Supplementary Information

Spectral data for polymers **2a**-**2c**

Polymer **2a**: ^{1}H-NMR (DMSO-d_6): 3.20 (Cγ-H*t*), 3.47-3.63 (Cγ-H), 3.70 (OCH_3), 4.28 (Cβ-H), 4.58 (Cγ-OH), 4.75 (Cα-H), 5.33 (Cα-OH), 6.68 (C5′-H), 6.77 (C6′-H), 6.85 (C6-H), 6.94 (C5-H), 7.00 (C2′-H), 7.02 (C2-H); ^{13}C-NMR (DMSO-d_6): δ 55.5 (OCH_3), 59.8 (γe), 59.9 (γt), 70.8 (αt), 71.4 (αe), 83.6 (βe), 84.4 (βt), 111.3 (2*t*), 111.7 (2*e*), 114.5 (5*t*), 115.0 (5*e*), 118.7 (6*t*), 119.1 (6*e*), 133.1 (1′), 134.7 (1*t*), 135.0 (1*e*), 145.2 (4′), 146.7 (4*e*), 147.0 (4*t*), 148.9 (3); 1′, 2′, 4′, 5′, 6′: phenolic end units; *e*: *erythro*, *t*: *threo*.

Polymer **2a** (acetate): ^{1}H-NMR ($CDCl_3$): δ 2.00, 2.06 (s, α, γ-OCOC$\underline{H}_3$), 2.29 (s, Ph-OCOC$\underline{H}_3$), 3.81 (s, OC$\underline{H}_3$), 3.95 (Cγ-H*t*), 4.14 (Cγ-H*e*), 4.24 (Cγ-H*t*), 4.37 (Cγ-H*e*), 4.61 (Cβ-H*t*), 4.67 (Cβ-H*e*), 6.00 (Cα-H*e*), 6.05 (Cα-H*t*), 6.85 (C5-H), 6.90 (C6-H), 7.03 (C2-H); ^{13}C-NMR ($CDCl_3$): δ 20.8, 21.0 (OCO$\underline{C}H_3$), 55.9 (OCH_3), 62.4 (γe), 63.1 (γt), 73.9 (αe), 74.7 (αt), 79.7 (βe), 80.1 (βt), 111.5 (2*t*), 111.9 (2*e*), 118.2 (5), 119.4 (6*t*), 119.7 (6*e*), 131.0 (1*t*), 131.3 (1*e*), 147.0 (4), 150.3 (3*t*), 150.6 (3*e*), 168.5 (Ph-O$\underline{C}OCH_3$), 169.5 (α-O$\underline{C}OCH_3$), 170.5 (γ-O$\underline{C}OCH_3$); *e*: *erythro*, *t*: *threo*.

Polymer **2b**: ^{1}H-NMR (DMSO-d_6): δ 3.23 (Cγ-H*t*), 3.39 (Cγ-H*e*), 3.65 (Cγ-H*t*), 3.73 (Cγ-H*e*), 3.72, 3.73, 3.74, 3.75 (OCH_3), 4.02 (Cβ-H*t*, Cγ-OH*e*), 4.12 (Cβ-H*e*), 4.34 (Cγ-OH*t*), 4.87 (Cα-H*e*), 4.90 (Cα-H*t*), 5.10 (Cα-OH*t*), 5.30 (Cα-OH*e*), 6.70 (C2-H*e*, C6-H*e*), 6.78 (C2-H*t*, C6-H*t*); ^{13}C-NMR (DMSO-d_6): δ 55.9 (OCH_3), 59.6 (γe), 60.1 (γt), 71.5 (αt), 72.2 (αe), 86.0 (βe), 86.7 (βt), 104.3 (2, 6), 134.2, 134.3 (4*e*), 134.7, 134.8 (4*t*), 137.8 (1*t*), 138.0, 138.1 (1*e*), 147.4 (3′, 5′), 152.0, (3*t*, 5*t*), 152.1 (3*e*, 5*e*); 3′, 5′: phenolic end units; *e*: *erythro*, *t*: *threo*.

