and finally stored in ethanol. These self-supporting films had a final thickness of about 50 μm.

To produce polymer-coated mica surfaces, a droplet of a highly viscous polymer solution was cast with a doctor on a freshly cleaved mica surface with a constant velocity. Films of about 50 μm thicknesses were obtained, which were immediately treated with ethanol for 2 min, and finally air-dried remaining on the mica surface.

AFM Studies on the Films

The polymer-coated mica surfaces were studied in the contact mode with a Topometrix-TMX 2000 scanning probe microscope (Topometrix GmbH Darmstadt, Germany) with an AFM Dry Scanner (130 μm scan range; 12 μm z-range) and silicon nitride standard tips (SFM Probes).

The self-supporting, wet films were dried using a critical point dryer CPD030 (BAL-TEC, Balzers, Lichtenstein). AFM studies were carried out in the non-contact mode with a DualScope C-21 (DME) and silicon nitride tips (60.0 N/m, 0.20 nN). The frequency applied was 310 kHz.

SEM Investigation of the Films

The wet films were dried using a critical point dryer CPD030 (BAL-TEC, Balzers, Lichtenstein) and mounted on stubs for SEM. After covering with gold using a sputter coating device BAL-TEC SCD005 (Balzers, Lichtenstein; 60 mA, 80 s, gold coating approx. 35 nm), the films were studied with a LEO-1450 VP (LEO, Oberkochen, Germany) scanning electron microscope operating at 15.00 kV. The micrographs were taken at a magnitude of 8.00k X and a working distance of 9 mm, 10 mm, and 12 mm, respectively.

Results and Discussion

Structural Specifics of the Polysaccharides used for the Synthesis of Organic Esters

Polysaccharides of different supermolecular structures were studied. Besides the widely applied polysaccharides cellulose (**1**) and starch (**4**) with well-known structures – for structural features see Table 1 – we used curdlan (**2**), dextran (**3**), and xylan (**5**).

Curdlan (**2**) formed by bacteria like *Agrobacterium biovar* and *Alcaligenes faecalis* is a homopolymer of β-(1 → 3)-D-glucose (Figure 1).[26] This β-glucan is unbranched like cellulose.

The commercially applied single strain of *Leuconostoc mesenteroides* NRRL B-512F produces extracellularly a dextran (**3**, Figure 2) that is linked predominately by α-(1 → 6) glycosidic bonds with a low level

Table 1.
Structures of polysaccharides used for esterification.

Polysaccharide				Reference
Type	Source	Structure		
Cellulose	Plants	β-(1 → 4)-D-glucose	**1**	[21]
Curdlan	Bacteria	β-(1 → 3)-D-glucose	**2**	[22]
Dextran	Bacteria	α-(1 → 6)-D-glucose main chain	**3**	[23]
Starch	Plants		**4**	[24]
Amylose		α-(1 → 4)-D-glucose		
Amylopectin		α-(1 → 4)- and α-(1 → 6)-D-glucose		
Xylan	Plants	ß-(1 → 4)-D-xylose main chain	**5**	[25]

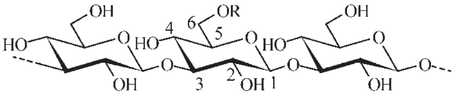


Figure 1.
Chemical structure of curdlan (R=H).

(~5%) of randomly distributed α-(1 → 3) branched linkages.[27,28]

Xylans of all higher plants possess β-(1 → 4) linked Xyl*p* units as the backbone, usually substituted with sugar units and *O*-acetyl groups. Figure 3 shows the chemical structure of xylan (**5**) from birch wood containing single side chains of 2-linked MeGA units.

