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1 **Non-targeted screening of extracts from polyester-phenolic can coatings:**

2 **identification of new aldehyde molecules from resole-based resins**

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14

15 **ABSTRACT**

16 Phenolic and substituted phenol based resoles are commonly used in the formulation of can  
17 coatings. However, migration analyses of these coatings are very little described compared  
18 to other coating technologies. While epoxy and polyester have well known migrants with  
19 defined formation mechanisms, Non-Intentionally Added Substances (NIAS) specifically  
20 related to the phenolic resin are hardly studied in the literature. The goal of the publication  
21 is to further explore the influence of the phenolic resole, used in the formulation of can  
22 coatings, on extracted NIAS's nature. Six different model polyester-phenolic can coatings  
23 were formulated each with a specific phenol, cresol or tertbutylphenol-based resole. Can  
24 coating films were extracted for 24 hours at 40°C in acetonitrile before analysis. NIAS  
25 identification was done using gas chromatography separation coupled to high resolution  
26 mass spectrometry (HRMS) and nuclear magnetic resonance (NMR) spectroscopy analyses.  
27 Cyclic polyester oligomers were found in all extracts, with oligomers found in a range of 10  
28  $\mu\text{g}/\text{dm}^2$  to 226  $\mu\text{g}/\text{dm}^2$ , without specific influence of the resole used in formulation. While  
29 very few or no peaks were detected from cresol- and phenol-based resoles, 48 peaks were  
30 specifically observed in coating extracts of formulas with tertbutylphenol-based resoles as  
31 well as in their respective resoles. The most intense peaks were identified as aldehyde  
32 compounds by HRMS and NMR analysis. These aldehydes were semi-quantified in similar  
33 proportions as polyester oligomers. The presence of such aldehydes has never been  
34 reported in the literature regarding NIAS in can coatings. Further study will then be needed  
35 to better understand the aldehyde formation mechanism and assess the toxicological profile  
36 of such chemicals.

37 **KEYWORDS**

38 **Food contact material, Can coating, Resole, NIAS, Non-targeted analysis, High resolution**  
39 **mass spectrometry**

#### 40 **Introduction**

41 As with any Food Contact Material (FCM), internal can coatings are strictly regulated to  
42 ensure that no substances may be transferred into the food in quantities which could  
43 endanger human health or impact organoleptic properties of the food [1]. The transfer of  
44 substances does not only concern unreacted substances such as residual monomers and  
45 additives, but Non-Intentionally Added Substances (NIAS) as well. NIAS are defined as all  
46 migrating substances which are not introduced in the FCM for technical reasons. They can be  
47 for example raw material impurities, side reactions and decomposition products [2]. There  
48 are a large variety of plausible NIAS due to resins syntheses, coating formulation and curing  
49 process. NIAS analysis is a significant task and essential to ensure the safety of can coatings.  
50 Many studies have been focused on NIAS, monitoring them in several main coating  
51 technologies: polyester oligomers [3–8], Bisphenol A, its analogues and derivatives in epoxy  
52 resins and coatings [9–12] and in acrylic based adhesives [13,14]. There are few studies  
53 specifically aimed at the influence of phenolic resins on the nature and quantity of the  
54 potential NIAS [15,16]. Moreover, to the best of the authors' knowledge, studies on NIAS  
55 extractions from coatings using substituted phenol based resole in their formulation were  
56 never published. Only one study has been reported on the compositions of the substituted  
57 resoles themselves [17].

58 Phenolic resins based on phenol and alkylated phenol resoles are frequently used as cross-  
59 linkers in internal coatings of metal cans for food contact application [18,19]. Resoles are the  
60 most used phenolic resin in the formulation of can coatings. These are produced through the

61 polycondensation of phenol or substituted phenol (cresol, 4-tert-butylphenol) with  
62 formaldehyde excess in alkaline conditions (**Figure 1**). The reaction leads to the formation of  
63 hydroxymethyl group substitutions in ortho and para positions of the phenolic ring, usually  
64 called methylol [15,20]. A self-condensation then takes place through the reaction of two  
65 methylol groups and produces oligomers consisting of a phenolic ring linked by a methoxy  
66 bridge. This latter is further transformed into a methylene bridge with the loss of  
67 formaldehyde. The condensation finally leads to the final network of the resole constituted  
68 of phenolic rings linked by methylene bridges [21,22]. In addition, resoless used for can  
69 coating formulations are usually solubilized in alcoholic solvents, such as butanol, which can  
70 lead to the etherification of residual methylol [15,16]. Several phenolic resins can be used in  
71 a coating formulation being added to polyester, epoxy or acrylic resins in order to give  
72 specific performances to the cured coating, thereby adding potential new NIAS due to the  
73 multiplicity of raw materials.

74 The present study focuses on the detection, identification and semi-quantification of NIAS  
75 extracted from polyester-phenolic can coatings. Model formulations were prepared with  
76 high concentrations of resole of different natures: based on phenol, cresol or 4-tertbutyl  
77 phenol (TbuP). Coatings with one resole each were applied and cured. Gas chromatography  
78 (GC) coupled to mass spectrometry (MS) and high resolution mass spectrometry (HRMS)  
79 analyses were conducted after extraction into acetonitrile. Liquid chromatography coupled  
80 to mass spectrometry (LC-MS) is one of the most used analytical techniques in literature for  
81 FCM extraction and migration analyses. But the chemical structure of phenolic molecules  
82 makes them not well adapted for LC-MS analysis. The expected phenolic molecules (**Figure**  
83 **1**) are difficult to charge with the usual positive ionisation, leading to a low sensitivity, while  
84 the overall signal is usually lower with a negative ionisation. These problems linked to the

85 ionisation could be one of the reasons for the scarce literature on phenolic NIAS. On the  
86 other side, GC-MS has already been used to analyse resoles [15–17], where the main  
87 oligomers were found between 100 and 600 Da, but never to identify extracted NIAS due to  
88 substituted phenol based resole in can coatings. Theoretical databases and HRMS were used  
89 for the identification of NIAS and further mono and bi-dimensional nuclear magnetic  
90 resonance (NMR) spectroscopy analyses were done to overcome identification uncertainty.

## 91 **1. Materials and methods**

### 92 **1.1. Reagents**

93 Acetonitrile (LC-MS Chromasolve grade, >99.9%) for extractions and calibration solutions  
94 was purchased from Honeywell (Levallois Perret, France). Acetonitrile is one of the best  
95 extractants for polyester coatings and does not lead to hydrolysis of polyester oligomers  
96 [23].

97 Deuterated acetonitrile-d<sub>3</sub> (99,6% D) from CEA (France) was used as solvent in NMR analysis.

98 Analytical standards 4-tert-butyl-2,6-diformylphenol (CAS 84501-28-0, >96%) was purchased  
99 from Sigma-Aldrich (Saint Louis, MO, USA), Diethyl terephthalate (CAS 636-09-9, >99,0%)  
100 from TCI Chemical (Tokyo, Japan) and Ethylene Terephthalate Cyclic Dimer (CAS 24388-68-9,  
101 98%) from Toronto Research Chemicals (Toronto, Canada). All chemicals used for coating  
102 preparation were supplied by Valspar and formulations are proprietary to Valspar.

### 103 **1.2. Coating's formulation and curing**

104 Six different polyester-phenolic coatings were prepared based on a model formula, using in  
105 each of them one specific phenolic resin:

106 – Phenol based (P-1, P-2 & P-3)

107 – Cresol based (C-1)

108 – Tertbutyl phenol (TbuP) based (TbuP-1 & TbuP-2)

109 Formulas were developed to feature 20% of resole in its non-volatile content. All coatings  
110 were prepared following the same protocol. To a polyester resin, solvents (acetate and  
111 diacetate mix), slip agent and defoamer were added under stirring. A caprolactam blocked  
112 isophorone diisocyanate solution and a resole were then added. Wax and catalyst were  
113 finally added to complete the formulation. In addition, a polyester coating without phenolic  
114 resin was prepared.

115 The polyester resin is based on isophthalic (IPA) and terephthalic acid (TPA), ethylene glycol  
116 (EG), neopentyl glycol (NPG), hexan-1,6-diol (HD) and trimethylolpropane. IPA and TPA are  
117 referred as phthalic acid as both isomers cannot be differentiated in mass spectrometry.  
118 Electrolytic tin plates were coated using a wire-wound bar to obtain a 10g/m<sup>2</sup> cured film.  
119 Coated plates were cured for 14min at 205°C in a calibrated electric oven to mimic real  
120 temperature profile of a 10min at 200°C industrial cure and take into account the loss of  
121 temperature due to the door opening and its restabilisation.

### 122 **1.3. Sample extraction and preparation**

123 Two extractions were done for each formulation. For each extraction experiment, a 6 cm x  
124 25 cm band (1,5dm<sup>2</sup> area) was cut from a coated panel. The band was then cut into smaller 3  
125 cm x 5 cm pieces. Pieces were folded in an accordion style, to ensure that the entire surface  
126 was available to the extraction solvent and placed in a glass bottle. 50 mL of acetonitrile was  
127 added, and the bottle was tightly shut and left for 24 hours at 40°C. Extractions at room  
128 temperature, 40°C and 60°C for 24 hours were carried out but no difference was observed.  
129 40°C extraction was chosen as final procedure.

130 20 mL of the extract were collected and concentrated to 2 mL by evaporation before GC-MS  
131 and GC-Orbitrap analysis. Diethyl terephthalate (DET) was spiked in the sample as an  
132 internal standard to ensure no matrix effect or injection failure may have occurred during  
133 the analysis.

