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1 **Organocatalyzed ring opening polymerization of lactide from the surface of**
2 **cellulose nanofibrils**

3 Michael Lalanne-Tisé^{1,2}, Maarten A. Mees¹, Samuel Eyley¹, Philippe Zinck^{2*}, Wim Thielemans^{1*}

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6 ¹ Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven, campus Kulak Kortrijk,
7 Etienne Sabbelaan 53, box 7659, B-8500 Kortrijk, Belgium

8 *wim.thielemans@kuleuven.be

9

10 ² Université de Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse
11 et Chimie du Solide, F-59000 Lille, France

12 *philippe.zinck@univ-lille.fr

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18 **Abstract:**

19 The surface initiated ring opening polymerization (SI-ROP) of cellulose nanofibers (CNF) with *rac*-Lactide
20 under mild conditions using N,N-dimethyl aminopyridine (DMAP) was investigated. The influence of
21 catalyst amount, monomer-to-initiator (cellulose surface –OH groups) ratio, temperature, and cellulose
22 preconditioning (lyophilization *vs* solvent exchange) were studied to determine the best SI-ROP conditions,
23 and to understand the effect of the parameters on grafting efficiency. The fibers modified after
24 lyophilization had a PLA content comparable to those obtained with traditional metal catalysts (e.g. tin-
25 (II)ethylhexanoate). Starting from a stable dispersion of CNF in dichloromethane obtained through solvent-
26 exchange showed better results at low catalyst amounts. Furthermore, DMAP was readily removed from
27 the products whereas metal catalysts can be hard to remove from the final material, potentially shortening
28 the material lifespan and making it unfit for some applications. Therefore, the use of an easily removable
29 and more efficient organocatalyst can be considered a good alternative to metal catalysts.

30 **Keywords:**

31 Cellulose nanofibrils, Organocatalysis, Polylactide, Biocomposite

32

33 **1. Introduction**

34 After playing an important role in the advent of the chemical industry and being replaced by petroleum-
35 based alternatives, carbohydrate polymers have again regained an increasing amount of attention.
36 Polysaccharides have been the focus of a large amount of work as the biggest fraction of renewable biomass,
37 with cellulose being the most common biopolymer on the planet with an estimated annual production of
38 well over 10¹⁰ tons (Habibi, Lucia, & Rojas, 2010). Cellulose has many potential uses, and can be made
39 into nanomaterials such as cellulose nanofibrils (CNF) (Siqueira, Bras, & Dufresne, 2010; Zhao, Du, Chen
40 W., Pan, & Chen D., 2019) and cellulose nanocrystals (Habibi et al., 2010; Zhao et al., 2019). CNF are
41 micron-length fibers that possess remarkable properties such as a high aspect ratio (width of 4 to 20 nm,
42 length of up to several microns), a high stiffness with a Young's modulus superior to 110 GPa, and a low
43 density of 1.6 g/cm³ (Dufresne, 2013), capable of forming a network structure. Unlike CNFs, CNCs do not
44 contain dislocated non-crystalline sections as the dislocated regions are removed during an acid hydrolysis,
45 making their length smaller and crystallinity higher (Bondeson, Mathew, & Oksman, 2006)**Erreur !**
46 **Source du renvoi introuvable.** Their high abundance, stiffness, and high aspect ratio make CNFs and
47 cellulose nanocrystals (CNCs) good candidates for use in composite materials as reinforcements (Eichhorn
48 et al., 2010). Moreover, nanocellulose can be produced at an industrial scale (Liu, Moon, Rudie, &

49 Youngblood, 2014; Trache, Hussin, Haafiz, & Thakur, 2017). Because of the lower aspect ratio of CNCs
50 when compared to CNFs, CNFs have a greater potential as reinforcing fiber and impact modifier in
51 composites (Xu et al., 2013), yet they have not received the same amount of attention as CNCs when it
52 comes to surface modification (Xie, Du, Yang, & Si, 2018). Using CNFs and CNCs in polymer matrices
53 comes with a few challenges; the compatibility between hydrophobic polymer matrices and hydrophilic
54 cellulose is limited, and the dispersion of nanomaterials in polymer can be quite poor. This in turn
55 diminishes the achievable mechanical strength and ductility improvements of the composite material as
56 these depend on individualization of the reinforcing fibers. Hence, some research has been carried out on
57 the surface modification of nanocellulose to enhance their dispersibility and to improve the compatibility
58 of cellulose nanomaterials with hydrophobic polymer matrices. Their surface hydroxyl groups allow for a
59 wide array of chemical modifications and these could thus be used to change the nanocellulose surface
60 energy to increase compatibility with polymer matrices (Eyley & Thielemans, 2014; Habibi, 2014).
61 Examples of modifications reported in the literature include non-covalent modification such as surfactant
62 adsorption (Bondeson & Oksman, 2007; Heux, Chauve, & Bonini, 2000), but also covalent surface
63 reactions such as sulfonation (Abitbol, Kloser, & Gray, 2013; Liimatainen, Visanko, Sirviö, Hormi, &
64 Niinimäki, 2013), oxidation (de Nooy, Besemer, & van Bekkum 2010; Isogai, Saito, & Fukuzumi, 2011),
65 acetylation (Yamamoto, Horii, & Hirai, 2006; Yang et al., 2013), etherification (Hasani, Westman, & Gray,
66 2008), silylation (Goussé, Chanzy, Excoffier, Soubeyrand, & Fleury, 2002), and amidation (Lasseuguette,
67 2008).

68 The combination of a biodegradable, biocompatible, and bio-based polymer with CNFs could lead to an
69 all-biodegradable and biocompatible composite material made completely from renewable materials.
70 Polylactide (PLA), a polyester that can be obtained from 100% renewable sources, is therefore an
71 interesting candidate (Drumright, Gruber & Henton, 2000). In addition, PLA is non-toxic and
72 biocompatible, allowing it to be used in many fields such as food-contact and biomedical application
73 (Munim & Raza, 2019). Combining cellulose fibers with PLA could thus lead to materials with a larger
74 range of mechanical and impact properties opening up a wider range of possible applications than those
75 now achievable (Avinc & Khoddami, 2009). Using the same monomer to graft on the cellulose as the
76 polymer matrix should provide the best possible compatibility between matrix and reinforcing fiber
77 (Nordgren, Lönnberg, Hult, Malmström, & Rutland, 2009). Surface modification of CNF with polymers
78 could also be useful for the production of co-continuous composites, where the polymeric surface graft acts
79 as the complete matrix phase with near-perfect compatibility between the matrix and the fiber (Labet,
80 Thielemans & Dufresne, 2007).

