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DOI: 10.1039/c6gc01081d www.rsc.org/greenchem Synthesis of biorenewable and water-degradable polylactam esters from itaconic acid†

Pengxu Qi, a Hsiao-Li Chen, a Ha Thi Hoang Nguyen, Chu-Chieh Lin and Stephen A. Miller* $\rm ^{a}$

Itaconic acid, a naturally occurring compound mass-produced via fermentation of glucose, was reacted with ethanolamine or ethylene diamine to afford hydroxy-acid or diacid monomers containing the 2-pyrrolidone lactam. Homopolymerization or copolymerization with diols, respectively, yielded polylactam esters with higher glass transition temperatures and faster hydrolytic degradation compared to the commercial polyester polylactic acid (PLA).

As the commercial plastics industry was born and thrived in the last century, a great portion of finite resources was dedicated to polymer production. A handful of commercial polymers—poly(ethylene terephthalate) (PET), polyethylene (PE), polyvinylchloride (PVC), polypropylene (PP), polystyrene (PS), and polycarbonate (PC)—have dominated the plastics market for many decades because of their low cost and unique thermal and mechanical properties.¹ However, the overutilization of these materials has revealed dire environmental issues. The depletion of fossil fuel resources, along with persistence in the environment—especially the oceans—have stimulated academic and industrial research programs that seek degradable polymers derived from biorenewable resources.^{2–4} Such alternatives to incumbent polymers could appreciably improve the sustainability of the short-term packaging industry.⁵

Among a wide variety of linear polymers, polyesters have great potential because (1) structural diversity allows tailoring of their properties, (2) the main-chain ester functionality is an obvious point of water-degradation or bio-degradation, and (3) many are accessible from natural building blocks.⁶⁻⁹ Thus, considerable research has focused on partially or completely biobased polyesters.^{4,10-12} The fastest growing, partially biorenewable polyester is 30% biobased PET (PlantBottle®), which is derived from bio-ethylene glycol and petrochemical terephthalic acid.¹³ Perhaps the most successful, fully biorenewable polyester is polylactic acid (PLA), made from corn starch or other carbohydrates.¹⁴ While PLA is 100% biobased, its useful temperature range is limited by its low glass transition temperature (T_g) of 50 °C¹⁵ and it composts very poorly in the environment,¹⁶ thus requiring *industrial* composting conditions.¹⁷ PET exhibits a notably higher T_g of 67 °C,¹⁸ making it suitable for a wider range of applications. The superior thermal properties seem to originate with the aromatic/aliphatic motif present in the polymer backbone (Fig. 1). Recreating this hard/soft motif with bioaromatics from lignin (vanillin) or lignocellulose (ferulic acid, coumaric acid), our research group¹⁹⁻²² has reported several new biogenic polyesters and copolyesters with T_{g} values ranging from 78 °C to 153 °C,²² surpassing the important benchmark of 100 °C for polystyrene (PS).23

In our continued pursuit of high T_g thermoplastics, we reasoned that certain biobased heterocycles might replace our



Fig. 1 The glass transition temperature (T_g) of polylactic acid (PLA) can be excelled by incorporating aromatic (PET), bioaromatic (PHFA), or bio-heterocyclic (PEPC) motifs into the polyester main-chain.

^aThe George and Josephine Butler Laboratory for Polymer Research, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA. E-mail: miller@chem.ufl.edu; Fax: +1-352-392-9741; Tel: +1-352-392-7773

