

Supporting Information to

Near-Ultraviolet Circular Dichroism of Achiral Phenolic Termini Induced by Nonchromophoric Poly(L,L-lactide) and Poly(D,D-lactide)

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1. Experimental procedure

1-1. Materials

L,L-lactide (LLA; Musashino Chemical Laboratory, Ltd., Japan) and D,D-lactide (DLA; Musashino Chemical Laboratory, Ltd., Japan) were recrystallized from ethyl acetate/*n*-hexane and cooled in a freezer at -20 °C. Then the obtained crystal was filtered, and dried under vacuum at room temperature. Vanillin, ethyl vanilate, 3-ethoxy-4-hydroxybenzaldehyde (ethyl vanillin), syringaldehyde, 4-fluorophenol, 4-tert-butylphenol, guaiacol, 4-amyphenol, and 4-chlorophenol were purchased from Tokyo Chemical Industry, Ltd., Japan. Methanol, chloroform, spectroscopic grade chloroform, 1-dodecanol, anhydrous toluene, and CHCl₃ (chloroform, super dehydrated, amylene added) were purchased from Wako Pure Chemical Industries, Ltd., Japan. Vanillin, ethyl vanilate, ethyl vanillin, syringaldehyde, 4-fluorophenol, 4-tert-butylphenol, methanol, chloroform, tetrahydrofuran (THF), and spectroscopic grade chloroform were used without purification. Anhydrous toluene was also dried by 4 Å molecular sieves (Nacalai tesque, Inc., Japan) under nitrogen atmosphere. Guaiacol, 4-amyphenol, 4-chlorophenol, and 1-dodecanol were distilled from 4 Å molecular sieves as a drying agent under nitrogen gas before use. Additionally 4 Å molecular sieves was used under vacuum at 200 °C for 24h.

1-2. Measurements

The number average of molecular weight of PLA was determined by size exclusion chromatography (SEC). A JASCO Chem NAV system was used with polystyrene standards at 40 °C, equipped with PU-2080, AS-2055, CO-2065, and RI-2031. Two commercial columns (TSKgel SuperH4000 and TSKgel GMH_{XL}) were connected in series and THF was used as an eluent. ¹H NMR spectra were measured with a NMR spectrometer (JEOL ECA-600) at 600 MHz. CD/UV spectral measurements were conducted at 20 °C using a J-820 spectropolarimeter (JASCO, Tokyo, Japan) equipped with Peltier-controlled thermostat (PTC-423L) housing unit using a SQ-grade cuvette, with a path length of 10 mm, PMT response of slow mode, a scanning rate of 50 nm min⁻¹, bandwidth of 4 nm, 1 nm interval data sampling, and a single accumulation. Fluorescent spectra were measured on a JASCO FP-6600 spectrofluorometer under a scanning rate of 50 nm min⁻¹, bandwidths of 10 nm (excitation) and 5nm (emission) for PL measurement, bandwidths of 5 nm (excitation) and 10 nm (emission) for PLE measurement, response time of 2 s, PMT gain high, and 0.5 nm interval data sampling at 20 °C. CPL/PL spectra were measured at 20 °C using a JASCO CPL-200 spectrofluoropolarimeter (JASCO, Tokyo, Japan) equipped with a Peltier-controlled housing using the SQ-grade quartz cuvette under a single accumulation, a path length of 10 mm, a bandwidth for excitation of 3000 μm, a bandwidth for CPL measurement of 3000 μm, a scanning rate of 50 nm min⁻¹, 1 nm interval data sampling, a response time of 8 s, and 280 nm excitation wavelength.

1-3. Synthesis of poly(L,L-lactide)-vanillin (PLLA-vanillin) (1) and poly(D,D-lactide)-vanillin (PDLA-vanillin) (2)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) and vanillin (0.053 g, 0.35 mmol) were dried under vacuum, and purged with nitrogen for three times. Then 2.2 ml of 1 vol% SnOct₂ (69 μ mol) in dry toluene solution was combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-vanillin was synthesized in a similar way as PLLA-vanillin. By changing the molar ratio of the vanillin initiator against the LLA monomer and DLA monomer, the three molecular weights of PLLA-vanillin were obtained (**1**, **1a**, **1b**, **2**, **2a**, and **2b** listed in Table S1). **1** (Yield: 89%, $M_n = 11400 \text{ g mol}^{-1}$, $M_w/M_n = 1.97$). **1a** (Yield: 58%, $M_n = 8600 \text{ g mol}^{-1}$, $M_w/M_n = 1.51$). **1b** (Yield: 41%, $M_n = 3600 \text{ g mol}^{-1}$, $M_w/M_n = 1.64$). **2** (Yield: 88%, $M_n = 16800 \text{ g mol}^{-1}$, $M_w/M_n = 1.95$). **2a** (Yield: 61%, $M_n = 10400 \text{ g mol}^{-1}$, $M_w/M_n = 1.51$). **2b** (Yield: 41%, $M_n = 4000 \text{ g mol}^{-1}$, $M_w/M_n = 1.55$).

1-4. Synthesis of poly(L,L-lactide)-guaiacol (PLLA-guaiacol) (3) and poly(D,D-lactide)-guaiacol (PDLA-guaiacol) (4)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) was dried under vacuum, and purged with nitrogen for three times. Then guaiacol (0.038 ml, 0.35 mmol), 2.2 ml of 1 vol% SnOct₂ (69 μ mol) in dry toluene solution were combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-guaiacol was synthesized in a similar way as PLLA-guaiacol. **3** (Yield: 91%, $M_n = 12900 \text{ g mol}^{-1}$, $M_w/M_n = 1.6$). **4** (Yield: 91%, $M_n = 10900 \text{ g mol}^{-1}$, $M_w/M_n = 1.63$).

1-5. Synthesis of poly(L,L-lactide)-ethyl vanilate (PLLA-ethyl vanilate) (5) and poly(D,D-lactide)-ethyl vanilate (PDLA-ethyl vanilate) (6)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) and ethyl vanilate (0.068 g, 0.35 mmol) were dried under vacuum, and purged with nitrogen for three times. Then 2.2 ml of 1 vol% SnOct₂ (69 μ mol) in dry toluene solution was combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-ethyl vanilate was synthesized in a similar way as PLLA-ethyl vanilate. **5** (Yield: 80%, $M_n = 18500 \text{ g mol}^{-1}$, $M_w/M_n = 1.71$). **6** (Yield: 82%, $M_n = 17200 \text{ g mol}^{-1}$, $M_w/M_n = 1.74$).

1-6. Synthesis of poly(L,L-lactide)-ethyl vanillin (PLLA-ethyl vanillin) (7) and poly(D,D-lactide)-ethyl vanillin (PDLA-ethyl vanillin) (8)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) and ethyl vanillin (0.058 g, 0.35 mmol) were dried under vacuum, and purged with nitrogen for three times. Then 2.2 ml of 1 vol% SnOct₂ (69 μmol) in dry toluene solution was combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-ethyl vanillin was synthesized in a similar way as PLLA-ethyl vanillin. **7** (Yield: 91%, $M_n = 26000 \text{ g mol}^{-1}$, $M_w/M_n = 1.55$). **8** (Yield: 92%, $M_n = 25300 \text{ g mol}^{-1}$, $M_w/M_n = 1.52$).

1-7. Synthesis of poly(L,L-lactide)-syringaldehyde (PLLA-syringaldehyde) (9) and poly(D,D-lactide)-syringaldehyde (PDLA-syringaldehyde) (10)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) and syringaldehyde (0.063 g, 0.35 mmol) were dried under vacuum, and purged with nitrogen for three times. Then 2.2 ml of 1 vol% SnOct₂ (69 μmol) in dry toluene solution was combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-syringaldehyde was synthesized in a similar way as PLLA-syringaldehyde. **9** (Yield: 16%, $M_n = 7600 \text{ g mol}^{-1}$, $M_w/M_n = 1.24$). **10** (Yield: 16%, $M_n = 7500 \text{ g mol}^{-1}$, $M_w/M_n = 1.25$).

1-8. Synthesis of poly(L,L-lactide)-4-tert-butylphenol (PLLA-4-tert-butylphenol) (11) and poly(D,D-lactide)-4-tert-butylphenol (PDLA-4-tert-butylphenol) (12)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) and 4-tert-butylphenol (0.052 g, 0.35 mmol) were dried under vacuum, and purged with nitrogen for three times. Then 2.2 ml of 1 vol% SnOct₂ (69 μmol) in dry toluene solution was combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-4-tert-butylphenol was synthesized in a similar way as PLLA-4-tert-butylphenol. **11** (Yield: 87%, $M_n = 9200 \text{ g mol}^{-1}$, $M_w/M_n = 1.73$). **12** (Yield: 88%, $M_n = 9200 \text{ g mol}^{-1}$, $M_w/M_n = 1.7$).

1-9. Synthesis of poly(L,L-lactide)-4-amyphenol (PLLA-4-amyphenol) (13) and poly(D,D-lactide)-4-amyphenol (PDLA-4-amyphenol) (14)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) was dried under vacuum, and purged with nitrogen for three times. Then 4-amyphenol (0.059 ml, 0.35 mmol), 2.2 ml of 1 vol% SnOct₂ (69 μmol) in dry toluene solution were combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times.

PDLA-4-amyphenol was synthesized in a similar way as PLLA-4-amyphenol. **13** (Yield: 90%, $M_n = 9900 \text{ g mol}^{-1}$, $M_w/M_n = 1.64$). **14** (Yield: 90%, $M_n = 8200 \text{ g mol}^{-1}$, $M_w/M_n = 1.71$).

1-10. Synthesis of poly(L,L-lactide)-4-chlorophenol (PLLA-4-chlorophenol) (15) and poly(D,D-lactide)-4-chlorophenol (PDLA-4-chlorophenol) (16)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) was dried under vacuum, and purged with nitrogen for three times. Then 4-chlorophenol (0.034 ml, 0.35 mmol), 2.2 ml of 1 vol% SnOct₂ (69 μmol) in dry toluene solution were combined to heat up at 120 °C for 2hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-4-chlorophenol was synthesized in a similar way as PLLA-4-chlorophenol. **15** (Yield: 90%, $M_n = 13,500 \text{ g mol}^{-1}$, $M_w/M_n = 1.72$). **16** (Yield: 86%, $M_n = 13,900 \text{ g mol}^{-1}$, $M_w/M_n = 1.78$).

1-11. Synthesis of poly(L,L-lactide)-4-fluorophenol (PLLA-4-fluorophenol) (17) and poly(D,D-lactide)-4-fluorophenol (PDLA-4-fluorophenol) (18)

To the round bottom flask, LLA (1.0 g, 6.9 mmol) and 4-fluorophenol (0.039 g, 0.35 mmol) were dried under vacuum, and purged with nitrogen for three times. Then 2.2 ml of 1 vol% SnOct₂ (69 μmol) in dry toluene solution were combined to heat up at 120 °C for 2 hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-4-fluorophenol was synthesized in a similar way as PLLA-4-fluorophenol. **17** (Yield: 86%, $M_n = 12,200 \text{ g mol}^{-1}$, $M_w/M_n = 1.71$). **18** (Yield: 87%, $M_n = 11,700 \text{ g mol}^{-1}$, $M_w/M_n = 1.74$).

