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1     **Release-killing properties of a textile modified by a layer-by-layer**  
2             **coating based on two oppositely charged cyclodextrin**  
3                     **polyelectrolytes**

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39 **Abstract**

40

41 Infections represent a major medical concern and have severe impact on the public  
42 health economy. Antimicrobial coatings represent one major solution and are the subject of  
43 many investigations in academic and industrial research. Polyelectrolyte multilayers (PEMs)  
44 consist in the step-by-step deposition of polyanions and polycations films on surfaces. The  
45 wide range of disposable polyelectrolytes makes this approach among the most versatile  
46 methods as it allows to design surfaces that prevent bacterial adhesion, and kill bacteria by  
47 contact or by releasing antibacterial agents. The present work focused on the release-killing  
48 effect of an active PEM coating of a polyethylene terephthalate (PET) textile support. This  
49 activity was obtained thanks to the PEM film build up using cationic and anionic  
50 polyelectrolytes both based on cyclodextrins (PCD- and PCD+) that provided a reservoir  
51 property and prolonged release of triclosan (TCS). To this effect, a PET non-woven  
52 preliminarily modified with carboxylate groups by applying a thermofixation process was  
53 then treated by dip-coating, alternating soaking cycles in cationic PCD+ and in anionic PCD-  
54 solutions. Samples coated with such PEM film were then loaded with TCS whose release was  
55 assessed in dynamic mode in a phosphate buffered saline solution (PBS) at 37°C. In parallel,  
56 TCS/PCD+ and TCS/PCD- interactions were investigated by Nuclear Magnetic Resonance  
57 (NMR) and phase solubility study, and the biocide activity was assessed against *S. aureus* and  
58 *E. coli*. Finally, the present study has demonstrated that our PCD+/PCD- PEM system  
59 presented release-killing properties that supplement the contact-killing effect of this system  
60 that was reported in a previous paper.

61

62

63

64 **Keywords:**  $\beta$ -cyclodextrin polymers, polyelectrolytes multilayer (PEM), textile, drug  
65 delivery system, antibacterial textile.

## 66 1. Introduction

67 Infections represent a major medical concern and has severe impact on the public  
68 health economy. Antimicrobial coatings of medical devices and implants is one major  
69 solution and is the subject of many investigations in academic and industrial research.  
70 Polyelectrolyte multilayers (PEMs) introduced by Decher *et al.* in 1992 (Decher et al., 1992)  
71 consist in the step-by-step deposition of polyanions and polycations building layer-by layer  
72 (LbL) films on surfaces. The wide range of disposable polyelectrolytes makes this approach  
73 among the most versatile methods for the design of antibacterial surfaces as PEMs present the  
74 great advantages (i) to be applicable to a large variety of substrates (Boudou et al., 2010;  
75 Hammond, 2012), (ii) to be tunable in terms of chemical, physicochemical and mechanical  
76 properties (Phelps et al., 2011) and iii) to embed and release a wide range of antimicrobial  
77 compounds. Three general strategies are commonly used in the design of LbL antimicrobial  
78 films (Lichter et al., 2009; Lichter and Rubner, 2009; Séon et al., 2015). The first approach  
79 consists in the prevention of the bacterial adhesion through the adjustment of the surface  
80 hydrophobicity (Chen et al., 2010; Genzer and Efimenko, 2006), the surface charge (Zhu et  
81 al., 2015) or the surface stiffness (Lichter et al., 2008). The second approach is based on  
82 contact-killing surfaces obtained by the immobilization into the LbL film of polymers  
83 carrying cationic groups. Antimicrobial peptides, synthetic polymers carrying amine groups  
84 such as polyallylamine (Lichter and Rubner, 2009), quaternary ammonium salts such as  
85 poly(diallyldimethylammonium chloride) (Zhu et al., 2015), chitosan biopolymer (Wang et  
86 al., 2012) and its quaternary ammonium derivatives (Graisuwan et al., 2012) are the most  
87 commonly used solutions (Lichter et al., 2009; Zhu and Loh, 2015). The third approach  
88 consists in the release of antimicrobial agents compound toward the tissues directly in contact

89 with the implant or the device such as copper or silver salts or nanoparticles (Dai and  
90 Bruening, 2002), antibiotics especially cationic ones such as gentamicin (Chuang et al., 2008),  
91 antimicrobial peptides (Shukla et al., 2010), nitric oxide (Cai et al., 2011), antiseptic agents  
92 (Agarwal et al., 2012; Nguyen et al., 2007; Séon et al., 2015; Wang et al., 2014) (triclosan,  
93 chlorhexidine) have been especially studied. Concerning the two later strategies, it is worth to  
94 mention that the antibacterial effect of contact killing surfaces often lasts longer than release  
95 based coatings since the LbL film degradation is in general slower than the release  
96 phenomenon.

97 Recently, our group successfully developed contact-killing PEMs films based on the one  
98 hand on cationic  $\beta$ -cyclodextrin polymers crosslinked with epichlorohydrin in the presence of  
99 glycidyl trimethylammonium chloride (PCD+), and on the other hand on an anionic  $\beta$ -  
100 cyclodextrin polymer crosslinked with citric acid (polyCTR-CD = PCD-). Such LbL system  
101 was built onto a nonwoven PET textile whose surface was preliminarily modified with  
102 carboxylic acid groups in order to provide the requested anionic character to the support  
103 (Junthip et al., 2015). Thanks to their high glycidyl trimethylammonium chloride content,  
104 such LbL systems presented a relevant intrinsic bacterial reduction up to 7.3 log against *S.*  
105 *aureus* and 4.5 log against *E. coli* (Junthip et al., 2016).

106 In the present work, the contact-killing PCD+/PCD- LbL system described above was  
107 loaded with triclosan (TCS), a broad-spectrum antimicrobial agent (Jones et al., 2000;  
108 Yazdankhah et al., 2006) commonly used in personal care products (Cheng et al., 2011) that  
109 conveniently exhibits a high host-guest complexation affinity with cyclodextrins (Duan et al.,  
110 2005; Loftsson et al., 1999; Lu et al., 2001). Thereby, a dual antimicrobial action system was  
111 expected, combining the contact-killing effect provided by the trimethylammonium groups of  
112 PCD+ on the one hand, and the release-killing effect obtained TCS release on the other hand  
113 (Figure 1). **To our knowledge, only a few dual release and contact killing LbL systems with**

114 multiple bactericidal components have been already described in the literature (Zhu and Loh,  
115 2015). Despite PEM integrating CDs have been particularly studied in drug delivery (Fagui et  
116 al., 2014; Leguen et al., 2007; Smith et al., 2009) and in biomaterials applications (Benkirane-  
117 Jessel et al., 2004; Chen et al., 2011; Martin et al., 2013a; Teo et al., 2015), the only existing  
118 work dealing with the concept of dual functionality was reported by Wong et al. who prepared  
119 a dual functional PEM coating including a poly(carboxymethylcyclodextrin) and N,N-  
120 dodecyl,methyl-polyethyleneimine that displayed both prolonged release of anti-inflammatory  
121 diclofenac and contact microbiocidal activity (Wong et al., 2010).

122 To achieve our objective, a nonwoven PET coated with an LbL film made of five  
123 PCD+/PCD- bilayers was prepared and characterized by Scanning Electron Microscopy  
124 (SEM). The release-killing effect was obtained by loading TCS on samples, whose release  
125 kinetics was performed in phosphate buffered saline (PBS) at 37°C in a dynamic system. TCS  
126 inclusion in CD cavities present in both PCD+ and PCD- were investigated by proton Nuclear  
127 Magnetic Resonance (NMR) and by phase solubility study. The antibacterial activities of the  
128 samples loaded with TCS dipped in PBS medium over a period of 28 days were assessed in  
129 parallel by diffusion test.

130

## 131 **2. Materials & Methods**

### 132 **2.1. Materials**

133  $\beta$ CD was a gift from Roquette (Kleptose®, Lestrem, France).  
134 Glycidyltrimethylammonium chloride (GTMAC), epichlorohydrin (EP), sodium dihydrogen  
135 hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ), sodium hydroxide (NaOH), citric acid (CTR), triclosan  
136 (TCS), phosphate buffered saline (PBS, for solution 0.15 M at pH=7.4) and potassium  
137 dihydrogen phosphate (for solution 50 mM at pH=6.5) were supplied from Sigma Aldrich  
138 (Saint-Quentin Fallavier, France).

139 The textile support was a polyethylene terephthalate non-woven (PET, thickness =  
140 0.24 mm, surface weight = 65 g/m<sup>2</sup>, reference NSN 365) donated by PGI-Nordlys (Bailleul,  
141 France).

142 Anionic water-soluble polymer of  $\beta$ -cyclodextrin (polyCTR-CD or PCD-) was  
143 prepared according to a method described by Martel et al. (Martel et al., 2005) by the  
144 solubilization of  $\beta$ -cyclodextrin, sodium hypophosphite as catalyst and citric acid as  
145 crosslinking agent in respective weight ratio 10g/ 3g/ 10g in 100 mL of water. After water  
146 removal by rotary evaporator, the resulting solid mixture was then cured at 140°C during 30  
147 min under vacuum. After water addition, the resulting suspension was filtered and the filtrate  
148 dialyzed during 72 hours against water using 6–8 kDa membranes (SPECTRAPOR 1,  
149 Spectrumlabs). Finally, the polyCTR-CD was recovered by freeze drying. Molecular masses  
150 in number (Mn) and in weight (Mw), measured by aqueous size exclusion chromatography  
151 (SEC) in water equipped with a light scattering detector, were 13.0 kg/mol and 22.6 kg/mol  
152 respectively (PDI = 1.7). The charge density of PolyCTR-CD (or COOH groups content) was  
153 4 mmol per gram (measured by acid-base titration). The weight composition determined by  
154 <sup>1</sup>H NMR was 50 wt.% in CD moieties and 50 wt.% in citrate cross-links.

155 Cationic water-soluble polymer of  $\beta$ -cyclodextrin (polyEPG-CD-10 or PCD+) was  
156 synthesized by reacting  $\beta$ CD with epichlorohydrin (EP) in the presence of  
157 glycidyltrimethylammonium chloride (GTMAC), with a molar ratio GTMAC/  $\beta$ CD = 10,  
158 under basic conditions as previously described (Junthip et al., 2015). Briefly 5g (4.4 mmol) of  
159  $\beta$ CD was dissolved in 8 mL of NaOH (22% (w/v)) aqueous solution and left under  
160 mechanical stirring overnight at room temperature. Then, 7.40 mL (44 mmol) of GTMAC  
161 (90%(w/v) in water) and 3.45 mL (44 mmol) of EP were rapidly added to solution heated to  
162 60°C during 3 hours before adding acetone. The aqueous phase was heated to 50°C overnight,  
163 neutralized with HCl (6 N), dialyzed (cut-off of 6–8 kDa, SPECTRAPOR 1, Spectrumlabs)

164 and finally freeze-dried before collecting polyEPG-CD samples as white powders. Mn and  
165 Mw, measured by aqueous size exclusion chromatography (SEC), were 16.1 kg/mol and 25.8  
166 kg/mol respectively (PDI = 1.6). The charge density (or trimethylammonium groups content)  
167 of polyEPG-CD-10 was 2 mmol/g of polymer (measured by colloidal titration). The weight  
168 composition determined by <sup>1</sup>H NMR, was 58 wt.% in CD moieties, 16wt.% in EP cross-links  
169 and 26 wt.% in GTMAC.

