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ARTICLE

## Thermal Stable Poly lactides by Stereocomplex Formation and Both Terminal Conjugation with Bio-based Cinnamic Acid Derivatives

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The novel poly lactides (PLAs) with both terminal conjugation of cinnamic acid (CA) derivatives showed high thermal stability and photoreactivity. Their stereocomplex formation was influenced by conjugation groups at both chain ends of PLAs, showed photoreactivity and a dramatic improvement in their 10% weight thermal decomposition temperature ( $T_{10}$ ) from 250 to 320 or 345 °C for conjugated CA or 3,4-diacetoxycinnamic acid (DACA). Interestingly, CA or DACA-conjugated stereocomplexes showed above 98% weight remaining, although the original PLAs showed a 23 wt% pyrolysis during isothermal degradation at 200 °C for 120 min. Thermal stability and photoreactivity of PLAs or their stereocomplexes were controlled by cinnamic acid derivatives. These PLAs and their stereocomplexes may be useful as functional bio-based materials for various application fields.

### Introduction

Poly lactides (PLAs) are a widely investigated as bio-based renewable material, which are synthesized from lactic acid and generates renewable resources.<sup>1,2</sup> Their products are degradable in nature and in the human body.<sup>3</sup> Furthermore, PLAs exhibit excellent physical properties compared to some general purpose plastics.<sup>4</sup> These properties have made PLA materials become a hot research area from the standpoint of both basic and applied research.<sup>5-7</sup> However, since the melting temperature ( $T_m$ ) and heat resistance of PLAs are relatively low, they are limited in the application fields. Therefore, further improvement of thermal stability of PLAs is still required especially for industrial applications. Ikada et al. discovered that stereocomplex (PLA-sc) formation between enantiomeric poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) showed a high melting point ( $T_m$ ), ca. 50 °C higher than that of the pure PLLA or PDLA, as evidenced by differential scanning calorimetry (DSC) and X-ray diffraction (XRD).<sup>8-12</sup> PLA-sc can be formed in the solution<sup>13-19</sup> and in the melt blending<sup>20-24</sup>. In PLA-sc formation by solution casting method, PLLA and PDLA homopolymers have to completely dissolve in volatile good organic solvents such as

chloroform, dichloromethane (DCM), etc. The melt blending process is another option in making PLA-sc.<sup>25</sup> Direct melt blending of the PDLA with PLLA is not desirable due to the high temperatures needed (over  $T_m$ ), and PLLA or PDLA homopolymers can be pyrolyzed.<sup>26,27</sup> The PLA-sc formed from linear and branched PLAs,<sup>28-31</sup> or multiarmed PLAs<sup>22,32-34</sup> have been reported. However, all PLAs used to form stereocomplexes were substituted by initiator in a chain end. PLAs which are modified at both chain ends have never been investigated for stereocomplex formation, except for our studies.<sup>35,36</sup> In addition, initiators which are used to ring-opening polymerize PLAs were almost aliphatic alcohols, particularly functional aromatic cinnamic acid derivatives have been never reported.

The cinnamic acid (CA) derivatives are known as 3,4-dihydroxycinnamic acid (DHCA), ferulic acid, coumaric acid etc., which exist in most plants, have photoreactive, biometabolizable and nontoxic properties. In previous studies, we reported that the thermal and mechanical properties of poly(coumaric acid) were improved when copolymerized with DHCA.<sup>37</sup> Therefore, 3,4-diacetoxycinnamic acid (DACA), which was obtained by acetylation of DHCA, was expected to enhance the thermal and mechanical properties of PLLA. As expected, the thermal stability of PLLA was improved by terminal conjugation of DACA. In particular,  $T_{10}$  showed an increase of over 100 °C, as compared to PLLA of the same molecular weight although the crystallinity and solubility of the PLLA were well-maintained after the conjugation of DACA.<sup>35,36,38-40</sup> The PLA-sc with natural aromatic compounds conjugated at both chain ends known as terminal and initiating groups was successfully formed in the mixing acetonitrile solution.<sup>35,36</sup> These stereocomplexes showed simultaneous improvements in both  $T_m$  and  $T_{10}$  regardless of the molecular weight. However, the effect of cinnamic acid derivatives on the thermal properties of PLAs or PLA-sc and photoreactivities of PLA-sc with both terminal conjugation of cinnamic acid derivatives have never been reported. If other cinnamic acid derivatives are also able to enhance the thermal properties of PLAs, PLA products will be diversified and their application fields will be widened as well.

