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# 1 **SI-ATRP grafting of polymers from polydopamine-** 2 **modified cellulose nanocrystals**

3  
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## 12 13 **ABSTRACT**

14 This work reports on the possibility of using polydopamine (PDA) as a tool to immobilize  
15 bromoisobutyryl moieties at the surface of cellulose nanocrystals (CNCs) and initiate Surface  
16 Initiated Atom Transfer Radical Polymerization (SI-ATRP) reactions from these sites. Two  
17 different strategies based on i) the stepwise modification of the CNCs with dopamine (DA) and  
18  $\alpha$ -bromoisobutyryl bromide (BiBB) (Protocol 1) and ii) the one-step treatment of the CNCs  
19 with a mixture of DA and BiBB-modified DA (Protocol 2), were compared. Only the CNC  
20 particles treated according to Protocol 1 guaranteed efficient anchoring of the SI-ATRP  
21 initiating sites in our experimental conditions (with limited impact on the CNCs crystalline  
22 structure), the coated layer being leached out by certain solvents in the case of Protocol 2. The  
23 brominated particles displaying the best performances were subsequently tested as potential  
24 ATRP macroinitiators, using methyl methacrylate (MMA) and styrene (St) as model monomers.

25 Polymer-grafted particles were successfully obtained, with a grafting density twice as high for  
26 Sty as for MMA, demonstrating the validity of this strategy.

27

## 28 **Keywords**

29 Cellulose nanocrystals; polydopamine; SI-ATRP; polymethyl methacrylate; polystyrene

## 30 **1. Introduction**

31 With the gradual implementation of the concept of low-carbon environmental protection, the  
32 development of environmentally friendly biomass resources has attracted more and more  
33 attention (Kobayashi & Nakajima, 2021; Velvizhi et al., 2022). Cellulose nanocrystals (CNCs)  
34 are rod-like nanoparticles, typically obtained by acid hydrolysis of cellulosic substrates (pulp,  
35 paper or microcrystalline cellulose), which are increasingly considered as building blocks for  
36 high-value applications in biotechnology, electronics, optics, energy, packaging or catalysis  
37 (Thomas et al., 2018). Their interest lies in particular in their renewable and biocompatible  
38 nature, outstanding mechanical properties, high aspect ratio, inclination for chiral nematic  
39 ordering, and reactive surface. The efficient use of CNCs however requires a fine control of  
40 their dispersive, interfacial and self-assembling properties, which is generally achieved by  
41 chemical functionalization of their surface. Polymer grafting by Surface Initiated Atom  
42 Transfer Radical Polymerization (SI-ATRP) is particularly attractive in this regard, as it allows  
43 nanohybrids with well-controlled surface properties to be obtained after introduction of  
44 halogenated sites from which controlled radical polymerization can be initiated (Wohlhauser et  
45 al., 2018; Z. Zhang et al., 2021). Until now, the most widely employed method to do so, makes  
46 use of an esterification reaction between the surface hydroxyl groups of the CNCs and  $\alpha$ -  
47 bromoisobutyryl bromide (BiBB). However, direct reaction with the surface cellulose chains  
48 can damage the crystalline structure of the particles through surface erosion and/or modification  
49 of the cellulose I native allomorph (partial conversion into cellulose II) (Z. Zhang et al., 2021).

50 To address this issue, an alternative strategy would be to coat the CNCs with a brominated layer  
51 made of polydopamine (PDA), which could then be reacted with BiBB, limiting the impact of  
52 the treatment on cellulose nanocrystals. Polydopamine (PDA) is a bio-inspired hydrophilic  
53 polymer produced by the oxidative polymerization of dopamine (DA) in alkaline conditions,  
54 and composed of dihydroxyindole, indolquinone and dopamine units, which are assumed to be  
55 covalently linked (Fig. 1). As biocompatible and biodegradable material, PDA has also  
56 excellent adhesive properties (Barclay, Hegab, Clarke, & Ginic-Markovic, 2017; Lee, Dellatore,  
57 Miller, & Messersmith, 2007; Liu, Ai, & Lu, 2014). Its catechol and amine moieties make it an  
58 excellent coating for almost any type of surface including metals, oxides, graphene and  
59 synthetic polymers, while at the same time providing reactive sites for further chemical  
60 modification (Barclay et al., 2017; Lee et al., 2007; Liu et al., 2014). The mechanism of  
61 attachment of PDA on organic and inorganic substrates remains poorly understood, but the  
62 presence of both catechol and amine groups seems to be critical; adhesion appears to be the  
63 results of a combined variety of noncovalent and covalent connections, within the coating and  
64 to the surface, such as  $\pi$ - $\pi$  stacking, van der Waals forces, hydrophobic associations, hydrogen  
65 bonds or electrostatic interactions (Barclay et al., 2017). PDA displays also remarkable  
66 properties, which can impart additional functions to the coated material, such as fluorescence,  
67 UV-absorption, paramagnetism, radical scavenging activity, electrical conductivity, metal ions  
68 chelating activity and redox activity (Barclay et al., 2017; Lee et al., 2007; Liu et al., 2014;  
69 Yang et al., 2020). Up to now, the functionalization of CNCs with PDA has been envisaged to  
70 graft PEG (Zheng et al., 2021), prepare Janus particles (Sun et al., 2022), crosslink nanofiber  
71 mats (Yang et al., 2022) or immobilize cellulase (Qin et al., 2023). Its utilization for the surface  
72 immobilization of ATRP initiators has been recently explored with metals (Zhu & Edmondson,  
73 2011), polystyrene (Kohri et al., 2013; Zhu & Edmondson, 2011), graphene oxide (Luo, Zhao,  
74 Fei, Liu, & Liu, 2016; Wang et al., 2019), carbon nanotubes (Huang et al., 2020; Song et al.,

75 2016), TiO<sub>2</sub> nanoparticles (Kopeć et al., 2018) or poly(vinylidene fluoride) (Dong et al., 2018).  
76 Two types of strategies were then used: in the first one (named Protocol 1 in the current paper),  
77 PDA was polymerized in alkaline water on the targeted surface, then the brominated initiator  
78 was anchored by reaction between the hydroxyl/amine groups of PDA and BiBB, in dry  
79 conditions (Huang et al., 2020; Kopeć et al., 2018; Song et al., 2016; Wang et al., 2019); in the  
80 second one (Protocol 2), the BiBB initiator was first reacted *in-situ* with an excess of DA in dry  
81 conditions, then the BiBB-modified DA was copolymerized in basic water with the remaining  
82 DA (Dong et al., 2018; Kohri et al., 2013; Luo et al., 2016; Zhu & Edmondson, 2011). This  
83 second method appears more convenient, as the DA functionalization and oxidative  
84 polymerization on CNCs are performed in the same flask, but fewer hydroxyl/amine groups are  
85 available after the reaction with BiBB, which may detrimentally impact the binding with the  
86 CNCs. To the best of our knowledge, none of these strategies have been applied to cellulose  
87 nanocrystals; yet this approach could limit CNCs degradation in ATRP reactions, while at the  
88 same time providing additional properties related to the PDA surface layer. There is also a lack  
89 of fundamental knowledge concerning the protocols mentioned in the literature, which are  
90 mostly implemented as a tool to reach other objectives.