All polysaccharides were esterified with a furan-2-carboxylic acid in order to introduce the unsaturated function leading to a desired photo-cross-linkable material. For esterification, Avicel® PH 101 (M_W 45,444 g/mol), curdlan from *Alcaligenes faecalis* (M_W 129,700 g/mol), dextran from *Leuconostoc mesenteroides* NRRL B-512F (M_W 54,800 g/mol), potato starch with an amylose content of 31% (M_W 40,000,000 g/mol), and xylan from birch wood (M_W 13,000 g/mol) were allowed to react with a furan-2-carboxylic acid in the presence of *N,N′*-carbonyldiimidazole (CDI), i.e. by *in situ* activation according to Ref.[29]. Cellulose furan-2-carboxylic acid esters (furoates) with degree of substitution (DS) values up to 1.97 were accessible both by homogeneous conversion in DMAc/LiCl[29] and in the solvent DMSO/tetrabutylammonium fluoride (TBAF).[30]

The carboxylic acid imidazolide in DMAc and DMSO, respectively, was simply added to the polymer solution and the reaction proceeded at 60 °C and 80 °C, respectively, for 24 h (Scheme 1). Pure products obtained by an usual work-up procedure were soluble in organic solvents dependent on the DS values. In case of xylan furoate it was shown that the DS was controlled by increasing the molar ratio of the furan-2-carboxylic acid to repeating unit, cf. Table 2. Xylan furoate with a DS of 0.86 (**10d**) was completely soluble in

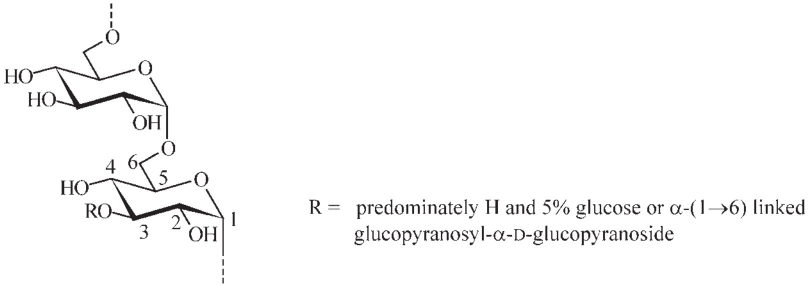


Figure 2.
Structure of dextran obtained from *Leuconostoc mesenteroides* NRRL B-512F.

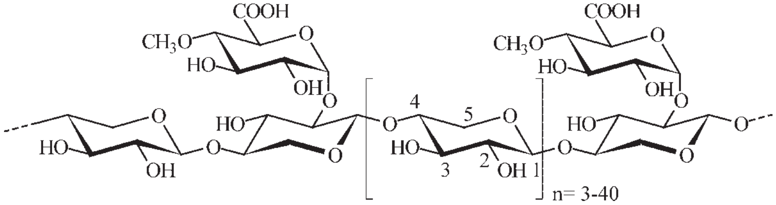
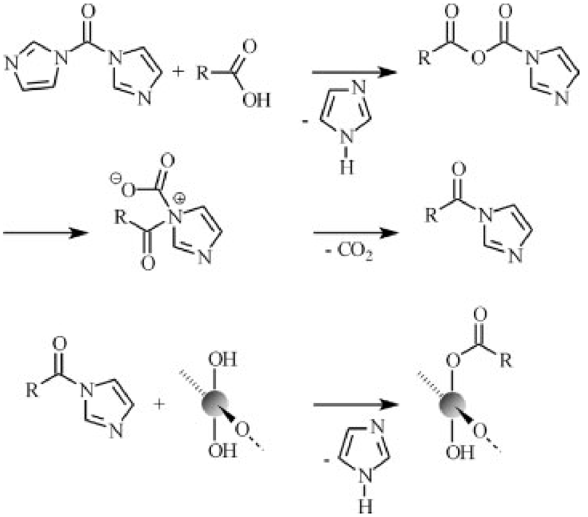


Figure 3.
Structure of 4-*O*-methylglucuronoxylan.

solvents like DMSO, DMAc, or DMF, and thus can be processed to films.

Polysaccharide ester films were prepared using a doctor or a spin coating device applying a solution of the polymer in DMSO containing 11–18% (w/w) of the polysaccharide furoate. The films formed were immediately treated with ethanol. If



Scheme 1.
General method for esterification of polysaccharides with furan-2-carboxylic acid.

Table 2.
Degree of substitution (DS) and solubility of the polysaccharide furan-2-carboxylic acid (FCA) esters synthesized homogeneously via *in situ* activation of the carboxylic acid with *N*,*N*′-carbonyldiimidazole (CDI).