Herein, we developed the series of PLA stereocomplex with both terminal conjugation using cinnamic acid derivatives, for the first time. The various PLAs were successfully prepared by the use of

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aromatic hydroxyl group of cinnamic acid derivative as initiator. The effect of cinnamic acid derivatives on their thermal stability and photoreactivity was also evaluated.

## Experimental Section

### Materials

L-Lactide (LLA) and D-lactide (DLA) (Musashino Chemical Laboratory, Ltd., Japan) were recrystallized from ethyl acetate and then dried under reduced pressure at room temperature for 24 h. Tin(II) 2-ethylhexanoate (SnOct<sub>2</sub>; assay: 96%), thionyl chloride (SOCl<sub>2</sub>; assay: > 95%), DHCA (assay: > 98%), acetic anhydride (assay: > 97%), cinnamoyl chloride (CC; assay: > 95%) (Wako Pure Chemical Industries, Ltd.) and ethyl ferulate (EF; assay: 98%) (Sigma Aldrich) were used without further purification.

### Synthetic procedures

**Synthesis of Poly(L-lactide) (PLLAEF) and Poly(D-lactide) (PDLAEF).** PLLAEF and PDLAEF (PLAEFs) were prepared according to the literature.<sup>38</sup> The typical procedure is as follows. In a round-bottom flask, the required amount of LLA, EF and SnOct<sub>2</sub> (0.3 wt% of monomer) which was dissolved in toluene, was mixed and mechanically stirred *in vacuo* at room temperature for 1 h to remove air. Next, the mixture reacted at 160 °C for 4 h in a nitrogen atmosphere. After the reaction, the product was dissolved in chloroform, purified by re-precipitation over methanol twice and dried under reduced pressure at room temperature for 24 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ = 1.33-1.78 (m, 3H of PLA and 3H of EF), 3.83 (m, 3H), 4.25 (m, 2H), 5.17 (t, 1H), 6.41 (d, 1H), 6.98-7.52 (m, 3H), 7.61 (d, 1H).

**Synthesis of DACA conjugated PLLAEF (DACA-PLLAEF), DACA conjugated PDLAEF (DACA-PDLAEF), CA conjugated PLLAEF (CA-PLLAEF) and CA conjugated PDLAEF (CA-PDLAEF).** DACA-PLLAEF, DACA-PDLAEF (DACA-PLAEFs), CA-PLLAEF and CA-PDLAEF (CA-PLAEFs) were prepared according to the literature.<sup>38</sup> The typical procedure of CA-PLLAEF is as follows. In a round-bottom flask, 5 g of PLLAEF ( $M_n = 25.6 \times 10^3$ ; 0.195 mmol) was dissolved in 20 ml of distilled dichloromethane (DCM) and 1 ml of distilled pyridine at 0 °C for 30 min, and 131 mg of CC (0.781 mmol; molar ratio of PLLAEF1 : CC = 1:4) was then added and stirred at this temperature for 1.5 h, and at room temperature for 24 h. After the reaction, the product was washed in HCl solution (pH 3), re-precipitated into ethanol by being dissolved in chloroform twice, and dried under reduced pressure at room temperature for 24 h. <sup>1</sup>H NMR of DACA-PLAEFs (CDCl<sub>3</sub>, 400 MHz) δ = 1.33-1.78 (m, 3H of PLA and 3H of EF), 2.17 (m, 6H), 3.83 (m, 3H), 4.25 (m, 2H), 5.17 (t, 1H), 6.38-6.44 (m, 2H), 6.98-7.57 (m, 6H), 7.61-7.71 (m, 2H). <sup>1</sup>H NMR of CA-PLAEFs (CDCl<sub>3</sub>, 400 MHz) δ = 1.33-1.58 (m, 3H of PLA and 3H of EF), 3.83 (m, 3H), 4.25 (m, 2H), 5.17 (t, 1H), 6.42-6.46 (m, 2H), 6.98 (d, 2H), 7.00-7.80 (m, 8H).

