Electronic Supplementary Information for:

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

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Contents **page**

1. Experimental procedure 2
2. ^{1}H NMR spectra 5
3. FT-IR/ATR spectra 7
4. SEC traces 9

1. Experimental procedure

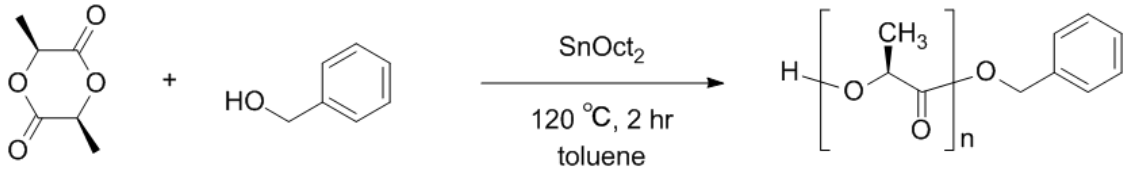
1-1.) Materials.

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 CaH_2 for purification. Thionyl chloride ($SOCl_2$), 3,4-dihydroxycinnamic acid (DHCA), acetic anhydride (Ac_2O) were used without purification.

1-2.) Measurements.

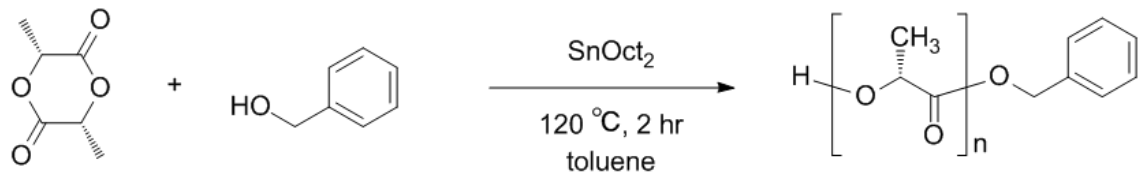
The number average of molecular weight of PLLA was determined by size exclusion chromatography (SEC). A JASCO Chem NAV system was used with polystyrene standards at 40 ºC, equipped with PU-2080, AS-2055, CO-2065, and RI-2031. Two commercial columns (TSKgel SuperH4000 and TSKgel GMH_{XL}) were connected in series and 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)



To the round bottom flask, LLA (2 g, 13.9 mmol) was dissolved in 2 mL of toluene under N_2 atmosphere, then benzyl alcohol (36 μL, 0.347 mmol) and $SnOct_2$ (28 mg, 0.0694 mmol) were combined to heat up at 120 ºC for 2 hr. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol twice. The yield was 92 %.

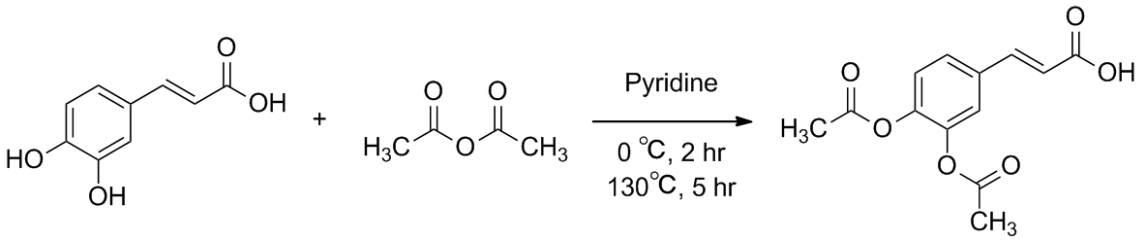
1-4.) Synthesis of poly(D-lactide) (PDLAb)



To the round bottom flask, DLA (10 g, 69.4 mmol) was dissolved in 10 mL of toluene under N_2 atmosphere, then benzyl alcohol (180 mL, 1.73 mmol) and $SnOct_2$ (70 mg, 0.173 mmol) were

