Supporting information

Grafting well-defined CO_2-responsive polymers *to* cellulose nanocrystals via nitroxide-mediated polymerisation: effect of graft density and molecular weight on dispersion behaviour

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Determination of molecular weight and styrene content by ^{1}H NMR spectroscopy

The molecular weight of the synthesized P(DMAPMAm-*co*-S)-SG1 macroalkoxyamines was determined by ^{1}H NMR spectroscopy end-group analysis as shown in Figure S1:

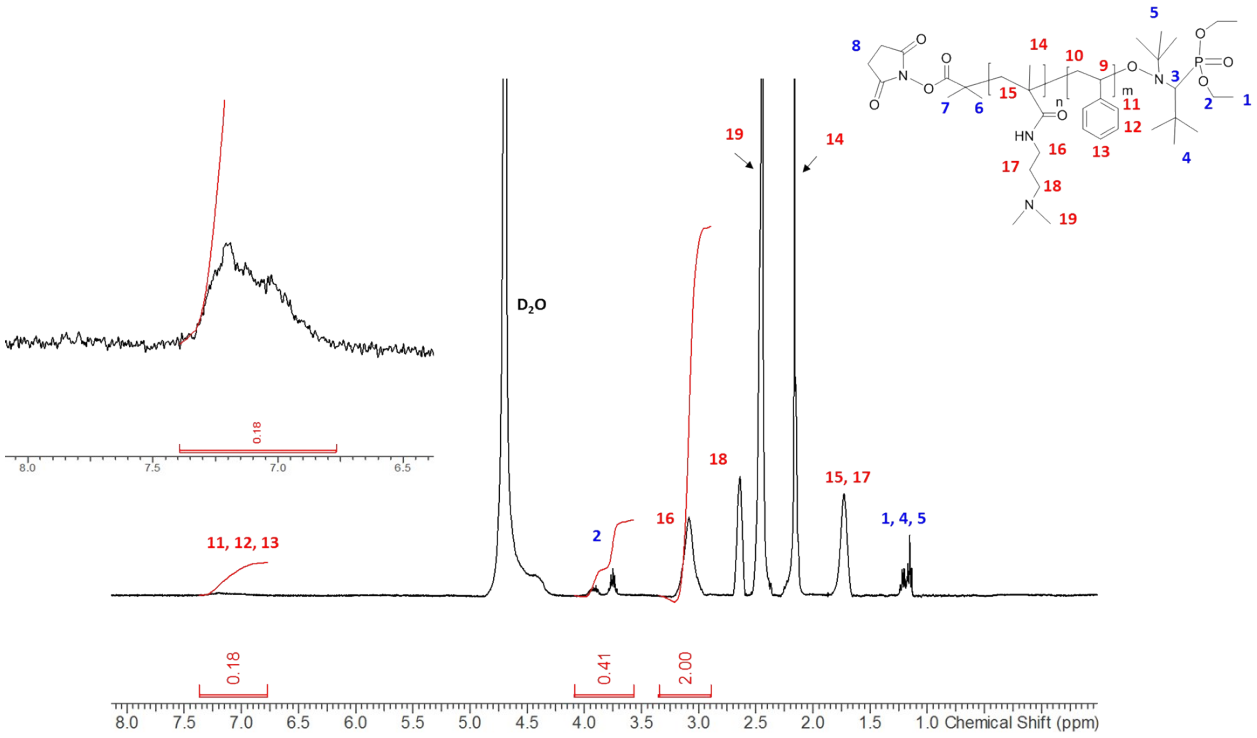


Figure S1 ^{1}H NMR (400.30 MHz, D_2O) of P(DMAPMAm-*co*-S)-SG1-1 with a calculated $M_n \approx 2200$ g/mol, showing the SG1 terminated chain end.