1-12. Synthesis of poly(L,L-lactide)-1-dodecanol (PLLA-1-dodecanol) (19) and poly(D,D-lactide)-1-dodecanol (PDLA-1-dodecanol) (20)

PLLA-1-dodecanol and PDLA-1-dodecanol were prepared according to the literature.^[S1] The typical procedure is as follows. To the round bottom flask, LLA (1.0 g, 6.9 mmol) was dried under vacuum, and purged with nitrogen for three times. Then 1.1 ml of 1 vol% 1-dodecanol (50 μmol) in dry toluene solution, 0.32 ml of 1 vol% SnOct₂ (99 μmol) in dry toluene solution were combined to heat up at 120 °C for 3hr under nitrogen atmosphere. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol three times. PDLA-1-dodecanol was synthesized in a similar way as PLLA-1-dodecanol. **19** (Yield: 82%, $M_n = 17,600 \text{ g mol}^{-1}$, $M_w/M_n = 1.46$). **20** (Yield: 85%, $M_n = 16,800 \text{ g mol}^{-1}$, $M_w/M_n = 1.47$).

Table S1. Results of Polymerization and g_{CD} Value of PLLA and PDLA Derivatives

Initiator + L-lactide + D-lactide $\xrightarrow[120\text{ }^{\circ}\text{C, 2hr}]{\text{SnOct}_2, \text{toluene}}$ PLLA-initiator + PDLA-initiator

Entry	Polymers	R ₁	R ₂	R ₃	g_{CD} (wavelength/nm)
1	PLLA-4-tert-butylphenol (11)	H	H	CH(CH ₃) ₃	-
2	PDLA-4-tert-butylphenol (12)	H	H	CH(CH ₃) ₃	-
3	PLLA-4-amyphenol (13)	H	H	(CH ₂) ₄ CH ₃	-
4	PDLA-4-amyphenol (14)	H	H	(CH ₂) ₄ CH ₃	-
5	PLLA-4-chlorophenol (15)	H	H	Cl	-
6	PDLA-4-chlorophenol (16)	H	H	Cl	-
7	PLLA-4-fluorophenol (17)	H	H	F	-
8	PDLA-4-fluorophenol (18)	H	H	F	-

1-13. CD and UV-vis measurement of polymers

All polymers **1-20** were dissolved in chloroform (r.t.) at concentrations of 0.050 mol L⁻¹ (**1**, **1a**, **2**, **5-8**, **11-20**), 0.025 mol L⁻¹ (**2a**, **3**, **4**, **9**, **10**), 0.063 mol L⁻¹ (**1b**, **2b**), as lactide repeating unit, respectively.

1-14. PL measurement of polymers

PLLA-vanillin (**1**) and PDLA-vanillin (**2**) were dissolved in chloroform, super dehydrated, amylene added (r.t.) at concentrations of 0.020 mol L⁻¹, respectively.

1-15. CPL measurement of polymers

PLLA-vanillin (**1**) and PDLA-vanillin (**2**) were dissolved in chloroform, super dehydrated, amylene added (r.t.) at concentrations of 0.10 mol L⁻¹, respectively.

1-16. Gaussian09, Revision E.01 Calculation.

Potential surface energy calculation of lactide-vanillin was performed using Gaussian09, Rev.E.01 program^{S1} running on an Apple MacPro2008 (8-Cores, 2.66GHz, 32 GB memory, MacOS ver.1.75). The geometries of lactide-vanillin were optimized by the PM3-MM followed by DFT (B3LYP, 6-311G(d)) calculations as a function of dihedral angles of L,L-lactide and vanillin aromatic rings (C₁-C₂-O₃-C₄) varying from -80° to +80° with 15° interval. Simulated CD and UV-vis spectra of lactide-vanillin conformers were obtained using the TD-DFT (B3LYP, 6-31G(d) basis set) protocol with a half-width-at-half-height of 0.15 eV.

2. ^1H NMR spectra of polymers

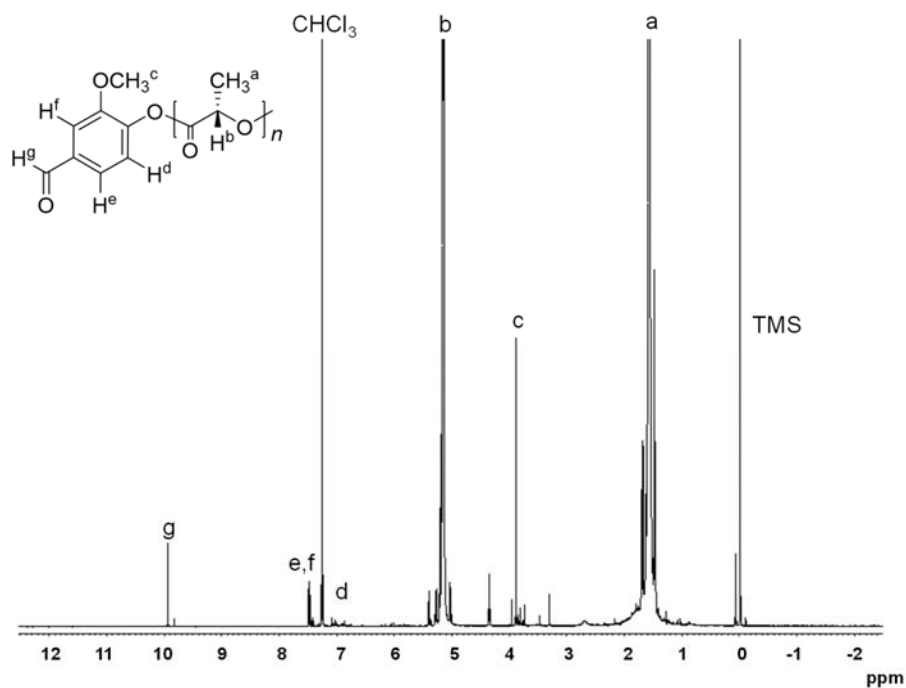


Figure S1. ^1H NMR spectrum of PLLA-vanillin (1) in CDCl_3 (600MHz).

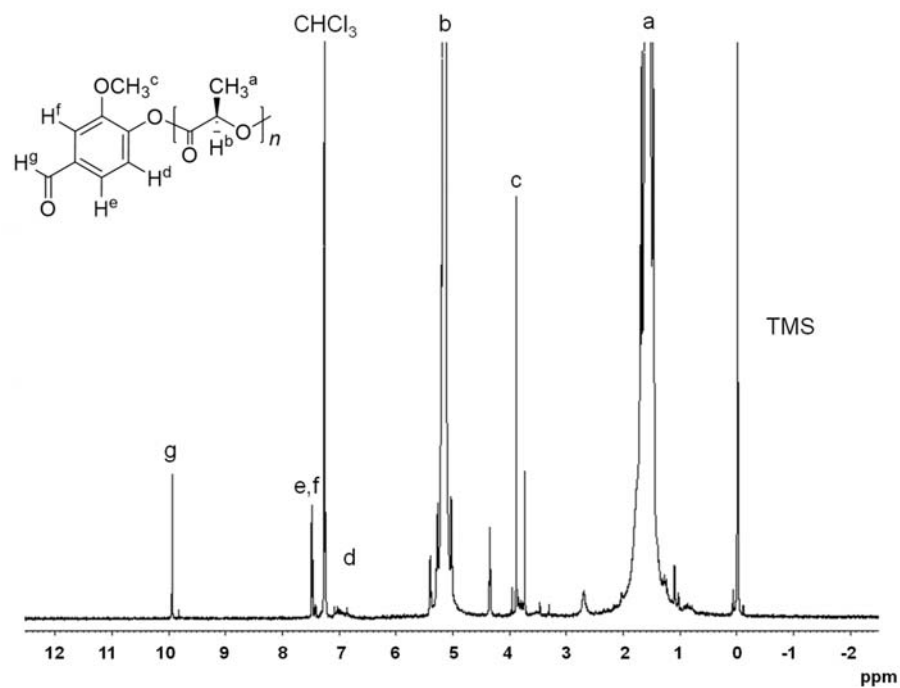


Figure S2. ^1H NMR spectrum of PDLA-vanillin (2) in CDCl_3 (600MHz).

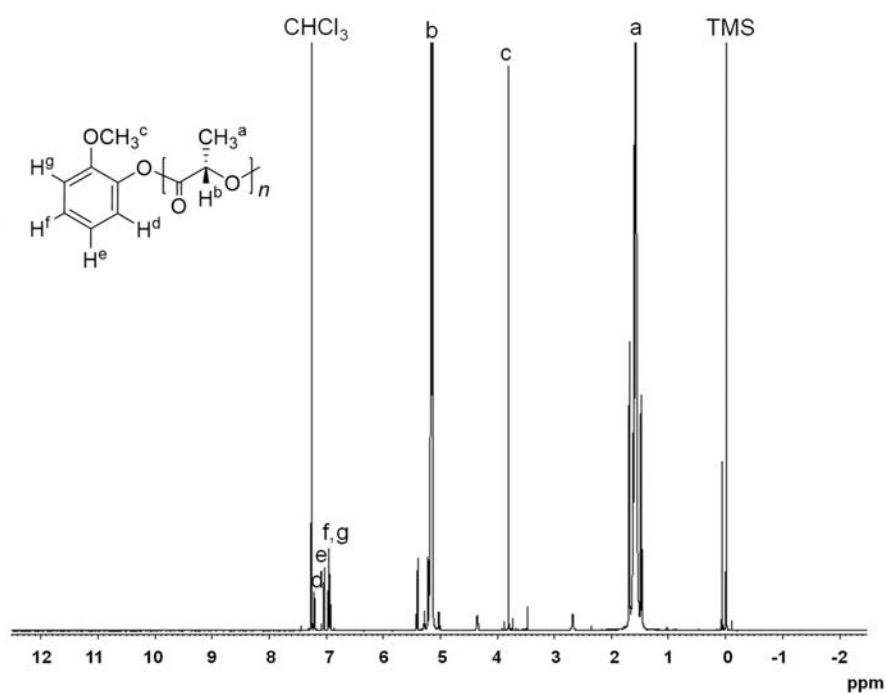


Figure S3. ^1H NMR spectrum of PLLA-guiacol (**3**) in CDCl_3 (600MHz).

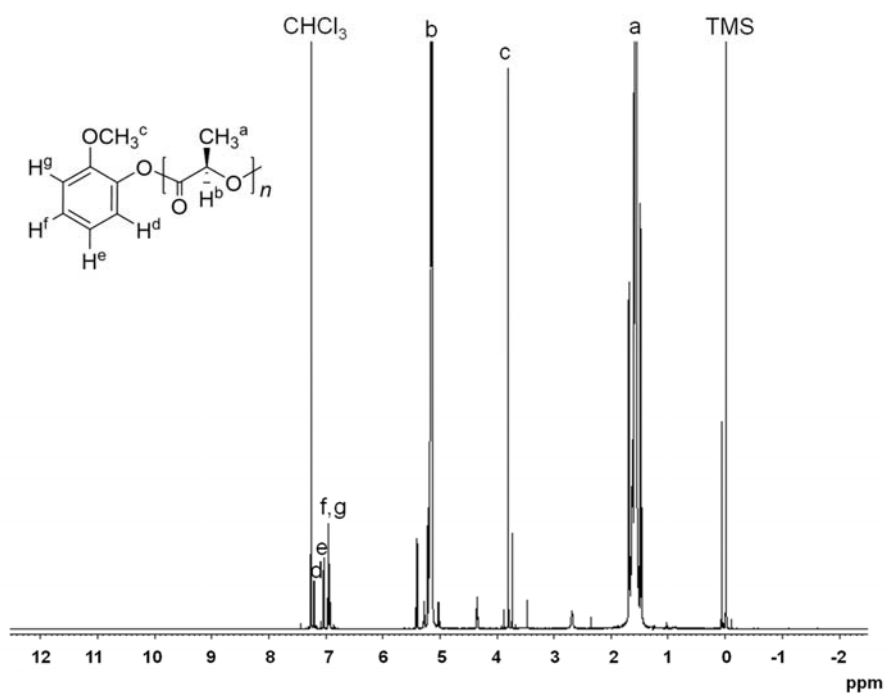


Figure S4. ^1H NMR spectrum of PDLA-guiacol (**4**) in CDCl_3 (600MHz).