91 In this work, we investigated the possibility of using PDA chemistry to introduce brominated  
92 sites at the CNC surface, and initiate SI-ATRP reactions from these sites. The two  
93 functionalization strategies (Protocols 1 & 2) were compared, using different characterization  
94 techniques such as X-ray Photoelectron spectroscopy (XPS), X-ray diffraction analysis (XRD),  
95 Fourier transform infrared spectroscopy (FT-IR) and solid state <sup>13</sup>C CP-MAS NMR  
96 spectroscopy. The brominated particles displaying the best performances were subsequently  
97 tested as potential ATRP macroinitiators, using methyl methacrylate (MMA) and styrene (St)  
98 as model monomers. The polymer-grafted CNCs obtained were then examined by FT-IR  
99 spectroscopy, <sup>13</sup>C CP-MAS NMR spectroscopy, thermogravimetric analysis (TGA) and

100 derivative thermogravimetry (DTG), while the polymerization kinetics were investigated by  
101 liquid  $^1\text{H}$  NMR and size-exclusion chromatography (SEC).

## 102 **2. Experimental section**

### 103 *2.1. Materials*

104 Cellulose nanocrystals (CNCs) were provided by the University of Maine (US). They were  
105 produced by acid hydrolysis of wood pulp with sulfuric acid, and are composed of rod-shape  
106 particles of  $110 \pm 48$  nm in length and  $4.8 \pm 1.1$  nm in thickness, as determined by atomic force  
107 microscopy in a previous study (Brand, Pecastaings, & Sèbe, 2017). The particles are decorated  
108 with negative sulfate half-ester groups at their surface, resulting from the sulfuric acid treatment.  
109 The amount of accessible hydroxyl groups at the surface was estimated at  $3.1 \pm 0.1$  mmol.g $^{-1}$   
110 in the same study.  $\alpha$ -bromoisobutryl bromide (BiBB, >98%), 3-hydroxytyramine  
111 hydrochloride (DA, >98%), tris(hydroxymethyl)aminomethane (Tris, >99%), copper(I)  
112 bromide (CuBr, >98%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, >99%)  
113 were purchased from TCI Europe. Triethylamine (TEA, 99%), methyl methacrylate (MMA,  
114 99%) were purchased from Alfa Aesar 99%. Ethyl  $\alpha$ -bromoisobutyrate (EBib, 98%) and styrene  
115 (St, 99%) purchased from Sigma Aldrich.

### 116 *2.2. Immobilization of the brominated sites.*

117 Protocol 1: the CNC-PDA<sub>P1</sub>-Br<sub>x</sub> samples (P1 = protocol 1; x = Br atomic % determined by  
118 XPS) were prepared by, first coating PDA on the CNCs, then reacting the CNC-PDA material  
119 with BIBB, taking inspiration from previous work (Song et al., 2016). In detail, 0.5 g of CNCs  
120 were dispersed in 20 mL water through 1 min sonication (Bandelin, MS72 probe). 0.6 g of DA  
121 and 70 mL of water were then added to this suspension, which was adjusted to pH = 8.5 with  
122 0.6 g of Tris. The mixture was stirred at room temperature for 24 h. The particles were recovered  
123 by centrifugation, washed three times with water/centrifugation cycles, then freeze-dried. The  
124 esterification reaction was performed in DMF, under nitrogen, in the presence of equal volumes

125 of TEA and BiBB. Before reaction, the CNC-PDA material was dispersed in 30 mL DMF  
126 (through 1 min sonication), while BiBB (1, 2, or 4 mL) was solubilized in 10 mL DMF. After  
127 solubilization of TEA in the CNC-PDA suspension, an ice bath was added and the BiBB  
128 solution was introduced dropwise. After 30 min, the ice bath was removed, and the reaction  
129 was conducted for 24 h. The particles were recovered by centrifugation, then  
130 washed/centrifugated with i) ethanol, ii) water (until the supernatant was colorless), and finally  
131 freeze-dried. To further probe the stability of the grafting towards the solvents used in the ATRP  
132 experiments, additional washing/centrifugation steps were later performed with i) DMF and ii)  
133 THF, followed by a dialysis in water for 3 days using a 3.5 kDa regenerated cellulose ester  
134 dialysis membrane.

135 Protocol 2: the CNC-PDA<sub>P2</sub>-Br<sub>x</sub> samples (P2 = protocol 2; x = Br atomic % determined by  
136 XPS) were prepared by co-polymerizing a mixture of DA and BiBB-modified DA on the CNCs  
137 surface, taking inspiration from previous work (Kohri et al., 2013). The BiBB-modified DA  
138 was first prepared by reacting DA with BiBB in DMF, under nitrogen, with equal volume  
139 amounts of TEA as catalyst (0.9 molar equivalents). 0.6 g of DA were solubilized in 5 mL DMF  
140 with TEA, then various amounts of BiBB (1, 2, or 4 mL) were added and stirred for 3h at room  
141 temperature. The reaction with the CNCs was performed in the same flask, in a second step.  
142 The CNCs suspension (0.5 g of CNCs in 20 mL water) was added to the previous mixture with  
143 70 mL of additional water, and the pH was adjusted to 8.5 with Tris. The direct reaction between  
144 the CNCs and unreacted BiBB cannot be totally excluded at this stage, but the hydrolysis of  
145 BiBB should be largely favored. The oxidative polymerization was allowed to proceed for 24  
146 h at room temperature, then the particles were centrifugated/washed with ethanol/water then  
147 DMF/THF as described before (Protocol 1).

### 148 2.3. *SI-ATRP grafting of PMMA and PS.*

149 The CNC-PDA<sub>P1</sub>-Br<sub>1.44</sub> sample was used as macroinitiator to initiate the SI-ATRP

150 polymerizations. Reactions were conducted in DMF, with methyl methacrylate (MMA) and  
151 styrene (St) as model monomers, Cu(I)Br as catalyst, pentamethyldiethylenetriamine  
152 (PMDETA) as ligand and ethyl  $\alpha$ -bromoisobutyrate (EiBB) as sacrificial initiator. Reactions  
153 with MMA were performed at 60°C, with a molar ratio of  
154 [MMA]:[EBib]:[CuBr]:[PMDETA]=300:1:1:1. Reactions with St were performed at 100°C,  
155 with a molar ratio of [St]:[EBib]:[CuBr]:[PMDETA]=500:1:1:1. In detail, 50 mg of CNC-  
156 PDA<sub>P1</sub>-Br<sub>1.44</sub> particles were dispersed in 11.6 mL DMF through sonication. 150 mmol MMA  
157 (15 mL) or 250 mmol St (28 mL), 0.5 mmol EBiB (70  $\mu$ L) and 0.5 mmol PMDETA (105  $\mu$ L)  
158 were added to the mixture. The dispersion was bubbled with argon for 30 min. And then 0.5  
159 mmol CuBr (70 mg, weighted in a glove box), was added to the mixture. After degassing by  
160 three freeze-pump-thaw cycles under argon, the reaction flask was immersed in an oil bath at  
161 the required temperature. Different operations were performed at designed polymerization time  
162 (20 min, 40 min, 60 min, 90 min, 120 min & 180 min): i) 40  $\mu$ L of the reaction medium was  
163 withdrew and added in 460  $\mu$ L CDCl<sub>3</sub> for <sup>1</sup>H NMR characterization (evaluation of the monomer  
164 conversion); ii) 1 mL of the reaction medium was withdrawn, centrifugated, passed through a  
165 neutral Al<sub>2</sub>O<sub>3</sub> column with THF as solvent (to remove copper and retain any dispersed CNC  
166 particles), then poured into methanol to precipitate the free polymer for SEC analysis. At the  
167 end of the SI-ATRP reaction (90 min for MMA, 7h for St), the whole reaction mixture was  
168 centrifuged several times with i) THF and ii) ethanol (until the supernatant was colorless), and  
169 the sedimented particles were dried under vacuum at 50 °C before FT-IR and CP-MAS <sup>13</sup>C  
170 NMR characterization. The supernatant from the final centrifugation was collected and  
171 characterized by <sup>1</sup>H NMR to confirm that no free macromolecules were left.

