Control of the aqueous solubility of cellulose by hydroxyl group substitution and its effect on processing

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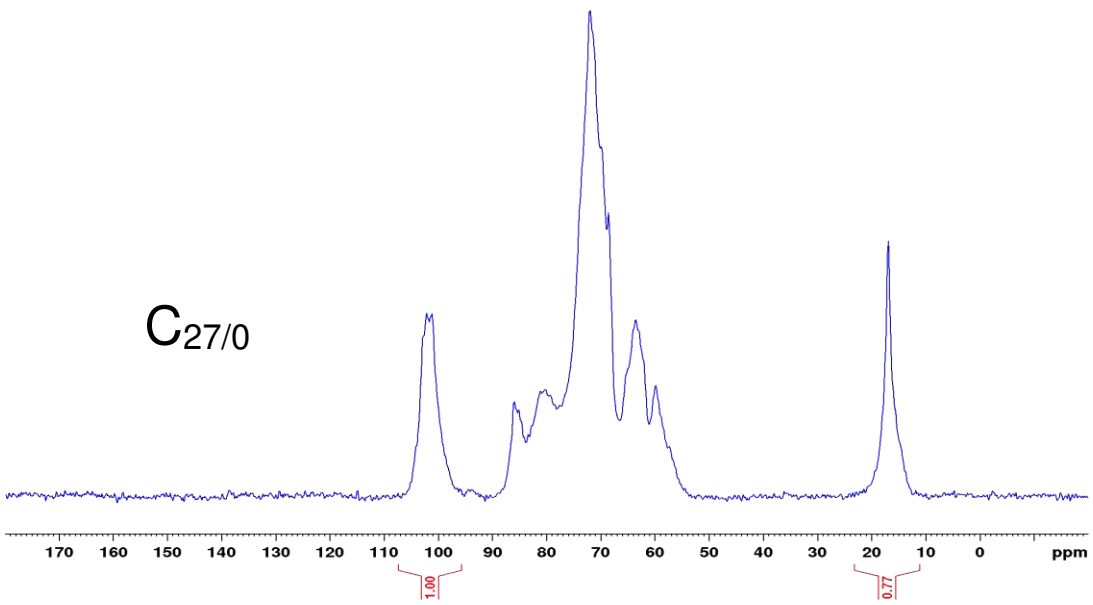
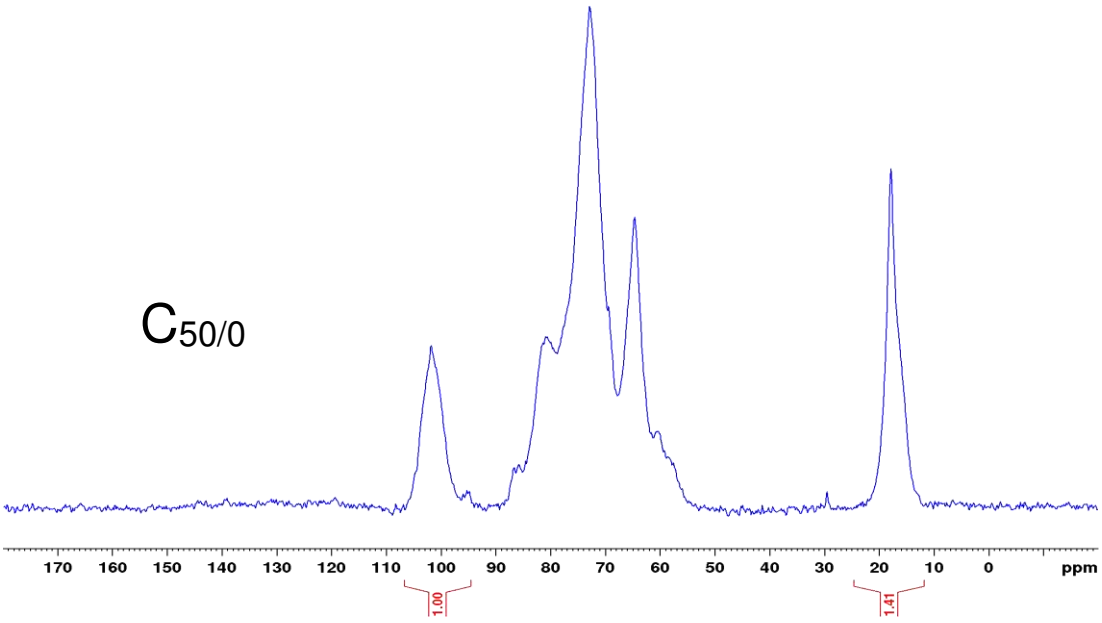
Supplementary data

