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The Green ChemisTREE: 20 years after taking root with the 12 principles

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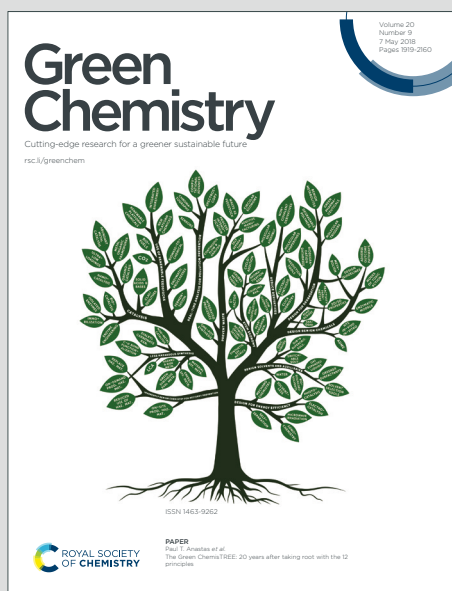
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1 Enzyme-catalyzed synthesis of malonate polyesters and their use as metal chelating

2 materials

3

4 Fergal P. Byrne[1,*], Jamie M. Z. Assemat[1], Amy E. Stanford[1], Thomas J. Farmer[1],

5 James W. Comerford[1, 2], Alessandro Pellis[1, 3, *]

6

7 [1] Green Chemistry Centre of Excellence, Department of Chemistry, University of York,

8 Heslington, York YO10 5DD, United Kingdom

9 [2] SINTEF, Forskningsveien 1A, 0373, Oslo, Norway

10 [3] University of Natural Resources and Life Sciences, Vienna, Department of

11 Agrobiotechnology, Institute of Environmental Biotechnology, Konrad Lorenz Strasse

12 20, 3430, Tulln an der Donau, Austria

13 * Correspondence to: Dr. Alessandro Pellis, alessandro.pellis@boku.ac.at and Dr.

14 Fergal Byrne, fergal.byrne@york.ac.uk

15

✓**Unprecedentedly high molecular weight (29<DP<38)**

✓Biobased monomers
✓Non-toxic catalyst
✓Green solvents
✓Metal removal
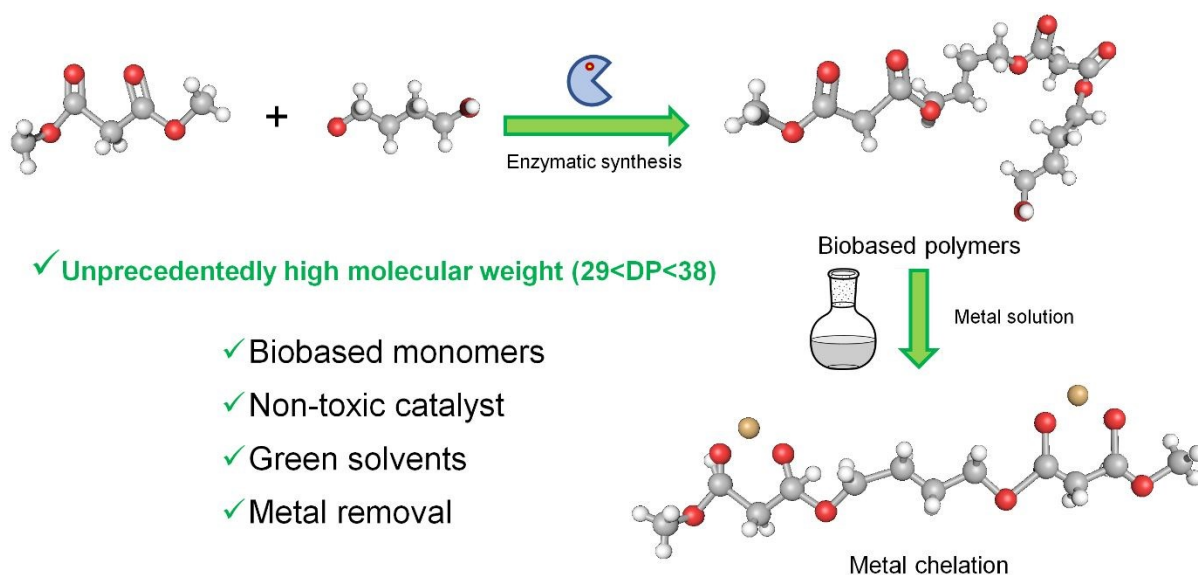
16

