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1 **Evaluation of the effect of chemical or enzymatic synthesis methods on biodegradability**
2 **of polyesters**

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6

7 **Abstract**

8 This work compares the biodegradability of polyesters produced by an esterification reaction
9 between glycerol and oleic di-acid (D 18:1) issued from green chemical pathways, via either
10 classical thermo-chemical methods, or an enzymatic method using the immobilized lipase of
11 *Candida antarctica* B (Novozym 435). An elastomeric polymer synthesized by enzymatic
12 catalysis is more biodegradable than an elastomeric thermo-chemical polyester synthesized by

13 _____

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25 a standard chemical procedure. This difference lies in percentage of the dendritic motifs, in
26 values of the degree of substitution, and certainly in cross-links inducing an hyper-branched
27 structure less accessible to the lipolytic enzymes in a waste treatment plant. However, when
28 the elastomeric polymer synthesized by enzymatic catalysis is processed at high temperature
29 as required for certain industrial applications, it presents an identical rate of biodegradation
30 than the chemical polyester. The advantages of the thermo-chemical methods are greater
31 speed and lower cost. Enzymatic synthesis appears be suited to producing polyesters, devoid
32 of metallic catalysts, which must be used without processing at high temperature to keep a
33 high biodegradability.

34 **Keywords** : chemical polyesters, enzymatic polyesters, biodegradability

35

36 **Introduction**

37 Production of synthetic polymers from petroleum compounds dates back to the beginning of
38 the 20th century and played a major role in the economic development of industrialized
39 countries. Since 1970, however, it has been recognized that these polymers are resistant to
40 degradation by microorganisms, once used, create problems of pollution and disposal both in
41 the natural medium and in waste treatment plants. When designing new materials, therefore,
42 efforts have been made to provide for not only their texture, their mechanical resistance or
43 their moistness, but also for their biodegradability [1], while ensuring that this does not occur
44 during use.

45 Taking polyethylene as an example, there is practically no diffusion of water and oxygen in
46 the polymer. Only the surface, with a reduced number of free chains, is open to attack by
47 extracellular enzymatic reactions. Addition of pro-oxidant derivatives (Manganese and Cobalt
48 salts) leads to release free radicals which, exposed to light, allow the formation of

49 hydroperoxides and then lead to the cleavage of the polyethylene [2,3]. These conditions [4]
50 reduce the molecular weight, but only 20 % of fragments with Mw < 1000 g/mole can be
51 mineralized by microorganisms. These fragments, which are hydrocarbons, follow various
52 known metabolic pathways for alkanes with terminal, di-terminal or sub-terminal oxidation
53 [5]. Thus, such polymers are not biodegradable according to norm NE 13432 for
54 compostability. The long-term effects of accumulation of oligo- and poly-olefins in soils are
55 not yet known [6].

56 Other biodegradable polymers can be synthesized using various natural resources and
57 processes [7]. Examples include agro-polymers produced from vegetal biomasses [8],
58 polymers produced from microbial metabolism such as poly-hydroxyalkanoates [9] and
59 polymers synthesized from monomers produced by bacterial fermentations, i.e. poly(lactic
60 acid) [10, 11] which is the principal polyester based on renewable raw material
61 commercialized at industrial scale [12].

62 There are two ways of catalysing the poly-condensation of poly-acids and poly-ols to obtain
63 polyesters: using either organo-metallic compounds [13] or enzymes [11]. The chemical
64 method is efficacious and rapid, allowing the synthesis of many important polymers. Yet the
65 various organo-metallic catalysers [14, 15] in these reactions cannot be fully eliminated after
66 synthesis with the ensuing risk that they will confer toxicity to the polymers, and
67 accumulation in soils. Chemical synthesis of polyesters requires high temperatures,
68 sometimes exceeding 200°C. Such temperatures can lead to secondary reactions liable to
69 modify the stoichiometry of the polymerization through, for example, dehydration of diols or
70 degradation of glycerol into acroleine. However, polymerization using chemical catalysis
71 allows for the production polymers on a large scale and in a short reaction time, with limited
72 purification steps afterwards.

73 The enzymatic synthesis of biodegradable polymers from renewable resources has attracted
74 great interest. Thus, lipases which are enzymes used in many biotechnological fields [16,17]
75 can hydrolyse polyesters or catalyse the inverse reaction, the esterification. Balance between
76 hydrolyse and esterification reactions is controlled by the quantity of water in the reacting
77 medium. For the esterification reactions, the quantity of water allowing the optimal activity
78 corresponds to the water molecules hardly bound to protein structure which are necessary to
79 maintain their enzymatic conformation.