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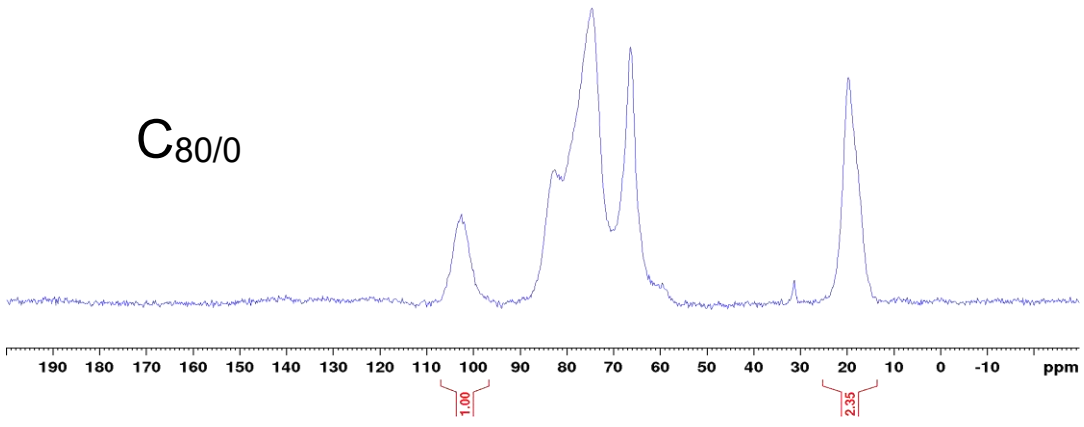
1.41