17 Graphical abstract

18

Abstract

Following the environmental problems caused by non-degradable plastics there is a need to synthesise greener and more sustainable polymers. In this work we describe, for the first time, the facile enzyme-catalysed synthesis of linear polyesters using dimethyl malonate as the diester. These polymers, containing a different aliphatic diol component (C_4, C_6 or C_8), were synthesised in solventless conditions using immobilized *Candida antarctica* lipase B as the biocatalyst. The potential of enzymes for catalysing this reaction is compared with the unsuccessful antimony- and titanium-catalysed synthesis (T>150 °C). The application of the synthesized polymers as effective metal chelators in biphasic, green solvent systems was also described, together with the characterisation of the synthesised materials.

Keywords: biobased polyesters, enzymatic synthesis, sustainable solvents, metal chelation, water detoxification

Introduction

Due to the functionality limitations and the pollution caused by fossil-derived polymers,[1] the chemical industry urges the development of greener routes to produce novel bio-based, degradable (or compostable) materials. Several steps in this direction were recently made, especially in the polyesters field, with the development of poly(ethylene 2,5-furandicarboxylate) (PEF) as a poly(ethylene terephthalate) (PET) substitute due to its similar mechanical and barrier properties[2,3] and better biodegradability.[4,5] Other furan- and pyridine-based polymers potentially useful for packaging and film applications were developed, but their synthesis remains limited to laboratory-scale.[6]

44 Recently, the potential of enzymes as green and selective biocatalysts has

45 been demonstrated on several aromatic and aliphatic monomers, which is of great

46 interest when the polycondensation of monomers carrying lateral functionalities is

47 desired, as highlighted in several review articles.[7, 8] Such functionalities - the vinyl

48 group of itaconic acid, the secondary hydroxy group of glycerol, sorbitol or mucic acid,

49 etc. - are prone to a wide array of side reactions (such as Ordelt saturation, radical

50 crosslinking, etc.) when traditional metal- or acid-catalyzed polymerization reactions

51 are carried out.[9, 10] In fact, previously synthesized metal-chelating polymers based on

52 a diethylenetriaminepentaacetic acid pendant group required a Michael addition of a

53 thiol to be carried out in a second reaction step, and the double bond of the itaconate

54 moiety was preserved only thanks to the use of very toxic chemicals such as 2-

55 furanmethanethiol and a phosphazene base as the initiator.[11]

56 In this work, attention was focused on malonate-derived aliphatic polyesters. Malonic

57 acid is a source of bio-based 1,3-diketone functionality, and it is produced

58 commercially by Lygos using engineered yeast strains.[12] To the best of our knowledge,

59 malonate-derived polyesters were reported before in the literature only in the form of

60 short oligomers having a maximum DP of around 5[13]. In fact, the reports dealing with

61 malonate polymers describe mainly the synthesis of aliphatic hyperbranched

62 polyesters (HBPE) from various monomers derived in one step from commercial

63 diethyl malonate.[14] The acid- and metal- catalyzed polycondensation of malonate

64 derivatives bearing aliphatic residues[15] was also reported together with the sequential

65 anionic polymerization of ethylene oxide and methylidene malonate to obtain

66 poly(ethylene oxide)-block-poly(methylidene malonate 2.1.2) block copolymers

67 bearing a primary amino group at the PEO chain end.[16] The only work where the

68 malonate unit was changed from a malonic acid or dialkyl ester to being part of the

69 main chain, is the work of Doğan and Küsefoğlu, published in 2008, that reported the

70 1,4-diazabicyclo[2.2.2]octane-catalyzed synthesis of a biodegradable polymeric foam

71 from epoxidized soybean oil and malonic acid.[17]