170

## 171 **2.2.Layer by Layer coating of the PET textile**

172 The virgin textile PET sample was preliminary functionalized by thermofixation using  
173 the *pad-dry-cure* process in order to obtain the negative charges provided by the resulting  
174 carboxylic groups strongly anchored on the surface (Martin et al., 2013a, 2013b). Virgin  
175 textiles (3 x 3cm<sup>2</sup>) were impregnated in 100 mL of solution containing β-cyclodextrin (10 g),  
176 sodium hypophosphite as catalyst (3 g) and citric acid as crosslinking agent (10 g). The textile  
177 was then roll-padded (BHVP model, Roaches, UK) and cured at 150°C in a ventilated oven  
178 (Minithermo, Roaches, UK). Samples were finally washed by soxhlet with water. This  
179 thermofixation treatment yielded samples provoked a 20wt.% weight gain of the samples  
180 (abbreviated PET20) measured with a precision balance ( $\pm 4 \cdot 10^{-4}$  g, Precisa 240A),  
181 corresponded to a surface density of 6.5 μmol COO<sup>-</sup>/cm<sup>2</sup> measured by using the calcium  
182 acetate titration method (Ducoroy et al., 2008).

183 The LbL build-up was carried out at room temperature by dipping process with both  
184 CD cationic and anionic polyelectrolytes solutions (4 g/L) in water at their natural pH, i.e 3.5  
185  $\pm 0.1$  (polyCTR-CD) and 6.5  $\pm 0.2$  (polyEPG-CD-10) (Junthip et al., 2015). The thermofixed  
186 PET20 samples were firstly dipped during 15 minutes in 50 mL of cationic polymer solution  
187 PCD+, drying at 90°C for 15 minutes, rinsing again with 50 mL of distilled water for 15  
188 minutes and drying at 90°C for 15 minutes. The similar sequence was then applied with the



189 anionic polymer solution PCD-. Both steps were repeated 4 times to obtain ten self-assembled  
190 layers, or five PCD+/PCD- bilayers onto the thermofixed PET supports (abbreviated PET20-  
191 PEM5) with a weight gain of  $75\% \pm 3\%$  (Junthip et al., 2016).

192 Finally, a thermal treatment of textiles was applied at  $140^{\circ}\text{C}$  in a ventilated oven  
193 (MEMMERT, DIN 40050- IP20) for 8 hours in order to improve the PEM film stability in  
194 contact with PBS medium.

195

### 196 **2.3. Triclosan adsorption**

197 The incorporation of TCS was performed by dipping the PET20 and PET20-PEM5  
198 samples into 15 mL of a saturated TCS solution during 24 hours under stirring 150 rpm at  
199  $37^{\circ}\text{C}$ . Then, samples were washed in 15 mL of distilled water during 5 minutes for three  
200 times before drying at  $45^{\circ}\text{C}$ .

### 201 **2.4. Scanning Electron Microscopy (SEM)**

202 Textile samples were characterized by SEM apparatus SEM instrument (Hitachi S-  
203 4700 SEM FEG (Field Emission Gun)), using an acceleration voltage of 5 kV. Textile  
204 samples were covered with a carbon layer before their analysis.

205

### 206 **2.5. Triclosan release study**

207 Drug release was measured with a fully automated flow-through cell dissolution  
208 apparatus (Sotax USP4, CE 7 Smart with CP7 piston pump, Switzerland) in a closed loop  
209 configuration combined with a UV-visible spectrometer (Perkin Elmer LAMBDA 25). Textile  
210 samples containing TCS (100 mg) were placed inside a cylinder flow cell (22.6 mm). The  
211 dissolution medium (filtered solution of PBS 0.15 M at  $\text{pH}=7.4$ ) under stirring (200 rpm) was  
212 circulated by pumping it through each cell at a rate of 50 mL/min and the temperature was  
213 maintained at  $37 \pm 0.5^{\circ}\text{C}$  during testing. The concentration of TCS was measured at time

214 intervals and calculated at each time point based on calibration curves (specific extinction  
215 coefficient of TCS in PBS at  $\lambda=282$  nm was  $0.0149 \text{ L mg}^{-1} \text{ cm}^{-1}$  with  $r^2=0.9974$ ).

216

## 217 **2.6. Complexation study of triclosan with PCD+ and PCD-**

### 218 **2.6.1. Proton Nuclear Magnetic Resonance**

219 The one and two dimensional  $^1\text{H}$  NMR spectra were recorded in  $\text{D}_2\text{O}$  using a Bruker  
220 AV 300 spectrometer at 300 MHz with 8 increments for polymers and complexed  
221 TCS/polymers, except for TCS with 13056 increments. Two-dimensional NOESY (Nuclear  
222 Overhauser Effect Spectroscopy) experiments were operated at 300 K using the standard  
223 Bruker parameters and a spin-lock mixing time of 350 ms with TPPI method. 2D spectrum  
224 consisted of a matrix of 2048 (F2) by 2048 (F1) covering a sweep width of 1929 Hz and 16  
225 increments were collected with 256 transients. A concentrated polymer solution was prepared  
226 (50mM) in  $\text{D}_2\text{O}$  before TCS addition in excess, and then it was maintained under agitation  
227 (150 rpm) 24 hours at  $25^\circ\text{C}$ . The supernatant was characterized by NMR.

228

### 229 **2.6.2. Phase solubility of TCS with PCD+ and PCD-**

230 Phase solubility of TCS in phosphate buffer (50 mM, pH 6.5) was carried out by  
231 adding an excess amount (5mg/mL) of TCS to 10 ml of polymer solution (0 to 8%(w/v)) and  
232  $\beta\text{CD}$  solution (0 to 1.6%(w/v)). The mixtures were mechanically shaken at  $25^\circ\text{C}$  for 24 hours  
233 (until equilibrium), centrifuged and the TCS concentration in the supernatant was determined  
234 by UV-visible spectroscopy (Shimadzu UV-1800) at 282 nm. Each experiment was  
235 performed in duplicate. In the case of the formation of a 1:1 inclusion complex, the stability  
236 constant  $K_{1:1}$  was obtained from the equation described by Higuchi and Connors (Higuchi and  
237 Connors, 1965) :

238

$$K_{1:1} = \text{Slope} / (S_0 (1-\text{Slope}))$$

239 where  $S_0$  represents the intrinsic solubility of TCS in PBS, and the molar concentration of CD  
240 polymers was calculated by considering that  $\beta$ -CD represented 58. wt % and 50. wt % in  
241 PCD+ and PCD- respectively.

242

## 243 **2.7. Antibacterial tests**

244 The diffusion test was applied to evaluate the antimicrobial activity through the  
245 measurement of the inhibition zone around the samples put on agar gel seeded with  
246 *Staphylococcus aureus*, CIP224 and *Escherichia coli*, K12. The textile samples of 11 mm  
247 diameter were sterilized with absolute ethanol during 1 minute before air-drying and then  
248 placed in a 24 well plate containing 1 mL of PBS sterilized solution (0.15 M, pH=7.4) under  
249 stirring (150 rpm) at 37°C. At the predetermined time points, the PBS solution of each well  
250 plate was removed and refilled with a new PBS solution, except at zero time. 100  $\mu$ L of the  
251 bacterial suspension ( $1 \times 10^4$  colony forming unit (CFU)·mL<sup>-1</sup>) were then plated on Müller-  
252 Hinton-Agar (MHA). Then, the textile samples were deposited on MHA and were incubated  
253 at 37°C during 24 hours. Inhibition zone radius (in cm) were measured and plotted as a  
254 function of the release time in PBS. The tests were repeated three times to obtain an average  
255 value.

256

## 257 **3. Results & Discussion**

### 258 **3.1. LbL film build-up onto PET20 samples**

259 LbL deposition of cationic polyEPG-CD-10 and anionic polyCTR-CD onto the  
260 nonwoven PET textile were realized as reported previously (Junthip et al., 2016, 2015). After  
261 the thermofixation step, textile samples underwent a weight gain of 20%wt and after the  
262 superimposition of five PCD+/PCD- bilayers, the weight gain increased up to 75%wt (Junthip  
263 et al., 2016). Micrographs displayed in Figure 2 show the evolution of the fibrous support

264 morphology at the fibers scale before treatment, after thermofixation (PET20 sample) and  
265 after the ten cycles of the dip coating process (PET20-PEM5). Both modification steps  
266 involved an increase of the diameter of the fibers synonym of their coating firstly by the  
267 thermofixed layer and then by the LbL film. In the latter case, ~~one can observe that~~ the textile  
268 structure was covered by the PEM coating, especially when focusing on the fibers crossings  
269 where fibers are bridged together. From this observation, ~~one can notice~~ a decrease of the  
270 ~~textile~~ porous volume ~~of the textile, and one can a~~ could also explain the stiffness increase  
271 noted upon samples handling, especially ~~observed~~ after the LbL process and the final thermal  
272 post-treatment at 140°C.

273

### 274 **3.2. Study of the complexation of TCS with PCD+ and PCD- by NMR**

275 TCS/polyEPG-CD-10 and TCS/polyCTR-CD interactions were investigated by  
276 Nuclear Magnetic Resonance (NMR). In Figure 3.a and 3.b the main signals in both  
277 cationic and anionic poly-cyclodextrins spectra could be attributed according to previous  
278 reports (Martin et al., 2013b) and (Junthip et al., 2016, 2015). ~~Spectrum in figure 3.a~~  
279 ~~relative to polyCTR-CD displayed the signal of the glucopyranosic units of cyclodextrins,~~  
280 ~~H1 at 5 ppm, H3, H5, H6, H4 and H2 situated between 3.5 and 4 ppm, the methylene~~  
281 ~~groups of the citrate crosslinks appearing between 2.7 and 3 ppm. Finally, two singlets at~~  
282 ~~6.25 and 7.8 ppm corresponding to cis and trans aconitic esters respectively issued from a~~  
283 ~~side reaction consisting of the dehydration of citrate crosslinks. Spectrum in figure 3.b~~  
284 ~~relative to polyEPG-CD-10 displayed the signal of anomeric proton (H-1) of cyclodextrin~~  
285 ~~near 5 ppm, the protons of quaternary ammonium of GTMAC at 3.2 ppm and the rest of~~  
286 ~~cyclodextrin protons and reactant protons (GTMAC and EP) in the range 3.2 to 4.5 ppm.~~  
287 In the presence of TCS, no signal shifts of H3 and H5 cyclodextrins protons could be  
288 observed in the 3.7 to 3.9 ppm interval. However, the spectrum magnification reported in  
289 Figure 3c displays spectral changes in the range from 6 to 8 ppm where aromatic protons

290 of TCS are situated (Jug et al., 2011; Qian et al., 2008). All aromatic protons of TCS  
291 shifted upfield or downfield (Figure 3c), in the presence of both polymers, revealing a  
292 possible complexation. This was confirmed by 2D-NOESY NMR spectra (Figure S1)  
293 where correlation peaks appeared consequently to the dipolar interaction between the TCS  
294 aromatic protons (6 to 8 ppm) with internal proton H3 and H5 of poly-cyclodextrins  
295 (around 3.8 to 3.9 ppm).

