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COMMUNICATION

Renewable and Water-degradable Polyimide-esters from Citric Acid

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Citric acid is an abundant, naturally occurring small molecule that affords a cyclic imide when condensed with a primary amine. The reaction of a reduced derivative of citric acid and glycine yields a cyclic imide diacid. This monomer was copolymerized with a variety of linear diols and sugar-dervied diols, yielding copolymers with a tunable glass transition temperature ranging from T_g = 25 to 134 °C. Unlike most polyesters, these polyimide-esters hydrolyze under environmentally-relevant conditions and thus, show promise as sustainable replacements for high T_g commodity plastics.

The commercial plastics industry thrived with the introduction of inexpensive petroleum-based products, such as polyethylene terephthalate (PET), polyethylene (PE), polyvinylchloride (PVC), polypropylene (PP), and polystyrene (PS). Their low cost of production and wide range of applications led to market domination, now accounting for greater than 70% of annual plastic production. However, the mismanagement of plastic disposal has resulted in untold negative environmental impacts.[1] Of the 438 billion kg of plastic produced globally in 2017, only 9% was recycled and about 2% entered aquatic ecosystems.[1,2,3] The aforementioned polymers do not hydrolyze under environmental conditions, but they can fracture into microplastics that enter our food supply via fish and, consequently, can be detected in human blood.[4] Such environmental concerns and dwindling fossil fuel resources have prompted a growing demand for sustainable polymers.[5, 6, 7, 8]

Bio-based plastics were first introduced commercially in the late 1980s. During 2021, the quantity of bioplastics produced reached 2.42 million kg, somewhat less than 1% of the plastics market.[9] Bioplastics have failed to gain significant market share because of their costly production and/or substandard thermal and mechanical properties. One such example is polylactic acid (PLA), which is similar in cost to PET, but suffers from a low glass transition temperature (T_g) of 55 °C compared to that of PET, 72 °C.[9,10,11,12] Moreover, the term bioplastics is often confusing since a polymer can be bio-based, but not biodegradable. An example is bio-polyethylene, which derives from sugarcane, but persists in the environment like fossil fuel-based polyethylene.[13] To confront these issues, researchers have targeted polymers that are both bio-based and biodegradable.[14,15,16]

Polyesters are particularly attractive since the ester group can be susceptible to hydrolysis and there is a plethora of biorenewable acids and alcohols available for polyester formation.[17,18] Unfortunately, many of these bio-available monomers possess an abundance of methylene groups, which generally confer low T_g values.[19] Our research group has investigated multiple biorenewable polyesters derived from biomass sources including: camphoric acid, coumaric acid, ferulic acid, itaconic acid, succinic acid, vanillin, isosorbide, and erythritan.[20,21,22,23] Our strategy to incorporate rings into the polymer main-chain generally increased the T_g values compared to similar polymers lacking rings. Here, we extend this strategy to another abundant bio-renewable small molecule, citric acid.

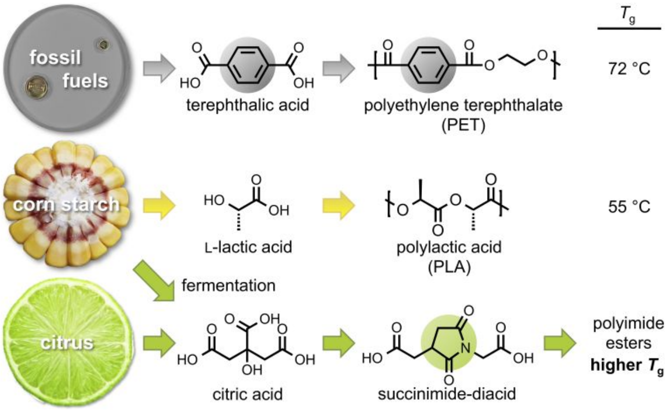

Figure 1. The T_g of fossil fuel-based polyethylene terephthalate (PET) exceeds that of bio-based polylactic acid (PLA). Our goal is to employ citric acid-based monomers to increase the bio-based content, the glass transition temperature, and the degradability of the polymer.