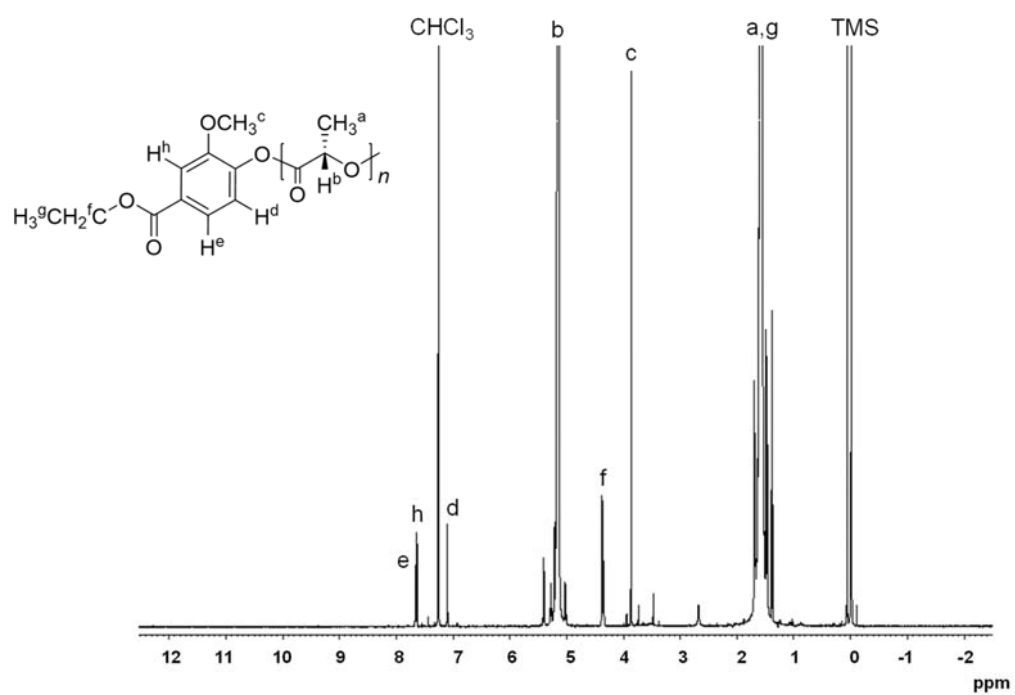


Figure S5. ^1H NMR spectrum of PLLA-ethyl vanilate (5) in CDCl_3 (600MHz).

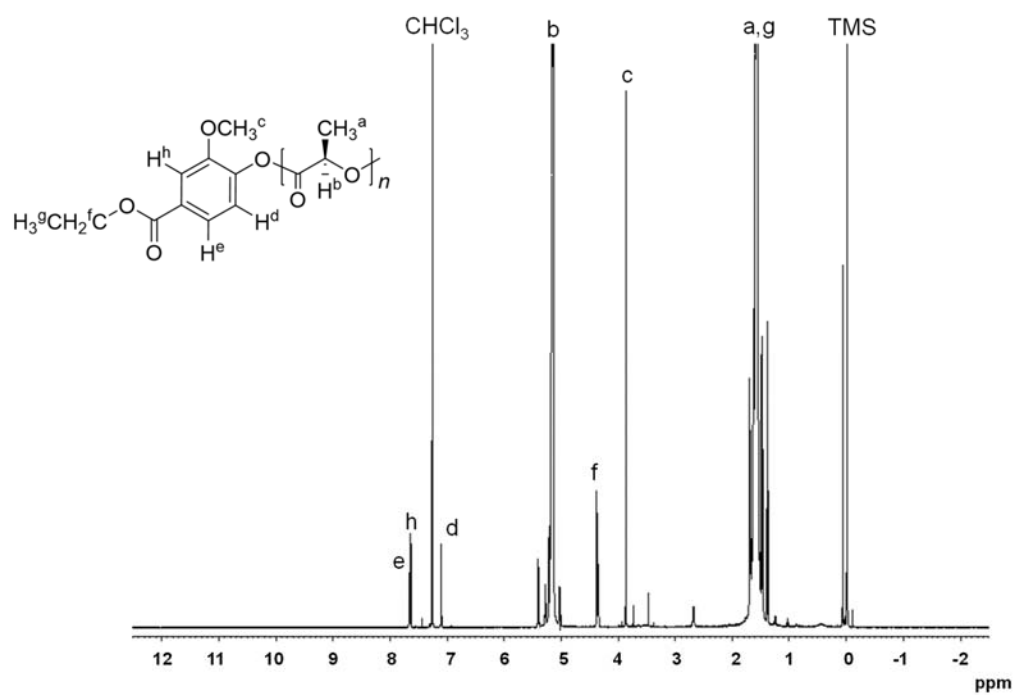


Figure S6. ^1H NMR spectrum of PDLA-ethyl vanilate (6) in CDCl_3 (600MHz).

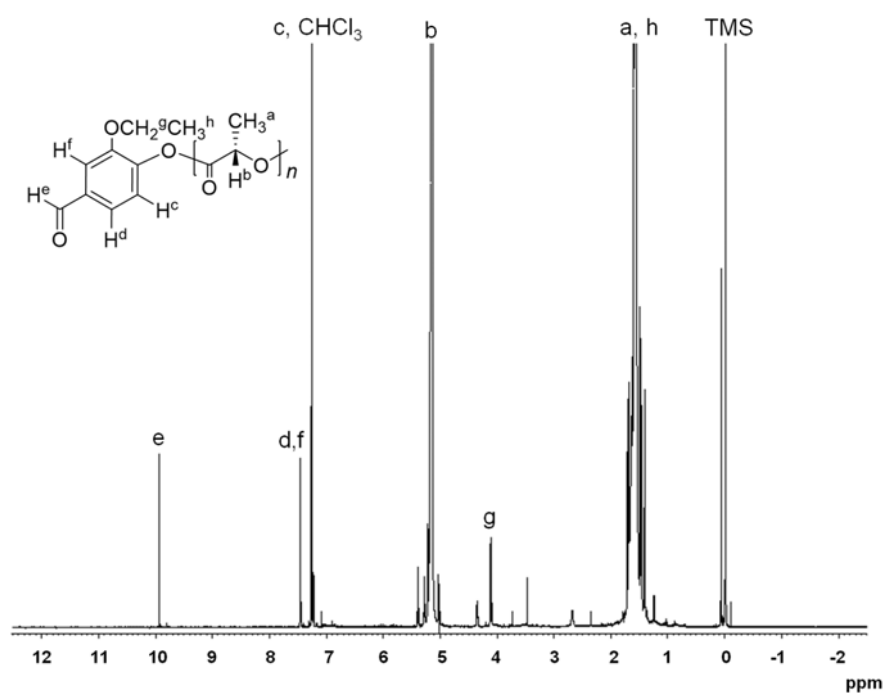


Figure S7. ^1H NMR spectrum of PLLA-ethyl vanillin (**7**) in CDCl_3 (600MHz).

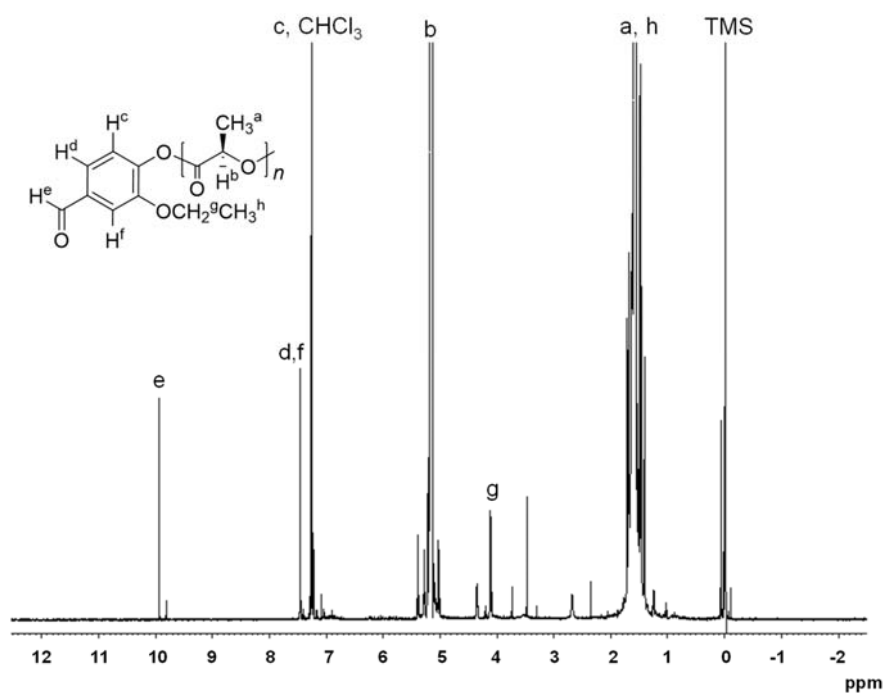


Figure S8. ^1H NMR spectrum of PDLA-ethyl vanillin (**8**) in CDCl_3 (600MHz).

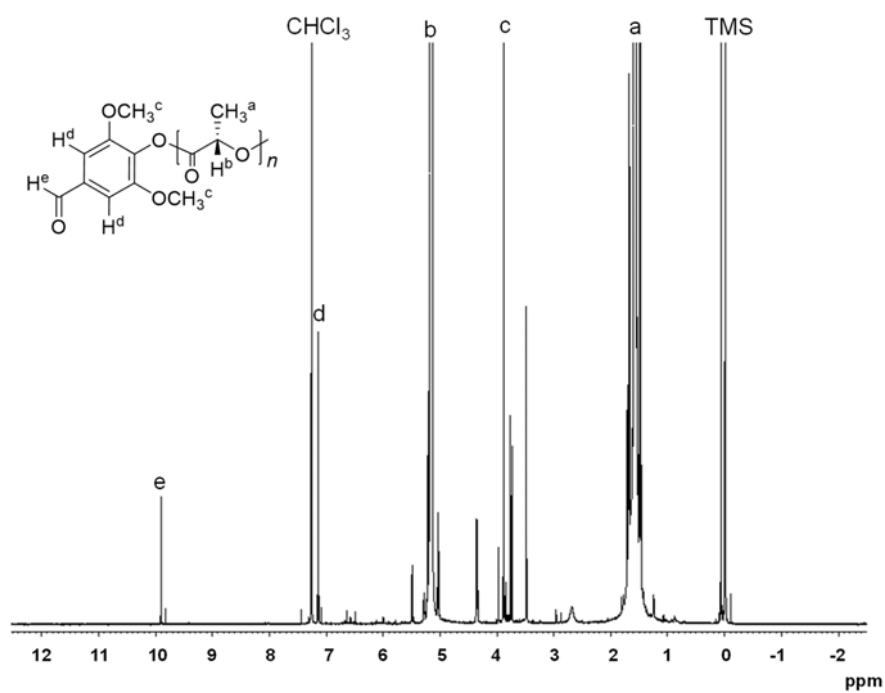


Figure S9. ^1H NMR spectrum of PLLA-syringaldehyde (**9**) in CDCl_3 (600MHz).