296

### 297 **3.3.Phase solubility study of TCS in the presence of PCD+ and PCD-**

298 Solubility enhancement studies of TCS in the presence of  $\beta$ CD, polyCTR-CD and  
299 polyEPG-CD-10 were carried out using the phase solubility method (Figure 4). TCS  
300 presented intrinsic solubility of 0.04 mM at 25°C that sharply increased by factors up to 10,  
301 60 and 220 in the presence of  $\beta$ CD, polyCTR-CD and polyEPG-CD-10, respectively. More  
302 specifically, Figure 4a shows an increase in TCS solubility in function of the  $\beta$ CD  
303 concentration up to 4.4 mmol/L, and then levels around 0.4 mmol/L. This is typical of a B-  
304 type phase-solubility profile (Higuchi and Connors, 1965) indicating the formation of  
305 complexes with limited solubility in the aqueous medium. The apparent association constant  
306 calculated from the slope of the plot ( $K_{1:1}$ ) was equal to 1870 M<sup>-1</sup>, in accordance with the  
307 literature in which  $K_{1:1}$  was equal to 2526 M<sup>-1</sup> for the complex  $\beta$ CD: TCS (Jug et al., 2011).  
308 TCS solubility linearly increases with both  $\beta$ CD polymers types concentration, displaying in  
309 both cases A<sub>L</sub>-type profiles (Figure 4b and 4c). The calculated association constants of TCS  
310 with polyEPG-CD-10 and polyCTR-CD were equal to 6650 and 1590 M<sup>-1</sup> respectively.  
311 Elsewhere, the  $K_{1:1}$  value of TCS with another type of cationic  $\beta$ CD polymer using choline  
312 chloride as cationizing agent was found to be equal to 3800 M<sup>-1</sup> in water (Qian et al., 2008).  
313 So, this study confirmed that both PCD+ and PCD- can form inclusion complexes with TCS.

314

315        **3.3.1. TCS Release study**

316        PET 20 and PET20-PEM5 samples were loaded with TCS and their release profile were  
317        assessed in PBS at 37°C and in dynamic mode at the flow rate of 50mL/min. Figure 5 shows  
318        a meaningful influence of the mode of functionalization on the release patterns. As a matter of  
319        fact, 4.6 mg of TCS /g of sample were loaded and then released by the textiles modified by  
320        thermofixation and then with five self-assembled bilayers, while samples that only underwent  
321        the thermofixation step adsorbed and then released only 1.1 mg/g. This result demonstrated  
322        that the multilayer film increased of a 3.5 factor the reservoir capacity of the textile. This  
323        result can be attributed to the inclusion complex formed between TCS and CD moieties  
324        present in both PCD+ and PCD- in the PEM coating.

325        **3.4. Antibacterial activity of samples**

326        PET20 and PET20-PEM5 samples cut in 11mm disks and then loaded with TCS were put  
327        in PBS batch at pH 7.4 at 37°C over a period of 28 days. The disks were withdrawn at  
328        different time points from the batches and deposited on agar plates pre-inoculated with *S.*  
329        *aureus* and *E. coli* (Figure 6a). After 24 hours of incubation, their residual antibacterial  
330        activities were reported by plotting the inhibition diameters of halos appearing around  
331        samples against the release time in PBS (Figure 6b and 6c). Despite TCS is a broad-spectrum  
332        antimicrobial agent, all test samples displayed larger inhibition diameters in the presence of *S.*  
333        *aureus* (minimum inhibitory concentration (MIC) of 0.025-1 mg/L) compared to *E. Coli* K12  
334        (MIC of 1mg/L), due to the higher sensitivity of Gram+ toward TCS (Assadian et al., 2011;  
335        Suller and Russell, 2000). On the other hand, inhibition diameters formed around PET20-  
336        PEM5 samples were sharply superior to those observed around PET20 samples loaded with  
337        TCS. This can be correlated with the kinetic study that showed that the release rates of TCS  
338        from PET20-PEM5 samples were sharply superior compared to PET20 samples. In the course  
339        of time of the batch experiments, PET20 samples displayed a fast loss of their antibacterial

340 activity against *E. coli* within 3 days as the inhibition diameters decreased from 2.3 cm to 1.1  
341 cm (corresponding to the diameter of disks) within this period. On the contrary, the  
342 antibacterial activity of PET20-PEM5 samples against *E. coli* only slightly decreased during  
343 the 28 days period as inhibition diameters decreased from 3.1 cm down to 2.7 cm. Besides,  
344 PET20 and PET20-PEM5 samples displayed a sustained antibacterial effect even after 28  
345 days against *S. aureus*. However, the antibacterial activity of PET20 samples against *S.*  
346 *aureus* quickly decreased within 3 days period as inhibition diameters decreased from 4.0 cm  
347 down to 2.2 cm. On the contrary, the antibacterial activity of PET20-PEM5 samples against *S.*  
348 *aureus* only slightly decreased during the 28 days period as inhibition diameters decreased  
349 from 5.0 cm down to 3.5 cm. So, diffusion tests realized after ageing samples in batch was  
350 maintained at high and almost constant level over at least 28 days against both bacterial  
351 strains. The test positive response in the diffusion test indicated that the amount of TCS  
352 released from aged samples in the agar gel was always maintained above the minimum  
353 inhibitory concentration (MIC). This slow and controlled release can be attributed to the high  
354 inclusion complex formation constants reported above between TCS and CD moieties in  
355 PCD+ and PCD-.

356 In our previous paper (Junthip et al., 2016), we reported that PET20-PEM5 sample  
357 without TCS, tested by the *kill-time* method, displayed bacterial reductions of 7.3 and 4.5  
358 log<sub>10</sub> against *S. aureus* and *E. coli*. This intrinsic antibacterial activity was found to be  
359 dependent of the trimethylammonium content of polyEPG-CD-10 in the self-assembled layer  
360 (Junthip et al., 2016). Interestingly, in our former studies dealing with PEM coatings based on  
361 PCD- as polyanion, and chitosan as polycations (Aubert-Viard et al., 2019; Martin et al.,  
362 2013a; Mogrovejo-Valdivia et al., 2019; Pérez-Anes et al., 2015) control samples not loaded  
363 with any antibacterial substances did not display such intrinsic antibacterial activity despite  
364 chitosan is often reported as an antibacterial polymer. The presence of quaternary ammonium

365 groups carried by PCD+ versus primary ammonium groups carried by chitosan can explain  
366 such result. These previous results combined to our new results showed that these  
367 PCD+/PCD- systems presented intrinsic contact killing property and also extrinsic release  
368 killing properties once loaded with TCS (up to 28 days).

369

## 370 **Conclusion**

371 Polyelectrolyte multilayer (PEM) assembly based on water-soluble cationic  $\beta$ -  
372 cyclodextrin polymer (polyEPG-CD) and anionic  $\beta$ -cyclodextrin polymer (polyCTR-CD) was  
373 built up by the layer-by-layer technique onto non-woven PET textile preliminarily modified  
374 by polyCTR-CD through a thermofixation process. TCS loading on the samples coated with 5  
375 self-assembled bilayers (PET20-PEM5 samples) reached 4.6 mg/g of textile, against only 1.1  
376 mg/g on the sample modified with one thermofixed layer consisting of polyCTR-CD (PET20  
377 samples). The PEM system displayed the sustained release of TCS over 14 hours in dynamic  
378 conditions. Besides, diffusion tests realized after ageing samples in batch was maintained at  
379 high and constant level over at least 28 days. These properties could be explained by the  
380 reversible inclusion complex formation between TCS and CD moieties present in both  
381 cationic and anionic crosslinked polymers. These results combined to our previous published  
382 paper (Junthip et al., 2016) showed that these PCD+/PCD- systems presented intrinsic contact  
383 killing property and also extrinsic release killing properties once loaded with TCS.  
384 PCD+/PCD- systems offer consequently an excellent potential for the prevention and curing  
385 of peri-operative infections on biomedical devices which often display dramatical  
386 consequences.

387

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394

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564 **Figure captions**

565

566 **Figure 1.** Schematic representation of cationic and anionic polyelectrolytes based on cyclodextrins (PCD- and  
567 PCD+) and of a nonwoven PET coated with an LbL film made of PCD+/PCD- bilayers, stabilized by a thermal  
568 crosslinking reaction at 140°C and loaded with Triclosan

569

570 **Figure 2.** SEM pictures of (a) and (d) virgin PET, (b) and (e) 20%wt thermofixed layer, (c) and (f) multilayers  
571 (10 layers). Magnification x 150 and x800 resolution; full scale 50 and 300 µm.

572

573 **Figure 3.** NMR study of TCS/polyEPG-CD-10 and TCS/polyCTR-CD complexation in D<sub>2</sub>O.  
574 <sup>1</sup>H NMR of the TCS/polyCTR-CD complex (a), the TCS/polyEPG-CD-10 complex (b) and the magnification at  
575 6-8 ppm of TCS (c1), TCS/polyCTR-CD complex (c2) and TCS/polyEPG-CD-10 complex (c3).

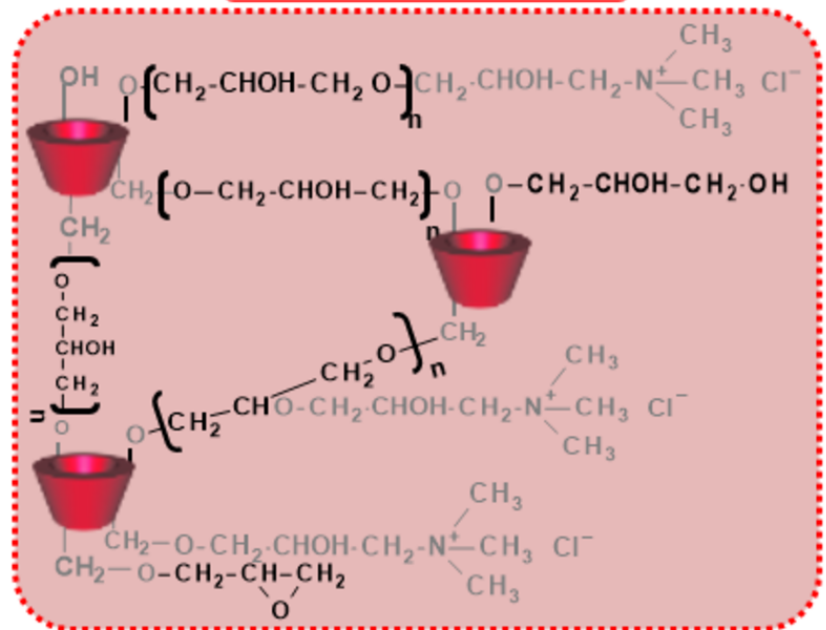
576  
577 **Figure 4.** Phase solubility diagrams of TCS with (a) βCD and (b) polyEPG-CD-10 and (c) polyCTR-CD, in  
578 phosphate buffer (50 mM, pH 6.5) at 25°C.

