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1 **EFFECTS OF ELECTRON BEAM STERILIZATION ON**
2 **POLYETHYLENE TEREPHTHALATE: PHYSICO-CHEMICAL**
3 **MODIFICATIONS AND FORMATION OF NON-VOLATILE ORGANIC**
4 **EXTRACTABLES.**

5 EFFETS DE LA STERILISATION PAR ELECTRONS ACCELERES SUR LE
6 POLY(ETHYLENE TEREPHTHALATE) : MODIFICATIONS PHYSICO-
7 CHIMIQUES ET FORMATION D'EXTRACTIBLES ORGANIQUES NON
8 VOLATILES.

9

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23

24 **ABSTRACT**

25 Our investigations hereby involve the effects of ionizing radiation as a
26 sterilization method, and especially electron beams, on a medical grade
27 Polyethylene Terephthalate (PET). Ionizing radiations are known to induce free
28 radicals formation in the polymer that will then either degrade or crosslink,
29 depending on its chemical nature, ionizing type and irradiation atmosphere [1–3].
30 The evaluation of packaging material modifications under radiation sterilization is
31 of great interest and the objective of our paper is to focus on both PET volume
32 modifications and extractable analyses after electron beam sterilization. As
33 regards the polymeric matrix and after sterilization, we did not observe by means
34 of spectral analyses, any single chemical modification whatsoever, whereas by
35 thermal techniques we evidenced polymer chain scissions. As for the non-volatile
36 organic extractables, we further substantiate the presence of numerous
37 compounds, namely oligomers and trimers especially, along with benzoic and
38 terephthalic acids in particular. With respect to pharmaceutical stakes however,
39 we claim herein that the 25 kGy sterilization dose used, triggers oligomers and
40 extractables formation, a result which is promising for further risk analysis.

41

42 **RÉSUMÉ**

43

44 Nous nous intéressons aux effets des rayonnements ionisants, utilisés comme
45 méthode de stérilisation, et notamment les électrons accélérés, sur un
46 poly(éthylène téréphtalate) (PET) de grade médical. Les rayonnements ionisants
47 sont connus pour induire la formation de radicaux libres dans le polymère qui,

48 selon sa nature chimique, le type de rayonnements et d'atmosphère d'irradiation,
49 va ensuite soit subir une dégradation soit une réticulation de ses chaînes
50 macromoléculaires [1–3]. Il est alors important d'évaluer la modification du
51 matériau de conditionnement sous stérilisation ionisante et l'objectif de ce travail
52 est d'étudier à la fois les modifications dans le volume du PET ainsi que
53 d'analyser les extractibles issus de la stérilisation par électrons accélérés. En ce
54 qui concerne la matrice polymérique et après stérilisation, nous n'avons pas
55 observé de modification chimique par analyse spectrale, en revanche, nous avons
56 pu mettre en évidence la coupure de chaînes par analyse thermique. De même,
57 pour les composés extractibles organiques non volatiles, nous confirmons
58 la présence de nombreux composés, en particulier des oligomères et des trimères,
59 avec en particulier les acides benzoïque et téréphtalique. En ce qui concerne les
60 recommandations pharmaceutiques, nous prétendons ici que la dose de
61 stérilisation de 25 kGy utilisée, engendre la formation d'oligomères et de
62 substances extractibles, un résultat qui semble prometteur pour une future analyse
63 de risque.

64

65 **KEY WORDS – MOTS CLÉ**

66

67 Extractables; PET; oligomers; electron beam sterilization; thermal analysis;
68 separation techniques.

69 Extractibles; PET ; oligomères ; stérilisation aux électrons accélérés ; analyse
70 thermique ; techniques séparatives.

71

72 INTRODUCTION

73

74 Polyethylene Terephthalate (PET) is widely used in the food packaging industry
75 thanks to its high-strength barrier and easy thermoforming (e.g.: bottles, frozen
76 products as well as packaged goods intended for microwave and convection oven
77 use). In the field of the medical and pharmaceutical industry, because of its
78 distinctive physical assets such as resistance, crystallinity, heat and solvent
79 resilience as well as its biological characteristics such as biostability and
80 promotion of tissue ingrowth, PET's applications include bottles, primary
81 packaging material as well as implantable sutures, surgical mesh, vascular grafts,
82 sewing cuffs for heart valves and components for percutaneous access devices.
83 For these purposes, PET can be submitted to ionizing radiation sterilization. The
84 evaluation of packaging material modifications under radiation sterilization is of
85 great interest. The objective of our paper is to study the electron beam effects on
86 the physico-chemical properties of PET as well on the formation of extractables.
87 This PET material comes from of a multi-layer laminated film with amorphous
88 polyethylene terephthalate (PET) combined with linear low density polyethylene.
89 A primer is applied to the PET film during the lamination process thus helping the
90 bonding between both films. This complex allows reservoir manufacturing for
91 BD-Uniject™ medical device. BD-Uniject™ prefillable injection device is for
92 packaging and administering parenteral drugs through intra-muscular or sub
93 cutaneous injections. It is aseptically filled, sealed and packaged by a
94 pharmaceutical manufacturer. It consists in the following components assembled
95 in open and ready to fill form ; reservoir which contains parenteral solution and
96 needle assembly with a port, a valve disc combined with valve seat, a hub and

97 cannula assembly, and finally the needle shield. The ready to fill form implies that
98 the product is radiosterilised. To anticipate the likely interaction between
99 container and content, we have to understand the effect of radiation among other
100 topics. We focused on the reservoir because of an immediately contact with
101 parenteral drug. Indeed, the effect of radiation can induce physical modifications
102 in PET such as change in the mechanical properties due to scission/cross-linking
103 of the macromolecular chains, oxidation, change of crystallinity and as a
104 consequence of permeability; but radiation can also induce degradation of the
105 additives into smaller molecules that have higher mobility through the
106 macromolecular chains and as a consequence become potential leachables.
107 Moreover, it is noteworthy that in the context of pharmaceutical packaging
108 sterilization processes, degradation products and oligomers are likely to appear
109 [4–7] and further, they may spread from the container/closure system into the
110 drug solution itself. Those compounds might have a bad effect on the stability of
111 the formulation and the adsorption of the formulation on the plastic container can
112 be modified. Hence, any thorough compatibility assessment needs to consider the
113 sterilization impact on physical properties and potential leaching impurities [5–9].
114 Polyethylene Terephthalate (PET) is a thermoplastic polyester synthesized by
115 polycondensation of ethylene glycol and dimethyl terephthalate [10–12].
116 Numerous publications to date provide extensive information as regards PET
117 oligomers identification, quantification [13–23] and migration in food simulants
118 [24]. However, few research papers have probed as yet the effects of sterilization
119 on PET used in medical or pharmaceutical applications. Within the realm of
120 pharmaceutical implementation, PET is used in containers intended for a wide
121 range of preparations but not in direct contact with parenteral drugs, where
122 acetaldehyde is solely referenced as a manufacturing residue: therefore its content

123 must never exceed 10 ppm in granules as a rule [25]. Whenever containers or
124 delivery-systems require proper sterilization before use, the above-mentioned
125 critical pre-requisite must be observed unequivocally.