81 Cellulose and other polysaccharides with PLA grafts have mostly been reported using a “grafting from”
82 approach (Gazzotti et al., 2019; Stepanova et al., 2019; Ouchi, Kontani, & Ohya, 2003; Miao, Rousseau,
83 Mortreux, Martin, & Zinck, 2011), but “grafting to” methods have also been used successfully to produce
84 similar materials (Ohkita & Lee, 2004). In the case of lactide and other similar cyclic monomers, the
85 grafting from approach makes use of ring-opening polymerization (ROP), using the polysaccharide
86 hydroxyl groups as initiating sites along with a catalyst, often tin(II) octoate (SnOct_2) (Gazzotti et al., 2019)
87 or DMAP (Miao et al., 2011; Ohkita & Lee, 2004). ROP reactions from nanocellulose have been performed
88 in solution and in bulk under a wide variety of condition (Labet & Thielemans, 2012; Ohkita & Lee, 2004).
89 A previous report of PLA-grafted cellulose nanofibrils using the “grafting from” approach and SnOct_2
90 achieved a grafting of around 20w% of PLA (Stepanova et al. 2019).

91 Metal-based catalysts, and in particular tin, have been used for a long time to perform ring-opening
92 polymerization of lactides, both for homogeneous PLA synthesis and for the grafting from carbohydrates
93 as described previously. However, metal catalysts can cause problems as they are prone to stay attached to
94 the chain end of the macromolecular product (Hafren & Córdova, 2005), requiring additional steps for
95 removal implying an increased cost for sensitive applications such as biomedical applications. Even these
96 steps in general do not fully remove the metal catalysts in the presence of cellulose, making trace pollution
97 a potential problem (Labet 2012).

98 Organic catalysis is an interesting alternative to metal-based catalysis and it has been heavily investigated
99 in the last few decades for the ROP of lactide (Dove, 2012; Kiesewetter, Shin, Hedrick, & Waymouth,
100 2010; Ottou, Sardon, Mecerreyes, Vignolle, & Taton, 2016). A wide range of organocatalysts can be used
101 including N-heterocyclic carbenes (Li, Ai, & Hong, 2018), pyridine-based compounds (Miao et al., 2011;
102 Ohkita & Lee, 2004), guanidine (Lohmeijer et al., 2006; Simón & Goodman, 2007) , amidine (Simón &
103 Goodman, 2007), and nucleobases such as adenine (Nogueira et al., 2016). Most of these have received
104 thorough studies for the ROP of lactide and were proven to be competitive with metal-based catalysts.

105 While both ROP of lactide initiated from polysaccharide hydroxyl groups and catalyzed by an
106 organocatalyst have been studied, the SI-ROP of PLA from nanocelluloses catalyzed by an organic
107 compound has not received such attention. In addition, the surface modification of cellulose nanocrystals
108 has been reported more often than surface modification on nanofibrils, with little work done on studying
109 the influence of different parameters on the reaction of polymerization initiated from nanocellulose
110 surfaces. Where such studies have been carried out, they proved to be quite valuable in bringing insights in
111 the reaction of SI-ROP and enabled optimization of the modification reaction (Labet & Thielemans, 2012).
112 Furthermore, while formation of homopolymer is also expected as trace water cannot be fully excluded
113 from the reaction mixture, little is known about the competition between homopolymerization and

114 polymerization from the nanocellulose surface. We report herein an investigation of the influence of
115 experimental parameters on the grafting efficiency of lactides in the DMAP catalyzed CNF hydroxyl groups
116 initiated ROP reaction to start developing the insights needed to optimize these reactions.

117

118 2. Materials and Methods

119 2.1. Material

120 Cellulose nanofibrils were obtained from SAPPI and received as a 1% suspension in water and was used as
121 the initiator for the reaction, and the main material used in this study. This product is available commercially
122 under the brand name Valida. Characterization data of non-modified cellulose is provided in Supplementary
123 Information. Dichloromethane (analytical reagent grade) was obtained from Van Waters Rogers (VWR)
124 and used as both the reaction solvent and for purification, acetone and ethanol were purchased from Acros
125 Organics and were used for purification. *Rac*-Lactide was used as the monomer and received from Fisher
126 Scientific and N,N-dimethyl aminopyridine was use as catalyst of the reaction and received from Sigma
127 Aldrich. All chemicals except for cellulose were used as received.

128

129 2.2. Surface-Initiated Ring Opening Polymerization (SI-ROP)

130 - SI-ROP from lyophilized cellulose nanofibrils

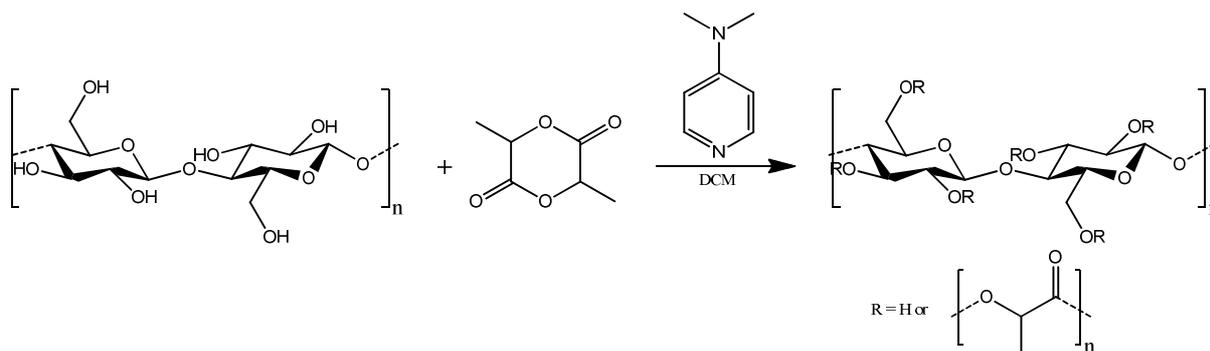


Figure 1: Reaction scheme of the Surface-Initiated Ring-Opening Polymerization (SI-ROP) of DL-Lactide from the surface of cellulose nanofibrils using N,N-dimethyl aminopyridine (DMAP) as catalyst dichloromethane (DCM) as the solvent

131 CNFs were first frozen using liquid nitrogen, and then freeze-dried for 4 days at -56°C with a Thermo Heto
132 PowerDry PL6000, under a vacuum of 2 mbar. After lyophilization, the CNFs were soxhlet-extracted with
133 ethanol for 24 hours to remove any impurities adsorbed on the surface of the cellulose fibers (Labet &
134 Thielemans, 2011). The CNFs were subsequently dried at 40°C for 24h, under vacuum at around 3 mbar.

