Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information

Grafting CO_2-responsive polymers from cellulose nanocrystals via nitroxide-mediated polymerization

Omar Garcia-Valdez,[a] Tiziana Brescacin,[a] Joaquin Arredondo,[a] Jean Bouchard,[b] Phillip G. Jessop,[c] Pascale Champagne,[a,d] and Michael F. Cunningham.[a]

[a] Department of Chemical Engineering, Queen's University, Kingston, ON, Canada.
[b] FPInnovations, 570 St. Jean Boulevard, Pointe-Claire, QC H9R 3J9, Canada
[c] Department of Chemistry, Queen's University, Kingston, ON, Canada.
[d] Department of Civil Engineering, Queen's University, Kingston, ON, Canada.

Synthesis of CNC-CMS

CNC were functionalised with CMS following previous reports.[32] Briefly, CMS (2.6 mL, 18.5 mmol) was added dropwise to a 3 wt% dispersion of CNC (2 g) in DMSO (60 g) in the presence of solid sodium hydroxide at room temperature. The reaction was allowed to proceed overnight before recovering the product by precipitation with a minimal amount of ethanol. Styrene-functionalised CNC (CNC-CMS) was collected by centrifugation and thoroughly redispersed in DI water. Centrifugation and redispersion were repeated again in water and twice with *t*-butanol to remove unreacted CMS. After the final sedimentation, the CNC-CMS was redispersed in a known quantity of t-butanol (~1 wt% CNC in *t*-butanol) before being used in the subsequent step.

Synthesis of CNC-BB

The synthesis of CNC-BB was performed following a similar procedure reported by our group.[32] A solution of 4.68 g (12.3 mmol) BB in 10 mL t-butanol was added to the CNC-CMS dispersion (100 mL) in a 3-neck round bottom flask equipped with a condenser and was bubbled with N_2 for 30 minutes. The solution was introduced to an oil bath at 95°C under nitrogen and the reaction was allowed to reflux for 90 min before being removed from the oil bath. CNC-BB was collected by centrifugation and redispersed in ethanol, and the procedure repeated 3 times. After the final sedimentation, a small portion of the CNC-BB was freeze-dried for characterization and the remaining CNC-BB was solvent exchanged with DMSO to yield a 5 wt% dispersion of CNC-BB in DMSO.

Figure S1 shows the apparatus used to assess the CO_2-switchability of CNC-g-PDMAEMA, CNC-g-PDEAEMA and CNC-g-PDMAPMAm. A measured amount of each sample was dispersed in DI water maintaining a concentration of 1 mg/mL in a 50 mL 3-neck round bottom flask equipped with a pH meter probe and a gas dispersion tube.

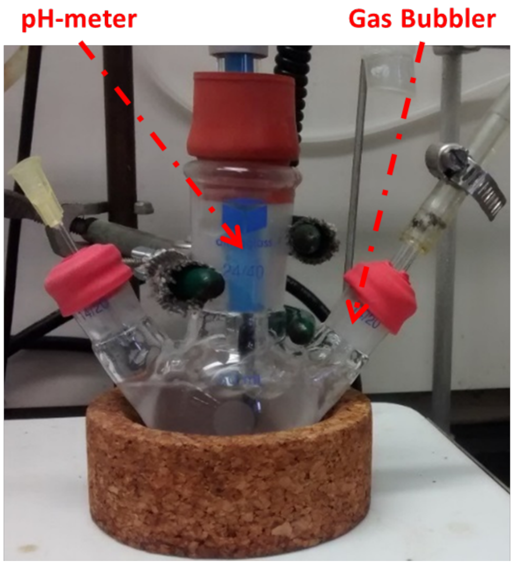

Figure S1. System adapted for bubbling CO_2 or N_2 to the aqueous dispersions of CNC-g-PDMAEMA, CNC-g-PDEAEMA or CNC-g-PDMAPMAm.

