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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, resoles 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-d₃ (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/m² 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 (1,5dm² 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/dm² for ethylene terephthalate cyclic
156 dimer and 6µg/dm² 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 10⁶ 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 10⁷, 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 ^1H and ^{13}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 ^1H , ^{13}C and DEPT135 mono-dimensional spectra as well as HSQC and HMBC
183 ^1H - ^{13}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 (Mn) 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 CH_3 ($m/z =$
266 191.0702) and C_3H_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}C NMR. The signal intensity was
296 sufficient to observe additional peaks in TbuP-1 by ^1H NMR. Specific peaks were observed
297 when compared to P-2 spectrum. Those protons were found with chemical shift (δ) 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 ^1H , ^{13}C and 135DEPT but ^1H - ^{13}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 ^1H NMR were correlated to their corresponding ^{13}C
310 NMR signals (**Table 3**). A peak at 199 ppm in ^{13}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 ^1H

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 ^1H 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
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421 France) and CTCPA (Centre technique de la Conserve et des Produits Agricoles, Bourg en
422 Bresse, France).

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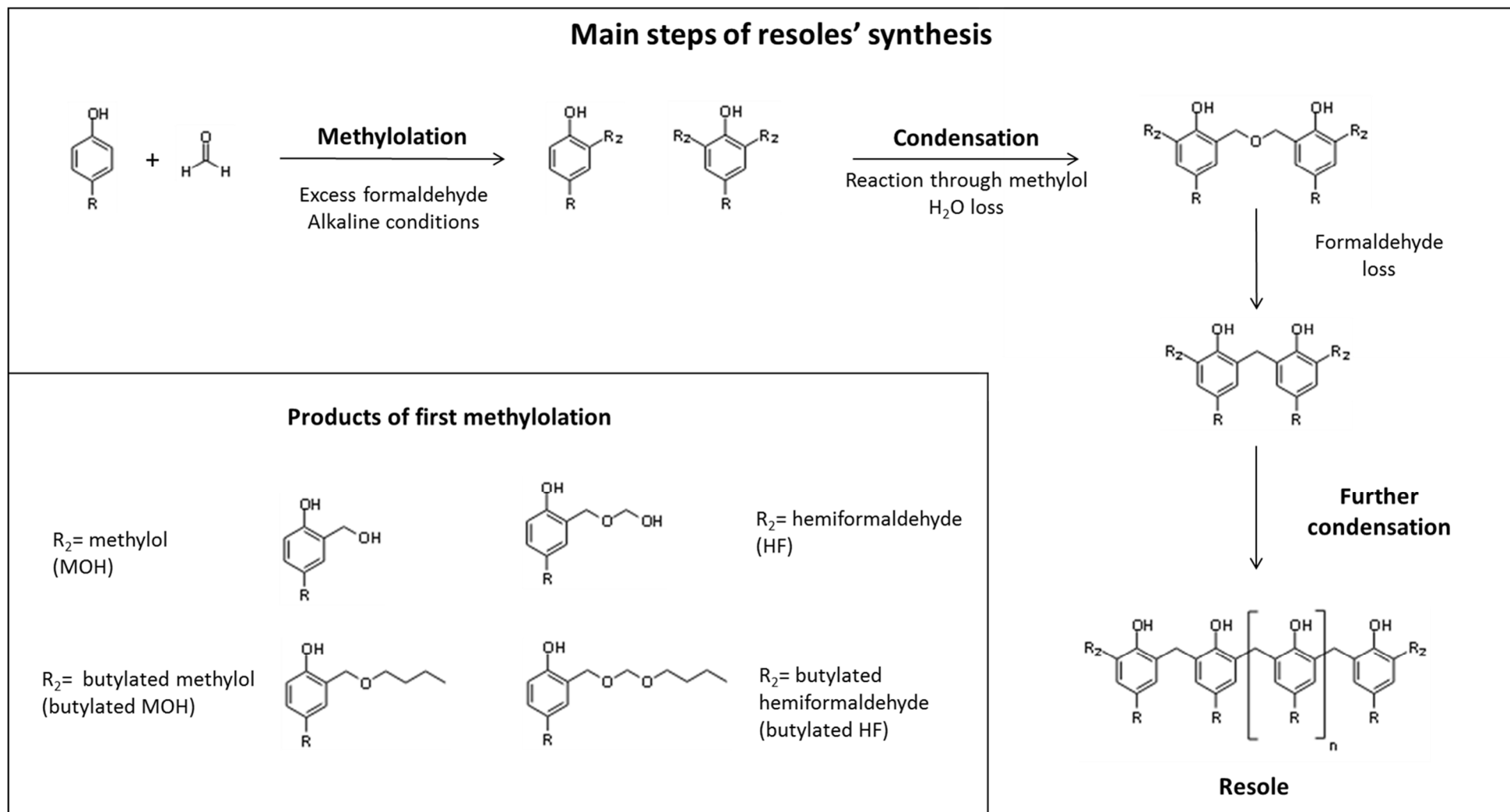
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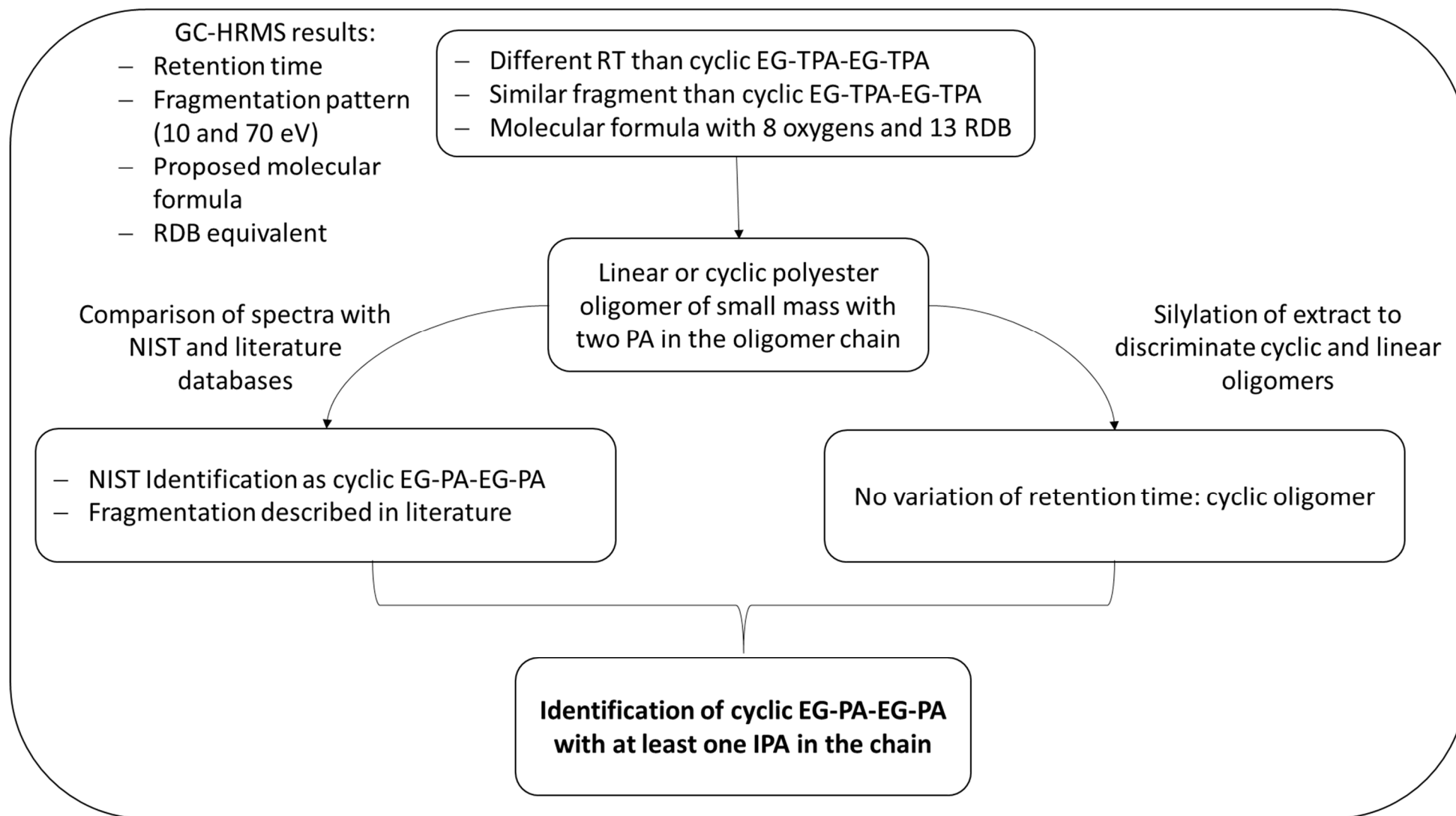
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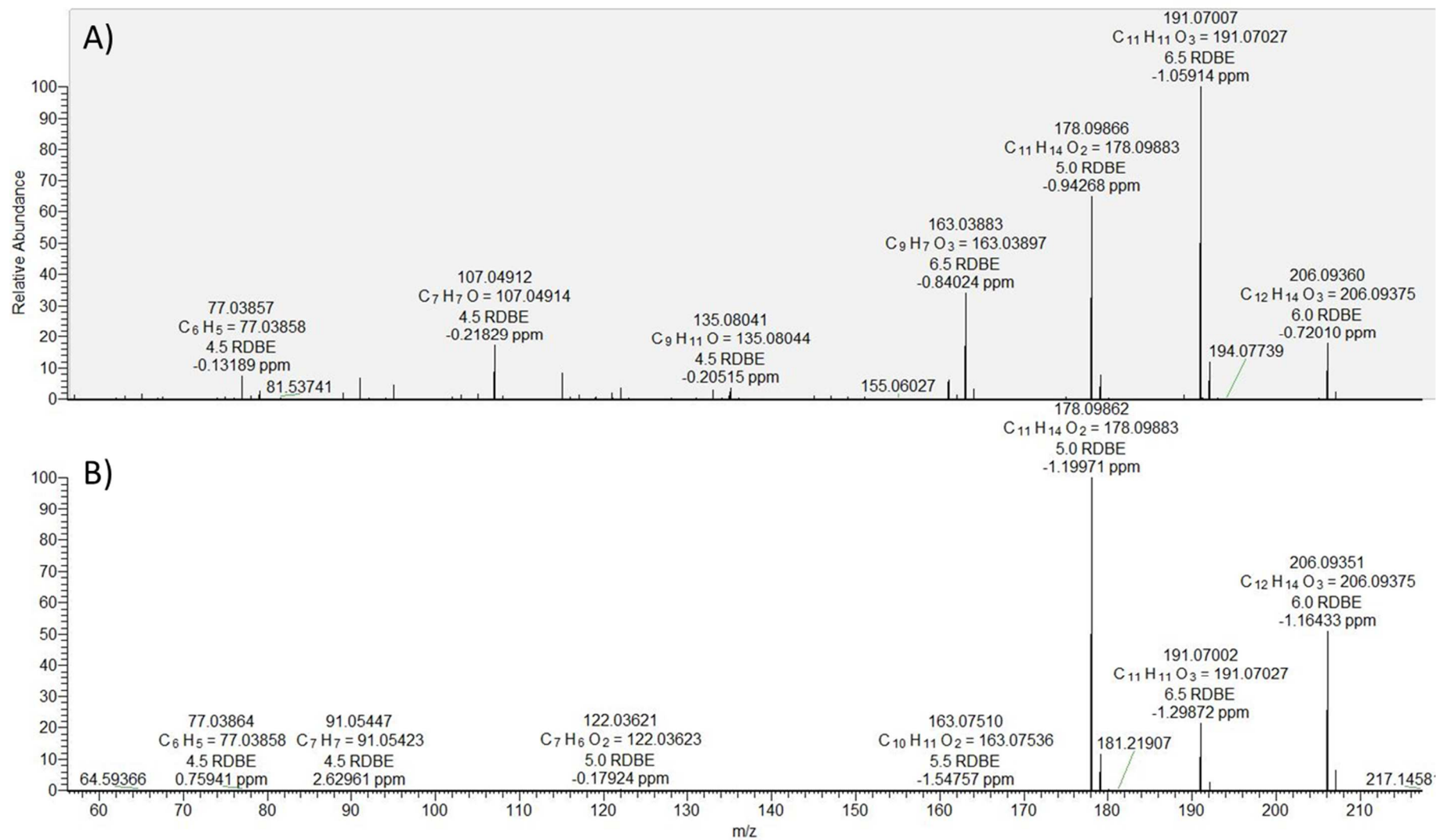
555 *Figure 1: Main steps of resoles' synthesis and products of first methylation*