Starting polysaccharide	Molar ratio AGU:FCA:CDI	No.	DS	Solubility$^{b)}$		
				DMSO	DMAc	DMF
Cellulose	1.0:5.0:5.0	**6**	1.81	+	+	+
Curdlan	1.0:3.0:3.0	**7**	1.59	+	nd	nd
Dextran	1.0:3.0:3.0	**8**	1.93	+	+	+
Starch	1.0:3.0:3.0	**9**	0.98	+	s	s
Xylan	1.0:0.5:0.5	**10a**	0.09$^{a)}$	s	—	—
Xylan	1.0:1.0:1.0	**10b**	0.44$^{a)}$	s	—	+/−
Xylan	1.0:1.5:1.5	**10c**	0.48$^{a)}$	+/−	—	—
Xylan	1.0:3.0:3.0	**10d**	0.86$^{a)}$	+	+	+

a) Degree of substitution detected by elemental analysis; b) s swollen, +/− partially soluble, + soluble, — insoluble, nd not determined; DMSO, dimethyl sulfoxide; DMAc, *N*,*N*-dimethyl acetamide; DMF, *N*,*N*-dimethyl formamide.

the polymer was given on a freshly cleaved mica surface prior casting and precipitation, the specimen was air-dried remaining on the mica surface. For the preparation of self-supporting films, the casted and ethanol-treated product was removed from the glass plate and finally stored in ethanol.

Starch furoates did not show any film formation, while cellulose-, curdlan-, and xylan furoates were suitable for the preparation of both films on mica surfaces and self-supporting films. Using dextran furoates, however, it was neither possible to receive self-supporting films after casting with a doctor nor after spin coating. This behaviour may be explained by the backbone structure of the biopolymer. Caused by additional linkages and side chains, the formation of self-supporting, compact films was not feasible. Here, partly aggregated films of non-detachable polymer structures with a high affinity to glass and ceramics were obtained predestining dextran derivatives for the surface coating of inorganic compounds.[31,32]

AFM Studies on Films on Mica Surfaces

Atomic force microscopy (AFM) was applied to investigate the structural features of the films, which were designated for the application in separation technology. The tests on polymer-coated mica surfaces resulted in significant different qualities of the polysaccharide ester films, i.e. the surface roughness of furan-2-carboxylic acid esters determined by AFM strongly depends on the backbone structure of the polysaccharides. Representative surface characteristics of the furan-2-carboxylic acid esters of cellulose, curdlan, dextran, starch, and xylan on the mica surfaces are shown in Figure 4.

For the roughness analysis (Table 3), different AFM figures were utilized, which were taken at a Topometrix instrument with a scanner size of 130 to 130 μm and a z-range of about 12 μm.

It could be proved by AFM studies that starch furoate (**9**) dissolved in DMSO was not able to form films on mica surfaces by a casting process. Instead of a homogenous film, single cluster of starch furoate were observed. This behaviour was obviously caused by the branched structure of the starch-based ester avoiding the desired formation of a compact "sheet structure". Contrary, the ability of film formation was proved for the other polysaccharides, i.e. in each case typical meshwork structures were observed. The films of cellulose furoate (**6**) on mica surfaces exhibited highest roughness values (Ra, approx. 170 nm) and maximum heights (R_{max}) of about 1,700 nm, followed by xylan furoate (**10d**) with $Ra \approx 150$ nm and $R_{max} \approx 1{,}500$ nm and dextran furoate (**8**, $Ra \approx 100$ nm, $R_{max} \approx 1{,}000$ nm), while curdlan furoate (**7**) always showed lowest values ($Ra \approx 25$ nm, $R_{max} \approx 370$ nm).

AFM Studies on Self-Supporting Films

Furthermore, self-supporting films of the polysaccharide esters were investigated by AFM. For this purpose, wet films of cellulose furoate (**6**) were dried by critical point drying, which preserved the pore structure. The AFM studies were performed in the non-contact mode at a DME Dualscope instrument with a scanner size of 40 to 40 μm and a z-range of about 2.7 μm. The atomic force micrographs visualized impressively the cleft surface of cellulose furoate films (Figure 5) and exhibited macro-pore sizes of about 500 nm.

Maximum height up to 1,750 nm was detected, which is in good agreement with results of cellulose furoate films on mica surfaces obtained by a Topometrix instrument. Due to the scanner restrictions in combination with the film's surface characteristics, however, the recording of extensive areas was difficult.

