Electronic Supplementary Material (ESI) for Green Chemistry.

Mercerisation of cellulose in aqueous NaOH at low concentrations: supporting information

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Additional diffractograms were acquired on wetted material using hermetically sealed sample holders in transmission mode. The samples were monitored after thawing while they still contained the NaOH solution, and after extensive rinsing with distilled water. Drying was avoided by simply squeezing the excess of solution out of the fibre lump and by immediately transferring the samples to the sample holder in order to proceed with the WAXD measurements. The spectra were vertically shifted and rescaled in order to emphasise peak positioning. An example of such a sample is given in Figure 1 for c = 3 wt.%. Similar diffractograms were obtained with c = 1 wt.% (data not shown here).

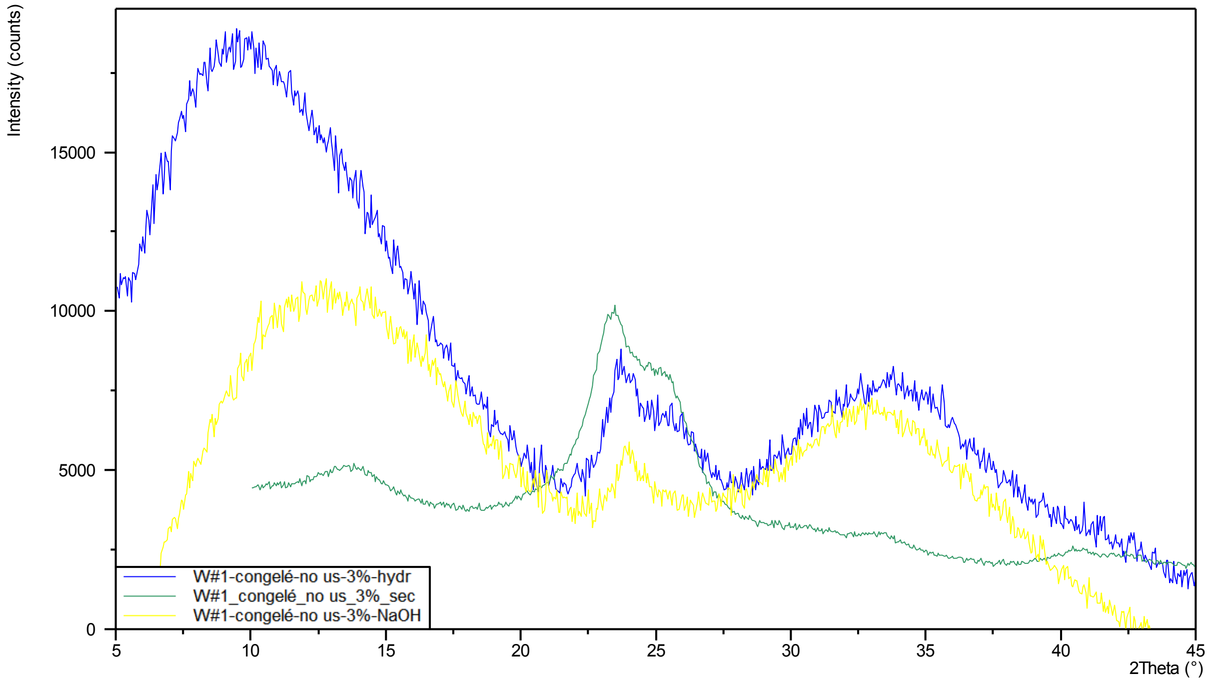

Figure S1. WAXD diffractograms of cellulose treated with a 3 wt.% NaOH (yellow), after rinsing with distilled water (blue) and after drying (green).

A fast peak fitting procedure was performed with the Fityk.[1] The method was the following:

- The area under the curve was normalized
- Background points were added manually
- The spectrum was stripped from its background
- Pearson VII peaks were added to the most prominent locations
- Fitting was performed with the implemented algorithm
- Peak parameters were exported. The peak width at half maximum was used to determine crystallite width using Scherrer equation (pure cellulose I (filter paper) or II (c = 1, 2 and 3 wt.%) only). The total peak area was used as an estimate of the crystallinity because the area under the curve was normalized before the background was subtracted.

Since the conversion from cellulose I to II was more than 90% complete with a 1 wt.% NaOH concentration (least square method), the peak fitting procedure was conducted ignoring the presence of cellulose I for c = 1, 2 and 3 wt.%.

