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The combination of the Williamson and Tishchenko reactions produced series of new  $\alpha,\omega$ -diene functionalized carboxylic ester monomers from both petrochemical and renewable resources, which were applicable in subsequent thiol-ene click and acyclic diene metathesis (ADMET) polymerizations, providing series of poly(thioether esters) and unsaturated aromatic-aliphatic polyesters with high molecular weights.

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## Introducing the Tishchenko Reaction into Sustainable Polymer Chemistry

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Taking advantage of the structural characteristics of lignin-derived phenolic compounds, a combination of the Williamson and Tishchenko reactions produced series of new  $\alpha,\omega$ -diene functionalized carboxylic ester monomers from both petrochemical and renewable resources, which were applicable in subsequent thiol-ene click and acyclic diene metathesis (ADMET) polymerizations, providing series of poly(thioether esters) and unsaturated aromatic-aliphatic polyesters with high molecular weights.

Polymeric materials play an important role in our daily life and in industry, and are mostly produced from petroleum-based monomers. However, there are increasing environmental concerns relating to both the feedstocks used to produce polymers and their end-of-life treatment options.<sup>1</sup> It is well recognized that the sustainable development of polymer science and any extension of the applications of polymers are heavily reliant upon the design of renewable monomers and the development of new polymerization strategies.<sup>2-4</sup>

Polyesters are an important class of polymers which are ubiquitous in daily life and have many industrial applications. Most commercially available polyesters are produced by polycondensations involving transesterification or by ringopening polymerization as shown in Scheme 1A,B. Usually, harsh conditions or complex procedures such as use of high temperature, vacuum, multiple polymerization steps and toxic metal catalysts are required in these synthetic protocols, particularly in the synthesis of aromatic polyesters.<sup>5</sup>

The biorefinery concept provides a large library of bio-derived chemicals, but most of these have to be upgraded into monomers with appropriate functionalities through environmentally unfriendly or complex protocols.<sup>6-8</sup> For example, the preparation of 5-hydroxymethyl-fufural (HMF) from carbohydrates has been widely studied. However, HMF has to be oxidized to 2,5-furandicarboxylic acid (FDCA) before being used as a monomer to prepare poly(ethylene-2,5-

furandicarboxylate) (PEF) with superior gas barrier properties to traditional polyethylene terephthalate.<sup>9, 10</sup> Therefore, major challenges remain in using sustainable resources for polyester production; especially the design and synthesis of monomers using environmentally friendly methods and their polymerization under mild reaction conditions.

Lignin is the main component in lignocellulosic biomass and is the most abundant renewable aromatic chemical source on Earth. The catalytic conversion of lignin can produce a library of

(A) Polycondensation



(B) Ring-opening polymerization



(C) This work: Ester-containing monomers via the Tishchenko reaction



Scheme 1 Preparation of polyesters.

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Scheme 2 Synthesis route to  $\alpha, \omega$ -diene monomers.

aromatic compounds, in which vanillin usually dominates.<sup>11-13</sup> Therefore, vanillin is regarded as a promising bio-derived aromatic building block for polymer synthesis through chemical upgrading by taking advantage of its phenol and aldehyde groups. For example, an acetyl dihydroferulic acid was prepared by reaction of vanillin with acetic anhydride, which could be polymerized to poly(dihydroferulic acid) with similar thermal properties to PET.<sup>14</sup> More recently, a fully bio-based ketone containing aromatic-aliphatic monomer was prepared by the condensation reaction of vanillin and levulinic acid. Its subsequent polycondensation resulted in formation of novel, fully bio-based, poly(keto-esters).<sup>15</sup> Other aromatic polyesters, such as polyalkylenehydroxybenzoates,<sup>16</sup> polyacetal ethers,<sup>17</sup> polyethylene ferulate<sup>18</sup> and divanillin-derived polyesters<sup>19, 20</sup> also have been prepared through traditional polymerization protocols.

