

SUPPORTING INFORMATION

Facile method to determine the molecular weight of polymer grafts grown from cellulose nanocrystals

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Supplementary Figures and Tables

1. Determination of average dimensions of neat CNCs

The average length and width of neat CNCs were determined by images analysis of TEM micrographs as reported elsewhere,¹ using a 0.001 wt% dispersion of CNCs, due to the well-known tip broadening effects on AFM images. The analysis resulted a length of 100 ± 23 and a width of 8 ± 1 (**Figure S1**). Note that even in well-dispersed suspensions of neat CNCs, they are commonly found in pairs, which may influence the width determined.

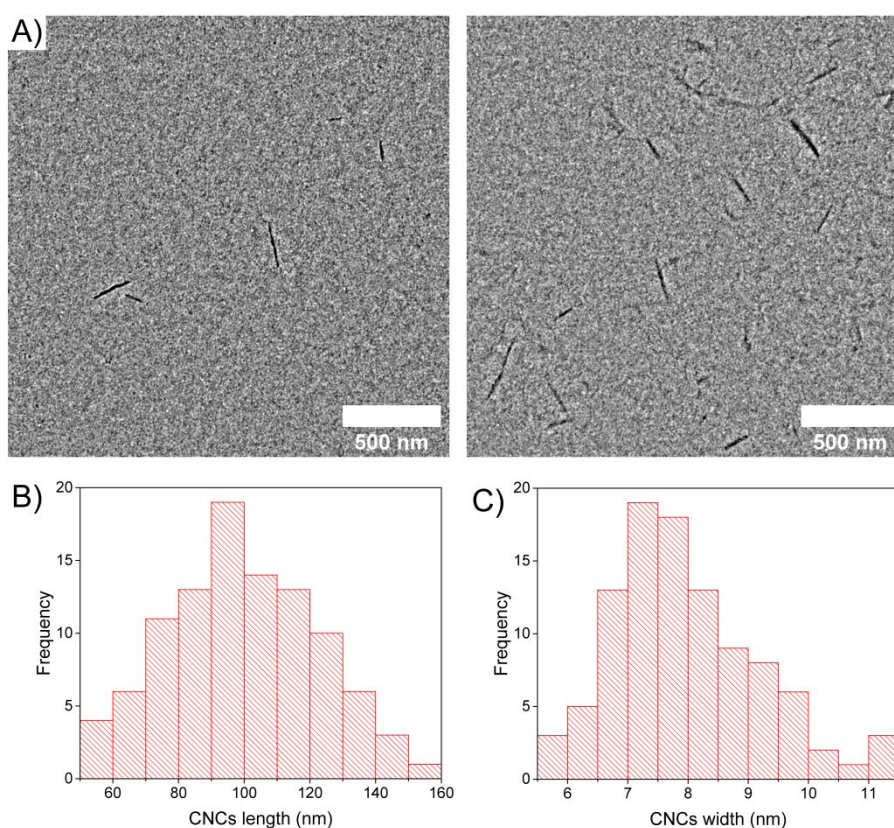


Figure S1. (A) TEM micrographs (two representative spots of one single TEM-grid) of a spin-coated 0.001 wt% aqueous dispersion of neat CNCs, scale bar = 500 nm. Histograms showing the (B) length and (C) width distributions of neat CNCs. Data were collected from the analysis of 100 CNCs observed in TEM micrographs.

In order to determine the average height of neat CNCs, image analysis of AFM tapping mode height image was employed. The analysis resulted in a height of 6 ± 2 nm (**Figure S2**). The sample was prepared by first functionalizing a freshly peeled mica with an aqueous solution of

poly-L-lysine by drop-casting (40 μL). After 0.5 min, the poly-L-lysine was washed off with milli-Q water and dried under a flow of nitrogen. Aqueous CNCs suspensions (0.0001 wt%, 40 μL) were then drop-casted onto the functionalized mica surface, washed with mili-Q water, and subsequently dried under nitrogen flow. The images were acquired with a Park NX10 microscope, in tapping mode with TAP300Al-G probes at room temperature. Images were recorded with 2048x2048 pixels of resolution.