126 Consequently, our goal is to evaluate the effects of electron-beam sterilization on
127 Polyethylene Terephthalate (PET) used as a medical device for drug delivery, and
128 subsequently to further lay the ground for compatibility studies involving a
129 pharmaceutical and/or a biological medium. Insofar as sterilization induces
130 modifications affecting all at once the polymeric bulk as well as the additives and
131 oligomers, an integrative two-fold approach had to be implemented (one slant of
132 approach focused on the matrix and the other slant concentrated on the additives,
133 the degradation products and oligomers).

134

135 **MATERIAL and METHODS**

136

137 **Materials and reagents**

138 Medical grade PET films, about 130 μm thick, 15 cm width were supplied by
139 Becton Dickinson Medical (France).

140 Tetrahydrofuran (THF) and Methanol (both HPLC grade) as well as benzoic and
141 orthophosphoric acids were provided by Prolabo, terephthalic acid was supplied
142 by Acros Organics.

143

144 **Irradiations**

145 The samples were irradiated at room temperature under air by an industrial
146 electron beam accelerator (Energy of 10 MeV, power 10 kW, speed of the
147 conveyor belt under the electron beam of 0.85 m/min) (Ionisos – Chaumesnil,
148 France).

149 The PET films were placed between paper sheets in plastic bags before
150 irradiation. The mean incident doses on the sample packages amounted to 25, 50
151 and 150 kGy. Around 140 g of PET films is dedicated for each dose. Chromic
152 dosimeters were used to measure the dose. 25 kGy is the sterilization dose that is
153 recommended by the Pharmaceutical authorities [26,27]. Once irradiated and
154 before being studied, samples were maintained 3-4 weeks at 5°C, so as to slow
155 down at best the decay of the radicals formed during irradiation, and to further
156 restrict potential component migration.

157 In order to check radiation effects on PET, we used specific analytical techniques.
158 Hence, we chose to further elicit in a first step, the effects of irradiation on the
159 polymer, subject to both chain scissions and cross-linking: such phenomena were
160 singled out by means of analytical techniques such as spectral (Fourier Transform
161 InfraRed spectroscopy (FTIR)) and thermal analyses (Differential Scanning
162 Calorimetry (DSC), Thermogravimetric Analysis (TGA)). In a second step, we
163 concentrate on the additives, the degradation products and oligomers, known as
164 extractables: they can be analyzed by means of weighing measurements along
165 with chromatographic methods, namely Size Exclusion Chromatography (SEC)
166 (providing some idea as regards oligomers molecular masses, albeit unspecific),
167 and Reversed Phase- High Performance Liquid Chromatography (RP-HPLC)
168 (more specific). In terms of compatibility studies involving the polymer combined

169 with pharmaceutical or biological media, toxicity tests still require further
170 developments to date.

171 **Characterization of the polymeric bulk**

172

173 **Fourier Transform InfraRed (FTIR) analysis**

174 FTIR spectra were recorded with a Perkin Elmer 2000 spectrometer (16 scans,
175 4 cm^{-1} resolution) equipped with a deuteriated triglycerine sulphate (DTGS)
176 detector. In transmission mode, the sample holder was tilted at the Brewster's
177 angle (also called the polarization angle) in order to eliminate interference fringes.
178 Ten different samples were analyzed for statistical reasons.

179

180 **Differential Scanning Calorimetry (DSC) analysis**

181 The DSC curves were recorded with a TA Q1000 calorimeter, under nitrogen
182 blanketing, for a temperature ranging between 35 and 280°C. The scanning rate
183 was optimized and finally set at 10°C/min. The calorimeter was calibrated before
184 use with indium and tin standards. For all PET samples a sequence was set as
185 follows: the temperature was initially set at 300°C over a 5 minute period in order
186 to melt the polymer and improve its contact with the crucible; subsequently a first
187 heating and cooling cycle was performed and the second heating scan was chosen,
188 since further heating scans gave the same DSC curve. For each dose, three
189 samples were analyzed.

190

191 **Thermogravimetric analysis (TGA)**

192 The TGA curves were recorded with a TA Q500 calorimeter, under nitrogen
193 blanketing, for a temperature ranging between 30 and 600°C at a scanning rate
194 optimized for 20°C/min. For each dose, three samples were analyzed.

195

196 **Characterization of the non-volatile extractables**

197

198 **Soxhlet extractions**

199 The soxhlet extraction was carried out on 20 g of PET accurately weighted, placed
200 in cellulose extraction thimbles, over a 2-hour period in methanol under reflux.
201 The extraction solution evaporated until dry. The 250 mL glass flask used for
202 collecting extracts were weighted before extraction and after evaporation, once
203 cooled. When ready for HPLC measurements, dry extracts collected in the glass
204 flask, were dissolved in 1 mL methanol (40°C) and 1 mL mobile phase. For each
205 dose, three extractions were performed and each extraction solution was injected
206 (20 μ L) three times in the HPLC apparatus. In the case of SEC analysis,
207 extractables were solubilized in methanol (40°C) prior to SEC analysis.

208

209 **Weighing**

210 An analytical Denver Instrument M-220D scale, capable of weighing from 1 mg
211 up to 31 g with a 0.01 mg sensitivity level was used to evaluate the quantity of
212 oligomers, additives and degradation products extracted from the polymer, by
213 calculating the difference of weight of the glass ampoules used before and after
214 extraction.

215

216 **Size Exclusion Chromatography (SEC) analysis**

217 Chromatograms were recorded with a PL-GPC 220 high temperature
218 chromatograph (Polymer Laboratories, UK), equipped with a refractometer (RI)

219 (Polymer Laboratories, UK) and an UV detector whose wavelength was set at
220 240 nm and 280 nm.

221 The chromatographic system had its temperature set at 35°C. Flow rate reached
222 1 mL/min in THF. The SEC system was controlled by the PL-GPC 220 Control
223 software (2.01 version). Acquisition and analysis were controlled by a Viscotek
224 software (Omnisec 4.0 version).

225 Two Polymer Laboratories (PL) 5 µm-mixed C and 100 Å-3 µm SEC columns
226 were set up in series. Their molecular weights linear range ranked between 200 –
227 2×10^6 for the first one, and 4000 - 2×10^5 for the second one, their length reached
228 300 mm and their internal diameter, 7.5 mm (supplier's data).

229 Six polystyrene (PS) standards (Polymer Laboratories, UK) of narrow molecular
230 weights (Mp) were used to perform a universal calibration.

231 Non irradiated PET extraction samples were obtained as described earlier and
232 extracts, containing oligomers and small weight molecules, was solubilized in hot
233 methanol prior to SEC analysis. Three different samples were analyzed such a
234 way for statistical reasons.

