

**Aromatic Polyesters from Biosuccinic Acid**

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## Aromatic Polyesters from Biosuccinic Acid

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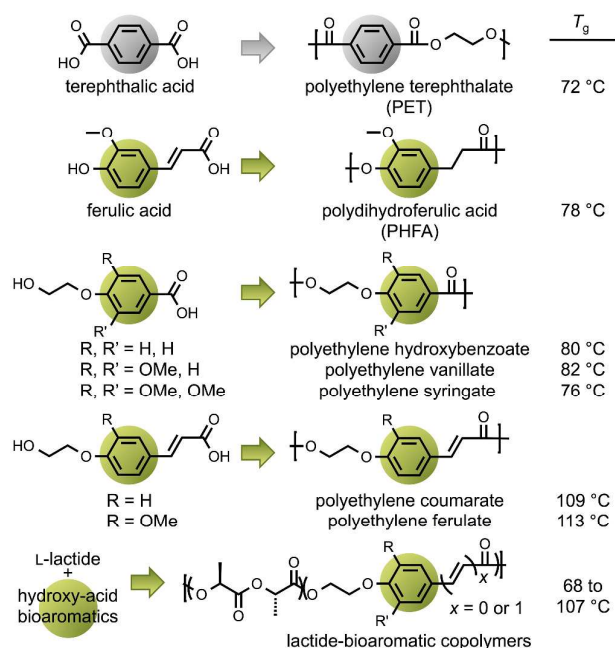
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Succinic acid, a promising biobased platform chemical, was used as a precursor to synthesize the aromatic monomers 2,5-dihydroxyterephthalic acid and 2,5-dimethoxyterephthalic acid. Two copolymer series were generated with linear diol comonomers, HO(CH<sub>2</sub>)<sub>n</sub>OH, of varying length with  $n = 2-10$ . For polyalkylene dihydroxyterephthalates, the glass transition temperature ( $T_g$ ) ranged from 36 to 168 °C. For polyalkylene dimethoxyterephthalates, the  $T_g$  ranged from 6 to 74 °C.

As one of the most important commodity plastics on the market, polyethylene terephthalate (PET) accounts for 13% of the plastics production worldwide.<sup>1</sup> PET has many applications which include packaging, films, and fibers, among others.<sup>2,3</sup> Single use beverage bottle consumption accounts for 81% of all PET packaging, corresponding to 12.5 million tons in 2013.<sup>4</sup> Total PET packaging usage is projected to reach 21.1 million tons by 2021.<sup>5</sup> PET is synthesized from ethylene glycol and terephthalic acid, both traditionally derived from fossil fuels.<sup>2</sup> Spurred by a rising demand for PET and a continued depletion of fossil fuels reserves,<sup>6,7</sup> the Coca-Cola company launched the PET *PlantBottle*® in 2009.<sup>8,9</sup> Its 30% biobased content is achieved with bio-ethylene glycol, which derives from bioethanol.<sup>10</sup> The remaining 70% of *PlantBottle* derives from terephthalic acid, which is still fossil fuel-based.<sup>2</sup>

Fully biorenewable PET or PET mimics<sup>11</sup> have been targeted in a number of ways including: designing new synthetic routes for converting biomass to terephthalic acid (TA);<sup>12,13,14,15</sup> synthesizing alternative diacids to supplant terephthalic acid;<sup>16,17,18</sup> and creating novel biorenewable polyesters with properties comparable to those of PET.<sup>19,20,21,22,23,24</sup> Among the efforts to mimic PET, the most successful to date is arguably polyethylene furanoate (PEF), produced by Avantium.<sup>16</sup> Biobased PEF bottles—reportedly not biodegradable<sup>25</sup>—are scheduled for use in the 2020 Summer Olympics in Japan.<sup>26</sup>