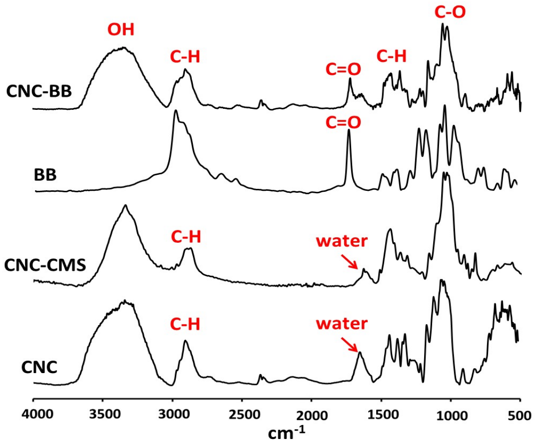

Figure S2. FT-IR spectra of CNC, CNC-CMS, BB and CNC-BB.

FT-IR spectra of native CNC shows the signals of the cellulose ring at 3448 cm^{-1}, stretching vibration of the O–H bonds at 2875 cm^{-1}, stretching vibrations from C–H, bending vibrations from $–CH_2$ and –CH groups at 1414-1315 cm^{-1}, stretching vibrations of C–O (ν, C–O) at 1160-1150 cm^{-1}, and at 1088 cm^{-1} the peak from the C–O–C (ν, C–O–C) bond. The spectra of CNC-BB shows the presence of a C=O group (1700 cm^{-1}) from the BB moiety.

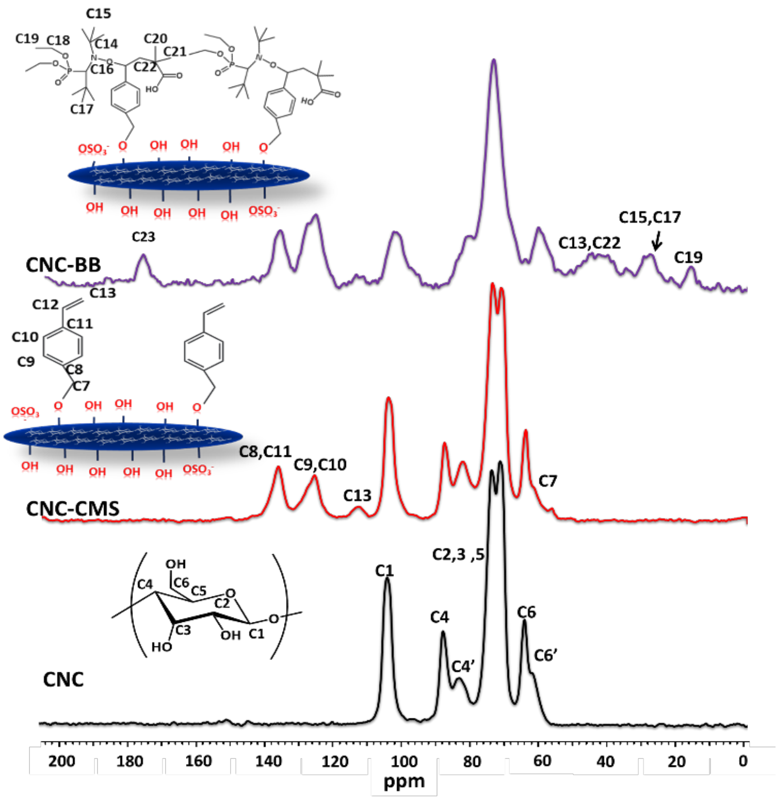

Figure S3. CP-MAS 13C NMR spectra of CNC, CNC-CMS and CNC-BB.

The structure of CNC-CMS and CNC-BB was confirmed by CP-MAS ^{13}C NMR (Figure 1) and FT-IR analysis (Figure S2). The CP-MAS ^{13}C NMR spectra of native CNC shows the signals of the cellulose ring at 105 (C1), 82-94 (C4), 70-80 (C2-5), and 62-70 (C6) ppm. The corresponding CP-MAS ^{13}C NMR spectra of CNC-CMS shows the signals from the aromatic rings at 122-136 (C9-10) and 136-146 (C8, C11) ppm. Solid state NMR shows the signals of the BB groups at 20-50 ppm, attributed to -C-, -CH-, -CH_2- and -CH_3- groups as well as the C=O group from BB.