172 2.4. *Fourier-Transform Infrared spectroscopy (FT-IR).*

173 FT-IR spectra were recorded in the 4000-450  $\text{cm}^{-1}$  range, using a Bruker Vertex 70  
174 spectrometer, at a resolution of 4  $\text{cm}^{-1}$  (64 scans). Sampling was performed with the potassium  
175 bromide method. For ease of comparison, the spectra were normalized to the C-O stretching  
176 vibration of cellulose at 1060  $\text{cm}^{-1}$ .

177 2.5. *X-ray photoelectron spectrometry (XPS)*

178 A ThermoFisher Scientific K-ALPHA spectrometer was used for XPS surface analysis, with  
179 a monochromatized Al-K $\alpha$  source ( $h\nu = 1486.6$  eV) and a 400  $\mu\text{m}$  X-Ray spot size. Powders  
180 were pressed onto indium foils. The full survey spectra (0-1100 eV) were obtained with a  
181 constant pass energy of 200 eV.

182 2.6. *Nuclear Magnetic Resonance spectroscopy (NMR)*

183 CP-MAS  $^{13}\text{C}$  NMR analysis of the CNC-PDA, CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub> and PMMA@CNC-  
184 PDA<sub>p1</sub>-Br<sub>1.44</sub> samples was performed by the CESAMO platform of the Institute of Molecular  
185 Sciences (ISM, Talence, France). Measurements were done at 25 °C, with a Bruker Avance II  
186 400 spectrometer operating at a frequency of 100.63 MHz (conventional CP-MAS method).  
187 The zirconium oxide rotors containing the samples were spun at 8 kHz, while the 90° pulse,  
188 contact time, and repetition time were set at 2.8  $\mu\text{s}$ , 2.0 ms, and 4 s, respectively. The PS@CNC-  
189 PDA<sub>p1</sub>-Br<sub>1.44</sub> sample was analysed by the Institut Européen de Chimie et Biologie (IECB,  
190 Pessac, France), using a Bruker Avance III spectrometer (Wissembourg, France) operating at  
191 125MHz, with a 4 mm double resonance HX-CPMAS probe. The sample packed in a 4 mm  
192 zirconium rotor (Cortecnet, Voisin Le Bretonneux) was spun at 11kHz, with the following  
193 acquisition parameters: 5 s recycling delay, 2k scans, 1 ms or 4 ms for contact time (temperature  
194 during acquisition  $\approx 35^\circ\text{C}$ ).  $^{13}\text{C}$  chemical shifts are reported relative to the carbonyl of glycine  
195 (external reference) at 173.6 ppm, and spectra are phased and baseline-corrected.

196 The monomer conversion during SI-ATRP reaction was evaluated by liquid  $^1\text{H}$  Nuclear

197 Magnetic Resonance (NMR), using a Bruker Avance 400 (<sup>1</sup>H at 400 MHz) spectrometer, with  
198 deuterated chloroform (CDCl<sub>3</sub>) as solvent.

### 199 2.7. *X-Ray Diffraction spectroscopy (XRD)*

200 XRD analyses were performed by the Centre de Recherche Paul Pascal (CRPP, Pessac,  
201 France). Measurements were conducted on a Rigaku Nanoviewer (XRF microsource generator,  
202 MicroMax 007HF), with a rotating anode coupled to a confocal Max-Flux® Osmic mirror  
203 (Applied Rigaku Technologies, Austin, USA) producing beam with a wavelength of 1,5418Å  
204 or an energy of 8KeV. The sample was put in a glass capillary and exposed to the X-Ray beam  
205 for 90min. Data were collected on a MAR345 image plate detector (MARResearch, Norderstedt,  
206 Germany) placed at a distance of 129 mm, providing access to 2Theta angle in the 5-40° range.  
207 Images were collected and spectra integrated with the FIT2D software (ERSF;  
208 <http://www.esrf.eu/>).

209 The crystallinity Index (CrI) was estimated from the diffractograms by the Segal method (Segal,  
210 Creely, Martin, & Conrad, 1959):

$$211 \quad CrI = \frac{I_{22.6^\circ} - I_{18.3^\circ}}{I_{22.6^\circ}} \quad (2-1)$$

212 where  $I_{22.6^\circ}$  represents the intensity of the (200) crystallographic plane of cellulose  $I_\beta$  and  $I_{18.3^\circ}$   
213 the intensity of the amorphous contribution. The average dimensions of the elementary  
214 crystallites perpendicular to the (200) plan ( $L_{200}$ ) were estimated from Scherrer's equation:

$$215 \quad L_{200} = \frac{0.9\lambda}{\beta \cos\theta} \quad (2-2)$$

216 where  $\theta$  is the diffraction angle,  $\lambda$  is the wavelength of the X-ray radiation, and  $\beta$  is the full  
217 width at half height of the diffraction peak.

### 218 2.8. *Size-Exclusion Chromatography (SEC)*

219 The molecular weight of the free polymers produced during SI-ATRP was measured by Size-  
220 exclusion chromatography (SEC), with tetrahydrofuran (THF) as the eluent. Samples were  
221 analyzed after vacuum drying and dispersion in THF (5g/L), using an Ultimate 3000 system

222 (Thermoscientific) equipped with a diode array detector, a multi-angles light scattering detector  
223 and differential refractive index detector (Wyatt technology). Polymers were separated on three  
224 G2000, G3000 and G4000 TOSOH HXL gel columns (300 x 7.8 mm) (exclusion limits from  
225 200 Da to 400 000 Da) with a flowrate of 1 mL/min at 40°C. The elution times were converted  
226 to molar mass using a calibration curve based on PS or PMMA standards.

### 227 2.9. Thermogravimetric analysis (TGA)

228 TGA experiments were conducted on a TGA Q500 instrument. Samples (8-10 mg) were  
229 heated up to 600°C, at a rate of 10 °C.min<sup>-1</sup> and under nitrogen atmosphere (flow rate:  
230 40 mL.min<sup>-1</sup> for balance, 60 for furnace). The weight loss was recorded as a function of  
231 temperature, and the temperature of maximum degradation was obtained from the maximum of  
232 the derivative curve. The grafting density after ATRP reaction was estimated from the  
233 thermograms of the PMMA@CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub> and PS@CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub> samples, by  
234 calculating the ratio of second weight loss due to the polymer (between 330 and 450 °C) relative  
235 to the first weight loss due to CNC-PDA degradation (between 120 and 330 °C). Ratios of 1.3  
236 and 1.1 were measured with PMMA and PS, respectively. These ratio were later converted in  
237 mmol of grafted polymer *per* gram of CNC-PDA material using the M<sub>n</sub>'s of free PMMA (22650  
238 g.mmol<sup>-1</sup>) and PS (5928 g.mmol<sup>-1</sup>) determined by SEC: grafting density with PMMA =  
239 1.3/22.650 = 0.057 mmol/g; grafting density with PS = 1.1/5.928 = 0.186 mmol.g<sup>-1</sup>. To improve  
240 the accuracy in the case of PMMA, the grafting density was re-calculated taking into account  
241 the 10 % weight loss that PMMA undergoes in the 150-330 temperature range: corrected second  
242 weight loss = (1.3x100)/90 = 1.44 g; corrected first weight loss = 1-(1.44-1.3) = 0.86 g;  
243 corrected grafting density = (1.44/0.86)/22.650 = 0.074 mmol.g<sup>-1</sup>.