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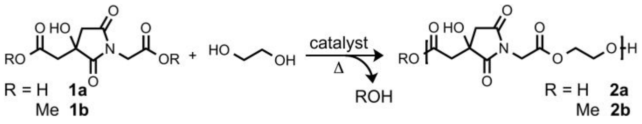
Electronic Supplementary Information (ESI) available: Synthetic details, complete polymer characterization data, and polymer degradation data. See DOI: 10.1039/x0xx00000x

Table 1. Synthesis and characterization of polyimide-esters derived from citric acid.[a]



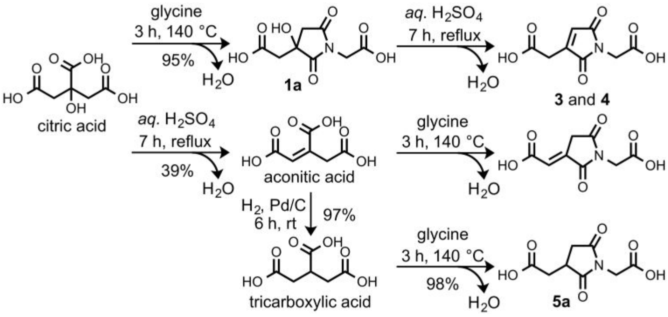
Entry	R	$T_{\text{p-max}}$ (°C)[b]	Solvent	Catalyst[c]	T_g (°C)[d]	M_n (Da)[e]
1	H	240	none	Sb_2O_3	–	–
2	H	220	none	Sb_2O_3	–	–
3	H	200	none	Sb_2O_3	97	–
4	H	180	xylene	–	70	1,900
5	H	180	xylene	*p*-TSA	83	–
6	H	180	xylene	Sb_2O_3	100	–
7	Me	200	none	Sb_2O_3	78	–

[a] See the ESI for complete reaction conditions. [b] The maximum polymerization temperature at the final stage. [c] All catalyst loadings were 2 mol%. [d] Determined by DSC. [e] M_n obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards.

Efficient sugar fermentation routes to citric acid have lowered its cost ($0.7/kg) and expanded its range of applications to chelating agents, pharmaceuticals, and beauty products.[24, 25] While useful as a small molecule, the tri-acid nature of citric acid relegates its use in polymers to crosslinking agents.[26, 27] An approach to transform this biorenewable molecule into a useful monomer is by cyclization. The cyclization of citric acid with primary amines is relatively unexplored. A few examples of the resulting cyclic imides can be found in the literature, but all are used as a minor component in biorenewable polyester resins having minimal or no characterization.[28,29,30,31,32] Herein, we describe a green synthetic route from citric acid to succinimide-based diacids and their corresponding degradable polyimide-esters.

One aim of this study was to optimize the synthesis of the succinimide-diacid (**1a**) from citric acid and glycine (Scheme 1). We began with the literature procedure for the synthesis of **1a**.[28] Stoichiometric equivalents of citric acid and glycine were combinded with xylene and heated to 150 °C for 4 hours. This procedure gave multiple products that were difficult to separate or purify. Product was collected in 72% yield only after several work-up steps, including the distillation of xylene. To synthesize **1a** through a greener procedure, citric acid and glycine were heated to 140 °C for 3 hours—without solvent—affording the product in 95% yield. Succinimide-dimethyl ester **1b** (Table 1) was synthesized via Fischer esterification with methanol and catalytic hydrochloric acid.