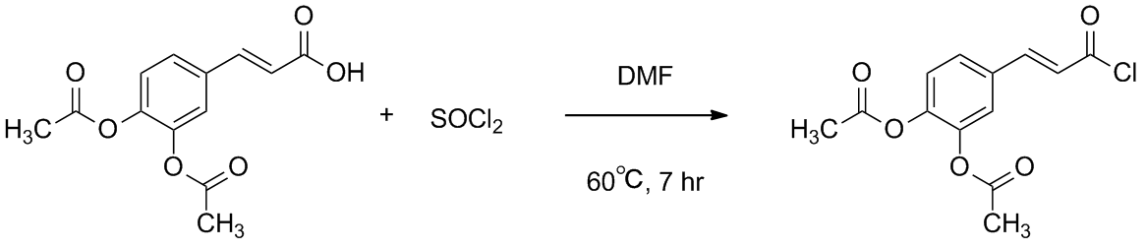
combined to heat up at 120 ºC for 2 hr. After the reaction, the product was dissolved in chloroform and purified by re-precipitation over methanol twice. The yield was 83 %.

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



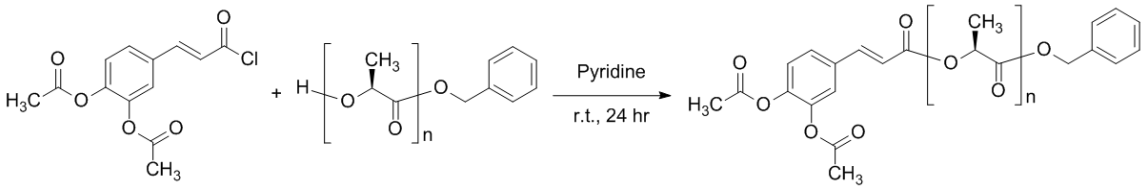
DACA was prepared according to the literature.[S1] To the round bottom flask, DHCA (10 g, 55.5 mmol) was dissolved in 20 mL of dry pyridine under N_2 atmosphere at 0 ºC. After 30 min, 30 mL of acetic anhydride (318 mmol) was added to stir for 30 min at 0 ºC. Then the reaction mixture was heated up to 130 ºC 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)



DACC was prepared according to the literature .[S1] To the round bottom flask, DACA (0.264 g, 1 mmol) was dissolved in 0.6 mL of dichloromethane. Then, 0.5 mL of $SOCl_2$ and 0.79 µL of dimethylformamide (DMF) were added to heat up to 60 ºC for 7 hr. The reaction mixture was directly transfered to the next reaction without further purification.

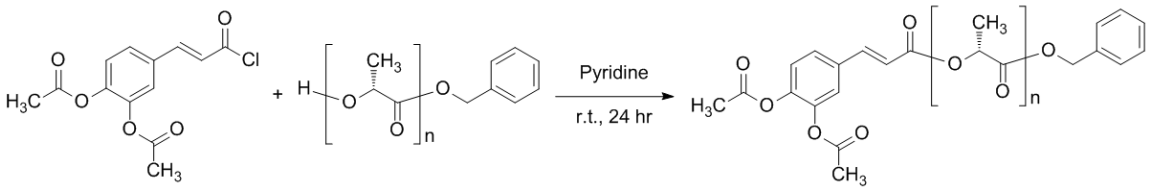
1-7.) Synthesis of DACA-PLLAb



DACA conjugation with PLLAb was achieved according to the literature.[S1] 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 ºC 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.[S1] 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 ºC 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.

