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Supporting Information

Curdlan Acetate Fibres with Low Degrees of Substitution Fabricated via Continuous Process of Chemical Modification and Wet Spinning Using Ionic Liquid

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The file includes Figure S1–S9 and Tables S1–S2.

Fourier-transform infrared (FT-IR) spectra

FT-IR spectra were recorded on a Nicolet Magna 6700 spectrometer (Thermo Fisher Scientific, Inc., Tokyo, Japan), which was equipped with an attenuated total reflection (ATR) unit. ZnSe was used as the ATR accessory. The measured wavenumber range was 4000–400 cm^{-1} and 64 scans were accumulated per spectrum. A resolution of 4 cm^{-1} was maintained throughout the measurements.

There are characteristic bands at 1030 and 889 cm^{-1} arising from the C–O–C linkages in the sugar backbone and *β*-glycosidic linkages between the glucose units of curdlan. The broad peak arising from OH groups from 3000 to 3500 $^{-1}$ was weaken with increasing the DS, whereas the strong bands clearly appeared at 1738, 1368, 1222 cm^{-1} corresponding to acetyl (Ac) group. Based on the results, it was suggested that the OH groups of curdlan was substituted with Ac group and the DS increased with increasing the used IPAc amounts.

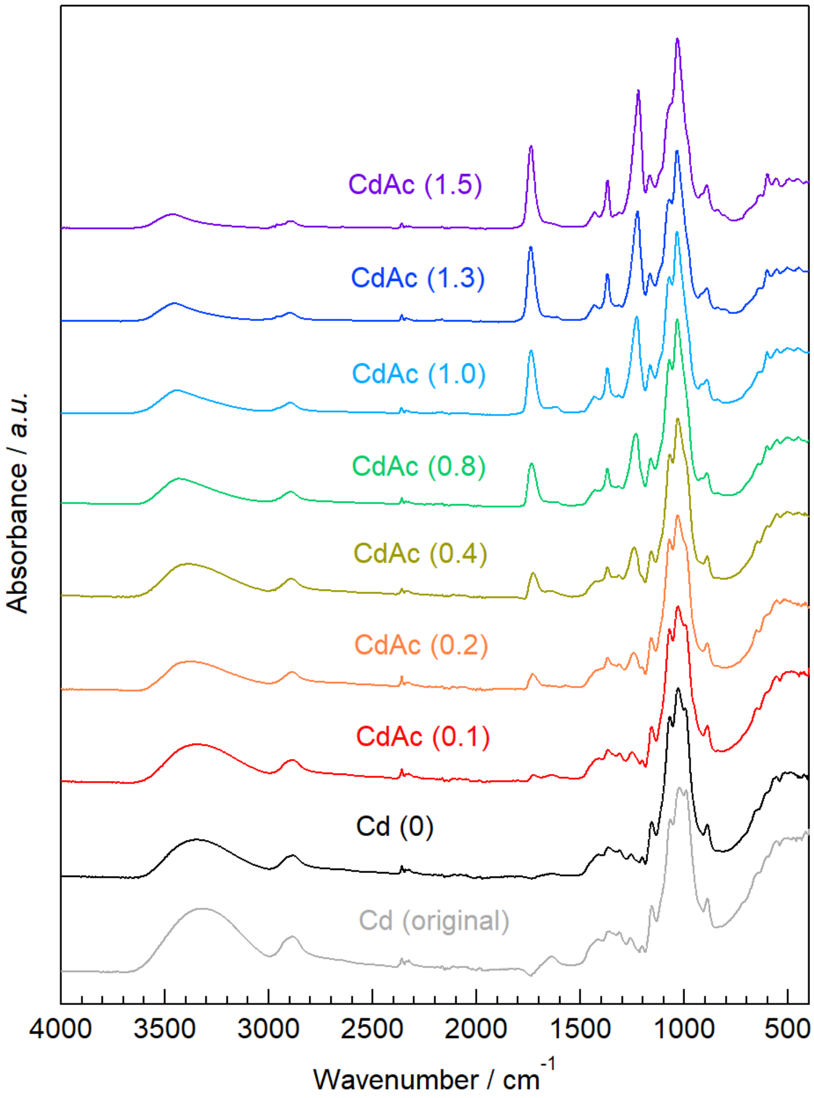


Figure S1. ATR-mode FT-IR spectra of curdlan and curdlan acetates.