C80/0
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1.00
2.35

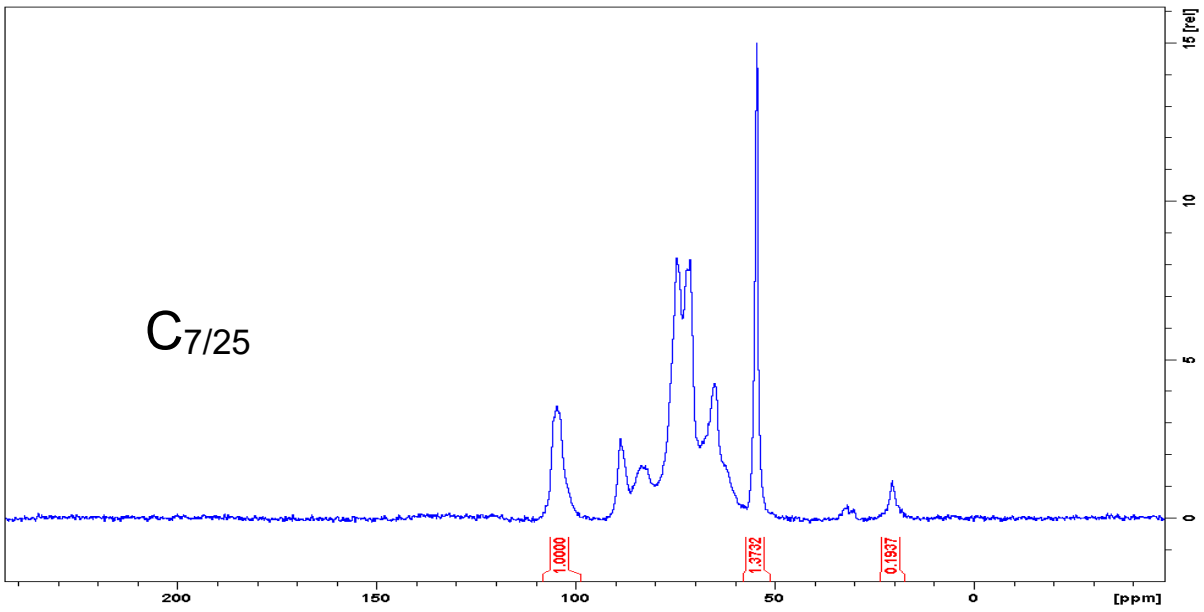

Figure S1. ^{13}C NMR spectra of $C_{27/0}$, $C_{50/0}$ $C_{80/0}$ and $C_{7/25}$. The C1 peak (carbon with glycosidic linkage between AGU) is at 100 – 110 ppm and the carbon from the methyl group of hydroxypropyl substituent is at 20 ppm. For example, the degree of substitution by HP (DS_{HP}) for $C_{80/0}$ and $C_{27/0}$ was calculated by dividing (2.35/3)*100 % = 78 % and (0.77/3)*100 % = 26 %, respectively. Molar hydroxyl substitution by HP per AGU (MS_{HP}) measured from CP/MAS ^{13}C NMR spectrum of hydroxypropylated celluloses: $C_{27/0}$ with MS_{HP} (DS_{HP}) = 0.77 (26 %), $C_{50/0}$ with MS_{HP} (DS_{HP}) = 1.41 (47 %), and $C_{80/0}$ with MS_{HP} (DS_{HP}) = 2.35 (78 %).