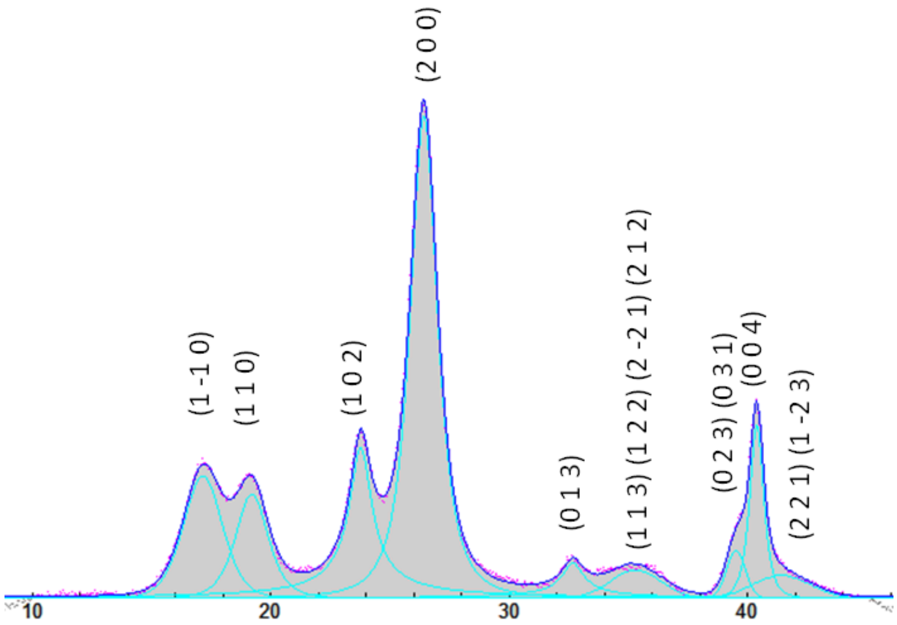

Figure S2. Fitted diffractogram of the raw cellulosic material. Peaks were indexed for cellulose I_β basis according to French (2014).[2]

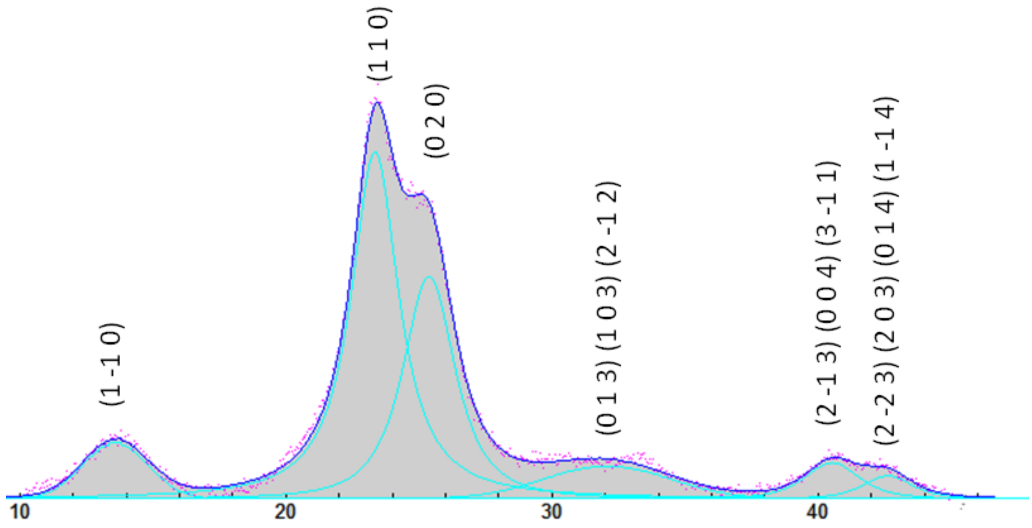

Figure S3. Fitted diffractogram of the dried cellulosic substrate treated with 3 wt.% NaOH at -17°C. Peaks were indexed for cellulose II according to French (2014).[2]

The score plots obtained after PCA can also be drawn as a function of the wavenumber.