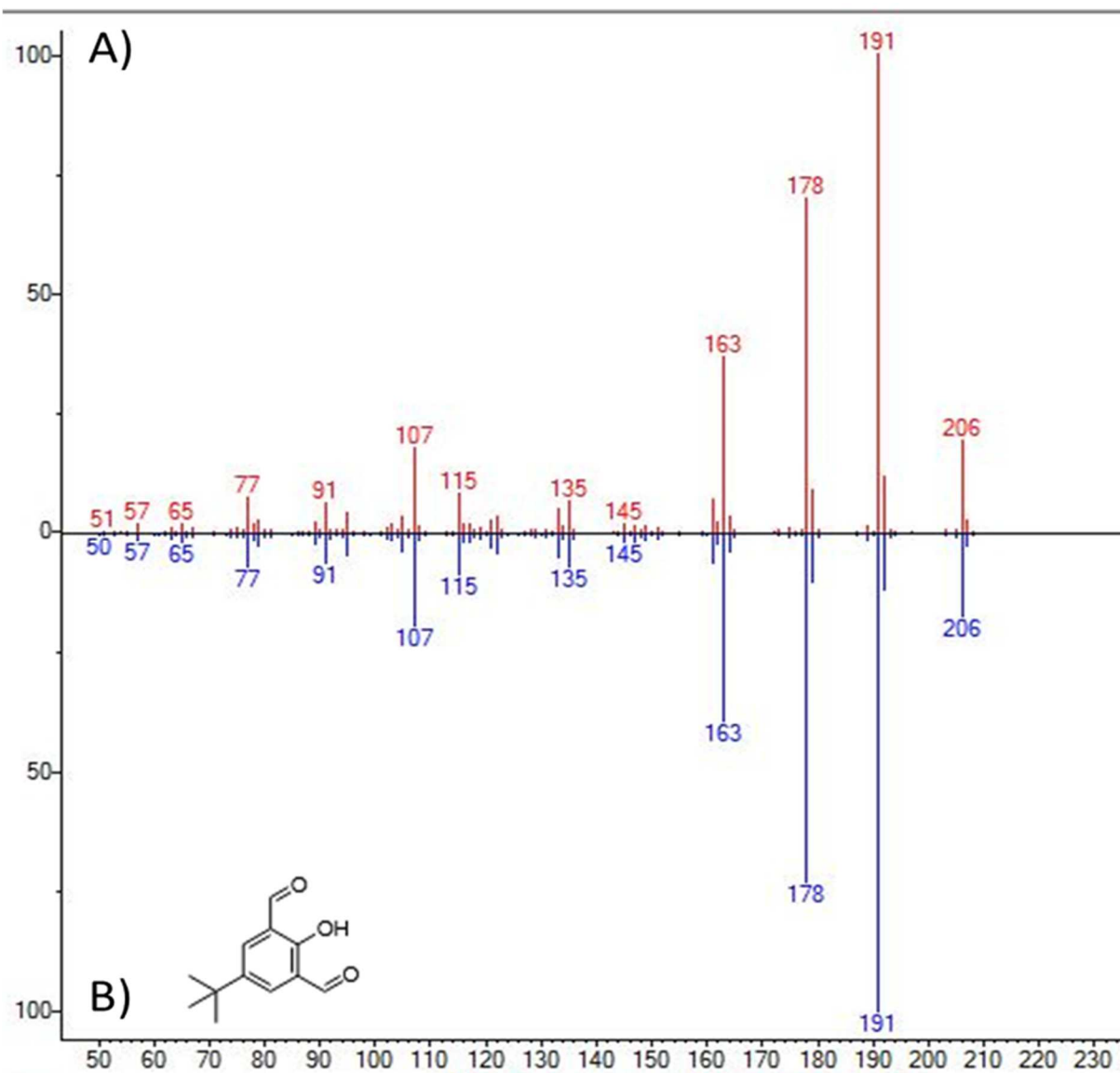
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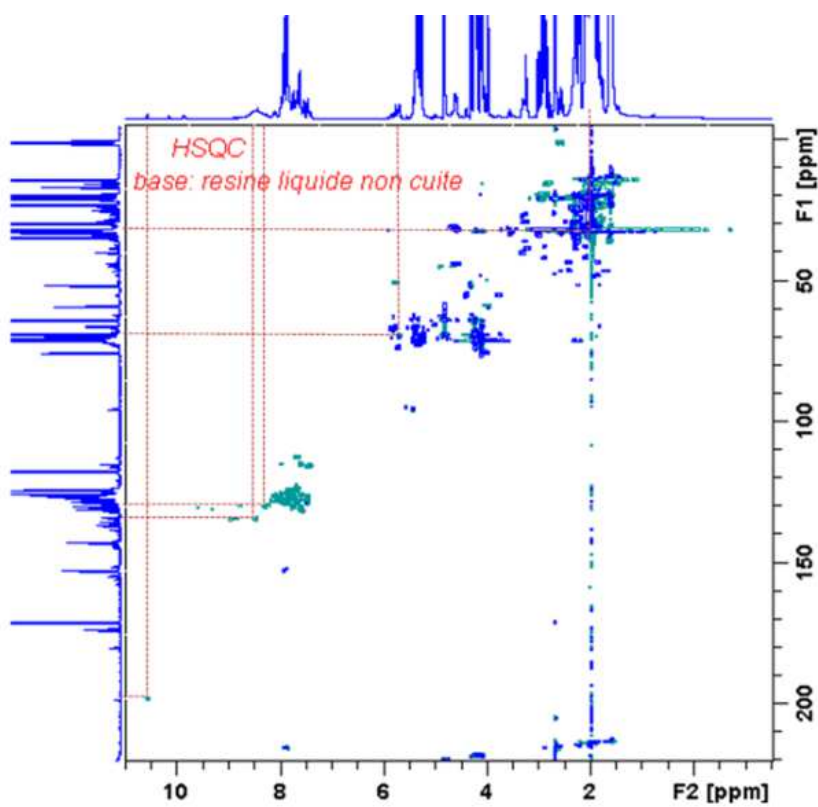
559 Figure 3: 70eV(A) and 10eV (B) mass spectra of unknown peak at RT=13.0 min in *TbuP* formulations



