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

Marcel Kluge, Sacha Pérocheau Arnaud, Tobias Robert

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	Organization	Fraunhofer Institute for Wood Research—Wilhelm-Klauditz-Institut WKI
	Address	Bienroder Weg 54E, 38108, Brunswick, Germany
	Phone	+49 531 2155-357
	Fax	
	Email	tobias.robert@wki.fraunhofer.de
	URL	
	ORCID	<a href="http://orcid.org/0000-0002-6530-9741">http://orcid.org/0000-0002-6530-9741</a>
Author	Family Name	<b>Kluge</b>
	Particle	
	Given Name	<b>Marcel</b>
	Suffix	
	Division	
	Organization	Fraunhofer Institute for Wood Research—Wilhelm-Klauditz-Institut WKI
	Address	Bienroder Weg 54E, 38108, Brunswick, Germany
	Phone	
	Fax	
	Email	
	URL	
	ORCID	
Author	Family Name	<b>Arnaud</b>
	Particle	
	Given Name	<b>Sacha Pérocheau</b>
	Suffix	
	Division	
	Organization	Fraunhofer Institute for Wood Research—Wilhelm-Klauditz-Institut WKI
	Address	Bienroder Weg 54E, 38108, Brunswick, Germany
	Phone	
	Fax	
	Email	
	URL	

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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.

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

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

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

4 Marcel Kluge<sup>1</sup> · Sacha Pérocheau Arnaud<sup>1</sup> · Tobias Robert<sup>1</sup>

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## 7 Abstract

8 Polyester resins are important raw materials for a myriad of applications especially in the field of coatings and radical curing  
9 polymers, such as wood and powder coatings, molding compounds, and UV-curing applications. In addition, polyols derived  
10 from polyester resins are precursors for the synthesis of polyurethanes and polycarbonates. Besides dicarboxylic acid, diols  
11 are used as monomers in these polyesters. To date most of the diols utilized are derived from petrochemical feedstock. To  
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16 cations. This article gives a brief overview over the utilization of 1,3-propanediol in high molecular weight polyesters for  
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  
A2 this work.

A3 ✉ Tobias Robert  
A4 tobias.robert@wki.fraunhofer.de

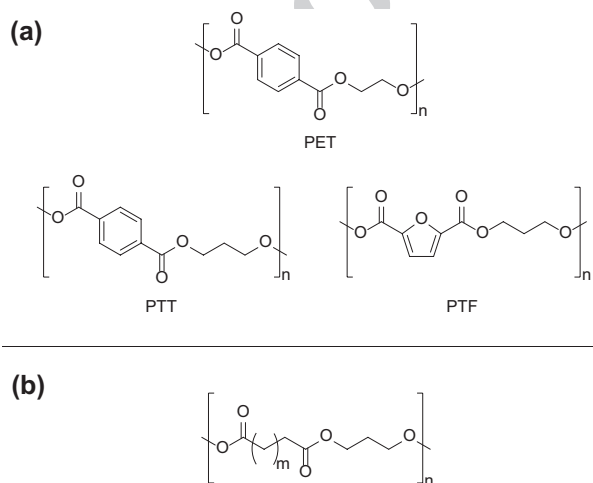
A5 <sup>1</sup> Fraunhofer Institute for Wood Research—Wilhelm-Klauditz-  
A6 Institut WKI, Bienroder Weg 54E, 38108 Brunswick,  
A7 Germany

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

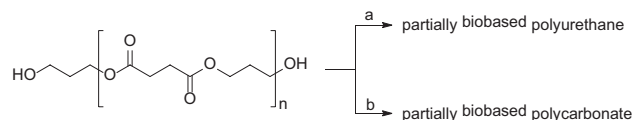
## 2 Polyester Resins from 1,3-Propandiol 88

