CITRIC ACID AS A BENIGN ALTERNATIVE TO METAL CATALYSTS FOR THE PRODUCTION OF CELLULOSE-*GRAFTED*-POLYCAPROLACTONE COPOLYMERS

Marianne Labet(1),(2),(3), Wim Thielemans(1)(2)*

(1) School of Chemistry, Faculty of Science, University of Nottingham, University Park, Nottingham NG7 2RD, UK

(2) Process and Environmental Research Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

(3) Current address: Materials and Engineering Research Institute, Sheffield Hallam University, Howard Street, Sheffield S1 1WB, UK

* Email: wim.thielemans@nottingham.ac.uk

ELECTRONIC SUPPLEMENTARY INFORMATION

Calculation of the number of surface OH groups

The number of surface hydroxyl groups on cotton nanocrystals can be calculated using the average size of a nanocrystal (150 nm × 27 nm × 7.3 nm) and the size of a unit cell composing this nanocrystal (0.7784 nm × 0.8201 nm × 1.038 nm). These calculations are an adaptation of Habibi *et al.*[A] from tunicin to cotton. While there are different reports of cotton nanocrystal dimensions, depending on the method of determination (e.g. TEM, cryo-TEM, XRD or CP-MAS SS-NMR), we based our calculations on the above values determined by... using cryo-TEM. However, using the equation ESI-5 shown below, the number of surface of hydroxyl groups can easily be adjusted if consensus in the community is reached on the most appropriate technique and lateral dimensions need to be adjusted.

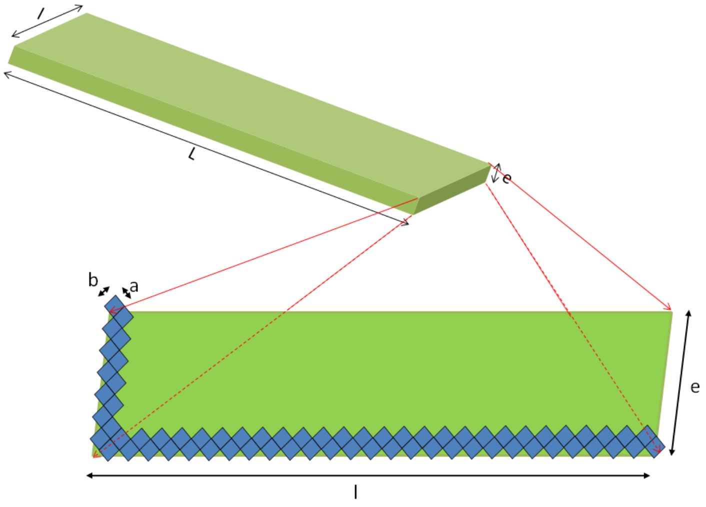


Figure ESI-1: Cross-section of a cotton nanocrystal and arrangement of the unit cells in the cross-section

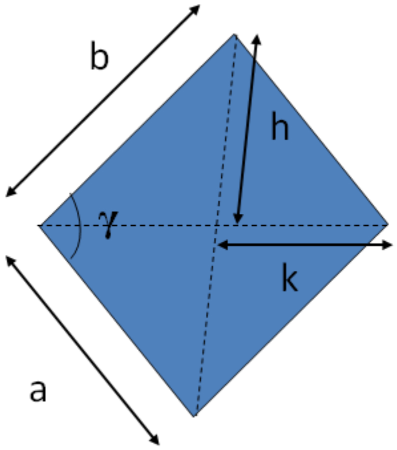


Figure ESI-2: Representation of the ab view of a unit cell showing the dimensions h and k

