Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid

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Electronic Supplementary Information (ESI)

Electronic Supplementary Information (ESI) Available: Synthetic details and complete polymer characterization data.

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General Considerations and Instrumentation

Unless otherwise noted, all solvents were sparged with nitrogen, dried over molecular sieves using an MBraun Solvent Purification System, dispensed into oven-dried Straus flasks, and degassed by stirring under reduced pressure for 20 minutes. Toluene for polymerization reactions was distilled from sodium/benzophenone under a nitrogen atmosphere and stored in an oven-dried Straus flask until used. All other chemicals and solvents were used as received.

Proton nuclear magnetic resonance (1H NMR) spectra were recorded using a Varian Mercury 300 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or residual proton in the specified solvent. Coupling constants (J) are reported in Hertz (Hz). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintuplet; m, multiplet; br, broad.

Differential scanning chromatographs were obtained with a DSC Q1000 from TA instruments. About 5-10 mg of each sample were massed and added to a sealed pan that went through a heat/cool/heat cycle at 10°C/min. Reported data are from the second full cycle. The temperature range depends on the experiment, but was limited to 300°C by the instrument.

Thermogravimetric analyses were measured under nitrogen with a TGA Q5000 from TA Instruments. About 5-10 mg of each sample were heated at 50°C/min from 25-600°C.

Viscosity measurements were performed at 35°C in a 1:2 mixture of phenol:1,1,2,2 tetrachloroethane with a CANNON-Ubbelohde type 150 viscometer.

Monomer Synthesis

3-(4-acetoxy-3-methoxyphenyl)acrylic acid (acetyldihydroferulic acid)

30.04 g of vanillin (0.197 mol) and 26.0 g of sodium acetate (0.317 mol) were dissolved in 200 mL of acetic anhydride (2.12 mol). About 1 mL of pyridine was added to the flask and the mixture was heated to reflux. After 24h, the brown solution was poured over about 500 g of crushed ice and the solution was stirred until the appearance of a yellow-brown solid. The flask was left overnight in the freezer and the dark yellow solid was then obtained by filtration. The crude solid was recrystallized in from acetic acid/water to give 32.3 g of yellow beige solid in a 69% yield.

1H NMR (DMSO): δ 12.35 (br s, 1H, COOH), 7.56 (d, J = 15.9 Hz, 1H, Ar–H), 7.46 (d, J = 1.7 Hz, 1H, Ar–H), 7.24 (dd, J = 8.2 Hz, 1.7 Hz, 1H, Ar–H), 7.09 (d, J = 8.2 Hz, 1H, Ar–H), 6.56 (d, J = 15.9 Hz, 1H, CHCOOH), 3.8 (s, 3H, OCH3), 2.24 (s, 3H, CH3).

13C NMR (DMSO): δ 168.4, 167.6, 151.1, 143.4, 140.8, 138.3, 123.2, 121.3, 119.5, 111.8, 56.0, 20.4.

3-(4-acetoxy-3-methoxyphenyl)propanoic acid (acetyldihydroferulic acid)

15.0 g (0.064 mol) of acetylfuralic acid were dissolved in a mixture of 150:80 mL of tetrahydrofuran:methanol. The solution was placed in a Parr pressure reactor along with 1.5 g of 10% palladium over charcoal. The reaction was stirred at room temperature under 60 psi of hydrogen for 5h. The black solution was filtered through celite, effectively removing the palladium. The resulting clear brown solution was dried over magnesium sulfate and condensed in vacuo. The solid was then dissolved in tetrahydrofuran and crashed with hexanes giving 12.8 g of off-white product in 85% yield.

1H NMR (DMSO): δ 12.15 (br s, 1H, COOH), 6.98 (s, 1H, Ar–H), 6.93 (d, J = 7.9 Hz, 1H, Ar–H), 6.76 (d, J = 7.9 Hz, 1H, Ar–H), 3.72 (s, 3H, OCH3), 2.79 (t, J = 8.0 Hz, 2H, Ar–CH2), 2.53 (t, J = 8.0 Hz, 2H, CH2COOH), 2.20 (s, 3H, CH3).

13C NMR (DMSO): δ 174.1, 168.9, 150.8, 140.1, 137.8, 122.7, 120.3, 113.1, 55.9, 35.5, 30.5, 20.7.