135 Surface modification of the freeze-dried CNFs was performed in a 100 mL 3-necked round bottom flask
136 under an inert atmosphere (argon) while stirring continuously. First CNF and lactide were introduced in the
137 flask, placed under vacuum, and flushed with argon for 15 minutes. Then dichloromethane (DCM) was
138 added and the mixture was left to stir for another 15 minutes. Finally, DMAP was introduced and the
139 mixture was heated to 35°C. A condenser was connected to the round bottom flask to avoid gas build-up
140 and pressure increase in the flask. After 48 hours, the reaction mixture was filtered over a cellulose soxhlet
141 extraction thimble and purified by soxhlet extraction with dichloromethane for 24 hours to remove
142 homopolymer. An additional soxhlet extraction with ethanol was performed for 24 hours to remove DMAP
143 from the surface of cellulose. The modified nanofibrils were subsequently dried *in vacuo* for 24 hours at
144 40°C and a pressure of 3 mbar. The reaction scheme for SI-ROP is presented in Figure 1.

145 For all those reactions, the temperature was set to 35°C for all reactions, and the monomer/cellulose ratio
146 was set at 30/1, while the catalyst loading was gradually increased from 0.5eq to 5eq.

147 - SI-ROP from never-dried CNF dispersion

148 A known amount of 1 wt% CNF/H₂O dispersion was poured in a 1L round bottom flask and mixed with an
149 equal part of ethanol. The resulting suspension was filtered through a large cellulose soxhlet extraction
150 thimble and purified by soxhlet extraction with acetone (8h) to remove water from the cellulose. The CNF
151 were then further purified by soxhlet extraction with ethanol (24h) and then with DCM (6,5h). Care was
152 taken to always keep the CNF in the extraction thimble in a wet state to avoid drying-induced aggregation.
153 The cellulose obtained was then mixed with additional DCM to obtain a 1% suspension of CNF in DCM.
154 Surface modification of cellulose was performed in a 100 mL 3-necked round bottom flask under inert
155 atmosphere (argon) while stirring continuously. DMAP was first introduced in the flask connected to a
156 condenser and flushed with argon for 15 minutes. Ten mL of the cellulose dispersion in DCM was then
157 added and stirred with DMAP to allow it to adsorb to the surface of cellulose. Five mL of pure
158 dichloromethane was then added to the mixture, followed by lactide. The reaction was subsequently heated
159 to the desired reaction temperature and stopped after 24 hours. The mixture was first filtered through a
160 cellulose soxhlet extraction thimble and then purified by DCM soxhlet extraction for 24h to remove
161 homopolymer formed during the reaction. Another 24 hours, an ethanol soxhlet extraction was then carried
162 out to clean cellulose of all the impurities still on its surface, especially DMAP. Finally, the solid was
163 dried *in vacuo* at 40°C and a pressure of 3 mbar for 24 hours.

164 During all these experiments, the temperature was tested between 25°C and 39°C, the monomer/cellulose
165 ratio was in a range between 1/1 to 30/1, and the catalyst loading was in a range of 0.5eq to 3eq.

166

167 **2.3. Characterization**

168 Elemental composition (C, H, N, and S) of CNFs was measured with a Thermo Scientific FLASH 2000
169 elemental analyzer (EA), using about 1 mg of dry sample. The standard used for calibration was 2,5-Bis(5-
170 tert-butyl-2-benzo-oxazol-2-yl)thiophene (BBOT, Elemental Microanalysis, UK. Vanadium pentoxide was
171 used to aid sulphur determination. All values reported are the average of 3 measurements.

172 Grafting percentage is evaluated by using the mass fraction of different elements in each sample, and then
173 comparing the elemental composition with unmodified CNF and lactide. Water content, determined by
174 TGA, is taken into account for the mass fraction of O and H for every measurement. The difference for
175 each element mass fraction between the modified and unmodified cellulose is then used to determine what
176 is the contribution of the grafts, which leads to the mass % of grafting done on CNFs. Unmodified CNF
177 composition used for this calculus is provided by elemental analysis of the starting product, while lactide
178 composition is assumed to be similar to its chemical formula.

179 A Netzsch TG 209 F3 Tarsus was used to carry out thermogravimetric analysis (TGA). Around 2 mg was
180 placed in an aluminum-(III)-oxide pan and heated from 30 to 600°C at a ramp rate of 10°C/min under argon
181 flow. Water content of the various samples was determined as the difference between the initial mass and
182 the stabilized mass around 100°C. The determined water content was taken into account in the
183 determination of the level of surface modification based on elemental composition results in line with our
184 earlier reported procedure (Eyley et al. 2018).

185 Infrared spectra of CNF were measured using a Bruker ALPHA Fourier-transform Infrared Spectroscopy
186 (FTIR) spectrophotometer to determine the success of the reaction on the CNF. Measurements were carried
187 out in attenuated total reflection (ATR) mode. Spectra were acquired as the sum of 16 scans over a
188 frequency ranging from 4000 to 400 cm⁻¹ on CNF deposited onto the spectrophotometer.

189 Surface-sensitive analysis of modified CNF was carried out by X-ray photoelectron spectroscopy (XPS) on
190 a Kratos Axis Supra photoelectron spectrometer using a monochromated Al K α ($h\nu = 1486.7$ eV, 5 mA)
191 X-ray source, hybrid (magnetic/electrostatic) optics, and a hemispherical analyzer with a pass energy of
192 160 eV for survey spectra and 20 eV for high resolution spectra. Spectra were acquired under charge
193 neutralization conditions using an electron flood gun within the field of the magnetic lens, and were charge
194 corrected to aliphatic carbon at 285.0 eV. Spectra were processed in CasaXPS with Tougaard 2-parameter
195 backgrounds used for integration and LA(α , m) lineshapes corresponding with a Voigtian function with
196 Lorentzian exponent α and Gaussian width m used for fitting high resolution spectra. Empirical relative
197 sensitivity factors supplied by Kratos Analytical (Manchester, UK) were used for quantification.