235

236 **Reversed Phase High Performance Liquid Chromatography (RP-HPLC)** 237 **analysis**

238 The liquid chromatograph was a Thermo Spectra Physics (TSP) system, involving
239 a P4000 pump, a Rheodyne sampling valve with a 20 µL loop, an AS 1000
240 automatic sampler, and was coupled with a photodiode array UV 6000 detector,
241 with pre-selected wavelength set at 240 nm. The software used was ChromQuest
242 (3.0 version) from Thermo Finnigan. The separation was achieved on a 250 by
243 4.6 mm inner diameter, 5 µm Lichrosphere, 60 RP Select B column (C8) (Merck),
244 heated at 30°C.

245 The elution gradient was a solvent mixture (phosphoric acid buffer / methanol)
246 with a 50/50 volume ratio. The phosphoric acid buffer was obtained from an
247 orthophosphoric acid solution prepared at 0.1 M and added to a 0.1 M NaOH
248 solution. The mobile phase had a pH adjusted to 2.8 with a 1 N HCl solution. The
249 flow rate of the mobile phase was set at 1 mL/min.

250

251 **RESULTS and DISCUSSION**

252 There is substantial existing evidence to the effect that irradiation induces
253 physical and chemical modifications in the polymeric bulk (e.g. chain scissions
254 and cross-linking), as well as oxidation groupment formation [1–3,28,29].
255 Irradiation also endorses a critical role in terms of extractable (oligomers and
256 additives) degradation. The entities formed thereby, display high mobility levels
257 in keeping with their low molecular weight, thus allowing for swift migration
258 capacity into the pharmaceutical and biological media. Both the effect of the
259 electron-beam radiation on PET bulk and non-volatile extractables are here
260 presented. It is worse notice here that the effect of radiation on polymer might be
261 different depending on the radiation type (electron-beam, gamma-ray, swift heavy
262 ions, X-rays), especially because of the dose rate and the depth of induced
263 radiation.

264

265 **1- Effect of the sterilization on PET bulk – Physico-chemical** 266 **methods.**

267 Several papers have been published on radiation effects on PET by means of high
268 energy ions beam [30–36] and gamma rays [28,29,37–41], but electron-beam

269 sterilization on PET is less described in the literature. Apel *et al.* [36] and
270 Buchalla *et al.* [37] mentioned the formation of a large amount of polar low-
271 molecular weight compounds. Buchalla *et al.* studied in depth the non-volatile
272 radiolysis products of PET by means of Liquid Chromatography - Mass
273 spectrometry (LC-MS). In their case, PET was irradiated by gamma rays at doses
274 of 25 and 50 kGy. They evidenced that every radiation resistant polymer can lead
275 to the formation of low-molecular weight degradation products.

276 1. 1- FTIR analysis

277 FTIR measurements enabled film structural analysis as a function of the radiation
278 dose. As shown on Figure 1, the transmission mode results revealed identical
279 spectra within the dose. Such a result underscored the lack of any volume-based
280 modification of PET chemical functions following irradiation (namely oxidation),
281 even at the highest dose. Likewise, authors such as Aytac *et al.* [38] evidenced no
282 change in the FTIR spectra of 150 kGy gamma irradiated cords used as tyre
283 reinforcing material.

284 PET is known to be radiation resistant, owing to the presence of aromatic groups
285 along with ester linkages in its backbone [39,42]. In keeping with findings
286 released by Liu *et al.* for doses above 6 MGy [30,31], we found that the 1579 cm⁻¹
287 band intensity assigned to the aromatic skeletal stretching band of benzene rings,
288 remained constant during irradiation. Several papers deal with the modification of
289 PET under high energy heavy ions irradiations: Steckenreiter *et al.* [32] as well as
290 Singh *et al.* [33] studied swift heavy ion effects over PET by FTIR and showed
291 alkyne formation near the track core and evidenced an enhanced degradation due
292 to the presence of oxygen. Zhu *et al.* [34] showed that a single ion bombardment
293 damaged the phenyl ring and the crystallinity of PET. As previously reported by

294 Dole [3], carbonyl groups are formed under radiation in oxygen atmosphere. In
295 our case, we observed no alkyne end group formation nor any oxidation functions.
296 It is noteworthy however, that we used a different radiation framework. Moreover,
297 we resorted to very small doses compared to the cited authors. Indeed, our goal
298 was to be the closest as possible to the sterilization dose.
299 Finally, under irradiation conditions used in our study, no chemical modification
300 was observed with reference to PET films.

301

302 *1. 2- Thermal analysis*

303 Thermal characteristics and especially crystallinity yield is an important parameter
304 to check after irradiation because a highly crystalline polymer will be more
305 efficient against the molecular diffusion than an amorphous one. Figure 2 gives
306 the DSC curve overlay obtained at the second heating stage for both non-
307 irradiated and irradiated samples. Glass transition was readily observed and
308 measured at a glass temperature (T_g) of 81°C, regardless of the dose. Radiation
309 effects were displayed with both subsequent thermal events, namely: the
310 endothermic transition emerging at about 176°C, and the shape of the melting
311 peak at 242°C approximately. Following irradiation, the endothermic transition
312 increases as well as the shoulder in the melting peak at a temperature below the
313 maximum level (about 228°C). Chain scissions may account for such a
314 phenomenon, insofar as they induce the formation of smaller molecular chains
315 involving a lower melting point compared to initial chains.

316 Jeon *et al.* [29] have referenced gamma irradiation PET degradation. Through
317 Size Exclusion Chromatography (SEC), they evidenced the molecular weights
318 decrease. Findings are congruent with results released by Buttafava *et al.* [28].

319 The latter carried out viscosity measurements, thus disclosing the following
320 trends: molecular weights decrease at 50-150 kGy gamma-rays doses, followed by
321 an increase up to 300 kGy, prior to a subsequent decrease recorded at higher doses
322 within the reach of 1000 kGy. In the course of our investigations, however, we
323 observed no single T_g value variation within our dose range, whereas Buttafava *et*
324 *al.* [28] and Kattan [40] reported a T_g decrease at higher gamma-rays doses (up to
325 3500 kGy): such a finding points out to a chain scission-induced macromolecules
326 mobility increase. Kattan took his research a step further: He calculated the
327 number of chain scissions by evaluating T_g decrease, a significant point when
328 considering the dose range used then.