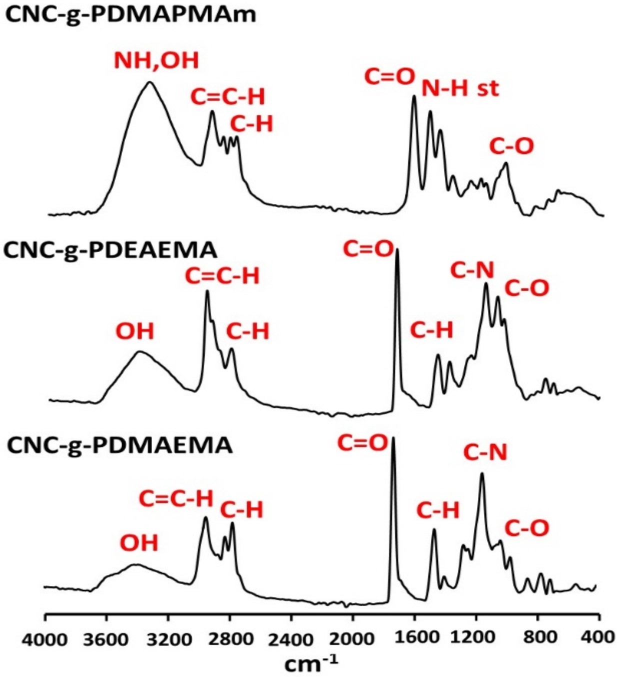

Figure S4.FT-IR spectra of CNC-g-PDMAEMA, CNC-g-PDEAEMA and CNC-g-PDMAPMAm.

The corresponding FT-IR spectra of the new polymer-modified CNC materials are shown in Figure 2. Each spectra shows the corresponding signals of the CNC previously discussed, and the grafted polymer; the spectra for CNC-g-PDMAEMA and CNC-g-PDEAEMA show the stretching of the C=C-H bonds from the styrene units at 3100 cm^{-1}, the stretching and flexing of the C-H groups at 2900 and 1400 cm^{-1} respectively, and the stretching of the C=O moieties of the ester groups of the methacrylic unit. The corresponding spectra for CNC-g-PDMAPMAm also shows the stretching of the C=C-H bonds at 3100 cm^{-1}, the stretching and flexing of the C-H groups at 2900 and 1400 cm^{-1}, the stretching and flexing of the N-H bonds at 3400 and 1500 cm^{-1} respectively, and the stretching of the C=O bonds of the methacrylamide unit.

Elemental analysis of CNC materials

Elemental analysis was carried out following the procedure reported by Hemraz et al.[1] Elemental analysis of was performed with a PerkinElmer 2400 Series II in CHN mode. The percent carbon (C), hydrogen (H) and nitrogen (N) contents (%) and standard deviation (±σ) of the unmodified cellulose nanocrystals (CNC) and the SG1-modified CNC (CNC-BB), CNC-g-PDEAEMA, CNC-g-PDEAEMA and CNC-g-PDEAEMA (obtained at different reaction times) are shown in Table S1. Also the Table shows the molar concentration (mmol/g) of switchable monomer units groups on CNC surface, the polymer% grafted on the CNC surface, taking into account the percentage of styrene incorporated into the polymer chains, the overall conversion of the monomers and the theoretical molecular weight of the grafted chains (obtained based on the Nitroxide concentration and the conversion).

Table S1. Elemental analysis of carbon (C), hydrogen (H) and nitrogen (N) for CNC, CNC-BB, CNC-g-PDEAEMA, CNC-g-PDEAEMA and CNC-g-PDEAEMA.