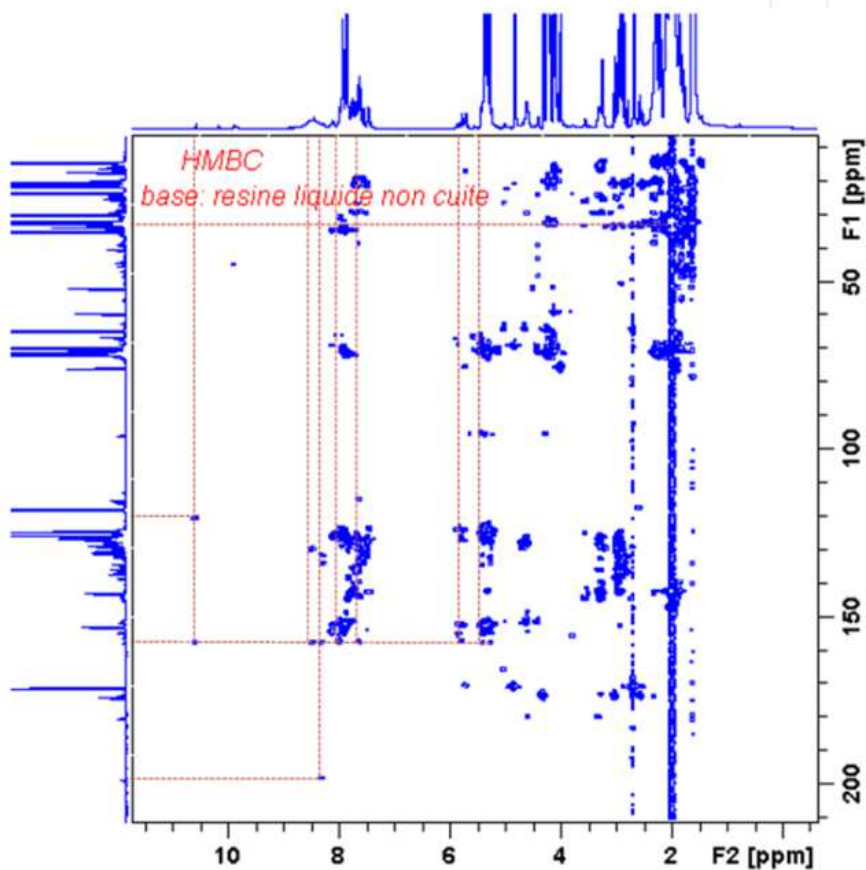
561 Figure 4: Comparison of mass spectra between A) Unknown peak at RT=13.0 min and B) 4-tert-butyl-
562 2,6-diformylphenol standard



