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# Preparation of novel aromatic-aliphatic poly(ketone ester)s through condensation of biomass-derived monomers

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**Abstract:** Novel unsaturated and saturated monomers with a hydroxyl group and a carboxylic group *via* aldol condensation reaction of lignin-derived aromatic aldehydes with levulinic acid were prepared through organocatalysis and hydrogenation, respectively. The catalytic process was optimized and the structure of the monomers were full characterized. The as-prepared monomers were ready for the subsequent condensation polymerization to achieve a serials of novel full biobased poly(ester ketone)s. The chemical-physical properties of the poly(ester ketone)s were evaluated. This provides a green upgrading strategy to prepare sustainable synthetic polymers from building blocks available on a large scale using a catalytic biorefinery approach.

The continuing depletion of fossil resources and increasing environmental consciousness stimulate our society to use renewable biomass feedstocks for energy, chemicals and materials production, in order to reduce our dependence on fossil resources.<sup>[1]</sup> Particularly, in the field of sustainable polymeric materials obtained from biomass, natural polymers and their derivatives have been widely used for a variety of applications, many of which play a significant role in our daily lives.<sup>[2]</sup> Simultaneously, the design and preparation of renewable monomers from biomass for polymers through controlled polymerization continues to be one of the most paramount challenges in current polymer research.<sup>[3]</sup> Lignocellulosic materials include three primary chemical fractions: (1) hemicellulose - a polysaccharide predominantly composed of pentoses; (2) cellulose — a glucose polymer; and (3) lignin — a complex polymer of phenylpropane units. The effective implementation of the lignocellulosic biorefinery concept, especially via chemical catalytic approach, will produce a portfolio of chemicals which can be potentially upgraded into monomers for polymer preparation (Scheme 1). The field of catalytic conversion of lignocellulosic biomass has been the subject of several excellent recent reviews.[1c, 4]

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Supporting information for this article is given via a link at the end of the document [synthesis and characterization of monomers and polymers and E-factor calculations].



**Scheme 1.** The choices of aromatic and aliphatic species available from lignocellulosic biomass for the synthesis of novel aromatic-aliphatic poly(ester ketone)s.

Lignin is one of main components in lignocellulose, and it is also the most abundant natural aromatic compound on the planet.<sup>[5]</sup> Recent catalytic conversions of lignin produced a broad library of aromatic compounds, including vanillin, syringaldehyde, p-hydroxybenzaldehyde, and creosol.<sup>[6]</sup> Amongst these, vanillin is regarded as a promising bio-based aromatic building-block for polymer synthesis and has received much attention. For example, Miller et al. used lignin-based vanillin aldehyde (VA) and acetic anhydride to prepare acetyldihydroferulic acid, (3-(3-methoxy-4acetoxyphenyl)propionic acid) which was subjected to polymerization to yield biorenewable poly(dihydroferulic acid).<sup>[7]</sup> This polyester exhibits thermal properties similar to those of polyethylene terephthalate (PET), which illustrates the huge potential of lignin-derived monomers for the preparation of aromatic polymers. As an extension of this investigation, a series of derivatives of VA were prepared using various chemical strategies for the production of sustainable monomers for not only polyesters, but also polyurethanes, and epoxy resins with good performance in thermal and chemical properties being observed.<sup>[8]</sup> For example, Wool et al. reported methacrylated lignin model compounds including methacrylated guaiacol and methacrylated eugenol as bio-based reactive diluents for liquid molding resins. Homopolymers of these methacrylates with glass transition temperatures similar to those of polystyrene and poly(methyl methacrylate) were then prepared by bulk polymerization.<sup>[8e]</sup> Zhu et al. have also prepared several highperforming lignin-based polymers.<sup>[9]</sup> Recently, they synthesized two novel vanillin-based diepoxides which exhibited similar curing reactivity to bisphenol A epoxy resin. The cured vanillin-based epoxides presented excellent flame retardancy and high T<sub>a</sub> together with outstanding mechanical properties.<sup>[9c]</sup>

Another promising pathway to prepare polymeric monomers from lignocellulosic biomass is the dehydration of cellulose and