Initial polymerizations were conducted under nitrogen and then dynamic vacuum from 180 °C to 240 °C with a catalyst loading of 2 mol% antimony oxide (Sb_2O_3) (Table 1, Entry 1). By 220 °C, the reactions increased in viscosity, a telltale sign that polymer has formed; however, the product appeared dark. To decrease polymer charring, the final reaction temperature was reduced from 240 °C to 220 °C or 200 °C (Table 1, Entries 2–3). The resulting products were brown and glassy. No molecular weights were determined for these polymers since they were insoluble in any the following gel permeation chromatography (GPC) solvents: tetrahydrofuran (THF), hexafluoroisopropanol (HFIP), or dimethylacetamide (DMAc). Solutions were left for two weeks and checked daily; however, the polymers did not swell or dissolve. The combination of various solvents with trifluoroacetic acid also proved ineffective to solubilize the polymers.



Scheme 1. Conversion of citric acid and reduced citric acid (tricarboxylic acid) to cyclic imide-based diacid monomers.

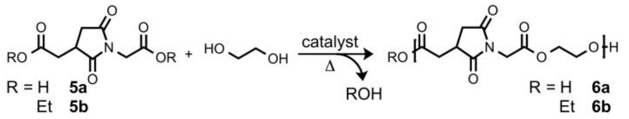
The polymer from Table 1 Entry 3 exhibited a T_g of 97 °C, but it was somewhat charred and brittle. To further remedy charring, the reaction temperature of the polymerization was reduced to 180 °C, xylene was added to improve mixing, and catalyst was varied. Since Sb_2O_3 has a high activation temperature over 200 °C,[33] *p*-toluenesulfonic acid (*p*TSA) was employed. The absence of catalyst led to oligomer formation as determined by GPC. Number average molecular weight (M_n) and nuclear magnetic resonance (NMR) were not possible with the other two polymers (Table 1, Entries 5–6) because of insolubility. It is highly possible that the products were crosslinked polymers. **1a** is a trifunctional monomer with two carboxylic acids and a tertiary alcohol. While tertiary alcohol esterification is sluggish, owing to steric hindrance, the extreme reaction conditions could create tertiary esters and few would be needed to form crosslinks that noticeably affect solubility.[34,35] ^1H NMR analysis of **1a**, following a thermal stability test at 180 °C (Figures S144 and S145), showed the evolution of alkene peaks resulting from the elimination of water. As good Michael acceptors, such α,β-unsaturated esters could lead to crosslinking of the polymer mainchain.[36]

To avoid these problematic crosslinking reactions, standard dehydration conditions (Scheme 1, *aq.* H_2SO_4) were applied to monomer **1a**. After workup, the supernatant was analyzed by ^1H NMR, which indicated a mixture of products (**3** and **4**) with unidentified side products. A second dehydration trial began with citric acid to form aconitic acid.[37] Imidation of aconitic acid was then attempted with glycine. ^1H NMR revealed many side products, apparently since aconitic acid is a good Michael acceptor for inadvertent reactions. The next approach reduced aconitic acid (H_2, Pd/C) to yield propane-1,2,3-tricarboxylic acid, which was then reacted with glycine to generate the succinimide-diacid **5a**, a reduced version of **1a** (Scheme 1). Computational results at the B3LYP/6-311++G** level of theory (Spartan) suggest formation of the 5-membered ring vs. the 6-membered ring is favored by 3.8 kcal/mol (Figures S1 and S2).

^1H NMR analysis confirmed that the 5-membered ring is the sole product. We then pursued **5a** as a diacid for polycondensations.

For AA/BB type copolymerizations at high temperatures, loss of the more volatile monomer prevents the optimal 1:1 stoichiometric ratio necessary for high molecular weight formation. Therefore, our copolymerizations were optimized utilizing **5a** and a slight excess of ethylene glycol with 2 mol% zinc acetate ($Zn(OAc)_2$) as the catalyst. Polymerizations with increasing ethylene glycol equivalents—from 1.0 to 1.3—revealed a broadening of the polymer dispersity with similar T_g values (Table 2, Entries 1–4). With 1.5 or 2.0 equivalents, polymer insolubility prevented acquisition of molecular weight data (Table 2, Entries 5–6). One explanation is that succinimide ring-opening occurs with excess ethylene glycol and the polymers can, thereby, become crosslinked. Although 1.1 and 1.3 equivalents of ethylene glycol afforded the highest measured molecular weights, 1.1 equivalents of ethylene glycol was selected as the optimal amount because of better polymerization control ($Đ$ = 3.5 vs. 4.9).