^{1}H nuclear magnetic resonance (NMR) spectra

^{1}H NMR spectra were recorded in deuterated dimethylsulfoxide (DMSO-d_6) on a JNM-ECA 600 spectrometer (JEOL Ltd., Tokyo, Japan). All NMR spectra were analyzed using a Delta NMR (JEOL Ltd., Tokyo, Japan), and the chemical shifts [δ, parts per million (ppm)] were referenced against tetramethylsilane (TMS, δ = 0 ppm) as the internal standard. The free induction decays of 80 were collected and averaged to obtain the ^{1}H NMR spectra. Notably, the concentration of the prepared sample solutions was very low due to the insufficient solubility of CdAc (1.3 and 1.5) in DMSO as shown in Figure S4, and thus, the scan numbers were increased to 4000 or 6000. These obtained spectra were exhibited in Figure S2 with a certain expansion.

Characteristic peaks arising from the sugar skeleton of curdlan were detected at 3.2–5.2 ppm. The chemical shifts at 1.9–2.1 ppm are assigned to the protons in Ac group,[1] indicating that the curdlan was acetylated. The number of the peaks due to the sugar skeleton increased with increasing the DS, and the chemical shifts might depend on the positions of the introduced Ac group.

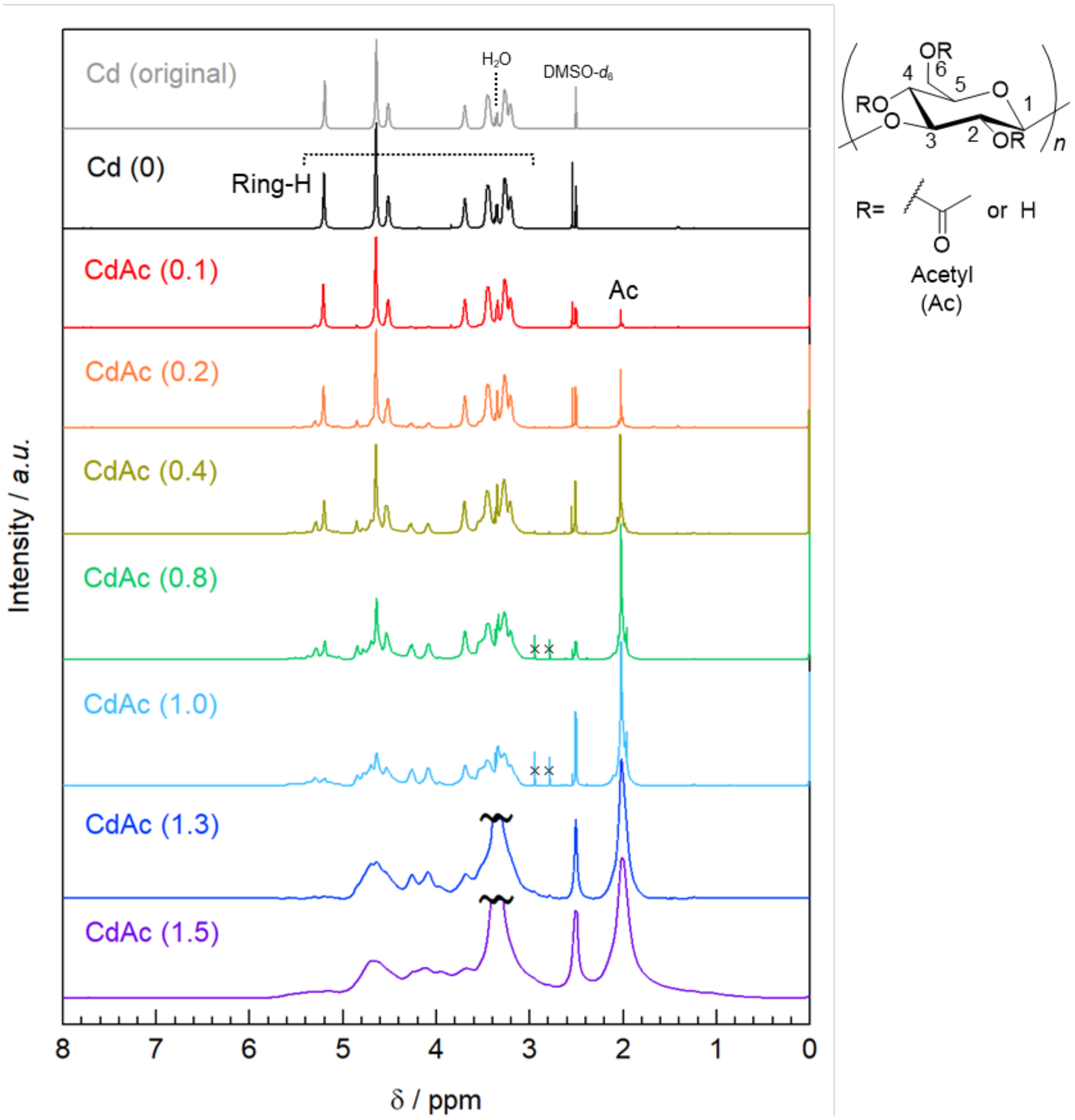
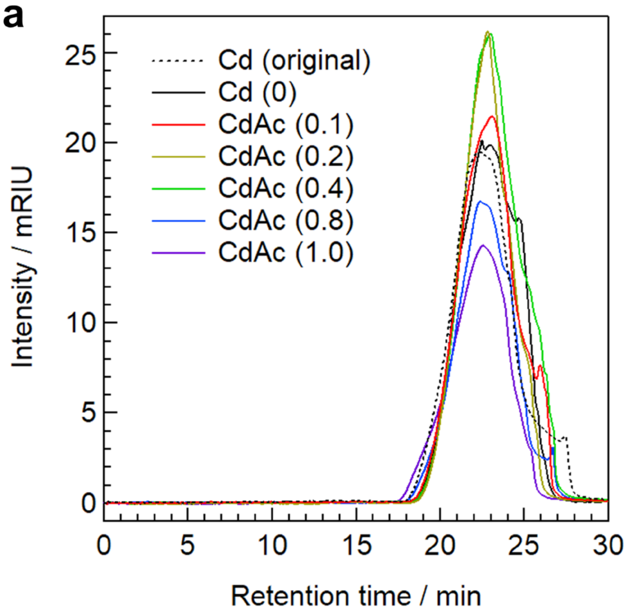