**Stereocomplex preparation.** The various DACA-PLAEFs or CA-PLAEFs were dissolved in DCM at a concentration of 4 mg mL<sup>-1</sup>. Then, corresponding 5 mL of DACA-PLLAEF and 5 mL of DACA-PDLAEF1 or DACA-PDLAEF2, 5 mL of CA-PLLAEF and 5 mL of CA-PDLAEF1 or CA-PDLAEF2 solutions were mixed in teflon petri dish (d = 3 cm). They were then dried at room temperature for 24 h to get films.

### Characterization

**Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR).** <sup>1</sup>H NMR spectra of PLAEFs, DACA-PLAEFs and CA-PLAEFs were obtained on a JNM-GSX-400 spectrometer (400 MHz; JEOL, Japan) in chloroform-*d*.

**Fourier transform infrared (FT-IR).** FT-IR spectra of PLAEFs, DACA-PLAEFs, CA-PLAEFs and their stereocomplexes were measured on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (Japan) in the region of 4000-400 cm<sup>-1</sup>.

**Gel permeation chromatography (GPC).** GPC data of PLAEFs were collected on a HLC 8120 GPC system with an R-M column (TOSOH Co., Ltd.) in chloroform and then calibrated with polystyrene standards with a flow rate of 0.6 mL min<sup>-1</sup> at 40 °C.

**Wide-angle X-ray diffraction (WAXD).** WAXD patterns of PLAEFs, DACA-PLAEFs, CA-PLAEFs and their stereocomplexes were obtained on a X-ray diffractometer (RINT UltraX18), equipped with a scintillation counter using CuKα radiation (40 kV, 200 mA; wavelength = 1.5418 Å).

**Thermal properties.** The thermal properties of the various PLAEFs, DACA-PLAEFs, CA-PLAEFs and their stereocomplexes were analyzed by differential scanning calorimetry (DSC; EXSTAR6000, Seiko Instruments Inc.) and thermal gravimetric analysis (TGA; EXSTAR6200, Seiko Instruments Inc.). The heating rate was 10 °C min<sup>-1</sup>, and the temperature ranged from 30 to 300 °C for the DSC measurements. The melting temperature ( $T_m$ ) was obtained from the DSC curves. The thermal degradation behavior of the samples was observed from the TGA curves by being heated from 30 to 500 °C at a rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere with a flow rate ca. 250 mL min<sup>-1</sup>. The heat resistance to pyrolytic measurements of representative PLLAEF, DACA-PLLAEF, DACA-PLAEF2-sc, CA-PLLAEF and CA-PLAEF2-sc were performed from 30 to 200 °C at a rate of 20 °C min<sup>-1</sup>, plus a hold at 200 °C for 120 min under a nitrogen atmosphere at a flow rate ca. 250 mL min<sup>-1</sup>.