Table 2. Polymerization results as a function of succinimide-diacid (**5a**; R=H) and ethylene glycol stoichiometry.[a]



Entry	R	Monomer ratio (diacid : EG)	T_g (°C)[b]	M_n (Da)[c]	$Đ$ [c]
1	H	1.0 : 1.0	76	9,300	3.0
2	H	1.0 : 1.05	75	9,900	3.3
3	H	1.0 : 1.1	74	10,600	3.5
4	H	1.0 : 1.3	73	10,600	4.9
5	H	1.0 : 1.5	77	–	–
6	H	1.0 : 2.0	78	–	–

[a] 180–200 °C under nitrogen for 20 hours, followed by a temperature ramp over 12 hours to 220 °C with dynamic vacuum. $Zn(OAc)_2$ catalyst loading was 2 mol%. [b] Determined by DSC. [c] M_n and $Đ$ obtained by GPC in HFIP at 40 °C versus PMMA standards.

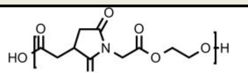
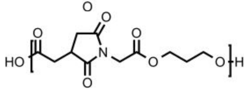
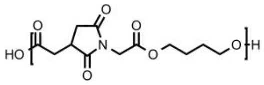
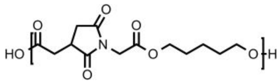
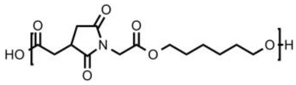
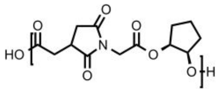
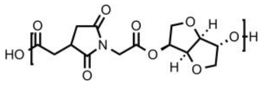
Table 3. Polymerization results as a function of catalyst and polymerization temperature for succinimide-diacid (**5a**; R=H) or succinimide-diethylester (**5b**; R=Et) with ethylene glycol.[a]

Entry	R	catalyst [b]	T_g (°C)[c]	M_n (Da)[d]	$Đ$ [d]
1	H	$Zn(OAc)_2$	74	10,600	3.5
2	H	Sb_2O_3	77	6,100	2.9
3	H	$Sn(Oct)_2$	75	8,900	12.1
4	H	*p*-TSA	70	8,200	2.8
5	H	H_2SO_4	71	11,000	7.7
6	H	Na_2HPO_4	77	5,300	3.7
7	H	K_2CO_3	78	–	–
8	H	$Sb_2O_3/Zn(OAc)_2$	77	7,100	3.3
9	H	none	73	7,700	3.1
10[e]	H	$Zn(OAc)_2$	73	6,100	3.2
11[f]	H	$Zn(OAc)_2$	68	4,400	2.8
12[g]	H	$Zn(OAc)_2$	76	10,600	5.1
13[g]	H	Sb_2O_3	80	4,800	2.5
14[hi]	H	$Zn(OAc)_2$	76	10,400	3.9
15[hj]	H	$Zn(OAc)_2$	75	9,500	3.5
16[hk]	H	$Zn(OAc)_2$	74	7,900	2.8
17	Et	$Zn(OAc)_2$	67	6,200	4.3
18	Et	Sb_2O_3	63	7,500	3.8
19	Et	none	21	1,000	2.5

[a] 180–200 °C under nitrogen for 20 hours, followed by a temperature ramp over 12 hours to 220 °C with dynamic vacuum. Monomer ratio (diacid:EG) was 1.0 : 1.1. [b] Catalyst loading was 2 mol%. [c] Determined by DSC. [d] M_n and $Đ$ obtained by GPC in HFIP at 40 °C versus PMMA standards. [e] Catalyst loading was 1 mol%. [f] Catalyst loading was 0.2 mol%. [g] 180–200 °C under nitrogen for 20 hours, followed by a temperature ramp over 12 hours to 240 °C with dynamic vacuum. [h] Succinimide-diacid was purified by crystallization. [i] Monomer ratio was 1.0 : 1.0. [j] Monomer ratio was 1.00 : 1.05. [k] Monomer ratio was 1.0 : 1.1.