SEM Investigation of Self-Supporting Films

Further characterisation of the film's surfaces was carried out by means of a scanning electron microscope (SEM). The macro-pore distribution and the investigation of polysaccharide esters regarding their ability to form self-supporting films were studied. For the SEM measurements,

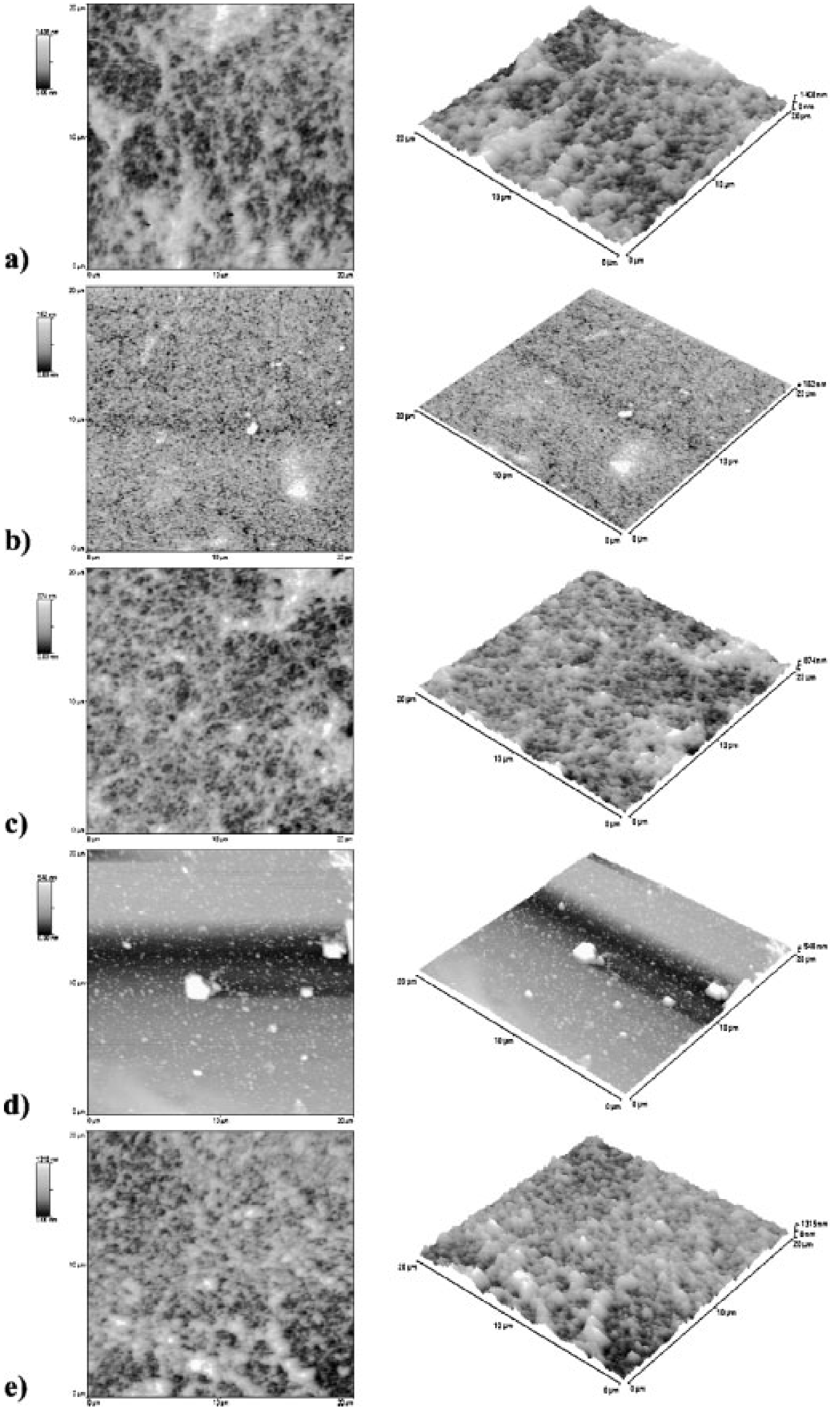


Figure 4.
AFM images (contact mode; scan range 20 × 20 μm) of the supermolecular structures of furan-2-carboxylic acid ester films on mica surfaces, a) cellulose (**6**, DS 1.81), b) curdlan (**7**, DS 1.59), c) dextran (**8**, DS 1.93), d) starch (**9**, DS 0.98), and e) xylan (**10d**, DS 0.86).