The development of mild, new polymerization protocols is also important for the development of sustainable polymer chemistry. For example, the introduction of multicomponent,<sup>21</sup>, <sup>22</sup> thiol-ene click<sup>23-26</sup> and acyclic diene metathesis (ADMET)<sup>27</sup> protocols into polymer chemistry has significantly promoted the development of polymer chemistry. Several studies have demonstrated that these polymerization protocols are applicable to vanillin-derived monomers, giving series of polymers with high molecular weights and satisfactory thermal properties.<sup>28-31</sup> Hence, there is now the potential to develop a sustainable polymers industry in which the vast majority of polymers are produced using bio-based monomers which are efficiently synthesized and which undergo facile polymerization.

The Tishchenko reaction is a 100% atom economical process in which aldehydes undergo disproportionation or dimerization to give the corresponding carboxylic esters. It has been known for more than a hundred years and is catalyzed by *N*heterocyclic carbenes, metal hydrides and alkali metal *tert*butoxides.<sup>32-37</sup> Although the Tishchenko reaction has been widely applied in fine chemicals synthesis, it is seldom applied in polyester chemistry, as the direct polymerization of a dialdehyde only produced polyester oligomers.<sup>38-43</sup> Herein, by utilizing the structural characteristics of lignin-derived phenolic aldehydes, we introduce a toolbox of combining the Williamson and Tishchenko reactions for the preparation of monomers ready for subsequent thiol-ene click and ADMET polymerizations (Scheme 1C).

Vanillin contains phenol and aldehyde groups. As expected, the direct Tishchenko reaction of vanillin does not occur using various catalysts including potassium tert-butoxide and the hydrides of calcium, sodium and potassium due to the weak acidic phenol group (Scheme S1).<sup>33, 34, 36</sup> However, Williamson allylation of vanillin produced 4-(allyloxy)-3methoxybenzaldehyde 2a in 96% yield (Scheme S1, Fig. S1-2). To our delight, compound 2a underwent a Tishchenko reaction under solvent-free conditions with sodium hydride as the optimal catalyst (Table S1), producing 4-(allyloxy)-3methoxybenzyl 4-(allyloxy)-3-methoxybenzoate 3a in 94% yield (Fig. S1-2). Monomer 3a is characterized by the presence of ester and  $\alpha, \omega$ -diene functional groups, which provide the opportunity to prepare polyesters via polymerization of the  $\alpha, \omega$ -dienes under appropriate polymerization protocols such as metal free thiol-ene click chemistry and acyclic diene metathesis (ADMET). These have been widely investigated and shown to be efficient and green polymerization protocols for monomers containing  $\alpha, \omega$ -dienes.<sup>44-49</sup>

The metal-free thiol-ene click polymerization of **3a** with 1,2dithioethane **4a** (Scheme 3) produced a poly(thioether ester) **P3a4a** with a M<sub>w</sub> of 50.0 KDa and a polydispersity index (PDI) of 1.4 in 96% yield. The ADMET polymerization of **3a** produced an unsaturated aromatic-aliphatic polyester **P3a** with a M<sub>w</sub> of 43.7 KDa and PDI of 1.1 in 97% yield when the second generation Hoveyda-Grubbs catalyst (HG-II) was used. The satisfactory molecular weight and PDI values of these polyesters demonstrated the feasibility of our strategy. To also demonstrate the scope of this methodology and to tune the properties of the prepared polyesters, series of ester monomers with  $\alpha, \omega$ -dienes containing different methylene spacers were

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Scheme 3 Novel aromatic polyesters obtained by thiol-ene polymerization and subsequent oxidation.

Table 1. Thermal properties and molecular weights of poly(thioether esters) P3a-h4a-d and poly(sulfone esters) PO3a,d-h4a