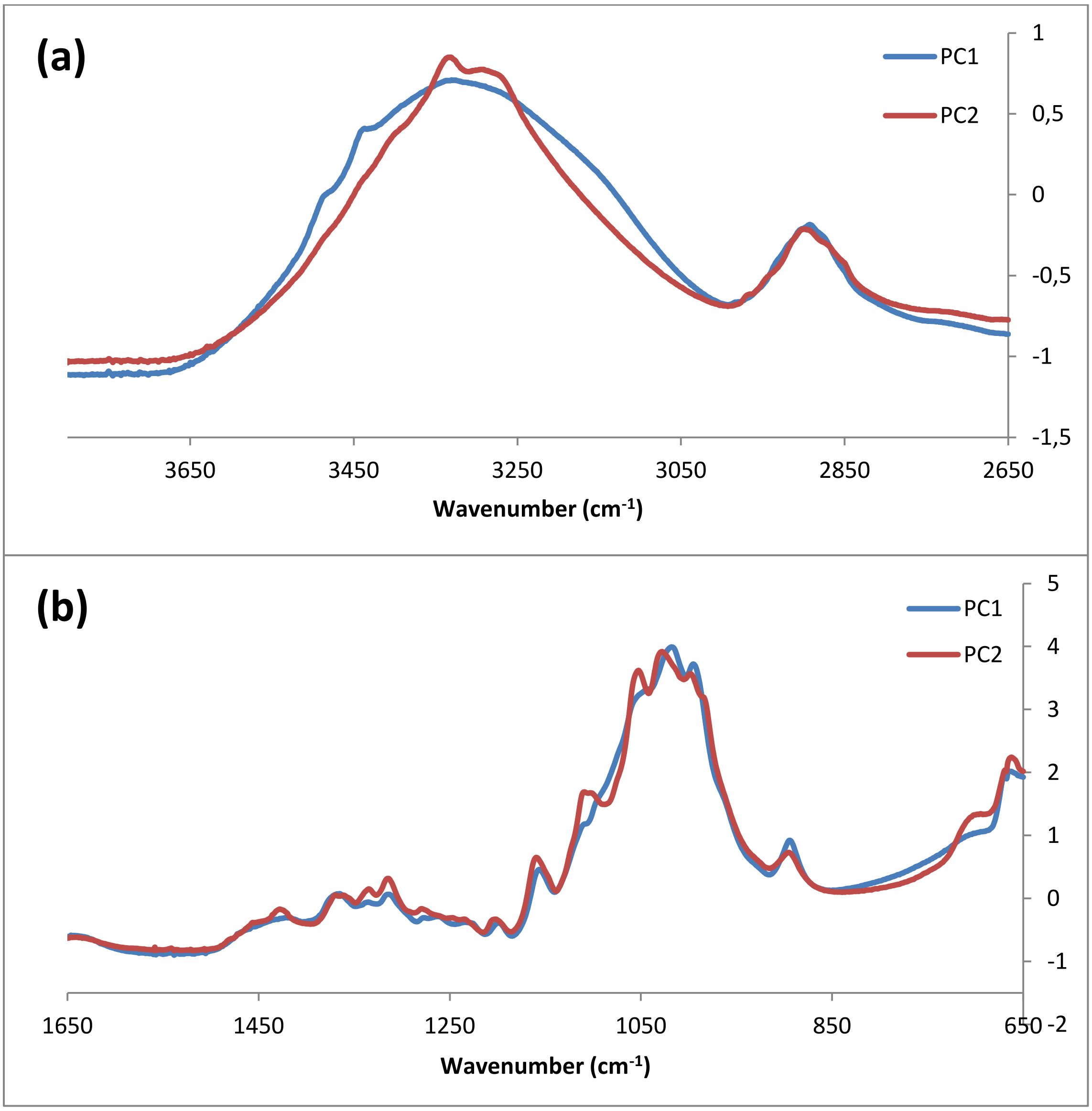

Figure S4. Score plots of the two principal components in the 3800-2650 cm^{-1} range (a) and in the 1650-650 cm^{-1} range.

The classical phase diagram of NaOH/H_2O/cellulose devised for ramie fibres by Sobue *et al.*was modified according to the results contained in this work and according to the following assumptions:[4]

- The cellulose substrate migrates to the liquid phase in the ice/liquid mixture below 0°C

- The NaOH concentration has to exceed 7 wt.% in order for the conversion to occur[5–8], which means that the treatment temperature has be below *circa* -7°C according the NaOH/H_20 phase diagram
- According to the results presented in this article, the liquid to cellulose ratio has to be kept superior to 7.7:1 for the full conversion to Na-cellulose I to occur.

