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Renewable (semi)aromatic polyesters from symmetrical vanillin-based dimers

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Two symmetrical biphenyl monomers derived from vanillin, a methylated divanillyl diol and a methylated dimethylvanillate dimer, were synthesized and employed as (co)monomers for the design of renewable (semi)aromatic polyesters. The reactivity in polytransesterification of these new monomers was investigated in bulk in the presence of various catalysts. The polytransesterification between methylated divanillyl diol and a series of bio-based diesters having different chemical structures led to amorphous thermoplastic polyesters with glass transition temperatures ranging from –5 to 139 °C and thermal stability up to 350 °C.

Introduction

Aromatic compounds constitute basic chemicals to manufacture everyday life items. Indeed, they play a key role in pharmaceuticals, perfumes, dyestuff and polymer industries.[1] In polymeric backbones, aromatic units offer rigidity, hydrophobicity as well as fire resistance. For instance, aromatic polyesters, such as poly(ethyleneterephtalate)s (PET), have widespread commercial applications, especially in food packaging and textile field due to their good thermomechanical and barrier properties.[2]

In terms of sustainability, various reports have been recently carried out on the investigation of bio-based substitutes of aromatic petroleum-based compounds.[3, 4, 5, 6] The main source of aromatic compounds, which can be found in Nature is lignin. However, despite extensive researches, efficient recovering of aromatic products from lignin remains a challenge.[7] Nowadays, the only commercial process is the production of vanillin from lignosulfonates, formed as a by-product of the sulfite pulping industry.[8, 9] Due to its carbonyl and phenolic group, vanillin can be easily derivatized into interesting aromatic monomers.[10, 11]

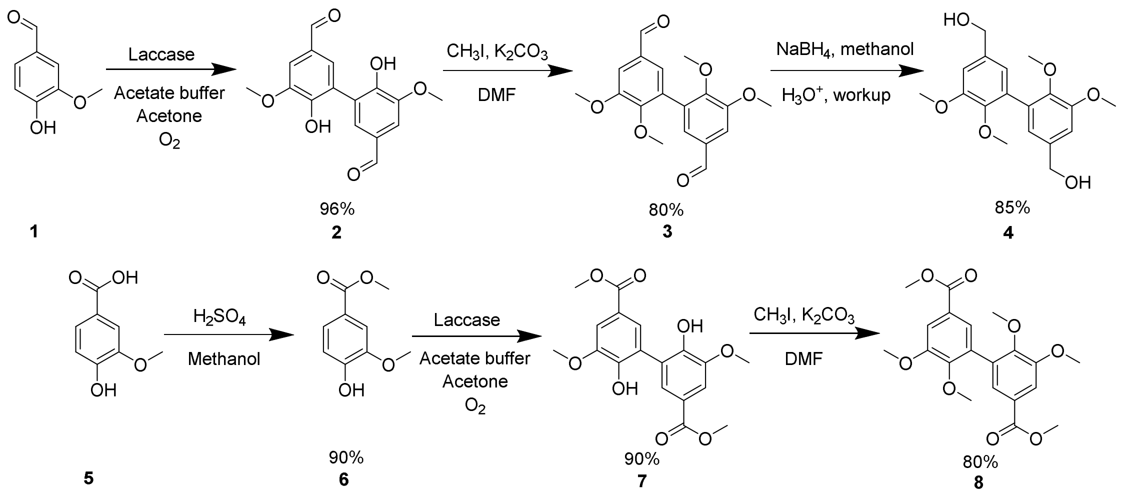
Pioneer work on the synthesis of polyesters from vanillin derivative, i.e. vanillic acid, and exhibiting thermomechanical properties similar to those of PET was reported in 1955.[12] Vanillic acid was also used as a comonomer in the synthesis of a multitude of thermotropic polymers, which exhibit liquid crystal formation in the melt form. Due to their high order and aromatic structure, such polymers possess high mechanical strength at high temperature, extreme chemical resistance and inherent flame retardancy.[13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23] Recently, with the increasing interest on renewable resources, several bio-based polymers were produced from vanillin or its derivatives. For instance, Ma and coworkers copolymerized the diester obtained by Williamson reaction of 1,4-dibromobutane and methylvanillate with vegetable oil-based polyols.[24] Meier and coworkers also reported the synthesis of 100% bio-based polymers from vanillin and vegetable oil derivatives by acyclic diene metathesis polymerization (ADMET), thiol-ene addition and polycondensation.[25] Allais and coworkers synthesized bisphenols by chemo-enzymatic coupling of ferulic acid with different diols and polymerized these building blocks by polycondensation or ADMET polymerization.[26, 27, 28, 29] Furthermore, Miller and coworkers used vanillin for the synthesis of renewable PET mimics.[30, 31]