Our group has designed and built various PET mimics from biobased aromatic monomers. These bioaromatics were included to emulate the terephthalate component of PET, which imparts conformational rigidity and chain-chain interactions, resulting in a PET glass transition temperature ( $T_g$ ) high enough (72 °C)<sup>27,28</sup> for a variety of packaging applications. Our reported biorenewable PET analogues (Figure 1) include: the homopolymer polydihydroferulic acid (PHFA) with a  $T_g$  of 78 °C;<sup>19,20</sup> polyethylene hydroxybenzoates with  $T_g$  values ranging from 76 to 82 °C;<sup>21,23</sup> polyethylene coumarate and polyethylene ferulate with  $T_g$  values of 109 and 113 °C, respectively;<sup>22</sup> and copolymers of L-lactide and bioaromatics with  $T_g$  values ranging from 68 to 107 °C.<sup>23</sup>



**Fig. 1** Biorenewable PET mimics built with naturally-occurring bioaromatics that exhibit glass transition temperatures ( $T_g$ ) competitive with fossil fuel-based PET.<sup>28,20,21,22,23</sup>

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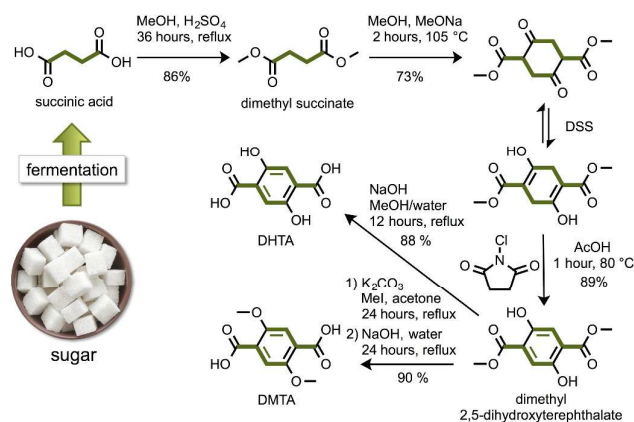
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Herein, our continued search for PET mimics is described. The targeted bioaromatic monomers are not naturally-occurring, but can be synthesized readily from non-aromatic, biobased succinic acid (SA). This diacid sugar fermentation product is recognized as one of the ten most promising biobased platform chemicals because of its low cost and chemical versatility.<sup>29</sup> The current uses of SA include: surfactants, additives, a precursor to various industrial chemicals (such as butanediol), and as a monomer for polyester and polyamide production.<sup>30</sup> The petrochemical production of this four-carbon diacid (butane to maleic anhydride) has continually yielded to sustainable glucose fermentation strategies.<sup>31</sup> The annual production of biosuccinic acid (bio-SA) was around 38,000 metric tons in 2013–2014 and is expected to reach 600,000 metric tons by 2020, mostly supplanting the petro-SA market.<sup>32,33,34</sup> The cost of bio-SA is estimated to be \$0.55–1.10 per kg.<sup>31</sup>

The low-cost and bioavailability of bio-SA are certainly features that render it attractive for high-volume polymer production.<sup>35</sup> However, its various polyesters generally have low glass transition temperatures, owing largely to conformational flexibility. For example, the  $T_g$  of polyethylene succinate is  $-11$  °C.<sup>36</sup> Hence, we sought cyclization chemistry of SA that would afford rigid ring monomers, structurally related to terephthalic acid. This search found the 1885 work of Ebert,<sup>37</sup> who first reported the Claisen condensation/Dieckmann cyclization of dimethyl succinate to afford dimethyl succinyl succinate (DSS, Scheme 1).<sup>38</sup> This cyclic dimerization product clearly resembles terephthalic acid, but is still not aromatic.