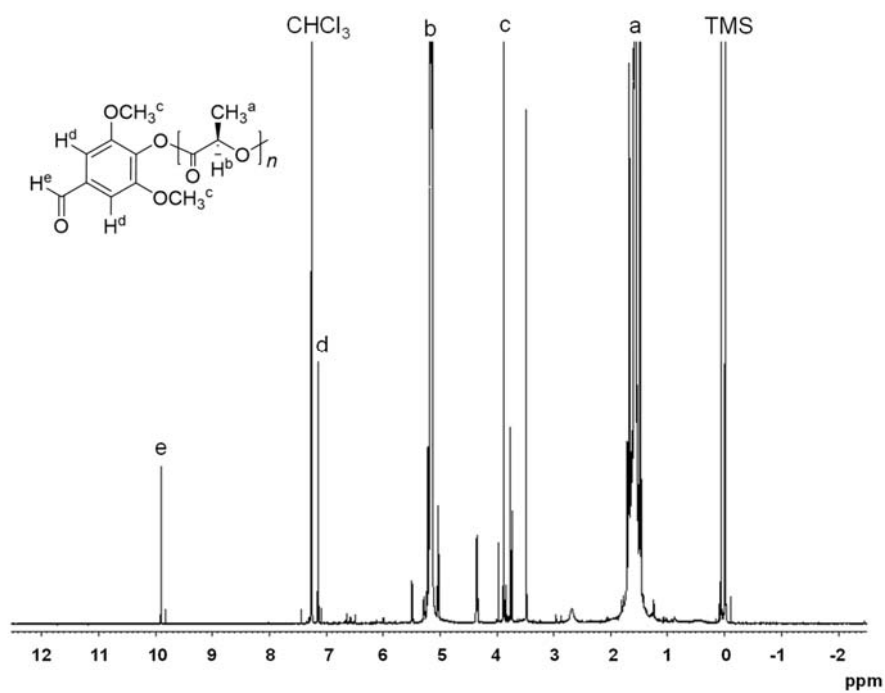


Figure S10. ^1H NMR spectrum of PDLA-syringaldehyde (**10**) in CDCl_3 (600MHz).

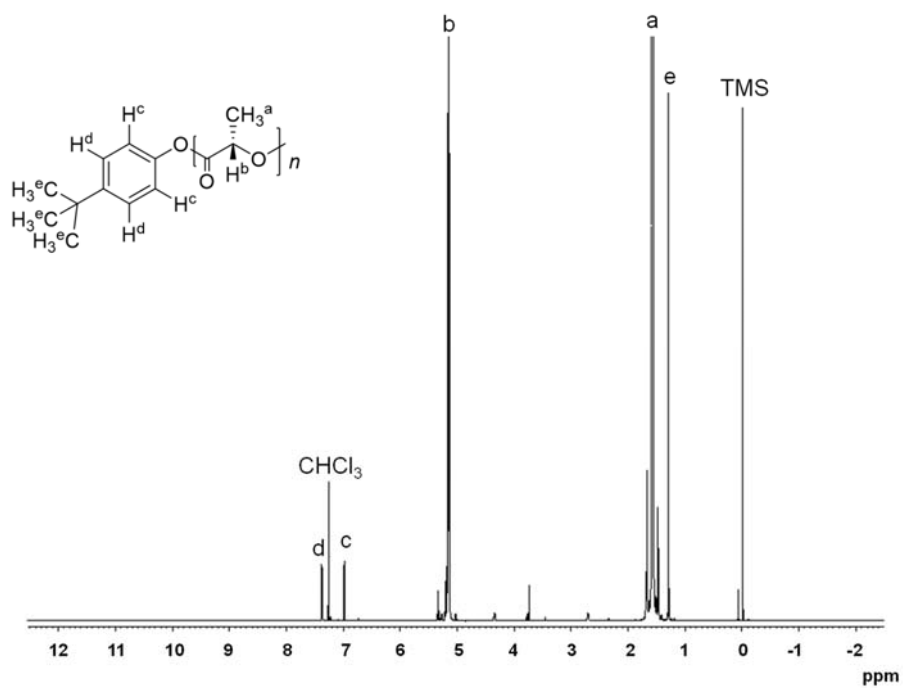


Figure S11. ^1H NMR spectrum of PLLA-4-*tert*-butylphenol (**11**) in CDCl_3 (600MHz).

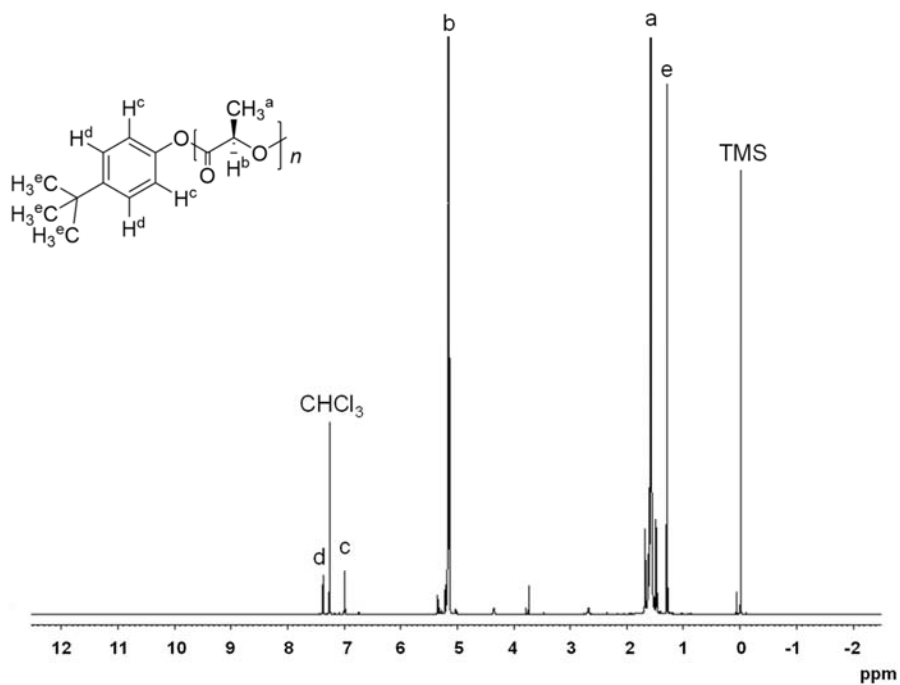


Figure S12. ^1H NMR spectrum of PDLA-4-*tert*-butylphenol (**12**) in CDCl_3 (600MHz).

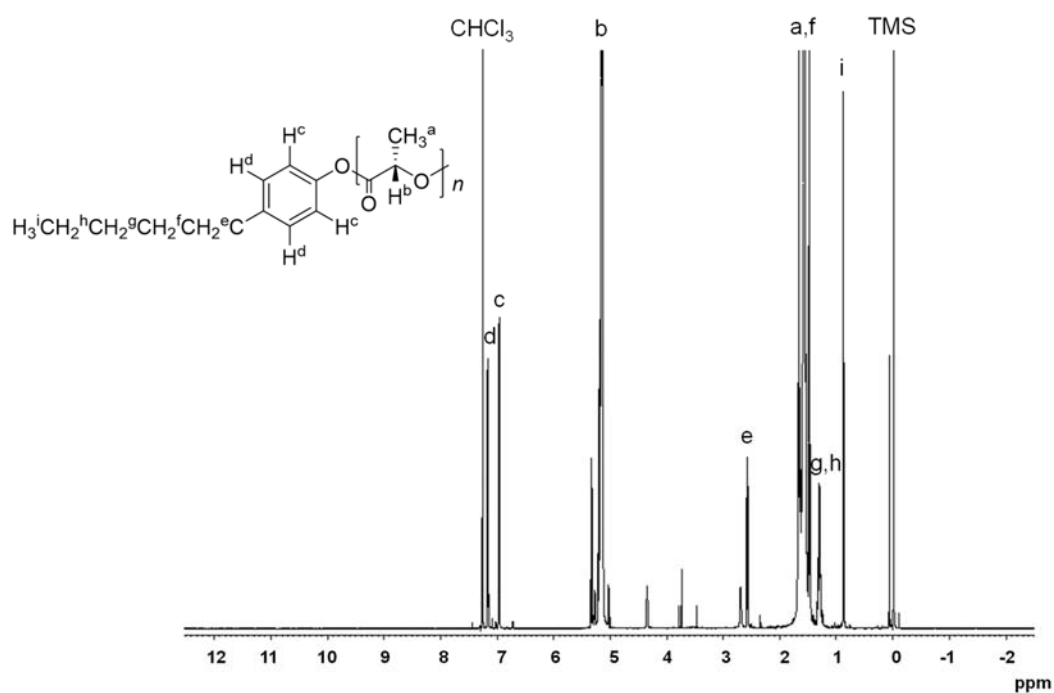


Figure S13. ^1H NMR spectrum of PLLA-4-amyphenol (**13**) in CDCl_3 (600MHz).

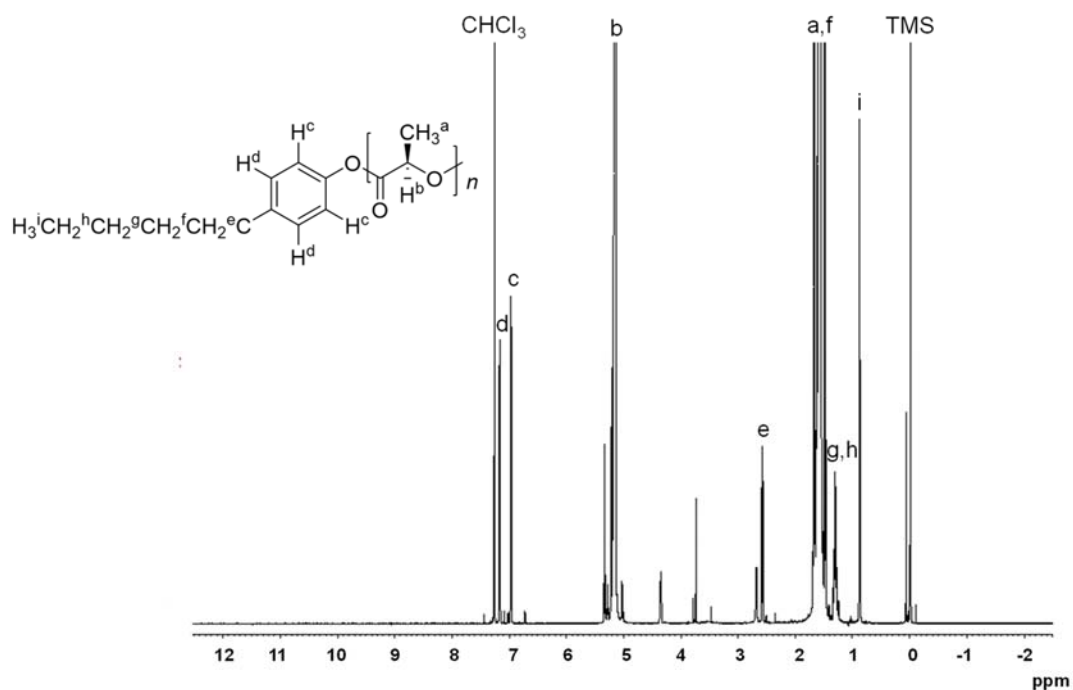


Figure S14. ^1H NMR spectrum of PDLA-4-amyphenol (**14**) in CDCl_3 (600MHz).