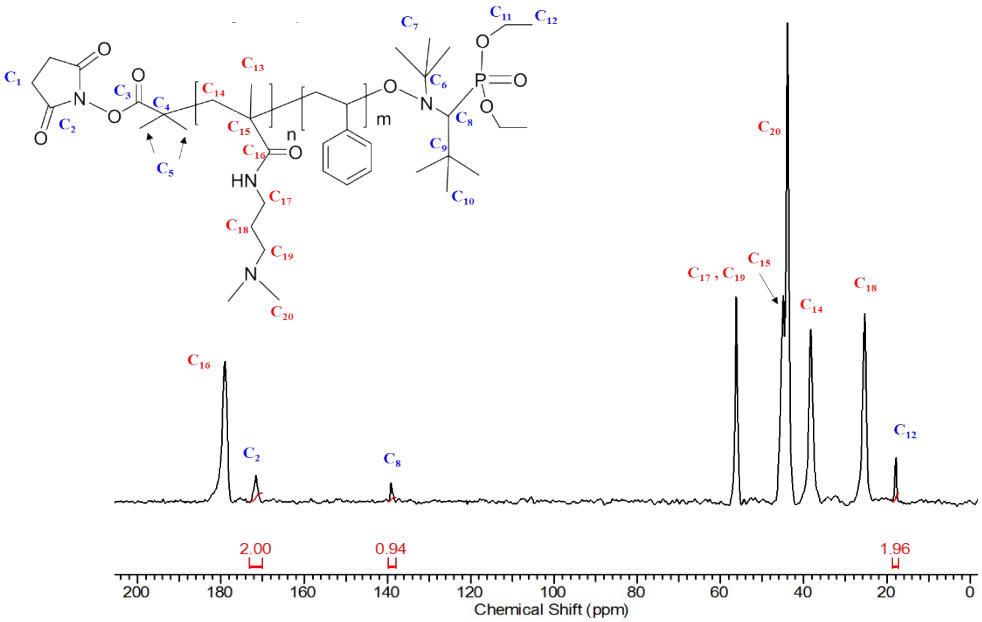
^{1}H NMR (400.30 MHz, D_2O, d, ppm) (Figure S1): 1.19 – 1.31 (m, 24H; H1, H4-5), 1.78 (s, 2H; H17), 2.22 (s, 3H; H14), 2.50 (s, 6H; H19), 2.69 (s, 2H, H18), 3.14 (s, 2H; H16), 3.76 – 4.07 (m, 4H; H2), 6.81 – 7.40 (m, 5H, H11-13).

The ratio of protons on the end-groups to protons on the polymer chain is determined by comparing the integral of the methylene protons H16 in DMAPMAm (2.0) and the aromatic protons H11-13 in styrene (0.18) to the integral of the methylene protons H2 in NHS-BlocBuilder (0.41). The integral per proton value is 2.0/2=1 for the H16 protons, 0.18/5=0.05 for the H11-13 protons, and 0.41/4=0.1 for the H2 protons, giving a ratio of 1:0.05:0.1. Taking into account the molecular weight of NHS-BB (478 g/mol), M_n is calculated as follows:

$$Mn = Mw\ (end\ groups + repeating\ unit) = 478.0\frac{g}{mol} + 10 \times 170.3\frac{g}{mol} + 0.5 \times 104.2\frac{g}{mol} \approx 2200\ \frac{g}{mol}$$

(1)

Similar calculations were performed for P(DMAPMAm-*co*-S) 4400 and 5700 g/mol as shown in Table S1. To estimate the end group fidelity of the prepared P(DMAPMAm-*co*-S)-SG1 macroalkoxyamines, inverse



gated (IG) ^{13}C NMR spectroscopy was performed (Figure S2).

Figure S2 IG ^{13}C NMR (100.66 MHz, D_2O) of P(DMAPMAm-*co*-S)-SG1-1 with a calculated $M_n \approx 2200$ g/mol, showing the SG1 terminated chain end.

IG ^{13}C NMR (100.66 MHz, D_2O, d, ppm) (Figure S2): 17.70 (s, C12), 25.27 (s, C18), 38.44 (s, C14), 42.28 – 46.85 (m, C15, C20), 56.10 (m, C17, C19), 139.06 (s, C8), 171.54 (s, C2), 179.12 (s, C16).