Figure S2. ^{1}H NMR spectra of curdlan and curdlan acetates, measured in DMSO-d_6 containing 0.05 vol.% TMS.

Gel permeation chromatography (GPC)

The molecular weight distributions of curdlan and the acetyl derivatives were measured by a GPC system equipped with a refractive index detector RID-10A (Shimadzu Co., Kyoto, Japan). All the GPC measurements were performed at 40 °C using KF-806L×KF-803L columns (Shodex®, Showa Denko K.K., Tokyo, Japan), and 20 mM of LiCl in *N*,*N*-dimethylacetamide (DMAc, GPC grade, FUJIFILM Wako Chemicals Co., Osaka, Japan) was used as an eluent at a flow rate of 0.6 mL min^{-1}. Pullulan (ReadyCal-Kit Pullulan high, Polymer Standards Service-USA, Inc.) was used as a standard sample.

Each sample solution was prepared by dissolution of 10 mg of samples in 2 mL of the eluent and subsequent filtration using a disposal syringe filter (ADVANTEC HP045AN, pore size: 0.45 μm). The filtered insoluble fraction increased with an increase of the DS of CdAc, which might lower the concentration of the sample solution, and the intensity of the GPC chromatogram gradually decrease although a constant injection volume (100 μL) was kept for all the measurements.