198 The crude homopolymer was extracted from dichloromethane soxhlet by removing the solvent using a
199 rotary evaporator, and placing the product obtained in a vacuum oven at 40°C for 24h. The number-average
200 molecular weight (M_n) and the dispersity (\mathcal{D}) of the crude product were determined by Size Exclusion
201 Chromatography (SEC) in tetrahydrofuran at 40 °C at a flow rate of 1 mL.min⁻¹. Sample concentration was
202 of 2g/l, M_n and \mathcal{D} were determined from the Refractive Index (RI) signal using a calibration curve based
203 on polystyrene (PS) standards from Polymer Standards Service, on a Waters apparatus equipped with
204 Waters Styragel columns HR2, HR3, HR5 and HR5E.

205 NMR was also used on some crude product extracted similarly to the one used for SEC analysis to
206 characterize the homopolymer formed and evaluate the presence or not of unreacted monomer. ¹H NMR
207 spectra were recorded on AVANCE III HD 300 Bruker spectrometer (7.1 Tesla) at room temperature
208 in deuterated dimethyl sulfoxide (0.6 ml) for the crude mixture, as well as DMAP and DL-Lactide
209 separately.

210

211 3. Results and discussion:

212 3.1. SI-ROP modification of lyophilized CNF

213 The effect of reaction temperature, catalyst loading, and monomer-to-cellulose ratio on the SI-ROP of PLA
214 from the surface of freeze-dried CNF was investigated in order to optimize and control CNF
215 functionalization. The reactions were first carried out in DCM using DMAP as the catalyst for 48h at 32°C.
216 Representative examples of the reactant ratios and % of grafted PLA are given in Table 1.

217 At a fixed temperature and reaction time (35°C and 48 hours), the PLA content of grafted nanocellulose
218 increased with the amount of catalyst, and reached a maximum for 3 equivalents of catalyst per surface
219 hydroxyl group (Table 1).

220 *Table 1: Evolution of grafted poly(lactide) content on the surface of cellulose using rac-Lactide, N,N-dimethyl aminopyridine*
221 *(DMAP) as catalyst, lyophilized cellulose nanofibrils (CNF), in dichloromethane. Determined by elemental analysis (EA),*
222 *calculation based on hydrogen and carbon content, corrected for water content.*

Entry	T (°C)	Lactide/CNF	Eq DMAP/CNF	Grafted PLA (wt%)
1	35	30	0.5	6
2	35	30	1	6
3	35	30	1.5	8
4	35	30	2.0	8
5	35	30	2.5	11
6	35	30	3.0	19

7	35	30	4	12
8	35	30	5	17

223

224 Water present during the reaction competes with cellulose nanofibrils surface hydroxyl groups to initiate
 225 the polymerization reaction (Figure 1), thus resulting in homopolymer formation. This side reaction is
 226 important due to the hydrophilic nature of cellulose. It is further exemplified at DMAP amounts above 3
 227 equivalents of the surface hydroxyl groups, where the grafted PLA content on the CNF dropped, indicating

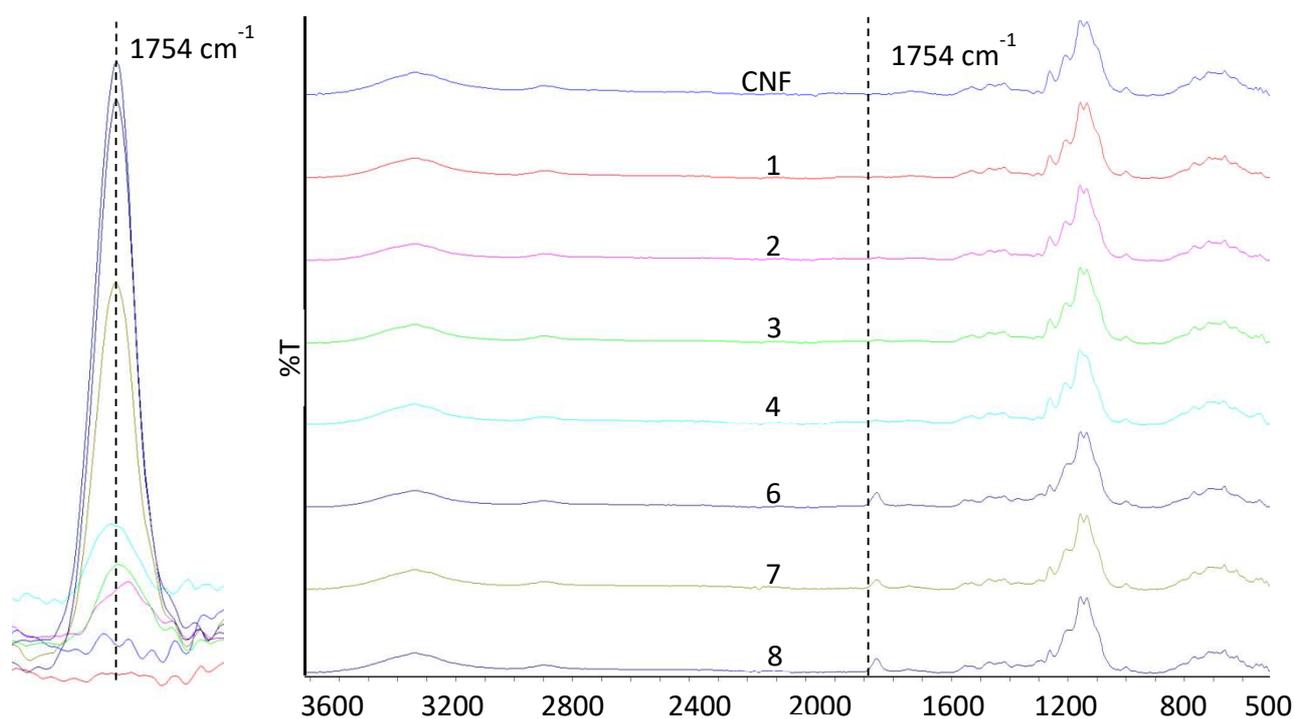


Figure 2: FT-IR spectra of cellulose nanofibrils (CNF) and modified CNF with different amount of grafting after purification by soxhlet extraction

228 that a higher catalyst amount leads to a faster initiation by water. Therefore a ratio [CNF]:[DMAP] of 3
 229 appears to be optimal for CNF surface modification. This catalytic ratio is in the range of values reported
 230 in the literature for DMAP-catalyzed homopolymerization of lactide and for the ROP of lactide from
 231 polysaccharides (Miao et al., 2011; Nederberg, Connor, Möller, Glauser, & Hedrick, 2001; Siqueira et al.,
 232 2010).