#### 134 **1.4. Instrumentation**

##### 135 **1.4.1. Screening and semi-quantification by GC-MS**

136 Initial screening used a 6890N GC gas chromatography equipped with a 7683 autosampler  
137 hyphenated to a 5975 inert XL MSD mass spectrometer from Agilent Technologies (Santa  
138 Clara, CA, USA) with electronic impact (EI) ionization (70eV). Extracts were injected without  
139 derivatisation to avoid unpredicted chemical reactions and ease the identification process.  
140 1µL of sample was injected in splitless mode with an injector temperature set at 280°C.  
141 Helium was used as carrier flow with a 1mL/min flow. An HP-5MS capillary column (30 m x  
142 0.25 mm x 0.25 µm, Agilent Technologies) was used for the separation. The oven program  
143 started at 80°C for 2 min, increased to 270°C at 10°C/min, held for 20 min before a last ramp  
144 to 320°C at 5°C/min and then held for 15 min. The scanning mass range was from 50 to 750  
145 Da.

146 Data treatment was done on MSD Chemstation software. Integration parameters set at a  
147 minimum peak area of  $10^5$  and a threshold of 15 while NIST 14 and Wiley 275 databases  
148 were used for tentative identification.

149 Semi-quantification was realised by an internal standard quantification with diethyl  
150 terephthalate as internal standard. As analytical standards were not available for most of the  
151 identified NIAS, the closest available molecules were used. 4-tert-butyl-2,6-diformylphenol  
152 calibration curve was used for phenol-based molecules and ethylene terephthalate cyclic



153 dimer for polyester oligomers. Response factors were considered as equivalent to those of  
154 their respective standard. Calibration curves were established from 1 to 50µg/mL with  
155  $R^2 > 0,99$ . The calibration curves lead to a LOQ of 10µg/dm<sup>2</sup> for ethylene terephthalate cyclic  
156 dimer and 6µg/dm<sup>2</sup> for 4-tert-butyl-2,6-diformylphenol.

#### 157 **1.4.2. Screening and identification by GC-Orbitrap**

158 A Q-Exactive Orbitrap mass spectrometer with EI ionisation, hyphenated to a Trace 1310 GC  
159 and TriPlus RSH autosampler from Thermo Scientific (Bremen, Germany), was used for GC-  
160 HRMS screening. PTV injector was set at 280°C and 1µL of sample was injected in splitless  
161 mode. Helium was used as carrier gas with a 1.2mL/min flow. Separation was done on a TG-  
162 5SILMS capillary column (30 m x 0.25 mm x 0.25 µm, Thermo Scientific). The oven  
163 temperature started at 80°C with an initial hold of 4 min before a ramp to 320°C at 10°C/min  
164 and held for 15 min. Mass spectrometer was set to a resolution of 60000 FWHM (m/z 200)  
165 on full scan with a range scan from 50 to 750 Da. The automatic gain control (AGC) was  
166 targeted at 10<sup>6</sup> with a maximum injection time of 200ms. Two different electron energies  
167 were used: 70eV and 10eV. Data were processed with Xcalibur and TraceFinder 4.1 (Thermo  
168 Scientific). Screening for compounds used TraceFinder with a threshold TIC of 10<sup>7</sup>, S/N of  
169 100 and ion overlap at 97%.

170 A fragmentation at 70eV was used for all samples, allowing spectra comparison with NIST 2.2  
171 database. A second analysis using 10eV fragmentation energy was carried out in order to  
172 avoid avoiding fragmentation and approaching the molecular mass of the compounds. The  
173 combination of both HRMS spectra is used for the identification process of unknown NIAS:  
174 the monoisotopic mass and molecular formulas of fragments were proposed by the software  
175 within a 5 ppm mass deviation between theoretical and experimental masses. NIAS could be

176 identified using combinations of molecular formulas, associated rings and double bonds  
177 (RDB) equivalent, fragmentation patterns, databases and literature.

### 178 **1.4.3. Identification by $^1\text{H}$ and $^{13}\text{C}$ -NMR**

179 For NMR analysis, extract samples and phenolic resins were taken up in deuterated  
180 acetonitrile after evaporation of the extraction solvent. A Bruker Avance III HD 400 from  
181 Bruker at 30°C with a 5mm PABBO BB/19F-1H/D Z-GRD probe was used. Samples were  
182 characterised by  $^1\text{H}$ ,  $^{13}\text{C}$  and DEPT135 mono-dimensional spectra as well as HSQC and HMBC  
183  $^1\text{H}$ - $^{13}\text{C}$  bi-dimensional experiments to observe proton-carbon correlations. Spectra were  
184 calibrated to the solvent signal.

### 185 **1.5. Theoretical databases**

186 To help the identification of NIAS, a predictive database was created, listing all possible  
187 polyester oligomers with a molecular weight less than 1000 Da. The limit of 1000 Da was  
188 chosen as only molecules with a molecular weight inferior to 1000 Da are considered to be  
189 possibly assimilated by the organism through the gastrointestinal tract [2,24]. Knowing the  
190 polyester resin monomeric composition, all the possible linear and cyclic oligomer  
191 combinations can be predicted from the successive esterifications. A set of iterative  
192 procedures were developed in Microsoft Excel Visual Basic for Applications (VBA) to  
193 automatize the process for any monomer composition and to calculate molecular mass for  
194 future analysis. More than 250 possible oligomers were obtained with the monomeric  
195 composition of the resin used in the formulas. A similar method was used for phenolic resin  
196 databases which proposed around 400 possible oligomers based on phenol and 150  
197 oligomers for each cresol and TbuP.

## 198 **2. Results and discussion**

## 199 2.1. NIAS associated to polyester resin

### 200 2.1.1. Identification by GC-HRMS

201 Due to their unexpected nature and the use of several raw materials in the coating  
202 formulation, NIAS analysis and identification are usually a complex analytical task [25].  
203 However, the generalisation of HRMS technology and the access to accurate mass is an  
204 important tool for the identification of unknown molecules which are absent from databases  
205 or without available analytical standards [26,27]. Although HRMS analysis treatment can be  
206 demanding, accurate mass coupled to calculated databases is a powerful aid to identify  
207 NIAS. Literature, particularly for polyester oligomers, was used as well to ensure the  
208 identification [6,28–31].

209 Identification in GC-MS is more complex due to the loss of the monoisotopic mass in most of  
210 the cases. The use of 10eV fragmentation energy, in addition to the usual 70eV, allows  
211 approaching the monoisotopic mass which coupled to accurate mass help to identify  
212 unknown compounds.

213 The polyester coating without phenolic resin was used to identify NIAS which were  
214 associated to the polyester resin. The identification has been done following the protocol  
215 presented in **Figure 2**.

216 In the case studied in **Figure 2**, fragmentation pattern and proposed molecular formula of  
217 the fragments indicate the presence of aromatic rings with at least 8 oxygens and 13 RDB,  
218 suggesting that the unidentified NIAS was a polyester oligomer composed of at least two PA.  
219 To refine identification, a silylation of the sample [32] to differentiate cyclic and linear  
220 oligomers was carried out, which led the identification to a cyclic oligomer. In parallel,  
221 available databases were compared to experimental results. As a result, the NIAS was

222 identified as a cyclic oligomer based on two EG and at least one IPA. This protocol allowed  
223 the identification of 13 different cyclic oligomers of polyester based on EG, NPG and HD with  
224 different isomers due to IPA and TPA combinations (Table 1).

225 Polyester oligomers were only identified as cyclic oligomers. This prevalence can be  
226 explained by the resin synthesis with high molecular weight. The polyester resin used is  
227 specified with an average molecular weight ( $M_n$ ) higher than 5000 Da, short linear chains  
228 are very small proportions of the initial resin. Furthermore, linear oligomers are expected to  
229 react during the curing of the coating with the diisocyanate cross-linker due to their pendant  
230 functions. On the contrary, once cyclic oligomers are formed during the resin synthesis, they  
231 would not be able to further react during the overall curing process. They would not be  
232 chemically linked to the coating network and therefore could be extracted [6,8]. This  
233 tendency is accentuated by the fact that extraction is done in a solvent with which no  
234 hydrolysis can occur [23].

### 235 **2.1.2. Polyester oligomers semi-quantification**

236 Polyester oligomers were quantified using the cyclic TPA-EG-TPA-EG calibration. The  
237 quantities of oligomers were compared to observe the influence of the resole chemistry on  
238 the quantity of extracted polyester oligomers (Table 2).

239 Formulas with phenol based resole have a total oligomer content ranging from 363 to 467  
240  $\mu\text{g}/\text{dm}^2$ . Results for the three other coatings have comparable levels of oligomers, 447 and  
241 506  $\mu\text{g}/\text{dm}^2$  in the two TbuP cases and 397  $\mu\text{g}/\text{dm}^2$  for the cresol-based formula.

242 Quantification results are in line with previous studies on polyester coatings where individual  
243 cyclic oligomers or total oligomer contents were quantified in acetonitrile and ethanol  
244 extractions [3,4,30]. The choice of resole used in the formulation has no specific impact on

245 the quantities of extracted oligomers of polyester. The noted variations from one formula to  
246 another are judged more likely to be due to the variation of resin quantity from one coating  
247 to another during its formulation rather than an effect of the resole. Moreover, the non-  
248 influence of the resole toward cyclic oligomers may be related to the absence of reactive site  
249 on the cyclic oligomers or any hydrolysis possibility during the coating formulation and cure.