80 Whatever the mode of polymer synthesis, it is necessary to distinguish degradation from
81 biodegradation. In the first case, the polymer undergoes an irreversible alteration of its
82 chemical structure, leading to loss of its properties and functions. These alterations can be
83 caused by abiotic phenomena such as mechanical hindrances, light, heat and hydrolysis or
84 oxidation reactions [18]. Biodegradation is a degradation catalysed by microorganisms which
85 can divide polymers into monomers. These monomers are then either mineralized into H₂O
86 and CO₂ with energy production, or transformed into biomass and secondary metabolites [19].
87 Contrary to transformation by abiotic phenomena, catalysis by microorganisms allows organic
88 matter recycling.

89 Here, we aimed to determine the effect of the mode of polyester synthesis, namely chemical
90 or enzymatic or even a combination of the two methods, on the chemical structure of these
91 polymers, and thus on their biodegradability. In particular, we focused on the effect of the
92 temperature during the thermic phase, used in certain processing, on the biodegradability of
93 polyesters obtained from glycerol and oleic di-acid (D18-1). These two compounds are issued
94 from a green chemical pathway: glycerol is issued from the biodiesel production [20] and the
95 oleic di-acid results of the enzymatic oxidation of the alkyl extremity of the oleic acid by
96 *Candida tropicalis* [21]. Kulshrestha et al [22], Yang et al [23] and Zhang et al [24] already
97 reported the use of glycerol and oleic di-acid as polymer precursor but only under the

98 chemical aspect of the synthesized products. Our study was conducted, either by chemical
99 techniques or by the lipase [25] of *Candida antarctica* B (Novozym 435) immobilized on a
100 polyacrylic matrix. To measure the biodegradability of polyesters, the lipase of *Rhizopus*
101 *arrhizus* was often used [26, 13], but in this work we chose the most common laboratory test
102 based on standardized respirometric techniques resulting in oxygen consumption and CO₂
103 release [27] when microorganisms present, for example, in activated mud or compost or soil,
104 are placed in contact with a polymer.

105 **Experimental**

106 Synthesis of polyesters

107 Monomers used: *cis* 9 octadecen dioic acid (oleic di-acid : D 18:1) was supplied by Cognis
108 (France). It was first purified by solubilisation in dichloromethane to remove insoluble
109 saturated by-products and then recrystallized in petroleum ether to remove soluble monoacids.
110 Its purity was evaluated by GC at 97 %. Glycerol was supplied by Acros Organics (purity 99
111 %).

112 Five polymers were synthesized from D 18:1 and glycerol in an equimolecular mixture: **1.** a
113 thermal polymer obtained by heating the monomer mixture at 65°C, the temperature used in
114 enzymatic methods; **2.** monomers mixed by rotary stirring and heated at 160°C for 3 h and at
115 180°C for 1 h; **3.** a polyester synthesized by first heating at 160°C under nitrogen flux for 8 h
116 in a 100 mL reactor with blade stirring and then dissolving the mixture in dichloromethane,
117 precipitated in cold methanol (-40°C < t° < -30°C) and recovering it; **4.** an enzymatic polymer
118 obtained with Novozym 435 (0.1 %) at 65°C in a glass reactor 100 mm high for 6 days; **5.** a
119 polyester synthesized by heating at 160°C for 4 h of a pre-polymer obtained by enzymatic
120 catalyse such as for the polymer 4 but stopped at a viscous liquid physical state.

121 Polymers 1, 4 and 5 were stirred in a glass reactor with an ARZR1 (Heidolph) motor equipped with a
122 rod supporting a mixing blade (4.5 cm diameter). All the reactor were immersed in an oil-bath.

123 Elementary analysis

124 Carbon, hydrogen and oxygen atom percentages in polymers were determined with a Thermo
125 Finnigan EA 1112 Elementary Analyser.