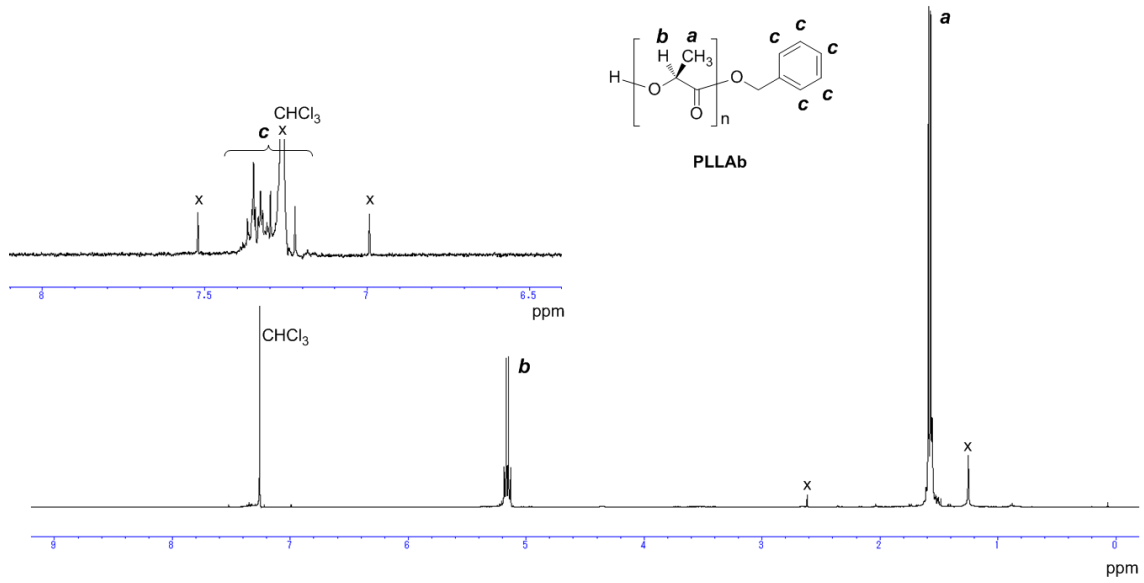


Figure S1. ^{1}H NMR spectrum of PLLAb in $CDCl_3$ at r.t. (600 MHz).

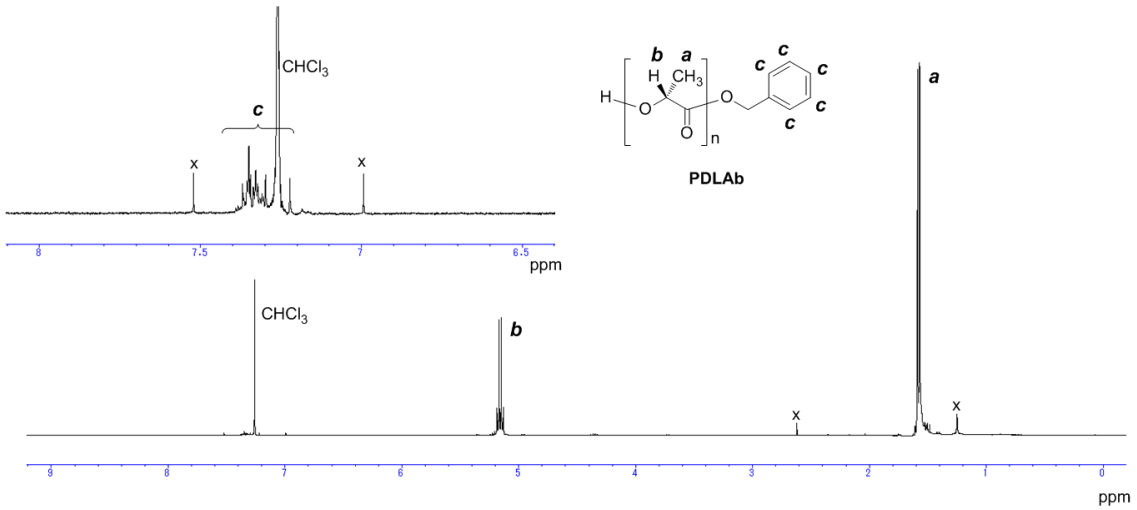


Figure S2. ^{1}H NMR spectrum of PDLAb in $CDCl_3$ at r.t. (600 MHz).