329 Many semi-crystalline polymers exhibit multiple melting behaviors from different
330 sources depending on authors. Regarding the issue of endothermic transition at
331 about 176°C, Kong [43] and Wang *alike* [44] argued that depending on PET
332 thermal treatment, a minor endotherm is likely to emerge due to secondary
333 lamellae melting processes. Authors evidenced the formation of two distinctive
334 lamellar thickness populations during the isothermal crystallization process at
335 long times: the thicker lamellae formed first, and the thinner lamellae formed both
336 during and after primary crystallization. Using isothermally crystallized PET,
337 Woo *et al.* [45] demonstrated the existence of doublet melting peaks in addition to
338 a series of multiple minor peaks. These results were related to the presence of
339 multiple lamellae population, a distinctive semi-crystalline polymer feature. Liu *et*
340 *al.* [46] used both morphological and calorimetric analyses to evidence such
341 multiple melting processes: hence, the lowest endotherm was attributed to the
342 melting of lesser quality subsidiary crystals and the highest endotherm to the
343 major crystallites.

344 Jeon *et al.* [29] proposed, from Nuclear Magnetic Resonance (NMR) results on a
345 10 kGy gamma-irradiated PET, a mechanism of formation of diethylene glycol
346 segments whereas Yoo *et al.* [47] worked on the cyclic tris (ethylene
347 terephthalate) (CTET) , a widely spread PET oligomer. Authors showed that the
348 316 °C melting endotherm, a distinctive CTET feature, would evolve to a double
349 melting behavior (252 and 313°C) depending on heat treatment. Insofar as melting
350 temperatures were substantially different from the endotherm observed in our
351 research (i.e.176 °C), we attributed it to the emergence of a new lamellar
352 population due to irradiation-induced polymer chain scissions. The formation of
353 small molecules did not seem to influence the Tg, presumably owing to their
354 scarcity. The high-temperature melting peak was construed as resulting from the
355 melting of thick lamellae generated during the industrial film process, whereas the
356 low-temperature melting peak was attributed to thin lamellae formed during
357 irradiation.

358 Crystallinity yields were calculated from the ratio of the melting enthalpy (ΔH)
359 measured by the total area under the melting peak to the melting enthalpy of a
360 fully crystalline PET, i.e. $\Delta H_0=138 \text{ J.g}^{-1}$ [48]. Integrations were conducted with a
361 linear function. Results are displayed in Table 1.

362 Considering the crystallinity yield calculated from both endotherms (between 140
363 up to 259 °C), a slight increase was observed over 50 kGy, due to secondary
364 lamellae formation. Congruent with our earlier statements, as irradiation dose
365 increased chain scissions developed, fostering thereby secondary lamellae
366 formation. Liu *et al.* [35] have reported crystallinity stability up to 4.0 MGy
367 absorbed doses delivered by swift heavy ions. On the contrary, Zhu *et al.* [34]
368 showed by both FTIR and X-rays Diffraction (XRD) that high energy heavy ions
369 could damage the benzyl ring of PET and induce a loss of crystallinity. According

370 to our research, as crystallinity increased permeability decreased, a double-fold
371 trend which entailed a valuable consequence, namely a lesser migration of low
372 molecular weight molecules. Small molecules are less likely to spread through
373 crystalline areas than through amorphous ones. Indeed, crystalline areas act as
374 barriers fending off any risk of spreading.

375

376 From TGA measurements, we obtained the sample degradation temperature from
377 the derivative curves. Results are given in Table 2. As dose increased, we
378 observed no single temperature variation or any degradation percentage alteration,
379 a fact which implies that even 150 kGy irradiation had no impact whatsoever over
380 PET temperature stability. Degradation temperature was akin to the one claimed
381 by Kinoshita *et al.* [49]: using TGA/FTIR simultaneous analysis, authors
382 evidenced the main gases from PET, i.e. benzoic acid and carbon dioxide.

383

384 Finally, in the first part, dedicated to the matrix, we have shown that for the dose
385 range used here, no chemical modifications were observed, whereas thermal
386 analysis evidenced physical modifications attributed to chains scissions.

387 Then, we chose to further extend our investigations on irradiation effects over
388 non-volatile organic extractables.

389

390 **2- Effect of the sterilization on PET's non-volatile extractables –** 391 **global analysis.**

392

393 First, we aimed at achieving a global analysis of extractables in PET films by
394 means of weight measurements. Extractables emerged following irradiation and

395 were chain scission-related, as stated earlier. Hence, we resorted to SEC in order
396 to determine extractable molecular weights. RP-HPLC was also used on account
397 of its enhanced separating efficiency.

398

399 2. 1- Weight measurements

400 PET is known to be radiation-resistant. Regarding mechanical features, authors
401 showed that PET and (High Density Polyethylene /Polyamide) HDPE/PA were
402 the most radiation-resistant and displayed moderate concentration of leachables.
403 Goulas *et al.* [39] have studied the overall migration of several gamma-irradiated
404 packaging materials in aqueous simulants and isooctane by weighing the samples.
405 We carried out three weight measures. As a result, the trend evidenced a
406 significant weight decrease ranging between 0 and 25 kGy (i.e. from $0.040 \pm$
407 0.006 g down to 0.018 ± 0.010 g). The loss of volatile compounds involving low
408 molecular weight molecules may indeed account for such a fact. Villain *et al.* [50]
409 reported aldehyde formation following PET thermal degradation. Komolprasert *et*
410 *al.* [41] argued that a 25 kGy gamma irradiation on PET triggered a significant
411 volatile compound increase, as opposed to non-volatile compounds.
412 50 and 150 kGy doses used in our investigations induced weight increase up to
413 0.056 ± 0.003 g. Chain scission-related oligomers formation may indeed account
414 for such an upward trend.

415

416 2. 2- SEC analysis

417 After weight analysis, we turned to SEC analysis. Although not specific, SEC
418 analysis stands as a semi-separative technique suited to releasing further

419 extractable-related information. Figure 3 shows the chromatograms obtained with
420 the RI and UV detectors set at 240 nm which is PET's most specific wavelength,
421 and at 280 nm specific of phenolic groupments. Several peaks are presented in
422 Figure 3. We determined molecular masses (Mp) based on calibration. Table 3
423 displays the masses of the different peaks. Peak n°1 was evidenced by
424 refractometry only, and corresponds to high weight extractables with a
425 34390 g.mol⁻¹ approximately Mp. As regards retention times exceeding 15
426 minutes, several peaks exhibit molecular weight variations within the 1275 to
427 221 g.mol⁻¹ Mp range. Regardless of the detector used, the top ranking peak
428 corresponds to peak number 3 with a 657 g.mol⁻¹ Mp (Figure 3). Chromatographic
429 profiles are similar for both wavelengths even though at 240 nm peaks are far
430 more distinctive.

431 Considering that the monomer molecular weight is of 192 g.mol⁻¹, we can propose
432 that oligomers observed have a polymerization degree varying from 2 to 6 approx.
433 (i.e. peaks 5 to 2, respectively).

434

435 Shiono *et al.* [21,22] used preparative SEC and mass spectroscopy on PET films
436 to demonstrate the presence of oligomers, as well as cyclic dimers and trimers in
437 particular. Molar masses reach 384 and 576 g.mol⁻¹, respectively. Cyclic trimer is
438 predominant because of ring tension [20,51,52]. Insofar as mass spectroscopy is
439 more acute, weight determination is therefore much more accurate. We may hence
440 consider that the top ranking peak in our study (peak number 3) corresponds to the
441 cyclic trimer, that has the highest concentration, and that the accuracy of the
442 calculation method accounts for the molecular mass difference (i.e. Mp=
443 576 g.mol⁻¹ instead of 657 g.mol⁻¹).