Aromatization conditions applied to DSS can yield several products, including dimethyl terephthalate,<sup>39</sup> 2,5-diaminoterephthalic esters,<sup>40,41,42</sup> and dimethyl 2,5-dichloro-3,6-dihydroxyterephthalate.<sup>43</sup> We were most interested in the simple aromatization conditions offered by *N*-chlorosuccinimide, which only serves to remove H<sub>2</sub> from DSS, thereby yielding dimethyl 2,5-dihydroxyterephthalate (DDHT).<sup>44,45</sup> This is a convenient precursor to terephthalic acid derivatives 2,5-dihydroxyterephthalic acid (DHTA) and 2,5-dimethoxyterephthalic acid (DMTA) (Scheme 1).<sup>46,47,48</sup> Because *N*-chlorosuccinimide is not an ideal oxidant for this aromatization, we have begun to explore more environmentally friendly strategies for this reaction, including sulfuric acid oxidation,<sup>49</sup> dimethylsulfoxide oxidation,<sup>50</sup> hydrogen peroxide oxidation,<sup>51</sup> and transfer dehydrogenation.<sup>52</sup>

In summary, the four-step syntheses of DHTA and DMTA were straightforward *via* adapted literature procedures: 1) esterification of SA to form dimethyl succinate,<sup>53</sup> 2) dimerization of dimethyl succinate to obtain dimethyl succinyl succinate (DSS);<sup>38,46</sup> 3) aromatization with *N*-chlorosuccinimide to produce dimethyl 2,5-dihydroxyterephthalate;<sup>44,54</sup> and 4) hydrolysis to produce DHTA<sup>55</sup> or one-pot methylation/hydrolysis to produce DMTA (Scheme 1).<sup>56</sup> DHTA and DMTA were obtained from succinic acid in good *overall* yields of 49.4% and 50.3%, respectively.

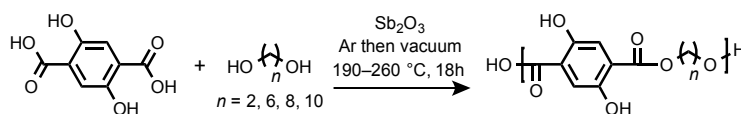


**Scheme 1** Synthesis of aromatic 2,5-dihydroxyterephthalic acid (DHTA) and 2,5-dimethoxyterephthalic acid (DMTA) in four steps from succinic acid, which can be obtained from sugar.

Prior polymerization chemistry has employed DHTA for the synthesis of polydiimidazoles,<sup>57,58,59</sup> polythioles,<sup>60,61</sup> and polybisoxazoles.<sup>47,62</sup> Three patents have described the use of petroleum-based DHTA, or its dimethyl ester, in polyester or terpolyester production.<sup>63,64,65</sup> However, key thermal properties were absent, or the aromatic feed fraction was less than 3%; hence, imperative comparisons to the structural analogue PET have not been made. Polymers made directly from DMTA have not been described, but the copolymer of its dimethyl ester and 1,2-propanediol has been claimed in a patent.<sup>66</sup> However, critical characterization and thermal property analysis was not conducted.

Polyalkylene dihydroxyterephthalates were synthesized from DHTA and four different  $\alpha,\omega$ -alkanediols (ethylene glycol, 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol) under argon during a 14-hour temperature ramp from 190 to 260 °C using 1 mol% of Sb<sub>2</sub>O<sub>3</sub> catalyst, followed by high dynamic vacuum to eliminate the water by-product for an additional 4 hours (Table 1). All four polymers were obtained in high isolated yields (above 80%) and showed good thermal stability with a 5% mass loss ( $T_{95}$ ) under nitrogen at temperatures from 211 to 334 °C. The poor solubility of three of these polymers in the gel permeation chromatography (GPC) solvent hexafluoroisopropanol (HFIP) precluded reliable molecular weight determinations. This poor solubility may be attributable to crosslinking via the aromatic hydroxy groups, or to persistent hydrogen bonding of the same groups. Only polydecylene dihydroxyterephthalate was suitably soluble in HFIP and thus, its number average molecular weight ( $M_n$ ) and dispersity ( $D$ ) were determined as  $M_n = 13,000$  Da and  $D = 1.7$  (Table 1, Entry 4).