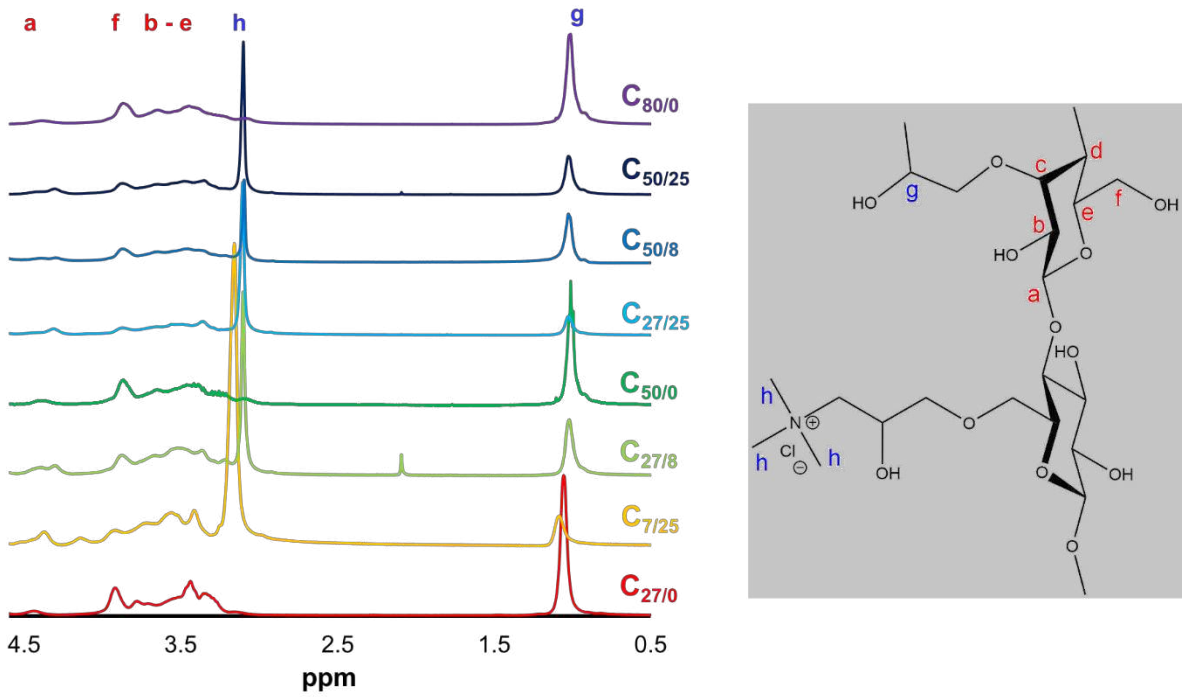

Figure S2. ^{1}H NMR spectra for all modified cellulose samples. Peak corresponding to the protons on C1 (4.5 ppm, a), C2 – 5 (3.3 – 3.8 ppm, b-e), C6 (3.9 ppm, f), the HP group (1.3 ppm, g) and the HPTMAC group (3.1 ppm, h) are labelled. HPTMAC degree of substitution (DS_{cat}) in Table S1 was calculated from the normalised ratio between the integrals of peaks h and b-e (I_h and $I_{b\text{-}e}$, respectively), through the equation $DS_{cat} = \left[\left(\frac{I_h/9}{I_{b-e}/4}\right)/3\right] \times 100\%$. The placement of the modified groups in the AGU units is not suggestive any possible stereoselectivity in the modification.

Table S1. Elemental analysis and ^{1}H NMR results analysing DS_{cat} values for $C_{7/25}$, $C_{27/8}$, $C_{27/25}$, $C_{50/8}$ and $C_{50/25}$.

Sample	Targeted HPTMAC Modification / %	Resulting HPTMAC Modification / %	
		^{1}H NMR	Elemental Analysis
$C_{7/25}$	25	16.5	24.7
$C_{27/8}$	8	13	13
$C_{27/25}$	25	34.5	28.0
$C_{50/8}$	8	8.5	8
$C_{50/25}$	25	22.9	18.7

Table S2. Overview of results for all samples including targeted modification of both hydroxypropyl (HP) and (2-hydroxypropyl)trimethylammonium chloride (HPTMAC) modification groups, the percentage solid content after modification (Solid Cont.), surface zeta potential (ξ), the length of nanocrystals (as determined by TEM), and the radius of gyration of the large aggregates (R_{gc}), molecules (R_{gm}) and the excluded volume parameter (ν), determined by SAXS.

Sample Name	DS / %			Solid Cont. / w/w %	ξ / mV	Length / nm	SAXS		
	HP	HPTMAC (cat)	Total				R_{gc} / nm	R_{gm} / nm	ν
$C_{27/0}$	27	0	27	52.8	- 2 ± 1	138 ± 33	40.9	14.9	0.44
$C_{7/25}$	7	25	32	45.7	25 ± 1	109 ± 31	1029.4	13.4	0.47
$C_{27/8}$	27	8	35	29.2	22 ± 1	100 ± 29	21.2	15.4	0.48
$C_{50/0}$	50	0	50	0.4	0 ± 1	122 ± 28	30.6	23.5	0.52
$C_{27/25}$	27	25	52	35.5	42 ± 2	101 ± 35	21.0	13.9	0.49
$C_{50/8}$	50	8	58	3.2	28 ± 1	118 ± 40	31.8	19.0	0.51
$C_{50/25}$	50	25	75	4.9	33 ± 4	91 ± 34	-	21.6	0.59
$C_{80/0}$	80	0	80	0.5	2 ± 1	-	-	19.5	0.55