## 250 **2.2. NIAS associated to phenolic resins**

### 251 **2.2.1. Identification by GC-HRMS**

252 Analysis of extracts from formulations with alkylated phenol-based resole had  
253 chromatograms with intense peaks which were not detected in phenol-based formula. This  
254 is particularly observed in TbuP-1 and Tbu-2 extracts, where respectively 42 and 26  
255 additional peaks were detected. With C-1-based coating, only 4 peaks were specifically  
256 observed, with lower intensities. The same protocol as for polyester oligomers had been  
257 applied on the experimental spectra to identify those compounds (**Figure 2**). Some of these  
258 new peaks could be identified as usual phenolic oligomers based on a tertbutyl-phenol base  
259 with methylol and butylated methylol substitutions. Yet, the most intense peaks could not  
260 be identified with this method. A conflict appeared between proposed molecular formula,  
261 expected phenolic oligomers and the NIST identification. Different alkylated phenols were  
262 proposed by the NIST database with low match results and accurate masses did not match  
263 with the molecular formula of predicted oligomers. Taking one of the most intense  
264 unidentified peaks as an example, proposed molecular formula and fragmentation patterns  
265 were indicating an expected tertbutyl substitution noticeable through the loss of  $\text{CH}_3$  ( $m/z =$   
266  $191.0702$ ) and  $\text{C}_3\text{H}_7$  ( $m/z = 163.0389$ ) from the monoisotopic mass ( $m/z=206.0937$ ) (**Figure**  
267 **3**). Its proposed formula was  $\text{C}_{12}\text{H}_{14}\text{O}_3$  and by considering the presence of tertbutyl  
268 substitution on the phenolic ring, the only possible structure was the addition of two

269 aldehyde functions on the aromatic ring. This particular compound identification was  
270 suspected to be 4-tert-butyl-2,6-diformylphenol. The presence of that aldehyde substitution  
271 was suspected for several unidentified NIAS.

272 The presence of multiple suspected aldehyde molecules was not expected as no mention of  
273 this chemistry appears in the literature relative to coating extraction, migration or even in  
274 other FCMs. Those compounds are linked to the use of TbuP resole since they were only  
275 observed in samples from coatings TbuP-1 and TbuP-2. Biederman and Grob highlighted the  
276 presence of compounds which did not fit the usual scheme of phenolic oligomers in the TbuP  
277 resole itself, but no identification was done [17].

278 Looking at C-1 extraction, specific peaks are fewer and less intense than those observed in  
279 TbuP analysis, but aldehyde molecules were suspected as well.

### 280 **2.2.2. Liquid coatings and TbuP resoles analyses**

281 The few studies mentioning aldehyde presence were done on the resole [33–36]. Both the  
282 liquid coatings and the TbuP resoles were directly extracted in acetonitrile by manual  
283 shaking followed by a 10min centrifugation at 1465 RPM. Supernatant was directly injected  
284 in GC-MS and chromatograms were compared with those of cured coating extractions.

285 All peaks specifically observed in the TbuP cured coating extracts were present in both liquid  
286 coating and initial resole. Therefore, these compounds were suspected as side products of  
287 TbuP resole synthesis.

### 288 **2.2.3. Validation of one specific NIAS identification**

289 A standard of 4-tert-butyl-2,6-diformylphenol was purchased and analysed with the same  
290 analytical method as for coating extracts. The standard showed the same retention time and

291 fragmentation in GC-MS analysis as its suspected peak (**Figure 4**). The presence of the  
292 multiple aldehyde molecules is then a plausible hypothesis and this standard was used for  
293 semi-quantification of NIAS from the phenolic resins.

#### 294 **2.2.4. Validation of the identification of aldehydes by NMR**

295 Cured coating extracts were insufficiently concentrated for  $^{13}\text{C}$  NMR. The signal intensity was  
296 sufficient to observe additional peaks in TbuP-1 by  $^1\text{H}$  NMR. Specific peaks were observed  
297 when compared to P-2 spectrum. Those protons were found with chemical shift ( $\delta$ ) of 10.6,  
298 multiple peaks from 8.5 to 7.6 ppm, 5.7 and 2 ppm. The signal at 10.6 ppm is specific to the  
299 presence of aldehyde or carboxylic acid functions. Protons at 8.5 and 7.6 ppm are in the  
300 range of aromatic protons and could be related to protons with specific chemical shifts due  
301 to the aldehyde substitution. Concerning the proton at 2 ppm, it is likely related to the  
302 hydrogen of the tertbutyl group.

303 In order to improve the signal intensity, extractions of liquid coatings TbuP-1 and P-2 were  
304 analysed. This way not only  $^1\text{H}$ ,  $^{13}\text{C}$  and 135DEPT but  $^1\text{H}$ - $^{13}\text{C}$  bi-dimensional experiments HSQC  
305 and HMBC (**Figure 5**) could be done to identify the presence of aldehyde functionality and its  
306 position in the molecule structure. HSQC shows correlations between carbons and  
307 hydrogens which are directly bonded while correlations between carbons and protons  
308 separated by two or three chemical bonds are obtained using HMBC.

309 The protons specifically detected by  $^1\text{H}$  NMR were correlated to their corresponding  $^{13}\text{C}$   
310 NMR signals (**Table 3**). A peak at 199 ppm in  $^{13}\text{C}$  NMR with a corresponding positive peak in  
311 135DEPT is correlated with the 10.6 ppm proton. This chemical shift and DEPT value are  
312 specific of primary and tertiary carbons from carbonyl functions. Considering the previous  $^1\text{H}$

313 NMR conclusions, the only possibility to observe such a carbon-proton correlation is the  
314 presence of an aldehyde function.

315 Moreover, using correlation in HMBC, the  $^1\text{H}$  signal of the aldehyde is correlated with  
316 aromatic carbons, with  $\delta^{13}\text{C}$  varying from 121 ppm to 158 ppm. These carbons are clearly  
317 identified as aromatic with their HSQC correlations with hydrogens with  $\delta^1\text{H}$  of 7.6 ppm to  
318 8.5 ppm. The aldehyde function is then substituted to the aromatic ring, which is in line with  
319 the suspected structure given to the NIAS.

320 Concerning the proton at 5.7 ppm, it was correlated in HSQC with a carbon at 70 ppm with a  
321 negative DEPT value. In parallel, the proton was correlated to the aromatic carbons by  
322 HMBC. This signal could be attributed to the methylol substitution as a secondary carbon  
323 was expected from DEPT spectrum and both chemical shifts are in line with theoretical ones.

324 In conclusion of the NMR analysis, using both chemical shifts and correlations, similar  
325 structures to 4-tert-butyl-2,6-diformylphenol matched the experimental specific signals in  
326 TbuP-1 spectra. The hypothesis stated with the GC-HRMS analysis was then validated: newly  
327 identified aldehydes are present in coating extractions. The origin of those compounds was  
328 attributed to the resole itself as a potential side-product of its synthesis.

#### 329 **2.2.5. Influence of resole nature on extracted NIAS from can coatings**

330 Following the validation of aldehyde presence, 28 NIAS from TbuP-based coatings could be  
331 identified and molecular formula proposed. A semi-quantification of all peaks due to  
332 phenolic resins was done using 4-tert-butyl-2,6-diformylphenol as standard (**Table 4 & Table**  
333 **5**).



334 Butyl substitution was identified as well and was related to the presence of butanol or  
335 tertbutanol in resole which can react with pendant methylol groups. Concerning methyl  
336 substitution, the methyl presence was not necessarily related to an etherification of a  
337 pendant methylol. From proposed molecular formula, more particularly the number of  
338 oxygens, methyl substitution has been suspected as a direct substitution on the aromatic  
339 ring.

340 No reference to aldehyde in resoles could be found in the literature regarding NIAS analyses  
341 in can coatings. As phenolic resins are used in other polymeric applications, a few studies  
342 have been found mentioning aldehydes presence in resole. TbuP+F had been identified in a  
343 TbuP based resin used in ink pen [33]. Aldehydes have been seen in phenol based resole  
344 [34–36]. Bouajila et al. proposed a mechanism using a cleavage of the methoxy bridge into  
345 an aldehyde and a methyl-substituted phenol. Such mechanism could explain the presence  
346 of the methyl substitution on the aromatic ring. Regardless, the oxidation of methylol into  
347 aldehyde could be the result of different mechanisms such as an oxydo-reduction reaction  
348 between phenolate and formaldehyde (**Figure 6**).

349 While tested phenol and cresol-based resoles were responsible for respectively none and  
350 very few extracted NIAS, TbuP-based resoles were sources of several phenolic compounds.  
351 Moreover, the presence of those compounds was not negligible, as the NIAS due to the TbuP  
352 resoles were more abundant in the film extracts than polyester oligomers (**Figure 7**). The  
353 most abundant phenolic NIAS was semi-quantified at 137 and 249  $\mu\text{g}/\text{dm}^2$  in TbuP-1 and  
354 TbuP-2 extracts. In comparison, the most abundant polyester oligomer was quantified at 226  
355 and 178  $\mu\text{g}/\text{dm}^2$  in the corresponding extracts. Moreover, while cyclic oligomer EG-PA-EG-PA  
356 is the only oligomers found in quantities higher than  $50\mu\text{g}/\text{dm}^2$ , 4 phenolic NIAS were found  
357 in higher concentrations in TbuP-1 and 3 in TbuP-2, notably with a concentration of 249

358  $\mu\text{g}/\text{dm}^2$  for TbuP + F + MOH , which is the most abundant NIAS found in all the analyses. The  
359 choice of the resole for the formulation of a can coating was then a major parameter to limit  
360 the extracted quantity of NIAS from can coatings.

### 361 **3. Conclusion**

362 To investigate the influence of phenolic resins on NIAS extractions of can coatings, six  
363 different model coatings were formulated, each using one specific resole. Different resoles  
364 based on phenol, cresol and TbuP were used.