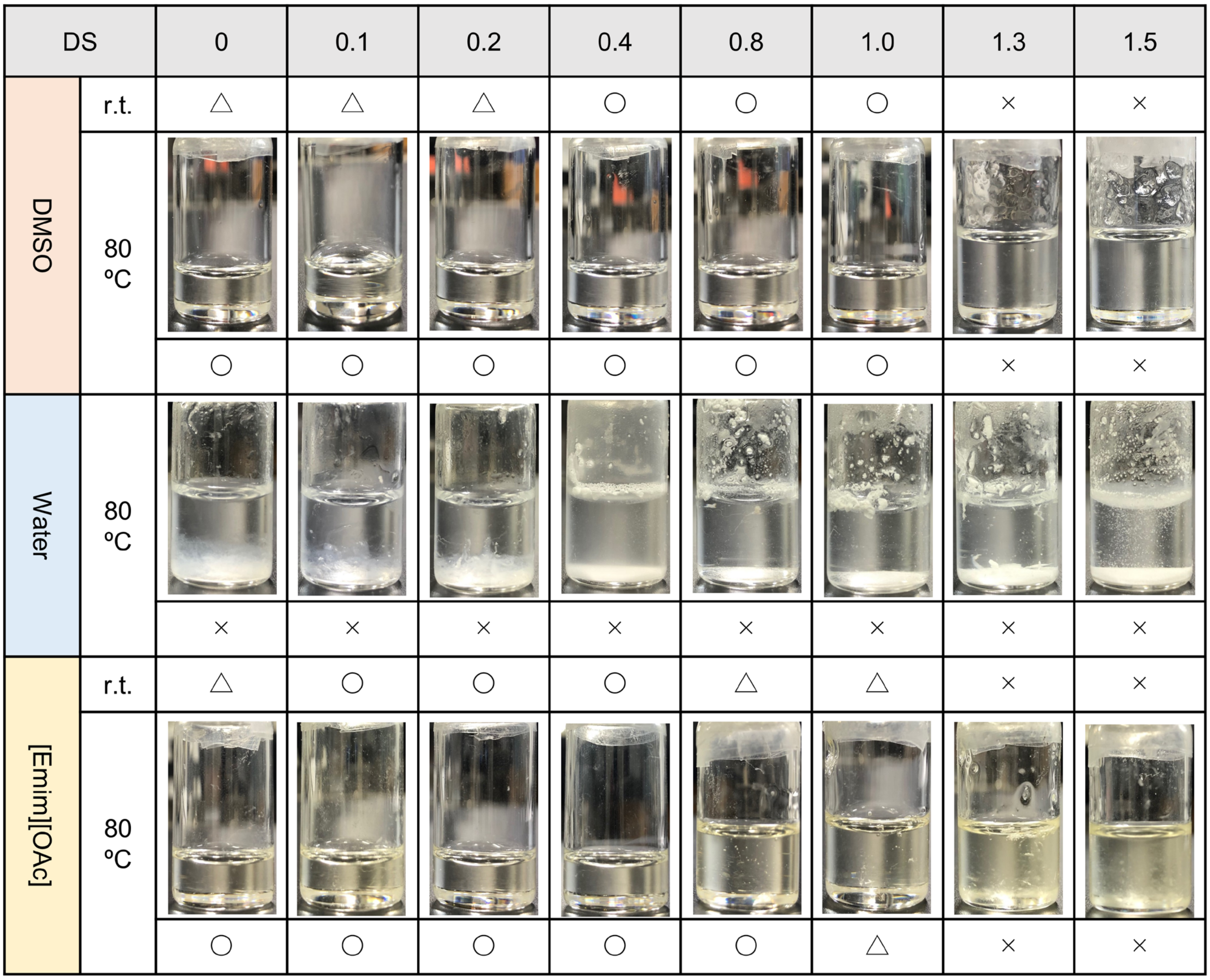
b

Entry	M_w / 10^5 g mol^{-1}	$Đ$
Cd (original)	11	21
Cd (0)	7.3	10
CdAc (0.1)	9.3	14
CdAc (0.2)	9.3	16
CdAc (0.4)	7.6	15
CdAc (0.8)	11	15
CdAc (1.0)	20	26
CdAc (1.3)	N/A	N/A
CdAc (1.5)	N/A	N/A

Figure S3. (a) GPC chromatograms of curdlan and curdlan acetates, measured in 1% LiCl/DMAc as an eluent with a flow rate of 0.6 mL min^{-1} and (b) the weight-average molecular weight (M_w) and polydispersity calculated using pullulan standards.