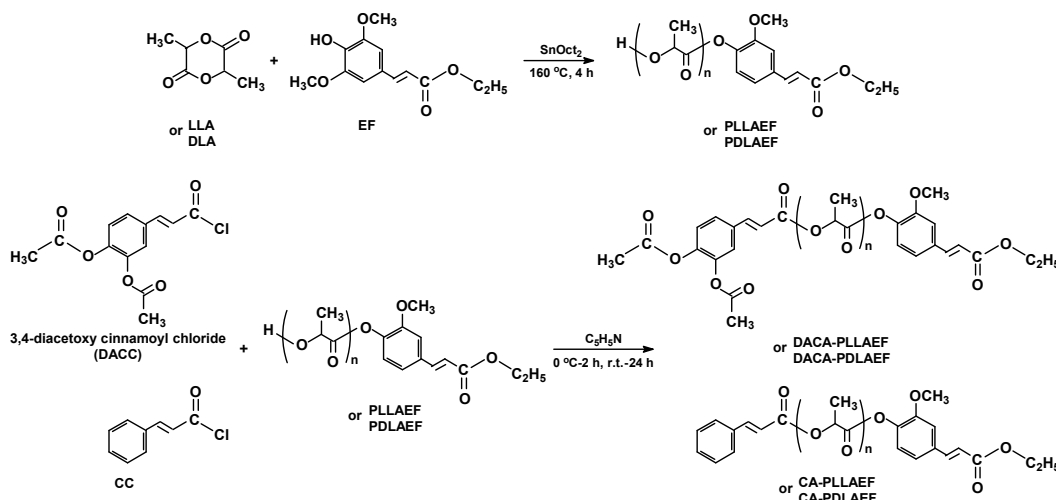
**Photoreactivities.** PLAEFs were dissolved in DCM to concentration of 1 mg mL<sup>-1</sup>. Their absorbance was monitored by UV-visible absorption spectroscopy using a HITACHI U3010 Spectrophotometer (Hitachi, Tokyo, Japan). The photoreactivities of representative DACA-PLAEF2-sc and CA-PLAEF2-sc films were evaluated using a glass-filtered high-pressure Hg Lamp ( $\lambda > 280$  nm, 56 mW cm<sup>-2</sup>, Supercure-352S-UV Lightsource; SAN-EI ELECTRIC) for irradiation. The time course of the photoreaction conversion was monitored by UV-visible absorption spectroscopy.

## Results and discussion

### Synthesis of PLAEFs

It is known that PLAs are synthesized by the direct condensation of lactic acids or ring-opening polymerization of lactides using initiators as alcohols. The direct condensation of lactic acids is difficult to obtain PLAs at high molecular weight due to degradation. On the other hand, ring-opening polymerization gives more higher molecular weight PLAs. Initiators which are used for ring-opening polymerization of lactides are almost aliphatic alcohols. In this study, we used a new aromatic initiator of bio-based ethyl ferulate which is cinnamic acid derivative to synthesize PLAs (Scheme 1), in order to introduce cinnamic acid derivatives at chain end group.

Table 1 shows the properties of PLAEFs. The yield was over 80 wt%, molecular weight ( $M_n$ ) of PLLAEF, PDLAEF1 and PDLAEF2 was 25.6, 11.1 and 94.6 kDa, molecular weight distribution (PDI) was 1.8, 1.4 and 1.5, respectively. The structure of PLAEFs was analyzed with FT-IR, <sup>1</sup>H NMR and UV-vis. All FT-IR spectra of the polymers exhibited a characteristic carbonyl (C=O) stretching band of the ester group at about 1758 cm<sup>-1</sup> for PLLA or PDLA, and low intensity of C=C stretching band of the cinnamoyl group at 1637 cm<sup>-1</sup> for EF, a methyl (CH<sub>3</sub>) stretching band from PLLA or PDLA at 1450 cm<sup>-1</sup> (Fig. 1a, 1b, and 1c). The peak intensity of cinnamoyl group compared to carbonyl group was decreased with increasing molecular weight of PLAEF (Fig. 1d, 1e, and 1f). <sup>1</sup>H NMR spectra of PLAEFs confirmed that the peak of both EF (6.98-7.52 ppm is