579  
580 **Figure 5.** Release kinetics study of TCS (dynamic mode at 50mL/min, in PBS at 37°C) from thermofixed  
581 (PET20) and 5 bilayers (PET20-PEM5) textile samples with (a) TCS released capacity in mg/g of sample, (b)  
582 TCS release capacity in %

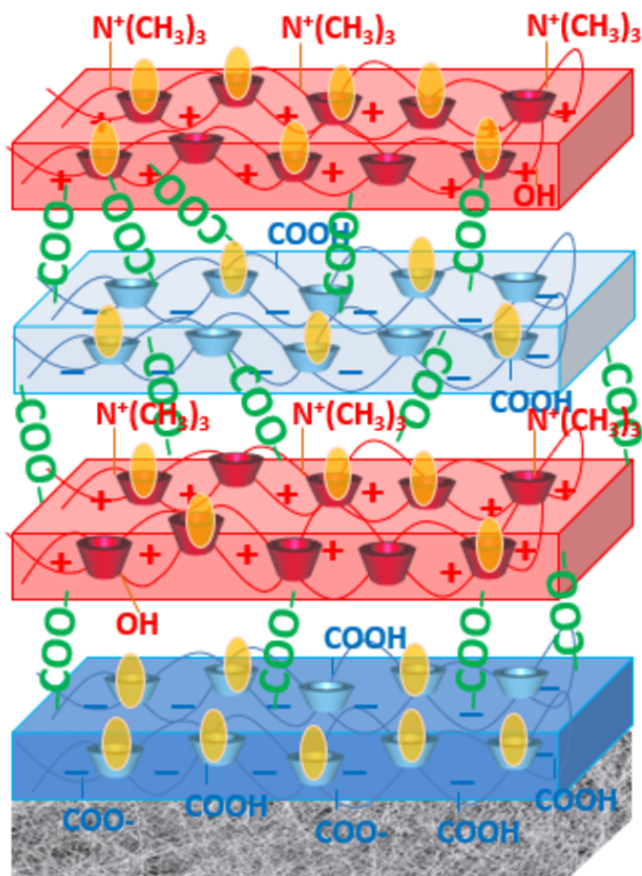
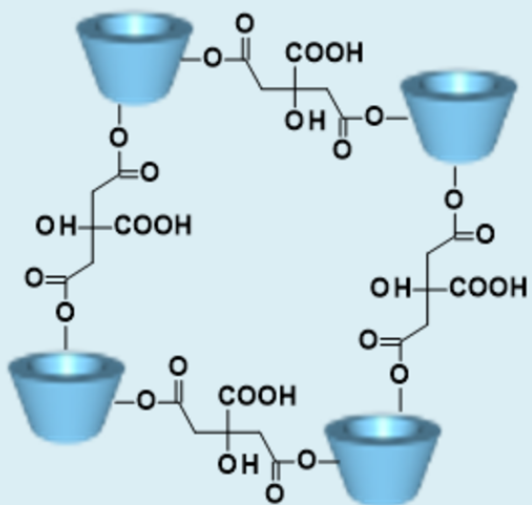
583  
584 **Figure 6.** (a) Representative images of Kirby-Bauer test on TCS impregnated PET20 and PET20-PEM5  
585 samples against *S. aureus* and *E. coli* with inhibition zone after 24 hours of TCS release in PBS at 37°C.  
586 Inhibition zone diameters around PET20 and PET20-PEM5 samples loaded with triclosan (TCS) against (b) *S.*  
587 *aureus* and (c) *E. coli* in function of contact time in PBS at 37°C after 24 hours incubation at 37°C over 28 days.

588  
589 **Figure S1.** 2D-NOESY NMR spectra of TCS/polyCTR-CD (a) and TCS/polyEPG-CD-10 (b) complexes.

**poly-EPG-CD-10 = PCD+**



**polyCTR-CD = PCD-**



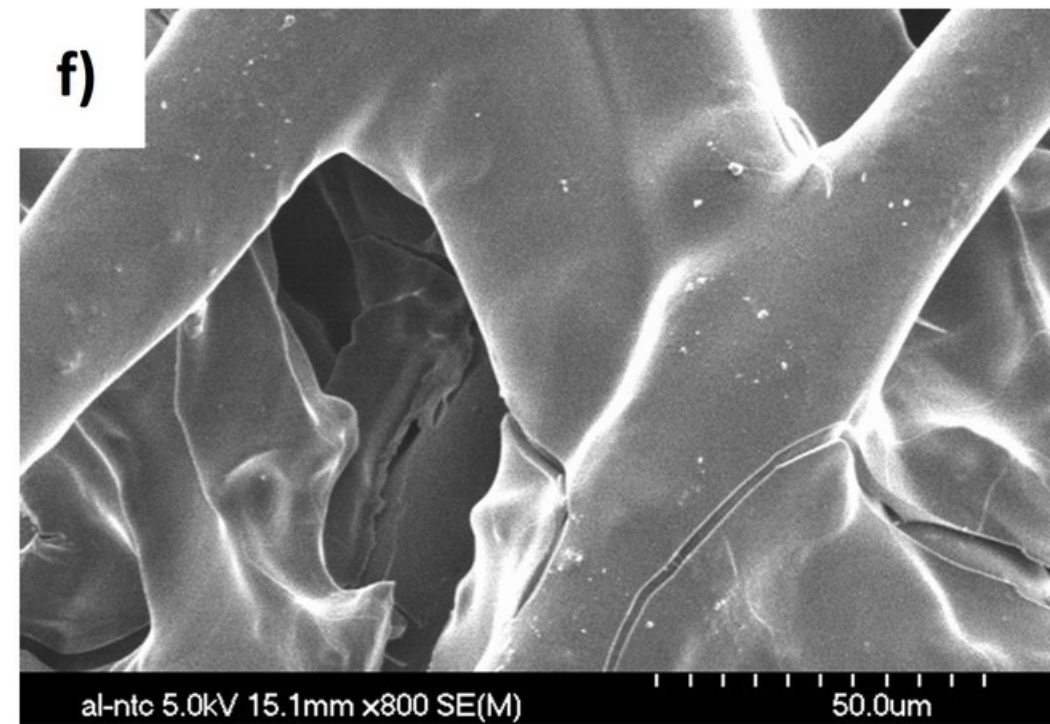
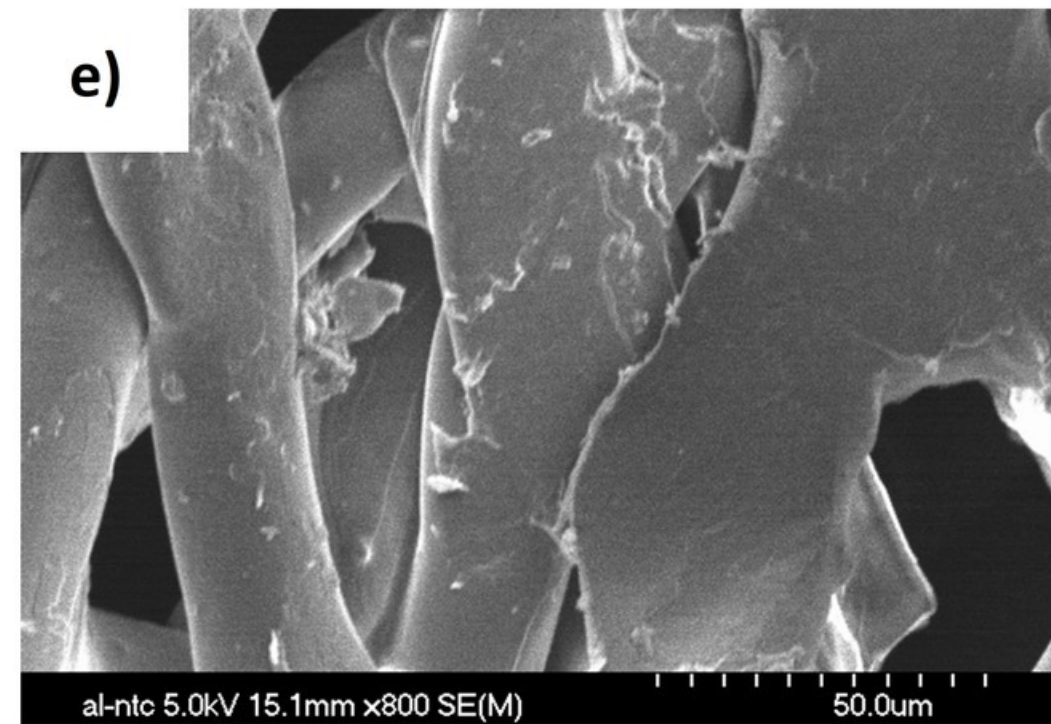
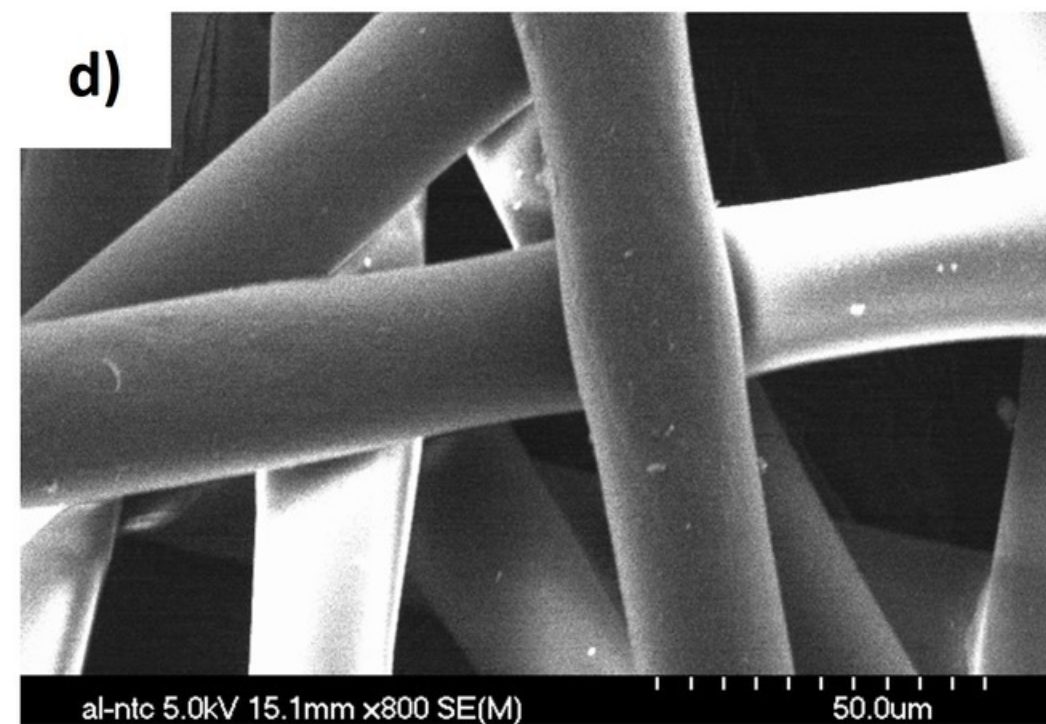
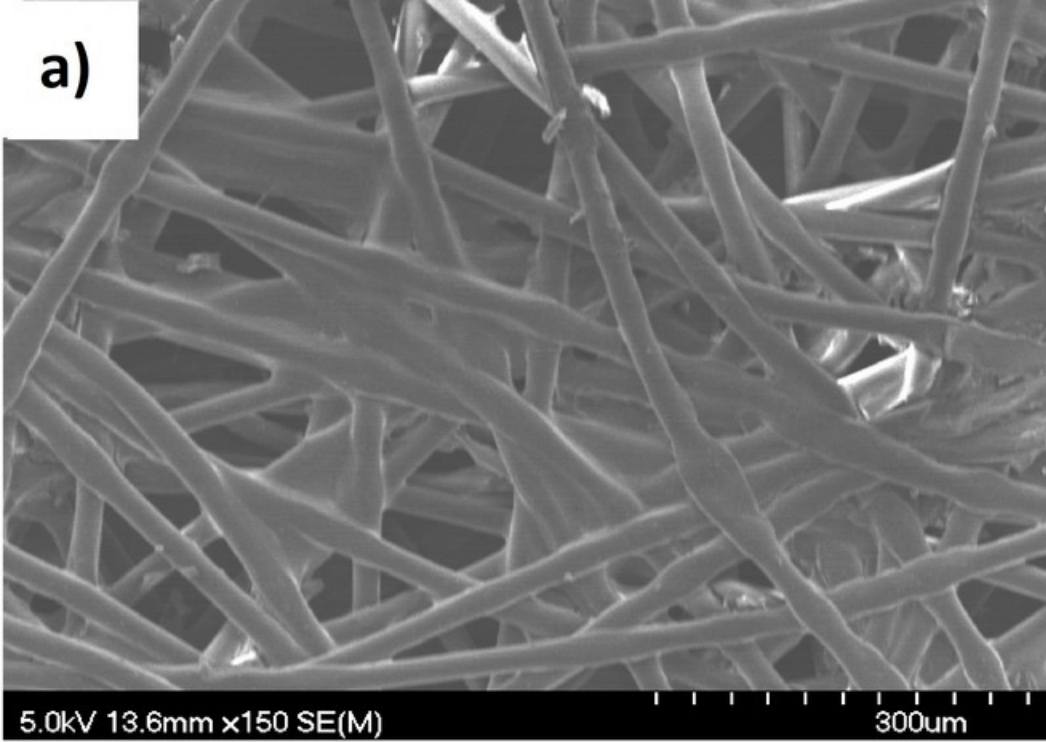
 **Triclosan**