For diacid/diol polycondensation at high temperatures, the loss of volatile diols would prevent the optimal 1:1 stoichiometric ratio necessary for ideal AA/BB copolymerization. Thus, a study was conducted with varying amounts of excess diol for the polymerization of DMTA and ethylene glycol. As described in Table 2, lowering the ethylene glycol equivalents from 6.0 to 3.0 to 2.0 to 1.2 (Entries 1–4)

**Table 1** Synthesis and characterization of polyalkylene dihydroxyterephthalates.<sup>a</sup>

Entry	Polymer	Yield (%)	$M_n^b$ (Da)	$M_w^b$ (Da)	$\mathcal{D}^b$	$T_g^c$ (°C)	$T_m^c$ (°C)	$T_{95\%}^d$ (°C)
1		80.0	<sup>e</sup>	<sup>e</sup>	<sup>e</sup>	168	n.o.	211
2		84.9	<sup>e</sup>	<sup>e</sup>	<sup>e</sup>	79	n.o.	334
3		89.5	<sup>e</sup>	<sup>e</sup>	<sup>e</sup>	51	171	331
4		81.4	13,000	22,100	1.7	36	160	327

<sup>a</sup>1 mol%  $Sb_2O_3$ ; melt polymerization under argon for 14 hours; temperature ramp from 190 to 260 °C; then 4 hours of dynamic vacuum. <sup>b</sup>Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. <sup>c</sup>Determined by DSC; n.o. = not observed. <sup>d</sup>Temperature at which 5% mass loss is observed under nitrogen. <sup>e</sup>Insolubility of the polymer in HFIP prevented GPC analysis.

revealed the following trends: a decrease of  $M_n$  from 10,200 to 5,900 Da; a narrowing of  $\mathcal{D}$  from 7.8 to 3.3; an increase in  $T_g$  from 59 to 74 °C; and a decrease in polymer solubility. The highest  $M_w$  polymer from ethylene glycol (Entry 1) showed the largest dispersity, which likely led to the lowest  $T_g$  value because of the abundant fraction of low molecular weight material. Although 1.2 equivalents did not afford the highest measured molecular weight, the 1.0:1.2 ratio was selected for further DMTA/ethylene glycol polymerizations because of optimal polymerization control (low  $\mathcal{D}$ ) and a high  $T_g$  value.

For the polymerization of DMTA and 1,3-propanediol, there is a drastic difference between 1.0 and 1.03 equivalents of the diol. For the stoichiometric case (Table 2, Entry 5),  $M_n$  values are about one-third those obtained with a slight excess (Table 2, Entry 6). Moreover, 1.03 equivalents yields better polymerization control (lower  $\mathcal{D}$ ) and a higher  $T_g$  value. Based on this, further DMTA/diol polymerizations with 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol (all liquids at room temperature) employed the 1.0:1.03 ratio. DMTA/diol polymerizations with larger diols (1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, and 1,10-decanediol) employed the 1.0:1.0 ratio as diol volatility is expected to be acceptably low (all solids at room temperature).

As shown in Table 3, polyalkylene dimethoxyterephthalates were obtained in good to high isolated yields (66 to 88%).  $M_n$  values were high and ranged from 19,500 to 36,200 Da, except for the polymerization with ethylene glycol, described above. Polymers made from the longer diols ( $n \geq 5$ ) displayed typical  $\mathcal{D}$  values for step-growth polymerizations, ranging from 2.2 to 2.7 (Entries 4–8). Higher  $\mathcal{D}$  values (3.3–4.6) were measured for polymers when shorter diols ( $n \leq 4$ ) were employed. We

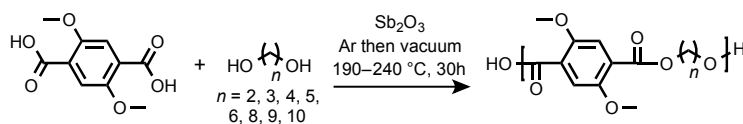
attribute this to the common deviation from ideal step-growth behavior associated with high polymerization viscosity.