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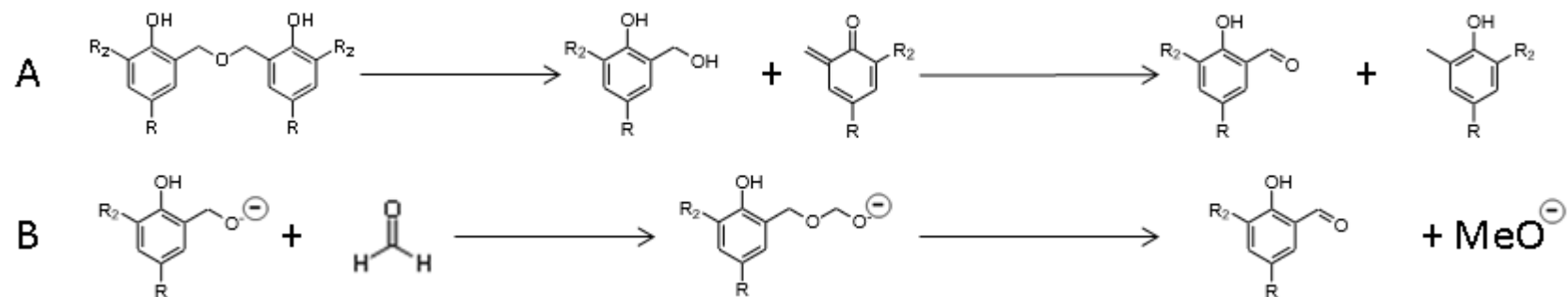