The spectrum in Figure S2 shows three signals of the end-group carbons: resonance of the carbonyl groups of NHS at 171.54 ppm (C2), resonance of the tertiary carbon in SG1 at 139.06 ppm (C8) and the resonance of both methyl groups of SG1 at 17.70 ppm (C12). The integral per carbon value is 2.0/2=1 for C2, 0.94 for C8 and 1.96/2=0.98 for C12, showing an estimated end group fidelity between 94 and 98%.

From the ^{1}H NMR spectrum of P(DEAEMA-*co*-S)-SG1-3 (Figure S3) the styrene content could be determined.

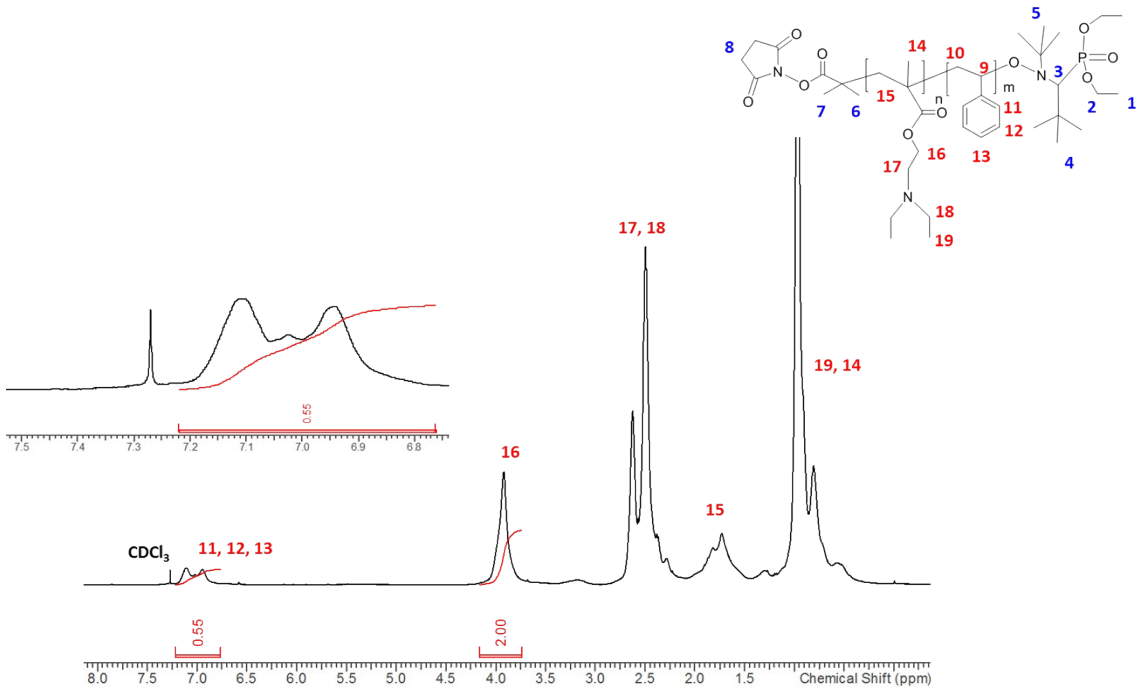


Figure S3 ^{1}H NMR (400.30 MHz, $CDCl_3$) of P(DEAEMA-*co*-S)-SG1-3 with $M_n \approx$ 19,700 g/mol.

^{1}H NMR (400.30 MHz, $CDCl_3$, d, ppm) (Figure S3): 0.64 – 1.18 (m, 9H; H19, H14), 1.44 – 2.04 (m, 2H; H15), 2.16 – 2.74 (m, 4H; H17, H18), 3.92 (s, 2H; H16), 6.76 – 7.22 (m, 5H, H11-13).

The integral of the methylene protons H16 in DEAEMA (2.0) was compared to the integral of the aromatic protons H11-13 in styrene (0.55). The integral per proton value is 2.0/2=1 for the H16 protons, and 0.55/5=0.11 for the H11-13 protons, giving an average styrene content of 11 %.