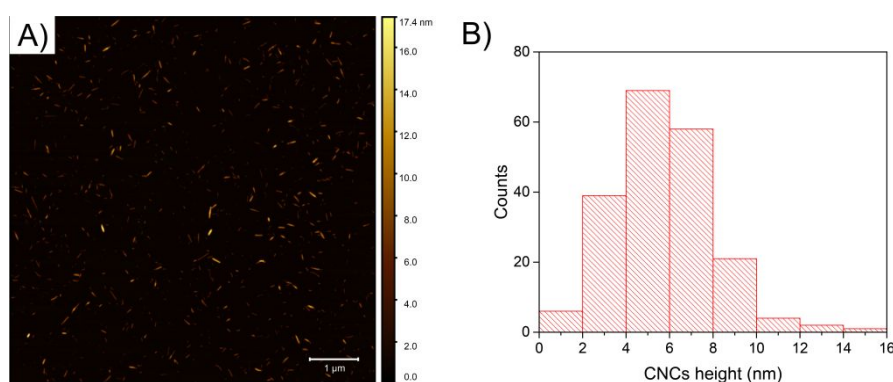


Figure S2. (A) AFM tapping mode height image of neat CNCs. Scale bar = 1 μm . (B) Histogram showing the height distribution of neat CNCs. Data collected from the analysis of 200 CNCs observed in an AFM height image.

2. Elemental composition of neat CNCs and CNC-Ini

Table S1. Elemental compositions (wt%) of neat CNCs and CNC-Ini determined by elemental analysis.

Sample	% C	% H	% N	% Br
CNCs	42.36	6.24	0.01	0.01
CNC-Ini	44.38	6.27	0.56	1.89

3. Determination of the sulfate half-ester content of neat CNCs by conductometric titration

The surface charge density of cotton CNCs was determined by conductometric titration according to a well-known procedure.² First, a dialyzed suspension of 0.55 wt% CNCs was passed through a previously washed strong acid cation exchange resin (DOWEX Marathon C hydrogen form, Sigma-Aldrich) column. Then, 20 mL of the resultant suspension, containing 1 mM NaCl, was titrated against 0.01M standardized NaOH solution using a SevenCompact Duo S213 pH/conductivity meter. The first equivalence point was assigned to the sulfate half ester groups content ($139 \text{ mmol R-OSO}_3\text{H kg}^{-1}$ CNCs), while the second equivalence point corresponds to the carboxylic groups (46 mmol kg^{-1} CNCs) (**Figure S3**).

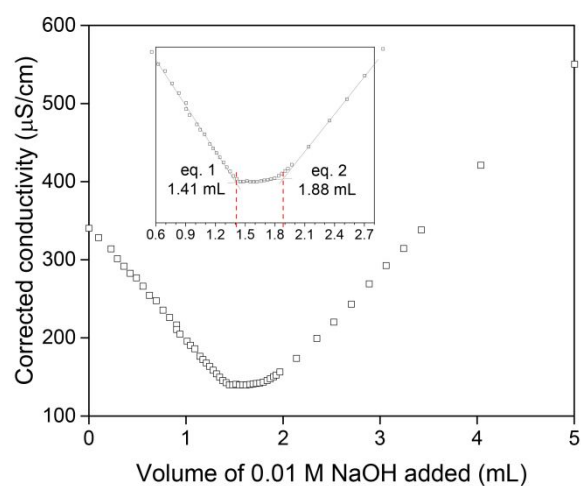


Figure S3. Conductometric titration curve for neat CNCs and the two equivalent points determined graphically (inset) corresponding to the surface half ester and carboxylic groups contents.