Figure ESI-1 represents the cross-section of a nanocrystal and shows how the unit cells are arranged. To determine the number of cellulose chains inside a nanocrystal, it is first necessary to determine the lengths **h** and **k** shown in Figure ESI-2. The dimension **h** corresponds to the distance between two planes ($1\bar{1}0$) while the dimension **k** corresponds to the distance between two planes (110). Both dimensions can be determined by applying the Al Kashi formula:

$$(2h)^2 = a^2 + b^2 - 2ab\cos\gamma \;\Rightarrow\; h = \frac{\sqrt{a^2+b^2-2ab\;\cos\gamma}}{2} \qquad \text{(eq ESI-1)}$$

$$(2k)^2 = a^2 + b^2 - 2ab\cos(180-\gamma) \;\Rightarrow\; h = \frac{\sqrt{a^2+b^2-2ab\;\cos(180-\gamma)}}{2} \qquad \text{(eq ESI-2)}$$

The numerical application of the equations ESI-1 and ESI-2 respectively give h = 0.5960 nm and k = 0.5305 nm. Knowing **h** and **k**, one can then easily determine the total number $\boldsymbol{N_T}$ of cellulose chains in a cotton nanocrystal (eq ESI-3) as well as the number $\boldsymbol{N_{surf}}$ of cellulose chains at the surface of a nanocrystal (eq ESI-4) and to deduce the proportion $\boldsymbol{p_{surf}}$ of surface chains in one nanocrystal (eq ESI-5).

$$N_T = n_l \times n_e = \frac{e}{h} \times \frac{l}{k} \qquad \text{(eq ESI-3)}$$

$$N_{surf} = 2 \times n_l + 2 \times n_e = 2 \times \frac{e}{h} + 2 \times \frac{l}{k} \qquad \text{(eq ESI-4)}$$

$$p_{surf} = \frac{N_{surf}}{N_T} \qquad \text{(eq ESI-4)}$$

where $\boldsymbol{n_l}$ and $\boldsymbol{n_e}$ are respectively the numbers of cellulose chains in the dimensions *l* and *e* of a cotton nanocrystal.

The numerical applications of equations ESI-3, ESI-4 and ESI-5 give respectively ***NT*** = 623, N_{surf} = 126 and p_{surf} = 0.20.

The amount $\boldsymbol{n_{OH\ surf}}$ of hydroxyl groups at the surface of the cotton nanocrystals can then easily be determined as follows:

$$n_{OH\ surf} = \frac{N_{OH\ cell} \times p_{surf}}{M_{cell}} \qquad \text{(eq ESI-5)}$$

where $\boldsymbol{N_{OH\ cell}}$ is the number of accessible hydroxyl groups in one cellobiose unit and ***Mcell*** the molecular weight of a cellobiose unit. The numerical application of eq ESI-5 gives $\boldsymbol{n_{OH\ surf}}f$ =1.87 mmol·g^{-1}.

Experimental conditions

Table ESI-1 – Reaction conditions for the optimization of the SI-ROP of ε-CL from cotton nanocrystals using citric acid as a catalyst (all reactions were performed in bulk)

Entry	[ε-CL]:[CA]:$[OH]_{surf}$	Reaction Temperature [°C]	Reaction Time
1	880:0:1	120	24 h
2	880:1:1	120	24 h
3	880:2:1	120	24 h
4	880:3.3:1	120	24 h
5	880:5:1	120	24 h
6	880:10:1	120	24 h
7	880:15:1	120	24 h
8	880:20:1	120	24 h
9	880:30:1	120	24 h
10	880:40:1	120	24 h
11	880:50:1	120	24 h
12	880:75:1	120	24 h
13	880:100:1	120	24 h
14	880:10:1	80	24 h
15	880:10:1	100	24 h
16	880:10:1	150	24 h
17	880:10:1	165	24 h
18	880:10:1	180	24 h
19	880:10:1	200	24 h
20	110:10:1	180	24 h
21	220:10:1	180	24 h
22	330:10:1	180	24 h
23	440:10:1	180	24 h

24	660:10:1	180	24 h
25	1100:10:1	180	24 h
26	330:10:1	120	30 min
27	330:10:1	120	1 h
28	330:10:1	120	2 h
29	330:10:1	120	4 h
30	330:10:1	120	7.5 h
31	330:10:1	120	14 h
32	330:10:1	120	24 h
33	330:10:1	120	65 h