Solubility test

The solubility of curdlan and the acetyl derivatives in common solvents and [Emim][OAc] was investigated by a brief test. All samples were vacuum dried at 70 °C for 24 h before testing. The dried sample (10 mg) was weighed into a 1 mL vial, and various solvents (i.e., DMSO, water, [Emim][OAc], acetone, and chloroform) were added. Solubility was observed by visual confirmation after standing at room temperature (25 °C) or 80 °C for 24 h. Regardless of the DS, all the samples were completely insoluble in acetone and chloroform.



DS		0	0.1	0.2	0.4	0.8	1.0	1.3	1.5
DMSO	r.t.	△	△	△	○	○	○	×	×
	80 °C	○	○	○	○	○	○	×	×
Water	80 °C	×	×	×	×	×	×	×	×
[Emim][OAc]	r.t.	△	○	○	○	△	△	×	×
	80 °C	○	○	○	○	○	△	×	×

Figure S4. Solubility of curdlan and curdlan acetates in DMSO, water, and [Emim][OAc] at room temperature (r.t.) or 80 °C, ○: Soluble; ≥ 10 g L^{-1}, △: partially soluble; ≥ 5 g L^{-1}, ×: Almost insoluble; < 5 g L^{-1}.

Thermal analyses

Thermogravimetric Analysis (TGA) was performed using a TGA-50 (Shimadzu Co., Kyoto, Japan) equipped with a gas-flow controller (FC-60A, Shimadzu Co., Kyoto, Japan) and an analysis system (TA-60, Shimadzu Co., Kyoto, Japan). All samples were vacuum dried at 70 °C for 24 h prior to use, and the measurement temperature range was set from 50 to 500 °C at a heating rate of 10 °C min^{-1} in a N_2-flow rate of 50 mL min^{-1}. A sample of *ca.* 10 mg was pre-dried at 120 °C for 2 h. The thermal decomposition temperature (T_d) was taken as the onset of a 5% weight loss ($T_{d\text{-}5\%}$).

The glass transition temperature (T_g) was investigated by dynamic mechanical analysis (DMA) using a DMA 8000 instrument (PerkinElmer Japan Co., Ltd., Yokohama, Japan) in a single cantilever mode. The powder samples (*ca.* 10 mg) were enclosed in a folded metal plate named "material pocket." The measurements were carried out under a N_2 atmosphere at a heating rate of 2 °C min^{-1} from 50 to 300 °C or to the temperature at which the T_g peak for each sample was clearly observed.