### 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.

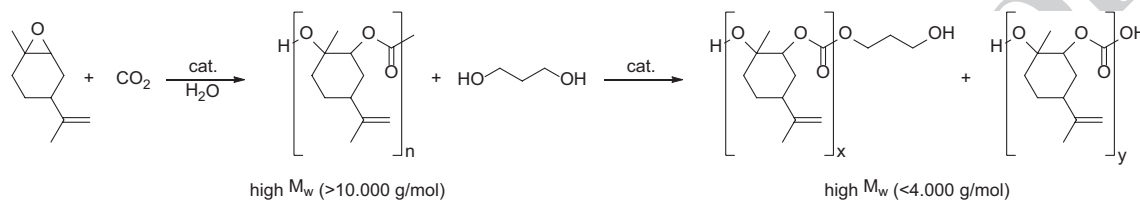
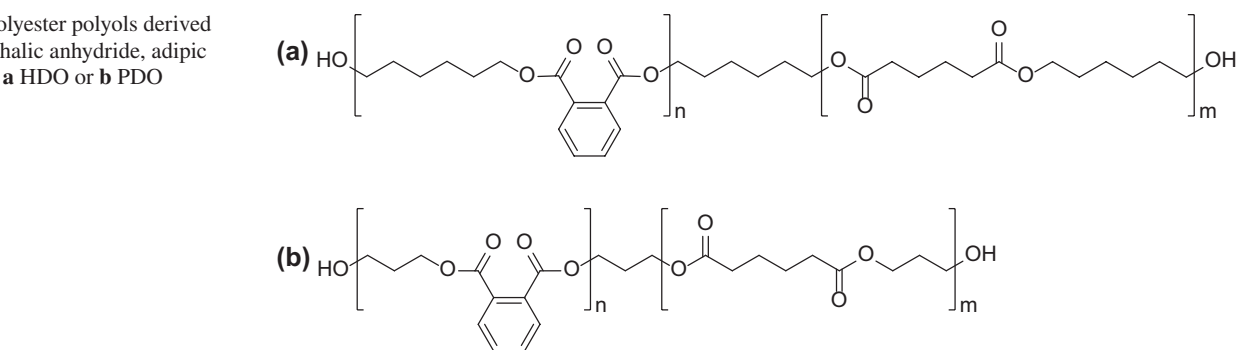
103 The polyester polyols also found application as building  
104 blocks for polycarbonates (Fig. 2b) [47]. After the polycon-  
105 densation step, the polyesters were chain extended by a two-  
106 step process using phosgene, a special amine and DMAP,  
107 which allows for an exact adjustment of 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 CO<sub>2</sub> 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

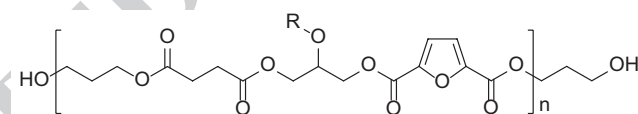


**Scheme 2** Synthesis of poly(limonene carbonate) and subsequent alcoholysis with PDO

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 recycling  
186 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 different  
197 ratios of an acrylic co-polymer, which resulted in an  
198 improved performance of the final coatings. The best properties  
199 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 viscosity,  
209 molecular weight, but also in coloring. Polyesters synthesized  
210 from PDO instead of PeDO were less disperse (1.3–1.6 against  
211 1.5–2.4 with PeDO). Increasing the amount of isosorbide led  
212 to a decrease in  $M_w$ , therefore the amount of isosorbide must  
213 stay under 50 mol % of the diol component. The incorporation  
214 of FDCA as well as isosorbide had a positive effect on the  $T_g$ ,  
215 as well as  $T_m$ , with isosorbide having a bigger influence.  
216 The use of PDO also improved the  $T_g$  and  $T_m$ , due to the  
217 lower chain flexibility of the shorter PDO chain. In addition,  
218 the polyester derived from IS and PDO exhibited a higher  
219 decomposition temperature compared to the similar polyester  
220 synthesized from PeDO.