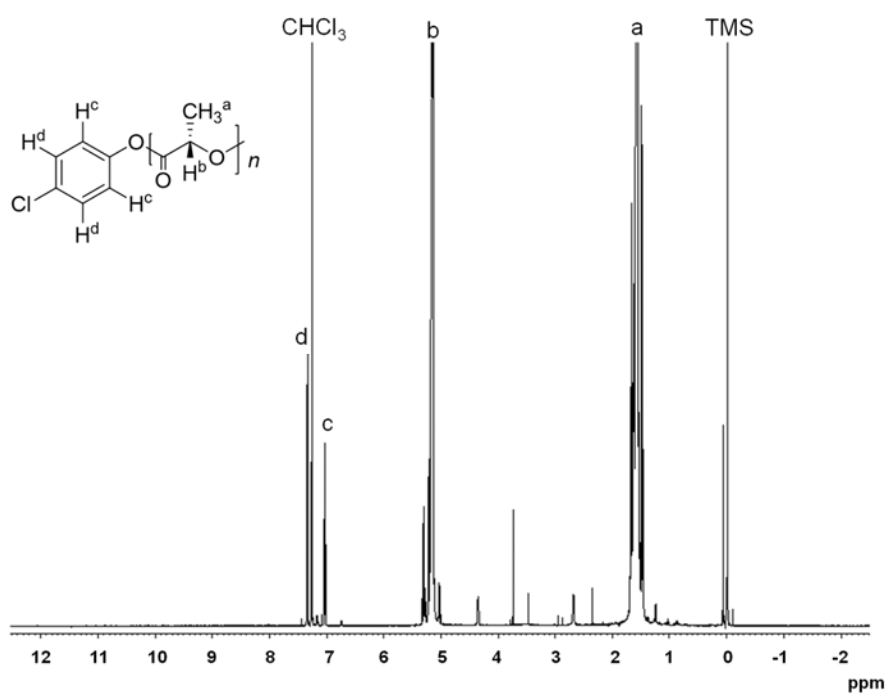


Figure S15. ^1H NMR spectrum of PLLA-4-chlorophenol (**15**) in CDCl_3 (600MHz).

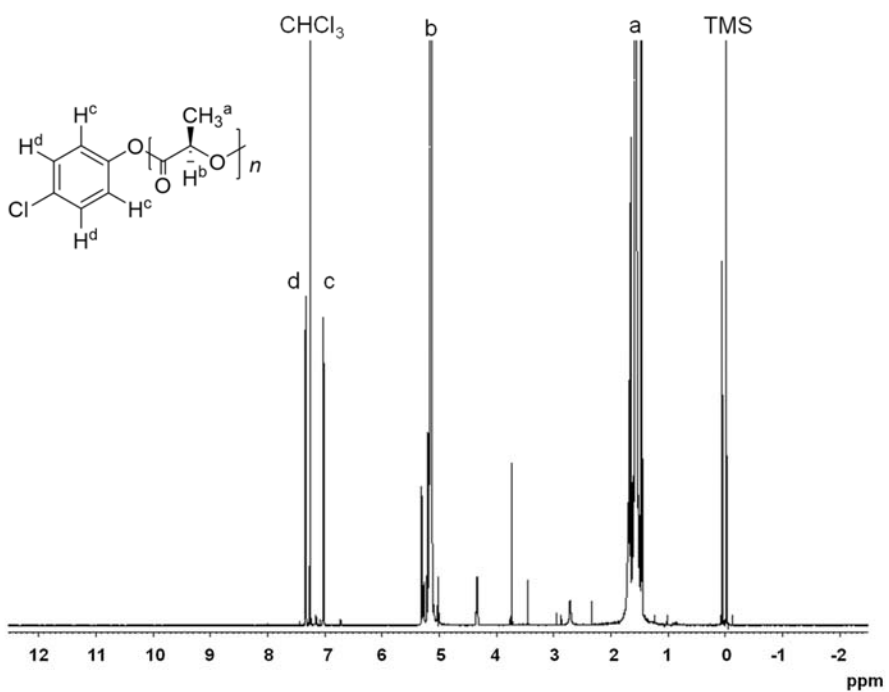


Figure S16. ^1H NMR spectrum of PDLA-4-chlorophenol (**16**) in CDCl_3 (600MHz).

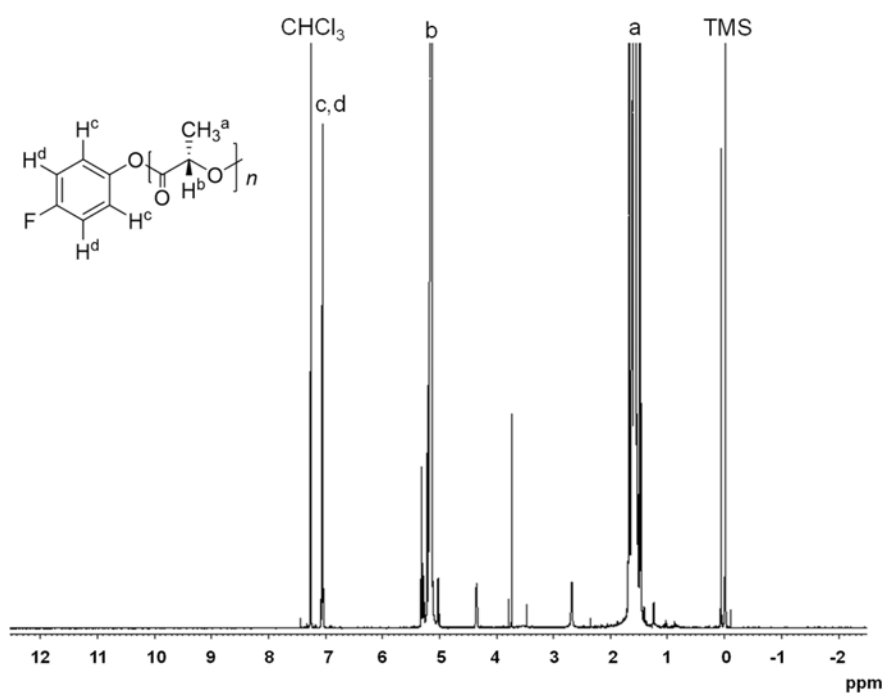


Figure S17. 1H NMR spectrum of PLLA-4-fluorophenol (**17**) in $CDCl_3$ (600MHz).

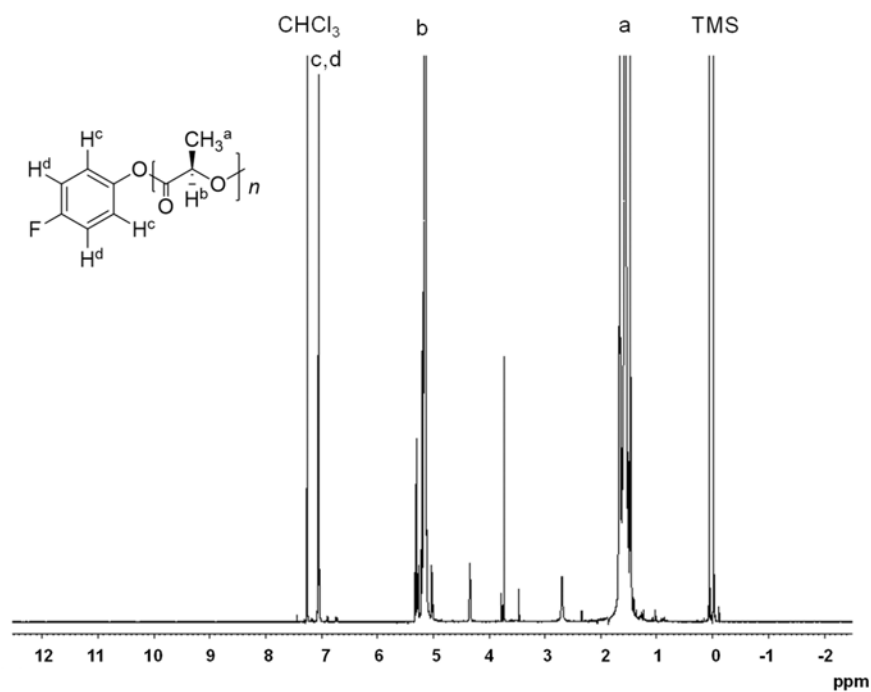


Figure S18. 1H NMR spectrum of PDLA-4-fluorophenol (**18**) in $CDCl_3$ (600MHz).

2. CD and UV-vis spectra of polymers

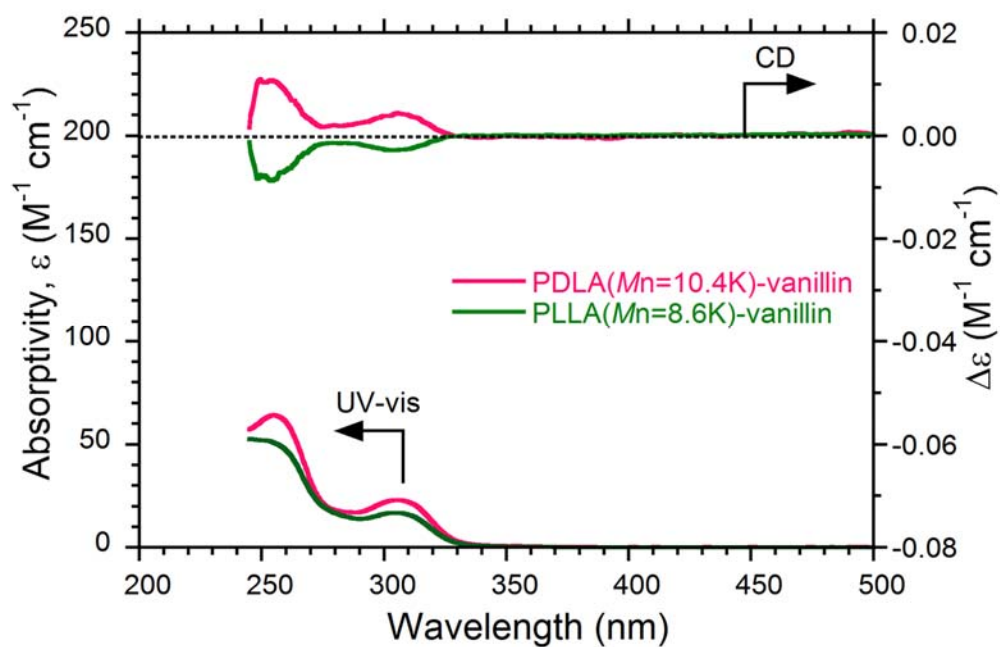


Figure S19. CD and UV-vis absorption spectra of the PLLA-vanillin (**1a**) and PDLA-vanillin (**2a**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹ in PLLA-vanillin (**1a**), and 0.025 mol L⁻¹ in PDLA-vanillin (**2a**).

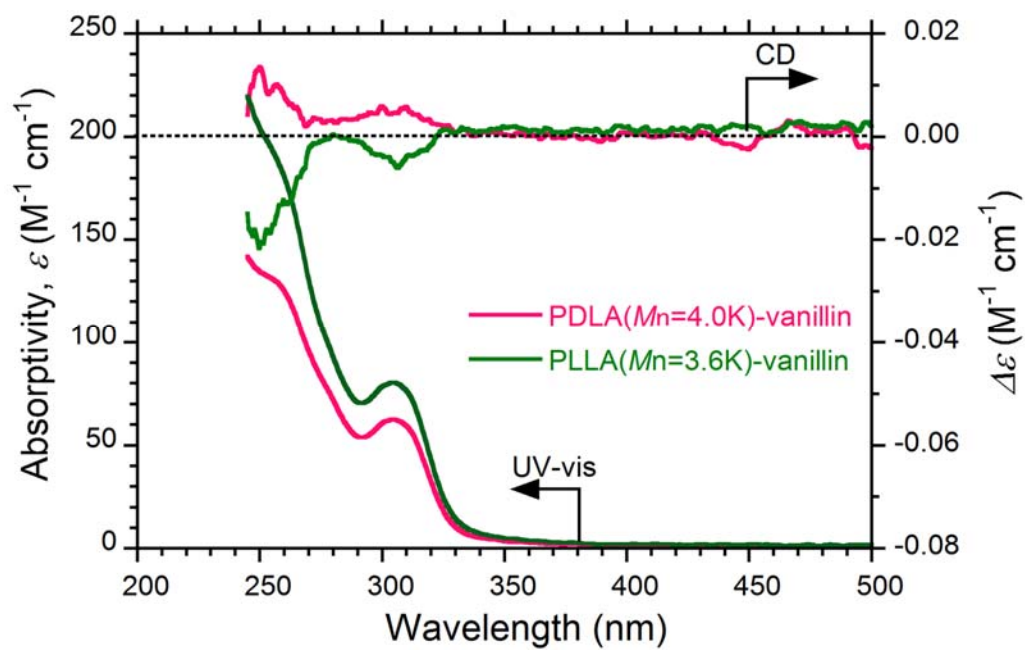


Figure S20. CD and UV-vis absorption spectra of the PLLA-vanillin (**1b**) and PDLA-vanillin (**2b**) in chloroform at 20 °C. Concentration of the solution is 0.063 mol L⁻¹ in PLLA-vanillin (**1b**) and PDLA-vanillin (**2b**).