**Table 2** Optimization of polymerization conditions for DMTA and ethylene glycol ( $n=2$ ) or DMTA and 1,3-propanediol ( $n=3$ ).<sup>a</sup>

Entry	$n$	Diacid: Diol	Yield (%)	$M_n^b$ (Da)	$M_w^b$ (Da)	$\mathcal{D}^b$	$T_g^c$ (°C)
1	2	1.0:6.0	79.4	10,200	79,600	7.8	59
2		1.0:3.0	61.4	11,500	74,800	6.5	72
3		1.0:2.0	70.1	4,000	16,000	4.0	75
4		1.0:1.2	66.1	5,900	19,500	3.3	74
5	3	1.0:1.0	73.2	6,800	37,400	5.5	57
6		1.0:1.03	87.5	21,900	81,000	3.7	63

<sup>a</sup>1 mol%  $Sb_2O_3$ ; melt polymerization under argon for 22 hours; temperature ramp from 190 to 240 °C; then 8 hours of dynamic vacuum. <sup>b</sup>Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. <sup>c</sup>Determined by DSC.

Figure 2 shows the glass transition temperature (solid lines) graphed as a function of the number of methylene spacers present in the diols ( $n$ ) of the two novel polymer series from Table 1 (diol + DHTA) and Table 3 (diol + DMTA). For comparison, literature data is also plotted for polyalkylene terephthalates.<sup>28</sup> Clearly, the polyalkylene dihydroxyterephthalates (Figure 2, orange squares) display significantly higher  $T_g$  values than the polyalkylene dimethoxyterephthalates (Figure 2, blue diamonds), for a given value of  $n$ . For example, polyethylene dihydroxyterephthalate (PEDHT,  $T_g = 168$  °C) has at  $T_g$  value that is 94 °C higher than that of polyethylene dimethoxyterephthalate (PEDMT,  $T_g = 74$  °C). The corresponding difference for the polydecylene ( $n =$

**Table 3** Synthesis and characterization of polyalkylene dimethoxyterephthalates.<sup>a</sup>

Entry	Polymer	Yield (%)	$M_n^b$ (Da)	$M_w^b$ (Da)	$D^b$	$T_g^c$ (°C)	$T_m^c$ (°C)	$T_{95\%}^e$ (°C)
1		66.1	5,900	19,500	3.3	74	n.o.	325
2		87.5	21,900	81,000	3.7	63	n.o.	338
3		84.9	19,500	89,700	4.6	47	149 <sup>d</sup>	328
4		66.0	31,700	76,100	2.4	33	n.o.	337
5		74.3	21,000	56,700	2.7	27	115	341
6		70.4	23,000	57,500	2.5	16	114 <sup>d</sup>	340
7		76.2	29,000	63,800	2.2	10	84	350
8		78.2	36,200	90,500	2.5	6	80	348