### 244 2.10. Atomic Force Microscopy (AFM)

245 The morphology of the polymer-grafted samples was assessed by AFM, in tapping mode.  
246 Samples were dispersed in water (0.2 g.L<sup>-1</sup>) by sonicating the mixture for 2 min (Bandelin,

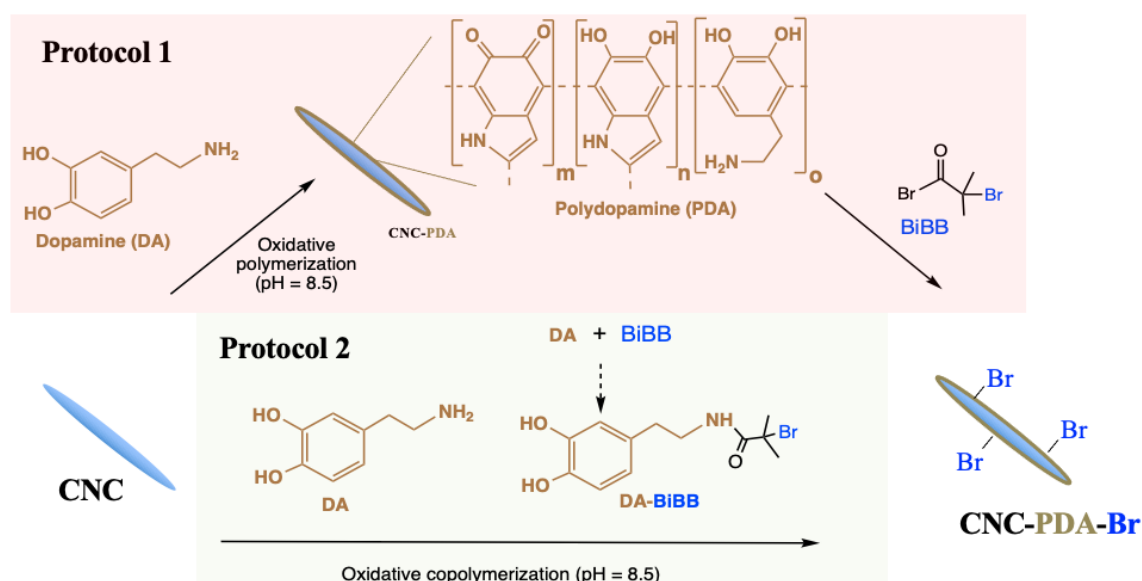
247 MS72 probe). One droplet of the dispersion was then deposited on a freshly cleaved mica  
248 surface priorly treated by a 10 mM MgCl<sub>2</sub> aqueous solution. After overnight air-drying, the  
249 samples were observed with a Dimension Fastscan AFM (Bruker) microscope in tapping mode  
250 (at 22°C), using a FastScan-A probe. The nominal spring constant was set to 18 N.m<sup>-1</sup> and the  
251 resonance frequency to 1.400 Hz. Height and phase images were obtained using a scan rate of  
252 3.8 Hz, and analyzed by the NanoScope Analysis software.

253

### 254 **3. Results and Discussion**

#### 255 *3.1. Immobilization of the brominated sites through PDA coating*

256 Two different strategies were investigated to introduce the brominated initiating sites at the  
257 surface of the CNCs (Fig. 1). With Protocol 1, the CNCs were reacted with DA and BiBB in a  
258 stepwise manner, while with Protocol 2, the CNC surface was modified in one step, by co-  
259 polymerizing a mixture of DA and BiBB-modified DA. After reaction, samples were  
260 extensively washed with ethanol and water, to remove any unreacted product and traces of  
261 triethylamine (Zeng et al., 2017; Zhu & Edmondson, 2011). The two protocols were compared  
262 in term of Br grafting achieved when an equal amount of BiBB was used in each process, the  
263 Br content being measured by XPS.



265

266 **Fig. 1.** Immobilization of the brominated initiating sites by polydopamine chemistry; two  
 267 different protocols were investigated (Protocol 1 & 2).

268

269 The reaction conditions and bromine content obtained after reaction with increasing amounts  
 270 BiBB are summarized in Table 1. The crystallinity index (CrI) and average dimensions of the  
 271 elementary crystallites perpendicular to the (200) plan ( $L_{200}$ ), measured for the particles treated  
 272 with Protocol 1, are also reported. The corresponding XPS survey spectra with the relative  
 273 elemental composition at the nanoparticles surface are presented in Fig. S1 & S2 and Tables S1  
 274 & S2 in Supporting Information. With protocol 1, the amount of Br sites immobilized at the  
 275 CNCs surface could be easily controlled by adjusting the BiBB volume, the reaction with the  
 276 PDA-modified CNCs being increasingly favored when more BiBB was used; but quite a large  
 277 excess of BiBB was required to achieve high bromine content. Higher grafting levels could be  
 278 obtained with Protocol 2, using lower amounts of BiBB, but this process required an  
 279 optimization of the BiBB amount (at about 2 mL), as the efficiency decreased when the BiBB  
 280 was too high (*i.e.* 4 mL). With this second protocol, the Br immobilization is achieved by first  
 281 partially functionalizing some of the DA molecules with BiBB, then co-reacting this DA-BiBB

282 precursor with pristine DA by reductive oxidation, in the presence of the CNCs. Since  
 283 hydroxyl/amine groups are required for both the coupling between DA-BiBB and DA, and the  
 284 binding with the CNC surface, a decreased efficiency is expected when the DA-BiBB monomer  
 285 is excessively substituted by the bromoisobutyryl moieties (*i.e.* when 4 mL of BiBB is used in  
 286 our case). The concentration of unmodified DA remaining in the medium may be also too low  
 287 when an excessive concentration of BiBB is used.

288

289 **Table 1.** Br content measured by XPS after modification with Protocol 1 or 2 and extensive  
 290 washing with ethanol and water.