126 Measure of the M_w and M_n polymers

127 This measure was realized by steric exclusion chromatography with a PLgel 5 μm MiniMIX-
128 D column (250 x 4.6 mm). This column was protected by a PLgel 5 μm MiniMIX-D Guard
129 pre-column (50 x 4.6 mm). Both columns were provided by Polymer Lab. They were supplied
130 continuously with a gas-free tetrahydrofurane (THF) via a Waters 515 pump with a 0.3 mL.
131 min^{-1} delivery. Prior to analysis, solutions were filtered through 0.45 μm Millex-HV filters
132 from Polymer Lab. Twenty μL at 3 g L^{-1} were injected at room temperature. This
133 chromatographic chain was equipped both with a Waters 410 refractometer (thermostated at
134 35°C) and a UV Waters 2487 detector. Data acquisition was realized with OmniSEC by
135 Viscotek.

136 Nuclear Magnetic Resonance

137 The insoluble samples were analyzed by ^{13}C High Resolution Magic Angle Spinning
138 (HRMAS) technique on a Bruker Avance 400MHz spectrometer operating at a ^{13}C resonance
139 frequency of 106 MHz and using a HRMAS Bruker double-bearing probe. About 3-4 mg of
140 sample were swollen with 50 μL of CDCl_3 in a 4 mm zirconium dioxide rotor, equipped with
141 Teflon spacers, and spun at 4 kHz. The soluble sample was analyzed by ^{13}C Liquid State
142 Bruker Avance 300 MHz spectrometer operating at a ^{13}C resonance frequency of 76 MHz and
143 using a commercial Bruker BBI probe. About 10 mg of sample were solubilized in a mixture

144 of CDCl₃-d₁ (77.1 ppm) and DMSO-d₆ (39.7 ppm) in a 5 mm NMR tube. Attributions of
145 carbons of the glycerol units were deduced from Rabiller and Maze [28] and Mazur et al [29].
146 All experiments were performed at room temperature and the ¹³C chemical shifts were
147 referenced to tetramethylsilane (TMS).

148 Respirometric method

149 Measures of respiratory activities were realized in an Oxytop System WTW apparatus
150 composed of a manometer and a one litre hermetic flask. Biomasses used were from sludge
151 sampled in the waste treatment plant of Brignoles (Var, France). Into the Oxytop flask were
152 introduced the polymer (0.25 g), mixed with the biomass (2.5 g) and a flask containing 50 mL
153 of 0.2 M NaOH. Oxytop flasks were incubated at 20°C. Quantities of oxygen consumed were
154 calculated from the lowering of pressure measured by the Oxytop manometers according to
155 the perfect gas law. They were expressed as mg of O₂ consumed per g of biomass.

156 Quantities of CO₂ released were measured by titration with barium hydroxide of Na₂CO₃
157 formed by reaction of CO₂ and NaOH. They were expressed as mg of CO₂ released per g of
158 biomass. Measures of CO₂ were realized every seven days when the Oxytop flasks refilled
159 with air and NaOH.

160 The biodegradability of polyesters 2, 3, 4 and 5 was compared to the biodegradability of
161 commercial polymers single-use cups formed either with a vegetal pulp (polymer 6) or with a
162 poly(lactic acid) commonly called PLA (polymer 7). The cups were pulverized and the
163 powder thus obtained was dispersed into the biomass in the Oxytop Flasks in the proportions
164 cited above for polyesters.

165 For each polymer tested, an assay was realized without polymer to measure the respiratory
166 activity of the biomass itself. All the assays were realized in triplicate.

167 **Results and discussion**

168 Effect of synthesis methods on polyester structure


169 Glyceridic motifs present in polyesters synthesized by esterification of glycerol by D18-1 di-
170 acid are presented in figure 1 and the respective ^{13}C Nuclear Magnetic Resonance (NMR)
171 spectrum is shown in figure 2 corresponding to the polymer 2. Glyceridic motifs were
172 identified, as further indicated in the experimental part, and their proportions were calculated
173 using integrals of signals of methine carbons. The differences observed in the chemical shifts
174 (1 to 1.5 ppm), compared to the attributions of Kulshrestha et al [22] were principally due to
175 the different mass concentration and the real sample temperature (about 10-15°C) due to
176 sample Magic Angle Spinning at 4 kHz.

177  Figure 1

178  Figure 2

179 Whether using chemical, enzymatic or mixed techniques for polyester synthesis, we observed
180 that proportions of the principal different glyceridic motifs (Fig. 1) depended on the
181 experimental conditions during the successive sequences of polymer synthesis (Table 1). In
182 particular, experiment 1, conducted at 65°C, shows that when this temperature is used for
183 enzymatic catalysis, weak, but not negligible polymerization, is induced.