72   There has been increased interest in elemental sustainability in recent years.

73 Commonly used metals such as cobalt, nickel, copper and zinc have reserves

74 expected to last only 50-100 years. Recovery of these metals from waste streams is

75 vital to maintain supplies of these dwindling resources.[18] One method of recovering

76 metals from aqueous waste streams is solvent-based hydrometallurgy.[19, 20] This

77 involved contacting an organic solution containing metal chelators with an aqueous

78 metal solution. A biphasic system emerges, in which metal ions can pass from the

79 aqueous phase to the metal chelators in the organic phase. The metals can be

80 recovered from the organic phase by re-extraction by an acidic solution, allowing the

81 free chelators in the organic phase to be reused.[20] However, issues of toxicity,

82 bioaccumulation and persistence in the environment of chelators are common.[21] In

83 addition, most currently available chelators are petroleum-derived with few examples

84 of bio-based products (Nouryon Dissolvine range being a rare example).[22] As such,

85 bio-based, safe, water-insoluble metal chelators are sought after.

86   Many functional groups can be used as chelators, such as oximes,

87 carboxylates, phosphorous acids, and 1,3-diketones. 1,3-Diketones such as LIX54

88 (Figure 1) are commercially available for this purpose,[19, 23] but naturally occurring other

89 1,3-diketones such as 14,16-hentriacontanedione are present in plant waxes.[24, 25]

90 Indeed, biphasic extraction systems have been proposed in the past using bio-derived

91 lipophilic chelators sourced from wheat straw wax,[25] as well as modified wax products

92 to produce super-chelators.[24]

Previous work

LIX54

14,16-Hentriacontanedione (HTD)
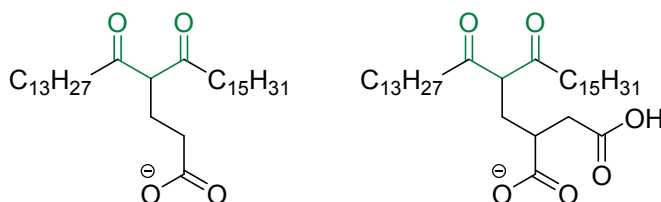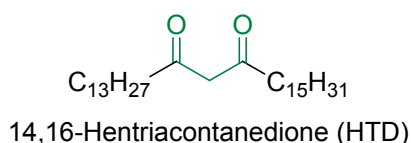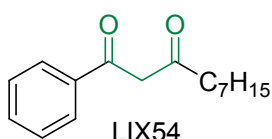
Modified HTD chelators using methyl
acrylate (left) and itaconic acid (right)
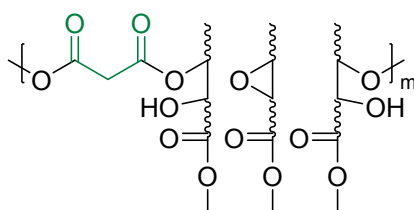
Epoxidised soybean oil/malonic acid polymers

This work

Dimethyl malonate   Diol   Malonate polymer

n = 2,3,4   n = 2,4
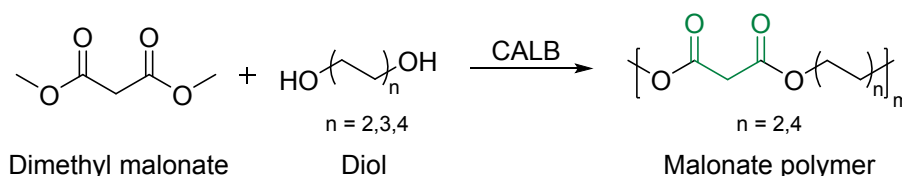
93

94

95   **Figure 1.** Structures of the previously described 1,3-diketone chelators LIX54, 14,16-

96   hentriacontanedione and the malonate-based polymers described in this work.