Polymer **2b** (acetate): ^{1}H-NMR ($CDCl_3$): δ 1.90, 1.92, 1.95, 2.02, 2.08, 2.14 (s, α, γ-OCOC$\underline{H}_3$), 2.32 (s, Ph-OCOC$\underline{H}_3$), 3.76, 3.79 (s, OC$\underline{H}_3$), 3.85 (Cγ-H*t*), 4.17 (Cγ-H*e*), 4.31 (Cγ-H*t*), 4.42 (Cγ-H*e*), 4.52 (Cβ-H*t*), 4.59 (Cβ-H*e*), 6.00 (Cα-H*e*), 6.08 (Cα-H*t*), 6.61 (C2-H, C6-H); ^{13}C-NMR ($CDCl_3$): δ 20.7, 20.8, 20.9, 21.1 (OCO$\underline{C}H_3$), 56.1 (OCH_3), 62.8 (γe), 63.8 (γt), 74.6, 74.7 (αe), 76.2 (αt), 80.7 (β), 104.5 (2, 6), 132.8 (1*t*), 133.2 (1*e*), 135.0, 135.3, 136.4, 136.6, 136.8 (4), 152.8, 153.1, 153.2 (3, 5), 168.4 (Ph-O$\underline{C}OCH_3$), 169.8 (α-O$\underline{C}OCH_3$), 170.6, 170.8 (γ-O$\underline{C}OCH_3$); *e*: *erythro*, *t*: *threo*.

Polymer **2c**: ^{1}H-NMR (DMSO-d_6): δ 1.64, 1.73 (Cβ''-H), 3.21 (Cγ-H*t*), 3.39 (OCH_3), 3.50-3.66 (Cγ-H), 4.29 (Cβ-H), 4.55 (Cα''-H), 4.68 (Cγ-OH), 4.73 (Cα-H), 5.38 (Cα-OH), 6.68 (C3′-H, C5′-H), 6.85 (C3-H*e*, C5-H*e*), 6.91 (C3-H*t*, C5-H*t*), 7.25 (C2-H, C6-H); ^{13}C-NMR (DMSO-d_6): δ 42.4 (β''), 58.1 (γ''), 59.8 (γe), 59.9 (γt), 69.3 (α''), 70.9 (αt), 71.2 (αe), 83.1 (β), 114.5 (3′, 5′), 115.4 (3*t*, 5*t*), 115.5 (3*e*, 5*e*), 126.6 (2″, 6″), 127.7 (2*t*, 6*t*), 127.9 (2*e*, 6*e*), 132.7 (1′), 134.1 (1*t*), 134.3 (1*e*), 138.4 (1″), 156.3 (4′), 157.7 (4*e*), 158.0 (4*t*); 1′, 3′, 4′, 5′: phenolic end units; 1″, 2″, 6″, α'', β'', γ'': non-phenolic end units; *e*:

erythro, *t*: *threo*.

Polymer **2c** (acetate): ^{1}H-NMR ($CDCl_3$): δ 1.99, 2.04 (s, α, γ-OCOC$\underline{H}_3$), 2.28 (s, Ph-OCOC$\underline{H}_3$), 3.94 (Cγ-H*t*), 4.14 (Cγ-H*e*), 4.20 (Cγ-H*t*), 4.31 (Cγ-H*e*), 4.73 (Cβ-H), 5.80 (Cα''-H), 5.98 (Cα-H*e*), 6.01 (Cα-H*t*), 6.91 (3*e*, 5*e*), 6.98 (3*t*, 5*t*), 7.08 (3′, 5′), 7.31 (2*e*, 6*e*), 7.34 (2*t*, 6*t*), 7.40 (2′, 6′); ^{13}C-NMR ($CDCl_3$): δ 20.7, 21.0 (OCO$\underline{C}H_3$), 35.1 (β''), 60.7 (γ''), 62.3 (γe) 62.8 (γt), 72.4 (α''), 73.8 (αe), 74.1 (αt), 78.1 (β), 116.4 (3*t*, 5*t*), 116.6 (3*e*, 5*e*), 121.7, 121.9 (3′, 5′), 128.0 (2″, 6″), 128.5 (2′, 6′) 128.9 (2, 6), 129.4 (1*t*), 129.5 (1*e*), 133.7 (1′), 150.8, 150.9 (4′), 158.2 (4*e*), 158.6 (4*t*), 168.7 (Ph-O$\underline{C}$OCH$_3$), 169.6, 169.8 (α-O$\underline{C}$OCH$_3$), 170.7 (γ-O$\underline{C}$OCH$_3$); 1′, 2′, 3′, 4′, 5′, 6′: phenolic end units; 2″, 6″, α'', β'', γ'': non-phenolic end units; *e*: *erythro*, *t*: *threo*.