184

185  Table 1

186

187 Table 1 shows that, for all the polymers, primary hydroxyls are more esterified than
188 secondary hydroxyls. This high percentage is partly due to monoglyceride formation in sn1 or
189 sn3 positions, the presence of monoglycerides in sn2 position (T_2 motif) not being detected.

190 Migration of acyl groups from the sn2 position towards sn1 and sn3 positions, and a higher
191 probability of forming 1- or 3- monoglyceride, explain the absence of 2-monoglyceride [30].

192 When a second esterification is realized on a 1- or 3-monoglyceride, the other external
193 position is preferentially esterified. The highest proportion of esters in sn2 position is present
194 in dendritic motifs (De), indicating that the decrease in the proportion of available primary
195 hydroxyl induces esterification in sn2 position.

196 Experiments 2, 3 and 4 show differences between chemical and enzymatic catalysis in
197 percentages of both the T_1 and dendritic motifs and values of the degree of substitution,
198 defined as the mean number of ester bindings by glycerol unit. Degree of substitution
199 increases with temperature in experiments 2 and 3 (2.1). The two polyesters 2 and 3 thus
200 obtained have 32 and 26 % of the dendritic motifs respectively, which means that their
201 hydroxyl functions sn2 are likely to be involved, in similar proportions, in the increase of the
202 degree of substitution. Nevertheless, the difference in their physical state and their M_n
203 corresponds to different proportions of the other glyceridic motifs. Enzymatic catalysis with
204 Novozym 435 (polymer 4) induces percentages of $L_{1,3}$ esters (36 %) identical to those
205 observed in polymer 2 obtained by thermal esterification (36 %), but great difference concern
206 the percentages of dendritic, $L_{1,2}$ and T_1 motifs.

207 For polymer 5, which presents an elastomeric state, the pre-catalysis with Novozym 435,
208 which leads to a viscous liquid ($MW = 28000$ g/mole, $M_n = 2830$ g/mole), has an effect on
209 the polymer structure. Its structure is closer to that of the polymer 4 than to that of the

210 polymer 2. Thus, polymers 2 and 5 differ greatly, particularly in proportion of both T₁ and
211 dendritic motifs and in degree of substitution in spite they both undergo a thermal phase.

212 Biodegradability of the polyesters

213 The degradation of these different polyesters by a biomass from urban sludge mud was
214 measured at 20°C by the oxygen consumed and the CO₂ released, taking into account the
215 endogen respiration of this biomass. It is important to note that all the polymers tested were
216 treated according to the same experimental protocol, i.e. they were not shaken in Oxytop
217 System. This test of biodegradability differs from the test using the lipase of *Rhizopus*
218 *arrhizus* [13, 26]. An urban sludge contains a great number of microorganism species able to
219 synthesise various types of lipases, thus increasing potentialities of ester-binding hydrolyses.

220 Two commercial polymers (polymers 6 and 7), considered as biodegradable under current
221 legislation, were selected as references to test the methodology used here to study the
222 biodegradability of the polyesters under consideration.

223 Consumption of O₂ and release of CO₂ by a biomass from sludge mud placed in contact with
224 polymers 6 and 7 are given in figure 3; only polymer 6 is degraded in the Oxytop System
225 condition, i.e. at 20°C.

226 Figure 3

227 The high potential of microorganisms to synthesize cellulases and hemicellulases may explain
228 this high biodegradation rate of the polymer 6 formed with a vegetal pulp. No degradation of
229 polymer 7 formed with PLA was observed in the Oxytop System. To eliminate the hypothesis
230 that the processing at high temperature [31] of the PLA cups could lead to a non-
231 biodegradable structure, a racemic mixture of polylactic acid isomers (white powder) was
232 subjected to the respiratory Oxytop System. Results are identical to those from experiments

233 conducted with PLA. The crystallinity of the PLA is certainly [32] an important parameter
234 which can be taken into account. Indeed, crystalline zones are less hydrolysable than
235 amorphous zones. Moreover, enzymes degrade only the surface of the solid substrate, because
236 they cannot penetrate the polymer systems [33]. As already demonstrated by Weir et al
237 [34,35], the increasing of temperature above 50°C, temperature reached in industrial compost
238 plants [36, 37], modifies the crystalline zones turning them into an amorphous structure, more
239 accessible and thus more biodegradable, so meeting the specifications of three international
240 standards: ASTM D5338, ISO1855 and NF14352. However, in a real soil environment and
241 home composting, the temperature usually does not exceed 30°C. These results corroborate
242 those of Rudnik and Briassoulis [38] who demonstrated by respirometric methods that PLA
243 materials are not degraded at 30°C. Consequently, the respiratory Oxytop System allows to
244 differentiate the biodegradability, measured at 20°C, of polymers studied in this work.