97

98   Herein we present the facile enzyme-catalyzed synthesis of dimethyl malonate-

99   based linear polyesters having a different aliphatic diol component (C_4, C_6 or C_8). The

100   reaction was conducted in solventless conditions using immobilized *Candida*

101   *antarctica* lipase B as the biocatalyst. The potential of enzymes for catalysing this

102   reaction is compared with the largely unsuccessful chemo-catalytic metal-catalyzed

103 synthesis. The application of the synthesized polymers as effective metal chelators in

104 biphasic, solvent-based hydrometallurgy is also described together with a detail

105 characterization of the synthesized materials. Moreover, these aliphatic polyesters are

106 known to be easily degraded to their constituent monomers (diacids and polyols) using

107 a variety of hydrolytic enzymes (eg. lipases, cutinases),[26, 27] therefore allowing the

108 recovery of such building blocks and the re-synthesis of the polymer in a closed-loop

109 circular economy concept.

110

111 <u>Synthesis of malonate-based aliphatic polymers</u>

112 Quite surprisingly, very few reports describing the use of malonic acid (or its esters)

113 as the diacid component of polyesters were found in the literature[28, 29] and none of

114 them focuses on the chelating properties of these polymers. We therefore initially

115 attempted to synthesize malonate polyesters using the most commonly known metal

116 catalysts for polycondensation reactions: antimony oxide and titanium butoxide,

117 catalysts widely known for the synthesis of PET,[30] PEF[31] and a wide range of other

118 aliphatic and aromatic polyesters.[32] Unfortunately, when using dimethyl malonate

119 (DMM) as the diester in combination with various aliphatic polyols, the metal-catalyzed

120 synthesis was unsuccessful, with obtained M_ns between 1000 and 2600 Da (DP of 6

121 and 16 respectively, Table 1).

122 The rather low molecular weights obtained in this work using metal catalysts

123 can be explained with the fact that β-diketones, such as malonates, are known

124 chelating agents and can therefore competitively chelate the catalyst metal ions,

125 reducing their capacity to promote the transesterification reaction. This idea is

126 supported by the fact that titanium forms complexes with dimethyl malonate[33] creating

127 a useful catalyst for the polymerization of polypropylene.[34] One of the few available

128 reports on malonate polyesters is the P_2O_5-catalyzed synthesis of poly(1,3-propyl

129 malonate), but also in this case the obtained molecular weights were really limited

130 since the maximum achieved DP was approximately 5.[13]

131

Table 1. Metal-catalyzed synthesis of malonate polyesters.

| Diol	Catalyst	M_n [Da]*	M_w [Da]*	Đ*
1,4-BDO	Sb_2O_3	2100	4000	1.90
	$Ti(O^tBu)_4$	2600	4600	1.79
1,8-ODO	Sb_2O_3	1000	2400	2.28
		1600	2800	1.68

* Calculated *via* GPC

132

133 Taking inspiration from recent papers on environmentally friendly synthesis of

134 polymers, and due to the impossibility to obtain polymers using traditionally-used

135 methods, an enzymatic approach was used in order to synthesize a series of

136 malonate-containing aliphatic polyesters using diols having a chain length from 4 to 8

137 carbon atoms. For the synthesis performed in this work, an immobilized preparation

138 of *Candida antarctica* lipase B (iCaLB) was used as the biocatalyst since this enzyme

139 was reported to be an excellent candidate for such synthesis reactions[7, 35]. The

140 polycondensation reaction progressed at very mild (85 °C, 1000/20 mbar, 6+18 h)

141 solventless conditions. The application of such environmentally-friendly synthesis

142 protocol was possible since DMM is a liquid at the used operational temperature while

143 the corresponding diacid, malonic acid, has a melting temperature reported to be

144 between 135 °C and 137 °C.

145 The enzymatic synthesis experiments show similar M_n values of around

146 6000 Da for all the used diols while the M_w values increase from 9000 Da to 12-14K Da

147 with the increase of the diol's chain length (Figure 1). The reported values are in line

148 with previous reports of solvent-free enzymatic polycondensations where the used

149 diester was dimethyl adipate that also showed similar M_n (~7000 Da) and increasing

150 M_w (from 11 to 14K Da) when the same three aliphatic diols having increasing carbon

151 chain length were used[35]. The decrease of the DP as the diol increases, as seen for

152 both the malonate and the adipate polyesters, is also a common trait (Figure 2).[7, 35]