Description of the interpretation of the analysis data

The extent of grafting was determined using FTIR and elemental analysis spectroscopy while homopolymer molecular weight recovered after extraction was determined using GPC. XPS spectroscopy was further used to confirm extent of grafting. Using FTIR, the PCL content was determined by normalising the intensity for the ester band located at 1732 cm^{-1} ($\boldsymbol{\nu}_{\mathbf{C=O}}$) with the intensity of the band at 1163 cm^{-1}, which corresponds to the antisymmetric stretching of C-O-C in the glycoside skeleton of cellulose [B,C]. This allows us to determine a relative extent of grafting. For elemental analysis, increased grafting results in an increase in carbon and hydrogen contents. This increase also allows the determination of an absolute extent of grafting by comparison with the carbon and hydrogen contents of unmodified cellulose nanowhiskers and pure polycaprolactone. The size of the grafts was estimated using GPC; if it can be assumed that the size of the grafts evolves similarly as the size of the free chains. However, since degrafting through ester link hydrolysis would also result in depolymerisation, this cannot be verified. The molecular weight of the free chains was compared to the theoretical molecular weight M_{calc} calculated as follows:

$$M_{calc} = M_{CA} + \frac{[\varepsilon\ CL] \times M_{\varepsilon\ CL}}{[CA] + [OH]_{surf}}$$

where M_{CA} is the molecular weight of citric acid ($M_{CA} = 192.124$ g.mol^{-1}), *[ε-CL]* is the initial concentration of ε-caprolactone used, $M_{\varepsilon\text{-}CL}$ is the molecular weight of ε-caprolactone ($M_{\varepsilon\text{-}CL} =$ 114.14 g.mol^{-1}), *[CA]* is the concentration of citric acid used and $[OH]_{surf}$ is the surface concentration of hydroxyl groups in the cotton nanocrystals. In this equation, it is assumed that the surface chains grow exactly the same way as the homogeneous chains.

Figures related to the optimization of the polymerization conditions

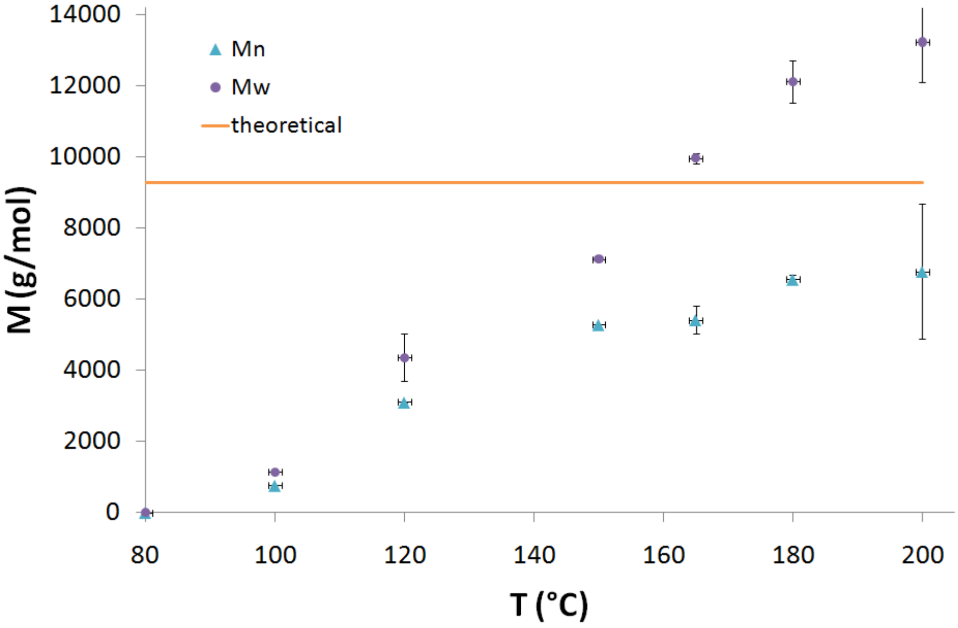


Figure 2-ESI- Evolution of the molecular weight of the homopolymer when increasing the reaction temperature, as determined by GPC. Molecular weight measured relatively to polystyrene standards and corrected by a factor of 0.56 specific to PCL [D]