365 Two groups of NIAS were identified in film extracts thanks to predictive databases of  
366 oligomers and HRMS treatment: cyclic polyester oligomers, already reported in literature,  
367 and NIAS specifically found in alkylated phenol-based resoles. While the choice of resole had  
368 no impact on the quantity of cyclic oligomers of polyester, the use of TbuP-based resoles led  
369 to the detection of an important number of specific NIAS among which the most abundant  
370 were identified as aldehydes. 4-tertbutyl-2,6-diformyl phenol was directly identified by GC-  
371 MS and the presence of a formyl group substituted on the phenolic ring had been  
372 demonstrated by bi-dimensional NMR. Moreover, the aldehyde components were not only  
373 found in film extracts but also in liquid coating and resole extracts, thus the NIAS were  
374 directly present in the native resole as side-products of their production process and were  
375 not produced within the formulation or the cure of the coating.

376 These new aldehyde molecules were never identified in FCM literature. While absent or only  
377 detected at marginal levels in phenol and cresol-based phenolic coatings, these aldehyde  
378 substituted phenols were semi-quantified in larger amounts than the polyester oligomers in  
379 TbuP-based phenolic coatings and should be further studied in future analysis. The absence  
380 of phenolic NIAS in phenol-based resole could be explained by the additional active site on

381 the phenolic ring. Contrary to alkylated phenols, aldehydes produced during the synthesis of  
382 the resole are more easily included in the overall polymeric network during the  
383 condensation thanks to the two remaining active sites, preventing their extraction. In the  
384 same way, the difference between cresol and TbuP may be due to the more sterically  
385 hindered tertbutyl group, decreasing the condensation rate and favouring side reactions of  
386 the smaller oligomers (**Figure 6**) leading to the formation of aldehydes. Another hypothesis  
387 could be the differences of process for the resoles synthesis. Because of the different end  
388 applications and reaction rates of monomers, specific processes for TbuP resole production  
389 could enhance the side production of aldehydes.

390 Finally, considering the risk assessment of these new NIAS, further studies are needed as  
391 current testing was performed on model formula designed to specifically study the presence  
392 of phenolic related NIAS. Migration tests on commercial can coatings should verify the  
393 presence and the quantities of these compounds in real situations of food contact with TbuP  
394 phenolic coatings, since food simulants and ultimately real foodstuff can have different  
395 extracting capacities than acetonitrile [23] and since commercial formulas usually use a mix  
396 of different phenolic resins at different ratios. Further evaluations of the identified aldehyde  
397 substances must be realised, especially regarding their more accurate quantification and  
398 toxicology in order to determine safe levels of exposure in case some would ultimately  
399 migrate into food. Organoleptic profile of the substances could as well be of interest, some  
400 aldehydes being known to be flavouring or fragrant. These findings, integrated in the  
401 selection of raw materials according to a Safety-by-Design approach may be very useful to  
402 contribute to the design of future low migration coatings.

403 **Authorship contribution statement**

404 **Julien Terrasse:** Conceptualization, Methodology, Validation, Formal analysis, Investigation,  
405 Writing – original draft, Writing – review & editing, Visualisation. **Marie Martin:** Formal  
406 analysis, Validation, Writing – review & editing. **Sarah Dubail:** Conceptualization,  
407 Supervision, Project administration, Funding acquisition, Writing – review & editing. **Hervé**  
408 **Casabianca:** Conceptualization, Supervision, Project administration, Funding acquisition,  
409 Writing – review & editing. **Patrice Dole:** Conceptualization, Supervision, Project  
410 administration, Funding acquisition, Writing – review & editing.

#### 411 **Declaration of competing interest**

412 The authors declare that they have no known competing financial interests or personal  
413 relationships that could have appeared to influence the work reported in this paper.

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422 Bresse, France).

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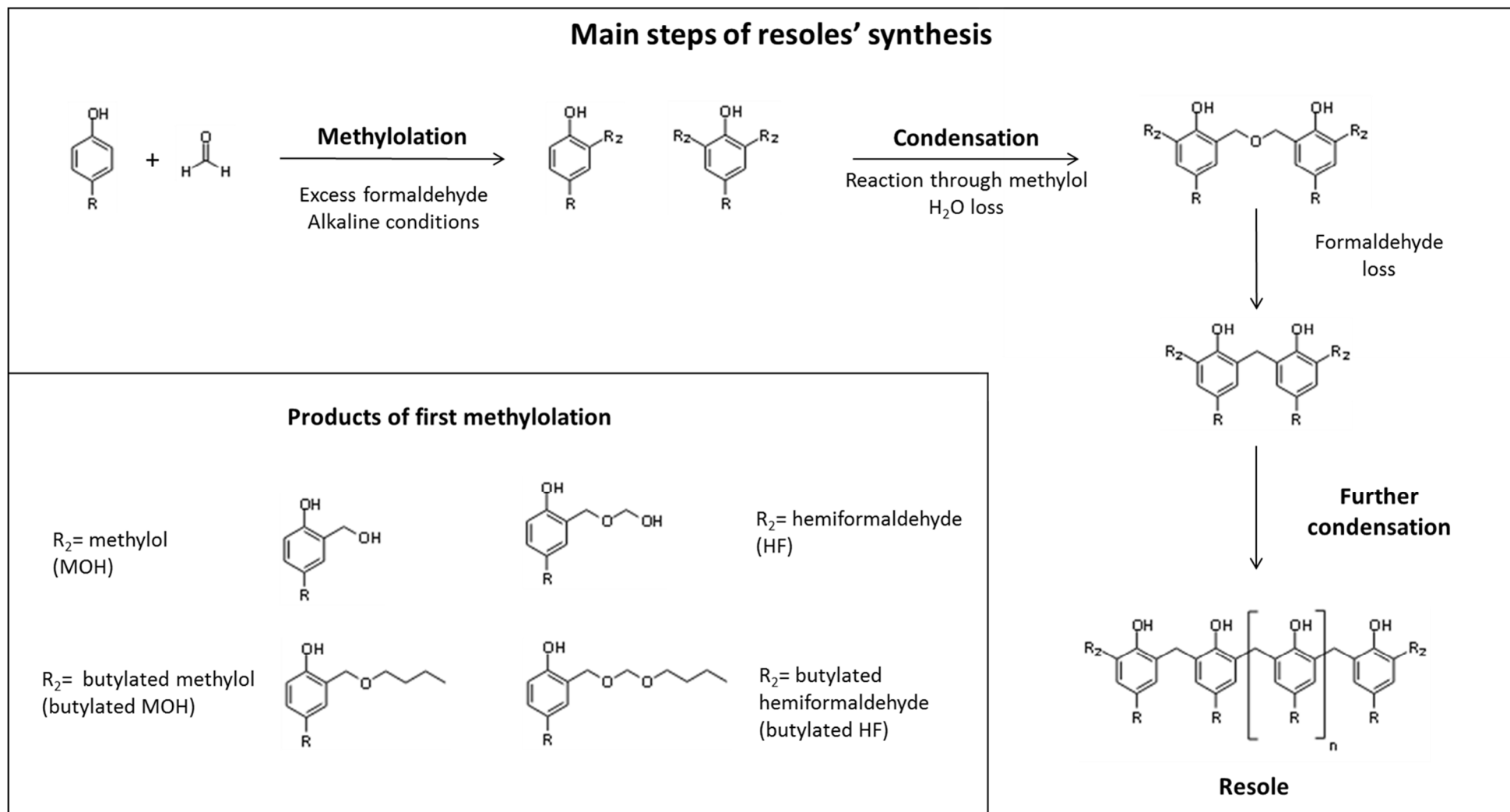
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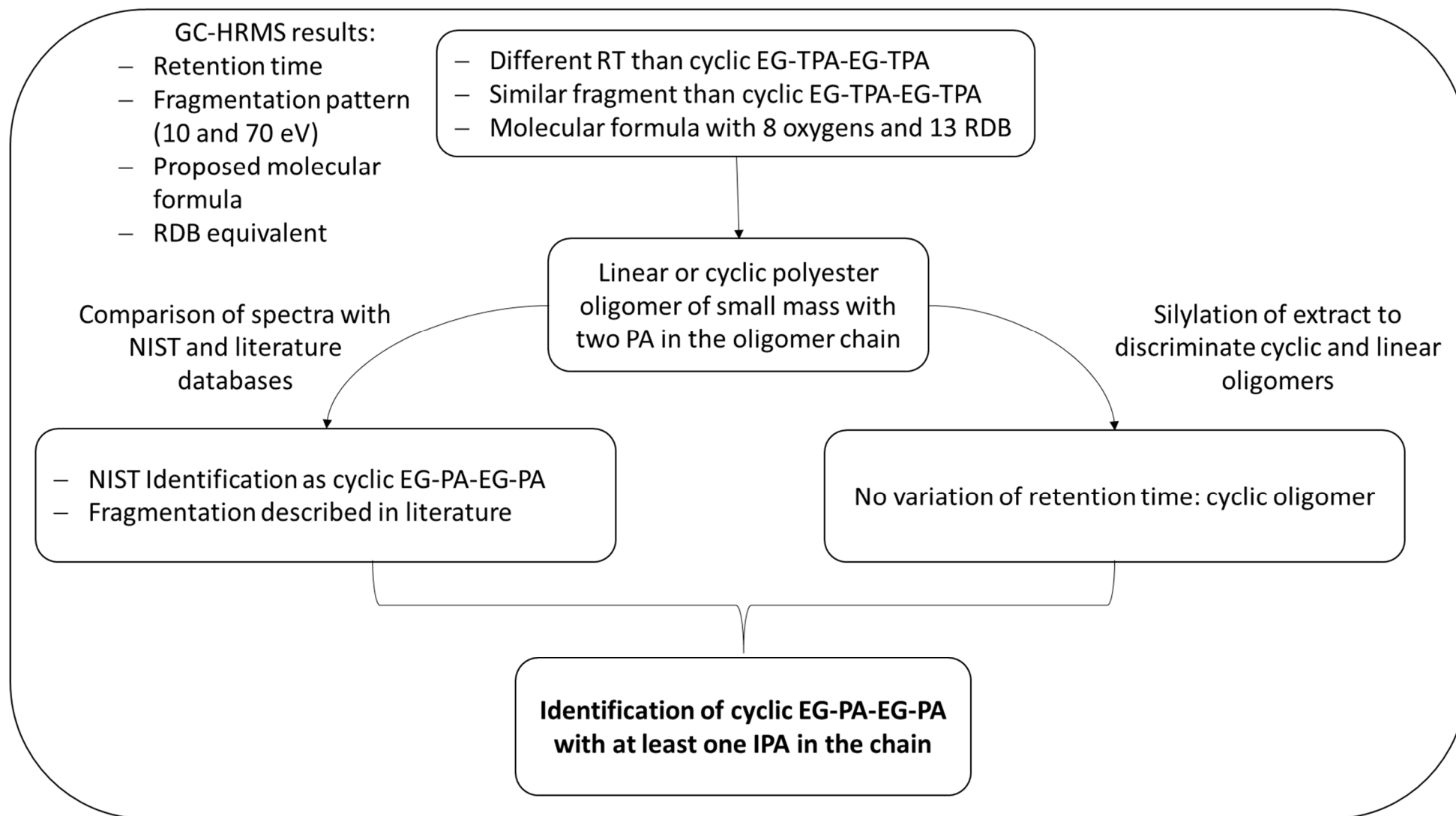
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555 *Figure 1: Main steps of resoles' synthesis and products of first methylation*