245 Figure 4 shows results of experiments 2, 3, 4 and 5, indicating that polymers obtained from an
246 equimolecular mixture of glycerol and D 18:1 are mineralized whatever the synthesis mode.
247 Yet the polymers 3 and 4 present a biodegradability higher than the polymers 2 and 5. Thus,
248 52 mg and 45 mg of CO₂ were respectively released for 35 days from polymers 3 and 4 by 1 g
249 of biomass from sludge mud. In the same conditions, only 10 mg of CO₂ were released from
250 the polymers 2 and 5. For the polymer 4, it is important to eliminate the hypothesis that the
251 residual Novozym may act in hydrolysis in the degradation system, thus releasing glycerol
252 and D 18:1. There is need to point out, first, that no free glycerol was detected in polymer 4 at
253 the end of its synthesis (results not shown). Second, when polymer 4 was mixed with urban
254 sludge mud, Novozym 435 was at a maximum concentration of 0.01%, versus 0.1 % for its
255 synthesis phase, and the temperature was at 20° C, whereas the maximum activity of this
256 enzyme occurs between 65 and 80°C [39].

257 Figure 4

258 These results seem indicate that the difficulties for microbial lipases to reach and thus to
259 hydrolyse the ester bindings are not only dependent of the dendritic structure of the polymer.
260 Probably, the thermic treatment subjected by the polymers 2 and 5 results in cross-links and
261 thus in a higher branched structure than in the enzymatic polymer. The higher degree of
262 branching between linear chains, as defined by Hölder et al [40], the greater the likelihood that
263 a hyper-branched polyester will have a typical globular dendrimer structure.

264 The thermic treatment subjected by the polymer 3, limited at a viscous liquid state, was
265 insufficient to create such structures. Its weak Mw and its viscous state certainly allowed a
266 better accessibility of the esters bindings to the microbial lipases as it was also observed by
267 Umare et al [41] with 1,3-propanediol based polyesters.

268 Polymers 4 and 5, despite having fairly similar structures and an elastomeric physical state,
269 are not biodegraded at the same rate. It seems that the enzymatic pre-polymerization interferes
270 with the thermal phase by reducing the proportion of dendritic motifs in polymer 5 as
271 compared to polymer 4, the processing at 160°C for 4 h then leading to cross-links which
272 confer to the polymer 5 the same biodegradability than the polymer 2.

273 Based both on the percentage of carbon in each polymer structure and on the rate of CO₂
274 production (Fig. 3 and 4), it is possible to estimate the approximate time required for 1 g of
275 biomass sampled in a waste treatment plant to transform 100 mg of polyester into CO₂. In the
276 Oxytop System, all the organic carbon can be considered to be transformed into CO₂, organic
277 carbon transformation into biomass probably being negligible. Indeed, the lack of no
278 renewable elements such as nitrogen and phosphorus induces an energy decoupling. An
279 extrapolation can be made from this result to a waste treatment plant, where there is
280 permanent nitrogen and phosphorus supplies, taking into account that about 50 % of carbon
281 (C) could be transformed into biomass [42, 43]. In this case, the time required to transform the

282 organic carbon into CO₂ and biomass in the Oxytop System, must be divided by
283 approximately 2.

284 Table 2 shows the approximate time required for mineralization by 1 g of biomass of 100 mg
285 of polymers 2, 3, 4, 5 and 6.

286 **Table 2**

287 The findings of this study indicate that the mode of synthesis of a polymer should be chosen
288 according both to its intended use and to the properties required. Enzymatic synthesis leads to
289 polyesters which are more biodegradable than those obtained by chemical means, while
290 providing an identical elastomeric state (polymers 2 and 4). A weak molecular mass and a
291 viscous state facilitate biodegradation. A thermal phase induces a higher proportion of
292 dendritic motifs, except after a pre-polymerization phase (polymer 5). The environmental
293 conditions to which the polyesters are subjected after use (compost, urban sewage sludge,
294 soil) also affect the action of microorganisms (polymer 7).