**Self assembled polyCTR-CD**

**Self assembled poly-EPG-CD-10**

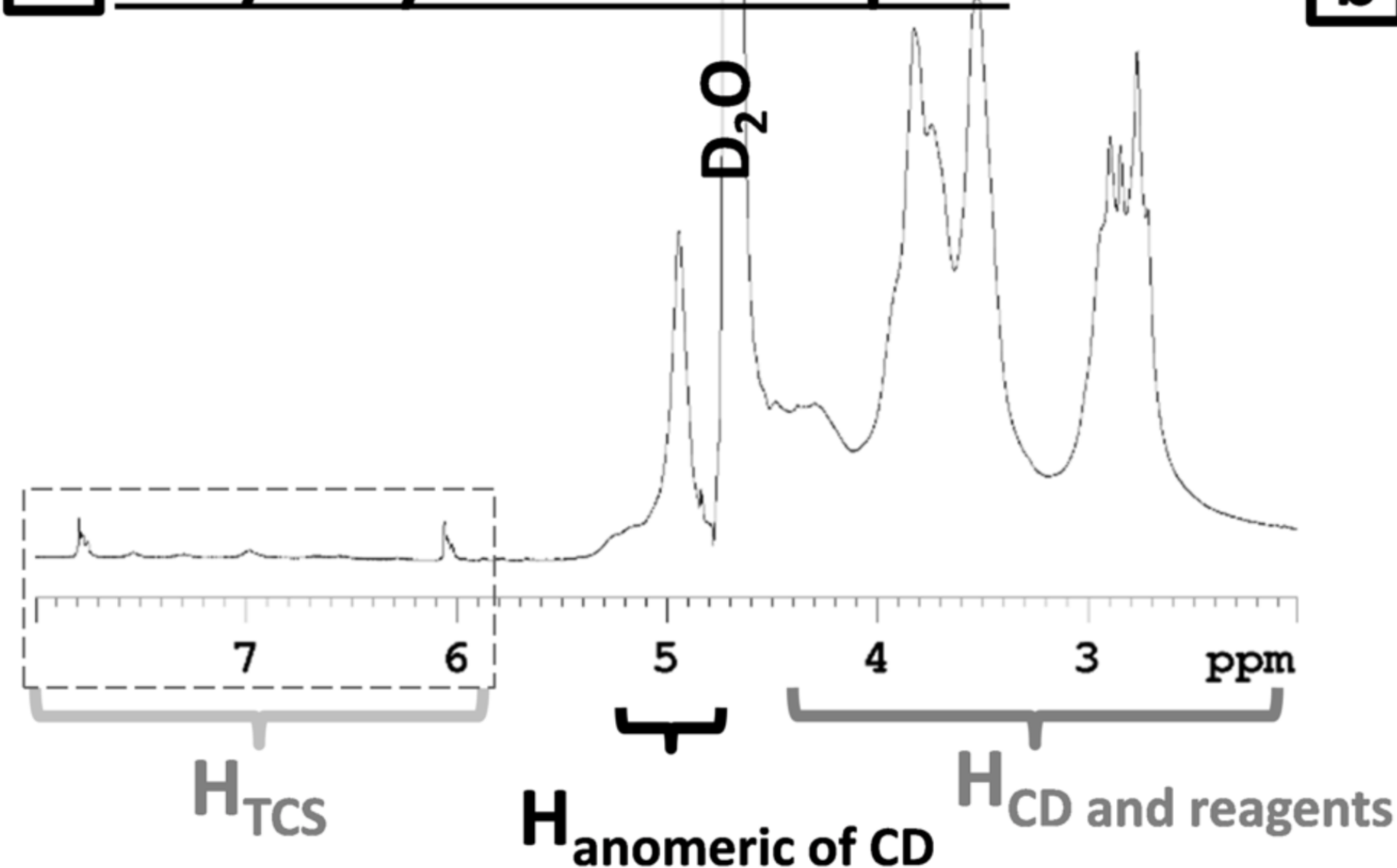
**Ester link formed by post-treatment at  $140^\circ\text{C}$**