444

445 Ultimately, SEC used on non-irradiated PET enabled us to evidence the presence
446 of oligomers obtained after extraction. Indeed, the medical grade PET used in our
447 research remains as such, additive-free, according to the European
448 Pharmacopoeia's specifications.

449

450 To extend further probing of extractables, we performed RP-HPLC analyses. The
451 latter prove far more acute than SEC. Hence, they stand as a relevant preparatory
452 task towards proper mass spectrometry coupling.

453

454 2. 3- HPLC analysis

455

456 To date, numerous researchers have granted special attention to PET oligomers on
457 the following grounds: highly radiation-resistant polymers such as PET, yield
458 measurable amounts of low molecular weight products. Cyclic n-mers (n=1 to 8)
459 have thus been identified. Among them, the cyclic trimer has been referenced as
460 the most concentrated form. Different methods have been developed and catered
461 to effective PET oligomer identification. As a case in point: Shiono *et al.* [21,22]
462 as well as Nasser *et al.* [20] carried out preparative SEC. They singled out
463 oligomers from dimer to pentamer (by ^1H and ^{13}C NMR). Küppers *et al.* [18]
464 implemented the Supercritical Fluid Extraction (SFE) technique towards selective
465 oligomers extraction in PET. Bartle *et al.* [53] demonstrated that cyclic trimer
466 molecules are not SFE accessible and that soxhlet extraction allows for enhanced
467 extraction yields. Others [17] studied oligomer extracts through Microwave
468 Assisted Extraction given its distinctive time-efficient and solvent saving features.
469 Mostly cyclic trimers and heptamers were thus extracted. HPLC coupled with UV

470 has also been used [16,19]. Lately, mass spectrometry involving thermospray [54]
471 and Positive Ion Atmospheric Pressure Chemical Ionization has been
472 implemented to study PET oligomers [14,55]. Such soft ionization, coupled with
473 an HPLC/MS method enables the identification of oligomers from $n=3$ to 8.
474 It is noteworthy however, that few researchers have issued to date studies
475 dedicated to low molecular weight compounds in irradiated PET. As a rare
476 example, Buchalla *et al.* [37] evidenced non-volatile PET radiolysis products such
477 as terephthalic acid methyl and ethylesters such as benzoic acid. They showed that
478 the concentration of terephthalic acid ethylester increased by a factor 2 after a
479 50 kGy gamma-irradiation (to ca. 2mg/kg) with a limit of detection of their
480 method of 10 $\mu\text{g/L}$. Moreover, pure ethylene terephthalate oligomers are neither
481 commercially available nor easy to prepare. In the framework of our
482 investigations, we focused therefore on terephthalic and benzoic acids exhibiting
483 close molecular structures (Figure 4): indeed, they stem from PET synthesis and
484 degradation respectively.

485

486 Figures 5a and 5b display the chromatographic profiles of both the acid standard
487 solutions and the extraction solutions at the 240 nm wavelength (wavelength
488 chosen from the maximum absorbance at 240 nm for the major peaks). Regarding
489 the chromatographic profiles of PET extraction solutions, the overall profile
490 remains complex and exhibits several major peaks. From the chromatographic
491 system characteristics, firstly held compounds disclose polar properties and/or
492 small molecular masses. As retention time increases, more apolar or larger
493 compounds are separated. Whenever retention times exceed 25 minutes, the major
494 peaks appear with regular 7-8 minutes approximative time intervals (25, 32, 41
495 and 48 min), while their dose-dependant intensities increase markedly. Such peaks

496 result most likely from the presence of oligomers with increasing polymerization
497 order as their 3D chromatograms display the same UV spectrum.

498 Retention times under 25 minutes yield numerous peaks that correspond to the
499 most polar compounds. We can observe in Figures 5a and 5b that very intense
500 peaks stand at about 4.5 minutes and 9 minutes. Those quickly eluted peaks
501 certainly correspond to dimer and trimer oligomers observed earlier by SEC.

502

503 Although low retention times generate numerous peaks, only terephthalic and
504 benzoic acids have been identified at 5.5 and 7.3 minutes retention times,
505 respectively. We performed a calibration with a linear regression on both acids
506 ($n=3$). Quantification results are presented in Figure 6. Acid concentrations were
507 calculated on the basis of calibration equation parameters. Concentrations were
508 further rationalized to the mass of PET extracted and to the volume of methanol
509 used to dissolve extraction products. Since extraction was performed in methanol,
510 we hypothesized therefore that trans-esterification could possibly affect acids
511 [16]. Hence, we chose to test such an assumption as follows: we let them boil
512 separately in methanol for two hours; subsequent analysis revealed no difference
513 whatsoever in HPLC with reference to native standards.

514

515 Figure 6 presents data pertaining to terephthalic acid concentrations: a slight
516 decrease is recorded between 0 and 25 kGy, before rising to 150 kGy. Benzoic
517 acid concentrations are about three times below terephthalic concentrations while
518 displaying similar dose-dependant trends. Since benzoic acid is considered as a
519 terephthalic acid degradation product, such a difference in terms of concentration
520 makes sense.

521 To the extent that terephthalic acid is a synthesis residue, concentration increase
522 stems therefore from the fact that extractables are easily forced out of the bulk
523 whenever macromolecular chains are degraded. One should notice that
524 regulation n°10/2011 [56], devoted to plastic materials and articles intended to
525 come into contact with food, specifies a specific migration limit of 7.5 ppm for
526 terephthalic acid.

527

528 **CONCLUSION**

529 Our investigations performed on electron beam irradiated PET films, demonstrate
530 that chain scissions can be evidenced. Thermal analyses reveal that the latter
531 reduce crystallite size without altering either global crystallinity yield, or stability
532 temperature. Findings are congruent with the study performed on PET
533 extractables which exhibit a dose-dependant extraction yield increase. Indeed, as
534 chain scissions occur, extractables prove more numerous; moreover, they are
535 likely to migrate swiftly towards the polymer matrix and may be easily extracted.
536 Further, we substantiated the presence of terephthalic and benzoic acids. Even
537 though concentration increase proves dose-dependant; the latter remain however
538 far below official pharmaceutical recommendations.

539

540 Within the framework of our experiments, we evidenced two kinds of organic
541 non-volatile extractables: low molecular weight extractables and oligomers, both
542 obtained under low irradiation doses. Concentrations increase, while mobility
543 becomes easier as crystallite size tends to decrease. SEC analysis singled out the
544 trimer as the predominant oligomer. HPLC further substantiated the presence of
545 oligomers. Any acute identification of extractable composition will however

546 require in the future, extended probing through mass spectroscopy coupled with
547 HPLC.

