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1,3-Propanediol and its Application in Bio-Based Polyesters for Resin Applications

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Abstract Polyester resins are important raw materials for a myriad of applications especially in the field of coatings and radical curing polymers, such as wood and powder coatings, molding compounds, and UV-curing applications. In addition, polyols derived from polyester resins are precursors for the synthesis of polyurethanes and polycarbonates. Besides dicarboxylic acid, diols are used as monomers in these polyesters. To date most of the diols utilized are derived from petrochemical feedstock. To increase the bio-based content of polyester resins, novel diols derived from renewable resources are of special interest. In this respect, 1,3-propanediol has drawn considerable attention over the last years. It is accessible via microbial fermentation of glucose from starch at a competitive price in sufficient amounts. Therefore, 1,3-propanediol could be a valuable alternative to petrochemical diols, such as 1,6-hexanediol and neopentylglycol, which are currently used as diols in most resin applications. This article gives a brief overview over the utilization of 1,3-propanediol in high molecular weight polyesters for plastic application followed by a more detailed discussion of the most relevant work in the field of polyester resins derived from 1,3-propanediol.

Keywords (separated by '-') 1, 3-Propanediol - Polyester resins - Coatings - Unsaturated polyesters

Footnote Information Marcel Kluge and Sacha Pérocheau Arnaud contributed equally to this work.



2 1,3-Propanediol and Its Application in Bio-Based Polyesters for Resin 3 Applications

4 Marcel Kluge¹ · Sacha Pérocheau Arnaud¹ · Tobias Robert¹

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7 Abstract

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17 plastic application followed by a more detailed discussion of the most relevant work in the field of polyester resins derived
18 from 1,3-propanediol.

19 **Keywords** 1, 3-Propanediol · Polyester resins · Coatings · Unsaturated polyesters

20 1 Introduction

21 The last decade has seen a growing interest in bio-based
22 materials. Especially in the polymer field, the demand
23 for alternatives from renewable resources is continuously
24 increasing. This trend is driven by the finite nature of fos-
25 sils fuels, but also a rising consumer awareness and lately
26 the problem of rising accumulation of (micro) plastic in
27 the environment, in particular in the oceans. The latter
28 results in an increasing attention towards the transition to
29 a circular economy and the development of bio-degradable
30 plastics [1]. Against this background, bio-based polyes-
31 ters are of special significance [2]. They are derived from
32 renewable resources and exhibit in many cases a higher
33

bio-degradability in comparison to other bio-based plastics,
such as bio-polyethylene. The most prominent examples in
the field of bio-based polyesters are polylactic acid (PLA)
[3–5] and polyhydroxyalkanoates (PHA) [4, 6–9], which are
both commercially available. Especially PLA is employed
in a variety of applications, such as packaging, composite
materials and biomedical applications [5, 10–14].

In addition, other bio-based polyesters have been in the
focus of both academic as well as industrial research and
are in different stages of commercial availability. A range
of bio-sourced monomers, such as furandicarboxylic acid
(FDCA), succinic acid, isosorbide, etc. have been used and
there are a range of extensive book chapters and review
articles that cover this topic of polymer and material science
[15–22]. Among these building blocks, 1,3-propanediol
(PDO) has been successfully applied in a several bio-based
polyesters.

Even though this diol is accessible by synthetic pathways,
for example from acrolein [23] or ethylene oxide [24] these
methods suffer from high production costs and undesired
and irritant impurities. This led to low interest in this mono-
mer from an industrial viewpoint and therefore very limited
applications. However, the situation changed when PDO was

A1 Marcel Kluge and Sacha Pérocheau Arnaud contributed equally to
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56 made accessible through microbial fermentation of glucose
57 [25, 26]. This biotechnological pathway led to an increased
58 availability of PDO at a competitive price and in turn to
59 more applications of this bio-based building block in poly-
60 mer materials.

61 As most promising examples, PDO was used as monomer
62 for the bio-based PET alternatives PTT (poly(trimethylene
63 terephthalate)) [27–29] and PTF (poly(trimethylenefuroate))
64 [30–32] (Fig. 1a). In comparison to PET, PTT shows high
65 resilience and has the ability to rapidly crystallize, which
66 makes it a promising candidate for fiber applications [33].
67 PTF on the other hand shows superior gas barrier proper-
68 ties than the (partially) petrochemical polymers PET and
69 PTT [34]. As another example in the field of bio-based poly-
70 esters with aromatic building blocks, PDO was utilized as
71 diol component with the difuranic monomer 5,5'-(propane-
72 2,2-diyl)-bis(furan-2-carboxylate) [35].