A typical synthetic procedure for monomer **a**

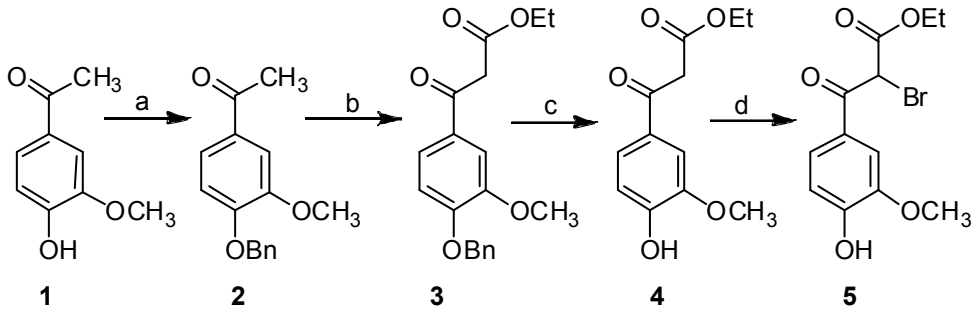
Compound **2**: To a stirred solution of compound **1** (16.6 g, 0.1 mol) in DMF (150 mL), benzyl chloride (13.8 mL, 0.12mol), potassium carbonate (21 g, 0.15 mol) and tetra-*n*-butyl ammonium iodide (3.69 g, 0.01 mol) were added at room temperature. The reaction mixture was kept at room temperature over night. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, and concentrated to dryness in *vacuo*. The product was recrystallized from ethanol/hexane (1/4, *v*/*v*) to afford colourless crystals.

Compound **3**: To a stirred suspension of sodium hydride (6g, 60-72% suspension in mineral oil) in anhydrous toluene (60 mL), ethyl carbonate (12.1 ml, 0.1 mol) was added at room temperature. Compound **2** (12.8 g, 50.0 mmol) in anhydrous toluene (60 mL) was added dropwise to the reaction mixture over a period of 2.5 h under reflux. After stirring for 0.5h under reflux, the reaction mixture was cooled to room temperature, and acetic acid was added until the mixture became neutral. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, and concentrated to dryness in *vacuo*. The product was triturated with hexane to afford a solid. The product was recrystallized from ethanol to afford crystals (13.57 g, 82.8%).

Compound **4**: A stirred solution of compound **3** (2.835 g) in ethanol (60 mL) was treated with 10% palladium carbon (300 mg) under H_2 at 0 °C for 2.5 h. The reaction mixture was filtered and concentrated to dryness *in vacuo*. The product was purified on a silica gel column with ethyl acetate/hexane (1/2, *v*/*v*) to afford a syrup (**4**, 2.00 g, 97.2%).

Ethyl 2-bromo-3-(4-hydroxy-3-methoxyphenyl)-3-oxopropanoate (**5**): To a stirred solution of compound **4** (2.10 g, 8.82 mmol) in chloroform (10 ml), a diluted solution of bromine (1.48 g, 9.26 mmol) in chloroform (10 ml) was added dropwise over a period of 2.5 h at

-5 °C. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, and concentrated to dryness in *vacuo*. The product was purified on a silica gel column with chloroform to afford colourless crystals (**5**, 2.31g, 82.6%). The crystals were further recrystallized from ethanol/hexane for polymerization in order to remove impurity completely: ^{1}H-NMR ($CDCl_3$): δ 1.26 (t, 3H, J = 7.1, OCH_2CH_3), 3.96 (s, 3H, OCH_3), 4.28 (q, 2H, J = 7.1, OCH_2CH_3), 5.63 (s, 1H, Cβ-H), 6.97 (d, 1H, J = 8.6, C5-H), 7.56-7.59 (m, 2H, C2-H, C6-H).

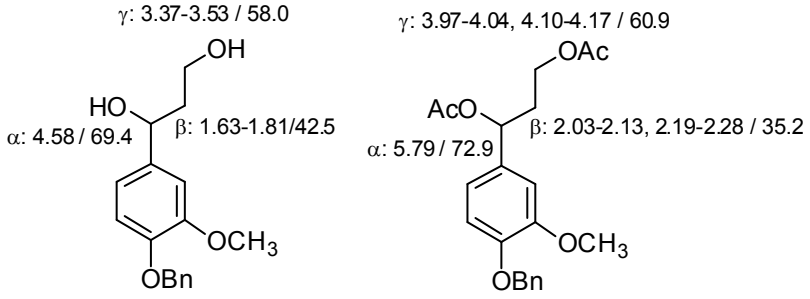


1 **2** **3** **4** **5**

Spectral data for non-phenolic end model compound **6**

Compound **6**: ^{1}H-NMR (DMSO-d_6): 1.63-1.81 (m, 2H, Cβ-H), 3.37-3.53 (m, 2H, Cγ-H), 3.76 (s, 3H, OCH_3), 4.39 (t, 1H, J = 5.0, Cγ-OH), 4.58 (m, 1H, Cα-H), 5.03 (d, 1H, J = 4.8, Cα-OH), 5.05 (s, 2H, C$\underline{H}_2$Ph), 6.79 (dd, 1H, J = 1.8, J = 8.2, C6-H), 6.94 (br s, 1H, C2-H), 6.95 (d, 1H, J = 8.2, C5-H), 7.29-7.45 (m, 5H, aromatics); ^{13}C-NMR (DMSO-d_6): δ 42.5 (β), 55.5 (OCH_3), 58.0 (γ), 69.4 (α), 70.0 (C$\underline{H}_2$Ph), 109.9, 113.4, 117.6, 127.7, 127.7, 128.4, 137.3, 139.6, 146.4, 148.9 (aromatics).