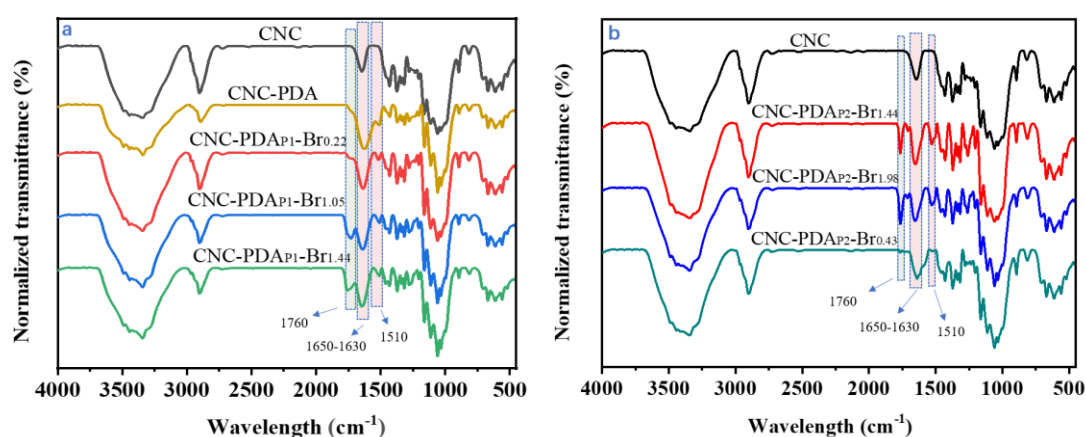
Reaction conditions				Protocol 1			Protocol 2		
CNCs (3.1 mmol OH/g)*	DA	BiBB		Samples	Br content (Atom. %)	CrI (%)	L <sub>200</sub> (nm)	Samples	Br content (Atom. %)
		Volume (mL)	Molar Content (mmol)						
0.5 g (1.55 mmol OH)	0.6 g (3.18 mmol)	1	8.1	CNC-PDA <sub>P1</sub> -Br <sub>0.22</sub>	0.22	85	4.3	CNC-PDA <sub>P2</sub> -Br <sub>1.44</sub>	1.44
		2	16.2	CNC-PDA <sub>P1</sub> -Br <sub>1.05</sub>	1.05	71	4.0	CNC-PDA <sub>P2</sub> -Br <sub>1.98</sub>	1.98
		4	32.4	CNC-PDA <sub>P1</sub> -Br <sub>1.44</sub>	1.44	70	4.0	CNC-PDA <sub>P2</sub> -Br <sub>0.43</sub>	0.43

291 CNCs: CrI = 86 %; L<sub>200</sub> = 4.4 nm; \*Brand, Pecastaings, & Sèbe, 2017

292

293 The grafting was further confirmed through the observation of the characteristic vibrations  
 294 of the bromoisobutyryl moieties in the infrared spectra (Fig. 2). The emerging bands observed  
 295 in the spectra of Fig. 2a and 2b indicate that the bromoisobutyryl moieties were grafted at both  
 296 the phenolic ( $\nu_{C=O}$  at 1760  $\text{cm}^{-1}$ ) and amine sites ( $\nu_{C=O}$  at 1650-1630  $\text{cm}^{-1}$ ,  $\delta_{N-H}$  at 1510  $\text{cm}^{-1}$ ) of  
 297 PDA, regardless of the protocol. To make sure that the grafting was resistant to the solvents  
 298 used in the subsequent ATRP treatment, the brominated samples were further washed  
 299 successively by DMF and THF (under sonication), and analyzed again by FT-IR spectroscopy  
 300 (Fig. S3 in Supporting Information). No modification of the infrared pattern was noted with  
 301 Protocol 1 (Fig. S3a), but the bromoisobutyryl signals of the protocol 2 samples disappeared  
 302 (Fig. S3b), indicating that the PDA coating was not strongly bonded in that case. Less

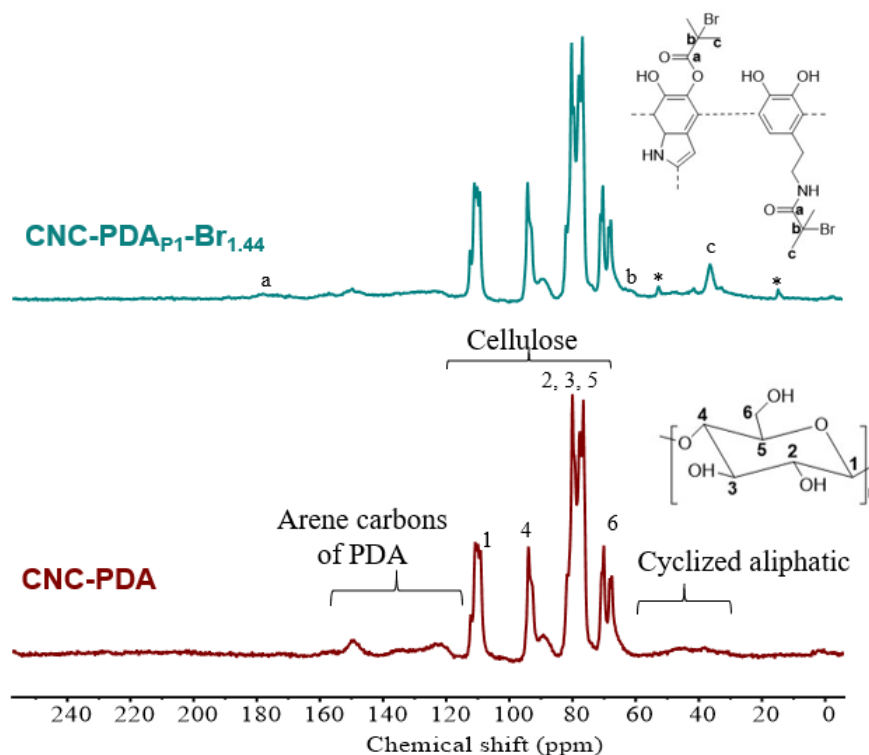
303 hydroxyl/amine groups are available for the bonding with the CNCs surface with Protocol 2, as  
304 part of these sites are already substituted by BiBB before the oxidative reaction. It is therefore  
305 likely that the amount of free hydroxyl/amine groups is not sufficient to guarantee an efficient  
306 anchoring at the CNCs surface, the PDA layer being solubilized by DMF and/or THF. In view  
307 of these results, only the particles modified with Protocol 1 were used in subsequent  
308 experiments.



309  
310 **Fig. 2.** FT-IR spectra of the brominated CNCs obtained from Protocol 1 (a) and Protocol 2 (b),  
311 after washing with ethanol and water.

312  
313 Further confirmation of the bromoisobutyryl grafting was provided by solid state  $^{13}\text{C}$  CP-  
314 MAS NMR analysis, as shown in Fig. 3. To help in the assignment, the spectrum of the CNCs  
315 modified with pure PDA (CNC-PDA) is also reported. The signals of cellulose are observed at  
316 110 ppm ( $\text{C}_1$ ), 95 ppm ( $\text{C}_4$  crystalline), 89 ppm ( $\text{C}_4$  amorphous), 76-80 ppm ( $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_5$ ), 69  
317 ppm ( $\text{C}_6$  crystalline), 67 ppm ( $\text{C}_6$  amorphous) (Atalla, Gast, Sindorf, Bartuska, & Maciel, 1980),  
318 while the PDA pattern can be seen in the 115-150 ppm (arene carbons) and 30-60 ppm (cyclized  
319 aliphatic carbons) regions (Dreyer, Miller, Freeman, Paul, & Bielawski, 2012). After reaction  
320 with BiBB, the bromoisobutyryl signals emerge at 178 ppm ( $\text{C}=\text{O}$ ), 60 ppm ( $\text{C}-\text{Br}$ ) and 37 ppm  
321 ( $\text{CH}_3$ ).