5a was then subjected to a solvent-free, two-stage melt-polymerization screening with a variety of catalysts. The first stage (oligomerization) occurred under nitrogen from 180 to 200 °C and thus, minimized loss of monomer to volatilization. Under these conditions, the bishydroxyethylester of **5a** was presumably created *en route* to oligomers. In the second stage (polycondensation), dynamic vacuum was engaged and the temperature was increased to 220 °C to remove evolved water and excess ethylene glycol. Seven different catalysts were tested for polymerization (Table 3) including Lewis acids (Entries 1–3), Brønsted acids (Entries 4–5), Brønsted bases (Entries 6–7), a dual catalyst system (Entry 8), and no catalyst (Entry 9). The resulting polymers had comparable T_g values and thermal stabilities according to thermogravimetric analysis (TGA; see Table S3). The Brønsted bases resulted in the lowest molecular weight polymers or insoluble polymers (Table 3, Entry 7), according to GPC analysis. The polymerization without catalyst reached a molecular weight of 7,700 Da, but afforded the lowest yield. Lewis acid and Brønsted acid catalyzed polymerizations gave similar yields and T_g values. Optimal results were obtained utilizing the Lewis acid $Zn(OAc)_2$ (Entry 1) with 88% yield, M_n = 10,600 Da, and $Đ$ = 3.5. For a $Zn(OAc)_2$ catalyst loading ranging from 0.2 to 2 mol% (Entries 1, 10, and 11), the optimal value appears to be 2 mol% (Entry 1). The lower catalyst loadings resulted in lower molecular weights (Entries 10–11). Higher polymerization temperatures (240 °C) gave lower molecular weights or higher polymer dispersities (Entries 12–13). Crystallization purification of monomer **5a** yielded similar results (Entries 14–16); therefore, **5a** was normally used without this additional purification step. For polyesterifications, transesterfication is often more effective than direct esterification. Thus, **5a** was converted to its diethyl ester **5b** but its polymerization with ethylene glycol using either $Zn(OAc)_2$ (Entry 17), Sb_2O_3 (Entry 18), or no catalyst (Entry 19) did not provide higher molecular weights or higher T_g values compared to the direct esterification of **5a**. One explanation is that the diacid monomer **5a** also functions as the esterification catalyst,[38,39] as evidenced by the decent yield (73%), M_n (7,700 Da), and T_g (73 °C) obtained for the catalyst-free reaction (Entry 9) versus the very low yield (8%), M_n (1,000 Da), and T_g (21 °C) for the catalyst-free reaction that employed the diethyl ester monomer **5b** (Entry 19).

Table 4. Polymerization and characterization of polyimide-esters from diacid **5a** and linear diols (Entries 1–5), erythritan (Entry 6), or isosorbide (Entry 7).