Poly(thioether ester)s P3a-h4a-d								Poly(sulfone ester)s PO3a,d-h4a							
Sample	Mn <sup>a</sup>	Mw <sup>a</sup>	PDI	Yield	T <sub>5%</sub> <sup>b</sup>	Tgc	Sample	$M_n^a$	$M_w^{a}$	PDI	Yield	T <sub>5%</sub> <sup>b</sup>	T <sub>g</sub> c		
	(KDa)	(KDa)		(%)	(°C)	(°C)		(KDa)	(KDa)		(%)	(%)	(°C)		
P3a4a	36.1	50.0	1.4	96	283.0	29.3	PO3a4a	39.1	47.4	1.21	90.9	173.06	78.0		
P3a4b	38.0	48.9	1.3	93	295.6	18.2									
P3a4c	46.4	50.0	1.1	97	295.3	11.0									
P3a4d	_d	_d	_d	93	316.0	-0.2									
P3d4a	38.6	46.8	1.2	93	276.0	7.6	PO3d4a	36.5	42.4	1.2	89	252.8	53.3		
P3e4a	20.2	23.0	1.1	89	259.5	8.1	PO3e4a	26.4	29.6	1.1	93	245.0	46.6		
P3f4a	43.9	50.8	1.2	89	288.5	1.5	PO3f4a	45.5	54.1	1.2	87	212.3	_ <sup>e</sup>		
P3g4a	41.9	47.4	1.1	93	277.4	31.5	PO3g4a	36.8	40.1	1.1	91	269.1	75.4		
P3h4a	26.7	33.0	1.2	98	297.2	19.7	PO3h4a	29.6	39.3	1.3	89	237.1	60.2		
P3b4a	35.2	45.7	1.3	88	304.3	10.5									
P3b4b	33.5	48.0	1.4	92	288.7	2.9									
P3b4c	43.2	48.3	1.1	94	312.7	-8.4									
P3b4d	32.1	51.9	1.6	93	323.9	-8.7									
P4c4a	44.5	51.0	1.2	91	300.3	-6.2									
P4c4b	_ <sup>d</sup>	_ <sup>d</sup>	_d	90	307.0	-14.3									
P4c4c	_ <sup>d</sup>	_ <sup>d</sup>	_d	90	306.9	-18.5									
P4c4d	_d	_d	_d	93	313.1	-17.5									

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The post-

<sup>a</sup>Determined by GPC in DMF (0.01 M LiBr) as the solvent against PS standards. <sup>b</sup>Polymer degradation temperature obtained at 5% mass loss by TGA. <sup>c</sup>Determined by DSC. <sup>d</sup>Insoluble in DMF or THF at room temperature. <sup>e</sup>No T<sub>g</sub> was detected by DSC.

prepared using both lignin-derived phenolic aldehydes (syringaldehyde para-hydroxybenzaldehyde) and and petrochemical-based phenolic aldehydes (meta-methyl-parahydroxybenzaldehyde, meta-bromopara-hvdroxybenzaldehyde and *meta*-fluoro-*para*-hydroxybenzaldehyde). Esters 3a-h were prepared in good yields (Scheme 2) and underwent thiol-ene click polymerization with dithiols 4a-d to produce poly(thioether esters) P3a-h4a-d in good yields ranging from 88-97% (Scheme 3). Poly(thioether esters) P3a-h4a-d have M<sub>w</sub> ranging from 23.0 to 50.8 KDa and narrow PDIs of 1.1 to 1.6.

To demonstrate the possibility of post-polymerization modifications, poly(thioether ester)s P3a,d-h4a were quantitatively oxidized to corresponding poly(sulfone ester)s PO3a,d-h4a using hydrogen peroxide as a green oxidant under mild conditions.<sup>50-52</sup> The molecular weight and PDI did not

significantly after the oxidation. change polymerization oxidation of thioether-containing polymers into the corresponding sulfoxide or sulfone derivatives can increase the polarity of the polymers, thus extending their applications into fields including organic light emitting diodes, organic solvent nanofillers, proton exchange resins, and gas separation membranes.53-57

The thermal properties of poly(thioether esters) P3a-h4a-d and poly(sulfone esters) PO3a,d-h4a were evaluated by TGA and DSC, and the results are summarized in Table 1. The TGA traces of the polymers demonstrated that both the poly(thioether esters) and poly(sulfone esters) show a one-step degradation pattern, indicating that the presence of thioether and sulfone groups in the polymer chain did not alter the thermal stability of the ester linkage (Figure S5-6). The

