Synthesis, characterization, and water-degradation of biorenewable polyesters derived from natural camphoric acid

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COMMUNICATION

Synthesis, characterization, and water-degradation of biorenewable polyesters derived from natural camphoric acid

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Camphoric acid, an inexpensive and biorenewable diacid derived from the terpene (+)-camphor, was copolymerized with a variety of diols to afford polyesters with glass transition temperatures (T_g) ranging from –16 °C to 125 °C. Polyethylene camphorate (PEC, 51 °C), polyerythritan camphorate (100 °C), and polyisosorbide camphorate (125 °C) exhibited T_g values matching or excelling those of important commercial polymers. Agitation of PEC in deionized water for 14 days dramatically degraded the polymer from M_n = 20,200 to M_n < 600. Incremental replacement of terephthalic acid with camphoric acid led to a series of polyethylene (camphorate/terephthalate) analogues with increased biobased content and T_g values (71 to 41 °C) that were diminished, but still competitive with that of polylactic acid (PLA).

Over the last 100 years, the commercial plastics industry has enjoyed fantastic growth via a somewhat small array of fossil fuel monomers. Many polymers have been commercialized and the success of these high volume materials can be attributed to a great balance of low production cost and good thermal and mechanical properties.[1,2] However, their increased production and usage is accompanied by a plethora of negative environmental impacts—notably, low recycling rates and poor environmental degradation behavior.[3,4] Additionally, the fossil fuel resources for these commercial polymers are dwindling.[5,6,7] This depletion of resources and the steady increase in demand for materials herald the need for sustainable polymers.[8,9]

To confront these problems, many researchers have designed and synthesized novel polymers with a variety of functional groups derived from renewable resources.[10,11,12,13,14,15] Polyesters are particularly attractive because they are potentially both renewable and degradable. The ester functionality is prone to water-degradation (hydrolysis) or biodegradation and it has been of great interest during the past few decades.[16,17,18] Polylactic acid (PLA), arguably the most successful, is a fully biorenewable polyester, made from corn starch or other carbohydrates (Figure 1). However, it still suffers from a low glass transition temperature (T_g) of 55 °C and it usually does not degrade apart from industrial composting conditions.[19,20,21] In pursuit of improved biorenewable polyesters, our group has focused on abundantly available biobased monomers such as ferulic acid[22,23,24] or itaconic acid,[25] striving to mimic the thermal properties of extant commercial polymers such as PLA or polyethylene terephthalate (PET, Figure 1).

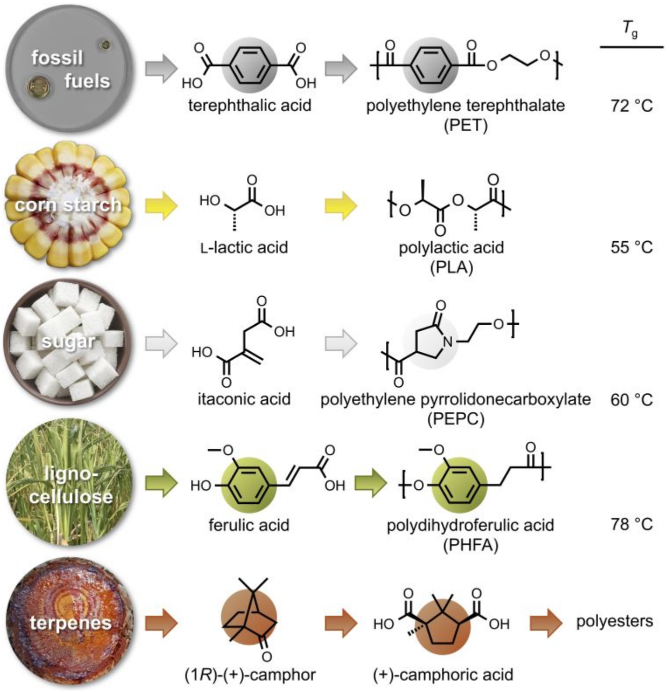

Fig. 1 Polyesters exhibit glass transition temperatures (T_g) rather dependent on structure, with rings generally conferring higher T_g values. A standing challenge is to employ inexpensive biobased feedstocks for the synthesis of high T_g polyesters.