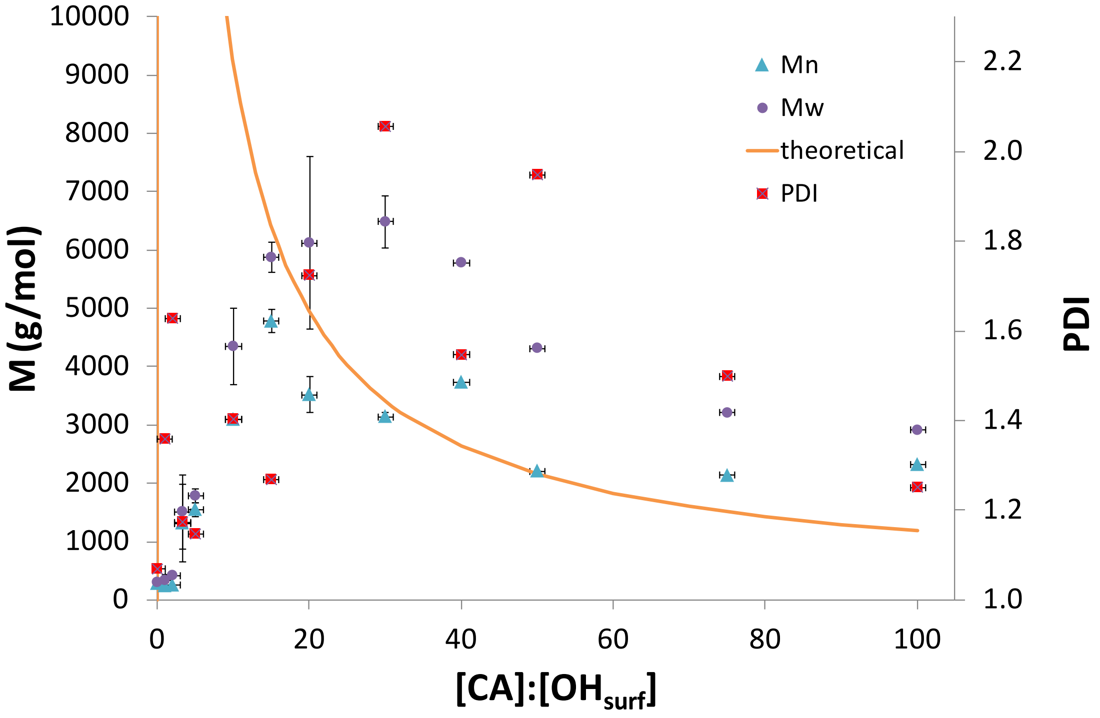


Figure ESI-3 – Figure 2 in manuscript with PDI included

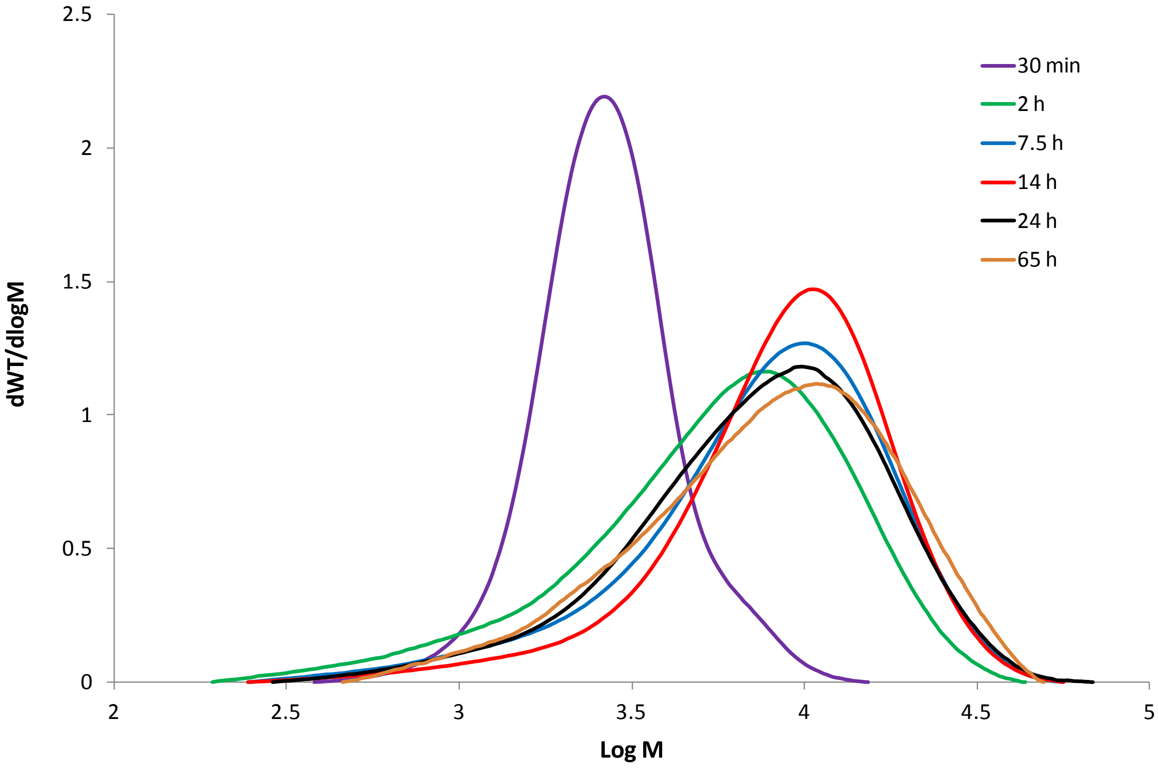


Figure ESI-4 – GPC traces of homopolymer for different reaction times. Molecular weight measured relatively to polystyrene standards and corrected by a factor of 0.56 specific to PCL.C Calculation of the theoretical molecular weight is detailed above. [ε-CL]:[CA]:[OH]$_{surf}$ = 330:10:1 and T = 120°C

Tables related to the optimization of the polymerization conditions

Table ESI-2 - FTIR and elemental analysis results for the cotton-g-PCL samples investigating the influence of the concentration of citric acid. Increase in h_{1732}/h_{1163} ratio (FTIR) and carbon content (elemental analysis) signifies increased PCL grafting

Entry	[ε-CL]:[CA]:[OH]$_{surf}$	FTIR	Elemental Analysis	
		$\frac{h_{1732}}{h_{1163}}$	%C	%H