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hemicellulose into 5-hydroxymethyl-furfural (HMF) and furfural,<sup>[10]</sup> and further oxidation of HMF yielding 2,5-diformylfuran<sup>[11]</sup> and 2,5furandicarboxylic acid,<sup>[12]</sup> which are regarded as promising alternatives to petroleum-based aromatic monomers for polyester preparation.<sup>[13]</sup> Levulinic acid (LA) is a renewable feedstock, which can be derived both from hemicellulose and cellulose in lignocellulose *via* acidic processing.<sup>[14]</sup> Notably, formic acid is a sustainable by-product from acidic hydrolysis of carbohydrate biomass, and can serve as an environmentally friendly hydrogen donor for catalytic transfer hydrogenation in biomass upgrading.<sup>[15]</sup> To the best of our knowledge, levulinic acid has not previously been used as a flexible precursor for the synthesis of sustainable aromatic polyesters.

Although significant progress has been made in the field of sustainable polyesters, there is still a substantial challenge to synthesize fully bio-based aromatic-aliphatic polyesters.[16],[17] It is believed that a short aliphatic component in the main chain will provide necessary flexibility to aromatic polyesters, thus increasing their subsequent processability. In many cases, a petroleum-based chemical was used for the introduction of a flexible chain into the aromatic polyester, in association with the use of lignin-derived aromatic or furan compounds.[4b] Considering the inherent structure characteristics of lignin-derived aromatic aldehydes and levulinic acid, herein we report a strategy to prepare monomers with a hydroxyl group and a carboxylic group via aldol condensation reaction of lignin-derived aromatic aldehydes with levulinic acid. These structural features offer the opportunity to prepare polymers using a single monomer instead of two co-monomers. A series of sustainable aromatic-aliphatic poly(ester ketone)s are prepared by using conventional bio-based obtainable catalytic chemicals from biorefining of lignocellulose.[4d]

Scheme 2 illustrates the strategy for the synthesis of the novel 100% bio-based aromatic-aliphatic poly(ester ketone)s. For the preparation of unsaturated aromatic monomers 3b, the influence of various parameters including catalyst structure, reaction temperature, and catalyst loading were investigated (Table1 and Table S1). The optimized catalyst was found to be 20 mol% of a combination of pyrrolidine and acetic acid and the best conditions involved carrying out the aldol condensation reaction at two different temperatures. Under these conditions, the α-methyl group of levulinic acid adds to the aldehyde carbon followed by dehydration to afford the arylidene keto acid derivatives 3a-c in moderate yields (supporting information). The stereochemistry of the monomers 3a-c were determined by <sup>1</sup>H NMR spectroscopy, and the results indicate the presence of a single E-isomer, as the coupling constants relating the two olefinic protons were in the range of 15-16 Hz.<sup>[18]</sup> In <sup>13</sup>C NMR the chemical shift at around 199, 175 ppm and 143, 130 ppm are attributed to the carbonyl and double bond, respectively (supporting information). Although L-proline is known to be an efficient bifunctional acid-base organocatalyst for aldol reactions,<sup>[19]</sup> only 20% yield was obtained under idential conditions. With acetic acid as the co-catalyst, neither linear secondary amines nor sixmembered cyclic secondary amines including morpholine and piperidine showed noticeable catalytic activity (Table 1, entries 2-6).

Table 1. Screening of the catalyst and co-catalyst to prepare unsaturated monomer  $^{\rm (a)}.$ 

Entry	Catalyst	Co-catalyst	Yield % <sup>[b]</sup>
1	L-Proline	None	20
2	n-Dibutylamine	AcOH	13
3	Diethylamine	AcOH	7
4	Tetramethylguanidine	AcOH	1
5	Morpholine	AcOH	28
6	Piperidine	AcOH	10
7	Pyrrolidine	AcOH	42
8	Pyrrolidine	HCI	12
9	Pyrrolidine	$C_2H_2O_4$	16
10	Pyrrolidine	F <sub>3</sub> CCOOH	21

[a] The solution of levulinic acid (16.4 mmol), catalyst (1.64 mmol) and cocatalyst (1.64 mmol) in 20 mL toluene were added dropwise to vanillin aldehyde (16.4 mmol) in 40 mL toluene at 40 °C under N<sub>2</sub>. The mixture was heated at 100 °C for 2 h and then at 140 °C for 1 h with Dean-Stark water trap. [b] Isolated yields.