Sample	C% (±σ)	H% (±σ)	N% (±σ)	Polymer N%	n (mmol)	Conv. (%)	M_n (theor)	Switchable Pol%	Total Pol%	CNC%
CNC	40.5 (0.17)	6.13 (0.02)	0.03 (0.07)	-	-	-	-	-	-	-
CNC-BB	48.0 (0.97)	8.3 (0.19)	2.6 (0.26)	2.57[f]	3.9[c]	-	-	-	-	-
CNC-g-PDEAEMA[a]	62.25 (0.28)	9.73 (0.31)	5.69 (0.14)	3.12[g]	1.58[d]	27	3100	41.29	41.68[e]	58.32
CNC-g-PDEAEMA[b]	64.31 (0.21)	10.95 (0.18)	7.42 (0.16)	4.85[g]	1.71[d]	45	5300	64.18	65.18[e]	34.82
CNC-g-PDMAEMA[a]	58.01 (0.12)	8.43 (0.06)	5.75 (0.11)	3.18[g]	3.53[d]	31	3100	35.71	36.08[e]	63.92
CNC-g-PDMAEMA[b]	59.97 (0.14)	9.52 (0.07)	7.23 (0.15)	4.66[g]	6.98[d]	49	4900	52.33	53.05[e]	46.95
CNC-g-PDMAPMAm[a]	53.39 (0.32)	9.44 (0.21)	8.98 (0.11)	6.41[g]	2.65[d]	34	3700	39.20	39.59[e]	60.41
CNC-g-PDMAPMAm[b]	54.31 (0.18)	10.28 (0.13)	10.51 (0.20)	7.94[g]	3.99[d]	52	5600	48.56	49.13[e]	50.87

[a] Reaction time of 0.5 h. [b] Reaction time of 1 h. [c] Molar concentration (mmol/g) of nitroxide on CNC surface. [d] Molar concentration (mmol/g) of switchable monomer units groups on CNC surface. [e] Polymer% grafted on the CNC surface, taking into account the percentage of styrene incorporated into the polymer chains. [f] N% total subtracting the nitrogen content present in CNC. [g] N% total subtracting the nitrogen content present in CNC-BB.

The molar concentration of SG1 groups on CNC-BB was estimated from the %N (Table S1) following the procedure reported by Hemraz et al..[1] It is assumed that 1 g of CNC was functionalized with n moles of SG1 (Mw=294.35 g/mol), therefore the weight of functionalized CNC is (1+n*294.35). The nitrogen content (Mw=14.0 g/mol) in CNC-BB comes from the SG1 moieties, and therefore the final nitrogen content can be derived as follows:

$$\frac{n * 14.0}{1 + n * 294.35} = \%Nitrogen$$

$$\frac{n * 14.0}{1 + n * 294.35} = 0.0257$$

Solving the equation for *n*:

n=0.0039, therefore n= 3.90 mmol of SG1/g of CNC.

For the compositional analysis of the CNC-g-PDMAEMA, CNC-g-PDEAEMA and CNC-g-PDMAPMAm, the molar concentration of monomer units incorporated to CNC was first determined, and then the total amount of polymer estimated. An example is shown below:

CNC-g-PDEAEMA obtained at 0.5 h of reaction time: It is assumed that 1g of CNC-BB was modified with n moles of DEAEMA (Mw=185.26 g/mol), therefore the weight of functionalized CNC is (1+n*185.26). The nitrogen content (Mw=14.0 g/mol) in CNC-BB comes from the DEAEMA moieties (the N% of the polymer-modified CNC samples was subtracted from %N reported by the instrument), therefore the final nitrogen content can be derived as follows:

$$\frac{n * 14.0}{1 + n * 185.26} = \%Nitrogen$$

$$\frac{n * 14.0}{1 + n * 185.26} = 3.12$$

Solving the equation for *n*:

n=0.00158, therefore n= 1.58 mmol of PDEAMEA units/g of CNC.

The weight percentage of PDEAEMA present in CNC-g-DEAEMA is:

$$\frac{(1.58 * 10^{-3}) * (185.26)}{1 + \left((1.58 * 10^{-3}) * (185.26)\right)} = 41.29\%$$

Similar calculations as above were performed for all the CNC products.