^bDepartment of Chemistry, National Chung Hsing University, Taichung City, 402,

Taiwan. E-mail: cchlin@dragon.nchu.edu.tw; Tel: +886-0422-840411

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chosen bioaromatics and confer the polymer chain rigidity and/or chain-chain interactions that are essential for high glass transition temperature materials.²⁴ Herein, we have focused on the 2-pyrrolidone ring system to function as the hard component of a repeating hard/soft motif. This lactam was selected for several reasons. It can be prepared by reaction of a primary amine with the inexpensive and naturally-occurring molecule, itaconic acid (IA). The α , β -unsaturated carbonyl functional group of IA reacts efficiently with a variety of primary amine nucleophiles in environmentally acceptable solvents with simple workup procedures.²⁵⁻²⁸ The five-carbon diacid IA has been promulgated as one of the top twelve renewable chemicals available from biomass by the U.S. Department of Energy National Renewable Energy Laboratory because of its scalability, sustainability, and nontoxicity.²⁹ It is presently mass-produced by glucose fermentation with Aspergillus terreus.³⁰ This biosynthetic method yields 40 to 80 million kg per year³¹ with a cost near \$1.5 USD per kg.³² Previous polymerization research with IA has generally followed two approaches:³³ polycondensation of itaconic acid with diols to yield polyesters;³⁴⁻³⁷ and radical homopolymerization or copolymerization of dialkyl itaconate with other unsaturated monomers to prepare acrylic polymers.³⁸⁻⁴¹ While polyamides from itaconic acid containing the pyrrolidone ring system have been reported,⁴² it appears that polyesters containing this lactam are novel. We predicted that such polylactam esters might be more degradable than the reported polylactam amides because of the greater hydrolytic sensitivity of esters versus amides, generally.43

Polyethylene 2-pyrrolidone-4-carboxylate (PEPC, Fig. 1) was selected as the paradigm polylactam ester because of its structural similarity to PET and polydihydroferulic acid (PHFA).¹⁹ For these three polymers, each repeat unit contains a rigid ring, two main-chain sp³ hybridized carbons, and ester connectivity (Fig. 1). Scheme 1 describes the aza-Michael addition of ethanolamine to itaconic acid (IA), affording an intermediate amino diacid. Intramolecular cyclization generates water and the γ -lactam ring, which is part of the targeted monomer *N*-(2-hydroxyethyl)-2-pyrrolidone-4-carboxylic acid (HEPC), formed as the racemate. Several polar solvents were explored



Scheme 1 The aza-Michael addition of ethanolamine to itaconic acid (green) followed by intramolecular cyclization affords racemic HEPC, a lactam/hydroxy-acid suitable for polymerization to the polylactam ester, PEPC, *via* Fischer esterification.

for this reaction, but water proved to give the highest yield (71% after recrystallization). No catalyst was necessary since ethanolamine was suitably active. Note that ethanolamine can be made in three steps from bioethanol or biosynthetically from serine.⁴⁴

The HEPC monomer was subjected to a solvent-free, twostage melt-polymerization protocol with a variety of catalysts. A pre-polymerization stage under nitrogen at 180 °C commenced oligomerization and thus minimized loss of monomer to evaporation during the second stage, which ramped to 240 °C with dynamic vacuum. Removal of the water byproduct ensured the condensation polyesterification reaction (Scheme 1).

Table 1 shows the polymerization results from a survey of eight different catalysts, including Brønsted acids (entries 1–3), Brønsted bases (entries 4–5), and Lewis acids (entries 6–11). Considering the polymer yield and molecular weight achieved with 1.0 mol% catalyst loading, the Brønsted bases excelled the Brønsted acids. But, the overall winner was Lewis acid Sb₂O₃ (entry 8) with 78% yield, $M_n = 15\,100$, and PDI = 2.7. The optimal loading of this catalyst was 2.0 mol%, which gave 84% yield, $M_n = 20\,800$, and PDI = 2.1 (entry 9). Other reaction conditions were varied, but did not improve the polymerization results. For example, a longer or hotter prepolymerization stage did not increase molecular weights. And higher ultimate polymerization temperatures (>240 °C) generally resulted in lower molecular weights and broader PDI values, possibly a consequence of decomposition.

Scheme 2 describes another strategy for synthesizing polylactam esters. In this case, two equivalents of itaconic acid (IA) are reacted with ethylene diamine in water to afford a monomer bearing two lactam rings, ethylene bis(pyrrolidone carboxylic acid) (EBPC, 78% yield). This diacid monomer was copolymerized with several α , ω -alkanediols, HO(CH₂)_nOH, where n = 2, 3, 4, 5, or 6 to give a homologous series of polyalkylene ethylene bis(pyrrolidone carboxylate) (PAEBPC) polymers. Table 2 summarizes the polymerization results and compares the formed polymers as a function of the number of