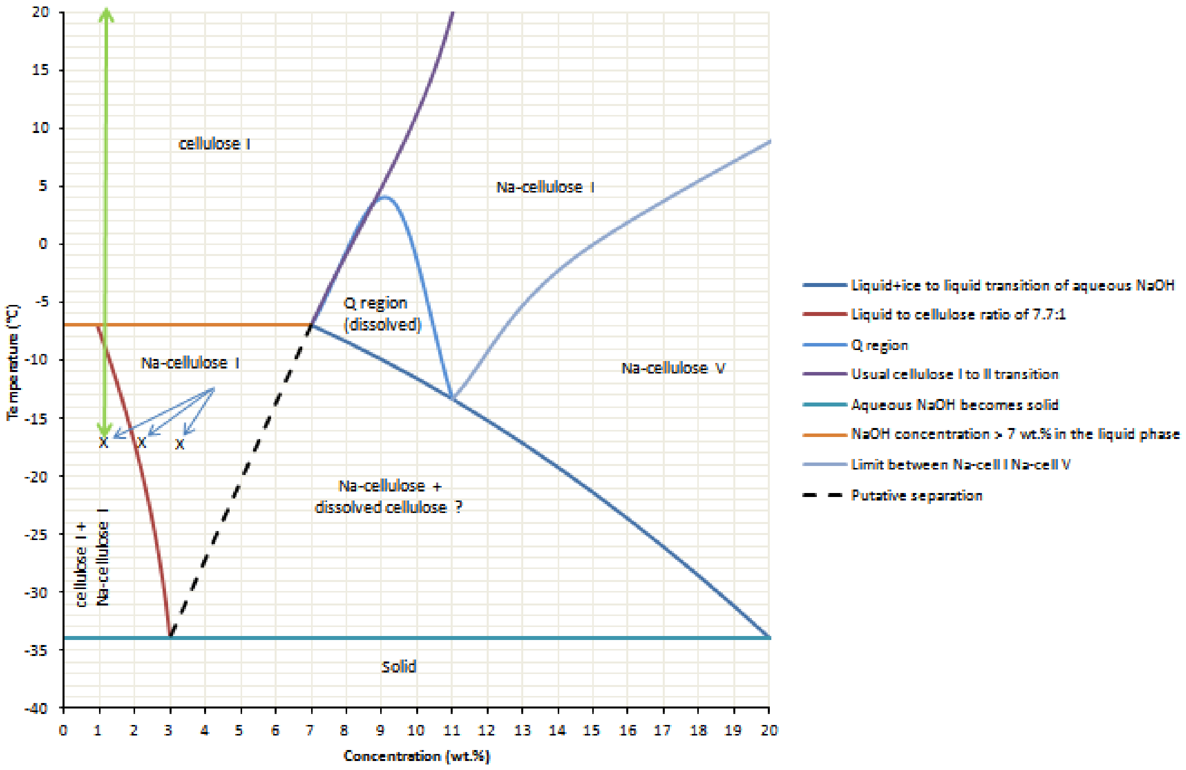

Figure S5. Putative phase diagram of 1 wt.% cellulose in aqueous NaOH. The green arrow represents the thermal path followed by the sample with c = 1 wt.% during the treatment.

Another treatment was conducted in order to test this method further with a different cellulose source. One gram of Avicel microcrystalline cellulose (MCC, Macherey Nagel, DP ~ 40-200) was mixed to 99 ml of aqueous sodium hydroxide (c = 1 wt.%). The experimental protocol was similar to the one described in the rest of the article: the suspension was stirred for 1 h at room temperature, the material was frozen to -20°C for 7 h. Thawing to room temperature was performed overnight. Rinsing and filtering against distilled water were performed three times. Drying was accomplished at room temperature.

Diffraction experiments were performed in reflection with powdered MCC. A control whatman#1 filter paper was prepared and measured in the same conditions and measured with XRD (Figure S6). The XRD data is presented below (Figure S7). The MCC diffractogram after treatment did not indicate any presence of cellulose II (Figure S7), whereas that of cotton was similar to the other one reported in the main body of the article. The crystallinity index of the starting material was evaluated using Segal's method, an amplitude method based on the strongest cellulose signal of the (200) diffraction plane that of the amorphous background.[3] The crystallinity index of Whatman #1, MCC before and after treatment were found to be, respectively, 0.73, 0.71 and 0.68. (Other materials were not assessed using this method as Segal's method doesn't apply to cellulose II or mixtures of cellulose I and II.) MCC thus appeared slightly less crystalline after treatment.