Table S1 Integral per proton values, degree of polymerisation DP_n, and final graft molecular weight M_n

	Integral per proton value			$DP_{DMAPMAm}$, DP_{DEAEMA}	$DP_{Styrene}$	Graft M_n [g/mol]
	H16	H11-13	H2			
P(DMAPMAm-*co*-S)-SG1-1	1	0.05	0.1	10	0.5	2200
P(DMAPMAm-*co*-S)-SG1-2	1	0.16	0.048	21	3	4400
P(DMAPMAm-*co*-S)-SG1-3	1	0.14	0.036	28	4	5700
P(DEAEMA-*co*-S)-SG1-1	1	0.11	-	19	2	4200
P(DEAEMA-*co*-S)-SG1-2	1	0.16	-	36	6	7800
P(DEAEMA-*co*-S)-SG1-3	1	0.11	-	98	11	19700

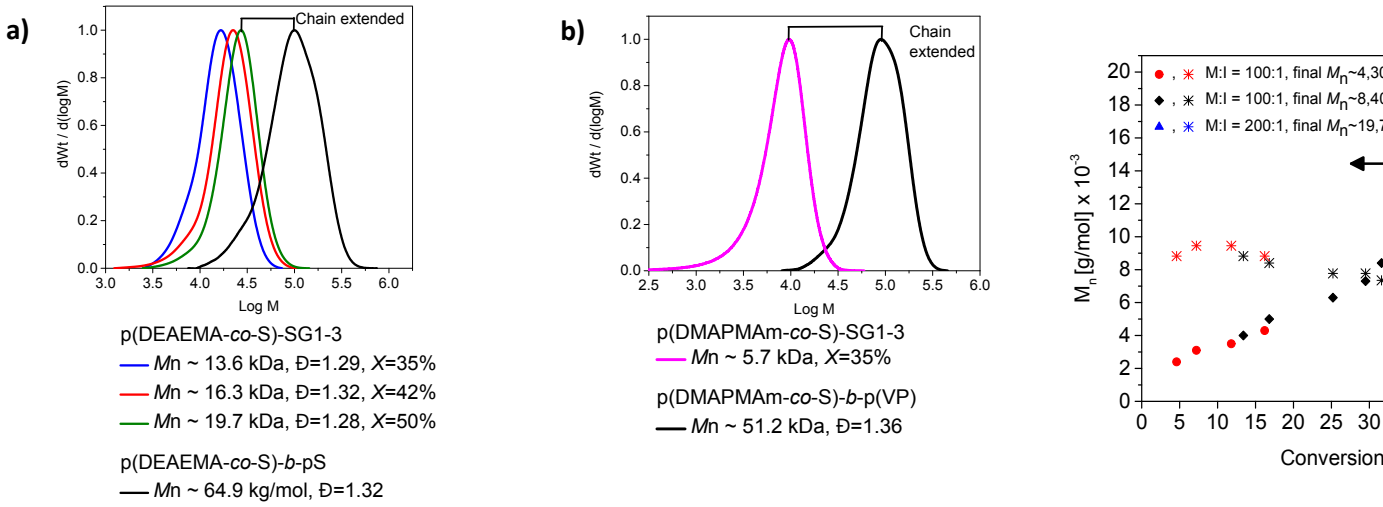


Figure S4 Evolution of normalized SEC chromatograms of (a) P(DEAEMA-*co*-S)-SG1-3 chain extended with styrene and (b) chain extensi P(DMAPMAm-*co*-S)-SG1-3 with 2-vinylpyrididine (VP), and (c) kinetic plot of the NMP of DEAEMA with 10 % styrene in bulk at 80 °C.