unmodified cotton NC		0.24 ± 0.01	42.57 ± 0.27	6.03 ± 0.05
1	880:0:1	0.19 ± 0.11	43.15 ± 0.26	6.03 ± 0.04
2	880:1:1	0.42 ± 0.11	43.56 ± 0.32	6.07 ± 0.07
3	880:2:1	0.42 ± 0.05	43.89 ± 0.33	6.13 ± 0.05
4	880:3.3:1	0.42 ± 0.16	44.43 ± 0.73	6.13 ± 0.17
5	880:5:1	0.65 ± 0.14	44.78 ± 0.13	6.25 ± 0.12
6	880:10:1	0.92 ± 0.11	50.45 ± 0.33	7.02 ± 0.06
7	880:15:1	0.89 ± 0.01	49.22 ± 0.50	6.89 ± 0.07
8	880:20:1	0.97 ± 0.13	49.06 ± 0.83	6.80 ± 0.10
9	880:30:1	0.83 ± 0.04	47.03 ± 0.41	6.54 ± 0.04
10	880:40:1	0.79 ± 0.09	45.98 ± 0.81	6.36 ± 0.10
11	880:50:1	0.67 ± 0.11	45.42 ± 0.77	6.25 ± 0.07
12	880:75:1	0.72 ± 0.10	44.20 ± 0.38	6.14 ± 0.04
13	880:100:1	0.63 ± 0.03	44.24 ± 0.32	6.06 ± 0.04

Errors come from different reaction runs (for both FTIR and elemental analysis results) and from repeats of the characterization method (for elemental analysis results).