Divanillin was also employed as building block for polymer synthesis. Razzaq and coworkers reported the synthesis of Schiff base polymers, exhibiting molar masses around 10 000 g/mol, by the reaction of divanillin with alkyl diamines, as well as the synthesis of polyvanillin by reductive coupling of the aldehyde group of divanillin through electrochemical polymerization.[32, 33] Divanillin was classically synthesized by oxidative phenol-coupling using iron(II) chloride ($FeCl_3$) or iron(II) sulfate ($FeSO_4$)[34, 35, 36, 37, 38, 39]. Nowadays, divanilllin can be produced by enzymatic pathways. Several studies on the dimerization of vanillin employing horseradish peroxidase and hydrogen peroxide were reported.[40, 41, 42, 43] The use of laccase as enzyme catalyst for oxidative coupling also attracted attention because such approach avoids the use of hydrogen peroxide. Thus, Beifuss and coll. employed laccase from *Trametes versicolor* to produce vanillidene derivative dimers with good yield and selectivity.[44] Also employing laccase from *Trametes versicolor* we recently developed an efficient enzymatic C-C coupling process –with a high yield and a high selectivity- yielding pure dimers of vanillin and some other phenol substrates.[45] Two of these symmetrical biphenyl monomers derived from vanillin, namely (i) a methylated divanillyl diol and (ii) a methylated dimethylvanillate dimer, have been tested in the present study as (co)monomers for the design of novel renewable (semi)aromatic polyesters. To this purpose, the conditions of polycondensation have been optimized. Indeed, a series of polyesters were prepared by polytransesterification of methylated divanillyl diol with various diesters having different aliphatic or aromatic structures. The thermomechanical and thermal properties of the resulting bio-based thermoplastic polyesters were investigated.

Results and Discussion

Synthesis of the monomers

The diol **4** and diester **8**, used as monomers in this study, were synthesized from vanillin, **1**, as a renewable resource (Scheme 1). On the one hand, vanillin was dimerized using a green process, employing a Laccase from *Trametes versicolor* as catalyst (see SI, Figures S1-S5). The phenols of the obtained divanillin **2** were then methylated yielding methylated divanillin **3** (see SI Figures S6-S8). Methylated divanillyl diol **4** was then prepared by reduction of **3** (see SI Figures S9-S11).[45]



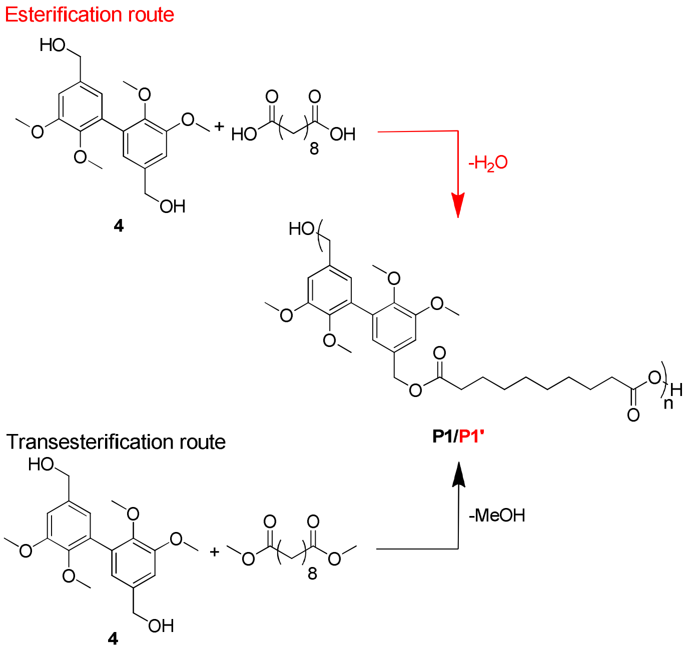
Scheme 1: Synthesis of methylated divanillyl diol **4** and methylated dimethyl divanillate **8** from vanillin with their respective yields

On the other hand, compound **5** is commercially available but can also be obtained by vanillin oxidation.[46] The carboxylic acid function of **5** was esterified into the methyl vanillate **6** (see SI Figures S12-S13). The latter was dimerized, employing the same enzymatic process as for the dimerization of vanillin, yielding the diester **7** (see SI, Figures S14-S17). Finally, the phenol groups of **7** were methylated yielding methylated dimethyl divanillate **8** (see SI Figures S18-

S20). The methylation of the phenol was performed before polymerization for two reasons: (i) the unprotected dimers were obtained as powders with lower degradation temperatures (around 200 °C) than melting temperatures thus impeding their polymerization in bulk (melting temperatures of methylated dimers: around 30 °C) and, (ii) the methylation reaction prevents the phenolic moiety to get involved during the polymerization.

Optimization of the bulk polymerization conditions

Polyesters can be produced either by esterification reaction of diols and diacids or by transesterification reaction between diols and diesters (Scheme 2). Preliminary, the reaction of **4** with dimethylsebacate and sebacid acid was investigated to produce **P1** and **P1'**, respectively. Titanium butoxide, Ti(OBu)$_4$, was employed as a catalyst at the concentration of 0.5 mol%, the temperature of polymerization was set at 200 °C. **P1** and **P1'** were characterized by means of FTIR spectroscopy; the latter display the same molecular structure (see Fig S21) but differ in terms of molar masses.



Scheme 2: Synthesis of polyester from vanillyl diol, **4**, and sebacic acid or dimethylsebacate.