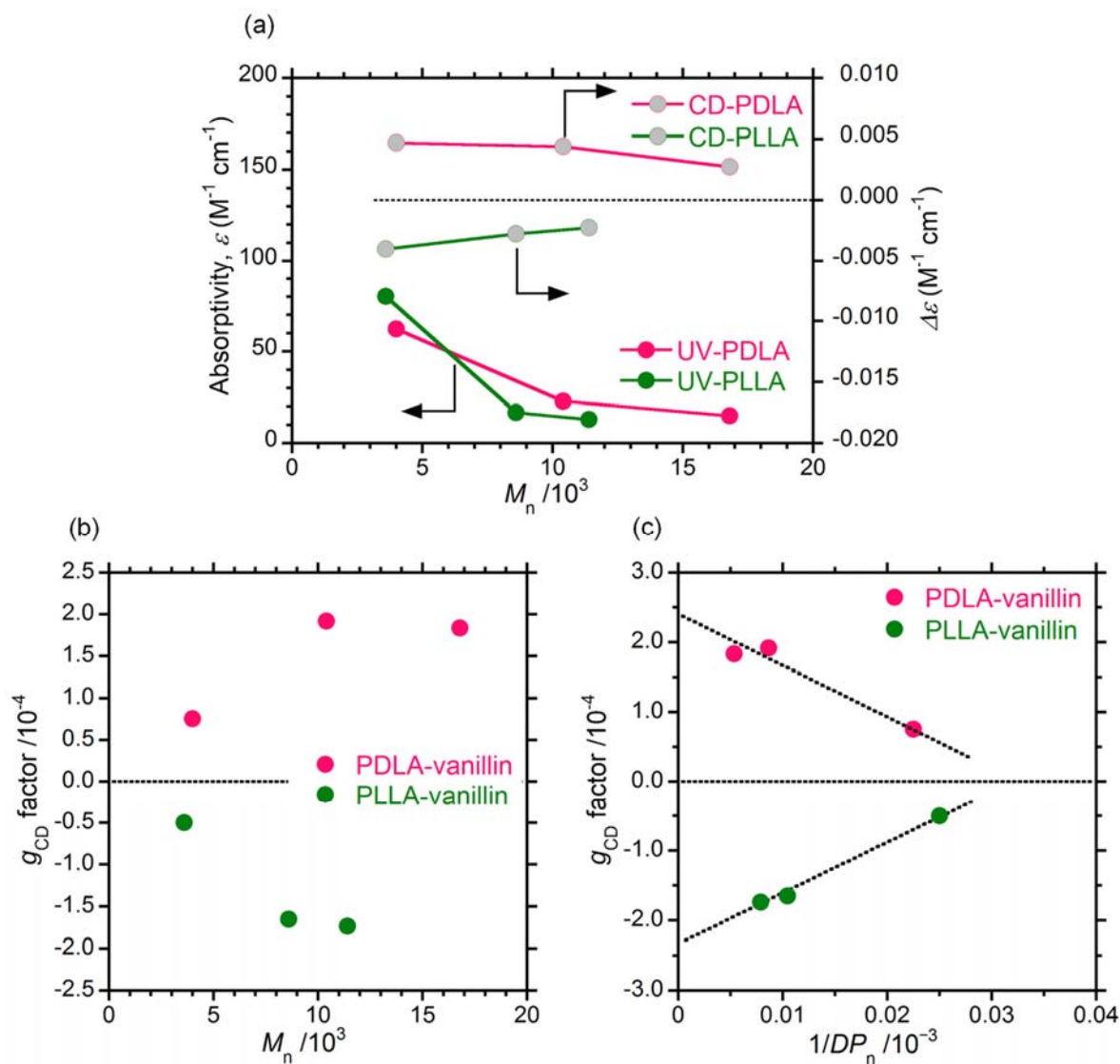


Figure S21. PLLA-vanillin and PDLA-vanillin in chloroform at 20 °C of (a) The absorptivity and ellipticity at the first Cotton band at 307 nm due to vanillin end terminus as a function of M_n (PDLA and PLLA bearing in chloroform at 20 °C). (b) The g_{CD} values at the first Cotton band as a function of M_n in chloroform at 20 °C. (c) The g_{CD} values at the first Cotton band as a function of reciprocal DP_n in chloroform at 20 °C.

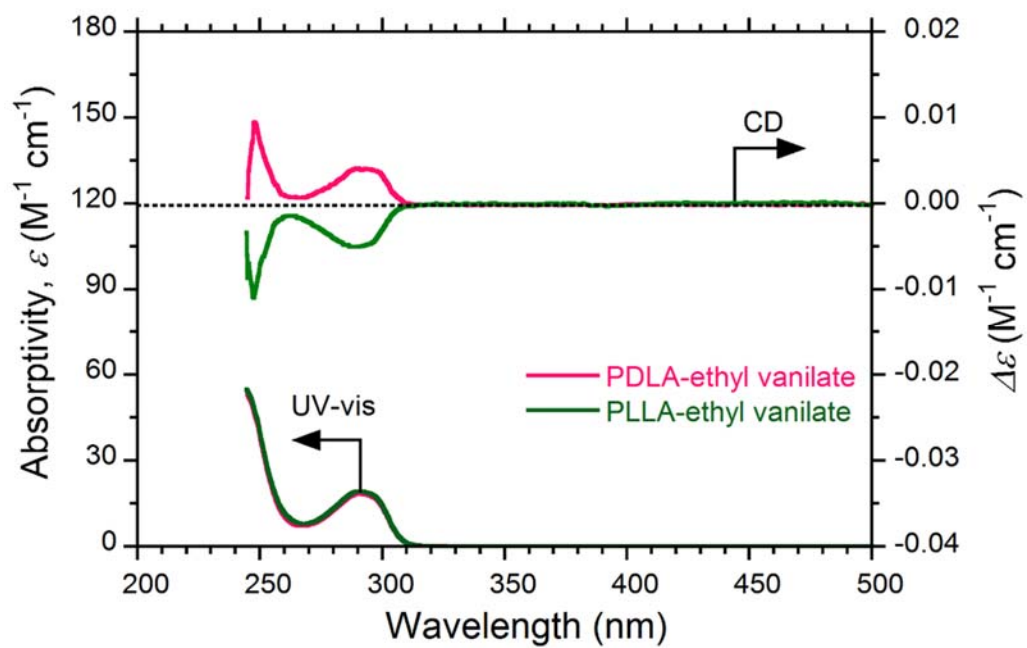


Figure S22. CD and UV-vis absorption spectra of the PLLA-ethyl vanilate (**5**) and PDLA-ethyl vanilate (**6**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

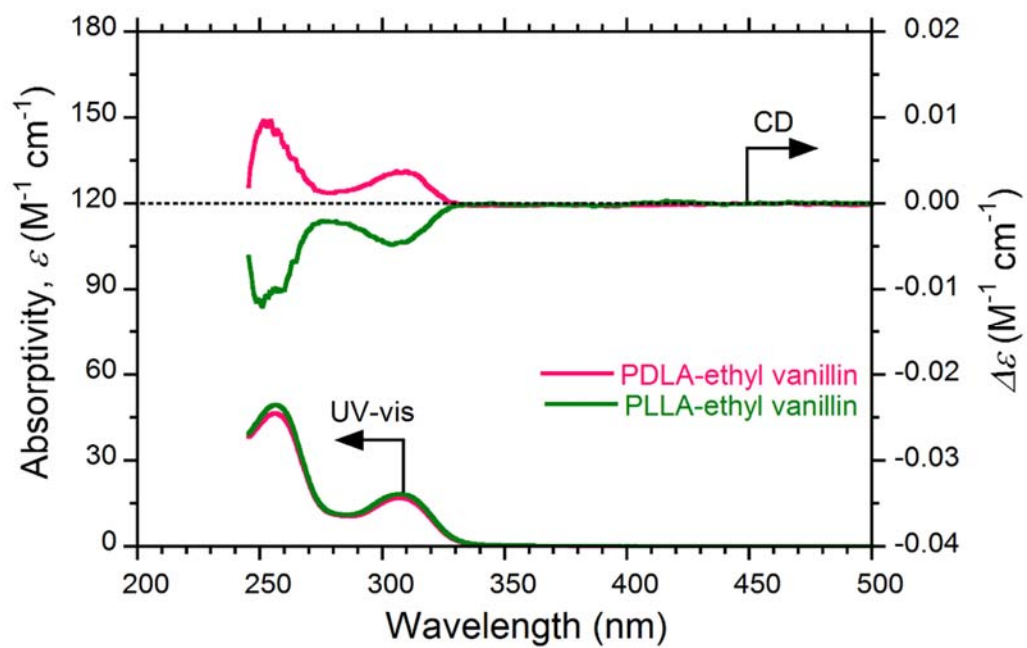


Figure S23. CD and UV-vis absorption spectra of the PLLA-ethyl vanillin (**7**) and PDLA-ethyl vanillin (**8**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

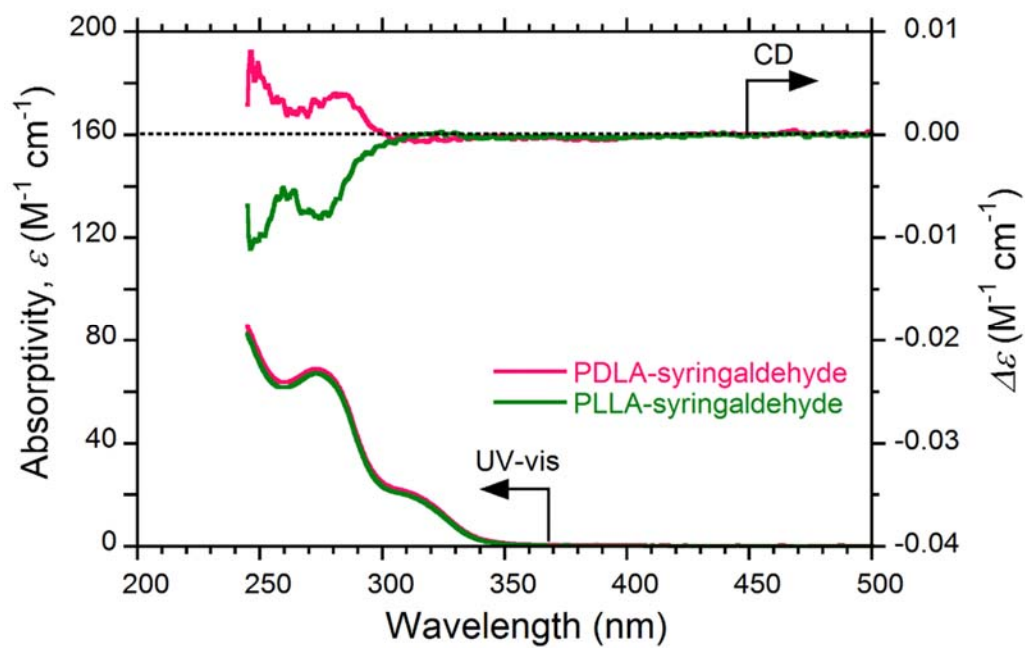


Figure S24. CD and UV-vis absorption spectra of the PLLA-syringaldehyde (**9**) and PDLA-syringaldehyde (**10**) in chloroform at 20 °C. Concentration of the solution is 0.025 mol L⁻¹.