4. ^1H NMR spectra of the supernatant extracted from the synthesis of CNC-g-PHMA in the absence and presence of EBiB as a sacrificial initiator

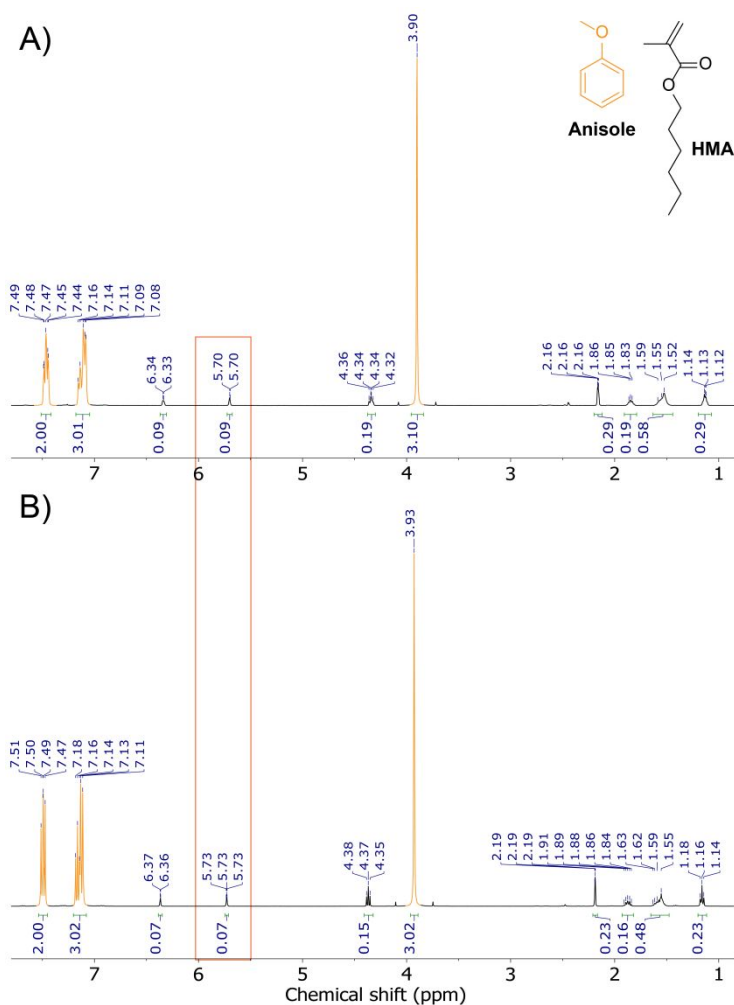


Figure S4. ^1H NMR spectra of the supernatant extracted from the synthesis of CNC-g-PHMA₂ (A) before and (B) after 2 h of reaction showing the proton signals of anisole (orange) and HMA (black).