Indeed, the molar masses of the resulting polyesters were determined by SEC analyses in DMF/DMSO 80/20 (w/w), using a PS calibration (Figure S22). **P1** exhibits a $\bar{M}_n$ of 65 000 g/mol and a dispersity of 2.1 whereas **P1'** shows a $\bar{M}_n$ of 20 000 g/mol and a dispersity of 1.7. While comparing the two routes, it appears that the transesterification method leads to polyesters with higher molar masses. This feature can be logically explained by the easier removal of methanol in comparison to water thus shifting more efficiently the reaction equilibrium towards the polymer. Consequently, all the polyesters described further in the study were synthesized by transesterification reaction.

Several polymerization reactions of methylated divanillyl diol **4** with dimethylsebacate were carried out employing different catalysts: triazabicyclodecene (TBD), titanium butoxide ($Ti(OBu)_4$), zinc acetate ($Zn(OAc)_2$), and dibutyltin oxide (DBTO). Molar masses of the resulting polyesters were compared with respect to the catalyst used (Table 1).

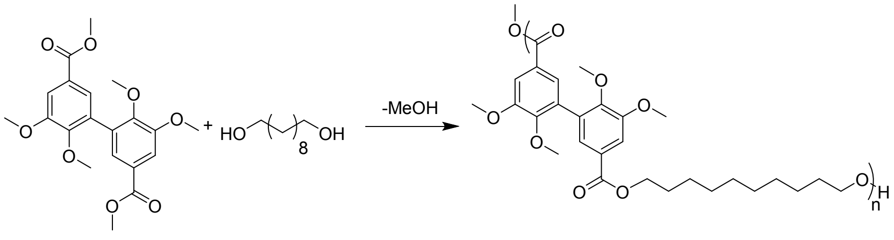
Table 1: Synthesis of polyesters from methylated divanillyl diol, **4**, and methyl sebacate in the presence of different catalysts.

Catalyst / conc.	Polymerization temperature (°C)	$\bar{M}_n$[a] (kg/mol)	Đ
TBD / 10 mol%	120	33	1.6
$Ti(OBu)_4$ / 0.5 mol%	200	65	2.1
$Ti(OBu)_4$ / 2 mol%	200	30	2.0
$Zn(OAc)_2$ / 2 mol%	200	43	1.8
DBTO / 2 mol%	200	44	1.9

[a]Determined by SEC in DMF/DMSO 80/20

Employing organocatalysts such as TBD generally requires higher catalyst loadings (10 mol%) in comparison to the transition metal-based catalysts (2 mol%) and lower polymerization temperature (120 °C) to avoid degradation/sublimation of the catalyst. In addition, a polyester sample was prepared with 0.5 mol.% of $TiOBu_4$, in order to investigate the influence of the catalyst concentration on the polymerization. It was observed that polyester molar masses decrease with the loading of $Ti(OBu)_4$. This reverse effect on the polymerization has already been observed in other studies reported in literature, for titanium alkoxide in general.[47, 48] $Zn(OAc)_2$ and DBTO presented lower catalytic activities, but the molar masses of the resulting polyesters remained high, at around 45 000 g/mol and the dispersity close to 2.0. TBD exhibited the lowest catalytic activity and produced polyesters with molar masses of 35 000 g/mol and a dispersity of 1.6.

A similar study on catalyst effect was conducted for the polymerization of methylated methyl vanillate **8** with 1,10-decanediol (Scheme 3, Table 2).



8

Scheme 3 Synthesis of polyester from methylated dimethyl divanillate, **8**, and 1,10-decanediol.

Table 2 Synthesis of polyesters from methylated dimethyl divanillate, **8**, and 1,10-decanediol in the presence of different catalysts.

Catalyst / conc.	**Polymerization temperature (°C)**	$\bar{M}_n$[a] **(kg/mol)**	**$Đ$**
TBD / 10 mol%	120	3	1.2
$Ti(OBu)_4$ / 0.5 mol%	200	20	1.8

$Ti(OBu)_4$ / 2 mol%	200	11	1.3
$Zn(OAc)_2$ / 2 mol%	200	3	1.1
DBTO / 2 mol%	200	12	1.6