Table ESI-3 - FTIR and elemental analysis results for the cotton-g-PCL samples investigating the influence of the reaction temperature

Entry	Reaction Temperature	FTIR	Elemental Analysis	
	[°C]	$\frac{h_{1732}}{h_{1163}}$	%C	%H
unmodified cotton NC		0.24 ± 0.01	42.57 ± 0.27	6.03 ± 0.05
1	80	0.15 ± 0.05	43.17 ± 0.08	6.04 ± 0.01
2	100	0.41 ± 0.09	44.15 ± 0.50	6.18 ± 0.11
3	120	0.91 ± 0.11	50.45 ± 0.33	7.02 ± 0.05
4	150	0.91 ± 0.14	51.44 ± 0.26	7.15 ± 0.06
5	165	1.03 ± 0.01	53.39 ± 1.38	7.35 ± 0.19
6	180	1.09 ± 0.01	52.91 ± 1.18	7.32 ± 0.20
7	200	1.07 ± 0.06	53.78 ± 1.03	7.45 ± 0.15

Errors come from different reaction runs (for both FTIR and elemental analysis results) and from repeats of the characterization method (for elemental analysis results).

Table ESI-4 - FTIR and elemental analysis results for the cotton-g-PCL samples investigating the influence of the amount of ε-CL

Entry	[ε-CL]:[CA]:[OH]$_{surf}$	FTIR	Elemental Analysis	
		$\frac{h_{1732}}{h_{1163}}$	%C	%H
Unmodified cotton NC		0.24 ± 0.01	42.57 ± 0.27	6.03 ± 0.05
1	110:10:1	0.82 ± 0.02	43.17 ± 0.08	6.04 ± 0.01
2	220:10:1	0.93 ± 0.01	44.15 ± 0.50	6.18 ± 0.11
3	330:10:1	0.86 ± 0.02	50.45 ± 0.33	7.02 ± 0.05
4	440:10:1	0.96 ± 0.02	51.44 ± 0.26	7.15 ± 0.06
5	660:10:1	1.05 ± 0.01	53.39 ± 1.38	7.35 ± 0.19
6	880:10:1	1.09 ± 0.01	52.91 ± 1.18	7.32 ± 0.20
7	1100:10:1	1.09 ± 0.05	53.78 ± 1.03	7.45 ± 0.15

Errors come from different reaction runs (for both FTIR and elemental analysis results) and from repeats of the characterization method (for elemental analysis results).

Table ESI-5 - FTIR and elemental analysis results for the cotton-g-PCL samples investigating the influence of the reaction temperature

Entry	Reaction time	FTIR	Elemental Analysis	
		$\frac{h_{1732}}{h_{1163}}$	%C	%H
unmodified cotton NC		0.24 ± 0.01	42.57 ± 0.27	6.03 ± 0.05
1	30 min	0.45 ± 0.02	44.41 ± 0.37	6.23 ± 0.06
2	1 h	0.63 ± 0.05	46.11 ± 0.54	6.40 ± 0.05
3	2 h	0.80 ± 0.07	47.71 ± 0.20	6.55 ± 0.02
4	4 h	0.79 ± 0.04	47.43 ± 0.58	6.55 ± 0.07
5	7.5 h	0.86 ± 0.04	48.29 ± 0.39	6.63 ± 0.08
6	14 h	0.79 ± 0.02	47.69 ± 0.32	6.44 ± 0.06
7	24 h	0.84 ± 0.02	48.30 ± 0.49	6.55 ± 0.11
8	65 h	0.89 ± 0.02	48.29 ± 0.01	6.55 ± 0.01

Errors come from different reaction runs (for both FTIR and elemental analysis results) and from repeats of the characterization method (for elemental analysis results).