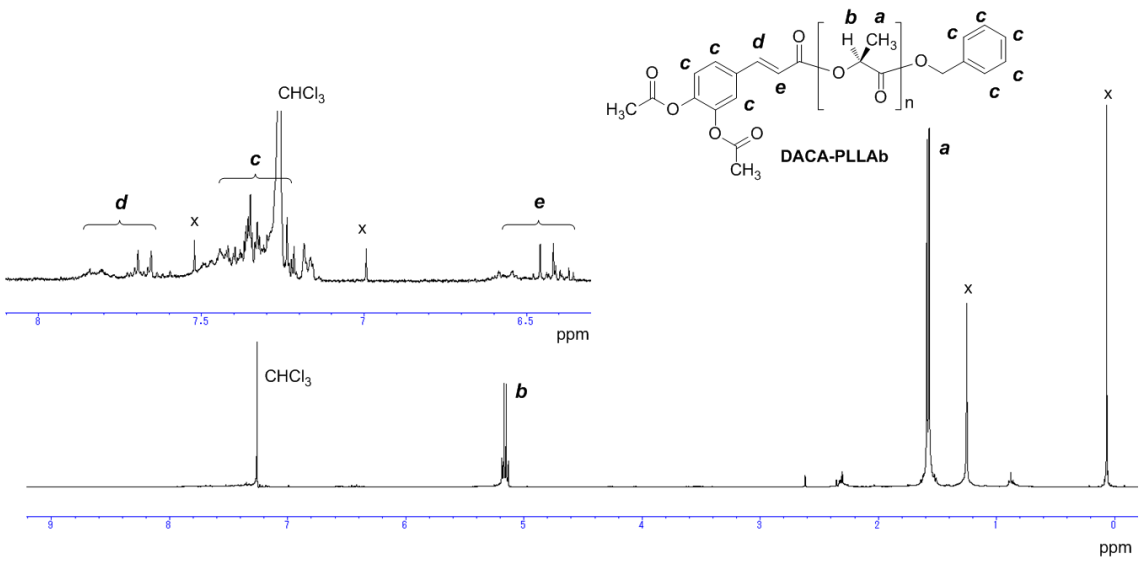


Figure S3. ^{1}H NMR spectrum of DACA-PLLAb in $CDCl_3$ at r.t. (400 MHz).

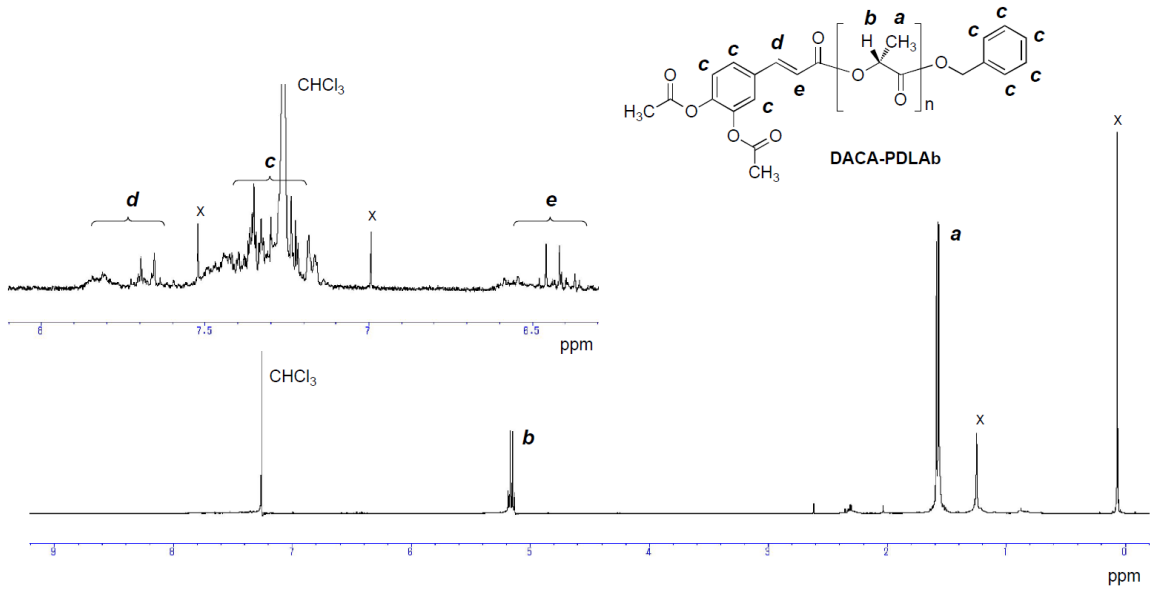


Figure S4. ^{1}H NMR spectrum of DACA-PDLAb in $CDCl_3$ at r.t. (400 MHz).