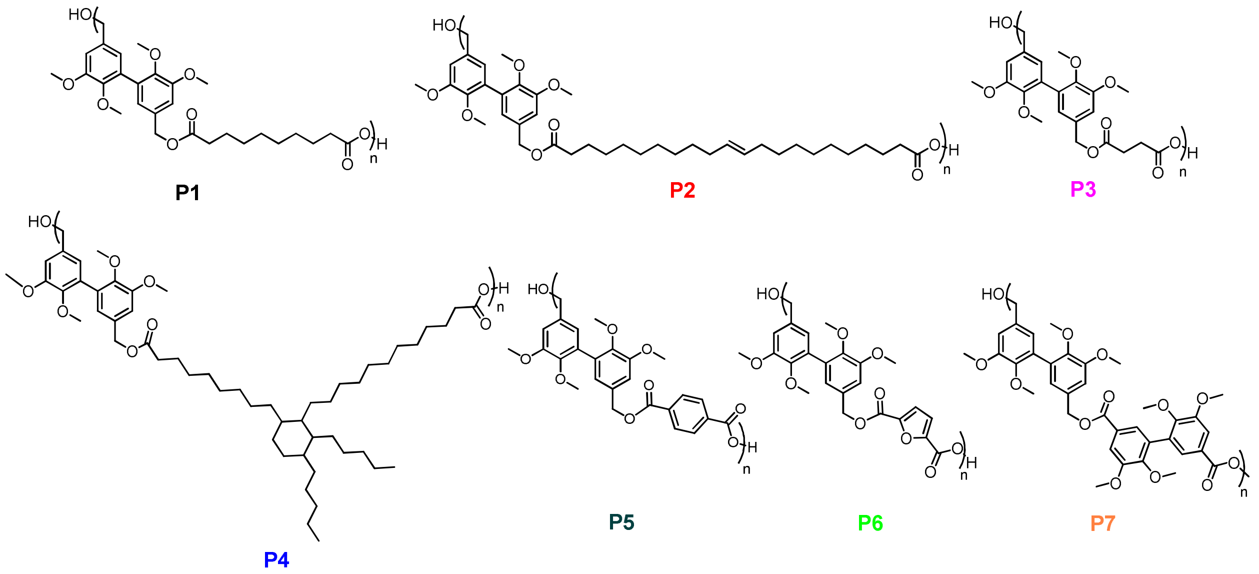
[a]Determined by SEC in DMF/DMSO 80/20

In such a case, a low catalytic activity of TBD and $Zn(OAc)_2$ was observed. Indeed, polyesters with a molar mass of 3 000 g/mol and a dispersity in the range of 1.1 to 1.2 were obtained. As previously, the polymerization with 0.5 mol.% of $Ti(OBu)_4$ afforded the highest molar mass, 20 000 g/mol, with a dispersity of 1.8.

The polyesters synthesized by polytransesterification of methylated dimethyl divanillate, **8**, with 1,10-decanediol exhibited lower molar masses than the polyesters prepared by polytransesterification of methylated divanillyl diol, **4**, with dimethylsebacate. This feature shows that methylated dimethyl divanillate, **8,** is less reactive toward polycondensation than the divanillyl diol, **4**. Indeed, the first reaction involves an aromatic ester and an aliphatic primary alcohol, whereas the second one involves an aliphatic ester and a benzyl alcohol. Aromatic esters are stabilized due to electronic effects, which lead to a decrease of reactivity in comparison to aliphatic esters. Moreover, **4** and **8** show different steric hindrances. Indeed, the ester moiety of **4** is closer to the aromatic ring than the benzyl alcohol group of **8**; it is thus more hindered and logically less reactive.

Synthesis and characterization of (semi)-aromatic polyesters

A series of polyesters were thus synthesized in the bulk based on methylated divanillyl diol, **4**, and several diesters with aromatic, aliphatic or cycloaliphatic structures using as catalyst $Ti(OBu)_4$ (0.5 mol%), in order to produce polymeric materials with a wide range of thermo-mechanical properties (Scheme 4). The copolymerization of **4** with dimethylsebacate, dimethylsuccinate and dimethyl-11-docosenoate produced polyesters **P1**, **P2** and **P3** with alternating aromatic and aliphatic sequences, the latter having different chain lengths. **P4** was synthesized by copolymerization of **4** with *Pripol 1009* (a fatty acid dimer from Croda), named **Pripol** in the following. The copolymerization of **4** with dimethyl terephtalate and with its common bio-based substitute, 2,5-furandimethylester, led to the aromatic polyesters **P5** and **P6**, respectively. Finally, an aromatic polyester, 100% derived from vanillin, **P7**, was prepared by polytransesterification of methylated divanillyl diol **4** and methylated dimethyl vanillate dimer **8**.



Scheme 4 Structures of polyesters synthesized from methylated divanillyl diol **4** and diesters with different structures in the presence of $Ti(OBu)_4$, 0.5mol.%.

Except **P1** that was characterized above, all the polyesters (**P2-P7**) were not soluble in any solvent impeding their characterization through NMR spectroscopy and SEC analysis. Thus, the chemical structure of these polyesters was determined by FTIR analyses. FTIR revealed the success of the transesterification reaction, i.e. full conversion, by: (i) the disappearance of broad peak between 3000 and 3500 cm^{-1}, characteristic for the hydroxyl stretching, whereas the typical C=C stretching vibration of the aromatic ring was found at 1 583 cm^{-1}, (ii) the presence of the C=O ester linkage at 1 730 cm^{-1} (Figure 1).