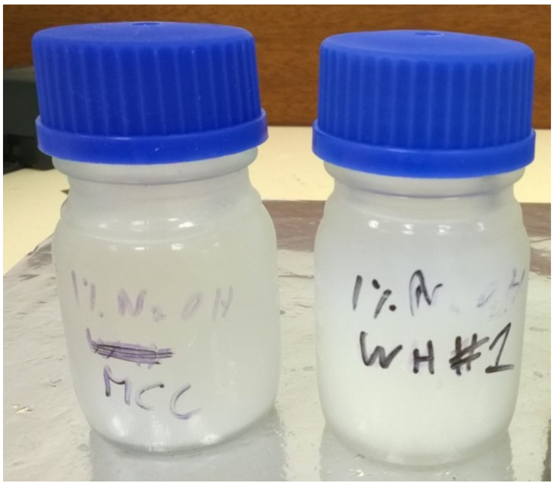

Figure S6. Frozen MCC (left), filter paper (right) suspensions in 1 wt.% aqueous NaOH solutions. Sedimentation is visible in the MCC sample.

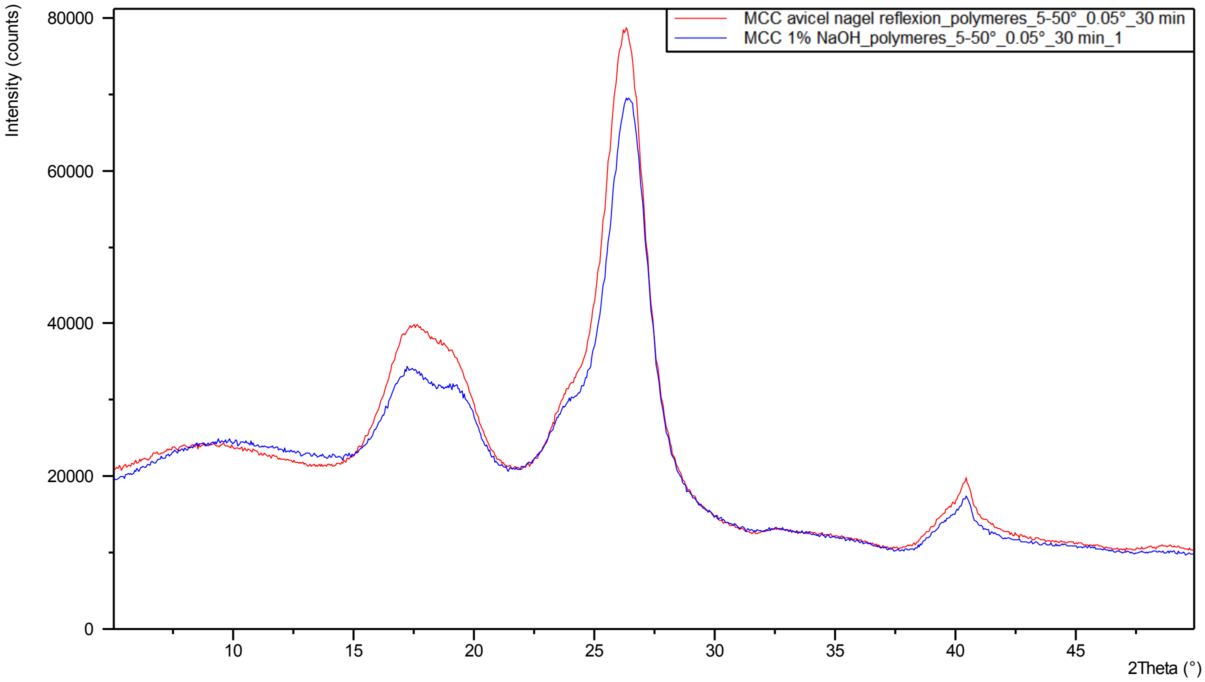

Figure S7. Microcrystalline cellulose before (red) and after (blue) a treatment in c = 1 wt.%.