The mechanism of pyrrolidine-acetic acid catalysed aldol condensations is proposed to proceed through the formation of an enamine intermediate. The formation of the enamine is the rate-determining step and largely depends on the nucleophilicity of the secondary amine.<sup>[20]</sup> It has been demonstrated that enamines are formed much more readily by pyrrolidines than by piperidines and the corresponding pyrrolidine enamines are known to be more nucleophilic.<sup>[21]</sup> Our results suggest that the combination of pyrrolidine and acetic acid could act synergistically to give high yields, which was supported by the lower yields obtained when hydrochloric, oxalic or trifluoroacetic acid were used as the co-catalyst. This result is in accordance with a previous report which demonstrated that the pyrrolidine-acetic acid combination was more efficient than other pyrrolidine-acid combinations in the formation of enamines.<sup>[20]</sup> The optmized catalytic system was extended to the aldol condensation reaction of other lignin derived aromatic aldyhydes with levulinic acid, including syringaldehyde and para-hydroxybenzaldehyde, giving 3a and 3c in moderate yields of 46% and 36% respectively.

Hydrogenation of arylidene derivatives **3a-c** using 10% palladium on carbon as catalyst in the presence of hydrogen or formate salts afford mainly compounds **4a-c** with satifactory yields and selectivities (Table S2). Lactone derivatives **5a-c** were also obtained as by-products. The formation of **5a-c** can be explained by further reduction of the carbonyl group to a hydroxyl group, which reacted with the carboxylic acid to form the lactone. The lactone derivatives are also potential monomers to prepare sustainable polymers via ring opening polymerization,<sup>[22]</sup> but this was not the main goal in this study.





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Scheme 2. General strategy to synthesize fully bio-derived aromatic-aliphatic poly(ester ketone)s.

Table 2. Polymerization an	d characterization of aromatio	c-aliphatic poly(ester ketone)s

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Entry	Monomer	poly(ester ketone)	T (°C)	T (h)	Cat (1 mol%)	Yield (%)	Mn	PDI	T50% (°C) <sup>[a]</sup>	W (%) <sup>[b]</sup>	Tg (°C)
1	4a	6a	220	12	Zn(OAc) <sub>2</sub>	52	20000	1.8	474	43.0	129
2	3b	6b'	170	5	Zn(OAc) <sub>2</sub>	33	23000	1.1	465	43.3	131
3	4b	6b-2	170	12	Zn(OAc) <sub>2</sub>	40	29000	1.6	397	32.6	80
4	4b'	6b-3	170	12	Zn(OAc) <sub>2</sub>	49	21000	1.8	407	26.4	81
5	4b'	6b-4	220	12	Zn(OAc) <sub>2</sub>	46	29000	1.5	409	36.1	95
6	4b'	6b-5	220	24	Sb <sub>2</sub> O <sub>3</sub>	38	32000	1.9	402	37.0	86
7	4c	6c	220	12	Zn(OAc) <sub>2</sub>	43	18000	1.8	464	44.5	137

[a] Temperature at which 50% weight loss was observed. [b] Remaining weight at 600 °C.

It is worth noting that formate salts are also good hydrogen donors for catalytic transfer hydrogenation.<sup>[15]</sup> As aformentioned, formic acid is a by-product from the preparation of LA from HMF, which indicates that a sustainable hydrogenation reagent also derived from biomass could be used in this synthesis.