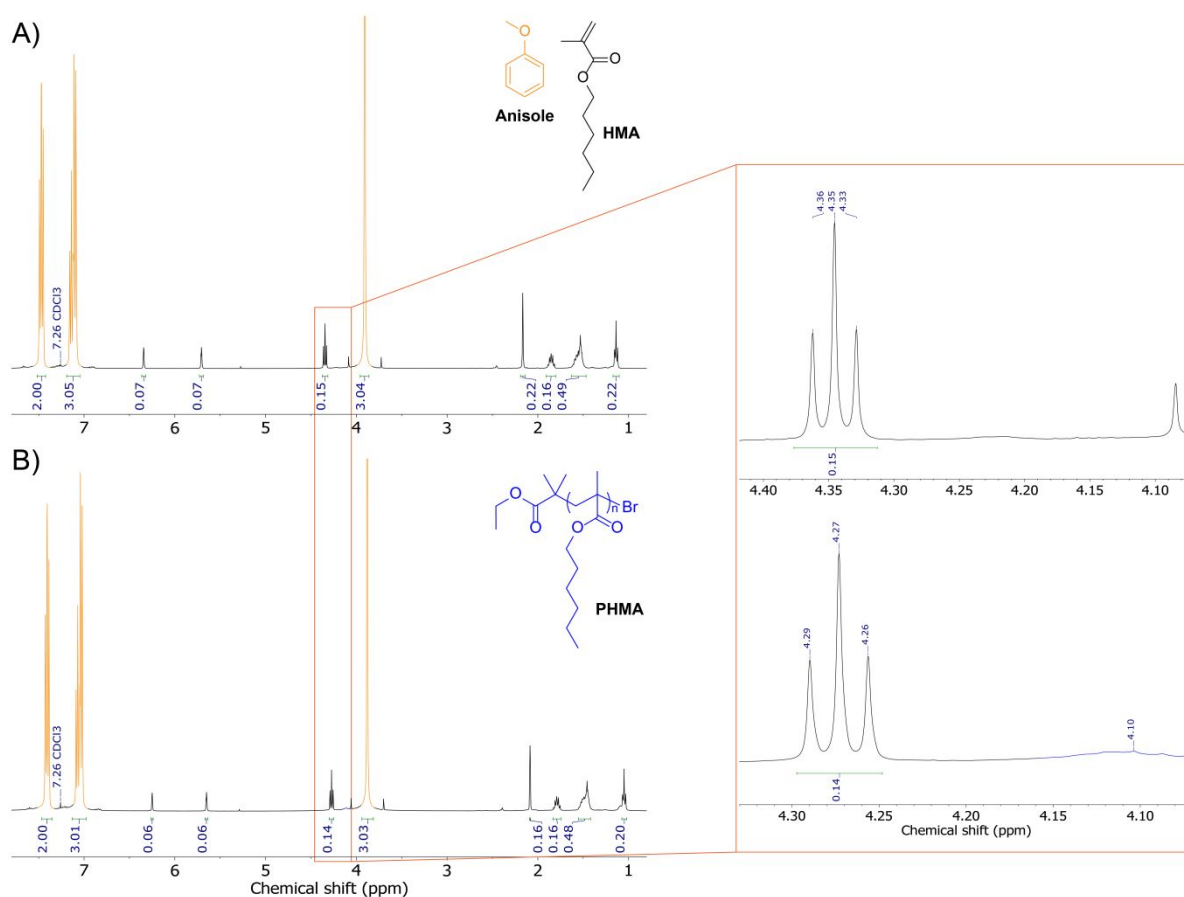


Figure S5. ^1H NMR spectra of the supernatant extracted from the synthesis of CNC-*g*-PHMA_(SII) in the presence of EBiB as sacrificial initiator, (A) before and (B) after 1 h of reaction showing the proton signals of anisole (orange), HMA (black) and free PHMA formed in solution (blue).

5. Size exclusion chromatography (SEC) of the free PHMA grown in solution from the sacrificial initiator

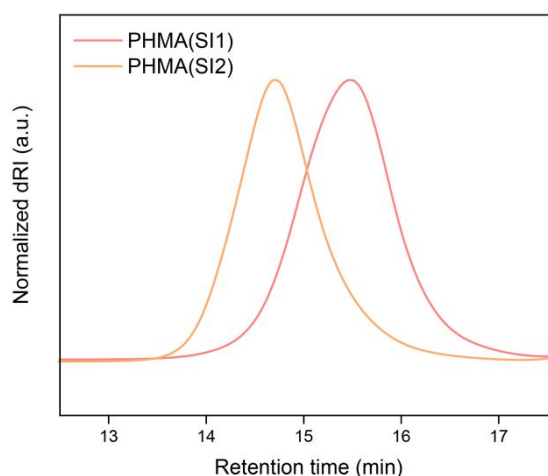


Figure S7. SEC traces of free PHMA isolated from CNC-g-PHMA_(SI1) (orange) and CNC-g-PHMA_(SI2) (pink) using THF as eluent.

6. Cleavage of grafted polymers from the CNCs

This protocol is based on reference 3. CNC-g-PHMA₁ or CNC-g-PHMA₂ (50 mg) was added to THF (2 mL) and the mixture was sonicated in a bath sonicator for 30 min before butanol (10 mL) fuming sulfuric acid containing 30% SO₃ (200 mg) were added. The suspension was heated to 100 °C under reflux for 7 days before the mixture was cooled and added to cold methanol (50 mL). The solvent was then evaporated in vacuo and the residue was washed with water; this afforded an organic and an aqueous layer. The organic layer was extracted and dried and the residue was used for NMR and SEC analysis.