233 In addition to elemental analysis, success of modification was confirmed by FTIR (Figure 2). The spectra
 234 of the product closely resembled that of cellulose as expected. The appearance of a band at 1754 cm^{-1} is
 235 characteristic of polylactide stretching frequencies for $\nu(\text{C}=\text{O})$ and confirms successful esterification on the
 236 CNF surface, as well as a signal at 1451 cm^{-1} and 1090 cm^{-1} , which are typical for PLA (Miao et al., 2011;
 237 Nogueira et al., 2016). As shown in the magnification in Figure 2, the relative intensity of the carbonyl
 238 signal in modified CNF increased with increasing amount of catalyst, reaching a maximum for 3 equivalent

239 of catalyst/surface hydroxyl, in line with the trend observed for the calculated amount of PLA obtained
240 from EA. This confirms the trend in surface modification and the maximum amount of PLA grafted on the

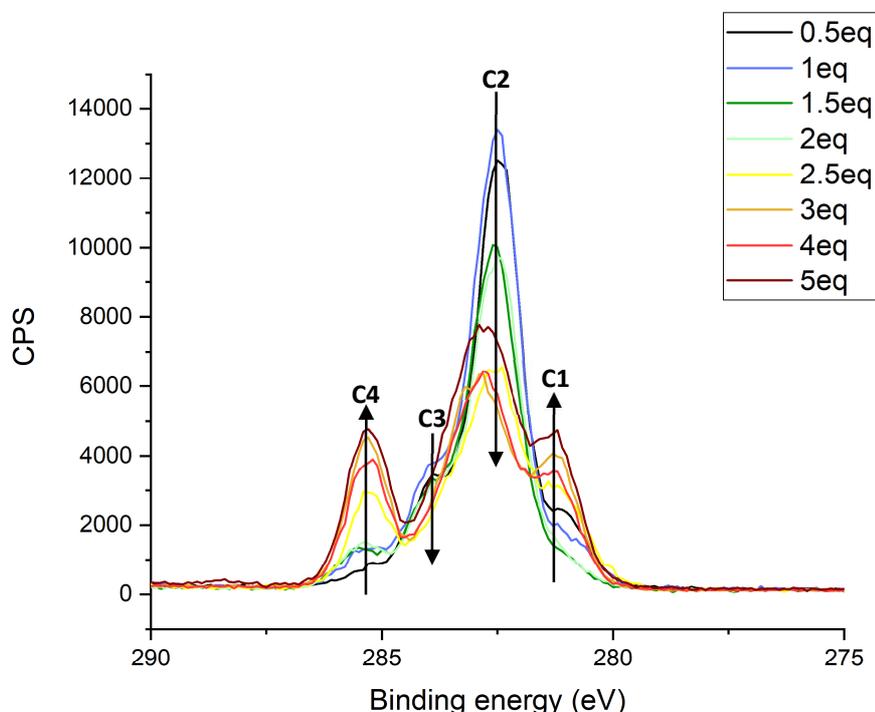


Figure 3: Carbon 1s X-ray Photoelectron Spectroscopy (XPS) scan of modified cellulose nanofibrils using different amounts of *N,N*-dimethyl aminopyridine

241 surface of cellulose for 3 equivalents of catalyst.

242 X-ray Photoelectron Spectroscopy (XPS) gives even more information on the surface composition and the
243 chemical environment of the CNFs. In Figure 3, C1 is the aliphatic carbon contribution at 285eV, which
244 initially increases with the amount of catalyst used. C2 and C3 correspond to C-O (at 286.41eV) and O-C-
245 O (287.45eV) contribution respectively and both decreased with an increasing amount of PLA grafted on
246 the surface of cellulose. C4 is the O-C=O contribution visible at 289.16eV, which increased with the amount
247 of modification on the fiber in agreement with C1. Both C4 and C1 are not present for unmodified cellulose,
248 confirming modification after purification of the CNF. All the positions reported for the different
249 contributions are in agreement with earlier reported results for poly(ϵ -caprolactone) grafted on
250 nanocellulose (Labet & Thielemans, 2011). XPS data thus confirmed the results obtained by elemental
251 analysis and FTIR, with the most amount of modification detected for 3 equivalents of catalyst.

252 3.2. SI-ROP modification on never dried CNF

253 Using the results obtained from the previous experiments, a different protocol was tested using never-dried
 254 CNF. Indeed, working with lyophilized CNF requires freeze-drying, giving CNF that are more difficult to
 255 redisperse and that require the use of more solvent than never-dried CNF suspensions to obtain a
 256 homogeneous reaction mixture. Therefore, different methods for preparing CNF dispersions in DCM, from
 257 a water 1% water dispersion, were tested. We optimized the procedure and came to the methodology as
 258 described in the Materials and Methods section. The results of the DMAP-catalyzed ROP grafting reactions
 259 are reported in Table 2. This method gave a product that was easier to characterize after drying (powder-
 260 like) and showed in general a superior quantity of PLA grafting on CNF, particularly at lower amounts of
 261 catalyst (*e.g.* compare entries 3 and 4 in Table 1 to entry 10 in Table 2).

262 Using a ratio of lactide/CNF/catalyst of 30/1/3, two similar reactions were performed at 39°C over 24h, one
 263 using freeze-dried CNF and the other never-dried CNF. After using elemental analysis and TGA, the
 264 grafting obtained from freeze-dried cellulose was 13% (entry 16, table 2), while never dried cellulose
 265 grafting reached 24% (entry 15, table 2). As the result found for never-dried cellulose was comparable to
 266 better grafting obtained using freeze-dried cellulose over 48h, experiments using never-dried cellulose were
 267 performed over 24h Using never-dried CNF suspensions in DCM, we also investigated the effect of
 268 temperature, monomer amount, and monomer/initiator ratio.