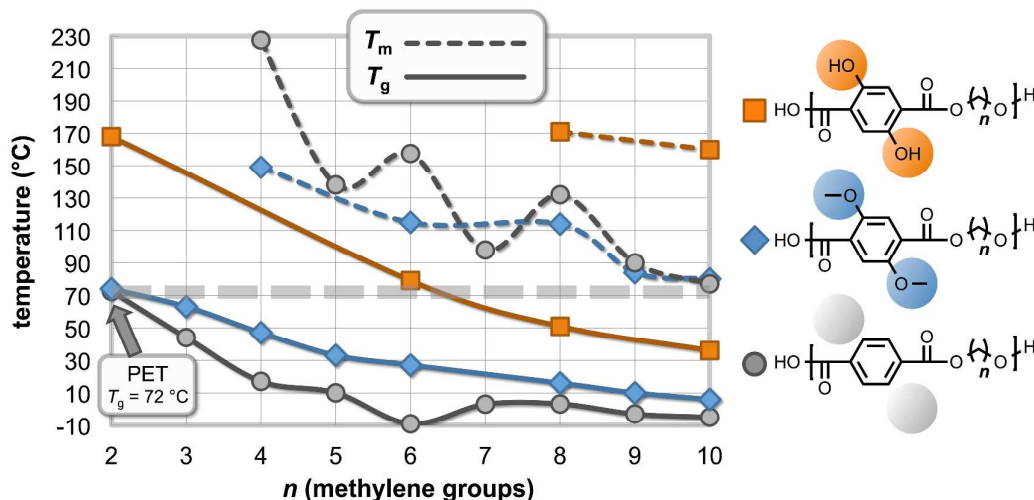
<sup>a</sup>1 mol%  $Sb_2O_3$ ; melt polymerization under argon for 22 hours; temperature ramp from 190 to 240 °C; then 8 hours of dynamic vacuum. <sup>b</sup>Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. <sup>c</sup>Determined by DSC;  $T_m$  values measured during the first thermal cycle; n.o. = not observed. <sup>d</sup> $T_m$  values measured during the second thermal cycle. <sup>e</sup>Temperature at which 5% mass loss is observed under nitrogen.

10) polyesters is lower at 30 °C (= 36 °C – 6 °C). The origin of this difference is likely the hydrogen bonding (intra- and intermolecular) present in the former, but absent in the latter. These interactions require greater thermal energy to be broken so that long-range segmental motion of polymers can occur and afford a rubbery state. Although we have not specifically detected branching/crosslinking via the aromatic hydroxy group, this is certainly possible and would also increase the  $T_g$  value. Typically, such aromatic esters are much less stable than aliphatic esters; but they could form under the forcing polymerization conditions employed.

Moreover, the polyalkylene dimethoxyterephthalates excelled the known polyalkylene terephthalates regarding measured  $T_g$  values.<sup>28,67,68</sup> Although polarity arguments likely pertain, an additional rationale is the larger conformational barriers imparted by the methoxy groups compared to

hydrogen substituents. The differences are not large, but consistently favor the more substituted polymer. For example, poly(pentylene dimethoxyterephthalate) ( $T_g = 33$  °C) shows a  $T_g$  value 23 °C above that of poly(pentylene terephthalate) ( $T_g = 10$  °C), while poly(ethylene dimethoxyterephthalate) (PEDMT) shows a  $T_g$  value just 2 °C above that of poly(ethylene terephthalate) (PET). In fact, PEDMT, with its  $T_g$  of 74 °C, is the best overall match among these novel polyesters to the fossil-fuel archetype PET, with its  $T_g$  of 72 °C.<sup>28</sup>

Polyalkylene terephthalates and other polymers with alkylene segments invariably exhibit lower  $T_g$  values as the alkylene segment length increases. The summary explanation for this is that such polymers possess a greater fraction of “flexible bonds,”<sup>28</sup> which can be interpreted as lower average conformational barriers and more facile segmental motion. The two novel polymer series reported herein are no exception. For polyalkylene dihydroxyterephthalates (Table 1),



**Fig. 2** Polymer melting temperature ( $T_m$ , dashed lines) and glass transition temperature ( $T_g$ , solid lines) for polyalkylene dihydroxyterephthalates (orange squares), polyalkylene dimethoxyterephthalates (blue diamonds), and polyalkylene terephthalates (gray circles)<sup>28</sup> as a function of methylene spacers ( $n$ ) present in the constituent diol employed for synthesis.

the addition of eight methylene groups to the repeat unit decreases the  $T_g$  by 132 °C (= 168 °C – 36 °C) for an average effect of 16.5 °C per methylene. For polyalkylene dimethoxyterephthalates (Table 3), the addition of eight methylene groups to the repeat unit decreases the  $T_g$  by 68 °C (= 74 °C – 6 °C) for an average effect of 8.5 °C per methylene.