322



323

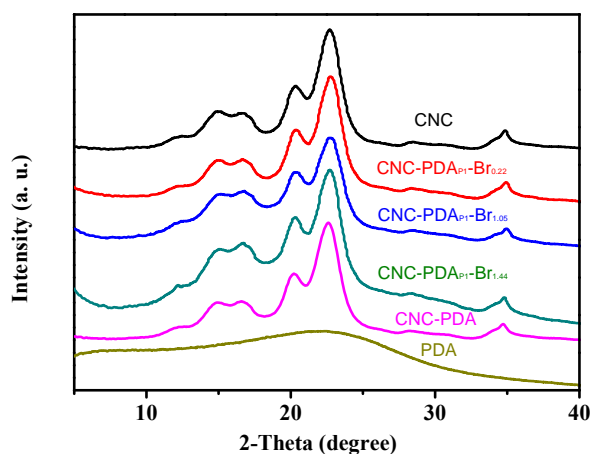
324

325 **Fig. 3.**  $^{13}\text{C}$  CP-MAS NMR spectrum of the  $\text{CNC-PDA}_{\text{P1-Br}_{1.44}}$  sample obtained from Protocol  
 326 1 (the peaks identified by an asterisk\* are assigned to traces of triethylamine). The spectrum of  
 327 the CNCs modified with pure PDA ( $\text{CNC-PDA}$ ) is also reported.

328

329 The impact of the Protocol 1 treatment on the CNCs crystalline structure was assessed by  
 330 X-ray diffraction analysis (XRD) (Fig. 4), through the calculation of i) the crystallinity index  
 331 (CrI) measured by the Segal method (Segal et al., 1959), and ii) the average dimension of the  
 332 elementary crystallites perpendicular to the (200) plan ( $L_{200}$ ) estimated from Scherrer's  
 333 equation (Sebe, Ham-Pichavant, Ibarboure, Koffi, & Tingaut, 2012). In Fig. 4, the characteristic  
 334 diffraction peaks of the cellulose I pattern can be seen at  $2\theta = 15, 17, 20, 22.3$  and  $34.5^\circ$ ,  
 335 corresponding to the  $(1\bar{1}0)$ , (110), (012), (200) and (004) diffraction planes, respectively, while  
 336 pure PDA is amorphous. The peak at  $2\theta = 12^\circ$  was assigned to traces of cellulose II. A slight  
 337 decrease in CrI and  $L_{200}$  was noted after the successive reactions with DA and BiBB, but the

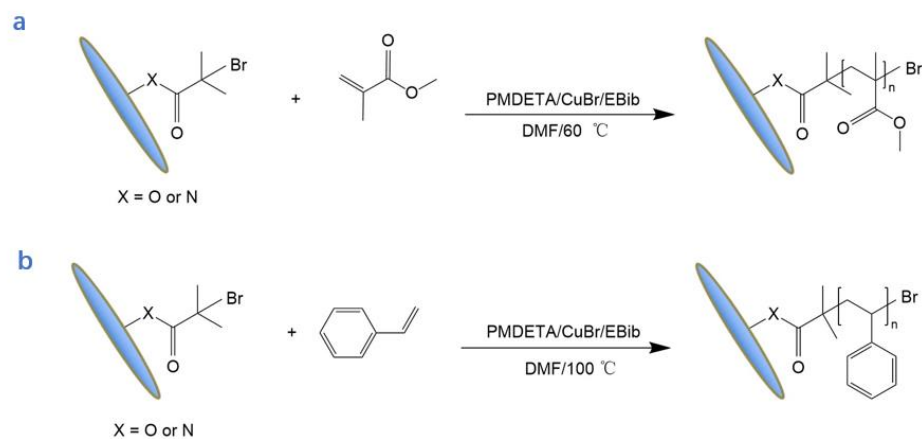
338 particles remained highly crystalline, indicating that the Protocol 1 treatment did not  
339 significantly impact the nanoparticles' structure. The slight decrease in crystallinity can be  
340 partly assigned to the amorphous fraction brought by the PDA layer. When the CNC surface  
341 was directly esterified with the classical method (without PDA), a significant decrease in  
342 crystallinity was noted when 2 and 4 mL of BiBB were used (Fig. S4), confirming the interest  
343 of Protocol 1 to preserve the nanoparticles structure.



344  
345 **Fig. 4.** XRD spectra of the brominated CNCs obtained with Protocol 1. The spectra of pristine  
346 CNCs and CNCs modified with pure PDA (CNC-PDA) are also reported.  
347

348 3.2. SI-ATRP grafting of PMMA and PS

349 ATRP experiments were performed with methyl methacrylate (MMA) and styrene (Sty) as  
350 model monomers, in a standard set of conditions inspired from the literature (Chun-xiang, Huai-  
351 yu, Ming-hua, Shi-yu, & Jia-jun, 2009; Z. Zhang, Wang, Tam, & Sebe, 2019). The CNC-PDA<sub>P1</sub>-  
352 Br<sub>1.44</sub> sample, with the highest bromine content, was used as initiating substrate. Reactions were  
353 conducted in DMF, with MMA and Sty as model monomers, Cu(I)Br as catalyst,  
354 pentamethyldiethylenetriamine (PMDETA) as ligand and ethyl  $\alpha$ -bromoisobutyrate (EiBB) as  
355 sacrificial initiator (Fig. 5).



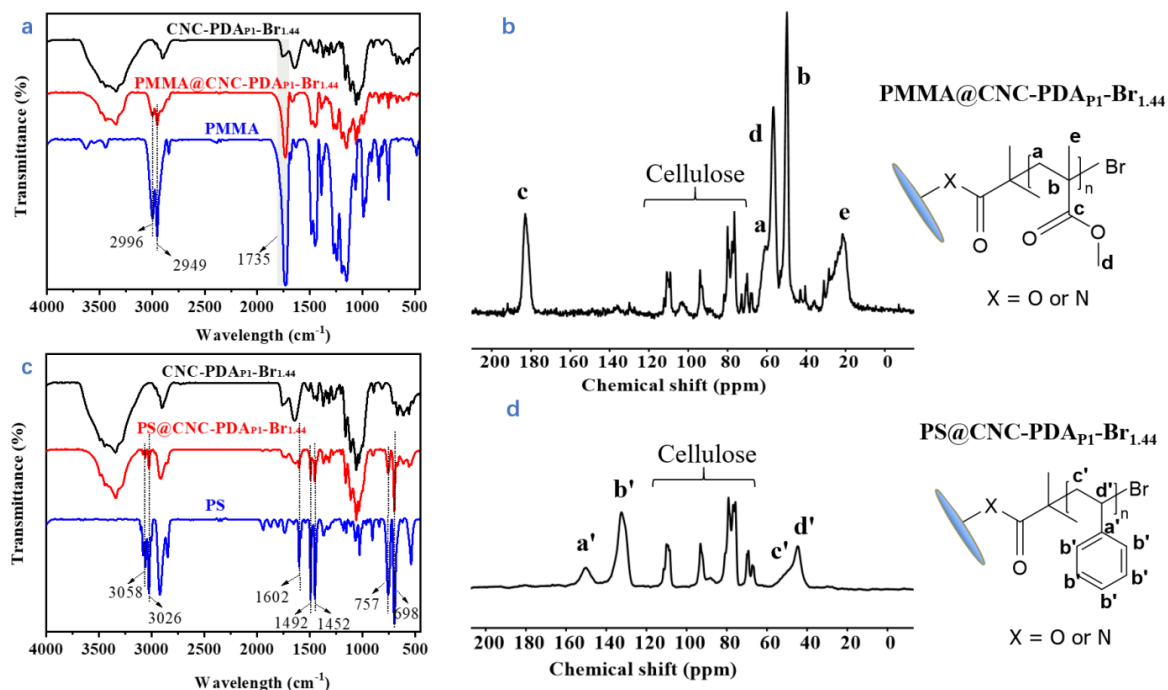
356

357 **Fig. 5.** SI-ATRP grafting of MMA (a) and Sty (b) from the CNC-PDA<sub>P1</sub>-Br<sub>1.44</sub> sample.