73 In addition, a lot of work was dedicated towards aliphatic
74 polyesters derived from PDO (Fig. 1b) [36–39]. These poly-
75 esters are especially interesting due to their high suscepti-
76 bility towards enzymatic degradation [37, 40]. This makes
77 these polymers promising candidates for degradable plastics,
78 as well as pharmaceutical applications.

79 Both the aromatic, as well as aliphatic polyesters derived
80 from PDO have been studied extensively and are the sub-
81 ject of several comprehensive review articles [22, 41–45].
82 PDO has also been used as monomer for polyester resins in
83 the coatings field. To the best of our knowledge, no review
84 for this type of polyesters derived from PDO for binder
85 resins has been made. Herein, we try to give an overview
86 of the most important work undertaken in this area in the
87 last years.

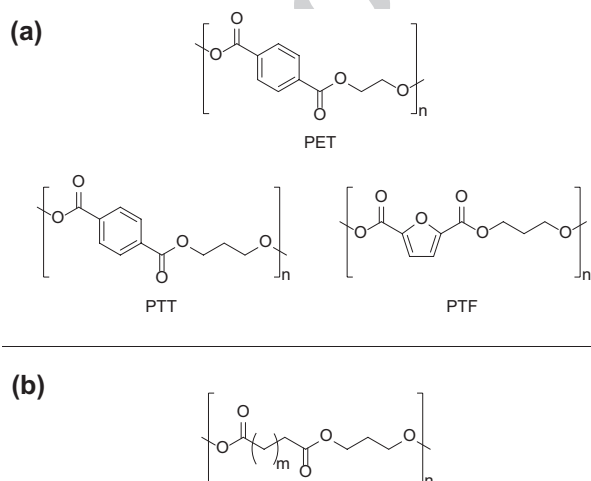


Fig. 1 Chemical structure of **a** aromatic and **b** aliphatic polyesters with PDO

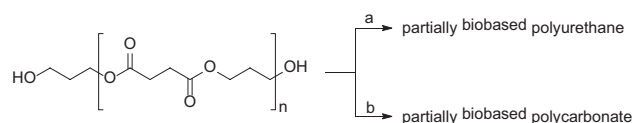
2 Polyester Resins from 1,3-Propanediol 88

2.1 Polyester Polyols for Polyurethanes and Polycarbonates 89

91 In 2001 Albertsson and co-workers reported the synthesis
92 of different bio-based poly (1,3-propylene succinate) oli-
93 gomers, by varying the diol/diacid ratio from 1.05 to 1.25
94 (Scheme 1a) [46]. This led to polyesters with different prop-
95 erties and low molecular weights up to 3400 g/mol. These
96 oligomers were further reacted with methylenediphenyliso-
97 cyanate (MDI) to obtain polyester urethanes with molecu-
98 lar weights up to 60.000 g/mol. The properties of these
99 polymers were examined in the dependency of the weight
100 percentage of the polyester polyol incorporated. The melt-
101 ing point varied in the range of 175–210 °C with properties
102 comparable to commercial thermoplastic polyurethanes.