548

549 With respect to extractables, leachables do also require further scrutiny. Hence,
550 ageing of materials under accelerated conditions needs to be experimented and
551 mathematical migration models developed accordingly. Ultimately, such results
552 provide a valuable contribution towards pharmaceutical and biological
553 applications: indeed, low molecular weight compounds can migrate out of the
554 polymer bulk and thus interact with the contact medium and we can wonder if
555 they are not able to induce potential toxicity-related risks.

556

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560

561 Conflicts of interest: none

562

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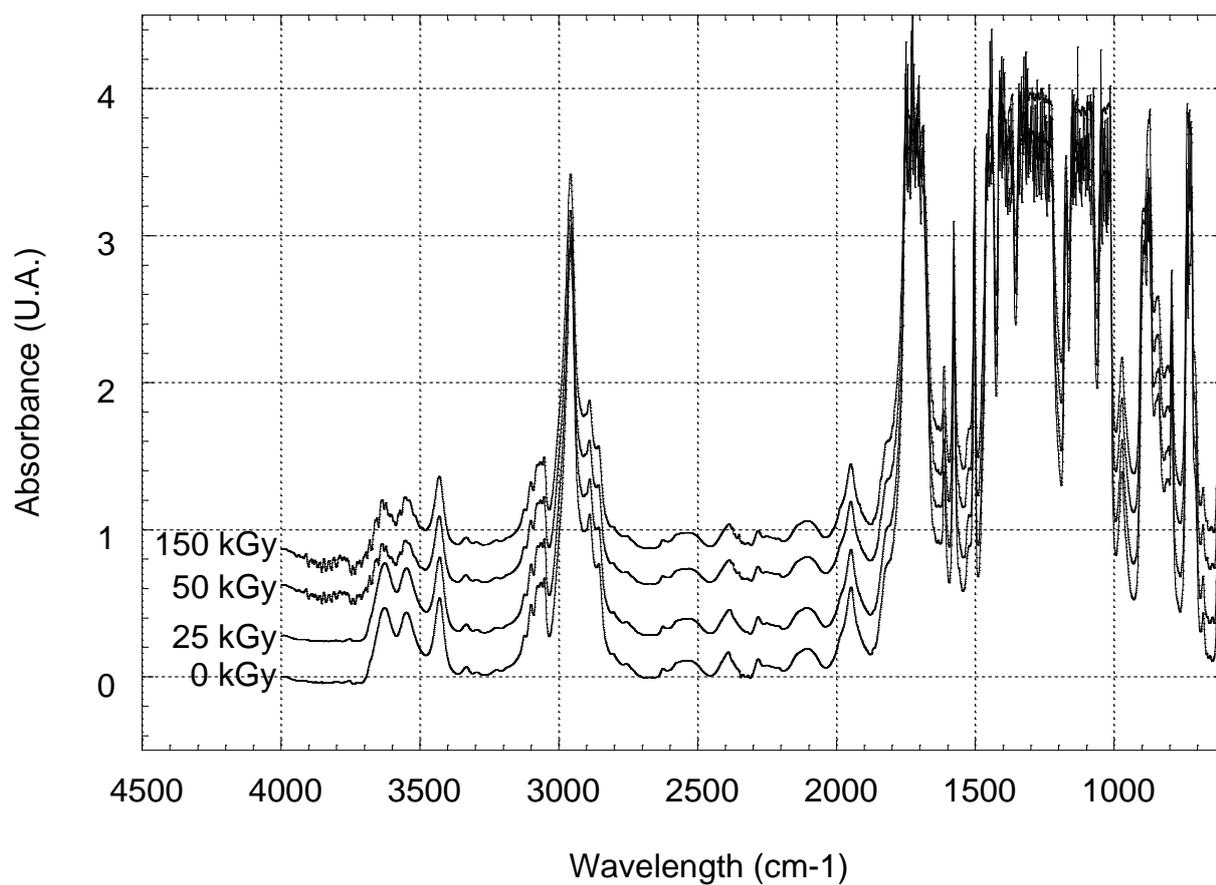


Figure 1: FTIR in transmission mode of PET irradiated at different doses (0, 25, 50 and 150 kGy). / Spectres IRTF en mode transmission du PET irradié à différentes doses (0, 25, 50 et 150 kGy).

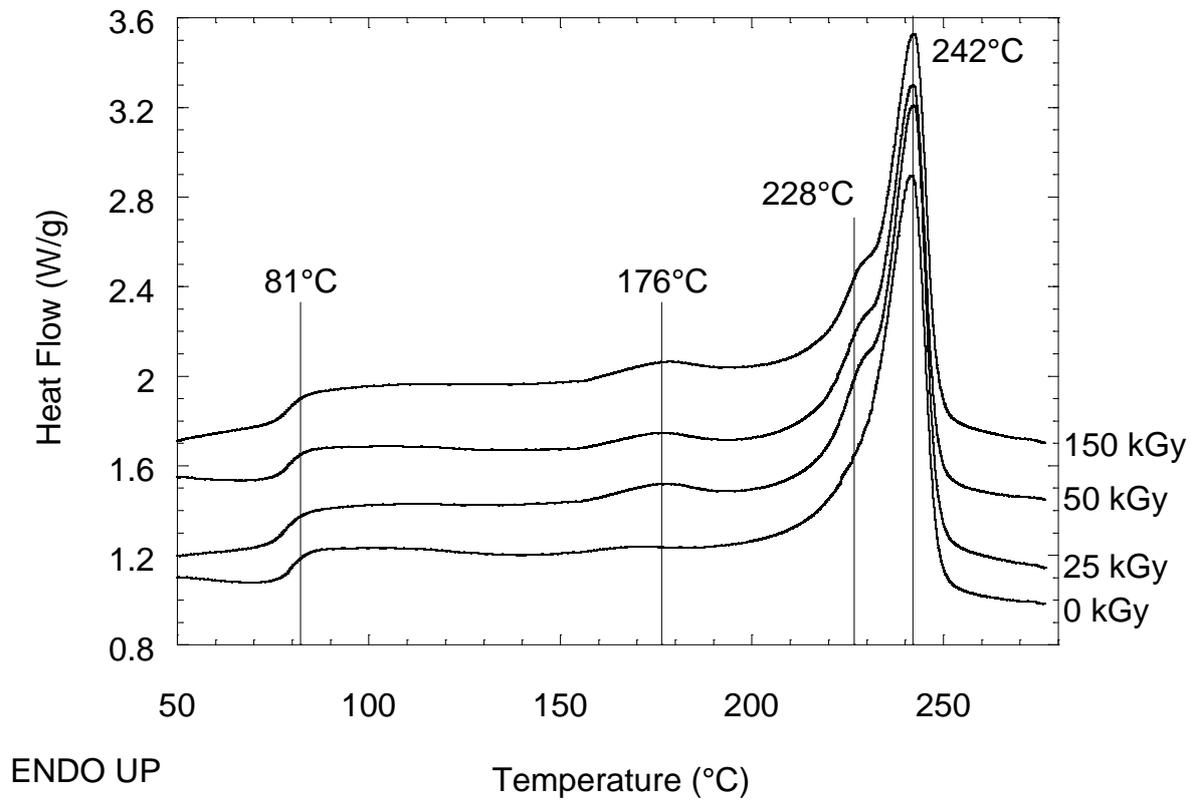


Figure 2: DSC curves of PET at different doses of irradiation (10°C/min, N₂ - Second heating). / Thermogrammes d'AED du PET à différentes doses d'irradiation (10°C/min, N₂ – Seconde montée en température).