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poly(thioether esters) exhibited a 5% weight loss (T<sub>5%</sub>) in the range of 259-324 °C (Fig. S7). Although post-polymerization oxidation of the poly(thioether esters) did not affect the molecular weight and PDI of the polymers, the T<sub>5%</sub> slightly decreased to 173-269 °C. All the polymers except for PO3f4a possess an obvious glass transition temperature (T<sub>g</sub>). **P3c4d** and P3h4a show an obvious cold crystallization peak and melting peak from the second heating run (at 98.7 °C and 113.6 °C; and 1.0 °C and 16.1 °C respectively) (Figures S5 and S6). PO3a4a shows exothermic and melting peaks from the second heating run at 136.2 °C, and 172.2 °C respectively (Figure S14). For the other polymers, no crystallinity or melting point was observed, and their amorphous structures are also confirmed by WXRD (Figures S10-13, and S15). As expected, the increase in number of methylene spacers in the dithiol and aliphatic  $\alpha, \omega$ -diene chain increases the flexibility of the aliphatic chain in the polymers and lowers the T<sub>g</sub> of the poly(thioether esters) (Figure S8). Oxidation of the thioethers into sulfones significantly increases the  $T_g$  of the polymers from 1.5-31.5 °C to 46.6-78.0 °C, which is comparable or higher than those of PLA and PET, indicating their potential applications as thermoplastics. The enhanced  $T_{e}$  can be ascribed to the synergetic effect of the regular tetrahedral structure of the sulfone moiety and the increased polarity of the polymers. The regular tetrahedral structure of the sulfone moiety may restrict the C-S bond rotation, thus decreasing the mobility of the macromolecular chains and leading to higher  $T_{g}$ , and the enhanced polarity will result in stronger dipole-dipole interactions, thus leading to higher  $T_{g}$ . It was found that the symmetry of the aromatic ring and the substituent group could have a great effect on the JgLOF the polymers. For example, polymers **P3d4**<sup>20</sup> and **P3e4**<sup>33</sup> with symmetric aromatic rings have similar and lower Tg's (8 °C). Other than *meta*-fluoro substitution, *meso*-substitution resulted in higher Tg than **P3d4a**, because the introduction of large substituent groups (e.g. -OCH<sub>3</sub>, -CH<sub>3</sub>, -Br) onto the aromatic ring decreases the symmetry and increase the free volume of the polymers. Although the symmetry of the polymer also decreased slightly by the introduction of small fluoro substituent, the strong electronegativity of fluorine can decrease  $\pi$ - $\pi$  interaction, thus facilitating the mobility of the macromolecular chains and resulting in a lower Tg of 1.5 °C.

To further demonstrate the versatility of polymer synthesis facilitated by the toolbox, monomers **3a-h** were submitted to ADMET polymerization to prepare polyesters catalyzed HG-II (Scheme 4). Gratifyingly, a series of unsaturated polyesters (P3a-h) were obtained in high yields (91-98%) with M<sub>w</sub> ranging from 26.2 KDa to 52.4 KDa and PDI ranging from 1.1 to 1.5 (Table 2). Furthermore, a series of saturated polyesters (PH3ah) can also be prepared by post-polymerization hydrogenation of P3a-h, and the molecular weight and PDI of the polyesters did not change, indicating the chemical stability of the polyesters during the hydrogenation. <sup>1</sup>H NMR spectra of P3a and PH3a allowed the success of the hydrogenation to be confirmed by the complete disappearance of the peaks assigned to the internal double bond at 6.1 ppm, and the appearance of new peaks at 2.1 ppm assigned to the newly formed methylene groups



Table 2 GPC and thermal properties of polyesters P3a-h and PH3	a-h
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ADMET polymers <b>P3a-h</b>								Hvdrogenated ADMET polymers <b>PH3a-h</b>							
Sample	$M_n^a$	M <sub>w</sub> <sup>a</sup>	PDI	Yield	T <sub>5%</sub> <sup>b</sup>	Tgc	Sample	M <sub>n</sub> <sup>a</sup>	$M_w^a$	PDI	Yield	T <sub>5%</sub> <sup>b</sup>	T <sub>g</sub> c		
	(KDa)	(KDa)		%	(°C)	(°C)		(KDa)	(KDa)		%	(°C)	(°C)		
P3a	38.6	43.7	1.13	97	225.6	59.1	PH3a	35.3	48.0	1.4	90	270.0	57.8		
P3b	42.1	49.3	1.2	95	268.0	23.4	PH3b	49.2	53.5	1.1	88	330.1	23.4		
P3c	44.7	51.9	1.2	96	348.6	0.8	PH3c	_d	_ <sup>d</sup>	_ <sup>d</sup>	94	344.2	7.2		
P3d	30.3	46.2	1.5	98	262.7	57.5	PH3d	29.4	44.5	1.5	93	288.4	20.6		
P3e	24.2	26.2	1.1	96	242.9	47.4	PH3e	22.0	24.0	1.1	92	303.5	46.3		
P3f	44.3	52.4	1.2	96	259.1	15.3	PH3f	46.8	52.7	1.1	90	323.8	14.8		
P3g	29.9	45.7	1.5	91	236.4	49.2	PH3g	35.4	45.9	1.3	86	293.1	44.8		
P3h	32.8	43.8	1.3	92	267.4	23.2	PH3h	_d	_d	_d	88	299.7	19.5		