358

359 The successful grafting of PMMA and PS was first confirmed by FT-IR spectroscopy (Fig.  
360 6a and 6c). The infrared vibrations of grafted PMMA are observed at 2996/2949 cm<sup>-1</sup> ( $\nu_{C-H}$ )  
361 and 1735cm<sup>-1</sup> ( $\nu_{C=O}$ ), while those of PS emerge at 3058/3026 cm<sup>-1</sup> ( $\nu_{CH\text{ aromatic}}$ ), 1602/1492/1452  
362 cm<sup>-1</sup> ( $\nu_{C=C}$ ), 698/757 cm<sup>-1</sup> ( $\gamma_{C-H}$ ). Further confirmation of the grafting was provided by the solid  
363 state <sup>13</sup>C CP-MAS NMR spectra, through the observation of the characteristic signals of PMMA  
364 at 183 ppm (c), 61 ppm (a), 57 ppm (d), 50 ppm (b) and 22 ppm (e) (Fig. 6b), and of PS at 150  
365 ppm (a'), 132 ppm (b'), 46-54 ppm (c'), 44 ppm (d') (Fig.6d). The AFM analysis of the  
366 polymer-grafted samples indicated that the rod-like morphology of the nanocrystals was

367 retained (Fig. S5), but an accurate estimation of the dimensions could not be inferred from the  
 368 pictures as the particles significantly aggregated during deposition on the mica surface.  
 369



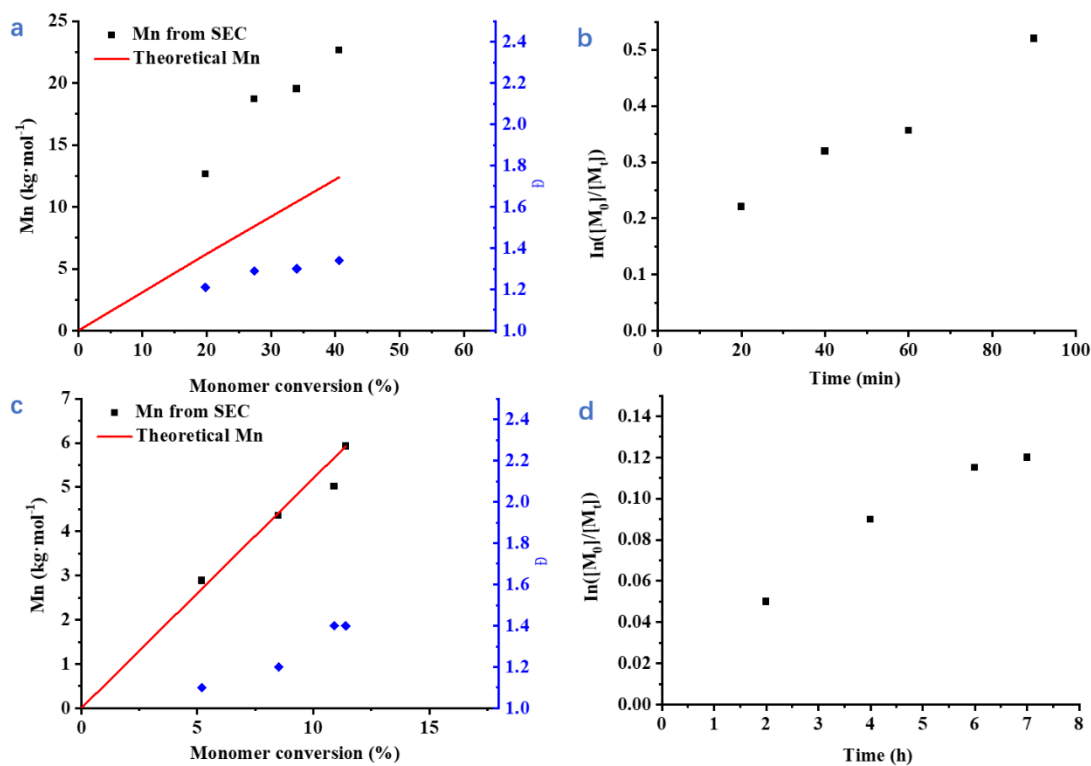
370  
 371 **Fig. 6.** FT-IR (a, c) and  $^{13}\text{C}$  CP-MAS NMR (b, d) spectra of the CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub> particles  
 372 before and after SI-ATRP grafting of MMA or Sty. The FT-IR spectra of the free polymers are  
 373 also reported.

374  
 375 The kinetics of the reactions were investigated by analyzing the free polymer produced by  
 376 the sacrificial initiator, assuming that the molecular weights of the grafted and free polymers  
 377 were similar (Fig. 7). With both monomers, the number-average molecular weight ( $M_n$ ) of the  
 378 PMMA and PS increased linearly with the monomer conversion and the dispersity ( $\mathcal{D}$ ) remained  
 379 relatively low (less than 1.3 for PMMA and 1.4 for PS). In the case of MMA, the  $M_n$  determined  
 380 by SEC was twice as high as expected (Fig. 7a), while the first-order kinetic plot of  $\ln([M_0]/[M_t])$   
 381 shows a positive intercept (Fig. 7b). Taken together, these elements suggest that a significant  
 382 amount of initial termination occurred with PMMA, leading to loss of approximately 50% of

383 the EiBB in the very early stages of the reaction, as the concentration of Cu(II)Br<sub>2</sub> built up to  
384 sufficient levels to control the reaction. These results are consistent with previous observations  
385 of low initiator efficiency of EiBB in ATRP polymerization of MMA (T. Zhang, Gieseler, &  
386 Jordan, 2016). After the first 20 minutes,  $\ln([M_0]/[M_t])$  increased linearly with time, indicating  
387 a first order reaction with a near constant concentration of radicals, as expected in ATRP  
388 reactions. In the case of Sty, good agreement between expected and  $M_n$  determined by SEC was  
389 observed (Fig. 7c), while the first-order kinetic plot showed some deviations from linearity,  
390 indicating a low level of ongoing termination reactions and gradual decrease in the radical  
391 concentration (Fig. 7d). The reactions proceeded at substantially different rates, reflecting the  
392 different reactivities of the chain ends towards activation and deactivation (Li, Wang, Li, & Zhu,  
393 2011): after 90 min of reaction, the MMA polymerization had reached *c.* 40% conversion and  
394 an  $M_n$  of 22650 g.mol<sup>-1</sup>, while that of Sty attained only *c.* 12% conversion and 5928 g.mol<sup>-1</sup>  
395 after 7 hours.