**Nonwoven with thermofixed polyCTR-CD layer**

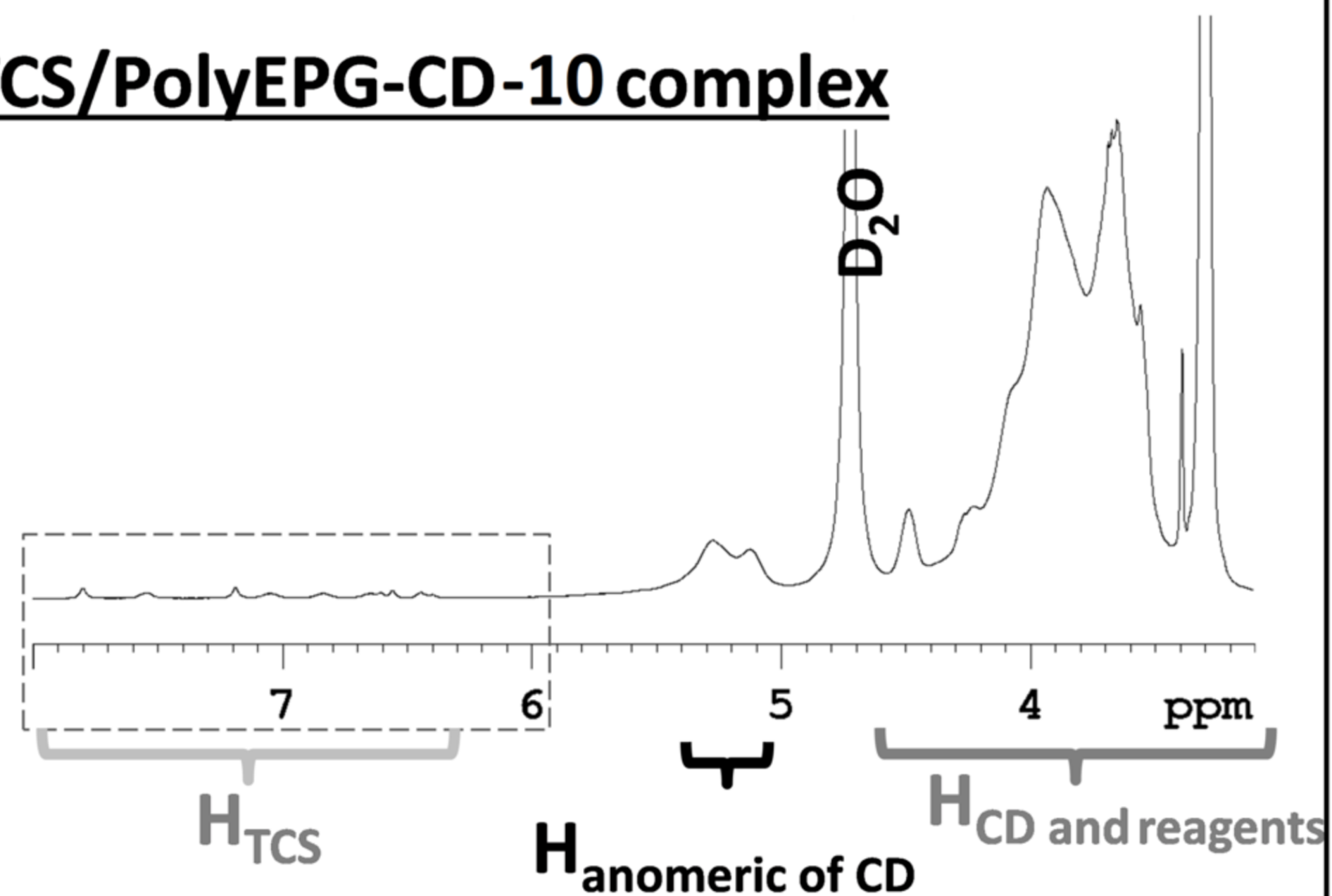


# 1D $^1\text{H}$ NMR ( $\text{D}_2\text{O}$ )

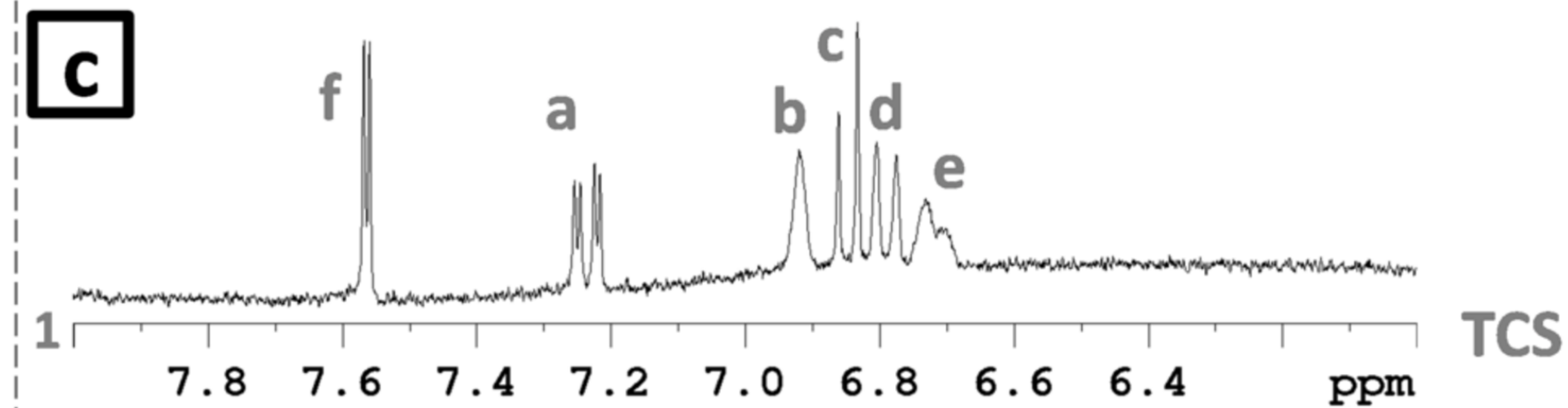
**a** TCS/PolyCTR-CD complex



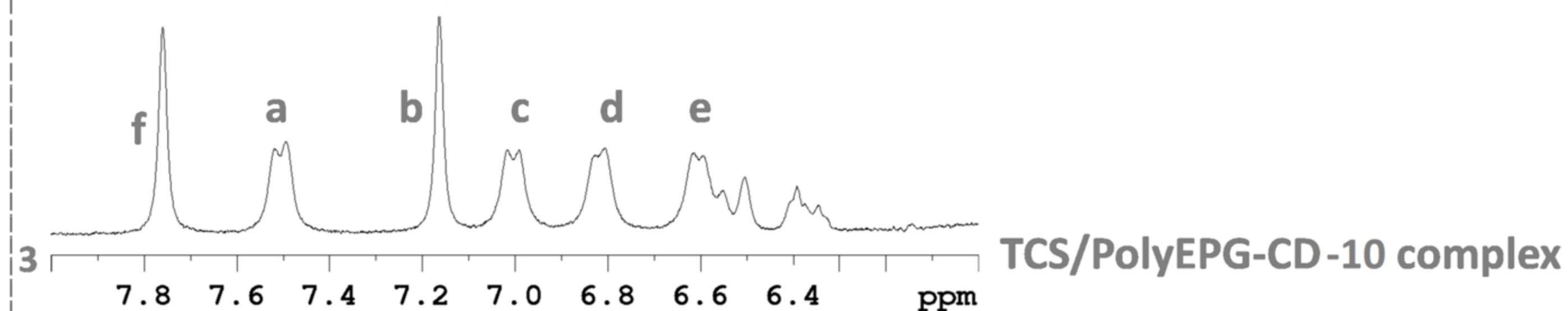
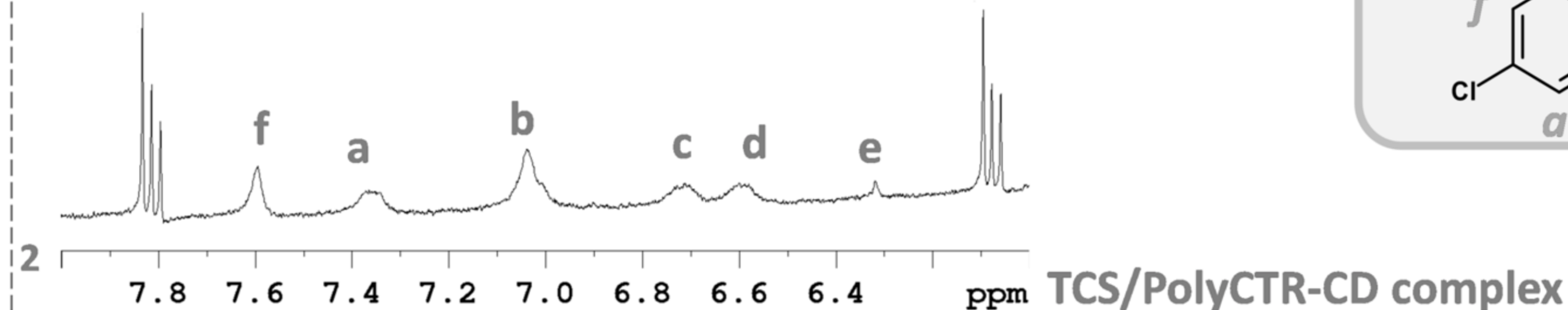
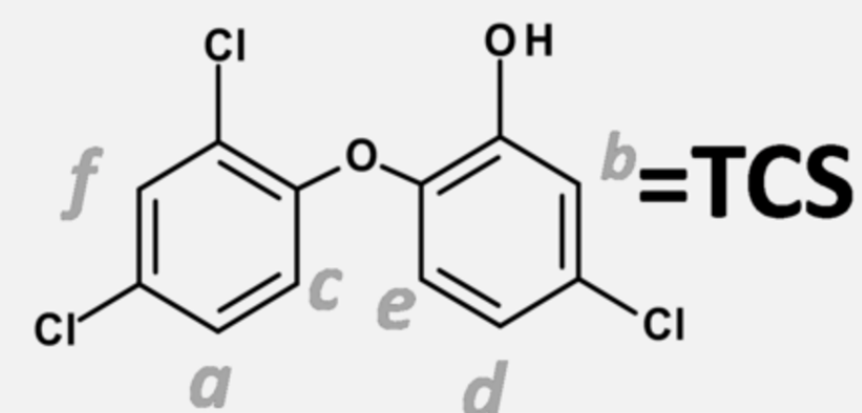
**b** TCS/PolyEPG-CD-10 complex



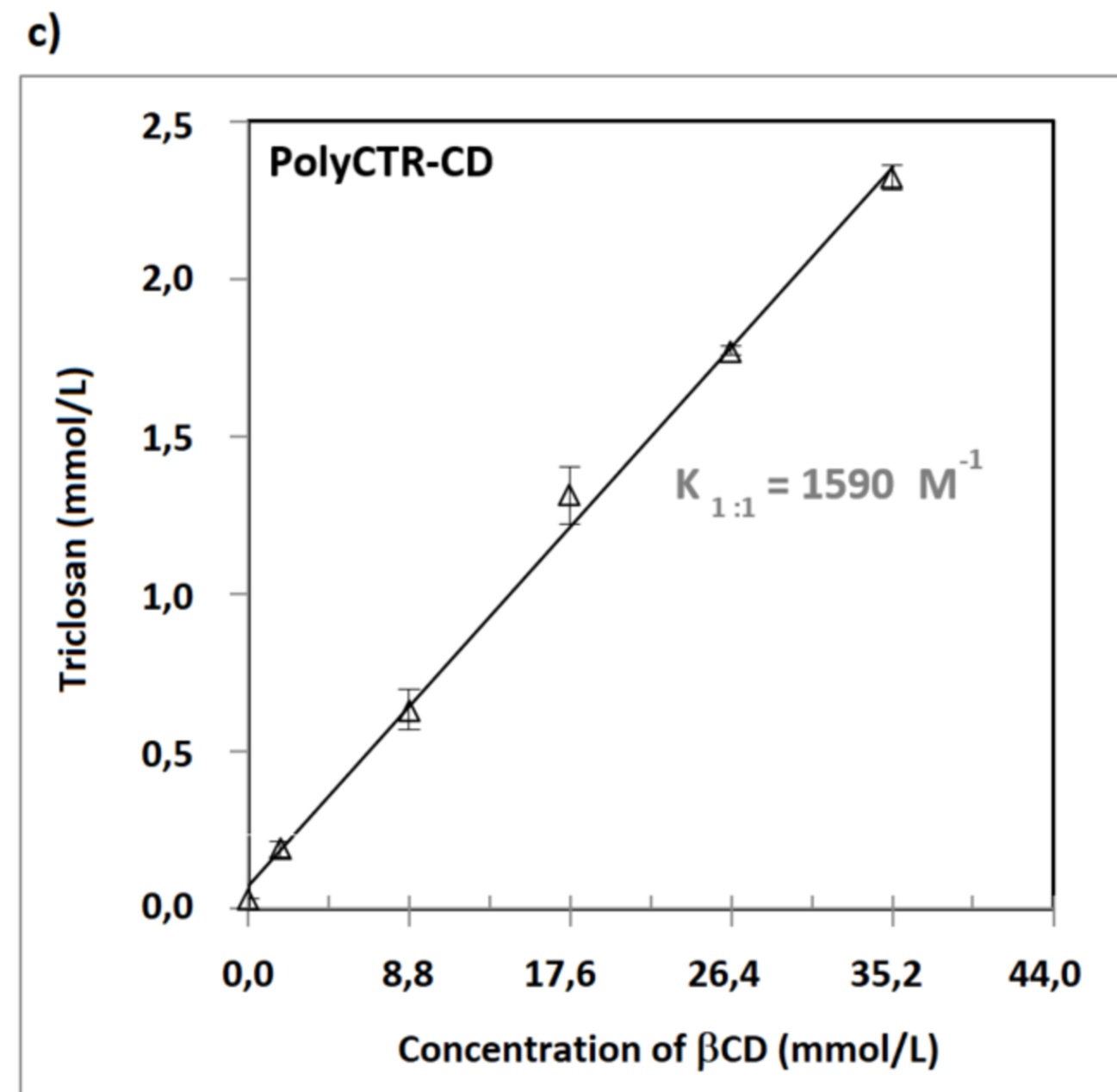
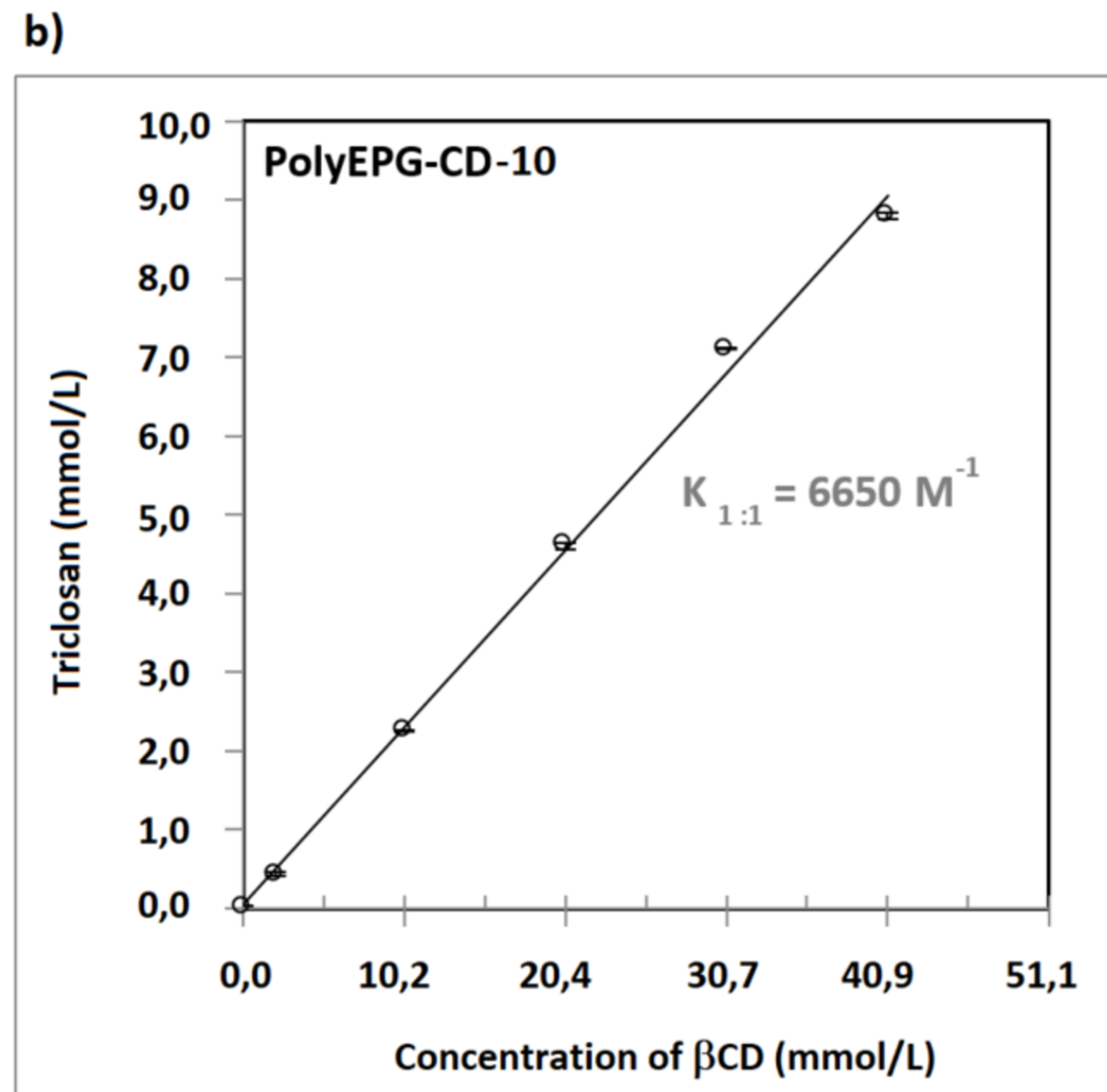
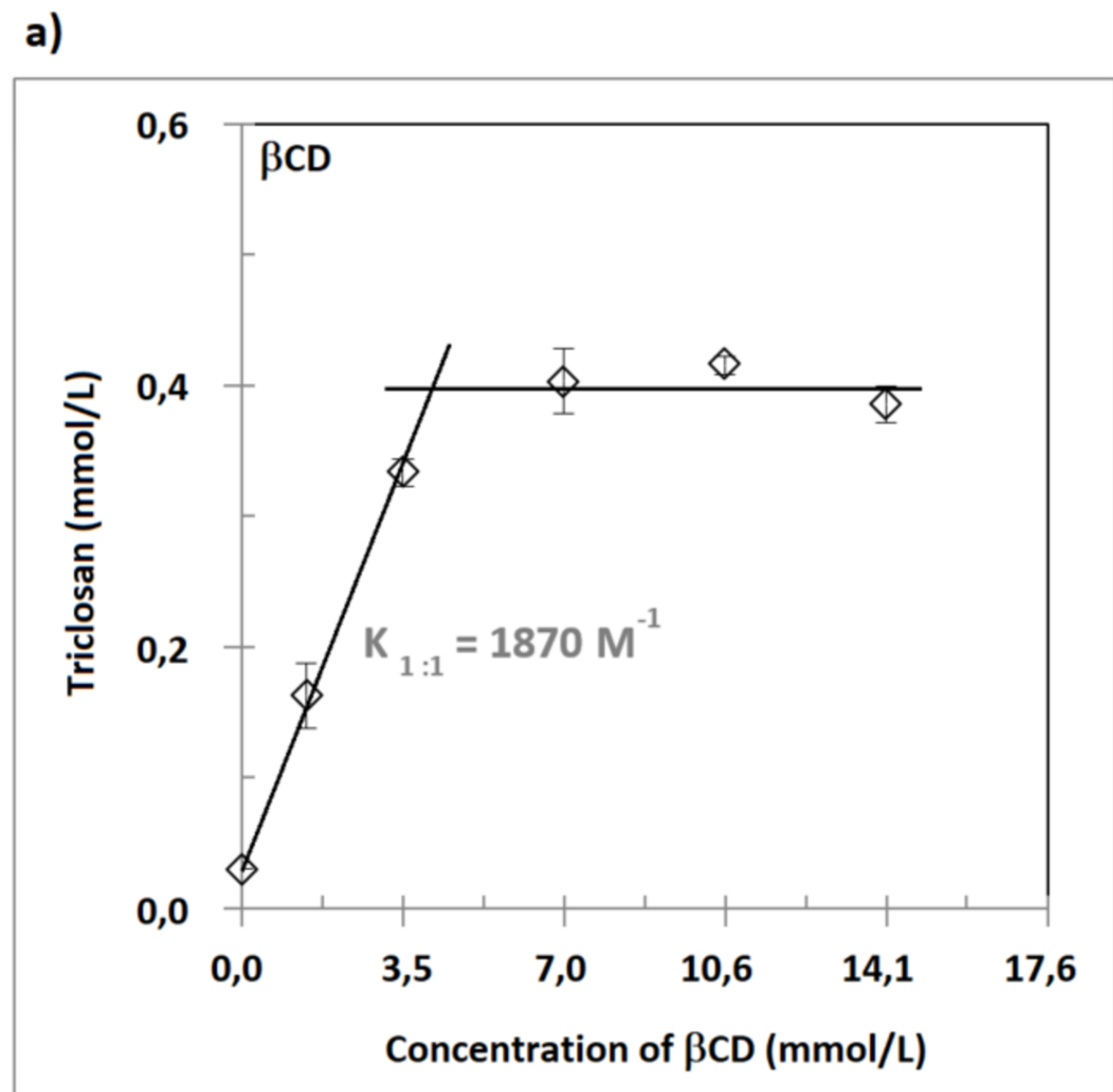
**c**