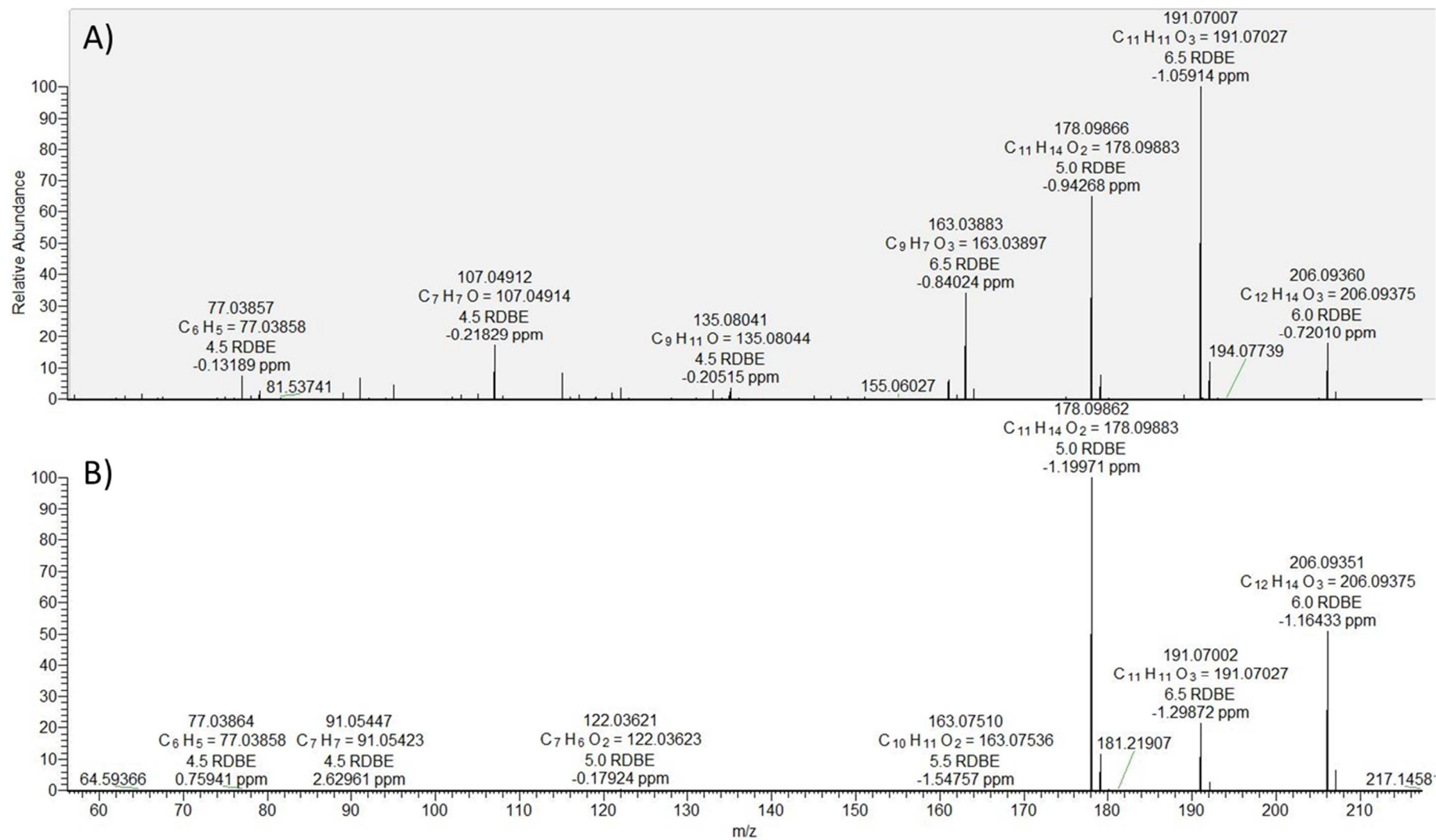


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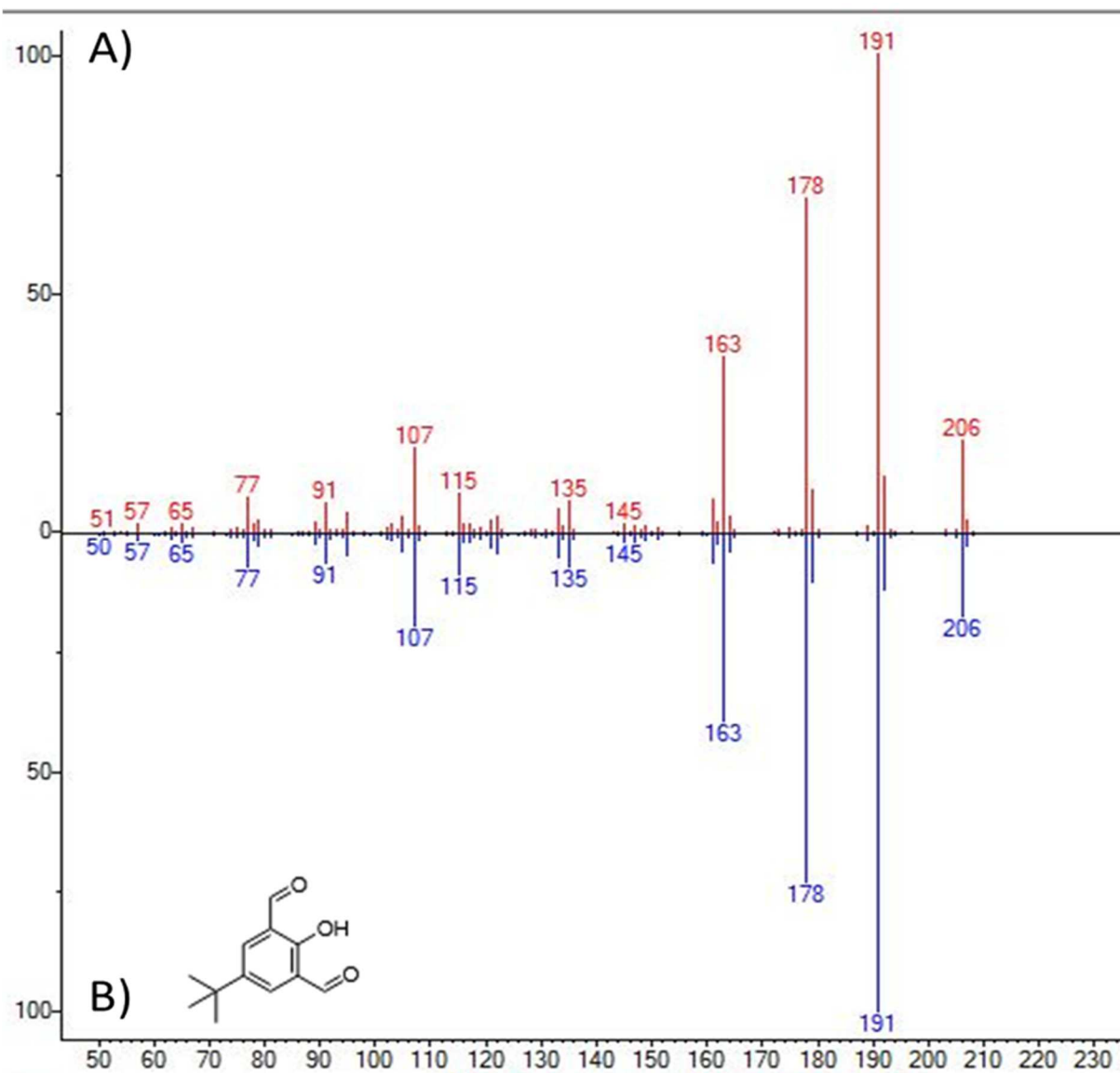