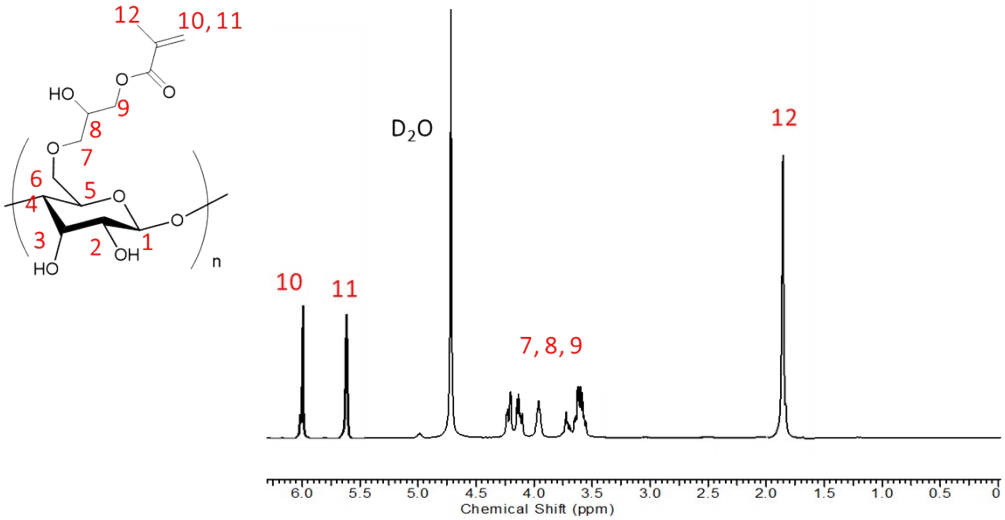


Figure S5 ^{1}H NMR (400.30 MHz, D_2O) of a CNC-GMA dispersion in D_2O.

Elemental Analysis and Calculation of Amine Groups on the CNCs Surface

Table S2: Elemental Analysis data for the grafted products and the consequent graft weight percentage, moles of grafts, and moles of switchable amine groups per 1 g of CNC.

	Graft M_n [g/mol]	%C	%H	%N	%N[a]	Switch-able polymer %	Total polymer % [b]	Graft density ×10^{-2} [chains/ nm^2]	Amine groups [mmol] [c]
Native CNC	-	39.9	6.3	0.0	-	-	-	-	-
CNC-*g*-P(DMAPMAm-*co*-S)-1	2200	46.2	7.9	3.9	3.1	19	23	14.2	1.36
CNC-*g*-P(DMAPMAm-*co*-S)-2	4400	45.5	7.3	2.7	2.2	13	18	5.2	0.91
CNC-*g*-P(DMAPMAm-*co*-S)-3	5700	43.5	6.7	1.1	1.0	6	7	1.4	0.38
CNC-*g*-P(DEAEMA-*co*-S)-1	4200	45.3	7.3	1.4	1.3	17	20	6.2	1.12
CNC-*g*-P(DEAEMA-*co*-S)-2	7800	43.6	6.5	0.9	0.9	12	14	2.2	0.73
CNC-*g*-P(DEAEMA-*co*-S)-3	19700	42.7	6.6	0.9	0.9	12	13	0.8	0.73

[a] Corrected value subtracting the nitrogen content from NHS-BB. [b] Per one gram of grafted CNCs, accounting for the amount of styrene and NHS-BB in the copolymer. [c] Maximum theoretical amount of switchable groups per one gram of grafted CNC.

The weight percent of polymer grafted from the surface of CNCs was estimated following the reported procedure by Tang et al..[1] Assuming 1 g of CNC powders is obtained after the grafting reaction, the moles of DMAPMAm (M_w=170.3 g/mol) or DEAEMA (M_w=185.3 g/mol) grafted to the surface of CNC can be calculated by considering the increased nitrogen content (M_w=14.0 g/mol) after subtracting the nitrogen coming from NHS and SG1. Since only SG1-capped macroalkoxyamines can react with CNC-GMA, there are two nitrogen atoms per graft that account for NHS and SG1. The %N from NHS and SG1 (NHS-BB) can then be obtained by considering the ratio of the nitrogen in NHS-BB to the nitrogen in DEAEMA and DMAPMAm (Table S2):

<u>CNC-*g*-P(DMAPMAm-*co*-S)-1 with a graft M_n of 2.2 kDa:</u>

Total %N − %N from NHS-BB $= 3.9\ \% - (\frac{2}{10} \cdot 3.9\ \%) = 3.1\ \%$ (%N from DMAPMAm only)