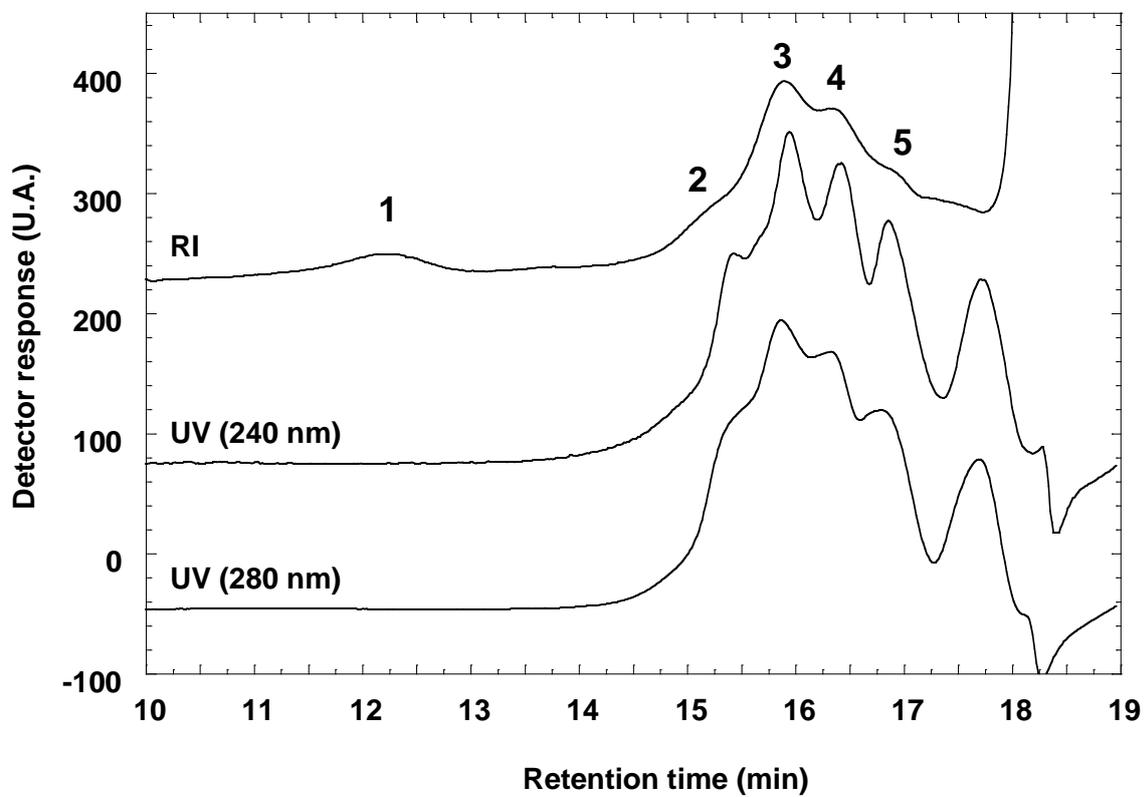
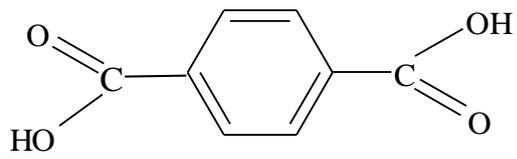
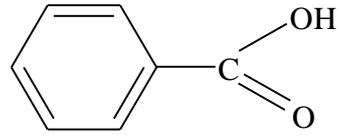


Figure 3: SEC profiles from non irradiated PET. / Profils de CES du PET non irradié.



a)



b)

Figure 4: Molecular structures of a) terephthalic acid and b) benzoic acid. / Structures des molécules a) acide téréphthalique et b) acide benzoïque.