153
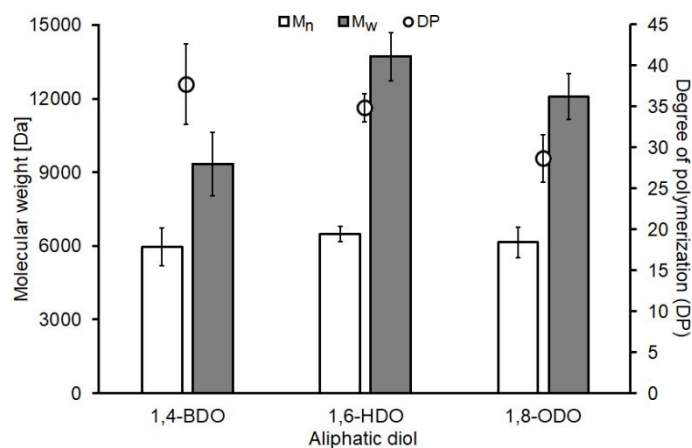
154

155 **Figure 2.** Enzymatic synthesis of linear malonate-based polyesters. Number average molecular

156 weights (M_n, white bars) and weight average molecular weights (M_w, grey bars) were determined via

157 gel permeation chromatography using polystyrene standards. The degree of polymerization (DP, white

158 circles) was determined dividing the M_n by the M_0 (weight of the repetitive unit of the polymer). All

159 experiments were performed in duplicates and shown ± the standard deviation.

160

161 All synthesized malonate-based polyesters have 29<DP<38, therefore presenting

162 molecular masses significantly higher in comparison of the short oligomers previously

163 synthesized using P_2O_5 and our own chemocatalytic synthesis approach (Table 1).

164 The polymers were recovered using a simple vacuum filtration that allowed the

165 removal of the immobilized enzyme and the work-up solvent was then removed *via*

166 rotary evaporation. All isolated polyesters were colourless viscous liquids and

167 subsequently used for the chelation experiments without further purification.

168 Polymer structures and relative monomer conversions were elucidated via ^{1}H-NMR

169 spectroscopy (Figures S1-S5 in ESI). Upon reaction, the $-CH_2-C\underline{H}_2-OH$ signal from the

170   diol has a characteristic change of chemical shift from 3.65 ppm to 4.14 ppm, proving

171   the formation of an ester bond. Additionally, the -OC$\underline{H}_3$ signal from the malonate,

172   observable at 3.75 ppm disappears due to the release of MeOH with the progression

173   of the reaction. The signals at 3.38 ppm (C-C$\underline{H}_2$-C of the malonate) and in the 1.3-

174   1.8 ppm range (-C$\underline{H}_2$-CH$_2$-OH of the diols) do not noticeably change chemical shift

175   upon elongation of the polymer chain. ^{13}C-NMR spectroscopy of the polymer reveals

176   the typical signals for these aliphatic polyesters (Figure S6 in ESI).

177

178   <u>Metal chelation in biphasic systems based on green solvents.</u>

179   The malonate polyesters were assessed for their ability to extract metal ions from

180   aqueous streams in a biphasic system. The biphasic system involved dissolving the

181   polyester in an organic solvent and mixing it with a metal-containing aqueous solution.

182   Upon contact between the two phases, metal transfer occurs from the aqueous phase

183   to the diketone chelating points on the polyester in the organic phase, purifying the

184   aqueous phase. Separation of the two phases and re-extraction of the organic phase

185   with an acidic stripping solution can recover the metal from the polyester for reuse,

186   and also regenerate the diketone chelating point on the polyester.

187   Copper was chosen as the target metal for chelation using the polyesters due

188   to it being a common pollutant in metallurgy waste streams[36]. Cl$^-$ was selected as the

189   counter ion as it has previously been shown to be effective in the chelation of copper

190   using diketone species due to it being a strong inner-sphere ligand.[24, 25] The chelation

191   tests were carried out across as pH range of 8.4–12.3.