295 **Conclusion**

296 This work shows that the synthesis method is a parameter allowing or not the biodegradability
297 of polyesters in an elastomeric state. Indeed, such polymers synthesized by enzymatic
298 methods are thus more biodegradable than those synthesized by chemical methods. However,
299 this difference disappears under processing at high temperature often required in industrial
300 applications of a biodegradable polymer, which could drastically decrease its
301 biodegradability.

302 The choice of the synthesis method depends on the utilisation envisaged for a polyester.
303 Chemical synthesis is rapid and can be applied to a large mass of monomers, or when
304 polymers need to have a slow biodegradation kinetic. Enzymatic synthesis is more expensive,

305 suitable for specific products with high added value which do not require processing at high
306 temperature. Enzymatic synthesis can also be used to obtain polymers intended to disappear
307 via biodegradation after use.

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311

312

313 **References**

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377

Captions of Tables

378

379 **Table 1.** Characteristics of the five polyesters synthesized by different methods

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381 **Table 2:** Approximate time theoretically required for 1 g of biomass in a waste treatment

382 plant to mineralize 100 mg of polymer

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Captions of Figures

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398 **Figure 1.** Principal glyceridic motifs present in the polyesters. Each letter corresponds to an
399 atom of carbon identified by ^{13}C NMR

400 R = oleic di-acid, De = dendritic motif

401 **Figure 2.** Extended zone of the ^{13}C NMR spectrum corresponding to the principal glyceridic
402 motifs in a polyester obtained from esterification of glycerol by oleic di-acid

403 Attributions (cf. Fig. 1): 62.3 ppm $\text{L}_{1,2}$ G ; 63.3 ppm De B; 63.6 ppm $\text{L}_{1,2}$ F ; 64.5 ppm T1 I ; 66.1 ppm
404 $\text{L}_{1,3}$ D ; 66.3 ppm T_1 H ; 69.1 ppm $\text{L}_{1,3}$ C ; 70.1 ppm De A ; 71.3 ppm T_1 J ; 73.3 ppm $\text{L}_{1,2}$ E

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406 **Figure3 :** Consumption of O_2 and release of CO_2 by a biomass from sludge mud placed in
407 contact with vegetal pulp (polymer 6, — —) and PLA (polymer 7, ———), endogen
408 respiration deduced. Error bars represent the standard error of mean three replicates (n= 3)

409 **Figure 4.** Consumption of O_2 and release of CO_2 by a biomass from sludge mud placed in
410 contact with polymers 2 (∇), 3 (\diamond), 4 (\square) and 5 (\triangle), endogen respiration deduced.
411 Error bars represent the standard error of mean three replicates (n= 3)

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	Thermo-chemical synthesis			Enzymatic synthesis	Enzymatic + thermo-chemical synthesis
Polymer number	1	2	3	4	5
T° Synthesis (°C)	65 (7d)	160 (3h)	160 (8h)	65 (6d)	65 (4d)
(time)		180 (1h)			160 (4h)
Catalyst :				Novozyme	Novozyme
Physical state	viscous liquid	elastomeric	viscous liquid	elastomeric	elastomeric
Mw (g/mole)	900	ND*	31280	ND*	ND*
Mn (g/mole)	500		9200		
Motif					
De (%)	8	32	26	18	13
L _{1,2} (%)	13	14	19	20	21
L _{1,3} (%)	26	36	40	36	38
T ₁ (%)	54	17	15	25	29
T ₂ (%)	0	0	0	0	0
Regioselectivity of the primary OH (%)	87	78	83	80	82
Degree of substitution	1.5	2.1	2.1	1.9	1.8

419 ND* Molecular mass not determined, this polyester being an insoluble cross-linked elastomer

420 De = dendritic motif

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422 **Table 1**

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	C %	In Oxytop System (month)	In an urban sludge plant (month)
Polymer 2	68.9	28.4	14.2
Polymer 3	68.0	5.4	2.7
Polymer 4	65.0	4.8	2.4
Polymer 5	67.4	23.0	11.5
Polymer 6	42.5	1.9	0.9