A similar effect is observed for the polymer melting temperatures ( $T_m$ ), as illustrated by the dashed lines in Figure 2. In this case, the strong polar interactions of the aromatic units are diluted by an increasing fraction of non-polar methylene groups, and a drop in  $T_m$  is observed.<sup>28</sup> For polyalkylene terephthalates, this trend is superimposed on an odd methylene/even methylene dependence, which directly impacts crystal lattice packing.<sup>69</sup> Those polymers with an even number of methylene groups pack better and display higher melting temperatures.

For the twelve novel polyesters reported in Table 1 and Table 3, melting temperatures were observed (by DSC) for only seven; five of these did not display a melting endotherm under the conditions employed—possibly because of slow crystallization kinetics. Still the aforementioned trend seems applicable, according to the dashed orange and dashed blue lines of Figure 2. For both series, the  $T_m$  decreases with increasing alkylene spacer length, albeit there are limited data points to unequivocally defend this trend. And, the odd/even dependence cannot be established since only one polymer with an odd number of methylenes exhibited a melting temperature ( $n = 9$ ; Table 3, Entry 7).

Note also that the hydroxy-substituted polymers melt higher than the corresponding methoxy-substituted polymers. For example, polyoctylene dihydroxyterephthalate has a  $T_m$  of 171 °C, while polyoctylene dimethoxyterephthalate has a  $T_m$  of only 114 °C. Most likely, the hydrogen bonding present in the former translates to better polymer packing and a greater

lattice energy. Interestingly, the less polar polyalkylene terephthalates generally melt higher than the more polar polyalkylene dimethoxyterephthalates (except for  $n = 10$ ). This could be attributed to simple space-packing effects, with two methoxy groups not fitting efficiently into the crystal lattice.

## Conclusions

Biobased succinic acid was converted into the terephthalic acid analogues 2,5-dihydroxyterephthalic acid (DHTA) and 2,5-dimethoxyterephthalic acid (DMTA) (Scheme 1). These were polymerized with linear diols of varying length to afford two polymer series: polyalkylene dihydroxyterephthalates and polyalkylene dimethoxyterephthalates. Both polymer series exhibited a logical relationship between structure and thermal properties. Specifically, the  $T_g$  value decreased with an increasing number of methylene groups ( $n = 2$ –10) in the polymer repeat unit. Hydroxy side groups conferred higher  $T_g$  values (168 to 36 °C); methoxy side groups conferred lower  $T_g$  values (74 to 6 °C). The known polyalkylene terephthalates exhibit still lower  $T_g$  values (72 to –9 °C).<sup>28</sup> The presumed participation of the pendant hydroxy groups in hydrogen bonding explains the high  $T_g$  values for that polymer series. Polymer melting temperatures followed a similar dependence on methylene spacer length. As the aromatic component was diluted with additional, non-polar methylenes,  $T_m$  diminished. Based on the polymeric properties, 2,5-dimethoxyterephthalic acid is an apt, biobased surrogate for terephthalic acid. With its  $T_g$  of 74 °C, polyethylene dimethoxyterephthalate (PEDMT) is a structural and functional analogue of polyethylene terephthalate (PET), which has a  $T_g$  of 72 °C.

Future work will investigate the polymer degradation behavior of these novel polyesters under environmentally relevant conditions. And, these polymers will be subjected to

additional characterization and mechanical testing to better define their capacity to replace PET, or other commercial polymers with even higher temperature applications.

### Conflicts of Interest

There are no conflicts of interest to declare.

### Acknowledgements

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## TOC Text and Graphic:

Biosuccinic acid, obtained via sugar fermentation, is cyclodimerized and oxidized to yield building blocks for aromatic polyesters with high glass transition temperatures.