3. FT-IR/ATR spectra of polymers

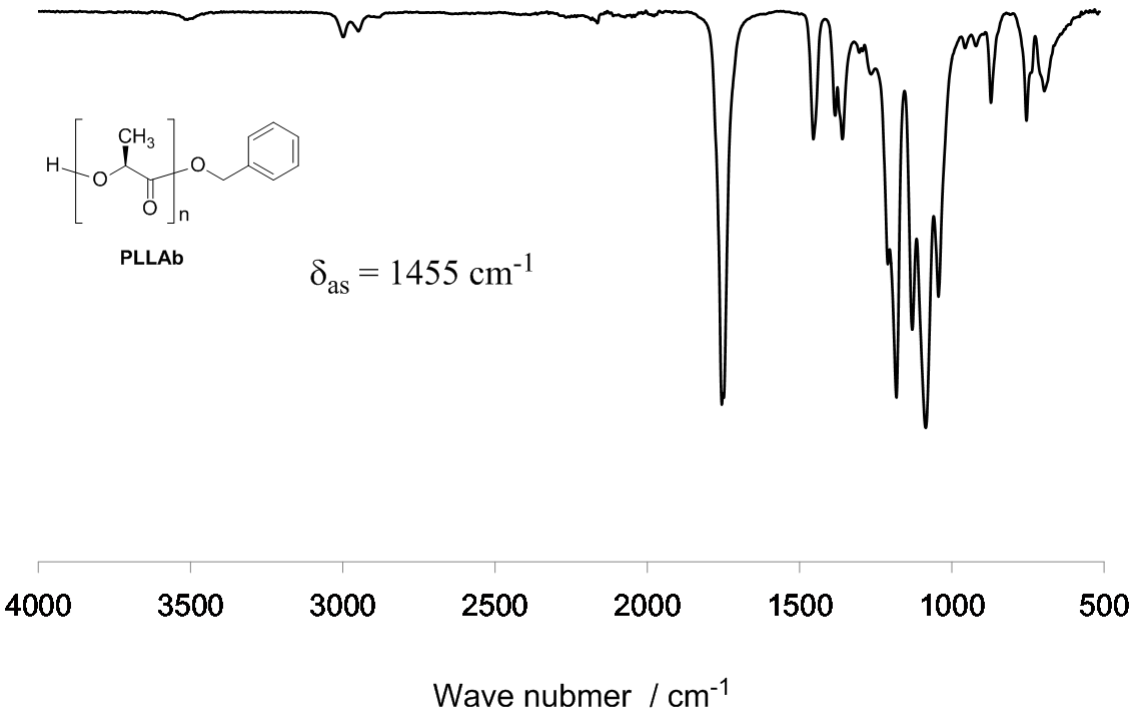


Figure S9. FT-IR/ATR spectrum of PLLAb.