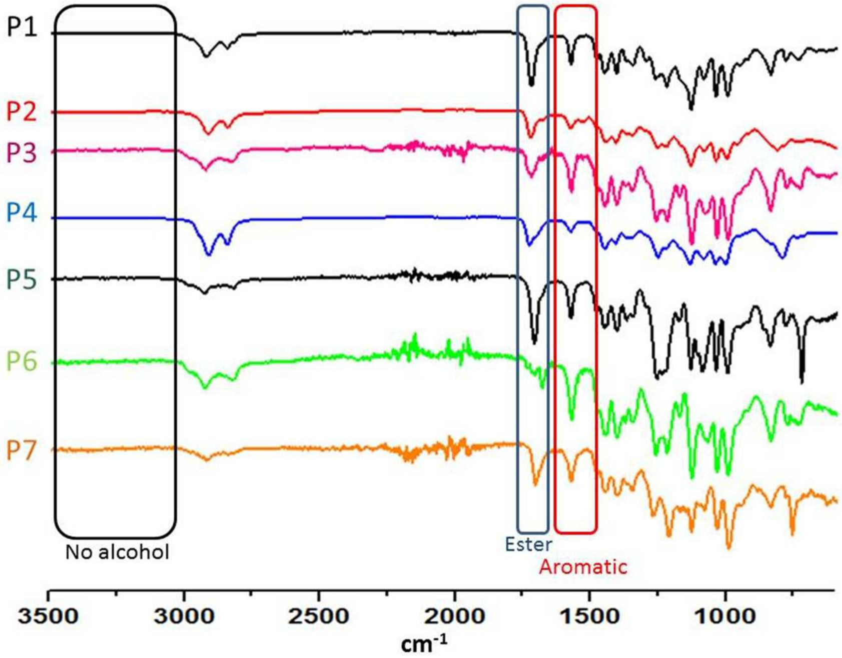


Figure 1 FTIR spectra of polyesters synthesized from methylated divanillyl diol **4** with different diesters, **P1** to **P7**.

The thermomechanical properties of the so-formed polyesters were determined by DSC, TGA and DMA. DSC traces did not show any melting transition between -70 and 200 °C (Figure 2). The polyesters displayed a glass transition temperature ranging from -5 to 139 °C, influenced by the structure of the co-monomer.

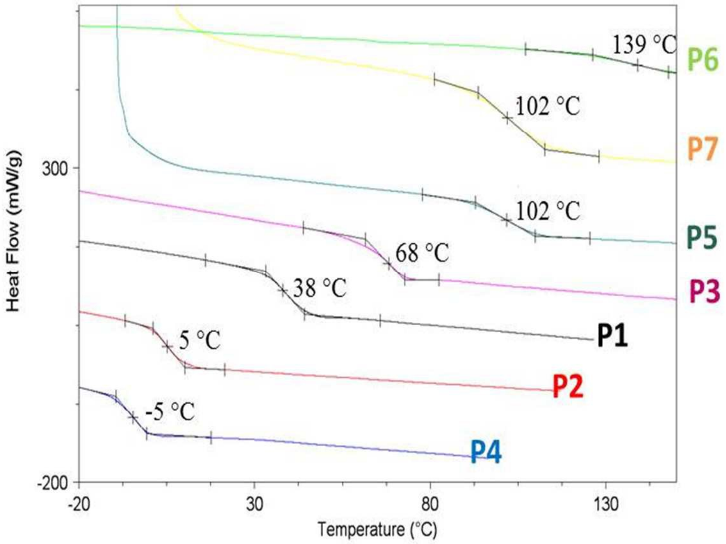


Figure 2 DSC traces (second heating cycle) of polyesters synthesized from methylated divanillyl diol **4** and different methyl diesters, **P1** to **P7**.

The absence of cristallinity of the polyesters so-formed is in agreement with the works of Miller and coworkers who showed the influence of methoxy groups attached to the aromatic ring. Indeed, the authors showed that polyacetals synthesized from vanillin derivatives are semi-crystalline while polyacetals from syringaldehyde are amorphous.[49] Indeed, the presence of two methoxy groups attached to the aromatic rings induces a higher free volume. This special disposition hinders the mobility and packing of the polymer chains, resulting in amorphous polymers.

Tg value depends on the molar mass and backbone flexibility of the polymer and also of the free volume. As expected, **P4,** which contains a ring with aliphatic dangling chains in the polymer backbone, exhibits the lowest glass transition temperature. The aromatic polyesters **P5**, **P6** and **P7**, exhibit the highest Tg of over 100 °C due to the inherent rigidity of the aromatic structures. In contrary, aliphatic chains give flexibility to the resulting polymers. Thus, the Tg of the semi-aromatic polymers **P2**, **P1** and **P3** ranged from 5 to 68 °C. Varying the aliphatic co-monomer structure allowed us tailoring the Tg of the resulting polyesters. In general, shorter aliphatic chains lead to polymer with higher Tg. Indeed, **P3** synthesized from the C4 diester exhibits a Tg higher than the one of **P2** synthesized from the C22 diester. Tg of **P5**, synthesized by copolymerization of methylated divanillyl diol, **4**, with dimethylterephtalate, and **P7**, synthesized by copolymerization of methylated divanillyl diol, **4**, with methylated dimethyl divanillate, **8**, are identical. Finally **P6,** synthesized by copolymerization of methylated divanillyl diol and 2,5-furandimethylester displays a remarkably high Tg of 139 °C. It is worth mentioning that differences in Tg values of **P5, P6** and **P7** can also be attributed to differences in molar masses.