269 *Table 2: Evolution of grafted poly(lactide) content on the surface of cellulose using rac-lactide, N,N-dimethyl aminopyridine*
 270 *(DMAP) as catalyst and 0.1g cellulose nanofibrils dispersed in dichloromethane. Reaction time 24h. Determined by elemental*
 271 *analysis, calculation based on hydrogen and carbon content. Corrected for water content. a: done using freeze-dried CNF*

Entry	T (°C)	Lactide/CNF	Eq DMAP/CNF	Grafted PLA (wt%)
1	25	1	0.5	7
2	25	1	3	13
3	25	15	1.75	7
4	25	30	0.5	16
5	25	30	3	18
6	32	1	1.75	5
7	32	15	0.5	9
8	32	15	1.75	11
9	32	15	3	9
10	32	30	1.75	12
11	39	1	0.5	6
12	39	1	3	17
13	39	15	1.75	12
14	39	30	0.5	18
15	39	30	3	24
16^a	39	30	3	13

272

273 Grafting onto CNF ranged from 5% to 24%: Overall an increase in catalyst ratio from 0.5 eq to 3 eq led to
 274 an increase in the amount of PLA grafted onto CNF, irrespective of the temperature (comparing entry 1 to
 275 2 and 12 to 11) or the quantity of lactide (comparing entry 1 to 2 and 5 to 4). As described previously, the
 276 polymerization reaction from the surface of CNF takes place in competition with the homopolymerization
 277 initiated by residual water. While DMAP is known to work better at higher quantities for ROP initiated by
 278 hydroxyl groups (Nederberg et al., 2001), the presence of a small amount of water means more catalyst is
 279 needed to ensure a proper initiation from the nanofibril surface.

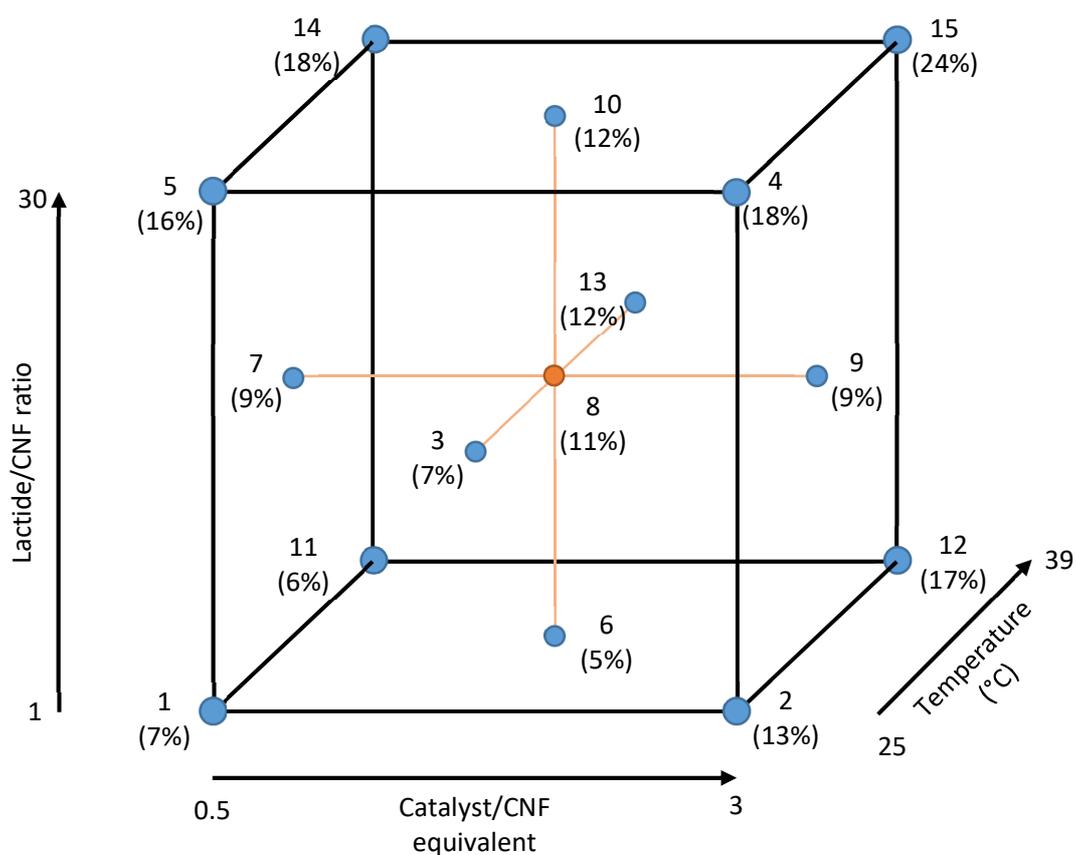


Figure 4: graphical representation of the grafting % of PLA on cellulose with different sets of parameters. Numbers correspond to entries in table 2

280 At higher temperatures but low monomer amount (entry 11 and 12), the increase in DMAP content has
 281 more of an impact on the amount of PLA grafted which increased by 11%, compared to a 5% increase at
 282 lower temperature. This is likely due to a faster polymerization of lactide at higher temperatures, but
 283 initiation being preferred for water as it is more mobile and available than cellulose OH groups, resulting
 284 in homopolymerization being heavily favored. An opposite effect is observed at lower temperatures and a
 285 high lactide amount (entry 5 and 4): An increase in the quantity of DMAP did not make a noticeable
 286 difference in the surface-grafted quantity of PLA (2%). If polymerization on cellulose “starts late” due to

287 initiation on water being faster, but there is a lot more monomer available and propagation is slower, then
288 grafting on cellulose still has time to occur. In that regard, adding more DMAP to ensure initiation on
289 cellulose can happen quickly does increase the amount of grafting found, but only by a small margin.

290 An increase in temperature (entry 1 to 11, 2 to 12, 5 to 14 and 4 to 15) in general led to a greater amount of
291 grafted PLA on the CNF, similarly to an increase in catalyst amount. However this effect was more
292 pronounced for higher catalyst amounts, as increasing the temperature from 25 to 39°C when only 0.5 eq
293 of DMAP was used (entry 1 vs. 11, 2 vs. 12, 5 vs. 14 and 4 vs. 15) did not make a significant difference
294 (2% or less) in the amount of PLA grafted on the CNFs, irrespective of amount of monomer. While
295 increasing the temperature was beneficial to the amount of PLA grafting, it may also lead to faster
296 polymerization, while the lower amount of catalyst may lead to a slower initiation on CNF surface hydroxyl,
297 both of which favor water-initiated homopolymerization.