Table 1Conditions for polymerizing HEPC to PEPC (see Scheme 1) a

Entry	Catalyst	Catalyst (mol%)	Yield ^b (%)	M_n^b (g mol ⁻¹)	PDI^b
1	p-TSA	1.0	56	9800	3.2
2	Amberlyst® ^c	1.0	42	7200	2.9
3	H_2SO_4	1.0	24	5600	6.4
4	K_2CO_3	1.0	63	11400	3.7
5	Na_2HPO_4	1.0	80	13 800	2.7
6	MgO	1.0	60	10 200	3.4
7	$Sn(Oct)_2$	1.0	81	5200	2.6
8	Sb ₂ O ₃	1.0	78	15 100	2.7
9	Sb_2O_3	2.0	84	20 800	2.1
10	Sb_2O_3	4.0	73	18 200	2.3
11	Sb_2O_3	0.5	67	6000	2.9

^{*a*} 180 °C under nitrogen for 4 hours, followed by a temperature ramp over 8 hours to 240 °C with dynamic vacuum. ^{*b*} GPC in hexafluoroisopropanol (HFIP) at 40 °C *vs.* polymethyl methacrylate standards. ^{*c*} Amberlyst® 15 hydrogen form (dry).



Scheme 2 Two equivalents of itaconic acid (green) react with ethylene diamine to afford the monomer ethylene bis(pyrrolidone carboxylic acid) (EBPC). Polyesterification at 180–240 °C with 2.0 mol% Sb₂O₃ catalyst with alkanediols (n = 2-6) yields polyalkylene ethylene bis(pyrrolidone carboxylate) (PAEBPC) polymers with properties dependent on n.

methylene spacers, n, present in the diol. These polymerizations employed the optimized conditions of Table 1: no solvent and 2.0 mol% Sb₂O₃ catalyst with a temperature ramp from 180 to 240 °C.

Table 2, entry 2 shows the result when the diacid : diol ratio is 1.0 : 1.0. In this case, the yield (63%) and molecular weight $(M_n = 10\ 000)$ are relatively low, and the PDI is somewhat broad (PDI = 4.1). Entry 3 shows that these numbers can be improved (yield = 88%; $M_n = 23\ 200$; PDI = 2.3) when a slight excess of diol is employed. Quite plausibly, the diacid : diol ratio of 1.0 : 1.2 ensures the incorporation of ethylene glycol into the initially formed oligomers, avoiding sub-stoichiometric diol during the vacuum stage, which would lead to low molecular weight polymer. With the capability of Sb₂O₃ to catalyze both direct esterification and transesterification, any excess, volatile diol can be removed during the vacuum stage of the polymerization. The excess diol strategy also worked for the longer diols (n = 3-6) of Table 2, entries 4–7, affording yields from 86 to 91% and good M_n values from 19 500 to 24 900.

Table 2 Molecular weight and thermal data for PEPC (entry 1), PAEBPC polymers made from diols of varying length (entries 2–7), and commercial samples of PLA (entry 8) and PET (entry 9)^a

Entry	Polymers	Monomer ratio (diacid : diol)	Yield (%)	$M_{\rm n}^{\ b}$ (Da)	$M_{\rm w}^{\ b}$ (Da)	PDI^{b}	$T_{\rm g}^{\ c}$ (°C)	$T_{50}^{\ \ d} \left(^{\circ} \mathbf{C}\right)$
1	но Ни Силонн		84	20 800	44 700	2.1	60	387
2	$\overset{HO}{\longrightarrow} \overset{HO}{\longrightarrow} \overset{NO}{\longrightarrow} \overset{NO}{\longrightarrow} \overset{NO}{\longrightarrow} \overset{O}{\longrightarrow} \overset{O}{\longrightarrow}$	1.0:1.0	63	10 000	40 800	4.1	56	359
3	$H_{0} \stackrel{\text{H}}{=} (\overset{\text{H}}{=} (\overset{\text{H}}{\to}) \stackrel{\text{H}}{\to}) \stackrel{\text{H}}{\to} (\overset{\text{H}}{\to}) \stackrel{\text{H}}{\to} (\overset{\text{H}}{\to}) \stackrel{\text{H}}{\to}$	1.0:1.2	88	23 200	52 500	2.3	62	374
4	но Ң См ~ №	1.0:1.1	90	19 500	50 300	2.6	50	368
5	но Ц Силонн	1.0:1.1	88	24 900	59 800	2.4	39	373
6	^{но} Ни Силони и Калании и Ка	1.0:1.05	91	21 200	47 300	2.2	29	373
7	$H_{(1)} \stackrel{\text{Ho}}{\longrightarrow} \stackrel{\text{Ho}}$	1.0:1.05	86	23 400	78 200	3.3	24	376
8	ᡟ᠋᠋ᢦ᠆ᢅᢩᢂ	Commercial samj	ple ^e	91 200	201 800	2.2	52	343
9	ᡟᢩ᠆᠆᠆ᢆ	Commercial samp	ple ^f	34 100	75 500	2.2	83	414