HSQC correlation



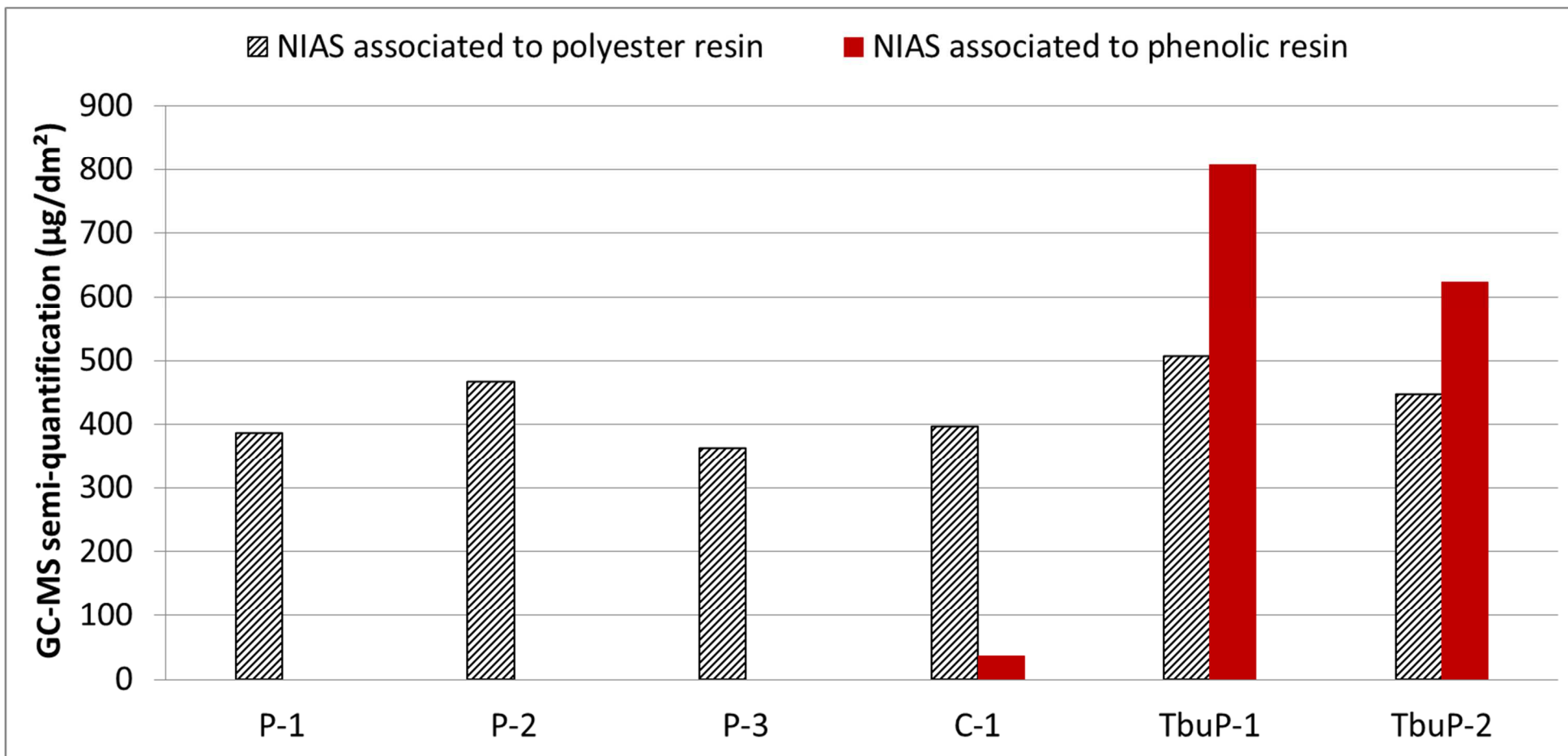
HMBC correlation

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



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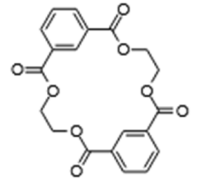
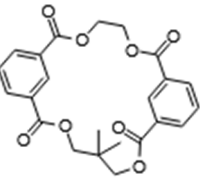
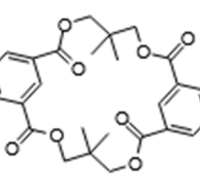
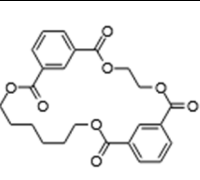
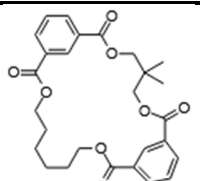
568 *Figure 7: Comparison of phenolic and polyester resin influence on extracted NIAS in GC-MS semi-quantification*

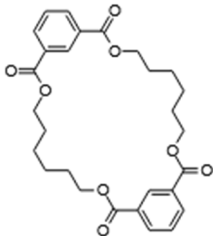


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570

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 ₂₀ H ₁₆ O ₈	384.0845 (not observed)	341.0653 / C ₁₈ H ₁₃ O ₇ / -0.88 ppm	
				359.0761 / C ₁₈ H ₁₅ O ₈ / -0.24 ppm	
35.2	cyclic EG-PA-NPG-PA	C ₂₃ H ₂₂ O ₈	426.1309 / -0.08 ppm	341.0653 / C ₁₈ H ₁₃ O ₇ / -0.88 ppm	
				359.0761 / C ₁₈ H ₁₅ O ₈ / -0.24 ppm	
				401.1229 / C ₂₁ H ₂₁ O ₈ / -0.41 ppm	
39.0	cyclic NPG-PA-NPG-PA	C ₂₆ H ₂₈ O ₈	468.1773 / -1.07 ppm	383.1122 / C ₂₁ H ₁₉ O ₇ / -0.81 ppm	
41.5				401.1229 / C ₂₁ H ₂₁ O ₈ / -0.41 ppm	
43.5				468.1773 / C ₂₆ H ₂₈ O ₈ / -1.07 ppm	
44.8	cyclic EG-PA-HD-PA	C ₂₄ H ₂₄ O ₈	440.1471 (not observed)	341.0653 / C ₁₈ H ₁₃ O ₇ / -0.88 ppm	
45.2				359.0761 / C ₁₈ H ₁₅ O ₈ / -0.24 ppm	
46.3				410.1359 / C ₂₃ H ₂₂ O ₇ / -0.32 ppm	
49.0	cyclic NPG-PA-HD-PA	C ₂₇ H ₃₀ O ₈	482.1935 / -0.62 ppm	383.1122 / C ₂₁ H ₁₉ O ₇ / -0.81 ppm	
49.3				415.1388 / C ₂₂ H ₂₃ O ₈ / 0.19 ppm	
50.3				482.1935 / C ₂₇ H ₃₀ O ₈ / -0.62 ppm	

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

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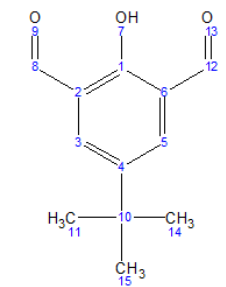
573 Table 2: Polyester oligomers semi-quantification by GC-MS

Retention time	Identification	P-1	P-2	P-3	C-1	TbuP-1	TbuP-2
		Average (µg/dm ²)					
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 ₃)	35	-	Carbon 10
-CH ₃	30	2.0	Carbons 11 / 14 / 15

576

577

578 Table 4: Proposed identification of compounds detected in TbuP-based coating extracts and semi-quantification by GC-MS - MOH: methylol group -CH₂OH / F:
579 formyl group -CHO / HF: Hemiformaldehyde -CH₂-O-CH₂-OH / bridge: methylene bridge -CH₂-