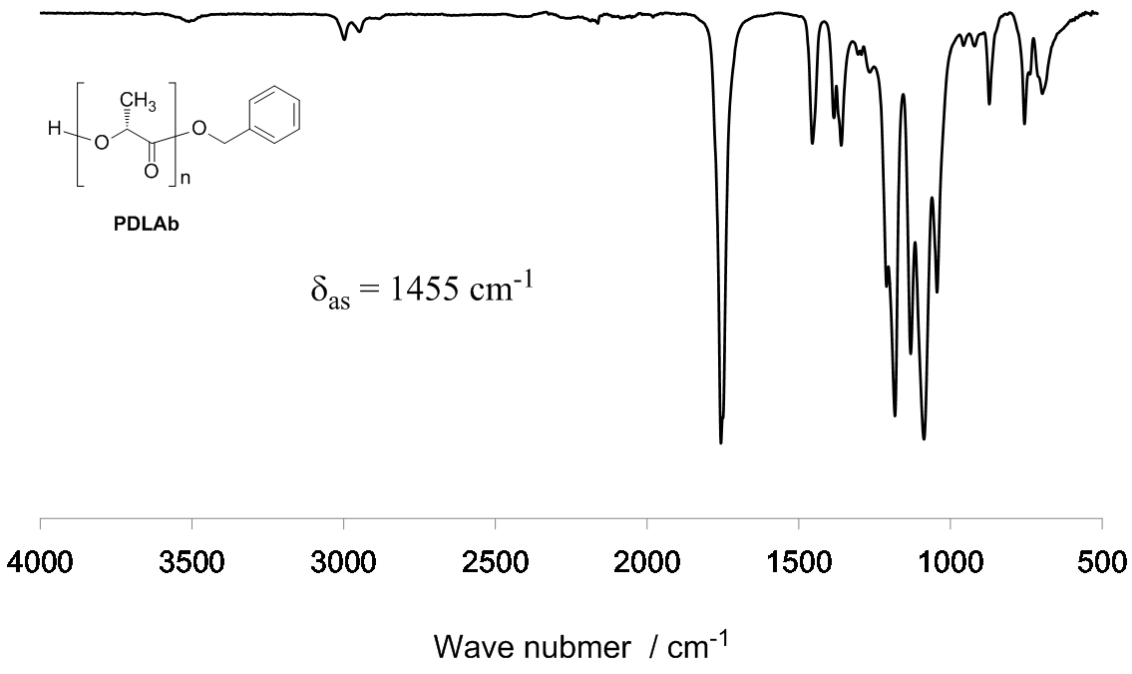


Figure S10. FT-IR/ATR spectrum of PDLAb.

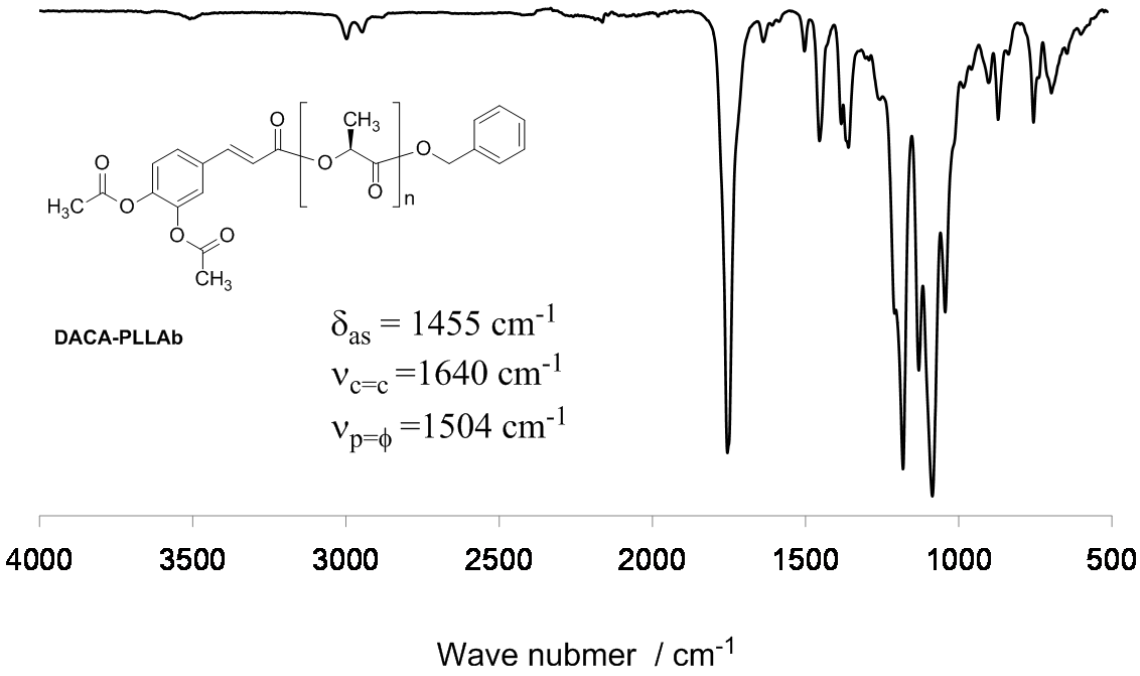


Figure S11. FT-IR/ATR spectrum of DACA-PLLAb.