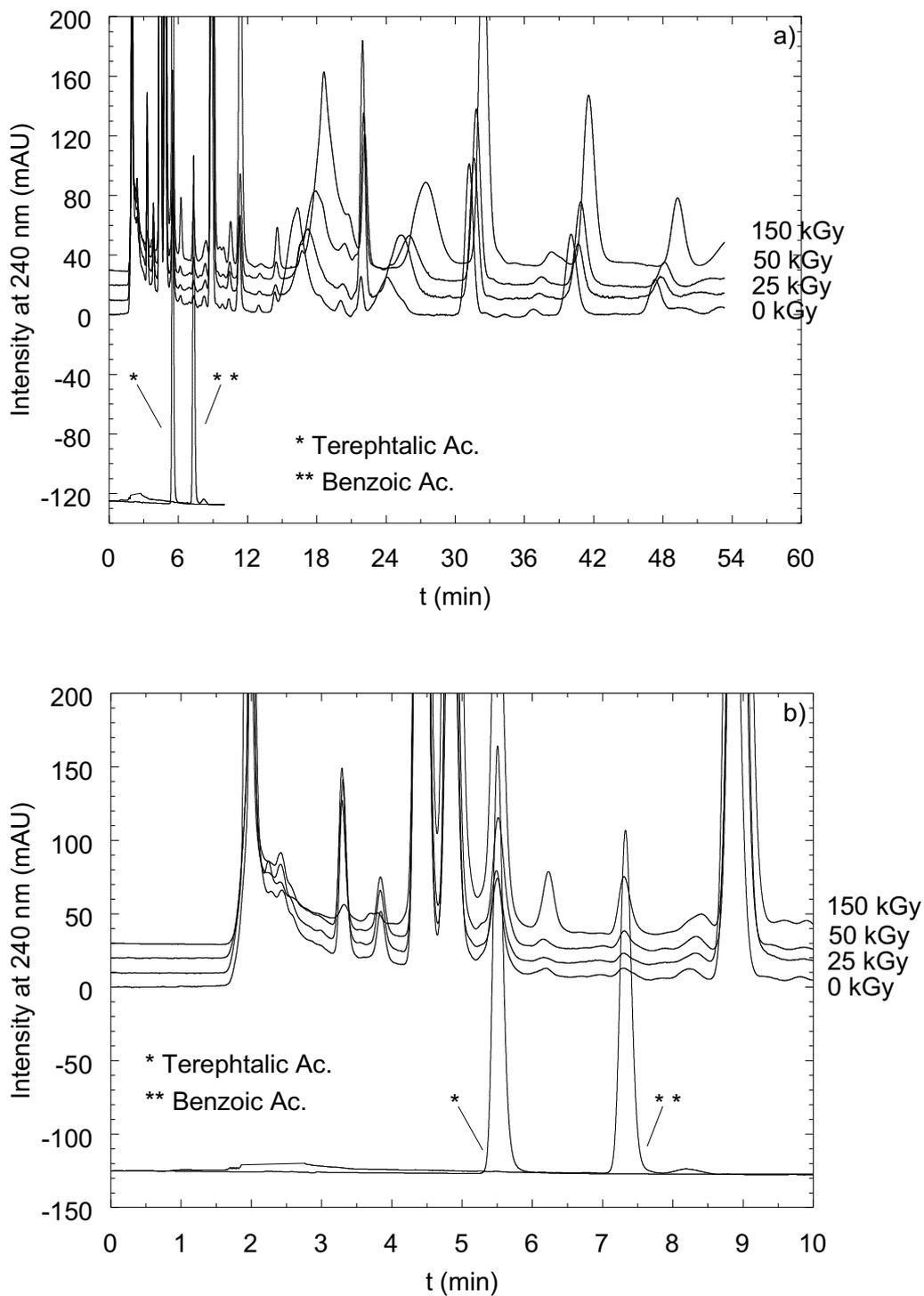


Figure 5: a).Chromatograms at 240 nm of extraction solutions of non-irradiated and irradiated PET, and chromatograms of terephthalic and benzoic acids, b) zoom of figure 5a. / a).Chromatogrammes à 240 nm des solutions d'extraction du PET non irradié et irradié, et chromatogrammes des acides téréphtalique et benzoïque, b) agrandissement de la figure 5a.

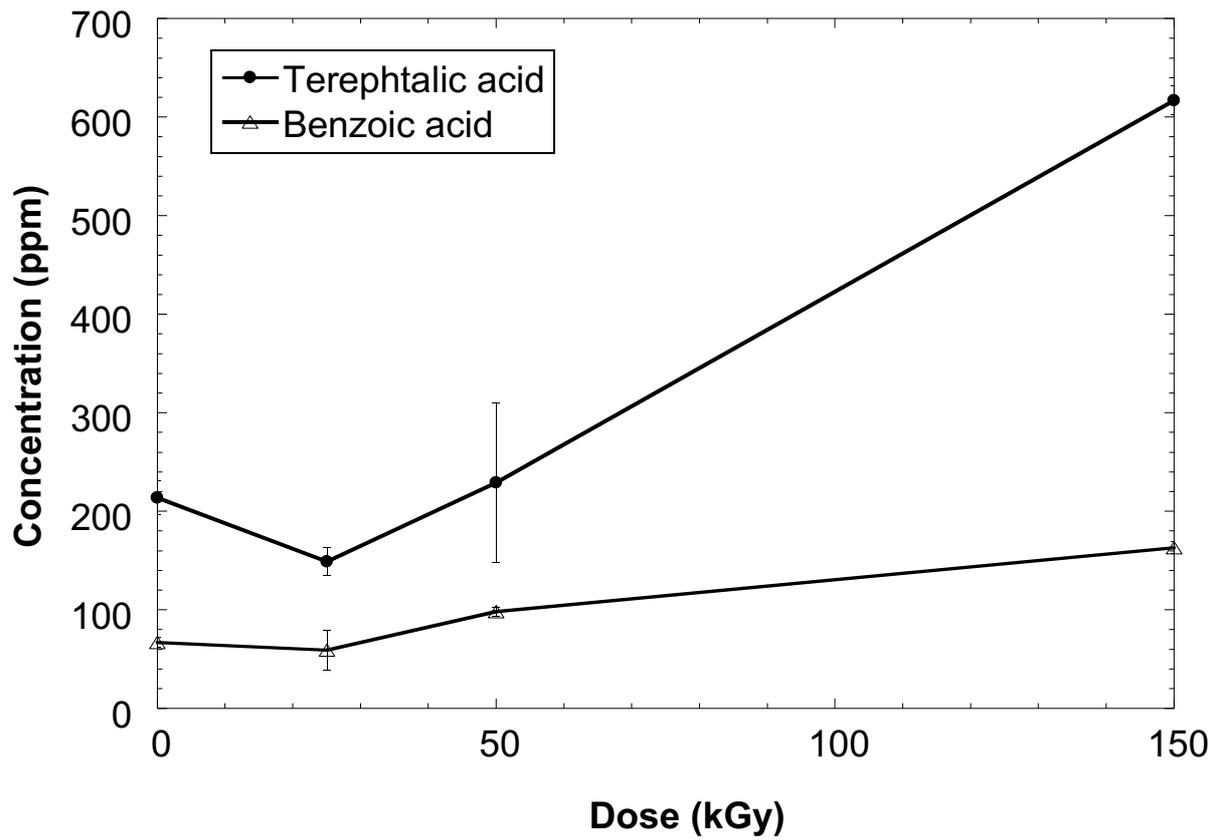


Figure 6 : Terephthalic and benzoic acids mean concentrations (n=3) in PET irradiated with different doses. / Concentrations moyennes en acides téréphtalique et benzoïque (n=3) dans le PET irradié à différentes doses.

Dose (kGy)	χ_c (J/g) (140-259 °C)	χ_c (J/g) (194-259 °C) ^o
0	26± 1	21± 2
25	29± 2	24± 1
50	28± 3	22± 1
150	34± 3	24± 2

Table 1: Crystallinity yields, χ_c , as a function of the dose, considering both endotherms in the temperature ranges of (140-259 °C) and (194-259 °C). / Taux de cristallinité, χ_c , en fonction de la dose, selon les deux endothermes entre (140-259 °C) et (194-259 °C).

Dose (kGy)	Mean degradation temperature (°C) (n=3)	Mean degradation percentage (%) (n=3)
0	446 ± 1	87 ± 6
150	447 ± 2	87 ± 4

Table 2: Temperatures and percentages of degradation as a function of the dose. /
Températures et pourcentages de dégradation en fonction de la dose.

Peak number	1		2		3		4		5	
Retention volume (min)	12.0		14.9		15.7		16.2		16.6	
	Mean (n=3)	CV	Mean (n=3)	CV	Mean (n=3)	CV	Mean (n=3)	CV	Mean (n=3)	CV
Mn (g/mol)	31401	3016	1230	148	702	8	434	4	307	15
Mw (g/mol)	38380	9335	1271	142	715	18	441	6	309	15
Mz (g/mol)	47896	19309	1320	134	730	30	448	9	311	15
Mp (g/mol)	34390	1440	1275	234	657	35	443	1	341	27

Table 3: Molecular masses of extractables observed in non-irradiated PET. / Masses molaires des extractibles observés dans le PET non irradié.