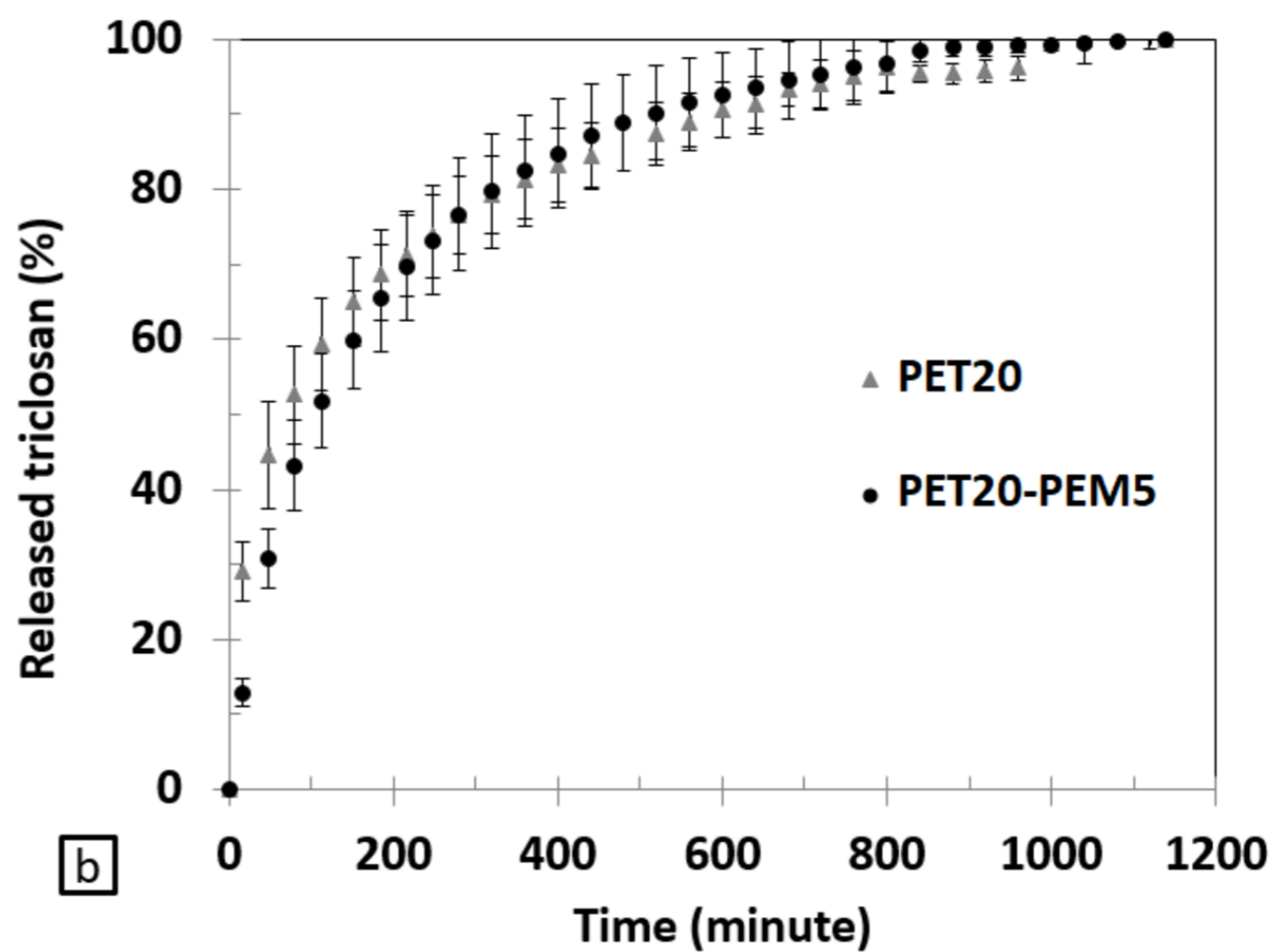
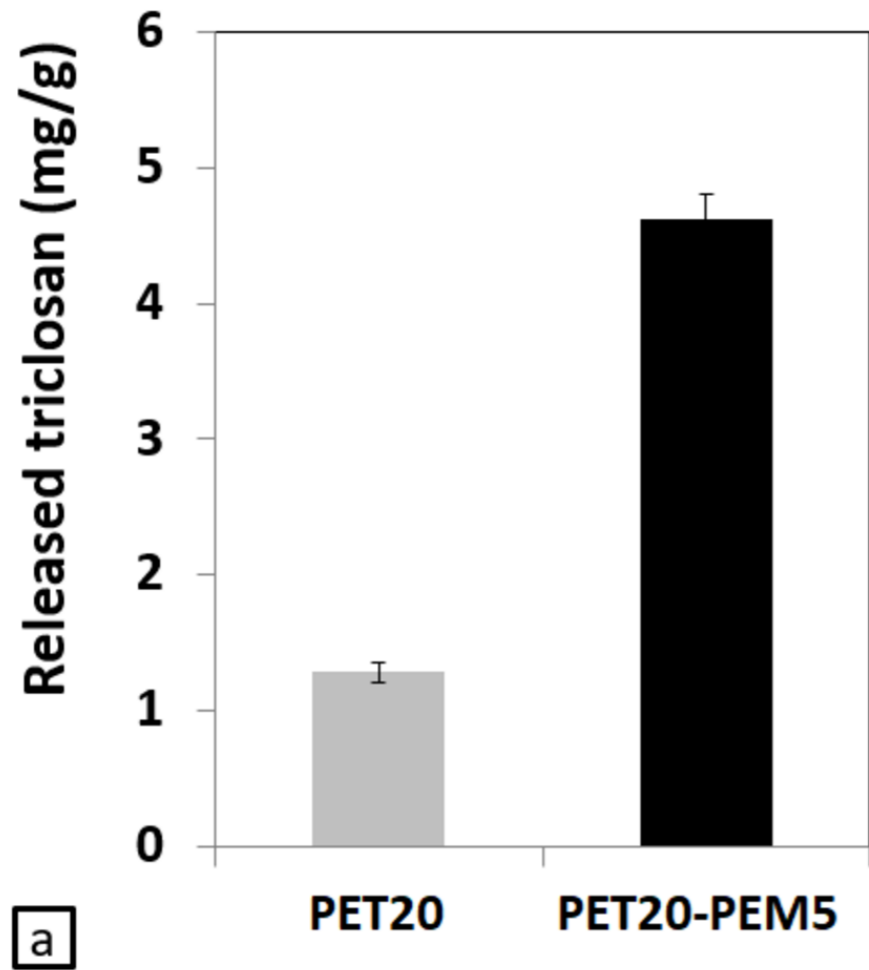