TGA experiments were performed under air (Figure 3). All the copolymers presented a 5 wt% degradation temperature of over 300 °C except for **P3** for which the 5% weight loss occurred at 270 °C, phenomenon that may be explained by the presence of residual impurities. **P4**, obtained by copolymerization of divanillyl diol and **Pripol**, surprisingly exhibited at 347 °C, the highest 5% degradation temperature (Table 3). Such a high degradation temperature may be explained by a cross-linked structure due to the presence of some trimers in **Pripol** precursor. As a conclusion, all these biphenyl compounds, derived from vanillin, are excellent candidates for the synthesis of polyesters with high thermal stability.

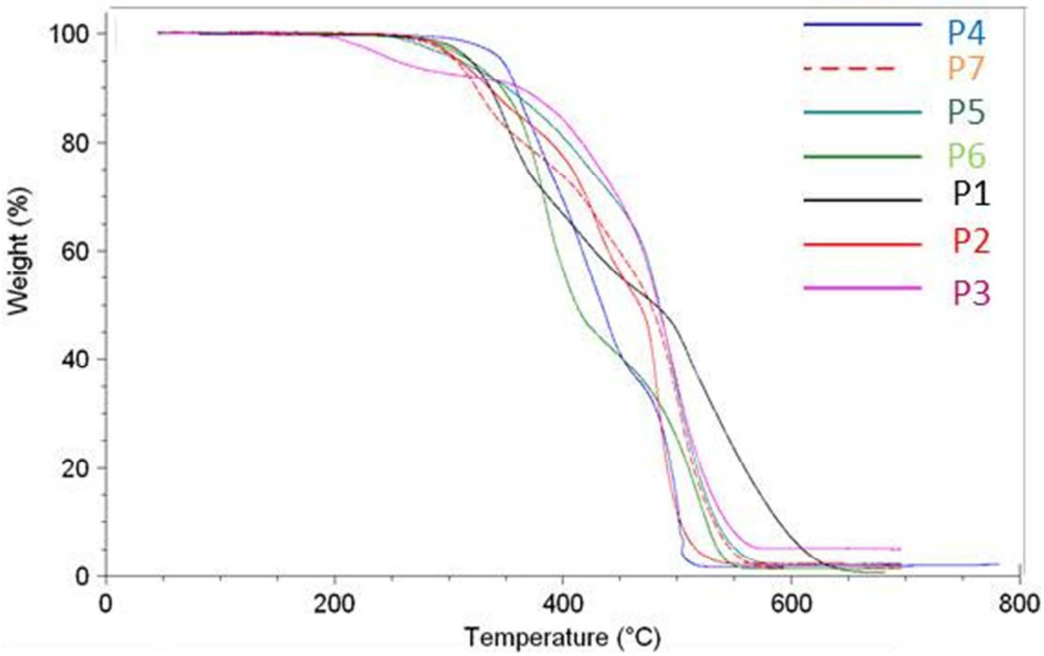


Figure 3: TGA thermogram (under air atmosphere) of polyesters synthesized from methylated divanillyl diol **4** and different methyl diesters.

The thermo-mechanical properties of the polyesters were also investigated by dynamical mechanical analyses (DMA) (see SI, Figure S23), performed on bar samples in a 3-point bending mode (Table 3). In agreement with DSC data, the decrease of the storage modulus was observed first for **P4,** then for the semi-aromatic polyesters **P2, P1** and **P3** and finally for the aromatic polyesters **P6**, **P5** and **P7**. The storage modulus in glassy state (E') of the semi-aromatic polyesters increases when the length of the aliphatic chain decreases, i.e. **P4** < **P2** < **P1**. **P3** and **P1** exhibits similar high storage modulus, in the range of 5-8 GPa. Unfortunately, the shape and thickness of the barrels could be not be well-defined, impeding in most cases a precise measurement of elastic modulus and Tα value.

Table 3: Thermo-mechanical properties of polyesters from methylated divanillyl diol, **4**, and different methyldiesters.

Polyester	**Tg (°C)**[a]	**Td5% (°C)**[b]	**Tα (°C)** [c]	**E' (GPa)**[c]
P1	38	319	42	8.1
P2	5	308	13	2.0
P3	68	270	72	5.1
P4	-5	347	8	0.1
P5	102	310	-	2.0
P6	139	342	-	1.4
P7	102	305	-	1.3

[a]Determined by DSC second heating cycle, [b] Temperature of 5% degradation [c]Determined by TGA, [c]Determined by DMA 3 point-bending mode

Conclusion

In conclusion, novel bio-based (semi)aromatic polyesters from original symmetrical vanillin-based dimers were synthesized. The experimental polymerization conditions were optimized in the bulk by polycondensation of the methylated divanillyl diol/dimethylsebacate system. Titanium butoxide at a loading of 0.5 mol.% was proven to produce the polyesters with the highest molar masses up to 65 000 g/mol, that exhibit a Tg of 38 °C, a storage modulus of 8.1 GPa and a Td5% of 319 °C. The same conditions were applied to the polymerization of methylated divanillyl diol with a series of bio-sourced diesters. Varying the structure of the diester allowed us tailoring the thermomechanical properties of the resulting polyesters, that all exhibit an amorphous morphology with a Tg ranging from -5 to 139 °C. The thermal stability of such (semi)aromatic polyesters is high with a 5% weight loss temperature over 300 °C. Such a new family of symmetrical aromatic monomers from vanillin clearly opens new perspectives in the challenging field of bio-based polymers. In addition, greener routes to phenol methylation still to be investigated together with the design of polyesters bringing free phenol functions, the latter giving additional properties to such materials.