^{*a*} With 2.0 mol% Sb₂O₃, 180 °C under nitrogen for 4 hours, followed by a temperature ramp over 8 hours to 240 °C with dynamic vacuum. ^{*b*} GPC in hexafluoroisopropanol (HFIP) at 40 °C *vs.* polymethyl methacrylate standards. ^{*c*} Determined by DSC. ^{*d*} TGA temperature at which 50% mass loss was observed under nitrogen. ^{*e*} Ingeo® PLA cup sample from NatureWorks, LLC. ^{*f*} Bottle grade PET copolymer from Trader Joe's® Natural Mountain Spring Water.

Table 2 summarizes the polylactam ester thermal properties, as measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The highest glass transition temperatures (T_{g}) of the series belong to PEPC (entry 1, 60 °C) and the PAEBPC from ethylene glycol (entry 3, n = 2, 62 °C). Note that the lower molecular weight of entry 2 negatively impacts its T_{g} value compared to the same polymer of entry 3 (56 vs. 62 °C). For the series of PAEBPC polymers with n = 2 to 6, it is evident that lactam ring dilution by increasing alkylene connector length proportionally decreases the glass transition temperature. The $T_{\rm g}$ ranged from 62 °C (n = 2) to 24 °C (n = 6); so each additional methylene group dropped the $T_{\rm g}$ by about 10 °C. According to DSC, these polymers are not crystalline; no melting temperatures are observed. This is somewhat expected since the polymers are likely atactic with insufficient long-range conformational order. Because lactam ring formation is stereorandom, the HEPC monomer is obtained as the racemate (R/S) and the EBPC monomer is obtained as a nearly equal ratio of diastereomers (55:45, see the ESI[†]). Finally, Table 2 shows the T_{50} values for these polylactam esters, the temperature at which 50% mass loss occurs according to thermogravimetric analysis (TGA) under nitrogen. The T_{50} decomposition temperatures (359–387 °C) excel that of commercial PLA (343 °C, entry 8) and approach that of commercial PET (414 °C, entry 9).

Since all polyesters potentially undergo hydrolysis, a preliminary degradation study was conducted under environmentally relevant conditions of (1) air or (2) neutral water. Six different polylactam esters (Table 2, entries 1 and 3–7) were molded into approximately 5 mm flattened pellets. These were simply exposed to air, or agitated continuously in deionized water with an orbital shaker. Interestingly, all polymers in water began to dissolve and their dissolution was complete after 30 days. After one year, the polymers exposed only to air exhibited just a slight decrease in molecular weight (10% or less) according to Gel Permeation Chromatography (GPC), whereas the polymers submerged in water were completely hydrolyzed to monomer ($M_n \sim 500$). Fig. 2 shows the time-dependent molecular weight analysis for the polylactam ester of Table 2, entry 4 (from HOCH₂CH₂-CH₂OH) over 360 days. Exposed only to air, the polymer M_n decreased 10% from 19 500 to 17 600 during this time, but for the submerged sample, the polymer M_n decreased steadily and completely from 19 500 to 570 (below the detection limit for polymer with this instrument). Most likely, the polymer dissolution enhanced the hydrolysis kinetics. The facile dissolution of these polymers can be appreciated because of the hydrophilicity of structurally-related lactams and polylactams: *N*-methylpyrrolidone (NMP), which is miscible with water;⁴⁵ and polyvinyl pyrrolidone (PVP), which is soluble in water.⁴⁶ In contrast, the water-insolubility of PLA⁴⁷ renders it much slower to hydrolyze, despite its similar sterics (alpha substitution) near the ester functional group.