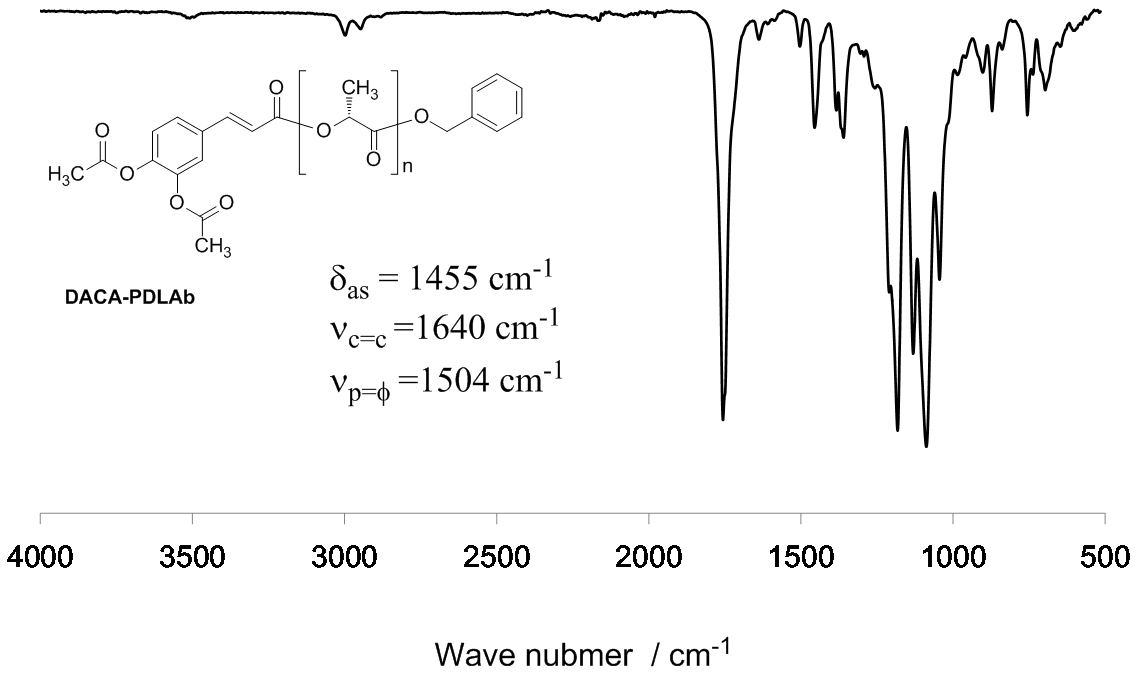
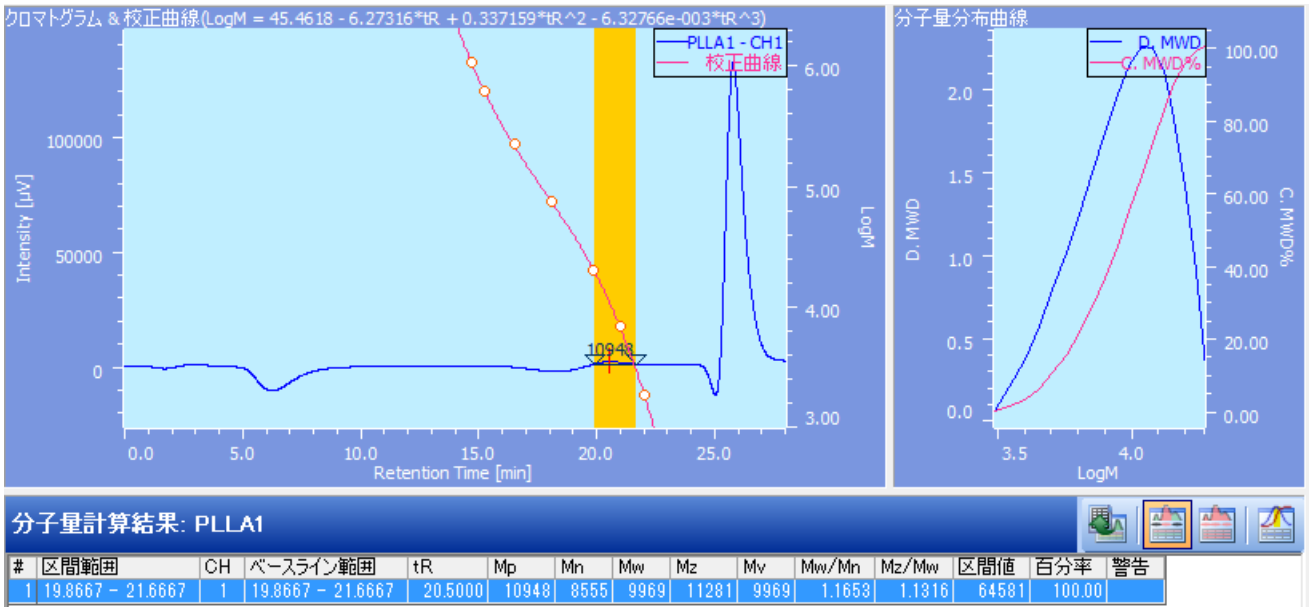