Experimental Section

Material

2,5-Furandicarboxylic acid (98.0%), 1,10-diaminodecane, dimethylsebacate (97.0%) and were supplied by TCI Europe. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), zinc acetate (99.999%), sodium acetate (99%), acetic acid (99.7%), Laccase from *Trametes versicolor*, sulphuric acid (95%), iodomethane (99%), dibutyltin oxide (98%), succinic acid (99%), dimethyl succinate (98%), dimethyl terephthalate (98%) were purchased from Sigma Aldrich. Titanium butoxide (99%) was bought from Fisher. *Pripol* was supplied by Croda. Sodium borohydride (98%), vanillic acid (98%) were bought from Alfa Aesar. Potassium carbonate (99%) and terephtalic acid (98%) were supplied by Prolabo. All products and solvents (reagent grade) were used as received, unless mentioned explicitly.

Instrumentations

All NMR experiments were performed at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz, in DMSO. Infrared spectra were obtained on a Thermoscientific Nicolet iS10 spectrometer using the attenuated total reflection (ATR) mode. HPLC was performed using a Spectra system instrument fitted with a Phenomenex Luna 5µ C18 100A column and compounds were detected with a Sedere Sedex 85 LT ELSD detector at 40°C (G=4, filter OFF). These analyses were performed in acetonitrile at a flow rate of 1 mL/min. The spectra were acquired using 16 scans. Size exclusion chromatography (SEC) analyses were performed in DMSO/DMF (20/80) (80 °C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of three columns from PLgel (PLgel 5 µm Guard (guard column 7.5 mm ID x 5,0 cm L); PLgel 5 µm MIXED-D (7.5mm ID x 30,0 cm L) and PLgel 5µm MIXED-D (7,5 mm ID x 30,0 cm L)). The elution of the filtered samples was monitored using simultaneous refractive index and UV detection. The elution times were converted to molar mass using a calibration curve based on low dispersity (Mw/Mn) polystyrene (PS) standards. Differential Scanning Calorimetry (DSC) measurements were performed on DSC Q100 (TA Instruments). The sample was heated from −70 °C to 200 °C at a rate of 10 $°C.min^{-1}$. Consecutive cooling and second heating run were also performed at 10 $°C.min^{-1}$. The glass transition temperatures were calculated from the second heating run, the reported temperature is the value at the mid point. Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 $°C.min^{-1}$ under nitrogen or air atmosphere as mentioned in the manuscript. DMA RSA 3 (TA instrument). The sample temperature was modulated from -80 °C to 220 °C, depending on the sample at a heating rate of 5 °C/min. The measurements were performed in a 3-point bending mode at a frequency of 1 Hz, an initial static force varying between 0.1 and 0.5 N and a strain sweep of 0.1%.

Experimental procedure

Synthesis of methylvanillate (6)

Vanillic acid (**5**) (15.0 g, 0,09 mol) was dissolved in methanol (75 mL). Sulfuric acid (2.1 mL) was added and the mixture was stirred and warmed to reflux for 8 h. After evaporation of methanol, the solid was dissolved in ethylacetate (60 mL), washed with a

$NaHCO_3$ solution (30 mL), water (twice) and brine (once). The organic phase was evaporated under reduced pressure. Yield: 90%.

^1H NMR (400 MHz, $CDCl_3$, δ (ppm)): δ 7.45 (m, 2H, Ar), 6.88 (d, 1H, Ar), 3.81 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3 ester)

^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)): δ 166,03 (OCH_3 ester), 151.22 (Ar-C), 147.20 (Ar-C), 123.38 (Ar-C), 120.30 (Ar-C), 115.13 (Ar-C), 112.42 (Ar-C), 55.27 (OCH_3), 51.60 (OCH_3 ester)

General procedure for dimerization: synthesis of divanillin (2) and dimethyl divanillate (7)

A solution of phenol (**1**) or (**6**) (1.5 g) in acetone (20 mL) was added to NaOAc buffer (180 mL, 0.1 M, pH 5.0). The solution was saturated in O_2 for 5 min. Laccase from *Trametes versicolor* (20 U, 12.4 mg) was added and the reaction was stirred at room temperature for 24 h. The precipitate was filtered off the solution and the product dried overnight at 80 °C under vaccum.

Divanillin (**2**): yield: 96%

^1H NMR (400 MHz, $CDCl_3$, δ (ppm)): δ 9.85 (s, CHO), 7.50 (s, 2H Ar), 4.00 (s, OCH_3).