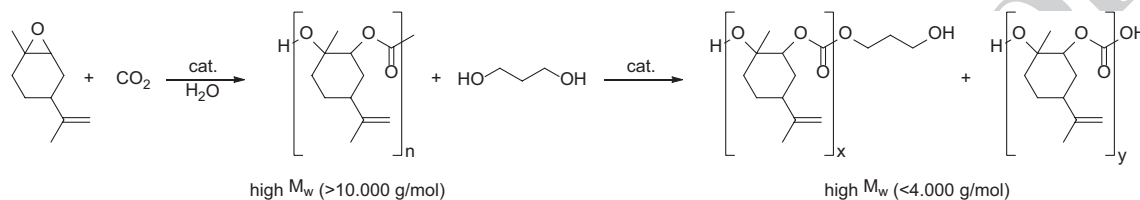
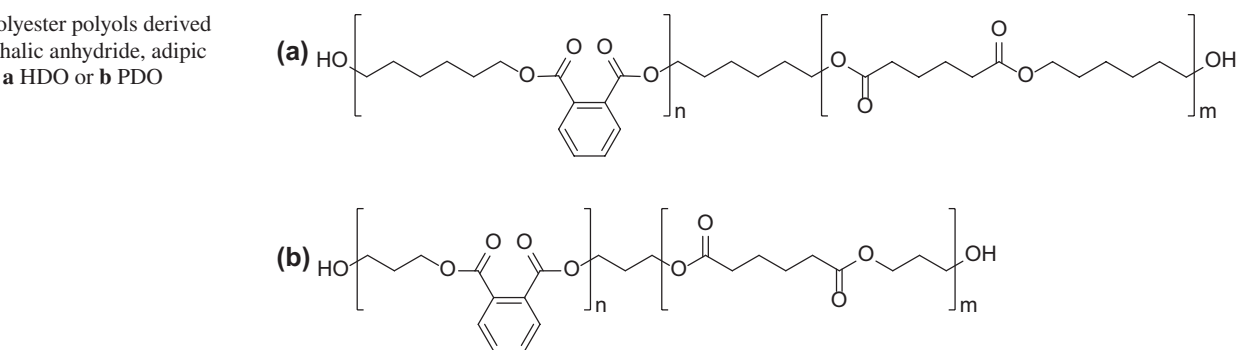
103 The polyester polyols also found application as building
104 blocks for polycarbonates (Fig. 2b) [47]. After the polycon-
105 densation step, the polyesters were chain extended by a two-
106 step process using phosgene, a special amine and DMAP,
107 which allows for an exact adjustment of the stoichiometry.
108 The corresponding polycarbonate was obtained with a
109 molecular weight of 48,000 g/mol. Surprisingly, the thermal
110 properties are close to those of the lower molecular weight
111 polyester precursors with only a slight increase of both glass
112 transition and melting temperature. In addition, the authors
113 state that the materials are potentially biodegradable as they
114 are derived from renewable resources. However, no studies
115 were conducted to confirm this statement. The same authors
116 later tried to improve the properties by replacing some of
117 the PDO with the cyclic building block 1,4-cyclohexan-
118 edimethanol [48]. However, the properties of the resulting
119 polycarbonates could not be substantially improved.

120 A very interesting approach to fully bio-based polycar-
121 bonates was reported by Koning and co-workers [49]. They
122 were synthesized by a phosgene-free reaction of limonene
123 oxide and CO₂ with high molecular weights ($M_n > 10.000$ g/
124 mol). To obtain material suitable for coating applications,
125 the polycarbonates were subsequently submitted to an
126 alcoholysis reaction using renewable diols, such as PDO
127 and 1,10-decanediol (scheme 2). The resulting OH-termi-
128 nated polycarbonates with reduced molecular weight were



Scheme 1 Bio-based poly (1,3-propylene succinate) as precursor for polyurethanes and polycarbonates through a reaction with **a** MDI and **b** phosgene, dimethylamino pyridine (DMAP) and a tertiary amine

Fig. 2 Polyester polyols derived from phthalic anhydride, adipic acid and **a** HDO or **b** PDO



Scheme 2 Synthesis of poly(limonene carbonate) and subsequent alcoholysis with PDO

129 preliminary examined on their potential as coating material.
 130 For this, they were mixed with a conventional isocyanate and
 131 applied on aluminum plates. The resulting coatings exhibited
 132 some interesting properties, such as good acetone resistance.
 133 In a subsequent paper, similar polycarbonates were further
 134 studied by post-polymerization modification [50]. In addition,
 135 the coating properties were examined in more detail,
 136 showing a high hardness of the polycarbonate coatings.

137 In another study the influence on the properties of PU-
 138 dispersions were examined when PDO was used to replace
 139 1,6-hexanediol (HDO) in the polyester polyol (Fig. 2) [51].
 140 In a first step, the polyesters were synthesized by polycon-
 141 densation of the two respective diols with adipic acid and
 142 phthalic anhydride. The hydrolysis resistance of the two dif-
 143 ferent polyols was examined at a buffered pH value of 4 and
 144 80 °C. In both cases, the molecular weight of the polyesters
 145 decreased slowly, with no significant difference when PDO
 146 or HDO are used as building block. Both polyesters were
 147 then used as polyol compounds for PU-dispersions synthe-
 148 sized by the acetone process. The solid content of the final
 149 dispersions was adjusted to 40%. The PU-dispersions were
 150 then blended with a commercially available acrylic resin
 151 and the blend was coated on wood panels. Weathering test
 152 revealed a significant difference in the performance between
 153 the blends and the pure acrylic resin used as a reference,
 154 with the blend outperforming the acrylic resin.