192

Keto-enol tautomerism
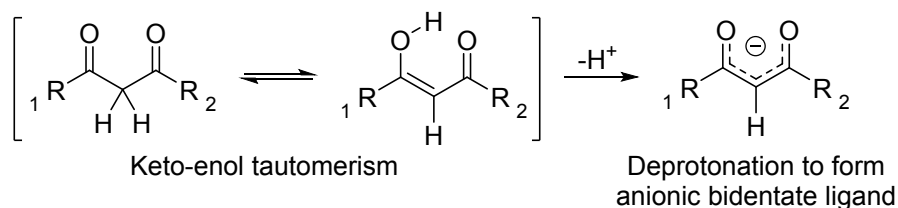
Deprotonation to form anionic bidentate ligand
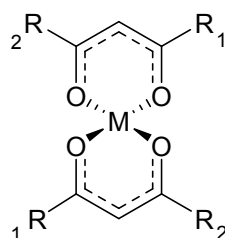
Suggested square planar structure of metal complex

193

194

195 **Figure 3.** Keto-enol tautomerism of 1,3-diketones followed by deprotonation to form negatively charged

196 bidentate ligand.

197

198 Several requirements exist for the choice of organic solvent for this purpose. It must

199 partition well with water; the chelating agent must favour solubility in the organic

200 solvent over water; it must facilitate enol formation; and it must not be reactive in the

201 extraction conditions. As the solvent does not need to be evaporated at any stage of

202 the extraction process, a low boiling point is not necessary. In fact, a higher boiling

203 point will reduce losses to the atmosphere, improving the economics of such an

204 extraction process. In addition, it will add to the green credentials of the process, as

205 emissions, exposure to workers and solvent demand are reduced. The CHEM21

206 solvent selection guide recommends a boiling point of between 70-139 °C.[37]

207   Three candidate solvents were ultimately selected using the CHEM21 solvent

208 guide[37]: *para*-cymene, ethyl levulinate and anisole. *para*-Cymene and anisole have

209 boiling points within the ideal range (70-139 °C), while that of ethyl levulinate is206 °C.

210 However, as the solvent/polymer mixture can be used repeatedly, this higher than

211 preferred boiling point is not a significant issue. All three candidates are aprotic,

212   meaning the enol form is more likely to be favoured[25] which is a prerequisite for

213   chelation ability (keto form is stabilised by intermolecular hydrogen-bonding in protic

214   solvents)[38]. Polymer insolubility in BDO MAL polymer prevented *para*-cymene from

215   being tested, while ethyl levulinate likely chelated with metal ions during extraction,

216   indicated by a green complex being formed when mixed with copper solutions. Anisole

217   could dissolve all polymers, and also scores well in the CHEM21 solvent selection

218   guide, being classified as "recommended"[37]. As such, anisole was chosen as the most

219   appropriate solvent for this process.

220   The 1,3-diketones functionality can exist in keto and enol forms (Figure 3). In

221   basic conditions, deprotonation of the acidic proton in the 2-position forms an anionic

222   bidentate ligand which are weak chelators. A square planar complex is suggested,

223   similar to that of bis(acetylacetonato)copper(II), as previously determined by single

224   crystal X-ray diffraction[39]. As the polymers existed as a viscous liquid, possibly due to

225   residual solvent that could not be removed *in vacuo*, powder XRD could not be carried

226   out to confirm the square planar complex in the malonate polymers of this work.

227   The polymers with the highest (ODO MAL) and lowest (BDO MAL) M_0 were

228   chosen as model to perform chelation tests with $CuCl_2$. A pH range of 8.4–12.3 was

229   used for the tests. Chelation tests were carried out in a biphasic system consisting of

230   a $CuCl_2$-rich aqueous phase (0.05 M $CuCl_2$, 0.25 M NH_3) and an organic solution of

231   the chelating polymer (0.05 M). Interestingly, the density of the aqueous metal

232   solutions at higher pH (10.4-12.3) changed such that the layers switched in the

233   biphasic system when the BDO MAL was used. This is due to the proximity of the

234   density of pure anisole (0.995 g mL^{-1}) to that of water (1.000 g mL^{-1}), which must be

235   taken into consideration in an industrial process.