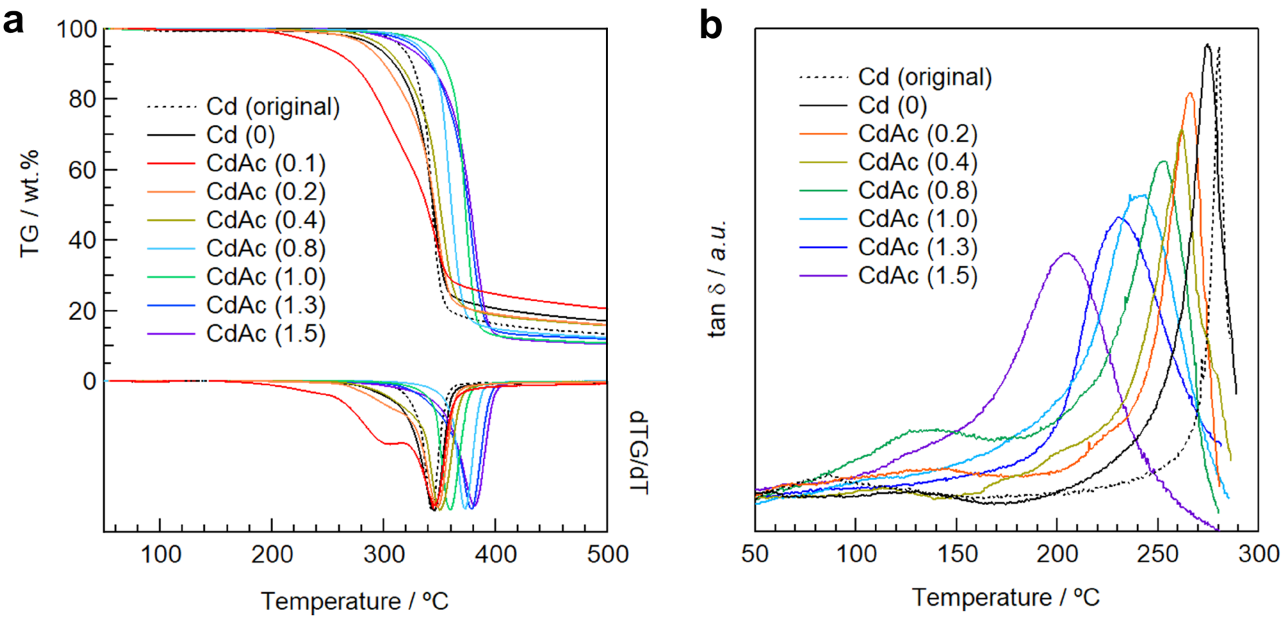


Figure S5. (a) TG and (b) DMA curves of curdlan and curdlan acetates.

Table S1 Thermal properties of curdlan and curdlan acetates with different DS

/ °C	Cd		CdAc							
	—[a]	0	0.1	0.2	0.4	0.8	1.0	1.3	1.5	3[b]
$T_{d\text{-}5\%}$	316	293	246	285	300	332	342	328	320	318
$T_{d\text{-}50\%}$	344	344	338	346	351	361	373	376	378	361
DTG_{max}	343	345	344	348	350	359	374	378	381	*n.d.*
T_g	280	274	251	265	253	254	231	230	206	171

[a] Original curdlan powder. [b] Refer to a previous work of Marubayashi *et al.* (2014).[1]

Hot-press tests

Curdlan acetate (powder, 0.5 g) with DS of 1.0, 1.3, and 1.6 was placed in a polytetrafluoroethylene (PTFE) mold (30 × 30 × 0.5 mm), covered between two PTFE sheets and hot-pressed for 1 min at a temperature of T_g + 20 °C under a constant pressure of 10 MPa using a MINI TEST PRESS・10 instrument (Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan) after pre-heating for 2 min. The molded film-like sample was naturally cooled and peeled off from the mold. The thermal processability of each sample was determined based on whether the heat-molded sample was a homogeneous self-standing film.

DS	1.0	1.3	1.5
T_g	231	230	206
Press temp.	250	250	230
Picture of hot-pressed film			
Thermal processability	×	△	○

Figure S6. Pictures of hot-pressed films prepared from curdlan acetate powders with DS of 1.0, 1.3, and 1.5. ○: Sufficiently processable, △: potentially processable with optimization of the molding condition, ×: Not applicable due to its significant thermal degradation.

Polarized optical microscope (POM) and birefringence measurements

The linear densities (titer) of the fibers were determined by a precise gravimetric measurement of each fiber, which was cut into a length of 3.0 cm.

An ECRIPSE E600 POM (Nikon Co., Tokyo, Japan) equipped with a DFC 450 charge-coupled device camera (Leica) was used to observe the orientation of the fiber. The polarizer and depolarizer were set at appropriate angles to obtain clear images. The average orientation of the amorphous and crystalline parts in each fiber sample was determined using the same POM equipped with a Berek compensator (Nichika Inc., Kyoto, Japan). The birefringence (Δn) of the fibers was calculated by dividing the retardation of the polarized light by the thickness of fiber, which was calculated from the linear density (titer) using the density of curdlan as 1.45 g cm^{-3}.[2] The total orientation factor (f_t) can be determined by dividing Δn by the maximum birefringence (Δn_{max}) of curdlan. However, the Δn_{max} of curdlan has never been determined, and thus, the value of Δn was considered as the analog factor for discussing the fiber orientation in this study.