Having established a strategy for the preparation of monomers **4a-c**, their bulk polycondensation was performed in the melt (170-220 °C) under dynamic vacuum with 1 mol% of zinc acetate as catalyst. The evolved water was efficiently removed by the dynamic vacuum to push the equilibrium toward the polymer. The structure of poly(ester ketone)s were determined by <sup>1</sup>H NMR and HSQC (Figure S1 to S8). In the <sup>1</sup>H NMR spectra of poly(ester ketone)s (**6a**, **6c**) derived from phenol carboxylic acid monomers (**4a**, **4c**) showed chemical shift above 8 ppm indicating the presence of hydroxyl end groups (Figure S1, 2 and S7, 8). The poly(ester ketone) of **6b-3** obtained from acetylated monomer **4b'** show weak acetyl end group at 2.2 ppm (Figure S5 and S6). The obtained unsaturated poly(ester ketone)s can be further modified

via post-functionalization such as Micheal addition, cyclization and thiol-ene click reaction. In Millers' study, the direct polycondensation of dihydroferulic acid only yielded oligomers under identical conditions, and application of the acetylated ferulic acid monomer for the polymerization yielded a polyester with molecular weights comparable to that of commercial PET  $(M_n=15000 \text{ to } 40000)$ .<sup>[7]</sup> Surprisingly therefore, our results show that both the unsaturated monomer 3b and saturated monomer yielding 4b undergo polycondensation, corresponding sustainable poly(ester ketone)s in moderate yields of 33 and 40% with molecular weights of 23000 (PDI=1.1) and 29000 (PDI=1.6) (Table 2, entry 2 and 3), respectively. The acetylated monomer 4b' was prepared by using acetic anhydride in the presence of 4dimethylaminopyridine in 54% yield. The yield of the poly(ester ketone) was increased to 49% when the acetylated monomer was applied under identical conditions, while the molecular weight slightly decreased to 21000 (Table 2, entry 4). Further increase in the polycondensation temperature from 170 °C to 220 °C does not

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lead to increases in either poly(ester ketone) yields or molecular weight. A poly(ester ketone) with molecular weight up to 32000 (PDI=1.9) was achieved when the acetylated monomer was polymerized in the presence of catalytic antimony(III) oxide. This indicates that antimony(III) oxide is a superior catalyst to zinc acetate to achieve a poly(ester ketone) with higher molecular weight, but at the cost of a slight reduced yield (Table 2, entry 6). Monomers **4a** and **4c** were also applied in the polymerization, and poly(ester ketone)s **6a**, **6c** with high molecular weight were obtained under identical conditions (Table 2 entry 1 and 7, Figures S9 and S15).

The use of biobased compounds and the new synthetic strategy to prepare polybutylene terephthalate (PBT) and polyhexylene terephthalate (PHT) analogues **6a-c** is anticipated to lead to new thermal behaviour of the poly(ester ketone)s, which is an issue of prime importance for the application of these polymers as potential thermoplastic materials. Therefore, their themal properties were evaluated by TGA and DSC and key data from these measurements are given in Table 2.

The TGA traces of poly(ester ketone)s 6a-c recorded under a nitrogen atmosphere are depicted in Figure 1. This comparative plot reveals that all the poly(ester ketone)s show a one-step degradation pattern, indicating that the presence of a conjugated double bond (6b', Table 2 entry 2) and acetyl end group (6b-4, Table 2 entry 5) did not significantly alter the thermal stability of the ester linkage. The poly(ester ketone)s exhibited a 50 wt% weight loss in the range of 395-474 °C indicating comparable thermal stability to fossil-based polyesters. The structures and molecular weights of the as-prepared bio- poly(ester ketone) do influence their thermal properties to some extent. As shown in Table 2, comparison of saturated and unsaturated poly(ester ketone)s of similar molecular weight suggests superior thermal properties for the unsaturated bio-poly(ester ketone) (Table 2 entries 2-4). The unsaturated poly(ester ketone) show higher residual weight at 600 °C than those saturated poly(ester ketone) indicating superior thermal stability.



Figure 1. TGA traces of newly prepared poly(ester ketone)s.

The semicrystalline aromatic polyester PHT has not achieved commercial applications, but it still deserves great attention because its relatively low melting point (144 °C) requires less severe processing conditions than PET and PBT (mp 255 and 224 °C, respectively).<sup>[23]</sup> However, PHT is not biodegradable and its potential utilization in applications above room temperature is

seriously limited because its glass transition temperature is rather low (-6.7 °C) compared to PET and PBT (67 and 38 °C, respectively). The poly(ester ketone)s possess the same functional groups but differ in the number of methylene units in the main chain, which resulted in a decrease in T<sub>g</sub> as the number of methylene units increased. The DSC results imply that although there are six methylene groups in the flexible chain repeat units of the as-prepared poly(ester ketone)s, their T<sub>g</sub>s are much higher than that of PHT, and comparable or even higher than those of PET and PBT (Table S3).