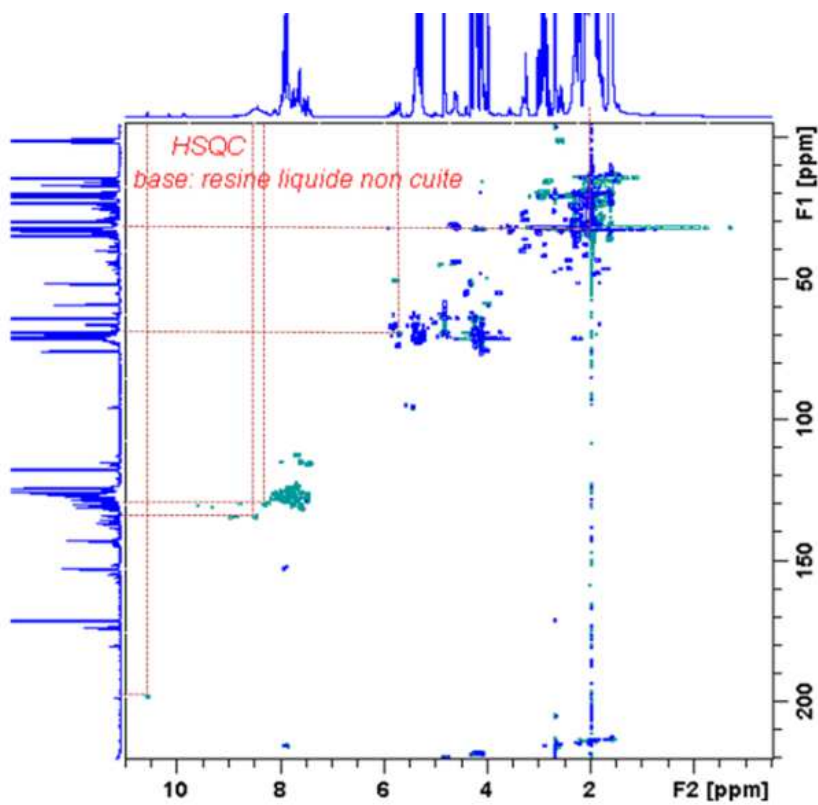
559 Figure 3: 70eV(A) and 10eV (B) mass spectra of unknown peak at RT=13.0 min in *TbuP* formulations



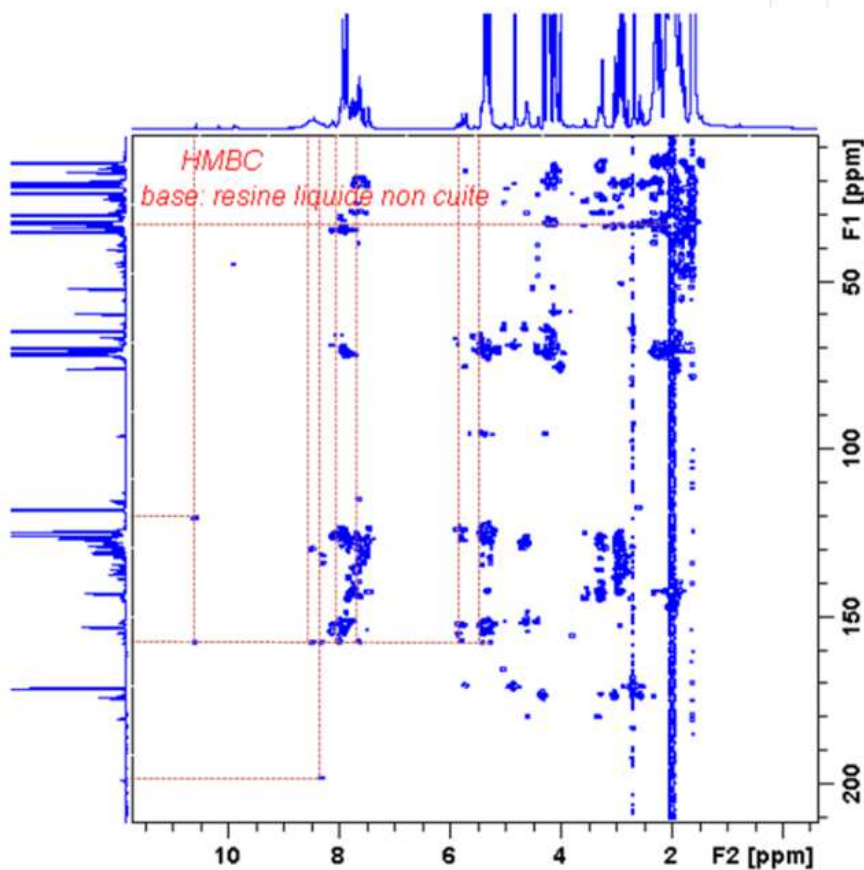
561 Figure 4: Comparison of mass spectra between A) Unknown peak at RT=13.0 min and B) 4-tert-butyl-  
562 2,6-diformylphenol standard



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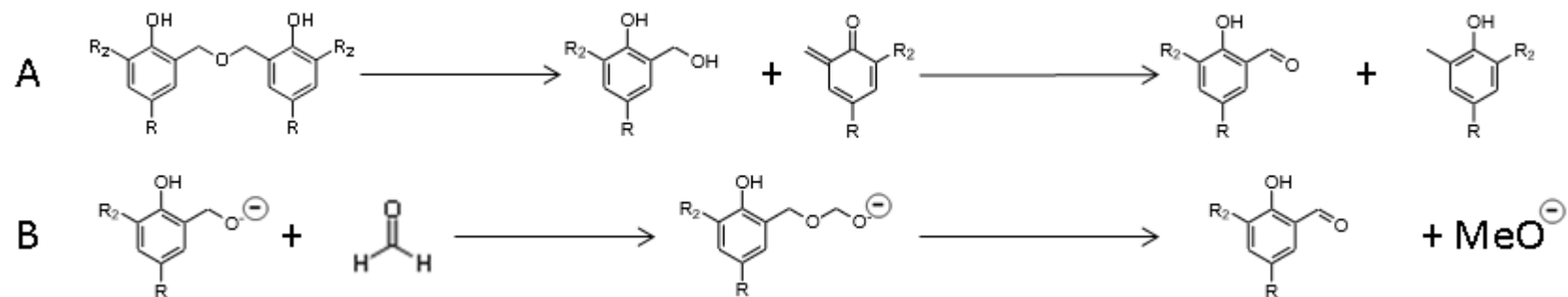


HSQC correlation



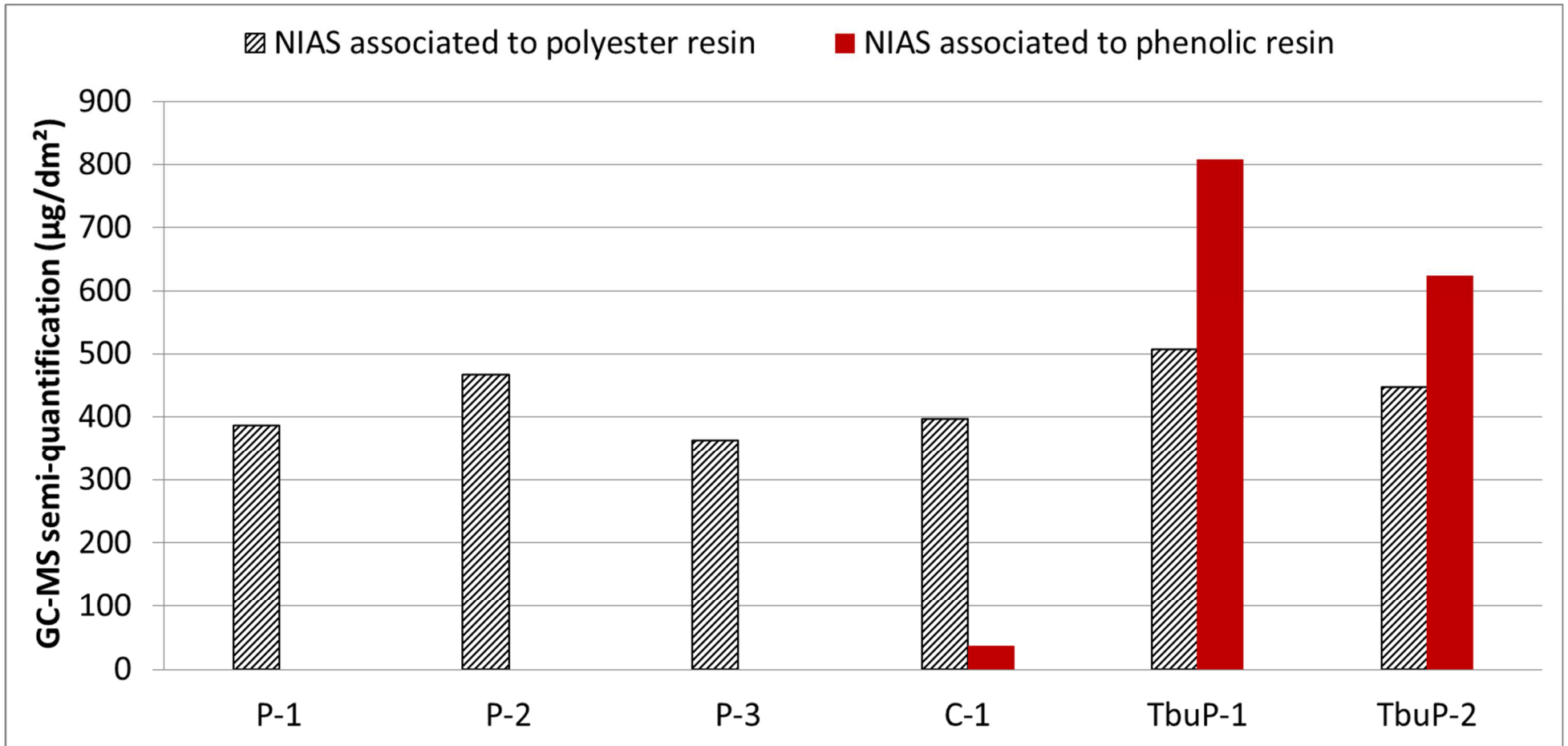
HMBC correlation

566 Figure 6: A) Mechanism of Bouajila et al - B) Oxydo-reduction of phenolate with formaldehyde



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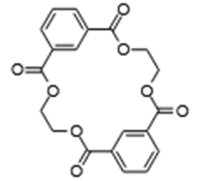
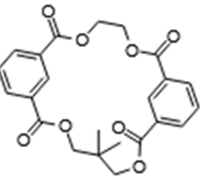
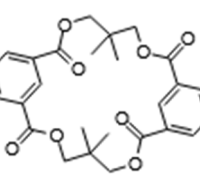
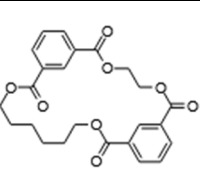
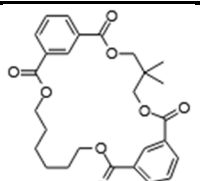
568 Figure 7: Comparison of phenolic and polyester resin influence on extracted NIAS in GC-MS semi-quantification