Tables related to the range of cotton-g-PCL samples with increasing amounts of PCL

Table ESI-6 – Surface composition of a range of cotton-*g*-PCL samples, as determined by XPS (wide scan). The wt% PCL was determined using elemental analysis based on carbon content.

Entry	wt% PCL	at% C	at% O	C/O
Unmodified nanocrystals	0	58.95 ± 0.13	41.00 ± 0.77	1.44 ± 0.03
1	8.9	67.22 ± 0.75	32.49 ± 0.13	2.07 ± 0.08
2	18.6	71.73 ± 0.31	27.43 ± 0.13	2.62 ± 0.06
3	25.5	73.41 ± 0.75	25.67 ± 0.13	2.86 ± 0.09
4	34.8	73.72 ± 0.22	25.27 ± 0.13	2.92 ± 0.04
5	42.3	74.00 ± 0.29	25.22 ± 0.13	2.93 ± 0.04
6	52.3	75.49 ± 0.50	23.82 ± 0.13	3.17 ± 0.03
7	58.2	73.57 ± 0.04	23.57 ± 0.13	3.12 ± 0.05
PCL homopolymer	100	77.72 ± 2.47	22.28 ± 0.13	3.79 ± 0.24

Table ESI-7 – Deconvolution of the C1s peak for a range of cotton-g-PCL samples (in italics, the cellulose-g-PCL sample reported by Habibi and co-workers [11] using tin (II) ethylhexanoate is given as a comparison)

Entry	wt% PCL	%C1	%C2	%C3	%C4
		-C-C-C-	-C-O-H, -C-O-C-	-O-C-O-	O=C-O-
Unmodified nanocrystals	0	5.17	74.31	20.01	0.51
15	8.9	31.43	49.68	10.18	8.7
Habibi *et al.* *[11]*		***40.2***	***43.0***	***6.4***	***10.5***
27	18.6	49.89	32.13	4.8	13.18
22	25.5	54.00	27.88	2.99	15.13
23	34.8	56.75	24.57	3.33	15.35
24	42.3	58.35	23.06	2.73	15.86
18	52.3	61.44	20.21	1.83	16.52
19	58.2	62.52	20.45	1.80	15.23
PCL homopolymer	100	62.93	18.55	0.00	18.55

Figures related to the range of cotton-g-PCL samples with increasing amounts of PCL