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<sup>a</sup> Determined by GPC in DMF (0.01 M LiBr) as the eluent against PS standards. <sup>b</sup> Polymer degradation temperature obtained at 5 % **mass loss by TGA.** <sup>c</sup> View Article Online DOI: 10.1039/C9GC03926K

### (Figure S16).

The thermal properties of polymers P3a-h and PH3a-h were evaluated by TGA and DSC and the results indicate that the unsaturated polyesters are thermally stable with 5% mass loss occurring between 225 and 348 °C (Figure S18-21, S24-27). The introduction of substituents at the meso-position in the aromatic ring results in decreased thermal stability. Conversely, an increase in the number of methylene spacer units results in increased thermal stability (Table 2). Although diffractive peaks were detected in the cases of P3d-f, and P3h by WXRD analysis, indicating the crystallinity of these polymers, no melting points were observed in their DSC curves (Figure S20-23). As expected, the corresponding  $T_{5\%}$  of **PH3a-h** are higher than those of **P3a**h due to the hydrogenation of the unsaturated C=C double bond to a C-C single bond. All the unsaturated polyesters (P3a-h) show a prominent Tg at 0.8 to 59.1 °C, and the hydrogenation usually slightly decreased the  $T_g$  of **PH3a-h** to between 7.2 and 57.8 °C. This can be explained by the hydrogenation of C=C bonds (sp<sup>2</sup>) with restricted rotation ability to C-C bonds (sp<sup>3</sup>) with a free rotation ability, as the rotation of the methylene groups can allow the polymer chains to bend or curl up in various ways, thus leading to a lower Tg. A similar effect of the substituent groups on the aromatic ring on the T<sub>g</sub> of polyesters (P3a-h and PH3a-h) to that discussed above for poly(thioether esters) P3a-h4a-d was observed. Similarly, no melting points were observed in the DSC curves of PH3a,d,f,h, although diffractive peaks were detected in the WXRD patterns, indicating the crystallinity of these polymers (Figure S26-29).

E-factors were calculated for novel polyesters P3a4a, P3a4b, P3a4c, P3a4d, PO3a4a, P3a, P3b, P3c and PH3a to obtain an overview of the environmental impact of our approach to polyester synthesis. The *E*-factors were determined to be 3.3, 3.4, 2.9, 2.8, 3.9, 6.1, 5.7, 5.1 and 10.8 respectively (Tables S2-19). These values are at the level of industrial processes for the manufacture of bulk and fine chemicals.<sup>58-60</sup> The polyesters obtained from thiol-ene polymerization showed lower *E*-factors than those obtained from ADMET polymerization indicating the lower environmental impact of the thiol-ene polymerization.

In summary, by taking advantage of the structural characteristics of lignin derived aromatic aldehydes, a toolbox of combining the Williamson and Tishchenko reactions has been demonstrated to be a highly efficient and sustainable strategy to synthesize  $\alpha, \omega$ -diene aromatic carboxylic ester monomers with high structural diversity. The monomers are suitable for thiol-ene click and ADMET polymerization to obtain new libraries of poly(thioether esters) and unsaturated polyesters with high molecular weights and satisfactory thermal properties as well as functional diversity, which open interesting possibilities for future applications. Furthermore, the functionality of the polyesters provides active sites for postpolymerization modification to produce a variety of new polymers with desirable properties and functionality. The applicability of both lignin-based and petroleum-based parahydroxy benzaldehyde derivatives demonstrated the potential of the strategy for sustainable polymer synthesis by enabling the use of other phenolic aldehydes and dithiols as well as different polymerization strategies.

### **Conflicts of interest**

There are no conflicts to declare.

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