Table 3.
Roughness analysis of the AFM images and macro-pore sizes of films based on polysaccharide furan-2-carboxylic acid esters (furoate). The standard deviations are given.

Furan-2-carboxylic acid ester of		Characteristics [nm]			
		Mean roughness (Ra)	Root mean square (RMS)	Maximum height (R_{max})	Pore size[a)]
Cellulose	**6**	174.0 ± 14.2	220.1 ± 17.4	1,725 ± 240	300 to 800
Curdlan	**7**	25.2 ± 08.7	33.4 ± 11.6	372 ± 190	200 to 550
Dextran	**8**	102.8 ± 10.4	132.0 ± 14.1	1,010 ± 161	—
Starch	**9**	67.3 ± 23.6	86.2 ± 31.7	776 ± 499	—
Xylan	**10d**	152.5 ± 20.1	193.7 ± 26.5	1,535 ± 424	250 to 750

[a)] Macro-pore size of self-supporting films determined by SEM.

the wet polymer films were dried by critical point drying and gold sputtered.

The scanning electron micrographs proved that the relatively unstructured rear side of cellulose furoate (**6**, Figure 6a) was attached to the glass plate during the casting process. This side was characterized by a homogeneous surface interrupted by single macro-pores smaller than 300 nm. Contrary, a rather high surface roughness was observed for the top side of the film (Figure 6b) showing a meshwork structure

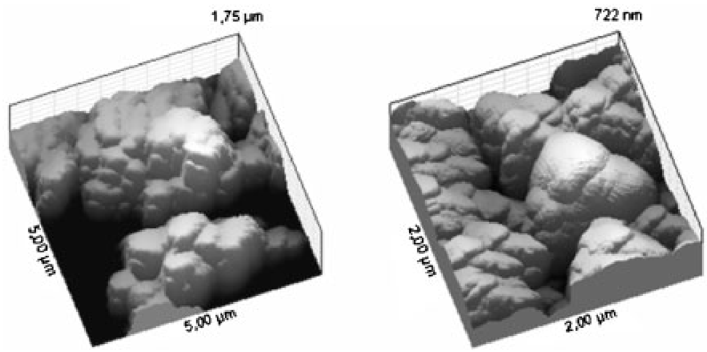


Figure 5.
AFM images (non-contact mode) of a self-supporting film of cellulose furan-2-carboxylic acid ester (both images sample **6**, DS 1.81).

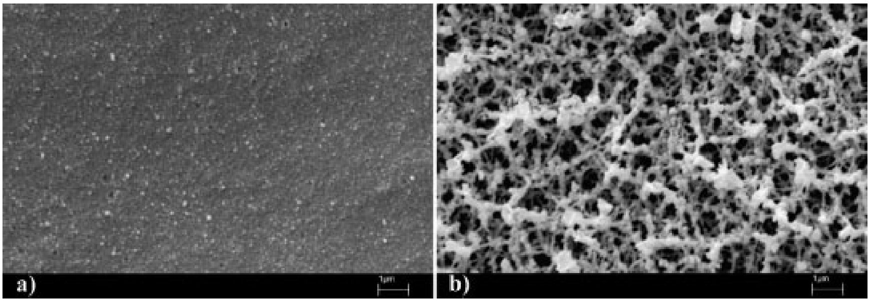


Figure 6.
Scanning electron micrographs of a self-supporting film of cellulose furan-2-carboxylic acid ester (**6**, DS 1.81); a) glass-film contact side, b) film-solvent contact side.