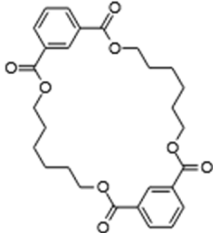


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571 Table 1: Identified polyester oligomers in coating extracts

Retention time (min)	Identification	Formula	Monoisotopic mass, mass deviation	Main fragment, associated molecular formula, mass deviation	Possible isomer IPA based
33.0	cyclic EG-PA-EG-PA	C <sub>20</sub> H <sub>16</sub> O <sub>8</sub>	384.0845 (not observed)	341.0653 / C <sub>18</sub> H <sub>13</sub> O <sub>7</sub> / -0.88 ppm	
				359.0761 / C <sub>18</sub> H <sub>15</sub> O <sub>8</sub> / -0.24 ppm	
35.2	cyclic EG-PA-NPG-PA	C <sub>23</sub> H <sub>22</sub> O <sub>8</sub>	426.1309 / -0.08 ppm	341.0653 / C <sub>18</sub> H <sub>13</sub> O <sub>7</sub> / -0.88 ppm	
				359.0761 / C <sub>18</sub> H <sub>15</sub> O <sub>8</sub> / -0.24 ppm	
				401.1229 / C <sub>21</sub> H <sub>21</sub> O <sub>8</sub> / -0.41 ppm	
39.0	cyclic NPG-PA-NPG-PA	C <sub>26</sub> H <sub>28</sub> O <sub>8</sub>	468.1773 / -1.07 ppm	383.1122 / C <sub>21</sub> H <sub>19</sub> O <sub>7</sub> / -0.81 ppm	
41.5				401.1229 / C <sub>21</sub> H <sub>21</sub> O <sub>8</sub> / -0.41 ppm	
43.5				468.1773 / C <sub>26</sub> H <sub>28</sub> O <sub>8</sub> / -1.07 ppm	
44.8	cyclic EG-PA-HD-PA	C <sub>24</sub> H <sub>24</sub> O <sub>8</sub>	440.1471 (not observed)	341.0653 / C <sub>18</sub> H <sub>13</sub> O <sub>7</sub> / -0.88 ppm	
45.2				359.0761 / C <sub>18</sub> H <sub>15</sub> O <sub>8</sub> / -0.24 ppm	
46.3				410.1359 / C <sub>23</sub> H <sub>22</sub> O <sub>7</sub> / -0.32 ppm	
49.0	cyclic NPG-PA-HD-PA	C <sub>27</sub> H <sub>30</sub> O <sub>8</sub>	482.1935 / -0.62 ppm	383.1122 / C <sub>21</sub> H <sub>19</sub> O <sub>7</sub> / -0.81 ppm	
49.3				415.1388 / C <sub>22</sub> H <sub>23</sub> O <sub>8</sub> / 0.19 ppm	
50.3				482.1935 / C <sub>27</sub> H <sub>30</sub> O <sub>8</sub> / -0.62 ppm	

54.9	cyclic HD-PA-HD-PA	C <sub>28</sub> H <sub>32</sub> O <sub>8</sub>	496.2090 / -0.39 ppm	397.1282 / C <sub>22</sub> H <sub>21</sub> O <sub>7</sub> / 0.02 ppm	
				415.1388 / C <sub>22</sub> H <sub>23</sub> O <sub>8</sub> / 0.19 ppm	
55.1				496.2090 / C <sub>28</sub> H <sub>32</sub> O <sub>8</sub> / -0.39 ppm	

572

573 Table 2: Polyester oligomers semi-quantification by GC-MS

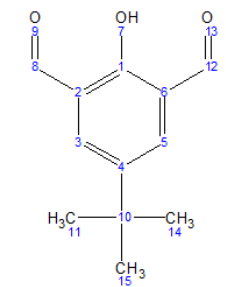
Retention time	Identification	P-1	P-2	P-3	C-1	TbuP-1	TbuP-2
		Average (µg/dm <sup>2</sup> )					
33.0	cyclic EG-PA-EG-PA	171	213	150	172	226	178
35.2	cyclic EG-PA-NPG-PA	24	27	21	25	32	25
39.0	cyclic NPG-PA-NPG-PA	13	15	11	13	16	13
41.5	cyclic NPG-PA-NPG-PA	<LOQ	10	<LOQ	<LOQ	11	10
43.5	cyclic NPG-PA-NPG-PA	18	21	18	21	23	22
44.8	cyclic EG-PA-HD-PA	N.D	N.D	N.D	N.D	<LOQ	<LOQ
45.2	cyclic EG-PA-HD-PA	35	41	34	36	45	42
46.3	cyclic EG-PA-HD-PA	21	24	21	22	25	25
49.0	cyclic NPG-PA-HD-PA	29	33	30	31	37	37
49.3	cyclic NPG-PA-HD-PA	28	29	27	29	33	32
50.3	cyclic NPG-PA-HD-PA	16	18	17	15	20	20
54.9	cyclic HD-PA-HD-PA	15	16	15	15	16	20
55.1	cyclic HD-PA-HD-PA	18	20	19	18	21	23



Total	386	467	363	397	506	447
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574

575 *Table 3: Correlation of experimental spectra and attribution on suspected structure*

Attribution of experimental peaks	$\delta^{13}\text{C}$ (ppm)	HSQC correlated $\delta^1\text{H}$ (ppm)	Attribution on:
Aldehyde	199	10.6	
Aromatic	158 - 135 - 121	8.5-8.3-8.0-7.6	Carbons 8 / 12 Carbon 1 Carbons 3 / 5 Carbons 2 / 6
C-(CH <sub>3</sub> )	35	-	Carbon 10
-CH <sub>3</sub>	30	2.0	Carbons 11 / 14 / 15

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578 Table 4: Proposed identification of compounds detected in TbuP-based coating extracts and semi-quantification by GC-MS - MOH: methylol group -CH<sub>2</sub>OH / F:  
579 formyl group -CHO / HF: Hemiformaldehyde -CH<sub>2</sub>-O-CH<sub>2</sub>-OH / bridge: methylene bridge -CH<sub>2</sub>-

Retention time	Proposed identification	Proposed formula	TbuP-1	TbuP-2	Monoisotopic mass / Mass deviation / RDB	Main fragment / Associated molecular formula / Mass deviation
			Average (µg/dm <sup>2</sup> )			
8.7	TbuP	C <sub>10</sub> H <sub>14</sub> O	34.3	10.3	150.1039 / 0.17 ppm / 4 RDB	138.0804 / C <sub>9</sub> H <sub>11</sub> O / -0.45 ppm
9.8	TbuP + F	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	23.0	11.7	178.0988 / -0.34 ppm / 5 RDB	163.0726 / C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> / -0.52 ppm
10.9	TbuP + F + methyl	C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>	24.7	19.3	192.1144 / -0.61 ppm / 5 RDB	177.0909 / C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> / -0.62 ppm
11.4	Undefined	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	10.0	11.0	194.0937 / -0.39 ppm / 5 RDB	179.0702 / C <sub>10</sub> H <sub>11</sub> O <sub>3</sub> / -0.54 ppm
12.5	TbuP + MOH	C <sub>11</sub> H <sub>16</sub> O <sub>2</sub>	14.3	16.0	180.1144 / -0.40 ppm / 4 RDB	147.0804 / C <sub>10</sub> H <sub>11</sub> O / -0.29 ppm
13.0	TbuP + 2 F	C <sub>12</sub> H <sub>14</sub> O <sub>3</sub>	78.0	86.7	206.0937 / -0.32 ppm / 6 RDB	191.0702 / C <sub>10</sub> H <sub>11</sub> O <sub>3</sub> / -0.53 ppm
13.5	TbuP + F + MOH	C <sub>12</sub> H <sub>16</sub> O <sub>3</sub>	11.7	14.7	208.1093 / -0.43 ppm / 5 RDB	175.0753 / C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> / -0.41 ppm
13.8	TbuP + F + MOH	C <sub>12</sub> H <sub>16</sub> O <sub>3</sub>	137.0	249.0	208.1093 / -0.43 ppm / 5 RDB	175.0753 / C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> / -0.41 ppm
13.9	TbuP + butylated MOH	C <sub>15</sub> H <sub>24</sub> O <sub>2</sub>	30.3	N.D	236.1771 / -0.01 ppm / 4 RDB	147.0804 / C <sub>10</sub> H <sub>11</sub> O / 0.02 ppm
14.4	TbuP + butylated MOH + methyl	C <sub>16</sub> H <sub>26</sub> O <sub>2</sub>	16.3	N.D	250.1927 / 0.01 ppm / 4 RDB	161.096 / C <sub>11</sub> H <sub>13</sub> O / -0.52 ppm
14.9	Undefined	C <sub>13</sub> H <sub>16</sub> O <sub>3</sub>	12.0	12.7	220.1094 / -0.05 ppm / 6 RDB	175.0753 / C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> / -0.29 ppm
15.1	TbuP + F + methylated MOH	C <sub>13</sub> H <sub>18</sub> O <sub>3</sub>	11.3	10.0	222.1248 / -1.08 ppm / 5 RDB	177.0908 / C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> / -1.12 ppm
15.3	TbuP + F + butylated MOH	C <sub>16</sub> H <sub>24</sub> O <sub>3</sub>	13.3	N.D	264.1721 / 0.47 ppm / 5 RDB	177.0908 / C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> / -1.13 ppm
15.7	TbuP + F + butylated MOH	C <sub>16</sub> H <sub>24</sub> O <sub>3</sub>	109.7	N.D	264.1721 / 0.47 ppm / 5 RDB	175.0753 / C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> / -0.47 ppm
16.6	Undefined	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	8.7	N.D	278.1511 / -0.74 ppm / 6 RDB	179.0701 / C <sub>11</sub> H <sub>11</sub> O <sub>3</sub> / -0.88 ppm
16.9	Undefined	C <sub>16</sub> H <sub>24</sub> O <sub>4</sub>	10.3	N.D	280.1667 / -0.71 ppm / 5 RDB	178.0986 / C <sub>11</sub> H <sub>14</sub> O <sub>2</sub> / -1.13 ppm
17.1	TbuP + F + butylated HF	C <sub>17</sub> H <sub>26</sub> O <sub>4</sub>	32.0	N.D	294.1825 / -0.31 ppm / 5 RDB	177.0909 / C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> / -0.63 ppm
17.4	TbuP + F + butylated HF	C <sub>17</sub> H <sub>26</sub> O <sub>4</sub>	14.0	N.D	294.1825 / -0.31 ppm / 5 RDB	177.0909 / C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> / -0.63 ppm