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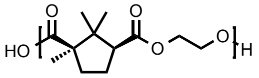
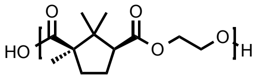
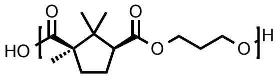
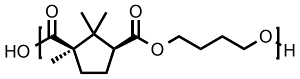
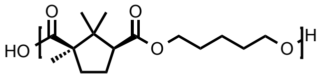
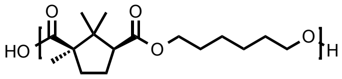
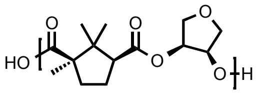
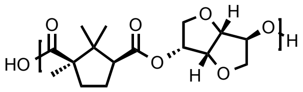
[a] *The George and Josephine Butler Laboratory for Polymer Research, Department of Chemistry, University of Florida Gainesville, Florida 32611-7200, USA. Fax: +1-352-392-9741; Tel: +1-352-392-7773; Email: miller@chem.ufl.edu*

Electronic Supplementary Information (ESI) available: Synthetic details, complete polymer characterization data, and polymer degradation data. See DOI: 10.1039/x0xx00000x

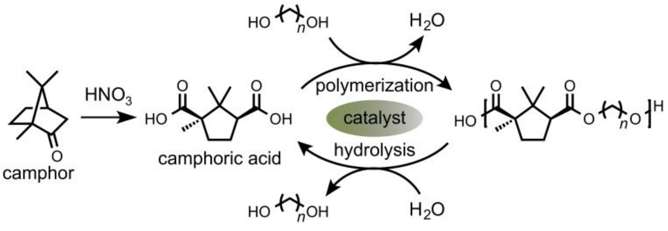
Table 1 Polymerization and characterization of polyalkylene camphorates from linear diols (Entries 1–6) and camphorate polyesters derived from erythritan (Entry 7) and isosorbide (Entry 8)[a]

Entry	Polymer from camphoric acid + diol	Catalyst	Yield (%)	Biobased Content (%) [b]	M_n (Da) [c]	M_w (Da) [c]	$Đ$ [c]	T_g (°C) [d]	T_5 (°C) [e]
1		$Zn(OAc)_2$ + Sb_2O_3	75	73.5	18,700	75,700	4.0	51	331
2		*p*-TSA	84	73.5	20,200	60,800	3.0	44	368
3		*p*-TSA	75	69.2	7,700	22,800	3.0	38	326
4		*p*-TSA	71	65.4	7,300	19,600	2.7	25	322
5		*p*-TSA	73	61.9	8,300	24,500	2.9	–1	352
6		*p*-TSA	96	58.9	8,000	35,800	4.4	–16	353
7		$Zn(OAc)_2$ + Sb_2O_3	73	100	9,000	25,000	2.8	100	304
8		*p*-TSA	98	100	6,900	42,000	6.1	125	355

[a] Polymerization conducted at 180 °C under nitrogen for 16 hours, followed by a temperature ramp over 12 hours to 230 °C under dynamic vacuum. [b] Calculated according to (166.22) / (166.22 + (diol$_{FW}$-2)), where 166.22 represents the atoms contributed by camphoryl and (diol$_{FW}$-2) represents the formula weight of the α,ω-diol minus the removed hydrogen atoms. [c] Gel permeation chromatography (GPC) in hexafluoroisopropanol (HFIP) at 40 °C *vs* polymethylmethacrylate standards. [d] Determined by DSC. [e] Temperature at which 5% mass loss was observed, determined by thermogravimetric analysis (TGA).

Another biobased monomer that has captured our interest is camphoric acid (Figure 1). Oxidation of the bicyclic terpene (1*R*)-(+)-camphor affords (1*R*,3*S*)-(+)-camphoric acid which, importantly, retains a conformationally rigid five-membered ring. Our previous work has demonstrated the importance of main-chain cyclics[26] or aromatics[22,23] for conferring high T_g values. Natural (+)-camphor itself can be obtained via the distillation of wood from the camphor laurel tree (*cinnamomum camphora*) found in Borneo, Taiwan, and East Africa, but also naturalized in many other parts of the world including North America.[27,28] Among all commercial aroma chemicals, camphor is one of the most widespread, garnering 100+ million US dollars in annual sales. Its commercial popularity led to the common industrial production process (near 17,000 tons per year[29]) via the readily available monoterpene α-pinene, found in the turpentine oil of wood pulp.[30,31,32,33,34] The commodity price of camphor is approximately $3.00 per kg.[35]