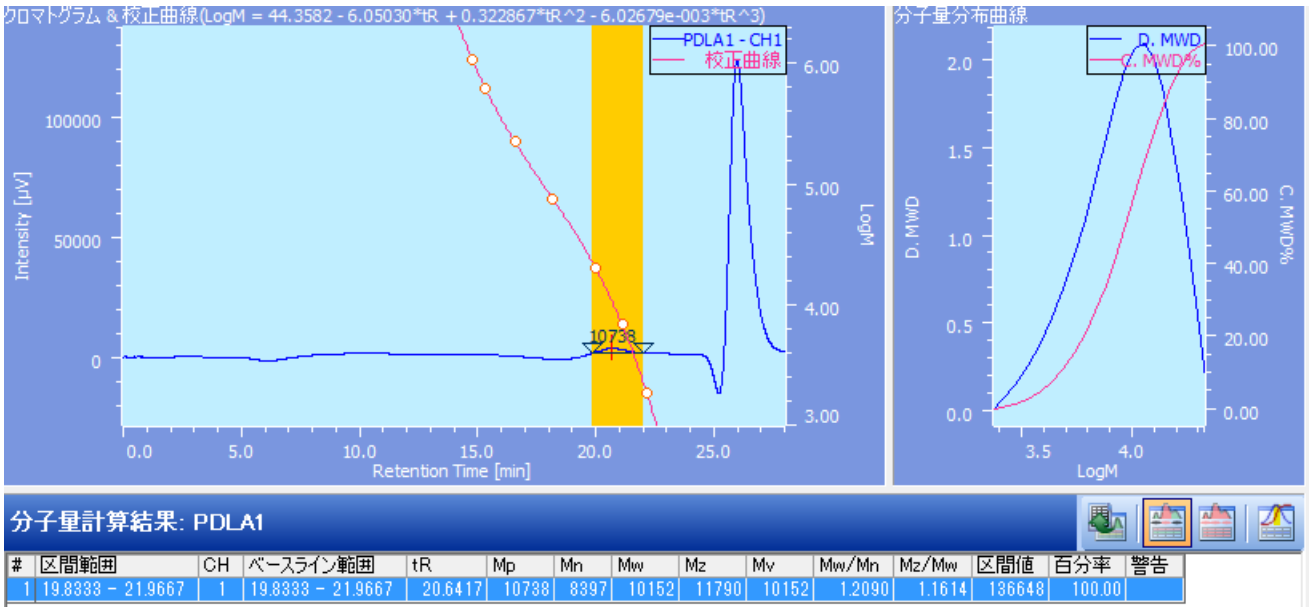
Figure S12. FT-IR/ATR spectrum of DACA-PDLAb.

4. SEC charts of polymers



#	区間範囲	CH	ベースライン範囲	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	区間値	百分率	警告
1	19.8667 - 21.6667	1	19.8667 - 21.6667	20.5000	10948	8555	9969	11281	9969	1.1653	1.1316	64581	100.00	

Figure S5. SEC chart of PLLAb in $CHCl_3$.



#	区間範囲	CH	ベースライン範囲	tR	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	区間値	百分率	警告
1	19.8333 - 21.9667	1	19.8333 - 21.9667	20.6417	10738	8397	10152	11790	10152	1.2090	1.1614	136648	100.00	

Figure S6. SEC chart of PDLAb in $CHCl_3$.

References

[S1] T. H. Thi, M. Matsusaki, and M. Akashi, *Chem. Commn.*, 2008, 3918-3920.