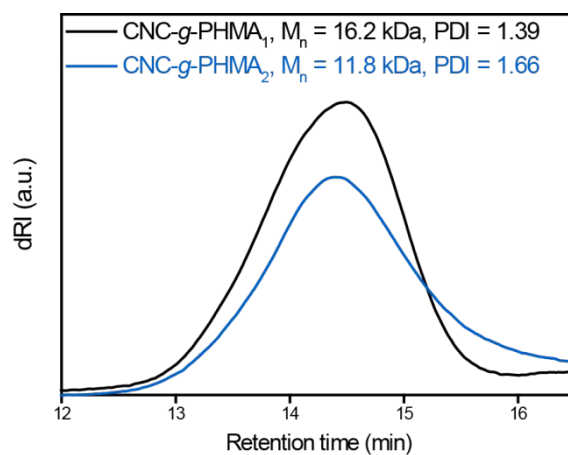


Figure S8. SEC traces of cleaved polymers from CNC-g-PHMA₁ (black) and CNC-g-PHMA₂ (blue) using THF as eluent.

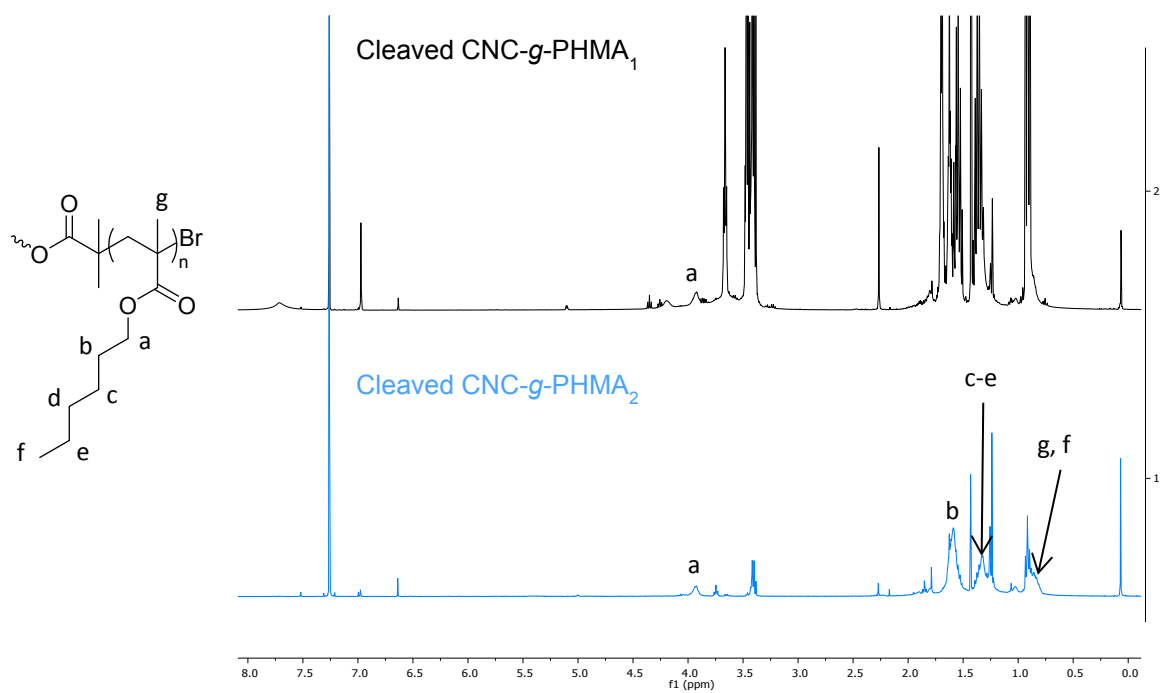


Figure S9. ¹H NMR spectra of the cleaved polymers from CNC-g-PHMA₁ (black) and CNC-g-PHMA₂ (blue) with CDCl₃ as the solvent.

7. References

1. Wohlhauser, S.; Delepierre, G.; Labet, M.; Morandi, G.; Thielemans, W.; Weder, C.; Zoppe, J. O., Grafting Polymers from Cellulose Nanocrystals: Synthesis, Properties, and Applications. *Macromolecules* **2018**, *51*, 6157-6189.
2. Beck, S.; Méthot, M.; Bouchard, J., General procedure for determining cellulose nanocrystal sulfate half-ester content by conductometric titration. *Cellulose* **2015**, *22*, 101-116.
3. Olszewski, M.; Li, L.; Xie, G.; Keith, A.; Sheiko, S.S.; Matyjaszewski, K. *J. Polym. Sci. Part A Polym. Chem.* **2019**, *57*, 2426–2435.