In organic synthesis, camphor-derived compounds have been extensively used as chiral templates in enantioselective synthesis, among other specific applications.[36,37,3839,40,] Yet, minimal work has been reported demonstrating the polymerization of camphor-derived monomers.[41,42,43,44,45,46,47,48] Because of its bioavailability and potential for scalability, camphor is an ideal building block for constructing novel polymers. Herein we report polyesters based on camphoric acid, a cyclic diacid readily made from camphor by oxidation with nitric acid (Scheme 1). To our knowledge, there are no reports of polyesters made from this renewable diacid and α,ω-alkanediols or other renewable diols. In this study, camphoric acid was copolymerized with various diols, including the homologous linear alkanediols $HO(CH_2)_nOH$, with n = 2, 3, 4, 5, and 6 to afford polyalkylene camphorate polyesters. Table 1 displays a summary of the polymerization results, including biobased content (%), molecular weight data, and thermal properties of the obtained polymers.



Scheme 1 Natural (+)-camphor is readily oxidized to camphoric acid, which is then subjected to polymerization with a variety of diols to afford linear polyesters. Various species can catalyze polyesterification.

During polymerization, a slight excess (1.2 equivalents) of diol was added to ensure its full incorporation into the initially formed oligomers. After 16 hours at 180 °C under 1 atm of nitrogen, vacuum was applied for 12 hours during a temperature ramp to 230 °C; this protocol was designed to remove water and any excess diol, thus increasing the molecular weight. The Brønsted acid catalyst *p*-toluene sulfonic acid (*p*-TSA, 4 mol%) proved effective for most diols, showing efficacy for both initial esterification and subsequent transesterification. Additionally, a sequential catalyst combination of zinc acetate (2 mol%) and antimony oxide (1 mol%) was investigated (Table 1, Entries 1 and 7). Zinc acetate was first added for the esterification stage at 180 °C under nitrogen, leading to the formation of oligomers. Prior to the temperature ramp and vacuum, antimony oxide was added because it is a known high-temperature (> 200 °C) transesterification catalyst.[49] This dual catalyst technique proved effective for camphoric acid/ethylene glycol (Table 1, Entry 1), but *p*-TSA afforded a marginally greater yield and number-average molecular weight (M_n) (Table 1, Entry 2).

For the linear diols of Table 1 (Entries 1–6), moderate to good molecular weights are obtained, with M_n values ranging from 7,300 to 20,200 Da and M_w values (weight-average molecular weight) ranging from 19,600 to 75,700 Da. Thus, dispersity (*Đ*) values were somewhat high and ranged from 2.7 to 4.4. Polyethylene camphorate (PEC) exhibits the highest molecular weight (Table 1, Entries 1 and 2) probably because ethylene glycol has the lowest boiling point among the linear diols; thus, excess ethylene glycol is most easily removed and the ideal 1:1 diacid:diol stoichiometry is most readily achieved. Longer diols afforded polymers with lower molecular weights (M_n = 7,300–8,300 Da), even with the aforementioned dual catalyst technique (M_n = 2,800–4,600 Da, see the ESI).

Table 1 provides a summary of the thermal properties for these camphoric acid/linear diol polyesters (Entries 1–6) as measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The highest glass transition temperature (T_g) obtained in this series belongs to PEC (from ethylene glycol, Entry 1, 51 °C). This T_g is comparable to that of polylactic acid (T_g of 55 °C)[50,51] and thus, PEC has the potential to mimic PLA. Noticeably, T_g decreases as the alkylene connector length (*n*) increases (see Figure 2). The observed range was 51 °C (*n*=2) to –16 °C (*n*=6). These polymers are apparently not crystalline, since no melting temperatures were detected by DSC. Note that camphoric acid is unsymmetrical and thus, should be incorporated with random regiochemistry into the main-chain. NMR analysis is consistent with a regioirregular structure. Hence, the polymers lack long-range stereochemical or conformational order typically necessary for crystallinity. Finally, Table 1 summarizes the T_5 values for these polyesters, which is the temperature at which 5% mass loss occurs according to TGA under nitrogen. The T_5 decomposition temperatures range from 322 °C to 368 °C.