<u>CNC-*g*-P(DEAEMA-*co*-S)-1 with a graft M_n 4.2 kDa:</u>

Total %N − %N from NHS-BB $= 1.4\ \% - (\frac{2}{19} \cdot 1.4\ \%) = 1.3\ \%$ (%N from DEAEMA only)

As DEAEMA bears one nitrogen atom and DMAPMAm bears two nitrogen atoms, the final moles of DEAEMA and DMAPMAm in the grafted products (i.e. the maximum theoretical amount of switchable amine groups) can be derived as:

<u>CNC-*g*-P(DMAPMAm-*co*-S)-1 with a graft M_n of 2.2 kDa:</u>

$$\frac{n \cdot 2 \cdot 14.0}{1 + n \cdot 170.3} = 3.1\ \%$$

Solving for n we obtain:

n = **1.36** mmol DMAPMAm / g CNC.

Thus, the weight percentage of PDMAPMAm in CNC-*g*-P(DMAPMAm-*co*-S)-1 is:

$$\frac{1.36 \cdot 170.3 \cdot 10^{-3}}{1 + 1.36 \cdot 170.3 \cdot 10^{-3}} = 19\ \%$$

Accounting for 5 % styrene and 10 % NHS-BB in P(DMAPMAm-*co*-S)-SG1-1 (Table S2), we obtain 0.05 * 1.36 mmol styrene (M_w=104.2 g/mol) and 0.1 * 1.36 mmol NHS-BB (M_w=462.5 g/mol) per 1 g of CNC. Hence, the total weight percentage of P(DMAPMAm-*co*-S)-1-SG1 in CNC-*g*-P(DMAPMAm-*co*-S)-1 is:

$$\frac{1.36 \cdot (170.3 + 0.05 \cdot 104.2 + 0.1 \cdot 462.5) \cdot 10^{-3}}{1 + 1.36 \cdot (170.3 + 0.05 \cdot 104.2 + 0.1 \cdot 462.5) \cdot 10^{-3}} = 23\ \%$$

<u>CNC-*g*-P(DEAEMA-*co*-S)-1 with a graft M_n 4.2 kDa:</u>

$$\frac{n \cdot 1 \cdot 14.0}{1 + n \cdot 185.3} = 1.3\ \%$$

Solving for n we obtain:

n = **1.12** mmol DEAEMA / g CNC

Therefore, the weight percentage of PDEAEMA in CNC-*g*-P(DEAEMA-*co*-S)-1 is:

$$\frac{1.12 \cdot 185.3 \cdot 10^{-3}}{1 + 1.33 \cdot 185.3 \cdot 10^{-3}} = 17\ \%$$

Taking into account the styrene (11 %) and NHS-BB content (2/19) in the copolymer in CNC-*g*-P(DEAEMA-*co*-S)-1, we obtain the total weight percentage of P(DEAEMA-*co*-S)-1-SG1 in CNC-*g*-P(DEAEMA-*co*-S)-1:

$$\frac{1.33 \cdot (185.3 + 0.11 \cdot 104.2 + 0.05 \cdot 462.5) \cdot 10^{-3}}{1 + 1.33 \cdot (185.3 + 0.11 \cdot 104.2 + 0.05 \cdot 462.5) \cdot 10^{-3}} = 20\ \%$$

Similar calculations as above were performed for CNC-*g*-P(DMAPMAm-*co*-S)-2, CNC-*g*-P(DMAPMAm-*co*-S)-3, CNC-*g*-P(DEAEMA-*co*-S)-2 and CNC-*g*-P(DEAEMA-*co*-S)-3 with data presented in Table S2.

Calculation of Graft Densities

Atomic force microscopy (AFM) was performed on a Veeco Dimension 5000 multimode atomic force microscope with a Nanoscope IV controller (Digital Instruments) by scanning in contact mode. After preparation of a dilute solution of water, one drop was deposited onto freshly cleaved mica. Tips of µmash NSC 15 type were used with a resonance frequency of 200 - 400 kHz, spring constants of 13-77 N/m, and a tip radius <10 nm. Micrographs were captured at a scan rate of 1 Hz and resolution of 256 number of samples/line. All images were treated with Nanoscope 1.50 software.