155 In 2012 Schirp et al. [52] reported the use of PDO as
 156 diol component in PU-dispersions derived from fatty acid-
 157 derived polyester polyols. The latter were synthesized by
 158 reacting either fatty acids or fatty acid methyl esters with the
 159 trimethylolpropane (TMP), isophthalic acid and PDO. The

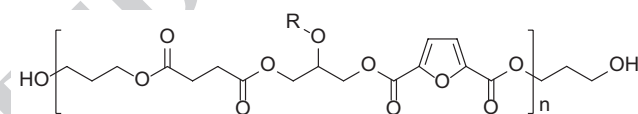


Fig. 3 Polyester polyol derived from 100% bio-based building blocks

160 resulting dispersions exhibited a good particle size distribu-
 161 tion and stability. In addition, the authors were able to show
 162 that the surface structure of the coated and dried dispersion
 163 strongly correlate to the amount of 2,2-bis(hydroxymethyl)
 164 propionic acid (bis-MPA).

165 More recently, another example of fully bio-based poly-
 166 ester polyols for polyurethanes coating was presented by
 167 García González and co-workers [53]. Based on a partially
 168 bio-based polyester binder that was reported by the same
 169 authors earlier [54], this new polyester was synthesized from
 170 glycerol, PDO, succinic acid, and FDCA (Fig. 3). The latter
 171 was used as a replacement for the previously used tereph-
 172 thalic acid. The properties of three different polyesters (0,
 173 75, and 100% bio-derived) and the resulting polyurethane
 174 materials derived from these three polyesters by a reaction
 175 with a petrochemical derived diisocyanate were studied. It
 176 could be shown that the polyesters exhibited similar molecu-
 177 lar weights from 1200 to 1800 g/mol, with the bio-based
 178 polyesters having a slightly lower T_g compared to the poly-
 179 ester derived from fossil resources. This was also true for
 180 the PU materials (14 °C against 34 °C for the petrochemical-
 181 derived PU). However, the PU derived from the 100% bio-
 182 based polyester proved to have superior properties than its
 183 fossil counterpart, such as better adhesion, higher stiffness

184 and improved surface tension. In addition to the synthesis
185 and material properties, the production, synthesis and recycl-
186 ing was evaluated by means of LCA. It was shown that
187 the bio-based PU emits 5.5 times less greenhouse gases and
188 exhibits a total non-renewable energy use that is 2.5 times
189 lower compared to the fossil-based material.

190 2.2 Alkyd Resins

191 PDO has also been used as diol component in bio-based
192 waterborne alkyd resins. Acar and co-workers prepared
193 acryl modified water reducible alkyd resins, where besides
194 TMP, PDO was used as sole alcohol component [55]. The
195 solid content of the acrylic modified alkyd resins was
196 60 weight-%. The others blended the resin with differ-
197 ent rations of an acrylic co-polymer, which resulted in an
198 improved performance of the final coatings. The best proper-
199 ties were found, when 40% (in respect to the alkyd resin) of
200 the acrylic co-polymer was used. In a consecutive study, the
201 same authors investigated the dilution effect of this kind of
202 acrylic modified alkyd resin on the coating properties, such
203 as film formation and thermal behavior [56].

204 2.3 Coil Coating

205 Polyester derived from FDCA, succinic acid, isosorbide and
206 either PDO or 1,5-pentanediol (PeDO) have been examined
207 in coil coatings applications by Lomelí-Rodríguez [57].
208 Increasing the ratio of FDCA led to an increase in vis-
209 cosity, molecular weight, but also in coloring. Polyesters
210 synthesized from PDO instead of PeDO were less disperse
211 (1.3–1.6 against 1.5–2.4 with PeDO). Increasing the amount
212 of isosorbide led to a decrease in M_w , therefore the amount
213 of isosorbide must stay under 50 mol % of the diol compo-
214 nent. The incorporation of FDCA as well as isosorbide had
215 a positive effect on the T_g , as well as T_m , with isosorbide hav-
216 ing a bigger influence. The use of PDO also improved the T_g
217 and T_m , due to the lower chain flexibility of the shorter PDO
218 chain. In addition, the polyester derived from IS and PDO
219 exhibited a higher decomposition temperature compared to
220 the similar polyester synthesized from PeDO.