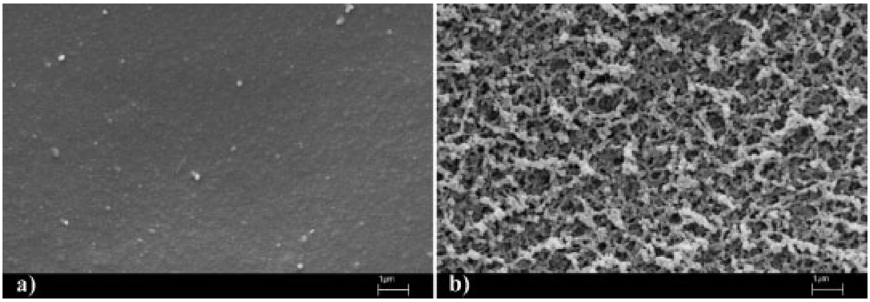


Figure 7.
Scanning electron micrographs of a self-supporting film of curdlan furan-2-carboxylic acid ester (**7**, DS 1.59); a) glass-film contact side, b) film-solvent contact side.

with macro-pores in the range from 300 to 800 nm, which is in good agreement with the AFM results described before. These results are comparable to macro-pore sizes of cellulose acetates, too.[33] It was shown that the linear homopolymer cellulose was very well suitable for the preparation of self-supporting films.

As described previously[34], the cellulose furoate can be modified specifically by UV irradiation yielding solvent-resistant, stable films. If samples were treated with light having a wavelength in the range of the absorption maximum of the furan moiety (290 nm), cross-linking succeeded presumably via a pericyclic reaction and yielded insoluble polymers. It was confirmed that the irradiation did not lead to a change in the surface roughness or the pore size.[29,34]

Contrary to cellulose furoate films, the rear side of curdlan furoate (**7**) films obtained by SEM (Figure 7a) exhibited rather smooth surfaces without single pores. The up side of curdlan furoate films showed again an exceedingly tender meshwork (Figure 7b) whereas the supermolecular structures of curdlan furoate films were much subtler compared to those based on cellulose. The dimension of the up side's macro-pores was between 200 and 550 nm and in average smaller than the macro-pores of cellulose furoate films.

The scanning electron micrographs of the xylan furoate (**10d**) film's rear side exhibited quite porous structures with a macro-pore size predominantly smaller than 250 nm (Figure 8a, upper picture). Contrary, the up side of xylan furoate films looked like a tender meshwork with pore-structures of about 400 nm size (Figure 8b). At some rear side's regions, however, sections of the meshwork were observed through extended macro-pores. At these regions, the pore structures were characterized by sizes up to 800 nm (Figure 8a, lower picture).

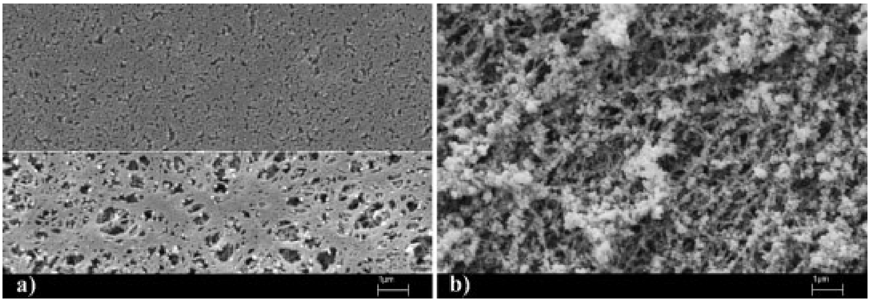


Figure 8.
Scanning electron micrographs of a self-supporting film of xylan furan-2-carboxylic acid ester (**10d**, DS 0.86); a) glass-film contact side, b) film-solvent contact side.

This fact implicated that the high-density rear side of a film would not control its separation properties, e.g. in activity as a membrane or filter material, and could be removed quite easily. Its tightness apparently depended on the feasibility of precipitation.

Conclusion

It was proved that the surface roughness of furan-2-carboxylic acid ester films of polysaccharides depends on the backbone structure of the biopolymer. On examination of the results of self-supporting films it became apparent that cellulose furoate with maximum macro-pore sizes exhibited highest roughness values and highest maximum heights, while curdlan furoate with slightest macro-pore sizes showed the lowest values. Starch furoate offered a surface roughness in the mean range, however, it was neither able to form self-supporting films nor films on mica surfaces. The furan-2-carboxylic acid esters of cellulose, xylan, and curdlan were well suited to form self-supporting films, which can be applied as membrane materials with varying features for different separation processes, while dextran derivatives were proved to be suitable for the surface coating of inorganic compounds.

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