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Table 2

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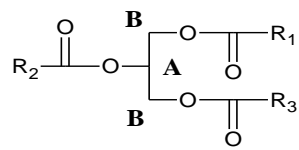
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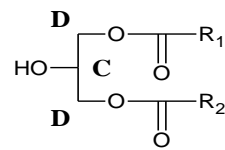
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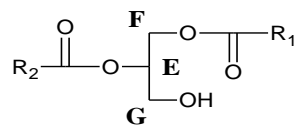
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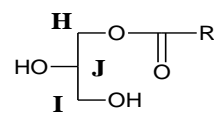
Motif De



Motif L_{1,3}



Motif L_{1,2}



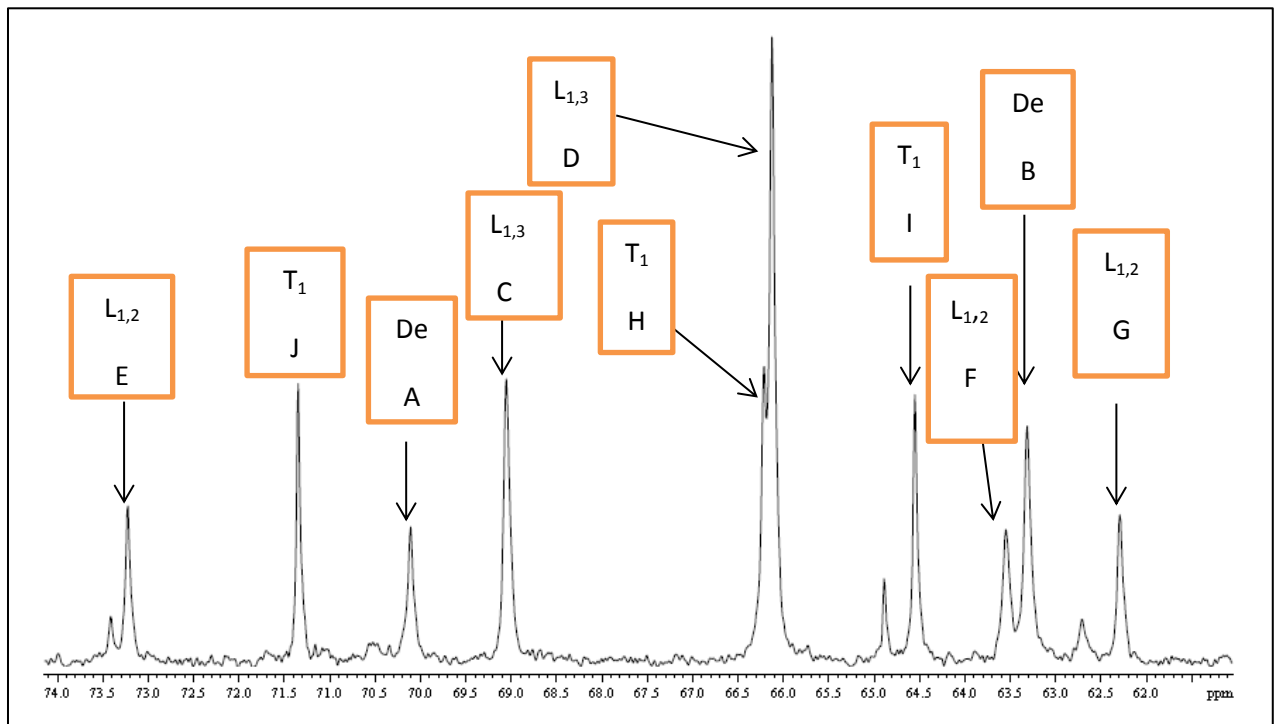