In order to increase the glass transition temperature of camphoric acid-based polyesters, other biobased, non-linear diols were investigated: erythritan and isosorbide. Erythritan is derived from erythritol by dehydration and thus, is also named *cis*-1,4-anhydroerythritol. Erythritol, in turn, is an inexpensive, naturally-occurring tetraol derived in large scale from glucose, employed mainly as a low calorie sweetener.[52,53] The rigid five membered ring of erythritan (Table 1, Entry 7) boosts the T_g of polyerythritan camphorate (Figure 2) to 100 °C—well above that provided by the comparably sized, 1,2-diol of ethylene glycol (T_g = 51 °C). Isosorbide is another renewable cyclic diol monomer derived from glucose that has already gained considerable attention from polymer chemists, particularly as a potential replacement for bisphenol A in epoxy resins and polycarbonates.[54,55,56] The rigid bicyclic isosorbide (Table 1, Entry 8) confers an even higher T_g value of 125 °C to polyisosorbide camphorate (Figure 2), the highest of Table 1. These glass transition temperatures compare favorably with those of polystyrene (PS, T_g = 95 °C) and atactic polymethylmethacrylate (PMMA, T_g = 105 °C). Although erythritan and isosorbide posses more sterically encumbered secondary alcohols, the obtained yields and molecular weights were similar to those of the long linear diols of Table 1.

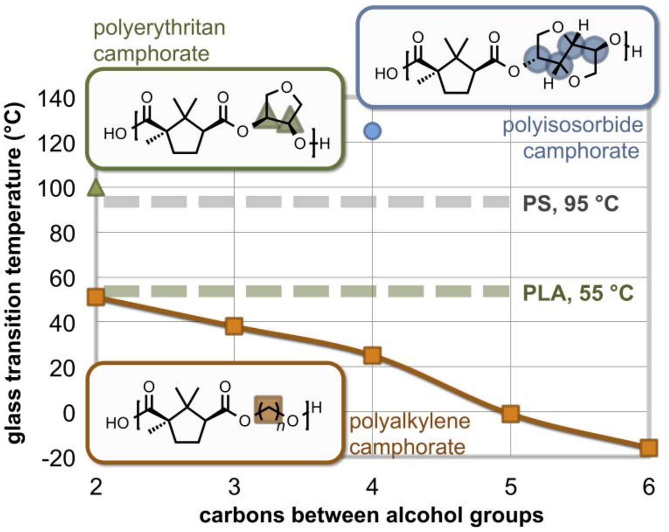
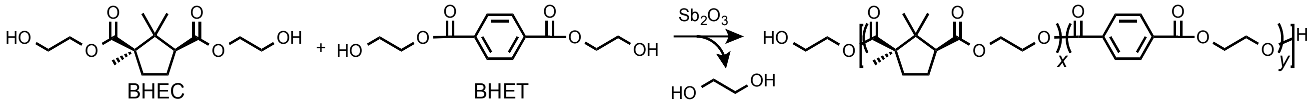


Fig. 2 Camphorate polyester glass transition temperature versus the number of carbons between the alcohol groups of the constituent diol.

Molecular weight and dispersity parameters of diacid/diol copolymerizations are sensitive to slight deviations of the ideal 1:1 stoichiometry. This prompted us to pursue a corrective strategy applied to PET production, wherein terephthalic acid is first converted to bis(hydroxyethyl) terephthalate (BHET).[57] Accordingly, bis(hydroxyethyl) camphorate (BHEC) was synthesized through Fischer esterification of camphoric acid with an excess of ethylene glycol under acidic conditions. Subsequent to isolation, this monomer was polymerized using catalytic antimony oxide (Sb_2O_3, 1 mol%) under high vacuum, thereby removing ethylene glycol as the small molecule by-product of transesterification. The procedure afforded relatively high molecular weight polyethylene camphorate (PEC) with M_n = 23,800, an almost ideal dispersity of 2.3, and a T_g value of 41 °C (Table 2, Entry 1).

Ongoing efforts to increase the biobased content of PET are vigorous, but currently remain at 30% since only biobased ethylene glycol is economical; biobased terephthalic acid is an important goal,[58] but its scalable production remains elusive.[59] Hence, we have targeted camphoric acid, a fully biobased diacid, as a potential mimic of fossil fuel-based terephthalic acid for incorporation into the PET structure to augment its biobased content. Ergo, we incrementally replaced the

Table 2 Copolymerization of bis(hydroxyethyl) camphorate (BHEC, from camphoric acid) and bis(hydroxyethyl) terephthalate (BHET, from terephthalic acid) [a]