17.6	Undefined	C <sub>16</sub> H <sub>24</sub> O <sub>4</sub>	19.7	N.D	280.1666 / -1.02 ppm / 5 RDB	191.0700 / C <sub>11</sub> H <sub>11</sub> O <sub>3</sub> / -1.28 ppm
18.3	TbuP + 2 butylated MOH	C <sub>20</sub> H <sub>34</sub> O <sub>3</sub>	12.3	N.D	322.2501 / -0.58 ppm / 4 RDB	161.0960 / C <sub>11</sub> H <sub>13</sub> O / -0.33 ppm
18.5	TbuP-bridge-TbuP	C <sub>21</sub> H <sub>28</sub> O <sub>2</sub>	N.D	10.0	312.2082 / -0.71 ppm / 8 RDB	241.1222 / C <sub>16</sub> H <sub>17</sub> O <sub>2</sub> / -0.43 ppm
20.9	TbuP-bridge-TbuP	C <sub>21</sub> H <sub>28</sub> O <sub>2</sub>	12.7	N.D	312.2082 / -0.71 ppm / 8 RDB	241.1222 / C <sub>16</sub> H <sub>17</sub> O <sub>2</sub> / -0.43 ppm
21.1	TbuP-bridge-TbuP + methyl	C <sub>22</sub> H <sub>30</sub> O <sub>2</sub>	13.3	N.D	326.2239 / -0.29 ppm / 8 RDB	255.11379 / C <sub>17</sub> H <sub>29</sub> O <sub>2</sub> / -0.38 ppm
21.2	TbuP-bridge-TbuP + F	C <sub>22</sub> H <sub>28</sub> O <sub>3</sub>	10.7	9.7	340.2032 / -0.23 ppm / 9 RDB	191.1066 / C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> / -0.47 ppm
21.4	TbuP-bridge-TbuP + F + methyl	C <sub>23</sub> H <sub>30</sub> O <sub>3</sub>	11.7	N.D	354.2188 / -0.42 ppm / 9 RDB	339.1953 / C <sub>22</sub> H <sub>27</sub> O <sub>3</sub> / -0.56 ppm
21.8	TbuP-bridge-TbuP + F + methyl	C <sub>23</sub> H <sub>30</sub> O <sub>3</sub>	24.7	26.3	354.2188 / -0.42 ppm / 9 RDB	339.1953 / C <sub>22</sub> H <sub>27</sub> O <sub>3</sub> / -0.56 ppm
22.3	TbuP-bridge-TbuP + 2 F	C <sub>23</sub> H <sub>28</sub> O <sub>4</sub>	N.D	11.7	368.1981 / -0.33 ppm / 10 RDB	353.1747 / C <sub>22</sub> H <sub>25</sub> O <sub>4</sub> / -0.15 ppm
22.4	TbuP-bridge-TbuP + 2 F	C <sub>23</sub> H <sub>28</sub> O <sub>4</sub>	11.0	N.D	368.1981 / -0.33 ppm / 10 RDB	353.1747 / C <sub>22</sub> H <sub>25</sub> O <sub>4</sub> / -0.15 ppm
22.6	TbuP-bridge-TbuP + 2 F	C <sub>23</sub> H <sub>28</sub> O <sub>4</sub>	68.3	82.0	368.1981 / -0.33 ppm / 10 RDB	353.1747 / C <sub>22</sub> H <sub>25</sub> O <sub>4</sub> / -0.15 ppm
23.3	TbuP-bridge-TbuP + 2 F + methyl	C <sub>24</sub> H <sub>30</sub> O <sub>4</sub>	21.7	12.3	382.2137 / -0.39 ppm / 10 RDB	191.1066 / C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> / -0.46 ppm
23.5	TbuP-bridge-TbuP + 2 F + methyl	C <sub>24</sub> H <sub>30</sub> O <sub>4</sub>	N.D	18.0	382.2137 / -0.39 ppm / 10 RDB	191.1066 / C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> / -0.46 ppm
49.4	TbuP-bridge-TbuP-bridge-TbuP + 2 F	C <sub>34</sub> H <sub>42</sub> O <sub>5</sub>	10.7	N.D	530.3027 / 0.02ppm / 14 RDB	191.1063 / C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> / -1.64 ppm
51.2	TbuP-bridge-TbuP-bridge-TbuP + 2 F + methyl	C <sub>35</sub> H <sub>44</sub> O <sub>5</sub>	N.D	12.7	544.3186 / 0.51 ppm / 14 RDB	241.1223/ C <sub>16</sub> H <sub>17</sub> O <sub>2</sub> / 0.01 ppm

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581 Table 5: Proposed identification of compounds detected in C-1 coating extracts and semi-quantification by GC-MS

Retention time	Proposed identification	Proposed formula	Average ( $\mu\text{g}/\text{dm}^2$ )	Monoisotopic mass / mass deviation / RDB	Main fragment / Associated molecular formula / Mass deviation
10.6	C + 2 F	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	8.7	164.0468 / -0.35 ppm / 6 RDB	163.0389 / C <sub>9</sub> H <sub>7</sub> O <sub>3</sub> / -0.47 ppm
20.7	C-bridge-C + 2 F	C <sub>17</sub> H <sub>16</sub> O <sub>4</sub>	10.7	284.1043 / -0.11 ppm / 10 RDB	255.1016 / C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> / 0.15 ppm

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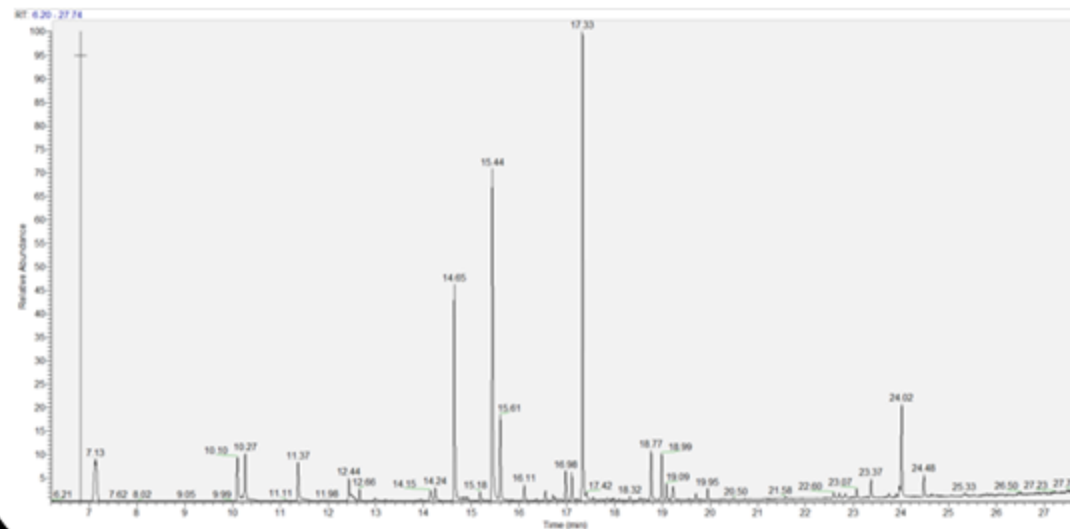
22.3	C-bridge-C + 2 F	C <sub>17</sub> H <sub>16</sub> O <sub>4</sub>	17.7	284.1043 / -0.11 ppm / 10 RDB	255.1016 / C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> / 0.15 ppm
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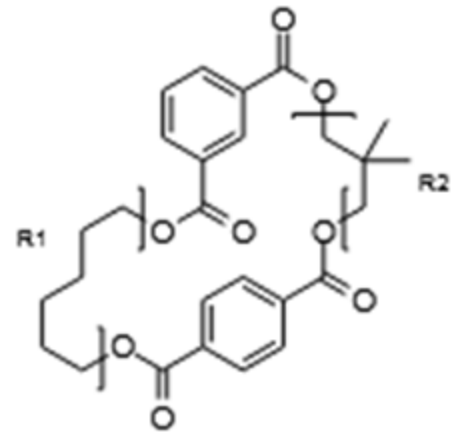
Extraction  
ACN 24h



GC-MS analysis and peak identification



Polyester oligomers



Phenolic compounds