As shown in Figure S7, the values of Δn increased with increasing the DS of curdlan acetate fibers. However, the Δn for curdlan acetate fibers with DSs of 0.8 and 1.0 were not determined by a limitation of our instrument setting, plausibly because their retardations of the polarized light were over from the measurable range of the used Berek compensator.

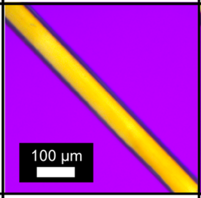
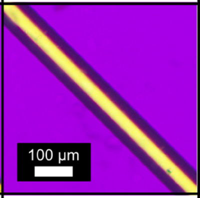
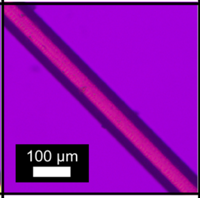
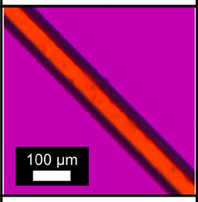
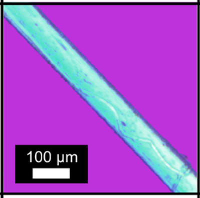
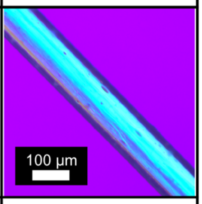
DS	0	0.1	0.2	0.4	0.8	1.0
tex	5.4 ± 0.1	5.5 ± 0.1	6.6 ± 0.1	6.5 ± 0.3	6.3 ± 0.1	6.6 ± 0.1
POM						
Δn	0.0040	0.0042	0.0050	0.0051	n.d.	n.d.

Figure S7. The average **l**inear density (titer, $N = 20$), POM images, and the values of Δn of regenerated curdlan fiber and curdlan acetate fibers with DS of 0.1−1.0.

Scanning electron microscopy (SEM)

SEM images were acquired with a field emission scanning electron microscope (S-4800, Hitachi Ltd., Tokyo, Japan) operating at an accelerating voltage of 1.0 kV after the fiber samples were coated with platinum for 30 s using an ion sputter (E-1030, Hitachi Ltd., Tokyo, Japan).

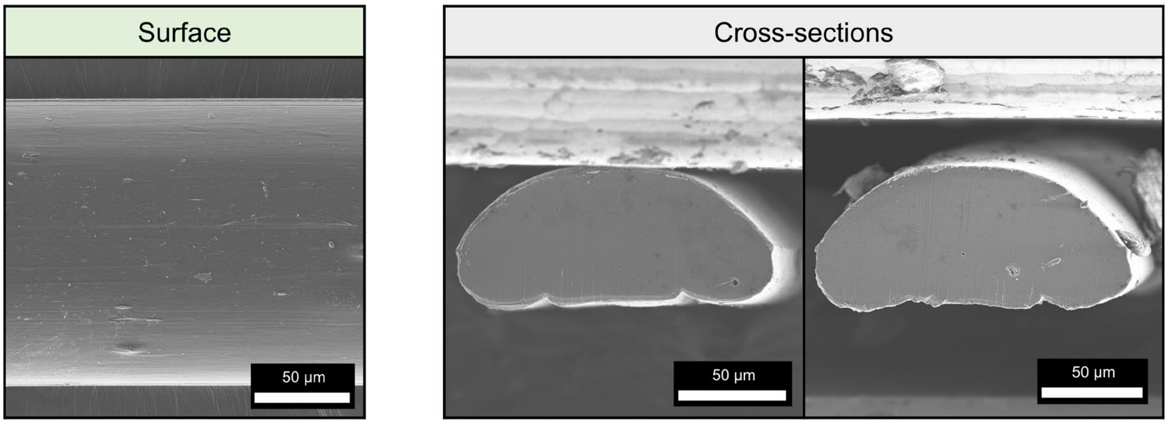


Figure S8. SEM images of the (a) surface and (b) cross sections of curdlan acetate fibers with DS of 0.8.

Tensile tests of fibers in the wet states

Tensile tests were performed using an EZ test instrument (Shimadzu Co., Kyoto, Japan) with a tensile speed of 10 mm min^{-1} at room temperature and an initial gauge length of 10 mm. The test was conducted for more than five times for each fiber sample in the wet state, and the average tensile strength was calculated and summarized in Table S1.