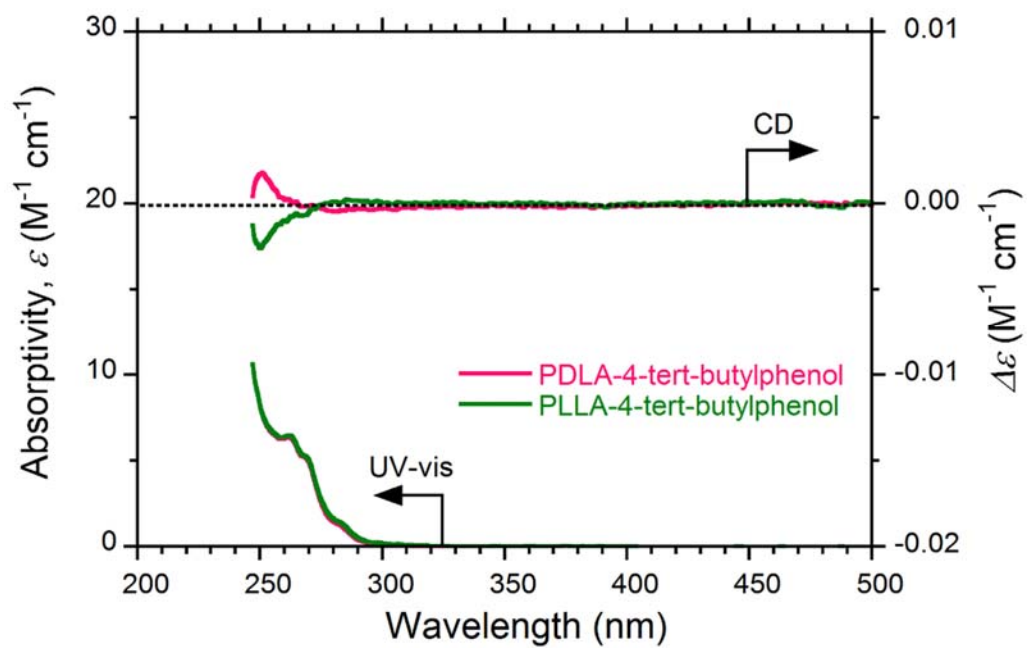


Figure S25. CD and UV-vis absorption spectra of the PLLA-4-*tert*-butylphenol (**11**) and PDLA-4-*tert*-butylphenol (**12**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

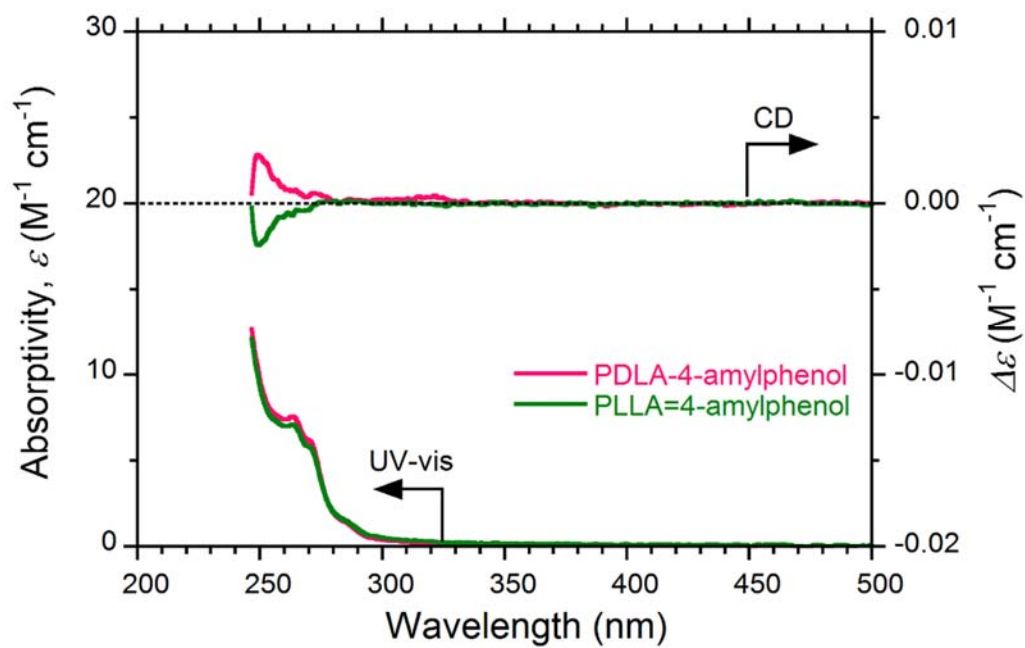


Figure S26. CD and UV-vis absorption spectra of the PLLA-4-amyphenol (**13**) and PDLA-4-amyphenol (**14**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

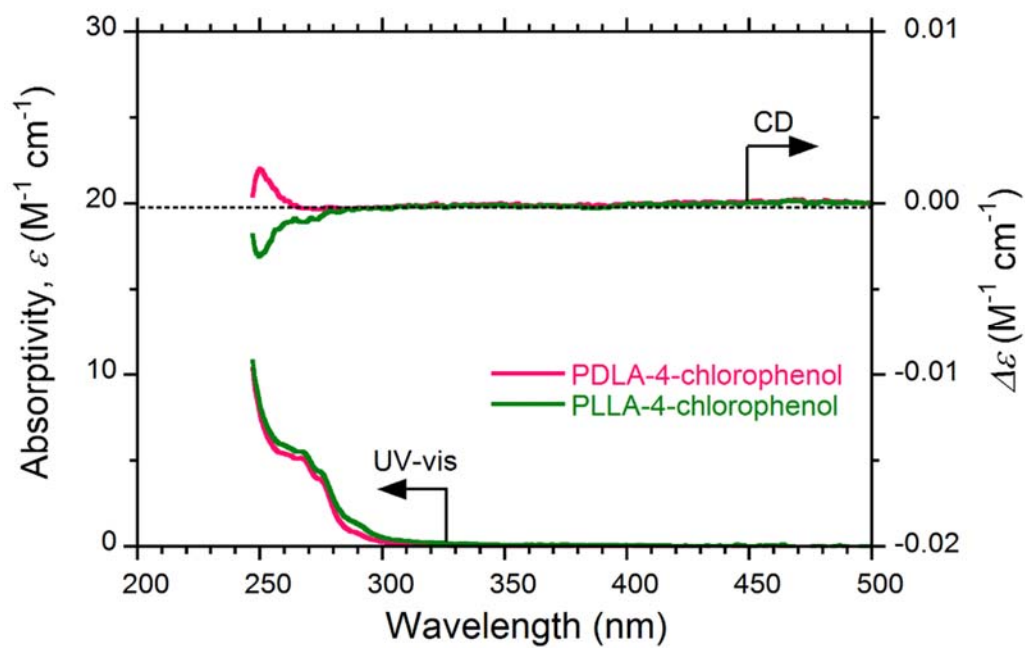


Figure S27. CD and UV-vis absorption spectra of the PLLA-4-chlorophenol (**15**) and PDLA-4-chlorophenol (**16**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

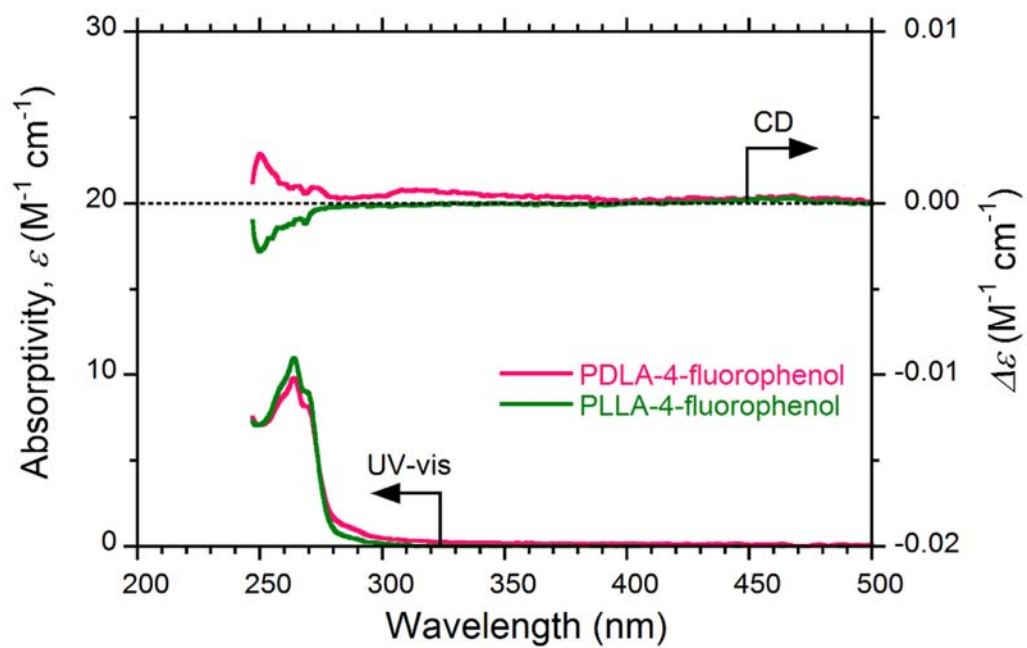


Figure S28. CD and UV-vis absorption spectra of the PLLA-4-fluorophenol (**17**) and PDLA-4-fluorophenol (**18**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

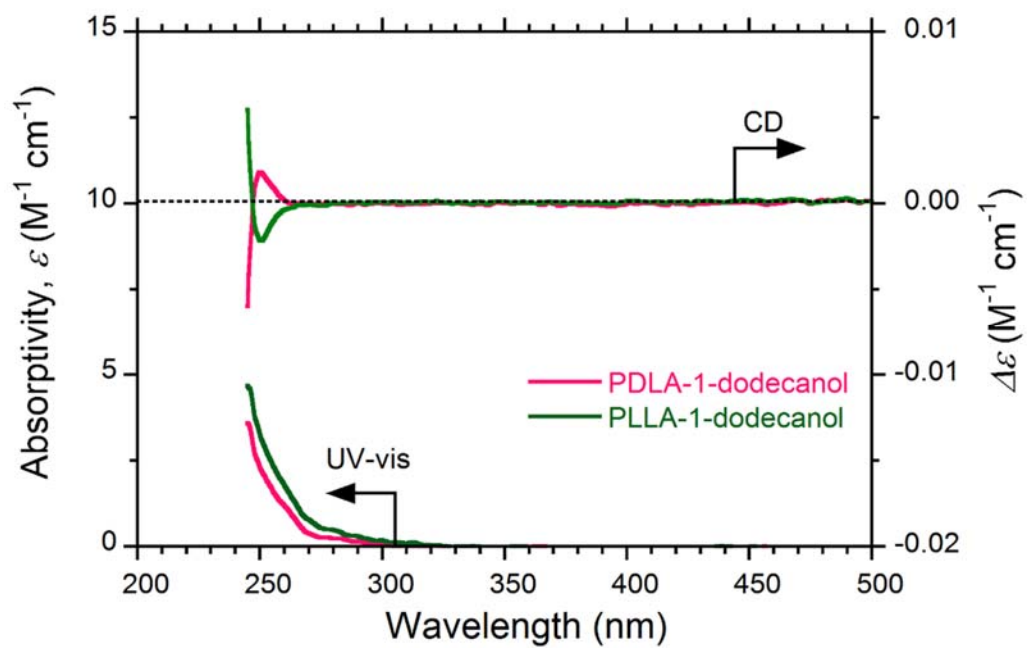


Figure S29. CD and UV-vis absorption spectra of the PLLA-1-dodecanol (**19**) and PDLA-1-dodecanol (**20**) in chloroform at 20 °C. Concentration of the solution is 0.050 mol L⁻¹.