C(sp<sup>2</sup>): Restriced rotation around carbon-carbon single bonds of C=C and C-C adjacent to the C=O

Scheme3: Structural comparison of traditional PHT, 6b and 6b'

This can be explained by the synergetic effect of the introduction of a methoxyl group onto the rigid aromatic benzene ring and ketones or  $\alpha,\beta$ -unsaturated ketones into the flexible aliphatic chain in the polymers. The introduction of a methoxyl group onto the aromatic benzene ring can decrease the symmetry and increase the free volume of the polymer, thus resulting in a higher T<sub>g</sub>. It is well known that in a linear sp<sup>3</sup>-carbon chain (e.g. in PHT), free rotations around carbon-carbon single bonds can allow the chains to bend or curl up in various ways, thus resulting in polymers with low T<sub>g</sub>. In carbon-carbon double bonds and carbon-oxygen double bonds, similar rotations cannot occur, and the polymeric segmental relaxation is restricted, thus resulting in a higher T<sub>g</sub> (Scheme 3).

In addition to their enhanced thermal properties, polyesters with  $\alpha$ , $\beta$ -unsaturated ketone moieties are anticipated to provide an important active site for post-polymerization modification via classic nucleophilic or electrophilic addition reactions, such as the Michael addition reaction. In this way a library of functional polyesters may be designed and prepared in the future.<sup>[24]</sup>

E-factor analysis was employed to evaluate the environmental impact of our approach and the details are shown in Tables S4-S15. According to our calculations, the E-factor of bio-based monomers **4a**, **4b** and **4c** were determined as 7.4, 6.7

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and 11.3 kg/kg respectively (Tables S4-S9) and the E-factor of bio-based poly(ester ketone)s **6a**, **6b** and **6c** were determined as 12.85, 13.1 and 20.8 kg/kg respectively (Tables S10-S15). These are in accordance with Sheldon's analysis of fine chemicals that have an E-factor of 5-50<sup>[25]</sup>. In this work, only moderate yields of the first aldol condensation reaction and the subsequent polymerization have been achieved which is responsible for the relatively high values of the E-factor. It is anticipated that these yields could be improved by using new catalytic and polymeric technology, such as solid basic catalysts,<sup>[26]</sup> and this is currently the subject of ongoing research in our laboratory.

In conclusion, fully bio-based aromatic-aliphatic monomers have been prepared via a green organocatalytic, atom economical aldol reaction between lignin-derived aromatic aldehydes and carbohydrate-derived levulinic acid. From these monomers, a series of novel aromatic-aliphatic poly(ester ketone)s were successfully prepared and characterized. These bio-based poly(ester ketone)s exhibit comparable thermal properties to conventional thermosetting materials. As the obtained functional phenol carboxylic acid monomers can be further derived to other polymeric monomers, such as bis-epoxy, which have great potential application in the area of polymers synthesis, therefore, future studies will focus on synthesis of new polymeric derivatives, polymer degradation behavior, postmodification of the poly(ester ketone)s as well as screening of new catalytic systems and polymerization technologies for the preparation of the monomers and polymers. The findings in this study open a new pathway to design sustainable polymers from lignocellulosic biomass.

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**Keywords:** Vanillin • Levulinic acid • Lignocellulose • Poly(ester ketone) • Aldol condensation

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## COMMUNICATION

#### **Entry for the Table of Contents**

### COMMUNICATION



Biobased poly(ester ketone)s were prepared via aldol condensation of aromatic aldehydes obtainable from lignin with levulinic acid available from cellulose and hemicellulose via green catalysis and polycondensation. Qin Chen, Tianhua Ren, Yang Chai, Yuanlong Guo, Ian D. V. Ingram, Michael North, Haibo Xie\*and Zongbao kent Zhao\* **Page No. – Page No.** 

Preparation of novel aromaticaliphatic poly(ketone ester)s through condensation of biomass-derived monomers