Prior to the test, the air-dried fibers (previously cut into a length of 3.0 cm) were immersed in distilled water and allowed to stand for 24 h. The water-absorbed fibers were taken from the water and gently wiped with paper to remove excess moisture on the surface, and immediately subjected to the tensile test.

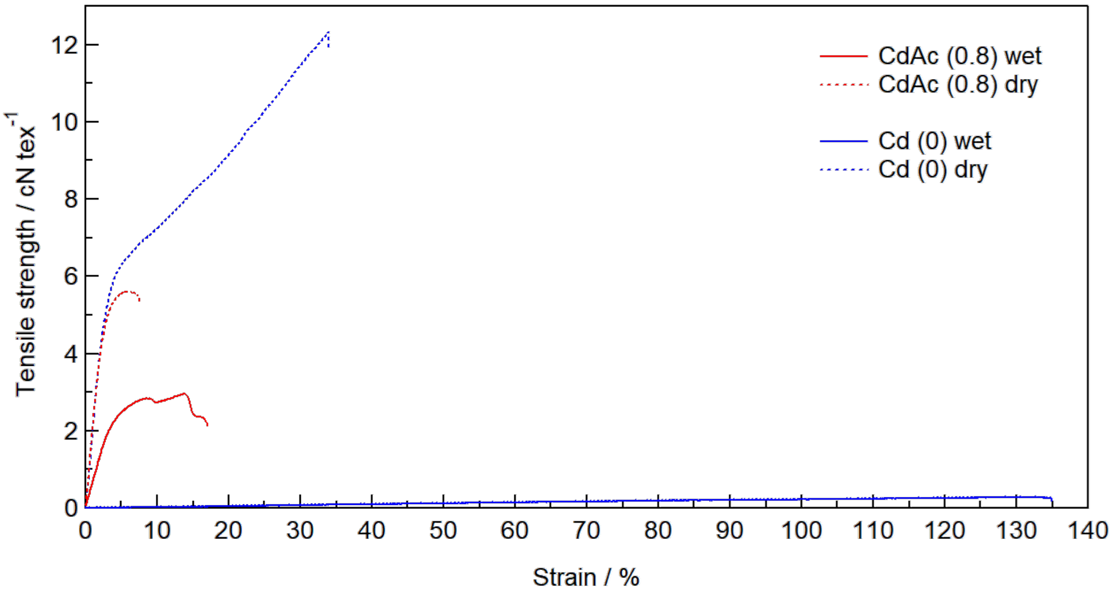


Figure S9. Stress-strain curves of regenerated curdlan fiber and curdlan acetate fibers with DS of 0.8 in dry and wet states, obtained by tensile tests.

Table S2 Water absorbency and tensile properties of regenerated curdlan fiber and curdlan acetate fiber in dry and wet states

Fiber sample	Water absorbency [a] / wt.%	Tenacity / cN tex^{-1}		Wet-to-dry tenacity ratio [b]	Elongation at break / %	
		Dry	Wet		Dry	Wet
Cd (0)	85 ± 1	12.6 ± 0.1	0.34 ± 0.0	0.03	34 ± 1	130 ± 8
CdAc (0.8)	15 ± 1	5.5 ± 0.1	2.8 ± 0.1	0.5	7.5 ± 0.2	19 ± 1

[a] $(W_{\mathrm{wet}} - W_{\mathrm{dry}}) / W_{\mathrm{wet}} \times 100$. Where W represents the average weight ($N \geq 10$).
[b] $T_{\mathrm{wet}} / T_{\mathrm{dry}}$. Where T represents the average tenacity ($N = 5$).

References

1. H. Marubayashi, K. Yukinaka, Y. Enomoto-Rogers, A. Takemura and T. Iwata, *Carbohydrate Polymers*, 2014, **103**, 427-433.
2. R. H. Marchessault, Y. Deslandes, K. Ogawa and P. R. Sundararajan, *Canadian Journal of Chemistry*, 1977, **55**, 300-303.