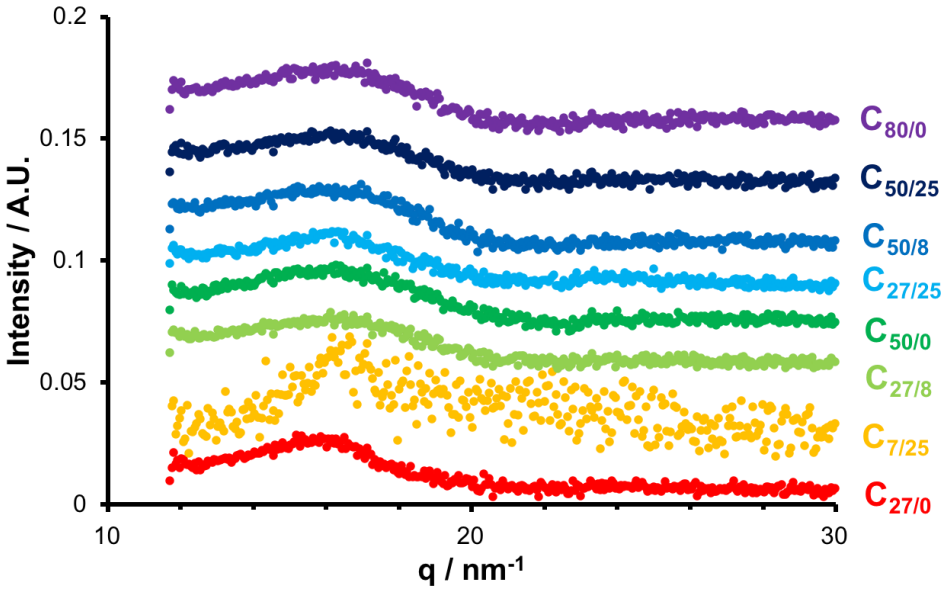

Figure S3. WAXS patterns of 1.0 w/w % modified cellulose aquesous dispersions. A broad peak can be seen in the region of 15 – 17 nm^{-1}, indicating the presence of amorphous cellulose. The patterns are offset for clarity. In order to minimize an effect of $C_{7/25}$ sedimentation on the scattering pattern, the $C_{7/25}$ WAXS pattern was recorded only for 60 s (instead of 15 min used for the others).

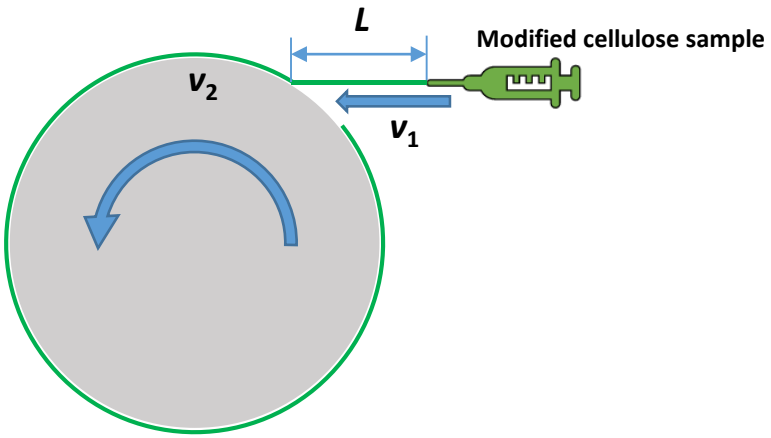

Figure S4. Schematic illustration of fibre spinning process. Dosing of an aqueous dispersion is performed using the syringe pump feeding the dispersion onto the rotating cylinder drum surface. In order to process $C_{50/0}$ 10 w/w % aqueous dispersion, the nozzle jet speed (v_1) and the drum surface speed (v_2) were set at 5.77 m/s (the syringe feed flow of 12 ml/min through the nozzle inner diameter of 210 µm) and 7 m/s, respectively, providing stretching ratio v_2/v_1 more than unity (1.21). The distance between the syringe needle tip and the drum surface (L) was set at 5 mm.