It is well-known that MCC shows more reluctance to chemical accessibility and mercerisation than less crystalline materials.[7] In the present work, sedimentation was visible in the preparation bottle (Figure S6). It is not clear as yet whether the sample didn't mercerize as efficiently because the local cellulose to alkaline solution ratio that formed was too high in the sediment at the bottom of the bottle.

Another explanation could be proposed. MCC is often assumed to be intrinsically more difficult to transform due to its high crystallinity. Nevertheless, its crystallinity is very similar to that of cotton.[6,7,9] The main difference between the presently used cotton and MCC lies in the extensive hydrolytic treatment of MCC, a treatment ensuing extensive scission of the longitudinal disordered regions by end-attack.[10,11] This hydrolytic scission results in a degree of polymerisation consistent in terms of extended chain length with single crystallite length. This degree of polymerisation is often called the level-off degree of polymerisation.[12,13] Consequently, since the main difference between MCC and cotton lies in the absence of longitudinal disordered regions (as opposed to lateral disordered regions), it is assumed that these longitudinal regions play an important role in the mercerisation process. This hypothesis coupled with a fringe-micellar view provides a volume of material with comingled chains, a pre-requisite still consistent with the interdigitation theory.[7,14,15]

References:

(1) Wojdyr, M. Fityk: A General-Purpose Peak Fitting Program. *J. Appl. Crystallogr.* **2010**, *43*, 1126–1128.
(2) French, A. D. Idealized Powder Diffraction Patterns for Cellulose Polymorphs. *Cellulose* **2014**, *21*, 885–896.
(3) Segal, L.; Creely, J. J.; Jr, A. E. M.; Conrad, M. C. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Text. Res J* **1959**, *29*, 786–794.
(4) Sobue, H.; Kiessig, H.; Hess, K. Das System Cellulose-Natriumhydroxyd-Wasser in Ahhängigkeit von Der Temperature. *Ztg. Phys. Chem.* **1939**, *B43*, 309–328.
(5) Mansikkamäki, P.; Lahtinen, M.; Rissanen, K. Structural Changes of Cellulose Crystallites Induced by Mercerisation in Different Solvent Systems; Determined by Powder X-Ray Diffraction Method. *Cellulose* **2005**, *12*, 233–242.
(6) Okano, T.; Sarko, A. Mercerization of Cellulose. I. X-Ray Diffraction Evidence for Intermediate Structures. *J. Appl. Polym. Sci.* **1984**, *29*, 4175–4182.
(7) Okano, T.; Sarko, A. Mercerization of Cellulose. II. Alkali–cellulose Intermediates and a Possible Mercerization Mechanism. *J. Appl. Polym. Sci.* **1985**, *30*, 325–332.
(8) Rånby, B. The Mercerisation of Cellulose. II. A Phase Transition Study with X-Ray Diffraction. *Acta Scand.* **1952**, *6*, 116–127.
(9) Ott, E.; Spurlin, H. *Cellulose and Cellulose Derivatives*; High polymers; 2nd ed.; Interscience, New York-London, 1955; Vol. 5.
(10) Wood, B. F.; Conner, A. H.; Hill Jr., C. G. The Heterogeneous Character of the Dilute Acid Hydrolysis of Crystalline Cellulose. *J. Appl. Polym. Sci.* **1989**, *37*.
(11) Hearle, J. W. . The Development of Ideas of Fine Structure. In *Fibre structure*; Butterworth, Ed.; The Textile Institute: London-Manchester, 1963.
(12) Battista, O. A.; Coppick, S.; Howsmon, J. A.; Morehead, F. F.; Sisson, W. A. Level-Off Degree of Polymerization. *Ind. Eng. Chem.* **1956**, *48*, 333–335.
(13) O'Sullivan, A. C. Cellulose: The Structure Slowly Unravels. *Cellulose* **1997**, *4*, 173–208.
(14) Dinand, E.; Vignon, M.; Chanzy, H.; Heux, L. Mercerization of Primary Wall Cellulose and Its Implication for the Conversion of Cellulose I→cellulose II. *Cellulose* **2002**, *9*, 7–18.
(15) Kim, N.-H.; Imai, T.; Wada, M.; Sugiyama, J. Molecular Directionality in Cellulose Polymorphs. *Biomacromolecules* **2006**, *7*, 274–280.