Electronic Supplementary Information for:

Stereocomplex of poly(lactide)s with chain end modification: simultaneous resistances to melting and thermal decomposition

Hiroharu Ajiro, a,b Yi-Ju Hsiao, a Tran Hang Thi, c Tomoko Fujiwara, *d Mitsuru Akashi* a,b

---

Contents

<table>
<thead>
<tr>
<th>Contents</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Experimental procedure</td>
<td>2</td>
</tr>
<tr>
<td>2. 1H NMR spectra</td>
<td>5</td>
</tr>
<tr>
<td>3. FT-IR/ATR spectra</td>
<td>7</td>
</tr>
<tr>
<td>4. SEC traces</td>
<td>9</td>
</tr>
</tbody>
</table>

---

* a Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan. Fax:+81-6-6879-7359;
  Tel: +81-6-6879-7356; E-mail: akashi@chem.eng.osaka-u.ac.jp
* b The Center for Advanced Medical Engineering and Informatics, Osaka University
* c Faculty of Technology of Organic Chemistry, College of Chemistry, Ministry of Industry, Tien Kien, Lam Thao, Phu Tho, Vietnam
* d Department of Chemistry, The University of Memphis
1. Experimental procedure

1-1.) Materials.

L-lactide (LLA; Musashino Chemical Laboratory, Ltd., Japan) and D-lactide (DLA; Musashino Chemical Laboratory, Ltd., Japan) were recrystallized from ethyl acetate, and then dried in vacuo at room temperature for 24h. Benzyl alcohol (Tokyo Chemical Industry, Ltd., Japan) was distilled with CaH2 for purification. Thionyl chloride (SOCl2), 3,4-dihydroxycinnamic acid (DHCA), acetic anhydride (Ac2O) were used without purification.

1-2.) Measurements.

The number average of molecular weight of PLLA 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 GMHXL) were connected in series and tetrahydrofran (THF) was used as an eluent. ¹H NMR spectra were measured with a NMR spectrometer (JEOL FX400) at 400 MHz and 600MHz.

1-3.) Synthesis of poly(L-lactide) (PLLAb)

\[ \text{To the round bottom flask, LLA (2 g, 13.9 mmol) was dissolved in 2 mL of toluene under N}_2 \text{ atmosphere, then benzyl alcohol (36 } \mu \text{L, 0.347 mmol) and SnOct}_2 \text{ (28 mg, 0.0694 mmol) were combined to heat up at 120 °C for 2 hr. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol twice. The yield was 92 %.} \]

1-4.) Synthesis of poly(D-lactide) (PDLAb)

\[ \text{To the round bottom flask, DLA (10 g, 69.4 mmol) was dissolved in 10 mL of toluene under N}_2 \text{ atmosphere, then benzyl alcohol (180 mL, 1.73 mmol) and SnOct}_2 \text{ (70 mg, 0.173 mmol) were} \]

2
combined to heat up at 120 °C for 2 hr. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol twice. The yield was 83 %.

1-5.) Synthesis of 3,4-diacetoxycinnamic acid (DACA)

![Chemical structure of DACA]

DACA was prepared according to the literature. To the round bottom flask, DHCA (10 g, 55.5 mmol) was dissolved in 20 mL of dry pyridine under N₂ atmosphere at 0 °C. After 30 min, 30 mL of acetic anhydride (318 mmol) was added to stir for 30 min at 0 °C. Then the reaction mixture was heated up to 130 °C for 5 hr. After the reaction, the solvent was evaporated and recrystallized from toluene. The obtained compound was washed by 0.1 N HCl repeatedly. The yield was 50 %.

1-6.) Synthesis of 3,4-diacetoxycinnamoyl chloride (DACC)

![Chemical structure of DACC]

DACC was prepared according to the literature. To the round bottom flask, DACA (0.264 g, 1 mmol) was dissolved in 0.6 mL of dichloromethane. Then, 0.5 mL of SOCl₂ and 0.79 μL of dimethylformamide (DMF) were added to heat up to 60 °C for 7 hr. The reaction mixture was directly transferred to the next reaction without further purification.

1-7.) Synthesis of DACA-PLLAb

![Chemical structure of DACA-PLLAb]

DACA conjugation with PLLAb was achieved according to the literature. 0.525 g of PLLAb was dissolved into 1.875 mL of dichloromethane and 0.094 mL of pyridine. The mixture was then, it was introduced into DACC (0.23 g, 0.83 mmol) at 0 °C to stir for 1.5 hr. The reaction mixture was kept to
stir at room temperature for 24 hr. After the reaction, the product was washed by 0.1 N HCl repeatedly and reprecipitated in ethanol.

**1-8. Synthesis of DACA-PDLAb**

DACA conjugation with PDLAb was achieved according to the literature.\[^{[8]}\] 0.525 g of PLLAb was dissolved into 1.875 mL of dichloromethane and 0.094 mL of pyridine. The mixture was then, it was introduced into DACC (0.23 g, 0.83 mmol) at 0 °C to stir for 1.5 hr. The reaction mixture was kept to stir at room temperature for 24 hr. After the reaction, the product was washed by 0.1 N HCl repeatedly and reprecipitated in ethanol.
2. $^1$H NMR spectra of polymers.

Figure S1. $^1$H NMR spectrum of PLLAb in CDCl$_3$ at r.t. (600 MHz).

Figure S2. $^1$H NMR spectrum of PDLAb in CDCl$_3$ at r.t. (600 MHz).
**Figure S3.** $^1$H NMR spectrum of DACA-PLLAb in CDCl$_3$ at r.t. (400 MHz).

**Figure S4.** $^1$H NMR spectrum of DACA-PDLAb in CDCl$_3$ at r.t. (400 MHz).
3. FT-IR/ATR spectra of polymers

![FT-IR/ATR spectrum of PLLAb.]

\[ \delta_{as} = 1455 \text{ cm}^{-1} \]

![Wave number / cm$^{-1}$](#)

**Figure S9.** FT-IR/ATR spectrum of PLLAb.

![FT-IR/ATR spectrum of PDLAb.]

\[ \delta_{as} = 1455 \text{ cm}^{-1} \]

![Wave number / cm$^{-1}$](#)

**Figure S10.** FT-IR/ATR spectrum of PDLAb.
**Figure S11.** FT-IR/ATR spectrum of DACA-PLLAb.

- $\delta_{as} = 1455 \text{ cm}^{-1}$
- $\nu_{c=c} = 1640 \text{ cm}^{-1}$
- $\nu_{p=\phi} = 1504 \text{ cm}^{-1}$

**Figure S12.** FT-IR/ATR spectrum of DACA-PDLAb.

- $\delta_{as} = 1455 \text{ cm}^{-1}$
- $\nu_{c=c} = 1640 \text{ cm}^{-1}$
- $\nu_{p=\phi} = 1504 \text{ cm}^{-1}$
4. SEC charts of polymers

**Figure S5.** SEC chart of PLLAb in CHCl$_3$.

**Figure S6.** SEC chart of PDLAb in CHCl$_3$. 
References