221 2.4 Powder Coatings

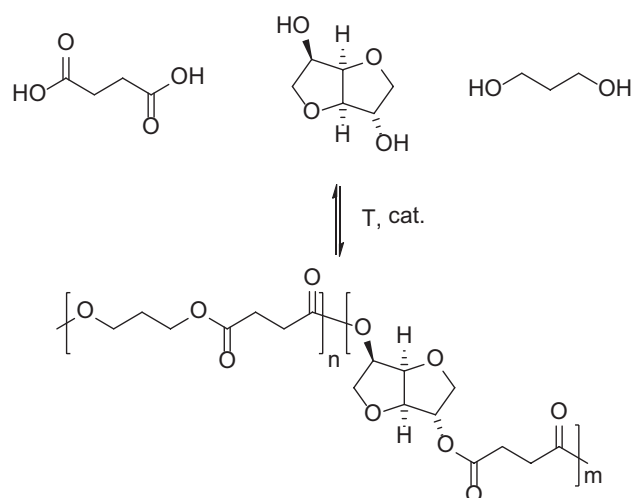
222 PDO was also examined as diol component in carboxyl func-
223 tional polyesters in the field of powder coatings [58]. In this
224 case, the powder coatings were formulated with triglycidyl
225 isocyanurate (TGIC) as hardener. It was shown that the
226 coatings based on polyester with PDO exhibited a superior
227 impact resistance and flexibility in comparison with those
228 without PDO. However, in this example PDO is the only
229 bio-derived monomer used.

To increase the amount of bio-based monomers in powder
coatings Koning and co-workers examined the use of PDO
in combination with succinic acid and Isosorbide [59]. The
latter was used as bio-based alternative to isophthalic and
terephthalic acid to obtain polyester oligomers with high T_g
necessary for powder coatings applications (scheme 3). It
was shown that PDO can be used to modify the T_g . Due to
the flexibility of this aliphatic monomer, the T_g decreases
with increasing amount of PDO. This shows that PDO could
be an alternative to petrochemical aliphatic diols such as
HDO.

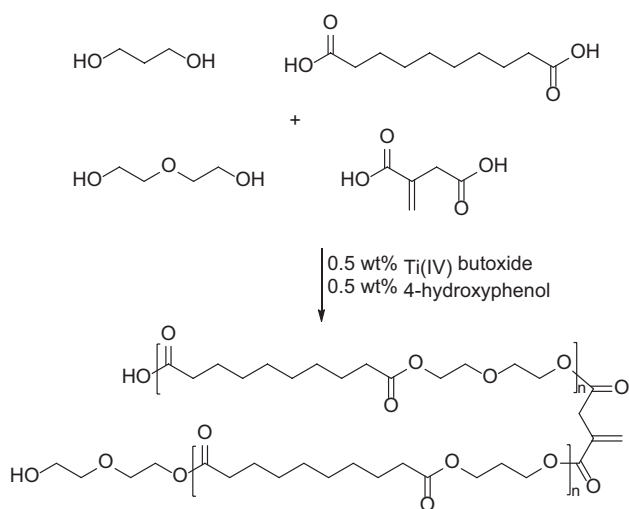
225 2.5 Unsaturated Polyesters

Unsaturated polyesters derived from PDO and itaconic acid
were used as shape memory polymers (SMP) [60]. In this
example, the synthesized PDO were almost exclusively com-
posed of bio-based monomers, such as itaconic acid, sebacic
acid and PDO. As only exception, diethylene glycol was
incorporated to influence the crystallinity of the polymers
(scheme 4). These polyesters were then subjected to com-
pression molding with dicumyl peroxide as radical initiator
resulting in a set of SMP with interesting properties and
potential fields of application.

1,3-Propanediol was also used as the only diol building
block for unsaturated polyester resins [61]. These resins
were then used as precursor for thermally curing composites
with nanoprecipitated calcium carbonate (NPCC). As other
components fumaric acid, succinic acid, and lactic acid were
used, resulting in a polyester with a high amount of bio-
based monomers. The resins were characterized by means
of IR and NMR. In addition to these resins, the authors syn-
thesized a novel reactive diluent as partial replacement for



Scheme 3 Bio-based polyesters based on succinic acid, isosorbide and PDO



Scheme 4 SMP derived from polyesters with PDO

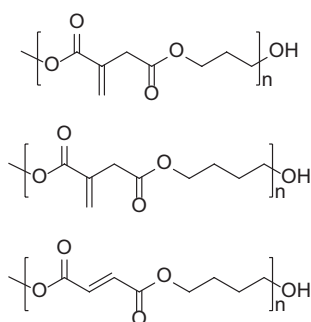


Fig. 4 Bio-based polyesters synthesized by Farmer et al. [62]

261 styrene. This reactive diluent was obtained by a reaction of
 262 lactic acid with 1,2-propanediol, followed by an end-capping
 263 reaction with itaconic anhydride. The resins were subse-
 264 quently cured with different amounts of reactive diluents
 265 (styrene and the bio-based component) and NPCC. It could
 266 be shown that the bio-based reactive diluent had a major
 267 influence on the properties of the composites.