^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)): δ 191.04 (CHO), 150.70 (Ar-C), 147.95 (Ar-C), 128.30 (Ar-C), 127.69 (Ar-C),124.52 (Ar-C), 109.10 (Ar-C), 55.88 (OCH_3)

Dimethyl divanillate (**7**): yield: 90%, Td = 200 °C, no Tm

^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): δ 9.60 (s, 2H, HO), 7.46 (s, 4H, Ar), 3.90 (s, 6H, OCH_3), 3.80 (s, 6H, OCH_3 ester)

^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)): δ 166,04 (OCH_3 ester), 148.60 (Ar-C), 147.27 (Ar-C), 125.25 (Ar-C), 123.93(Ar-C), 119.21 (Ar-C), 110.89 (Ar-C), 55.97 (OCH_3), 51.75(OCH_3 ester)

General procedure for phenol methylation of (2) and (7): synthesis of methylated divanillin (3) and methylated dimethyl vanillate (8)

Bisphenol (**2**) or (7) (7.9 g of (**2**) or 9.4 g of (**7**), 26 mmol) was dissolved in DMF (120 mL). Potassium carbonate (15.2 g, 110 mmol) was added before a slow addition of iodomethane (9.6 mL, 158 mmol). After 15 h of stirring at 80 °C, the mixture was filtered and the resulting solution poured into cold water. The methylated compound, which precipitated was filtered off and dried under vacuum.

Methylated divanillin (**3**): yield: 80%

^{1}H NMR (400MHz, $CDCl_3$, δ (ppm)): δ 9.94 (s, CHO), 7.58 (s, 2H Ar), 7.55 (s, 2H Ar),3.95 (s, OCH3), 3.68 (s, OCH_3)

^{13}C NMR (400MHz, $CDCl_3$, δ (ppm)): δ191.83 (CHO), 152.80 (Ar-C), 151.21 (Ar-C), 131.90 (Ar-C), 131.58 (Ar-C), 125.96 (Ar-C), 111.14 (Ar-C), 60.47 (OCH3), 55.93 (OCH_3)

Methylated dimethyl divanillate (**8**): yield: 80%, Td=215 °C, Tm=33 °C

^{1}H NMR (400MHz, CDCl3, δ (ppm)): δ 7.59 (s, 2H Ar), 7.41 (s, 2H Ar),3.92 (s, OCH_3), 3.84 (s, OCH_3), 3.62 (s, OCH_3)

^{13}C NMR (400MHz, $CDCl_3$, δ (ppm)): δ 165.63 (OCH_3 ester), 152.16 (Ar-C), 149.95 (Ar-C), 131.19 (Ar-C),124.44(Ar-C), 123.81 (Ar-C), 112.43 (Ar-C), 60.38 (OCH_3), 55.7

Synthesis of methylated divanillyl diol (4)

Methylated divanillin (**3**) (6.6 g, 20 mmol) was dissolved in ethanol (100 mL). The flask was put in an ice bath and sodium borohydride (3.6 g, 100 mmol) was added slowly. Then the mixture was stirred at room temperature for 30 min. Water (45 mL) was added to stop the reaction and the solution is acidified with HCl to pH 7 and warmed for 5 min at 50 °C. The solvent was evaporated; the resulting solid was solubilized in dichloromethane and washed 3 times with water. Yield: 85%. Td=230 °C, Tm=26 °C

^{1}H NMR (400MHz, CDCl3, δ (ppm)): δ 6.99 (s, 2H Ar), 6.67 (s, 2H Ar), 5.15 (t, 2H OH), 4.47 (d, 4H CH_2OH), 3.83 (s, OCH_3), 3.51 (s, OCH_3)

^{13}C NMR (400MHz, $CDCl_3$, δ (ppm)): δ 151.93 (Ar-C), 144.86 (Ar-C), 137.52 (Ar-C), 132.14 (Ar-C), 120.27 (Ar-C), 110.20 (Ar-C), 62.69 (CH_2OH), 59.83 (OCH_3), 55.53 (OCH_3)

Polyester synthesis

Methylated divanillyl diol (1 equivalent) and diacid or diester (1 equivalent) were solubilized and stirred in a minimum amount of THF. THF was evaporated yielding a homogeneous mixture. The mixture was then stirred at 160 °C for 2 h under nitrogen flow and at 200 °C under vacuum for 6 h in the presence of 2 mol% of catalyst (titanium butoxide, zinc acetate or dibutyltin oxide) or in the presence of 0.5 mol% of titanium butoxide or stirred at 120 °C for 24 h in the presence of 10 mol% of TBD.

Supporting Information.

Supporting information is available and includes: ^{1}H NMR, ^{13}C NMR, HSQC, HMBC and mass spectra of the compounds, HPCL profile of the dimers, TGA thermogram DMA analysis and of the polyesters.

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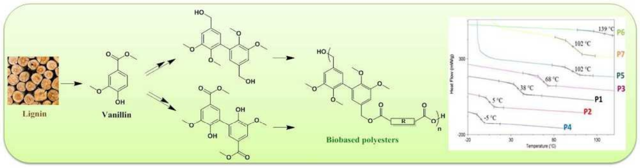

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