3-(4-hydroxy-3-methoxyphenyl)propanoic acid (dihydroferulic acid)

8.0 g (0.034 mol) of acetyldihydroferulic acid and 4.7 g (0.118 mol) of sodium hydroxide were dissolved in 100 mL of water. The solution was refluxed for 5h. After cooling to room temperature, the aqueous solution was acidified with hydrochloric acid and extracted with dichloromethane. The organic layer was washed with brine and dried over magnesium sulfate and condensed in vacuo. The resulting clear yellow crude product that was dissolved in dichloromethane and crashed with excess hexanes. The work up gave 5.5 g of an off-white powder in 83% yield.

1H NMR (CDCl3): δ 6.87 (d, J = 8.0 Hz, 1H, Ar–H), 6.73 (br s, 1H, Ar–H), 6.71 (d, J = 8.0 Hz, 1H, Ar–H), 3.88 (s, 3H, OCH3), 2.90 (t, J = 7.8 Hz, 2H, Ar–CH2), 2.70 (t, J = 7.8 Hz, 2H, CH2COOH).

13C NMR (CDCl3): δ 179.2, 146.4, 144.1, 132.0, 120.8, 114.4, 110.9, 55.8, 36.0, 30.3.

Polymerizations

poly(3-(4-hydroxy-3-methoxyphenyl)propanoic acid) (poly(dihydroferulic acid), PHFA)
Table S1, Entry 1. 1.61 g (6.8 mmol) of acetyldihydroferulic acid were melted under nitrogen for 2h and vacuum was applied for 2h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid/dichloromethane and precipitated with methanol. 1.0 g of off-white product was obtained by filtration in 83% yield.

$^1$H NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 6.92 (m, 3H, Ar–H), 3.84 (s, 3H, OCH$_3$), 3.11 (m, 2H, CH$_2$), 3.00 (m, 2H, CH$_3$).
$^{13}$C NMR (DMSO): $\delta$ 176.1, 150.9, 140.6, 138.3, 123.2, 121.8, 113.9, 56.6, 36.2, 31.2.

Table S1, Entry 2. 1.61 g (6.8 mmol) of acetyldihydroferulic acid and 0.021 g (0.072 mmol) of antimony trioxide (1 mol%) were melted under nitrogen for 2h and vacuum was applied for 2h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid/dichloromethane and precipitated with methanol. 0.8 g of off-white product was obtained by filtration in 67% yield.

$^1$H NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 6.88 (m, 3H, Ar–H), 3.80 (s, 3H, OCH$_3$), 3.07 (m, 2H, CH$_2$), 2.96 (m, 2H, CH$_3$).
$^{13}$C NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 175.5, 150.4, 140.1, 137.8, 122.6, 120.0, 113.4, 56.1, 35.8, 30.7.

Table S1, Entry 3. 1.63 g (6.8 mmol) of acetyldihydroferulic acid and 0.018 g (0.082 mmol) of zinc diacetate dihydrate (1 mol%) were melted under nitrogen for 2h and vacuum was applied for 2h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid/dichloromethane and precipitated with methanol. 1.0 g of off-white product was obtained by filtration in 82% yield.

$^1$H NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 6.90 (m, 3H, Ar–H), 3.83 (s, 3H, OCH$_3$), 3.10 (m, 2H, CH$_2$), 2.99 (m, 2H, CH$_3$).
$^{13}$C NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 175.5, 150.4, 140.0, 137.7, 122.6, 121.1, 113.3, 56.0, 35.7, 30.7.

Table S1, Entry 4. 1.63 g (6.8 mmol) of acetyldihydroferulic acid and 0.018 g (0.082 mmol) of zinc diacetate dihydrate (1 mol%) were melted under nitrogen for 2h and vacuum was applied for 6h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid/dichloromethane and precipitated with methanol. 1.1 g of off-white product was obtained by filtration in 91% yield.

$^1$H NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 6.90 (m, 3H, Ar–H), 3.83 (s, 3H, OCH$_3$), 3.10 (m, 2H, CH$_2$), 2.99 (m, 2H, CH$_3$).
$^{13}$C NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 175.5, 150.4, 140.0, 137.7, 122.6, 121.1, 113.3, 56.0, 35.7, 30.7.

Table S1, Entry 5. 1.61 g (6.8 mmol) of acetyldihydroferulic acid and 0.017 g (0.077 mmol) of zinc diacetate dihydrate (1 mol%) were melted under nitrogen at 220-250°C for 2h and vacuum was applied for 6h leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid/dichloromethane and precipitated with methanol. 0.82 g of off-white product was obtained by filtration in 68% yield.

$^1$H NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 6.88 (m, 3H, Ar–H), 3.80 (s, 3H, OCH$_3$), 3.07 (m, 2H, CH$_2$), 2.96 (m, 2H, CH$_3$).
$^{13}$C NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 175.0, 150.4, 139.8, 137.7, 122.5, 121.0, 113.1, 56.0, 35.7, 30.7.