Compound **6** (acetate): ^{1}H-NMR ($CDCl_3$): δ 2.03, 2.06 (s, 6H, α, γ-OCOC$\underline{H}_3$), 2.03-2.13, 2.19-2.28 (m, 2H, CβH), 3.90 (s, 3H, OC$\underline{H}_3$), 3.97-4.04, 4.10-4.17 (m, 2H, Cγ-H), 5.14 (s, 2H, C$\underline{H}_2$Ph), 5.79 (dd, 1H, J = 5.8, J =8.2, Cα-H), 6.82-6.89, 7.27-7.44 (aromatics); ^{13}C-NMR ($CDCl_3$): δ 21.1, 21.4 (OCO$\underline{C}H_3$), 35.2 (β), 56.2 (OCH_3), 60.9 (γ), 71.2 ($\underline{C}H_2$Ph), 72.9 (α), 110.5, 113.9, 119.2, 127.4, 128.0, 128.7, 133.0, 137.2, 148.3, 149.8 (aromatics), 170.4, 171.1 (α, γ-O$\underline{C}OCH_3$).



6 **6** acetate

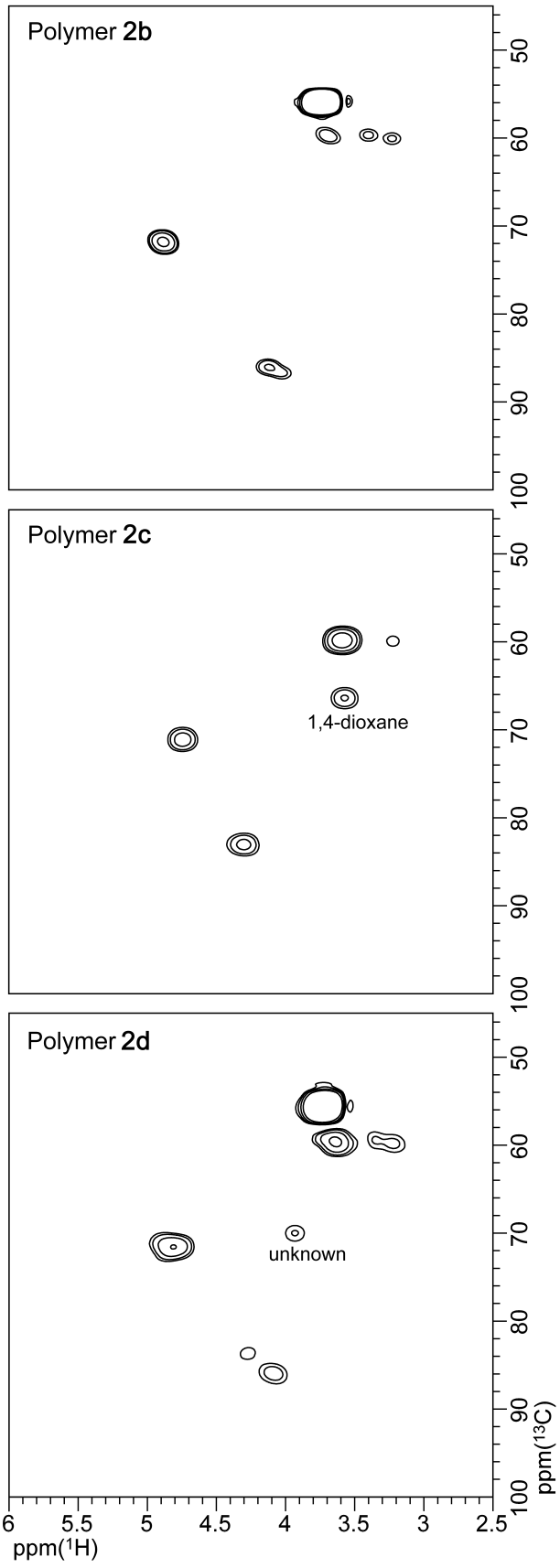


Fig. HMQC spectra of polymers **2b**-**2d** in DMSO-d_6