Furthermore, ¹H NMR analysis of the immersed polymers after one year shows regeneration of the corresponding diol and the EBPC di-carboxylic acid monomer. Fig. 3 shows the ¹H NMR spectra for the polyethylene [ethylene bis(pyrrolidone carboxylate)] polymer (PEEBPC, Table 2, entry 3), the degradation products after one year of agitation in water, and authentic EBPC monomer. By integration, about 94% of the ester functional groups have hydrolyzed to afford ethylene glycol. The matching of the degradation spectrum to that of the original EBPC monomer confirms that hydrolysis has occurred at the ester group, but not at the amide functional group leaving the lactam ring intact.

This degradation pathway is also confirmed by MALDI-TOF and ESI-TOF analysis, which clearly shows PEPC (Table 1, entry 1) yielding the monomer HEPC (173 Da) + sodium (23 Da) = 196 Da and higher oligomers with repeat units of 155 Da, upon acid-catalyzed hydrolysis (see the ESI†). Similarly, PPEBPC (Table 1, entry 4) yields its monomer PEBPC (342 Da) + sodium (23 Da) = 365 Da and higher oligomers with repeat units of 324 Da. Thus, it is clear that the main-chain



Fig. 2 According to molecular weight analysis, complete hydrolytic degradation of polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table 2, entry 4) was observed in neutral water over 360 days, whereas minimal degradation is observed in air.



Fig. 3 ¹H NMR spectra of polymer PEEBPC (top, from Table 2 entry 3) and ester hydrolysis degradation products EBPC and ethylene glycol (middle) obtained after agitation in water for one year. Authentic monomer EBPC (bottom) is shown for comparison.

ester group is the key feature that allows for polymer degradation. Compare this hydrolysis behavior to that of polylactam amides reported by Kaneko *et al.*,⁴² which resemble PEPC (Fig. 1) except they are constructed with alkylene diamines and thus bear no ester functionality. In this case, strongly alkaline solutions (pH > 10), one year's time in soil, or UV-irradiation (250–450 nm) in water effected pyrrolidone ring opening (hydrolysis) and polymer solubilization, but not chain scission. Apparently the remaining amide main-chain functionality is robust and survives these various conditions.

Conclusions

The pyrrolidone lactam ring has been incorporated into an aliphatic polyester and this hard/soft motif of the polymer repeat unit was targeted to mimic that of aromatic/aliphatic polymers such as polyethylene terephthalate (PET). Importantly, the hydroxy-acid monomer (HEPC, with one lactam ring) and the diacid monomer (EBPC, with two lactam rings) are synthesized from biogenic itaconic acid, an inexpensive, scalable platform chemical increasingly available via glucose fermentation. The solvent-free, melt homopolymerization of HEPC or copolymerization of EBPC with diols is catalyzed by several species, but 2.0 mol% Sb₂O₃ afforded the best yields (84-91%) and the highest molecular weights ($M_n = 19500-24900$). For these polylactam esters, the lactam : methylene (-CH₂-) ratio scaled proportionally to the glass transition temperature (T_g) . For the highest ratio of 1:2, the $T_{\rm g}$ is 60 to 62 °C (Table 2, entries 1 and 3). For the lowest ratio of 1:4, the T_g is 24 °C (Table 2, entry 7). Intermediate T_{g} values were observed for ratios of 1:2.5, 1:3, and 1:3.5 (Table 1, entries 4, 5, and 6, respectively). Upon exposure to air for one year, polylactam ester molecular weight decreased modestly by about 10%. However, agitation in water fully dissolved the polymers in one month and fully hydrolyzed them to monomers over one year. Hence, these biorenewable polylactam esters show great potential to compete with polylactic acid (PLA) in various dry applications because of their improved thermal properties ($T_{\rm g}$ of 62 vs. 50 °C) and self-remediation in the environment via facile water-degradation. Note that PLA is water-insoluble and requires fairly demanding industrial composting conditions for assured degradation.17

The synthetic methodology outlined in Schemes 1 and 2 is amenable to reacting itaconic acid with various alternative amines. Thus, substantial modification of monomeric and polymeric structure is possible and will allow significant expansion of the polymer thermal properties—likely to excel the T_g value of PET or polystyrene (PS) by incorporation of rigid or aromatic moieties, conceivably acquired from Nature. Structural modification could also slow down the hydrolytic degradation, expanding the utility of these materials for water contact applications. Future studies will also aim to measure the mechanical properties of polylactam esters and compare these results to those of incumbent packaging materials.

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