Entry	Polymer	Monomer ratio (diacid : diol)	Catalyst[d]	Yield (%)	M_n (Da)[e]	M_w (Da)[e]	$Đ$[e]	T_g (°C)[f]	T_{d5} (°C)[g]
1[a]		1.0 : 1.1	$Zn(OAc)_2$	88	10,600	37,400	3.5	74	374
2[a]		1.0 : 1.0	$Zn(OAc)_2$	84	6,400	19,800	3.1	54	369
3[a]		1.0 : 1.0	Sb_2O_3	89	6,100	22,800	3.7	37	362
4[a]		1.0 : 1.0	Sb_2O_3	87	6,500	23,200	3.6	31	366
5[a]		1.0 : 1.0	Sb_2O_3	85	8,600	28,000	3.2	25	369
6[b]		1.0 : 1.0	Sb_2O_3	72	5,700	24,000	4.2	112	365
7[c]		1.0 : 1.0	Sb_2O_3	88	5,900	23,800	4.0	134	377

[a] 180–200 °C under nitrogen for 20 hours, followed by a temperature ramp over 12 hours to 220 °C with dynamic vacuum. [b] 180–200 °C under nitrogen for 20 hours, followed by a temperature ramp over 4 hours to 240 °C with dynamic vacuum. [c] 180–240 °C under nitrogen for 20 hours, followed by a temperature ramp over 2 hours to 255 °C with dynamic vacuum. [d] Catalyst loading was 2 mol%. [e] Obtained by GPC in HFIP at 40 °C versus PMMA standards. [f] Determined by DSC. [g] Temperature reported upon 5% mass loss by thermogravimetric analysis (TGA) under nitrogen.

After optimizing the polymerization of diacid **5a** with ethylene glycol, we investigated a wider range of diols. Excess diol was unnecessary for longer diols because their higher boiling points minimized volatilization. As recorded in Table 4, the polymer yields ranged from 72 to 89%, with M_n values from 5,700 to 10,600 Da. For step-growth condensation polymerizations, it is well-known that high melt viscosities limit conversion and thus, molecular weight growth, as given by the Carothers equation. Still molecular weights near or above 10,000 Da can be achieved. Catalyst screening indicated that Sb_2O_3 was preferred over $Zn(OAc)_2$ for the longer diols and rigid diols, as measured by higher molecular weights and narrower polymer dispersities (Table S4). Despite many polymerizations, the molecular weights did not compare favorably to literature polyesterification reactions, such as those yielding polybutylene succinate (80,000 Da)[40] or polyethylene camphorate (20,200 Da).[20] It is possible that the Lewis acid catalysts are somewhat deactivated by the imide functional groups, which are more basic than ester functional groups.[41,42] This polymer series showed great thermal stability with T_{d5} (the temperature at which 5% of the polymer mass is lost according to TGA) values exceeding 360 °C in all cases—with no discernable dependence on the diol chain length. As expected, the T_g values were inversely proportional to the number of methylene groups provided by the linear diol. For $n = 2$, $T_g = 74$ °C; for $n = 3 – 5$, $T_g = 54 – 31$ °C; and for $n = 6$, $T_g = 25$ °C (Table 4, Entries 1–5). Besides the linear diols, two sugar-derived diols, erythritan and isosorbide, were copolymerized with **5a**. For **5a**/isosorbide, the polycondensation temperature was elevated to 255 °C to overcome the high melt viscosity of this polymerization. With these sugar-derived diols, the T_g values were significantly boosted to 112 °C (Table 4, Entry 6) and 134 °C (Table 4, Entry 7), owing to diminished conformational flexibility of the formed polyimide-esters. The corresponding molecular weights were expected to be lower than those from the primary/primary linear diols because of the additional steric congestion imposed by erythritan and isosorbide, which are secondary/secondary diols. According to DSC, none of the polymers was crystalline since no melting temperatures were observed. Because the monomer **5a** is both unsymmetrical and racemic, the polyimide-esters are both regioirregular and atactic, resulting in disorganized chain-chain interactions and no crystallite formation.