268 As another example in the field of unsaturated polyes-
 269 ters, Farmer et al. [62] reported their study on the synthesis
 270 of itaconic- and fumaric acid-containing polyesters starting
 271 from the corresponding methylesters of itaconic and fumaric
 272 acid. Besides PDO, 1,4-butanediol (1,4-BDO) was used as
 273 diol component for these completely bio-based polyesters
 274 (Fig. 4).

275 The structure of the polyesters as well as side reac-
 276 tions occurring during the polycondensation reaction were
 277 thoroughly studied by means of NMR spectroscopy. For
 278 example, the degree of mesomerization of the itaconic to
 279 the corresponding mesaconic acid species was analyzed.
 280 Furthermore NMR was used to elucidate the multiplet

281 complexity of the protons in α -position to the C–O-bond of
 282 the ester linkage. In addition, the crosslinking mechanism
 283 of polyester itaconates was examined. According to their
 284 studies, the crosslinking proceeds through an oxo-Michael-
 285 addition, the so called Ordelt reaction [63–65]. However, the
 286 abilities of these polyesters to undergo radical crosslinking
 287 or post-polymerization modification was not further exam-
 288 ined in the course of this study.

289 In a recent example, PDO was also used as building
 290 block for unsaturated polyesters with itaconic acid as dicar-
 291 boxylic acid [66]. Polyesters of this kind have been used as
 292 binder resins for wood coatings [51, 67]. However, the use
 293 of PDO under acid-catalyzed azeotropic polycondensation
 294 conditions led to undesired cross-linking and gelation. An
 295 effect that is not observed, when other diols, such as HDO
 296 or neopentylglycol were used. By screening at set of differ-
 297 ent Brønsted- and Lewis acids as condensation catalysts,
 298 it could be shown, that the use of Brønsted acids, such as
 299 methansulfonic acid leads to an enhanced rate of a compet-
 300 ing etherification reaction. This eventually leads in combi-
 301 nation with some crosslinking through radical or polar
 302 pathways to the gelation of the polyester. This etherification
 303 is observed to a much smaller degree, when Lewis acids,
 304 such as $Zn(OAc)_2$ or $Ti(OBu)_4$ are used. By employing these
 305 catalysts, the gelation can be prevented and polyesters with
 306 100% 1,3-PDO can be synthesized, setting the stage for the
 307 replacement of petrochemical diols with the bio-based PDO.
 308 Polyesters of this type have been employed as binder resins
 309 in UV-curing offset inks, resulting in binder resins with a
 310 renewable content from 47 to 100%, replacing commonly
 311 used diols in the preparation of polyester polyols [68].

3 Conclusion

312 The aim of this mini review was to highlight the poten-
 313 tial of PDO in the field of coating resins. Even though a
 314 lot of work has been dedicated to plastics derived from
 315 this interesting diol, such as PTT or PFT, examples in the
 316 coatings field are still somewhat scarce, especially in the
 317 scientific literature. The examples presented herein show
 318 that PDO can be used as building blocks in a broad field
 319 of application, such as polyurethane, polycarbonate, alkyd,
 320 and unsaturated polyester resins. In addition, some appli-
 321 cations in powder and coil coatings were given. It is worth
 322 mentioning that most of the studies focus on other aspects
 323 than the mere replacement of traditional diols with PDO.
 324 However, the wide range of applications show that PDO
 325 can be a bio-based alternative to diols usually used as
 326 monomers in the field of polyester resins, such as HDO or
 327 neopentylglycol. Depending on the diol being substituted
 328 and the composition of the polyester, it can alter the T_g and
 329 flexibility of the polymers, allowing for new properties of
 330

331 the resulting materials. PDO can therefore be considered
332 as an additional and valuable tool in the toolbox of poly-
333 meric chemistry, for plastics as well as coating materials.

334 Compliance with ethical standards

335 **Conflict of interest** The authors declare no conflict of interest.

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