Table S1, Entry 6. 1.61 g (6.8 mmol) of acetyldihydroferulic acid and 0.017 g (0.077 mmol) of zinc diacetate dihydrate (1 mol%) were melted under nitrogen for 2h and vacuum was applied for 10 min, leaving a brown solid that was dissolved in a mixture of trifluoroacetic acid/dichloromethane and precipitated with methanol. 0.90 g of off-white product was obtained by filtration in 75% yield.

$^1$H NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 6.88 (m, 3H, Ar–H), 3.80 (s, 3H, OCH$_3$), 3.07 (m, 2H, CH$_2$), 2.96 (m, 2H, CH$_3$).
$^{13}$C NMR (CF$_3$COOD/CDCl$_3$): $\delta$ 176.0, 150.5, 140.4, 138.0, 122.8, 121.6, 113.7, 56.2, 35.9, 30.9.

**oligo(3-(4-hydroxy-3-methoxyphenyl)propanoic acid)**

(oligo(dihydroferulic acid))

Table S1, Entry 7. 1.61 g (8.2 mmol) of dihydroferulic acid and 0.0195g (0.067 mmol) of antimony trioxide (1 mol%) were heated under nitrogen for 5h and vacuum was applied for 6h. At the end of the 6h period, the product was still a brown melt in the flask. The product was dissolved in dichloromethane/trifluoroacetic acid and only 0.07g (5%) of product precipitated upon addition of methanol. The methanol was subjected to rotary distillation, leaving 1.5 g of brown, amorphous solid that was analyzed by GPC showing only low molecular weight material.
## Summary of Polymerization Data

**Table S1.** Polymerization results and characterization of poly(dihydroferulic acid), PHFA.

<table>
<thead>
<tr>
<th>entry</th>
<th>$T_p$ (°C)</th>
<th>catalyst$^a$</th>
<th>melt time (h)</th>
<th>vacuum time (h)</th>
<th>stirring stops (h)</th>
<th>yield (%)</th>
<th>$[\eta]^b$</th>
<th>$M_v^c$</th>
<th>DP$^d$</th>
<th>$M_n^d$</th>
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<td>2</td>
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<td>31</td>
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<td>n.d.</td>
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<td>630$^e$</td>
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<table>
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<tr>
<th>entry</th>
<th>$T_p$ (°C)</th>
<th>catalyst$^a$</th>
<th>melt time (h)</th>
<th>vacuum time (h)</th>
<th>stirring stops (h)</th>
<th>yield (%)</th>
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$^a$Catalyst loading = 1 mol%. $^b$Intrinsic viscosity measured with an Ubbelohde viscometer in a 1:2 solution of phenol/1,1,2,2-tetrachloroethane at 35°C. $^c$Intrinsic viscosity (mL/g) calculated with $[\eta] = 1.09 \times 10^{-2} M_v^{0.84}$. $^d$Degree of Polymerization measured by $^H$ NMR end group analysis. $^e$GPC analysis.

**Table S2.** Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) data for PHFA from Table S1, entries 1–6.$^a$

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<th>major $T_m$ (°C)</th>
<th>minor $T_m$ (°C)</th>
<th>$\Delta H$ melt (J/g)</th>
<th>$T_c$ (°C)$^a$</th>
<th>$\Delta H$ cryst (J/g)$^a$</th>
<th>$T$ 50% decomp. (°C)$^b$</th>
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$^a$Crystallization was observed on the cooling scan, but not the heating scan. $^b$The temperature at which 50% mass loss is observed. TGA was performed under nitrogen.

**Table S3.** Reference codes for samples from Tables S1 and S2.

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NMR Spectra

Figure S1. $^1$H NMR spectrum of 3-(4-acetoxy-3-methoxyphenyl)acrylic acid (acetylferulic acid).

Figure S2. $^{13}$C NMR spectrum of 3-(4-acetoxy-3-methoxyphenyl)acrylic acid (acetylferulic acid).
Figure S3. $^1$H NMR spectrum of 3-(4-acetoxy-3-methoxyphenyl)propanoic acid (acetyldihydroferulic acid).

Figure S4. $^{13}$C NMR spectrum of 3-(4-acetoxy-3-methoxyphenyl)propanoic acid (acetyldihydroferulic acid).
Figure S5. $^1$H NMR spectrum of 3-(4-hydroxy-3-methoxyphenyl)propanoic acid (dihyroferulic acid).