298 Finally, the effect of the monomer quantity was studied. When comparing the results of entry 1 vs. 5, 2 vs.
299 4, 11 vs. 14, 12 vs. 15 and 6 vs. 10, the PLA weight content on modified CNF increased significantly with
300 increasing amounts of lactide. This particular effect was more pronounced for a smaller quantity of catalyst,
301 leading to an increase of 9% (entry 1 to 5) and 12% (entry 11 to 14) in PLA grafting. Comparatively,
302 increasing the monomer amount at higher DMAP loading increased the PLA amount on CNF by 5% (entry
303 2 to 4) and 7% (entry 12 to 15) respectively. This result agrees with the previous observations, showing that
304 a small amount of catalyst favors initiation by residual water, which then will quickly turn the monomer
305 into homopolymer. When more lactide is added to the reaction, this effect is mitigated as more monomer
306 takes longer to react away allowing for surface-grafting on the nanocellulose.

307 Comparing all reactions, the monomer amount comes out as the most influential parameter, as an increase
308 in *rac*-lactide always led to the most significant increase in grafting amount on CNF. However, increasing
309 the amount of catalysts can achieve comparable results, especially at higher temperatures. This can be more
310 advantageous as the amount of catalyst needed to yield such result is significantly less than the amount of
311 monomer required, as an increase by a factor 6 for the quantity of catalysts can yield similar amount of
312 grafting as an increase by a factor 30 for the quantity of monomer.

313 Reactions with intermediate values for all parameters were also performed to verify the trends. While those
314 observations stayed true for most experiments, some specific combinations gave low PLA grafting onto
315 cellulose, meaning some parameter combinations do not favor grafting, but rather water-initiated
316 homopolymerization. In particular, increasing the temperature was detrimental to PLA grafting on CNF for
317 low DMAP and lactide quantities, explained by the temperature increasing the speed of
318 homopolymerization.

319 Compared to the results for freeze-dried CNF, solvent-exchanging CNF allows for a higher maximum
320 grafting efficiency, but significantly better results are obtained for reactions performed with less than 3 eq
321 of catalysts, all the while requiring shorter reaction times. In addition, elemental analysis showed no

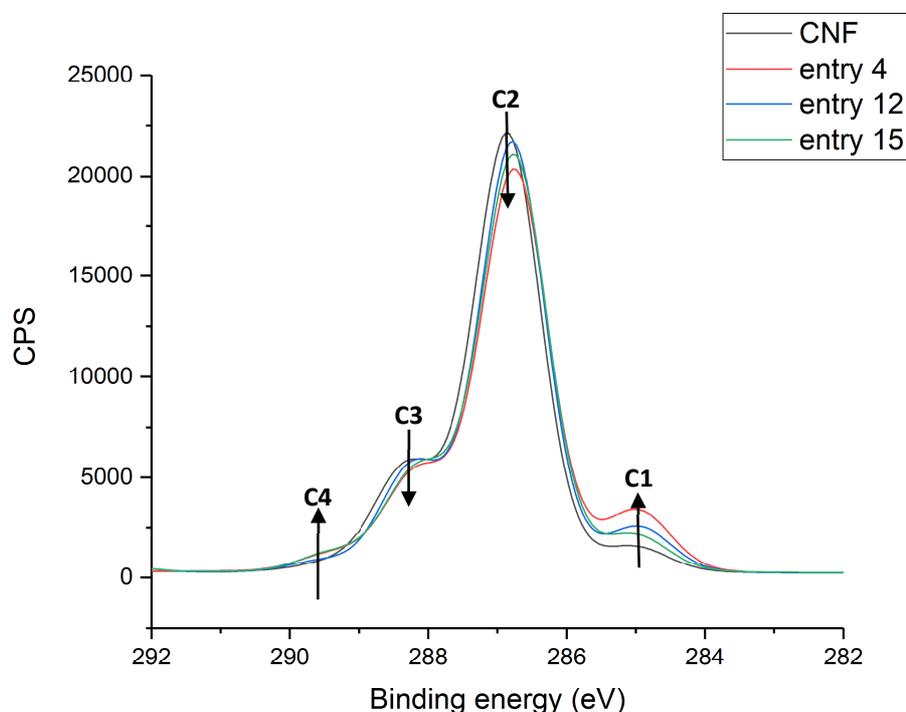


Figure 5: Carbon 1s XPS scan of modified cellulose nanofibrils (CNF) obtained from dispersion in dichloromethane, with different entries corresponding to the samples in Table 2

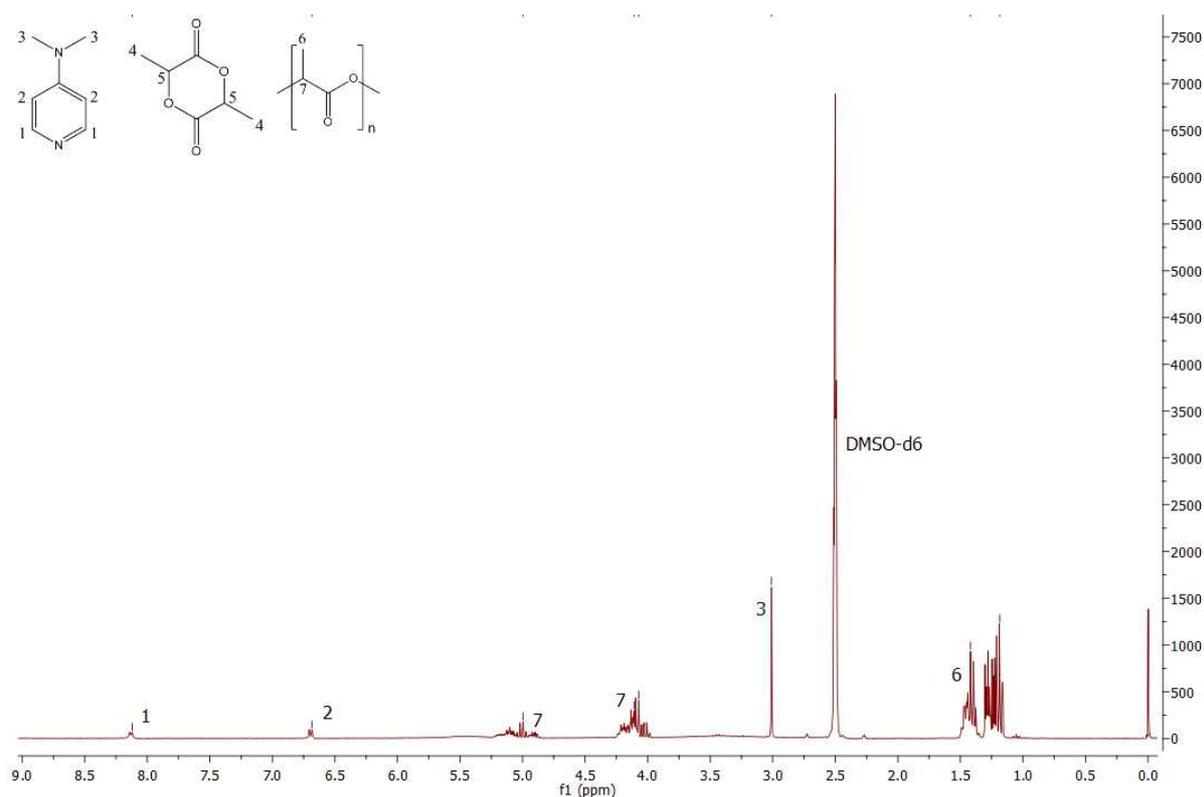
322 significant retention of DMAP in the grafted CNF, indicating a near complete removal of the catalyst from
323 the product. FT-IR (Supporting Information Section 2) analysis showed a band around 1750 cm^{-1} ,
324 characteristic of a stretching frequency for $\nu(\text{C}=\text{O})$. A characteristic ester band is seen at 1454 cm^{-1} and is
325 more important for the cellulose with a higher PLA content. As shown in the magnification the carbonyl
326 signal increase, following the same trend as the amount of grafting calculated using EA. Comparing the
327 spectra obtained using the freeze-dried CNF, the overall signal is similar, and the relative intensity of the
328 ester band is similar for samples with equal PLA content calculated with EA.