236   Figure 4 shows that optimal pH for extraction was similar in both cases, with

237   ~pH 10 being optimal for ODO MAL and BDO MAL polymers (specific pH's and

238   absorbances for chelation tests are shown in Table S2 and S3 in ESI). This is

239   consistent with previous observations of 1,3-diketones being more effective in basic

240   conditions[17]. Superior extraction was obtained with the ODO MAL, with mean Cu

241   extraction of 22.7% compared to 15.7% for the BDO MAL polymer. Extraction with the

242   malonate polymers is comparable with the commercial LIX54 (18% in a 50:50 mix of

243   LIX54/kerosene, 40% using pure LIX54),[23] demonstrating the potential of such a

244   chelating polymer for use in an industrial setting. Further work is required on optimising

245   the conditions for extraction (polymer loading, further solvent investigation, more

246   robust pH control), their stability over multiple uses and their affinities for other metals

247   in mixed aqueous streams which will be the focus of a subsequent full article.

248

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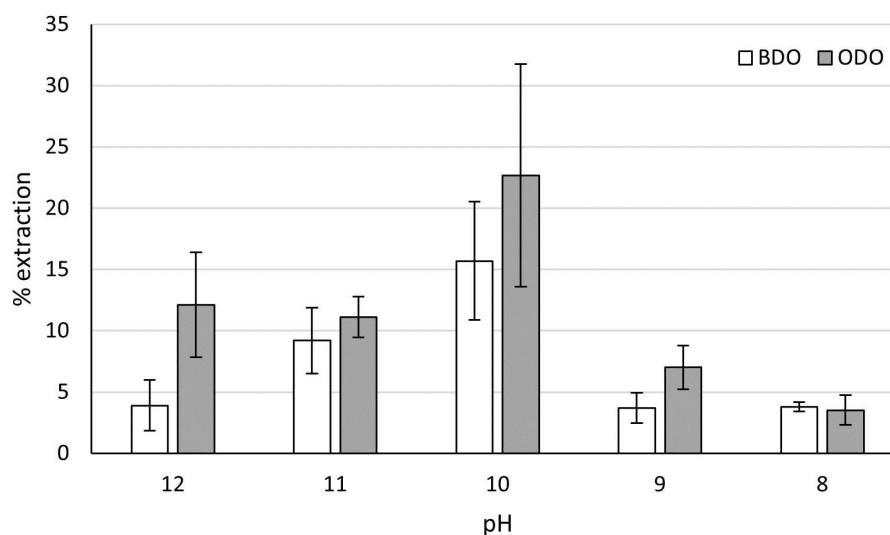
250   **Figure 4.** The % extraction of Cu(II) from ammoniacal solutions using "BDO" MAL and "ODO" MAL at

251   different pHs and 1:1 by weight loading of chelator:Cu(II). The pH shown in the graph has been rounded

252   to the nearest whole number for visual clarity. Exact pH values are shown in the electronic

253   supplementary information.

254

Conclusions

A series of malonate polymers were successfully synthesized using environmentally-friendly conditions (enzymatic catalyst, T<90 °C, solvent for the workup: MeTHF) and used to achieve the efficient chelation of copper, a common pollutant in metallurgy waste streams. A superior extraction efficiency of 23% was obtained with the ODO MAL polymer that is comparable with commercially-available LIX54 (18% in a 50:50 mix of LIX54/kerosene, 40% using pure LIX54), demonstrating the potential of this new class of polyesters for use in an industrial setting. Enzymatic catalysis, showing high selectivity, low operational temperatures and benign reaction conditions, is emerging as a useful tool to complement chemo-catalytic routes for the synthesis of multifunctional polymers having structures that are otherwise not possible to obtain using traditional metal- and acid based-methods.

Author contributions

A. P., J. M. Z. A. and A. E. S. performed the enzymatic polymer synthesis and material's characterization. F. P. B., J. M. Z. A. and A. E. S. performed the chelation experiments. A. P. and J.W.C. performed the chemo-catalytic synthesis. A.P. and F. P. B. planned the experiments and wrote the manuscript. F. P. B., A. P. and T. J. F. supervised the work. All authors corrected the manuscript and discussed the data prior to submission.

280

281 Notes

282 The authors declare no conflict of interests.

283

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