Motif T₁

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Figure 1

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449 **Figure 2**

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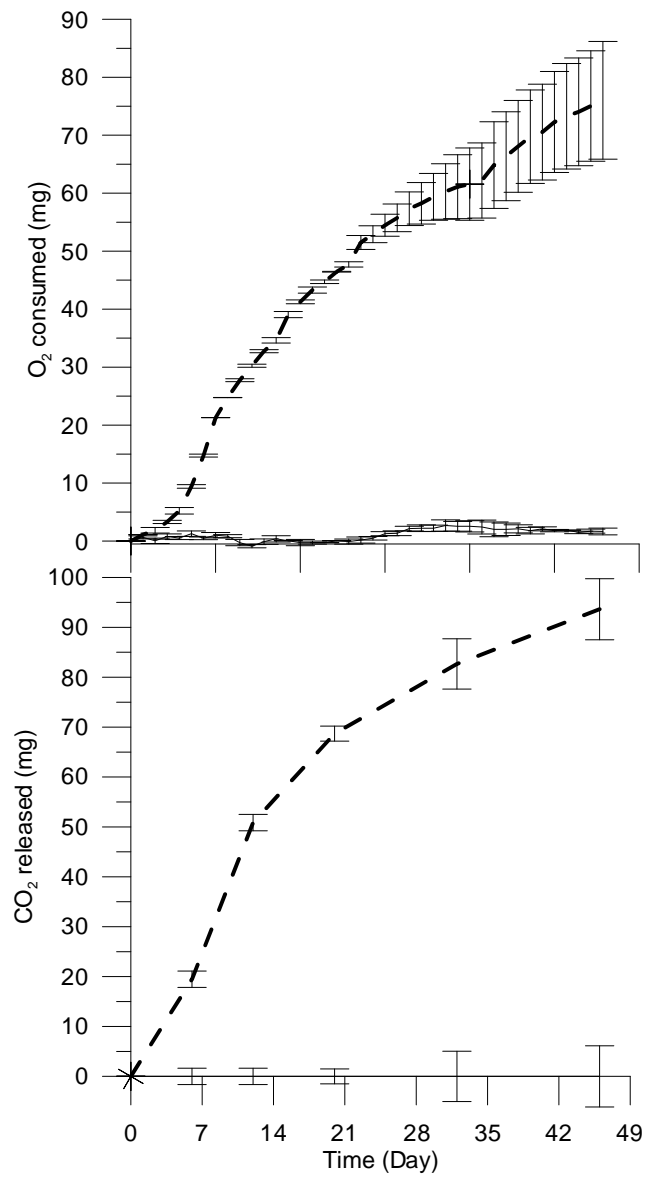
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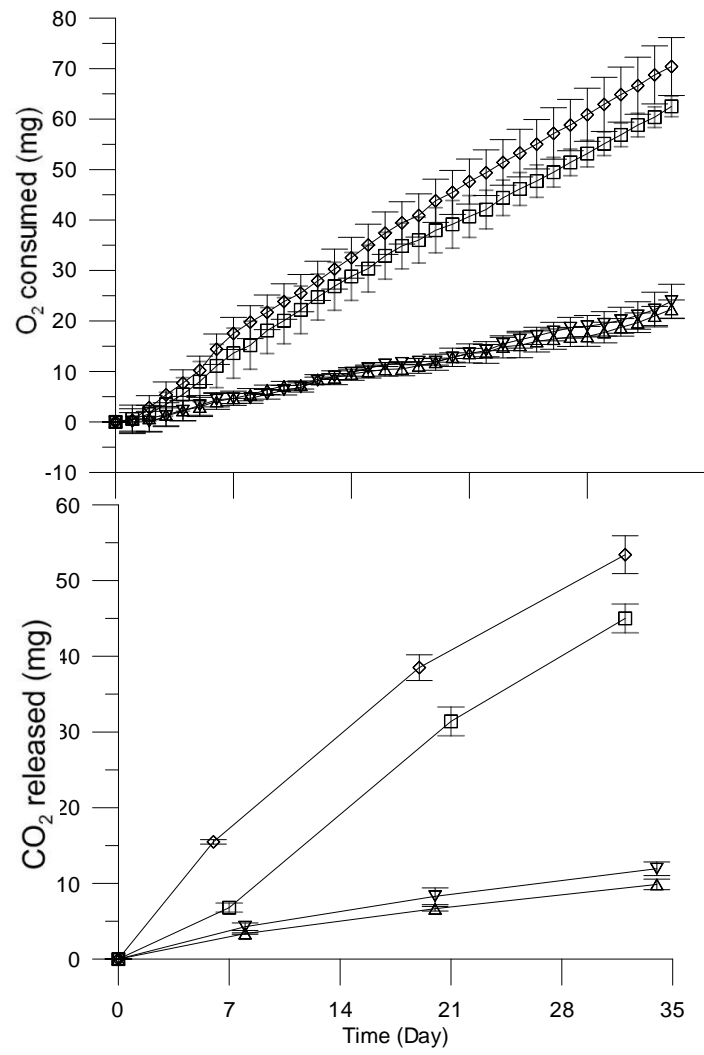


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457 **Figure 3**

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461 **Figure 4**

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