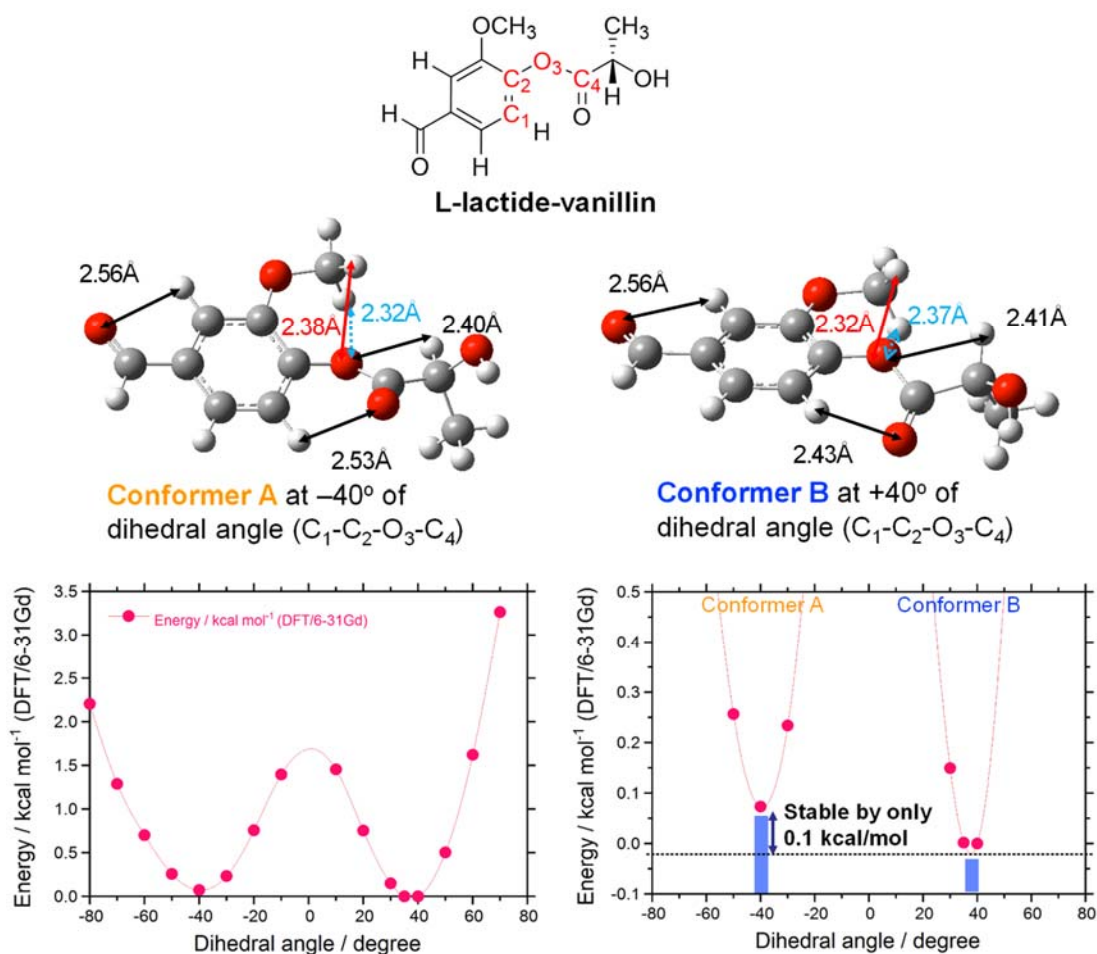


Figure S30. (Top). The model structure of L-lactide-vanillin for calculation (TD-DFT, B3LYP/6-31G(d) basis set). (Middle, left) Conformer A of L-lactide and benzene ring of vanillin as a function of dihedral angle ($C_1-C_2-O_3-C_4$) at -40° . (Middle, right) Conformer B of L-lactide and benzene ring of vanillin as a function of dihedral angle ($C_1-C_2-O_3-C_4$) at 40° . Noting that C–H/O distance led by Bondi is 2.72 Å, when C–H/O interaction was absent. (Bottom, left) Potential energy surface of L-lactide and benzene ring of vanillin as a function of dihedral angle with 10° . (Bottom, right) Magnified y axis of the bottom left Figure of potential energy surface. The energy difference between conformers A and B was 0.1 kcal mol⁻¹.

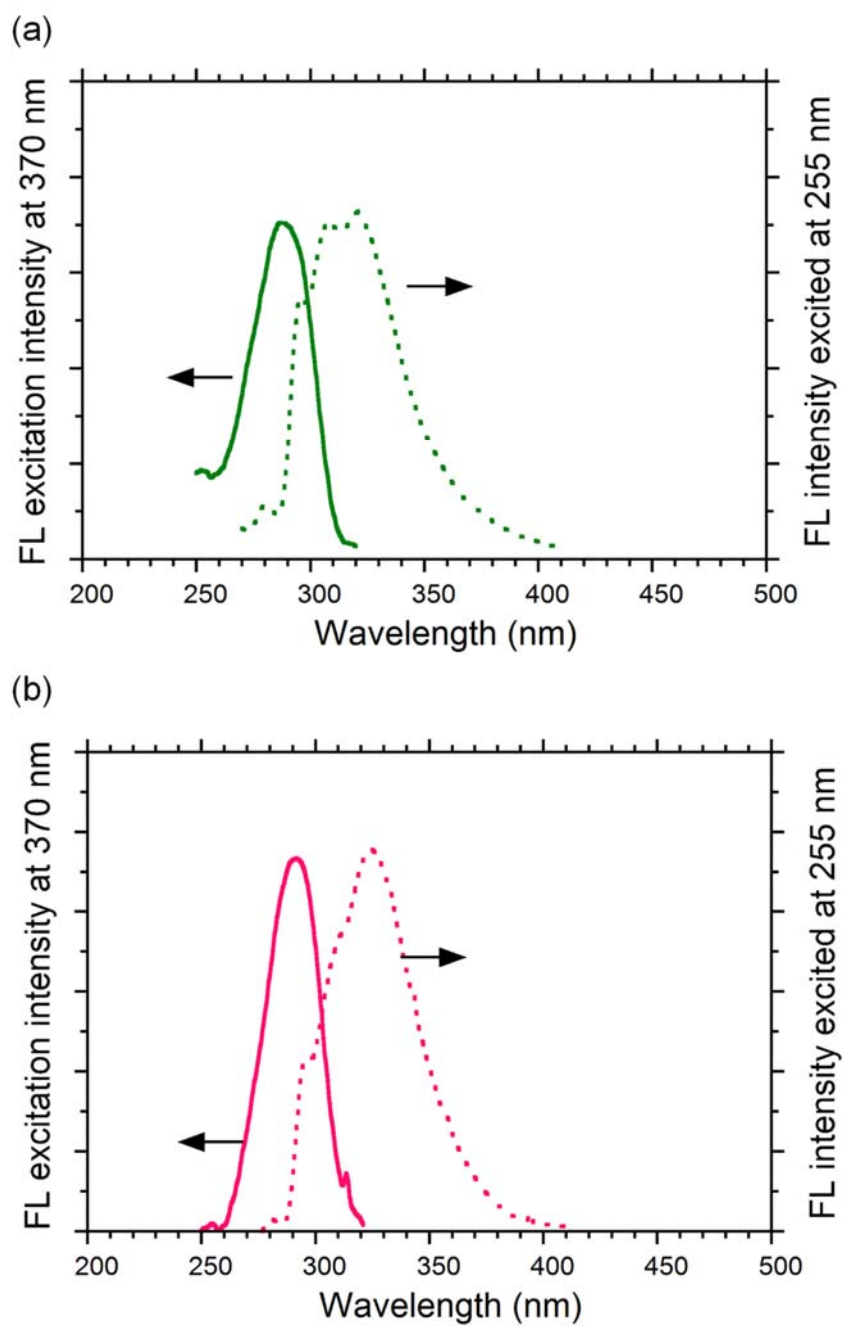


Figure S31. Fluorescent (excited at 255 nm) and the corresponding fluorescent excitation (monitored at 370 nm) spectra of (a) PLLA-vanillin (**1**) and (b) PDLA-vanillin (**2**) in CHCl_3 (chloroform, super dehydrated, amylene added). [repeating unit] = 0.020 mol L^{-1} .

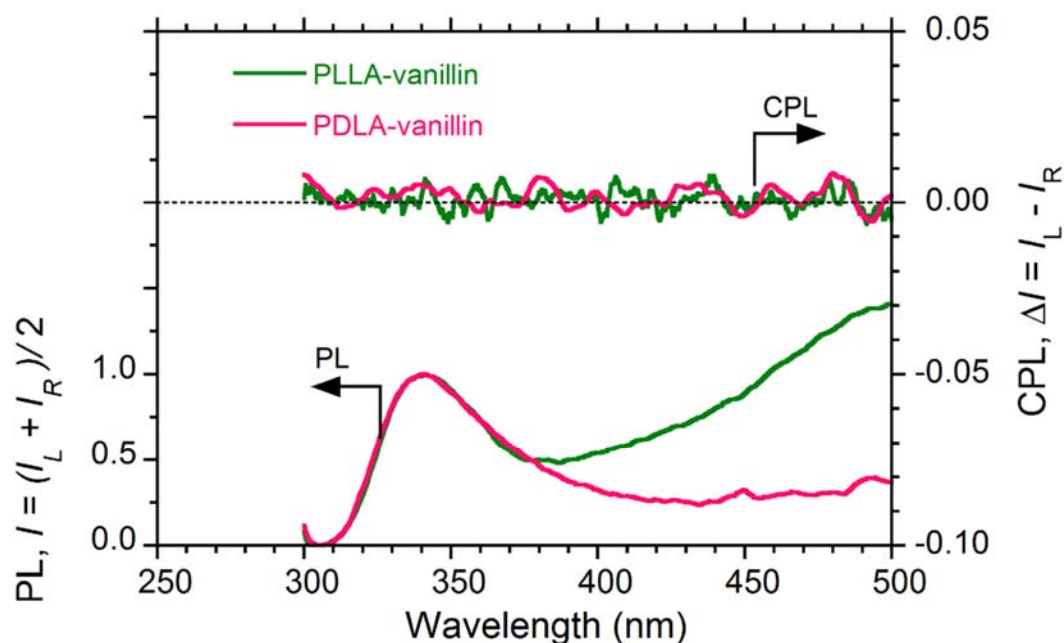


Figure S32. CPL and PL spectra of PLLA-vanillin (**1**) and PDLA-vanillin (**2**) in CHCl_3 (Wako, spectroscopic-grade chloroform, super dehydrated, amylene added). [repeating unit] = 0.10 mol L^{-1} . λ_{ex} = 280 nm.

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