Entry	BHEC % Feed	BHEC % Incorporation [b]	Biobased Content (%) [c]	Yield (%)	M_n (Da) [d]	M_w (Da) [d]	$Đ$ [d]	T_g (°C) [e]	T_m (°C) [e]	T_5 (°C) [f]
1	100	100.0	73.5	84	23,800	54,400	2.3	41	n.o.	343
2	90	82.9	62.5	64	13,300	34,100	2.6	42	n.o.	335
3	80	65.8	51.0	74	14,600	42,700	2.9	50	n.o.	344
4	70	52.7	41.7	86	17,300	56,600	3.3	46	n.o.	344
5	60	34.0	27.7	83	19,500	54,600	2.8	52	n.o.	342
6	50	31.6	25.9	95	21,300	59,200	2.7	54	n.o.	345
7	40	22.2	18.5	90	14,800	38,300	2.6	54	n.o.	351
8	30	19.8	16.5	97	13,700	33,100	2.4	59	180	352
9	20	12.3	10.4	99	16,800	42,200	2.5	64	193	348
10	10	7.6	6.5	99	22,300	55,900	2.5	66	209	361
11	0	0.0	0.0	99	19,800	55,100	2.8	71	229	371

[a] Polymerization conducted from 190 to 230 °C under dynamic vacuum with antimony oxide as a catalyst (Sb_2O_3, 1–2 mol%). [b] BHEC and BHET % incorporation determined by ^{1}H NMR by integrating the 1-methyl group of the camphoric acid ring (0.77 ppm) versus the aromatic protons (near 8.1 ppm). [c] Calculated according to (166.22 x BHEC %) / [(226.27 x BHEC %) + (192.17 x BHET %)], where the numerical values represent the atoms contributed by camphoryl, oxyethyl camphoryl, and oxyethyl terephthaloyl, respectively. [d] Gel Permeation Chromatography (GPC) in hexafluoroisopropanol (HFIP) at 40 °C *vs* polymethylmethacrylate standards. [e] Determined by DSC; n.o. = not observed. [f] Temperature at which 5% mass loss was observed under nitrogen, determined by TGA.

terephthalic acid of PET with camphoric acid via the copolymerization strategy described in Table 2.

Bis(hydroxyethyl) camphorate (BHEC) and bis(hydroxyethyl) terephthalate (BHET) were copolymerized with varying feed fractions via transesterification with antimony oxide (1 mol%). The BHEC incorporation fraction is consistently lower than its feed fraction, validating theconclusion that BHEC is harder to polymerize than BHET. A reactivity ratio analysis (Figure 3; see also the ESI) revealed that r_{BHEC} = 0.47 and r_{BHET} = 2.26 (RMS error = 2.67). A reasonable explanation for this is that steric encumbrance hinders the reactivity of BHEC, compared to BHET. This comports with reported small molecule esterification rates, which decrease with increasing steric encumbrance (quantified by a van der Waals radii parameter, ν) from benzoic acid (aryl; ν = 0.57) to isobutyric acid (2°; ν = 0.76) to pivalic acid (3°; ν = 1.24).[60]

Suitably high molecular weight copolymers were obtained (Table 2), with M_n ranging between 13,300 and 23,800 Da and an average of about 17,900 Da. All but one of the dispersity values were found between 2.3 and 2.9. Copolymer T_g values ranged between 41 and 71 °C, with an observed trend that BHEC lowered the T_g while BHET raised the T_g. Hence, BHEC incorporation increases the biobased content of the copolymer, but also lowers the T_g. Note the biobased content is about 25% (Table 2, Entry 6) when the copolymer has a T_g competitive with that of PLA (54 °C). For this polymer, the biobased content would measure about 55% if the ethylene glycol were biosourced. When the BHET incorporation fraction was 80% or greater, then the materials exhibited crystallinity and a melting temperature in the range of 180 to 229 °C. According to thermogravimetric analysis under nitrogen, the 5% decomposition temperatures (T_5) were high, ranging from 335 to 371 °C.

Polyethylene camphorate (PEC) with M_n = 20,200 Da (Table 1, Entry 2) was subjected to heterogeneous degradation conditions on an orbital shaker at room temperature: aqueous pH = 1, aqueous pH = 2, and deionized water with pH = 7. After 14 days, GPC analysis of all three samples showed only a broad distribution of low molecular weight oligomers and monomers, with M_n < 600 Da (the M_n of the lowest PMMA standard employed). Moreover, the physical appearance of the polymer changed significantly, transforming from an insoluble solid to a swollen gel. This is an important observation for PEC because it starkly contrasts the very slow hydrolysis observed with PLA, even at pH = 1 over 45 days.[61] Although polyglycolic acid is rather susceptible to hydrolytic degradation,[62] more substituted polyesters generally resist hydrolysis. Preliminary computations suggest that