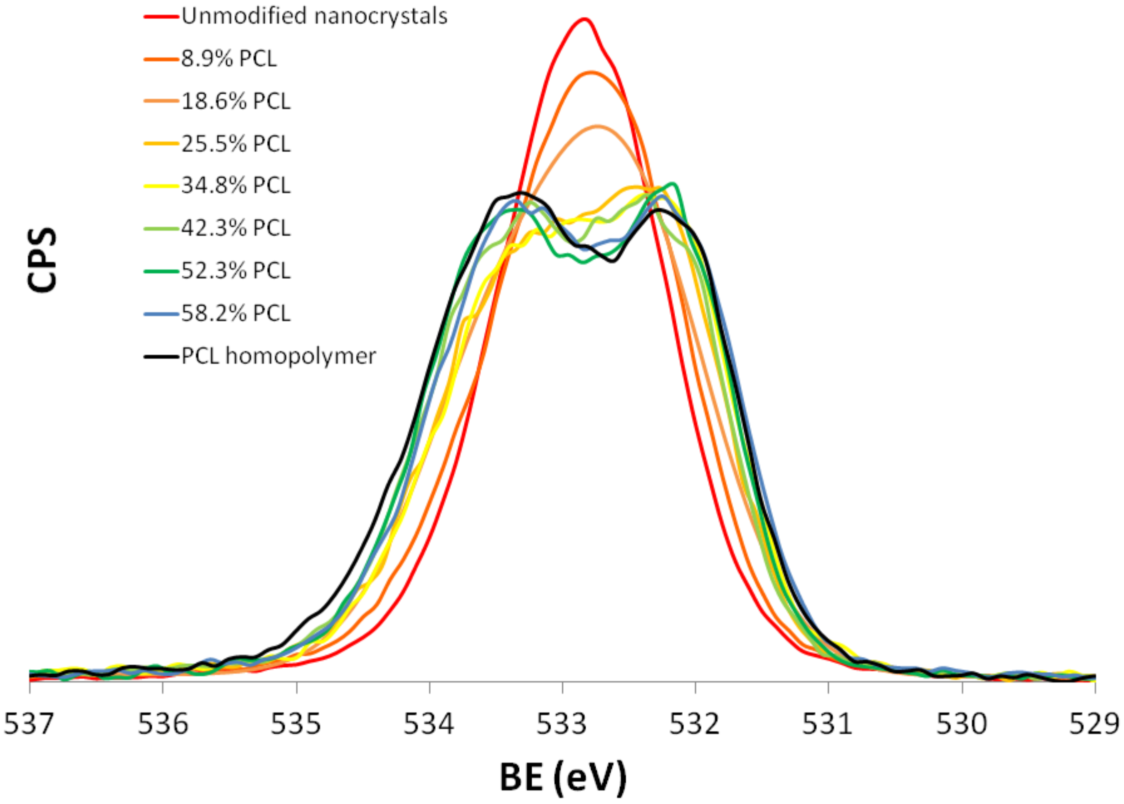
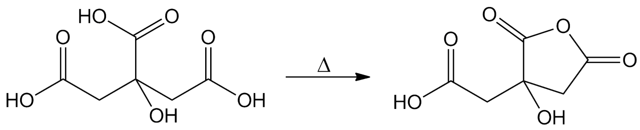
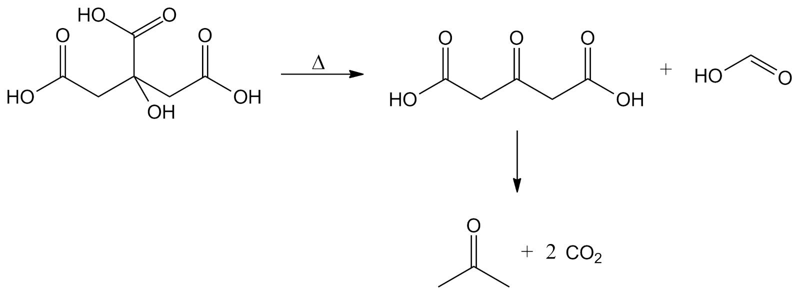


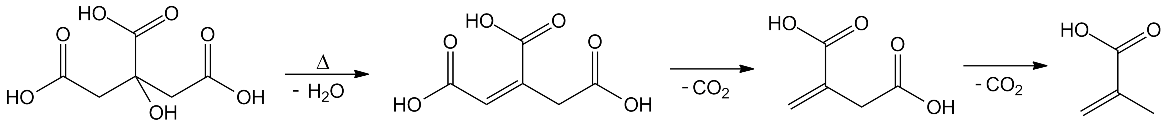
Figure ESI-5 – Evolution of the O1s peak when increasing the PCL content



Scheme ESI-1 - Dehydration of citric acid to form citric anhydride



Scheme ESI-2 - Thermal decomposition of citric acid



Scheme ESI-3 - Alternative thermal decomposition of citric acid

References

[A] Y. Habibi, H. Chanzy, M.R. Vignon, *Cellulose*, 2006, **13**, 679.

[B] Liu S, Yu H, Huang Y (2005) Structure and morphology of cellulose in wheat straw. Cellulose 12:25–34.

[C] Kondo T, Sawatari C (1996) A Fourier transform infra-red spectroscopic analysis of the character of hydrogen bonds in amorphous cellulose. Polymer 37:393–399.

[D] 46 G. Zhang, T.L. St-Clair, C.L. Fraser, *Macromolecules*, 2009, **42**, 3092