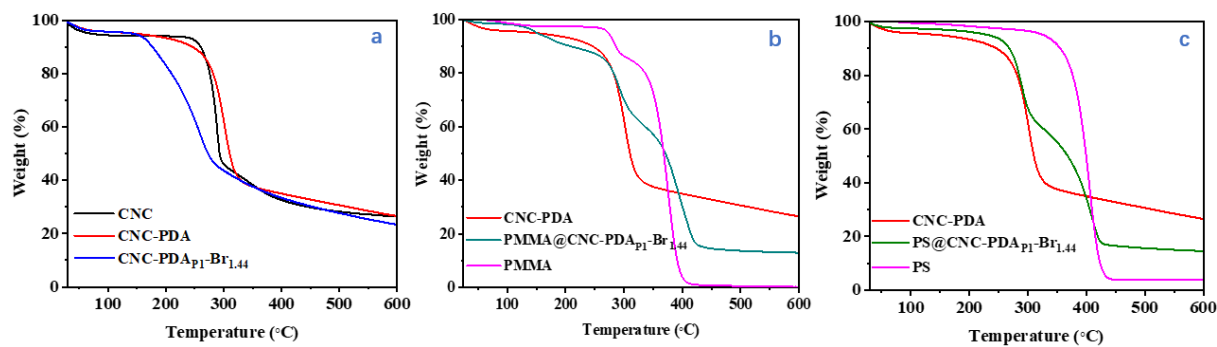
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398  
 399 **Fig. 7.** Kinetics of the ATRP reactions with MMA (a, b) and Sty (c, d): (a), (c)  $M_n$  and dispersity  
 400 ( $D$ ) vs. monomer conversion; (b), (d)  $\ln([M_0]/[M_t])$  vs. time.

401  
 402 The thermal stability of the polymer-grafted particles was investigated by thermogravimetric  
 403 analysis (TGA), the thermograms at each step of the treatments being gathered in Fig. 8, with  
 404 the data of the free polymers. The corresponding DTG curves are presented in Fig. S6.



411 **Fig. 8.** TGA thermograms of the different samples before (a) and after the ATRP reaction with

412 MMA (b) and Sty (c). The data obtained with the free polymers and CNC-PDA particles are  
413 also reported in b and c.

414

415 The thermogram of unmodified particles in Fig. 8a is characteristic of CNCs produced by  
416 sulfuric acid hydrolysis, with first, evaporation of water at 25-100 °C, then decomposition of  
417 cellulose with a temperature of maximum rate of degradation ( $T_{\max}$ ) of 287 °C. After the DA  
418 treatment (CNC-PDA), a slight increase in  $T_{\max}$  is noted (at 300 °C), indicating that the PDA  
419 layer retarded cellulose degradation to some extent. Further modification with BiBB (CNC-  
420 PDA<sub>p1</sub>-Br<sub>1.44</sub>) led to a significant decrease in the thermal stability of the cellulosic material  
421 (degradation started at 150 °C), which may be related to the strong hydrobromic acid released  
422 upon heating, due to the labile bromine (Wohlhauser, Rader, & Weder, 2022). After the PPMA  
423 or PS grafting on the other hand (PMMA@CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub> and PS@CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub>,  
424 respectively in Fig. 8b and 8c), the thermal stability is recovered, the cellulose chains being  
425 now protected by the grafted polymers, while the brominated moieties are no longer in close  
426 proximity to the nanocrystals (see Fig. 5). A two-step profile is now observed, corresponding  
427 to, first the degradation of cellulose coated with PDA (at  $T_{\max}$  = 289 °C for PMMA@CNC-  
428 PDA<sub>p1</sub>-Br<sub>1.44</sub> and 290 °C for PS@CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub>), followed by the degradation of grafted  
429 PMMA (at  $T_{\max}$  = 387-404 °C) or PS (at  $T_{\max}$  = 407 °C). The ratio of the second weight loss  
430 (polymer) relative to the first weight loss (CNC-PDA material) was then used to estimate the  
431 grafting density, expressed in mmol of grafted polymer *per* gram of CNC-PDA material, based  
432 on the  $M_n$ 's measured by SEC (see experimental section). The method is expected to be quite  
433 accurate for the PS-grafted particles, as the degradation of PS and CNC-PDA material do not  
434 overlap. An underestimation of the grafting density is however expected in the case of  
435 PMMA@CNC-PDA<sub>p1</sub>-Br<sub>1.44</sub>, as 10 % of the polymer degrades in the same temperature range  
436 as the CNC-PDA material (see thermogram of free PMMA in Fig. 8b). This weight loss,

437 observed under nitrogen, has been assigned in the literature to the decomposition of the PMMA  
438 end-chains (at about 290°C), while random scission (main degradation) takes place between  
439 300 and 400 °C (Hirata, Kashiwagi, & Brown, 1985; Meneghetti & Qutubuddin, 2006). Hence,  
440 to improve the accuracy of the grafting density estimation with PMMA, we re-calculated it  
441 taking into account this 10 % weight loss, which was added to the polymer loss and subtracted  
442 from the CNC-PDA loss (see experimental section). A grafting density of 0.074 mmol.g<sup>-1</sup> was  
443 found for PMMA, which was roughly half that observed for PS (0.186 mmol.g<sup>-1</sup>). The reduced  
444 grafting density of PMMA may be a result of the high level of termination observed in the early  
445 stages of the PMMA polymerization, which led to loss of approximately 50% of the EiBB, and  
446 may be assumed to have consumed a similar fraction of grafted initiator sites.

447

#### 448 **4. Conclusions**

449 We have developed a convenient method to immobilize SI-ATRP initiating sites at the  
450 surface of cellulose nanocrystals (CNCs), using polydopamine (PDA) as an intermediate layer.  
451 The stepwise modification of the CNCs with dopamine (DA) and  $\alpha$ -bromoisobutyryl bromide  
452 (BiBB) led to the strong anchoring of brominated sites, with limited impact on the CNCs  
453 structure. Weaker anchoring was observed when the CNCs were treated in one step, with a  
454 mixture of DA and BiBB-modified DA, presumably because this second approach produced  
455 fewer anchoring sites for the bonding with the CNCs. The coating produced in this case resisted  
456 solvent washing by ethanol and water, but not by DMF and THF. The best-performing  
457 brominated particles were subsequently tested as potential ATRP macroinitiators, using methyl  
458 methacrylate (MMA) and styrene (St) as model monomers. First order reactions with a near  
459 constant concentration of radicals were inferred from the analysis of free polymers produced  
460 by the sacrificial initiator, as expected in ATRP reactions. Reaction with Sty proceeded at  
461 substantially lower rate than with MMA, although the grafting density at the CNCs surface was

462 twice as high. These results illustrate the potential of PDA chemistry as a tool for tailoring the  
463 surface chemistry of CNCs by SI-ATRP, while limiting deterioration of the nanoparticles  
464 structure. The method may also provide functionality related to the specific properties of PDA  
465 (UV-absorption, paramagnetism, radical scavenging activity, electrical conductivity...), which  
466 will be investigated in future work.

467

#### 468 **Supplementary material**

469 Additional information includes i) the XPS survey spectra with elemental composition of the  
470 brominated CNCs, ii) the FT-IR spectra after DMF/THF washing of the brominated CNCs, iii)  
471 the XRD spectra of the brominated CNCs obtained by direct esterification with BiBB, iv) the  
472 AFM topography images of the samples after SI-ATRP grafting and v) the DTG curves of the  
473 samples after SI-ATRP grafting.

474

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480 Moléculaires (ISM, Talence, France) for the NMR experiments, and the PLACAMAT platform  
481 of the Institut de Chimie de la matière Condensée (ICMCB, Pessac, France) for the XPS.

482

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