## 221 2.4 Powder Coatings

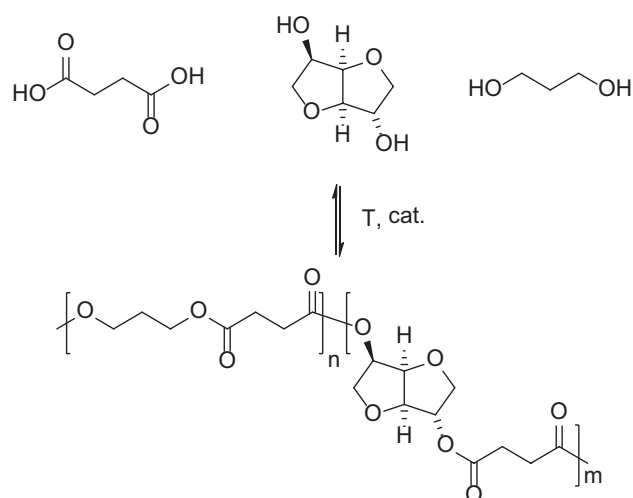
222 PDO was also examined as diol component in carboxyl functional  
223 polyesters in the field of powder coatings [58]. In this case,  
224 the powder coatings were formulated with triglycidyl isocyanurate  
225 (TGIC) as hardener. It was shown that the coatings based on  
226 polyester with PDO exhibited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

To increase the amount of bio-based monomers in powder  
230 coatings Koning and co-workers examined the use of PDO  
231 in combination with succinic acid and Isosorbide [59]. The  
232 latter was used as bio-based alternative to isophthalic and  
233 terephthalic acid to obtain polyester oligomers with high  $T_g$   
234 necessary for powder coatings applications (scheme 3). It  
235 was shown that PDO can be used to modify the  $T_g$ . Due to  
236 the flexibility of this aliphatic monomer, the  $T_g$  decreases  
237 with increasing amount of PDO. This shows that PDO could  
238 be an alternative to petrochemical aliphatic diols such as  
239 HDO.  
240

## 241 2.5 Unsaturated Polyesters

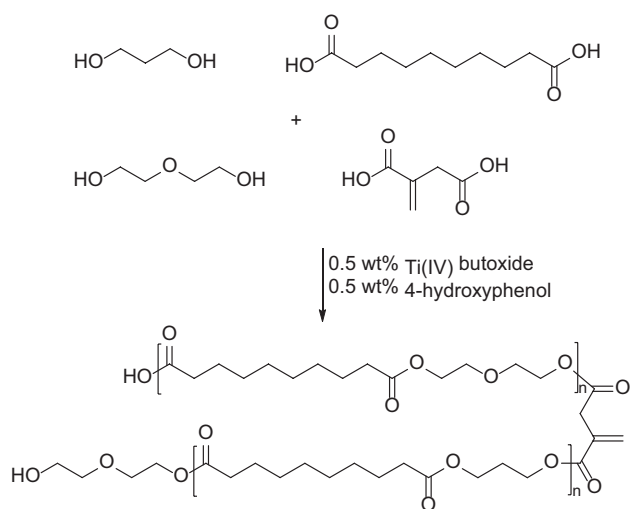
242 Unsaturated polyesters derived from PDO and itaconic acid  
243 were used as shape memory polymers (SMP) [60]. In this  
244 example, the synthesized PDO were almost exclusively composed  
245 of bio-based monomers, such as itaconic acid, sebacic acid  
246 and PDO. As only exception, diethylene glycol was incorporated  
247 to influence the crystallinity of the polymers (scheme 4). These  
248 polyesters were then subjected to compression molding with  
249 dicumyl peroxide as radical initiator resulting in a set of SMP  
250 with interesting properties and potential fields of application.  
251

252 1,3-Propanediol was also used as the only diol building  
253 block for unsaturated polyester resins [61]. These resins  
254 were then used as precursor for thermally curing composites  
255 with nanoprecipitated calcium carbonate (NPCC). As other  
256 components fumaric acid, succinic acid, and lactic acid were  
257 used, resulting in a polyester with a high amount of bio-based  
258 monomers. The resins were characterized by means of IR and  
259 NMR. In addition to these resins, the authors synthesized a  
260 novel reactive diluent as partial replacement for

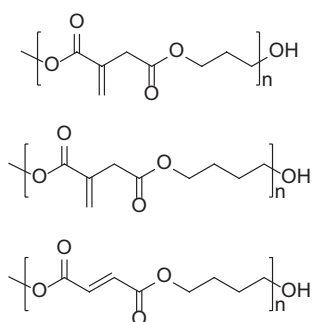


**Scheme 3** Bio-based polyesters based on succinic acid, isosorbide and PDO





**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  $\alpha$ -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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