## Zoom at 6-8 ppm

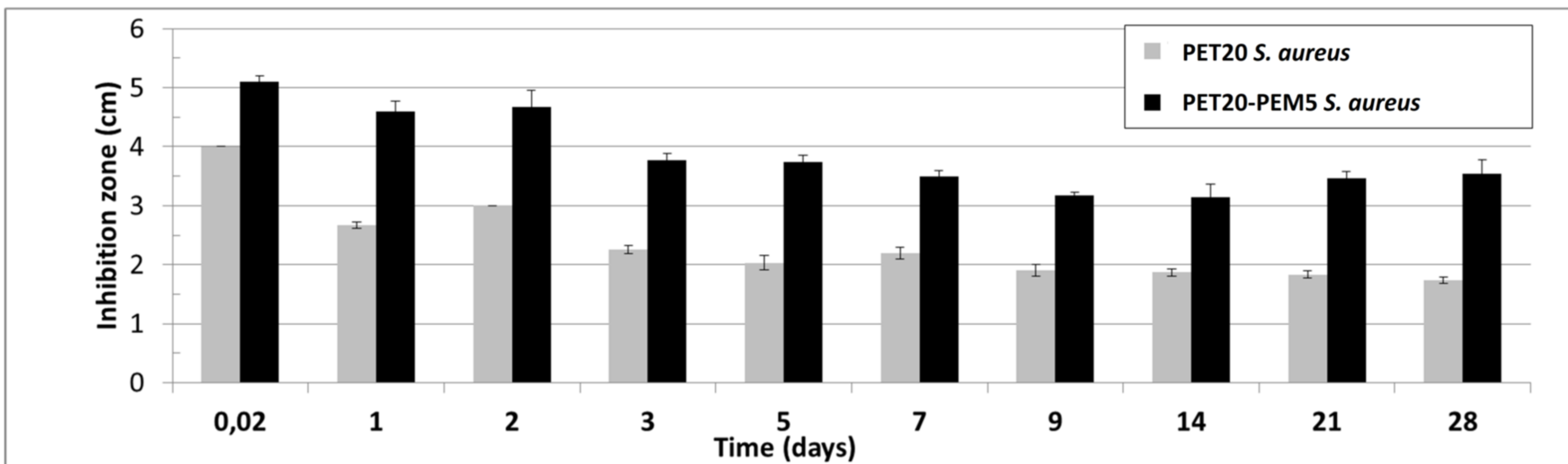
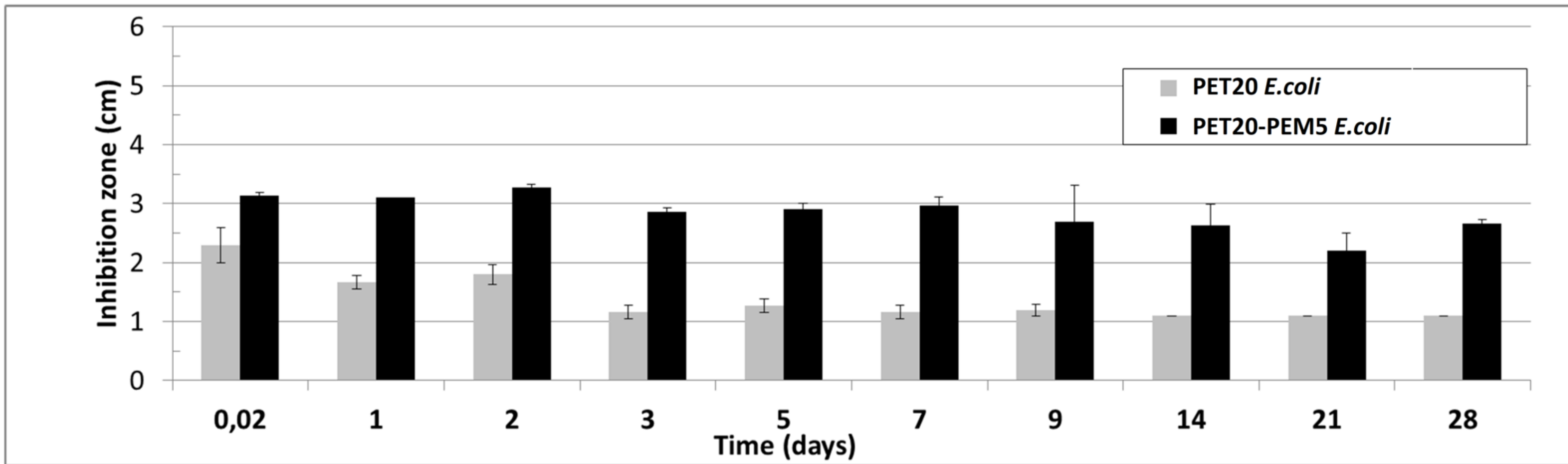
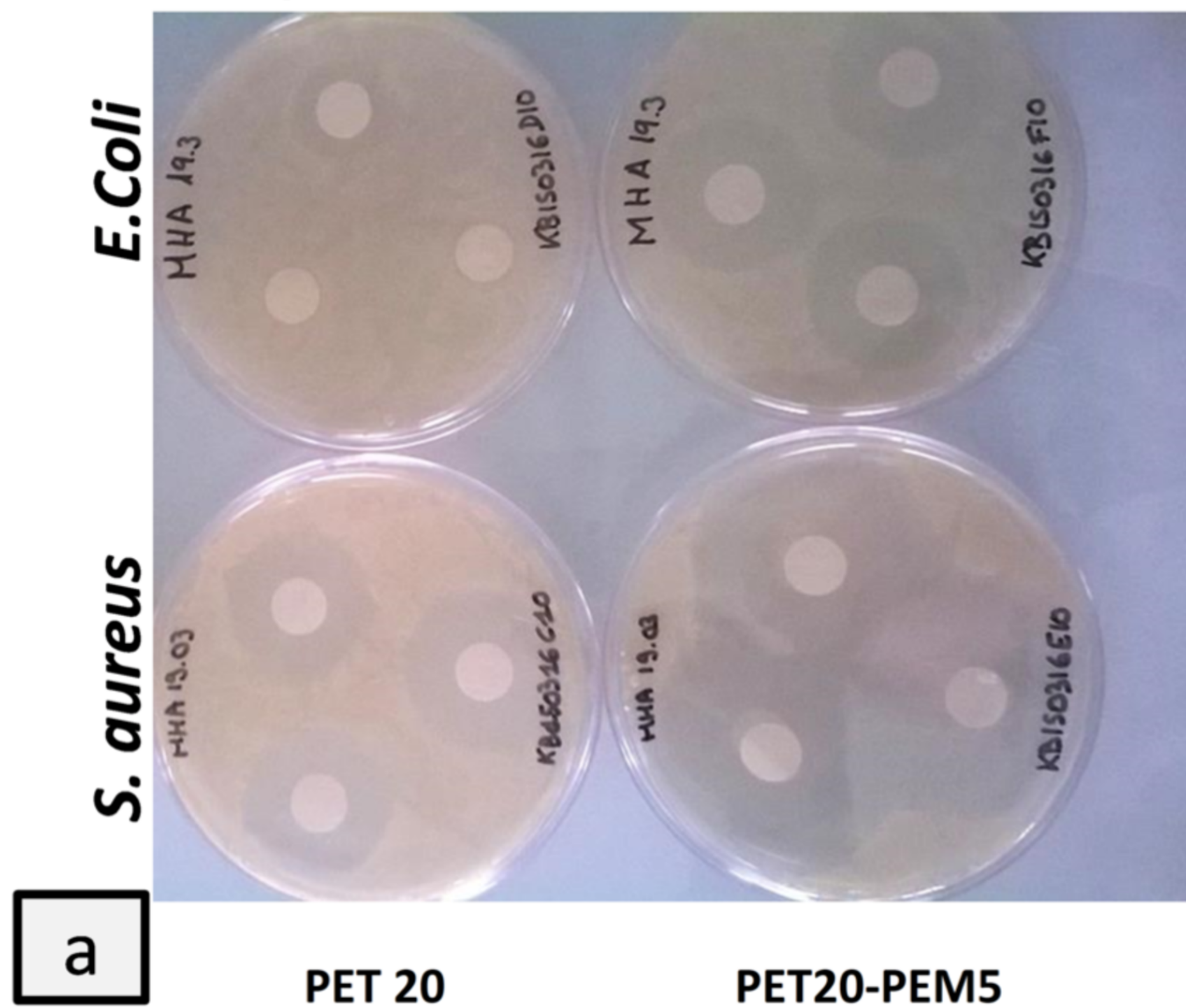




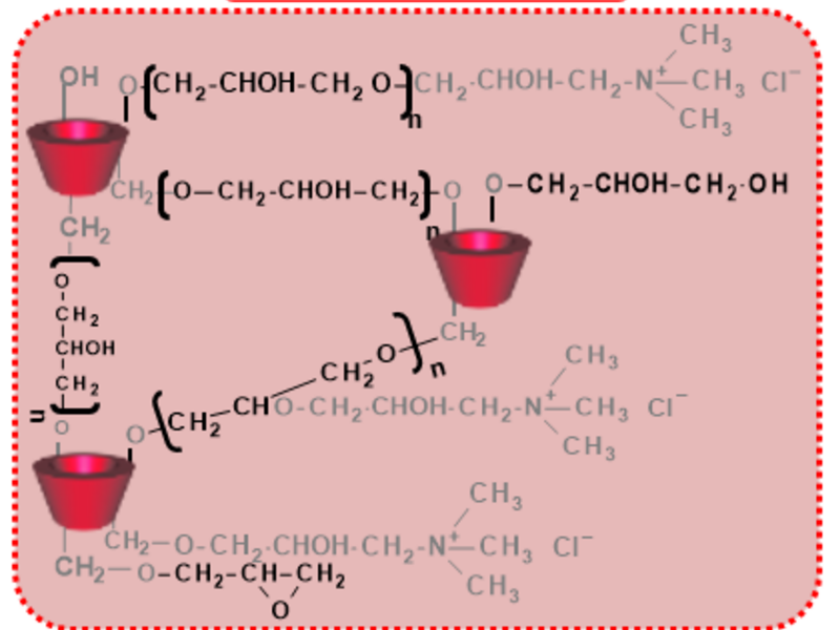




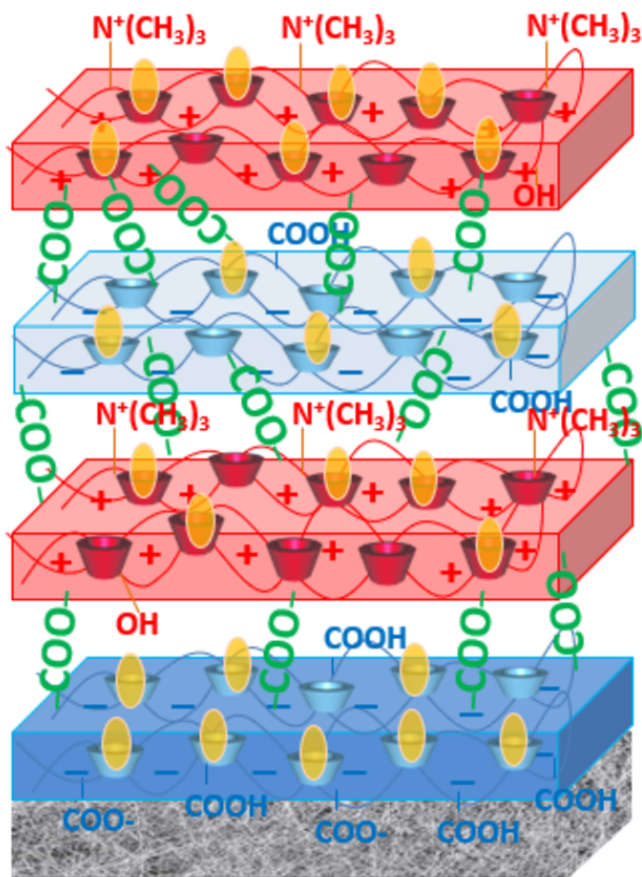
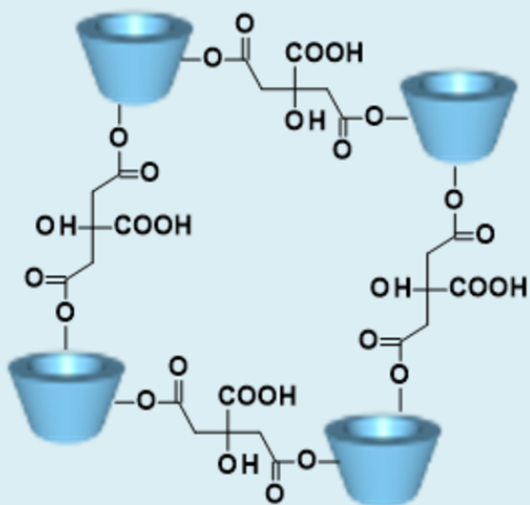
# Samples after 24 hours of TCS release



**poly-EPG-CD-10 = PCD+**



**polyCTR-CD = PCD-**



 **Triclosan**

**Self assembled polyCTR-CD**

**Self assembled poly-EPG-CD-10**

**Ester link formed by post-treatment at 140°C**

**Nonwoven with thermofixed polyCTR-CD layer**