Figure S6. $^{13}$C NMR spectrum of 3-(4-hydroxy-3-methoxyphenyl)propanoic acid (dihyroferulic acid).
Figure S7. $^1$H NMR spectrum of PHFA (Table S1, entry 1).

Figure S8. $^{13}$C NMR spectrum of PHFA (Table S1, entry 1).
Figure S9. $^1$H NMR spectrum of PHFA (Table S1, entry 2).

Figure S10. $^{13}$C NMR spectrum of PHFA (Table S1, entry 2).
Figure S11. $^1$H NMR spectrum of PHFA (Table S1, entry 3).

Figure S12. $^{13}$C NMR spectrum of PHFA (Table S1, entry 3).
Figure S13. $^1$H NMR spectrum of PHFA (Table S1, entry 4).

Figure S14. $^{13}$C NMR spectrum of PHFA (Table S1, entry 4).
Figure S15. $^1$H NMR spectrum of PHFA (Table S1, entry 5).

Figure S16. $^{13}$C NMR spectrum of PHFA (Table S1, entry 5).
Figure S17. $^1$H NMR spectrum of PHFA (Table S1, entry 6).

Figure S18. $^{13}$C NMR spectrum of PHFA (Table S1, entry 6).
$^1$H NMR Assignment of PHFA

Figure S19. $^1$H NMR spectrum and assignment of PHFA (Table S1, entry 3).
Polymer Molecular Weight Analysis

**Viscosity measurements.** Intrinsic viscosity measurements were performed with an Ubbelohde viscometer. 15 mL of a 1:2 mixture of phenol:1, 1, 2, 2-tetrachloroethane were poured in the viscometer and allowed to thermally equilibrate (35 °C) for 2h. Exactly 1 mL of about 8 g/L solution of polymer was added for each measurement until the final volume is 20 mL in the viscometer giving a final concentration of about 2 g/L.

\[
\eta = \lim_{c \to 0} \frac{\eta_{sp}}{c} \quad \text{with} \quad \eta_{sp} = \frac{t - t_0}{t_0}
\]

By creating a Kramer plot and extrapolating to infinitely dilute solution (c \(\to\) 0), we can obtain the intrinsic viscosity. The value is then related to the Mark-Houwink constant for PET in the same solvent and temperature [K. Kamide, Y. Miyazaki and H. Kobayashi, Polym. J., 1977, 9, 317-327].

\[
[\eta] = 1.09 \times 10^{-2} M_v^{0.84}
\]

**End group analysis.** End group analysis is one way to determine the number average molecular weight of a polymer. In an NMR analysis, the chemical environment for the end group is different from that of the repeat unit in the middle of the polymer chain. For polymers 2.22-2.27 the end groups will be a carboxylic acid and the acetyl group, which bears a methyl group that has a chemical shift of about 2.4 ppm. Four aliphatic hydrogens, associated with each repeat unit of the chain, resonate near 2.9 to 3.1 ppm.

![Figure S20](image)

**Figure S20.** End group analysis for molecular weight determination.

By measuring the integration of the methyl group hydrogens (I_{end}) by ^1H NMR and that of the methylene hydrogens (I_n) present in each repeat unit, we can obtain the number of repeat units (the degree of polymerization, DP) in the polymer chain with the following equation.

\[
DP = \frac{3}{4} \times \frac{I_n}{I_{end}} \quad \text{and} \quad M_n = RU \times DP
\]
**Differential Scanning Calorimetry (DSC) Thermograms**

The first heating and cooling pass of the DSC is shown by the dashed blue line. A second heating cycle is shown by the solid green line. Thermal analysis is calculated for the second scan, except for the crystallization event, which occurred during the first cooling cycle.

![DSC thermogram of PHFA](image)

**Figure S21.** DSC thermogram of PHFA (Table S1, entry 1).
Figure S22. DSC thermogram of PHFA (Table S1, entry 2).
Figure S23. DSC thermogram of PHFA (Table S1, entry 3).
**Figure S24.** DSC thermogram of PHFA (Table S1, entry 4).
Figure S25. DSC thermogram of PHFA (Table S1, entry 5).
Figure S26. DSC thermogram of PHFA (Table S1, entry 6).
Thermogravimetric Analysis (TGA)

Figure S27. TGA analysis of PHFA (Table S1, entry 1).
**Figure S28.** TGA analysis of PHFA (Table S1, entry 2).
Figure S29. TGA analysis of PHFA (Table S1, entry 3).
**Figure S30.** TGA analysis of PHFA (Table S1, entry 4).
Figure S31. TGA analysis of PHFA (Table S1, entry 5).
Figure S32. TGA analysis of PHFA (Table S1, entry 6).