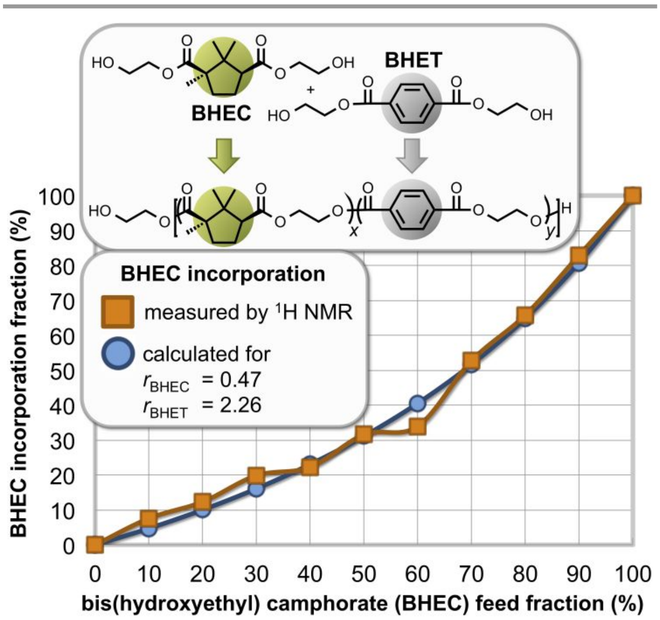


Fig. 3 The BHEC incorporation fraction is consistently lower than its feed fraction, suggesting that BHET is more easily incorporated into the formed polyethylene (camphorate/terephthalate) copolymers.

camphorate esters possess a peculiar conformation with a sterically accessible carbonyl LUMO at the right ester as drawn in Table 1, Entry 2 (the less sterically hindered ester). Continuing studies will investigate the origins of this apparent sensitivity to hydrolysis (Scheme 1), along with characterization of the degradation products.

Conclusions

Novel polyesters were synthesized from biorenewable (+)-camphoric acid, derived from the abundantly available and inexpensive terpene (+)-camphor. As a diacid, camphoric acid was readily polymerized with a homologous series of linear diols or with cyclic diols. The observed glass transition temperature for polyethylene camphorate (PEC, T_g = 51 °C, from ethylene glycol) was comparable to that of polylactic acid (PLA, 55 °C), but the T_g values decreased with increasing diol length. Cyclic diols erythritan and isosorbide, both derived from glucose, markedly increased the T_g to 100 and 125 °C, respectively. These are somewhat rare examples9 of fully biobased polyesters possessing T_g values surpassing that of polystyrene (T_g = 95 °C). The polycondensation between camphoric acid and linear diols was catalyzed effectively with *p*-toluene sulfonic acid and proceeded without solvent, yielding the highest molecular weight for PEC (M_n = 20,200). Camphoric acid was employed as an incremental replacement for the terephthalic acid of polyethylene terephthalate (PET). This copolymer was readily made via the solvent-free polymerization of bis(hydroxyethyl) camphorate (BHEC) with bis(hydroxyethyl) terephthalate (BHET), catalyzed by antimony oxide. Camphorate incorporation increased the biobased content of the resultant polymer, but also diminished the T_g from that of PET itself; the T_g dropped from 71 to 41 °C. Preliminary degradation studies showed the unexpectedly facile degradation of PEC after 14 days of agitation in water at pH 1, 2, or 7. The M_n dropped from 20,200 to < 600 Da in all cases. Future studies will subject PEC and other camphorate polyesters to environmentally relevant conditions and characterize their degradation products. We have demonstrated that (+)-camphoric acid is a versatile monomer for synthesizing biobased polyesters with commercially attractive thermal properties. Assuredly, it will be a useful building block for constructing a variety of polymers with other architectures and functional groups, beyond the polyesters described herein.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgements

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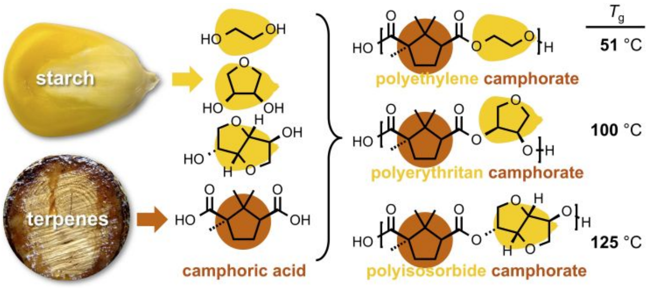

Sugar-derived diols are copolymerized with terpene-derived camphoric acid to yield polyesters with high glass transition temperatures and an unusual susceptibility to hydrolytic degradation.