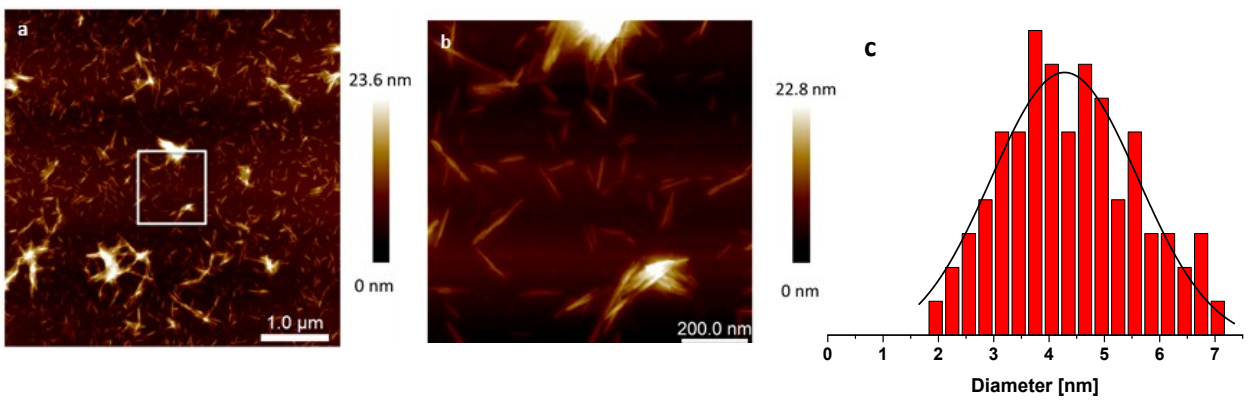


Figure S6 Characterization of CNC. (a) AFM height image with a height-range of 23.6 nm. (b) Zoom-in height image of CNC particles highlighted in part (a) by the white box with a height range of 22.8 nm. (c) Statistical analysis of the height of about 200 CNC particles illustrating the average diameter of ca. 4.4 nm.

The average center diameter of CNC determined by statistical analysis from the AFM images in Figure S5 is $d \approx 4.4$ nm. For simplicity an infinitely long cylinder was assumed resembling the shape of CNC rods with a radius of $r \approx 2.2$ nm. From this, a cylindrical volume segment with a height of h=1 nm is considered and the volume calculated according to (2):

$$V = \frac{1}{2}\pi r^2(2h) \approx \quad 1.52 \times 10^{-26}\, m^3 \qquad (2)$$

The surface area is given by:

$$S = r\,\pi\,(2h) \approx \quad 13.8\, nm^2 \qquad (3)$$

Using the M_w of anhydroglucose (162 g/mol) and the density of crystalline cellulose (ca. 1.58 g/mL)[2] the molar amount of anhydroglucose within one volume segment is $n(C_6H_{10}O_5) = 1.48 \times 10^{-22}$ mol and the mass $m(C_6H_{10}O_5) = 2.4 \times 10^{-20}$ g.

The specific surface area of CNC equals:

$$A_{spec} = \frac{13.8\ nm^2}{2.4 \times 10^{-20}\ g} = 5.75 \times 10^{20}\ \frac{nm^2}{g} \quad (4)$$

And finally, the grafting density ρ of the graft can be calculated by:

$$\rho = \frac{w}{M_n} A_v\ /\ ((1 - w) \cdot\ A_{spec}) \quad (5)$$

Whereby w is the weight fraction of P(DEAEMA-*co*-S) and P(DMAPMAm-*co*-S) as determined by EA, M_n is the number-average graft molecular weight and A_v is Avogadro's number.

References

1 J. Tang, M. F. X. Lee, W. Zhang, B. Zhao, R. M. Berry and K. C. Tam, *Biomacromolecules*, 2014, **15**, 3052.

2 J. Majoinen, A. Walther, J. R. McKee, E. Kontturi, V. Aseyev, J. M. Malho, J. Ruokolainen and O. Ikkala, *Biomacromolecules*, 2011, **12**, 2997–3006.