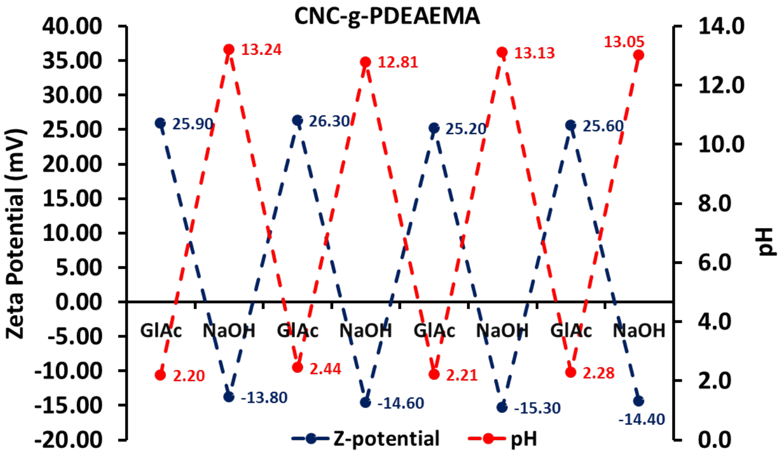

Figure S5. ζ-potential vs pH of CNC-g-PDEAEMA with alternating cycles of added GlAc/NaOH.

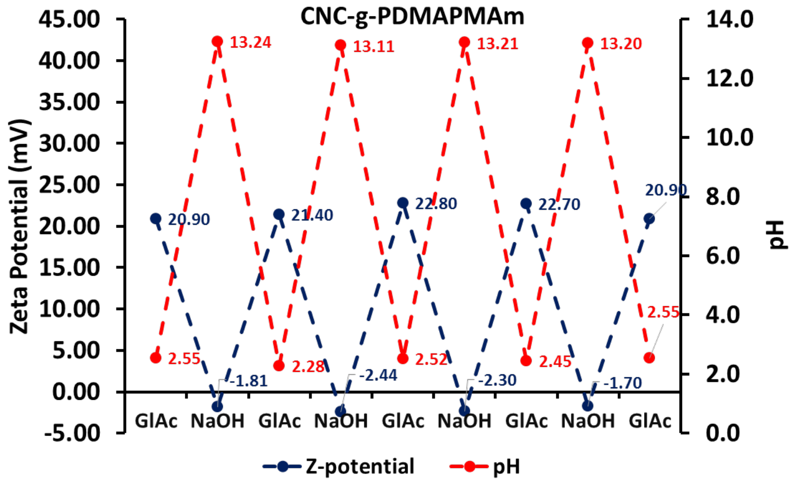

Figure S6. ζ-potential vs pH of CNC-g-PDMAPMAm with alternating cycles of added GlAc/NaOH.

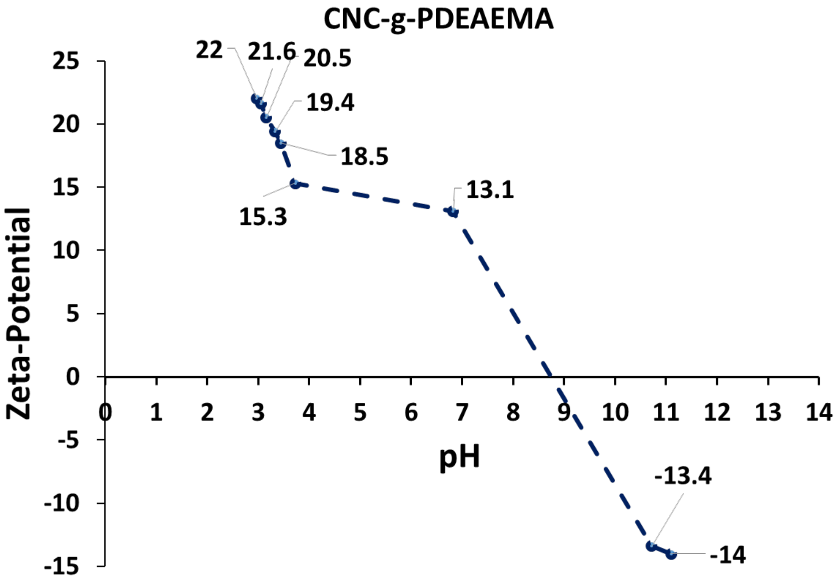

Figure S7. ζ-potential vs pH of CNC-g-PDEAEMA at different pH values under GlAc and NaOH.

References

1. U. D. Hemraz, K. A. Campbell, J. S. Burdick, K. Ckless, Y. Boluk and R. Sunasee, *Biomacromolecules*, 16, **1**, 319-325.