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

17.6	Undefined	C ₁₆ H ₂₄ O ₄	19.7	N.D	280.1666 / -1.02 ppm / 5 RDB	191.0700 / C ₁₁ H ₁₁ O ₃ / -1.28 ppm
18.3	TbuP + 2 butylated MOH	C ₂₀ H ₃₄ O ₃	12.3	N.D	322.2501 / -0.58 ppm / 4 RDB	161.0960 / C ₁₁ H ₁₃ O / -0.33 ppm
18.5	TbuP-bridge-TbuP	C ₂₁ H ₂₈ O ₂	N.D	10.0	312.2082 / -0.71 ppm / 8 RDB	241.1222 / C ₁₆ H ₁₇ O ₂ / -0.43 ppm
20.9	TbuP-bridge-TbuP	C ₂₁ H ₂₈ O ₂	12.7	N.D	312.2082 / -0.71 ppm / 8 RDB	241.1222 / C ₁₆ H ₁₇ O ₂ / -0.43 ppm
21.1	TbuP-bridge-TbuP + methyl	C ₂₂ H ₃₀ O ₂	13.3	N.D	326.2239 / -0.29 ppm / 8 RDB	255.11379 / C ₁₇ H ₂₉ O ₂ / -0.38 ppm
21.2	TbuP-bridge-TbuP + F	C ₂₂ H ₂₈ O ₃	10.7	9.7	340.2032 / -0.23 ppm / 9 RDB	191.1066 / C ₁₂ H ₁₅ O ₂ / -0.47 ppm
21.4	TbuP-bridge-TbuP + F + methyl	C ₂₃ H ₃₀ O ₃	11.7	N.D	354.2188 / -0.42 ppm / 9 RDB	339.1953 / C ₂₂ H ₂₇ O ₃ / -0.56 ppm
21.8	TbuP-bridge-TbuP + F + methyl	C ₂₃ H ₃₀ O ₃	24.7	26.3	354.2188 / -0.42 ppm / 9 RDB	339.1953 / C ₂₂ H ₂₇ O ₃ / -0.56 ppm
22.3	TbuP-bridge-TbuP + 2 F	C ₂₃ H ₂₈ O ₄	N.D	11.7	368.1981 / -0.33 ppm / 10 RDB	353.1747 / C ₂₂ H ₂₅ O ₄ / -0.15 ppm
22.4	TbuP-bridge-TbuP + 2 F	C ₂₃ H ₂₈ O ₄	11.0	N.D	368.1981 / -0.33 ppm / 10 RDB	353.1747 / C ₂₂ H ₂₅ O ₄ / -0.15 ppm
22.6	TbuP-bridge-TbuP + 2 F	C ₂₃ H ₂₈ O ₄	68.3	82.0	368.1981 / -0.33 ppm / 10 RDB	353.1747 / C ₂₂ H ₂₅ O ₄ / -0.15 ppm
23.3	TbuP-bridge-TbuP + 2 F + methyl	C ₂₄ H ₃₀ O ₄	21.7	12.3	382.2137 / -0.39 ppm / 10 RDB	191.1066 / C ₁₂ H ₁₅ O ₂ / -0.46 ppm
23.5	TbuP-bridge-TbuP + 2 F + methyl	C ₂₄ H ₃₀ O ₄	N.D	18.0	382.2137 / -0.39 ppm / 10 RDB	191.1066 / C ₁₂ H ₁₅ O ₂ / -0.46 ppm
49.4	TbuP-bridge-TbuP-bridge-TbuP + 2 F	C ₃₄ H ₄₂ O ₅	10.7	N.D	530.3027 / 0.02ppm / 14 RDB	191.1063 / C ₁₂ H ₁₅ O ₂ / -1.64 ppm
51.2	TbuP-bridge-TbuP-bridge-TbuP + 2 F + methyl	C ₃₅ H ₄₄ O ₅	N.D	12.7	544.3186 / 0.51 ppm / 14 RDB	241.1223 / C ₁₆ H ₁₇ O ₂ / 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 (µg/dm ²)	Monoisotopic mass / mass deviation / RDB	Main fragment / Associated molecular formula / Mass deviation
10.6	C + 2 F	C ₉ H ₈ O ₃	8.7	164.0468 / -0.35 ppm / 6 RDB	163.0389 / C ₉ H ₇ O ₃ / -0.47 ppm
20.7	C-bridge-C + 2 F	C ₁₇ H ₁₆ O ₄	10.7	284.1043 / -0.11 ppm / 10 RDB	255.1016 / C ₁₆ H ₁₅ O ₃ / 0.15 ppm

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22.3	C-bridge-C + 2 F	C ₁₇ H ₁₆ O ₄	17.7	284.1043 / -0.11 ppm / 10 RDB	255.1016 / C ₁₆ H ₁₅ O ₃ / 0.15 ppm
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