Since some aliphatic polyesters are known to hydrolyze, heterogeneous hydrolysis studies were conducted on polymer **6a** (Table 2, Entry 3). Small samples (5 mg) of **6a** were placed in aqueous buffers with pH = 2 or 5, as well as deionized (DI) water or seawater and subjected to orbital shaking at room temperature. After six months, all polymers lost most of their brownish color. After twelve months, all polymers showed a meaningful loss of molecular weight by GPC analysis, with a 31–54% decrease of M_n from 10,600 to 7,300–4,900 Da. Interestingly, the degradation behavior was similar for the acidic buffers and seawater, while the DI water hydrolysis was somewhat slower, as illustrated in Figure 2. For comparison, polymer **6a** exhibited an insignificant decrease of molecular weight, from M_n = 10,600 to 10,200 Da, when stored under ambient conditions over 25 months—indicating that meaningful hydrolysis requires contact with *liquid* water.

An accelerated hydrolysis study explored the degradation of polyimide-ester **6a** at 60 °C in deionized water. Samples swelled in 24 hours and fully dissolved after 2 months. This suggested hydrolysis to small oligomers and/or monomers since these are soluble in hot water, but the polymer **6a** is insoluble in hot water. According to GPC, the M_n decreased dramatically from

10,600 to ~150 Da, indicating full hydrolysis to the monomers (Table S6), which have molecular weights of 215 (**5a**) and 62 (ethylene glycol). ^{1}H NMR analysis after 2 months clearly showed monomers **5a** and ethylene glycol. The elevated temperature results are encouraging, as they suggest that the polyimide-ester **6a** could completely hydrolyze within a decade in various natural environments.[43]

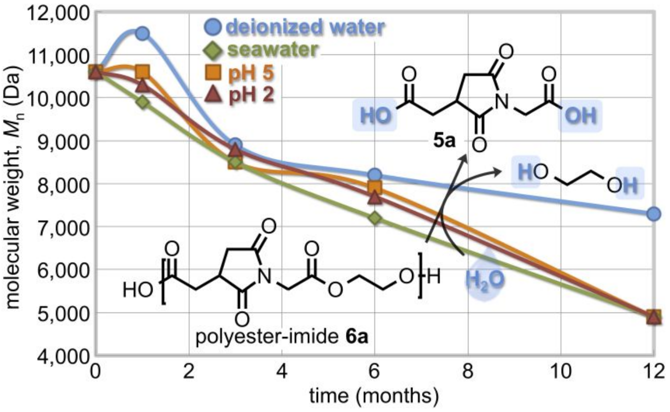


Figure 2. The polyimide-ester **6a** with initial M_n = 10,600 Da hydrolyzes at room temperature in various aqueous media: deionized water, seawater, pH 5, and pH 2. All conditions effected appreciable ester hydrolysis over 12 months, decreasing the M_n by 31–54%.

Conclusions

Citric acid was converted into the succinimide-diacid **1a** with glycine through a green procedure and was polymerized with ethylene glycol. Despite several polymerization optimizations, the polymers were insoluble in GPC and NMR solvents. The intractability is blamed on crosslinking via the tertiary alcohol or side reactions of alkenes generated upon dehydration at high temperatures. This monomer was redesigned to lack the tertiary alcohol, resulting in a new succinimide-diacid **5a**, obtained efficiently through dehydration and reduction of citric acid, followed by imidation with glycine. Condensation polymerization of **5a** with linear diols of different carbon chain lengths yielded polyimide-esters with tunable T_g values from 25 to 74 °C. To achieve higher T_g values, two structurally rigid and sugar-derived diols, erythritan and isosorbide, were polymerized with **5a**, yielding T_g values of 112 and 134 °C—greatly expanding the potential applications of these polyimide-esters. Ambient temperature heterogeneous hydrolysis studies of the polyimide-ester **6a** (made from **5a** and ethylene glycol) showed a 31–54% loss of molecular weight in pH = 2 and 5 aqueous media, deionized water, and seawater over 12 months. In deionized water at elevated temperature (60 °C), the polymer was completely hydrolyzed to monomers within 2 months. These studies suggest that novel and water-degradable polyimide-esters are potential sustainable candidates for replacing PET or other commodity polymers used in various dry packaging or fiber applications.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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