329 X-ray photoelectron spectroscopy (Figure 5), shows the aliphatic carbon contribution C1 increasing for
330 modified CNF compared to non-modified ones due to the methyl-bearing lactide units grafted on the
331 cellulose. The same conclusion can be made for the C4 contribution, related to $\text{O}-\text{C}=\text{O}$ visible at 289.54 eV
332 present only on the grafts.

333 When comparing the XPS results for the never dried CNF to the one in Figure 3, the same peaks can be
334 seen. However, increases are more pronounced for samples prepared with freeze-dried cellulose, despite

335 EA showing higher grafting for never-dried CNF. A plausible explanation could be that XPS is a surface
336 analysis, only revealing the composition of the top 10 nm of the material. Freeze-dried CNF is more
337 aggregated in the reaction mixture and in the final product. The majority of grafting will thus occur on the
338 surface of aggregated CNF particles, leading to a stronger signal in XPS, yet a lower EA amount. The well-
339 dispersed CNF form a powdery product however, and it is likely that the better dispersion leads to a better
340 separation of the fibrils, giving more surface area for the graft to occur, thus graft may be present deeper in
341 the material.

342 To confirm that lactide polymerization did indeed occur during the reaction and determine the potential
343 length of the PLA chains obtained, size-exclusion chromatography (SEC) was used to determine the length
344 of the homopolymer separated from the CNF during the soxhlet extraction. Overall, the results showed that
345 short oligomer chains were obtained, with a number average molecular weight between 600 and 1400
346 g/mol, confirming the successful polymerization reaction and the presence of chains initiated by water.



347

348 *Figure 6: ¹H NMR spectra of crude mixture after reaction in DMSO-d₆. Crude product separated from modified CNF*
349 *corresponding to entry 15 in table 2*

350 As a complementary approach to determine polymerization of lactide, NMR was used on some crudes
351 samples separated from CNF, similar to the one used for SEC analysis. Samples separated from CNF with

352 different % of grafting (according to EA) were analyzed and compared to the spectra of DL-Lactide and
353 DMAP.

354 ¹H NMR (DMSO-d₆, 300 MHz) δ (ppm) 8.16 (s, 2H), 6.72 (s, 2H), 4.86-5.21 (m, 1H), 4.10-4.24 (m, 1H),
355 3.01 (s, 6H), 1.16-1.49 (m, 3H)

356 Characteristic doublet are observed at 8.16 and 6.72 ppm, corresponding to protons on the pyridine ring
357 of DMAP. Additionally, a singlet corresponding to CH₃ moieties of DMAP is also observed at 3.01 ppm.

358 As the analysis was performed on crude product separated from cellulose, the presence of catalyst was
359 expected.

360 Complex signals can be observed between in the region 4.86-5.21 ppm and 4.10-4.24 ppm. This
361 corresponds to the proton in the polymerized lactide chain. Protons closer to chain ends have a different
362 chemical shift, which leads to 2 complex multiplet. Due to the short length of the oligomer produced,
363 protons next to chain ends have a strong signal in NMR.

364 A similar phenomenon can be observed between 1.16 and 1.49 ppm, which corresponds to methyl
365 protons.

366 Interestingly, the signal for lactide in DMSO, particularly for the proton in the 6 membered ring, is not
367 observed around 5.43 ppm where a quartet should be in the presence of DL-Lactide. This shows that
368 while the grafting measured on CNF is low, and only short oligomers are produced, the conversion of
369 monomer does occur.

370 Overall using never-dried CNF with DMAP and *rac*-lactide has been the more promising grafting method.
371 While both method used for never-dried and freeze-dried CNF are different, and a quantitative comparison
372 cannot be done, the second method used shows more promising results, in particular when trying to use
373 lower quantities of catalyst. It also does not require freeze-drying, a method than can at times take several
374 days, and leads to a better dispersed state of cellulose which is overall easier to analyses.

375

376 **4. Conclusion**

377 We performed SI-ROP of *rac*-lactide using an organocatalyst, N,N-dimethyl aminopyridine (DMAP), and
378 CNFs as the initiator. The effect of different parameters on the reaction were investigated as well as the
379 interaction between these parameters on the modification of cellulose. The highest modification amount
380 was achieved for never-dried CNF suspensions transferred into DCM by solvent exchange, as opposed to
381 the more common lyophilization procedure. The highest grafting was obtained for a 3/1 ratio of

382 DMAP/CNF, 3 g of *rac*-lactide, a reaction time of 24 h at 39°C under inert atmosphere. The amount of
383 modification was similar to earlier reports using tin(II) octoate as the catalyst in solution at 90°C or in bulk
384 at 120°C (Stepanova et al. 2019), while we used a simple one-step reaction and an organic catalyst under
385 mild conditions. In addition, most of the catalyst could be removed from the final product. We were also
386 able to elucidate the effect of changing parameters on the effect of residual water interference of the grafting
387 reaction.

388

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396

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