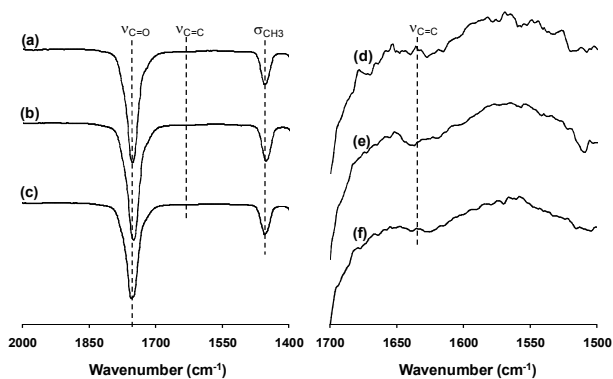


**Scheme 1** Synthesis of various PLAEFs, DACA-PLAEFs and CA-PLAEFs.

**Table 1** Properties of various PLAEFs<sup>a</sup>

Run	Sample	Yield <sup>b</sup> (wt%)	$M_n$ <sup>c</sup> ( $\times 10^3$ Da)	PDI <sup>c</sup>	$T_m$ <sup>d</sup> (°C)	$T_{10}$ <sup>e</sup> (°C)
1	PLLAEF	88	25.6	1.8	176	255
2	PDLAEF1	85	11.1	1.4	174	240
3	PDLAEF2	89	94.6	1.5	177	254

<sup>a</sup>PLAs were prepared by ring-opening polymerization with each lactide. <sup>b</sup>Yield present results after the purification. <sup>c</sup>The molecular weight and distributions were estimated by GPC in chloroform with polystyrene standards. <sup>d</sup>The  $T_m$  was measured by DSC at heating rate of 10 °C min<sup>-1</sup>. <sup>e</sup>The 10% weight-loss temperature,  $T_{10}$ , was measured by TGA under nitrogen atmosphere at heating rate of 10 °C min<sup>-1</sup>.



**Fig. 1** FT-IR spectra of PDLAEF2 (a) PDLAEF1 (b), and PLLAEF (c) in the range of 1400-2000 cm<sup>-1</sup>, and PDLAEF2 (d), PDLAEF1 (e), and PLLAEF (f) in the range of 1500-1700 cm<sup>-1</sup>.

typical of protons of phenyl group, 6.41 and 7.61 ppm is typical of protons of cinnamoyl group, 4.25 ppm is typical of protons of CH<sub>2</sub> group) and PLAs (5.17 ppm is typical of protons of CH group and 1.58 ppm is typical of protons of CH<sub>3</sub> group) (Fig. 2a). Furthermore, to confirm the presence of EF, UV-vis spectra were measured in DCM for PLLAEF, PDLAEF1 and PDLAEF2 (data not shown). The presence of the peak at the wavelength of 279 nm was typical of the absorbability of cinnamoyl group. These

results suggest that PLAEFs were successfully synthesized and EF could be an initiator for ring-opening polymerization of lactides to obtain novel functional PLAs.

#### Synthesis of CA-PLAEFs and DACA-PLAEFs

In previous studies, we successfully conjugated the DACA into PLLA, PDLA, poly(DL-lactide), poly( $\epsilon$ -caprolactone) and poly(ethylene glycol) chain ends.<sup>35,36,38,40</sup> With the same method, DACA-PLAEFs and CA-PLAEFs were synthesized (Scheme 1). The obtained FT-IR spectra were similar to those in Fig. 1 (data not shown), but the peak intensity of cinnamoyl group compared to carbonyl group were greater than that in Fig. 1 due to plus one cinnamoyl group of DACA or CA in the polymer chains. In addition, the peak intensity of cinnamoyl group compared to carbonyl group was decreased with increasing molecular weight of PLAs. <sup>1</sup>H NMR spectra of DACA-PLAEFs showed a peak of 2.3 ppm which is typical of CH<sub>3</sub> protons of DACA (Fig. 2b). These results suggested that DACA or CA was successfully conjugated into PLAEFs chain end.

#### Formation of PLA stereocomplexes (CA-PLAEF-sc and DACA-PLAEF-sc)

It is known that PLA stereocomplexes could be formed in the presence of some solvents, such as chloroform, DCM, and acetonitrile solution. It is also formed in the absence of solvent, such as direct melt blending and bulk polymerization. For example, PLA stereocomplexes obtained by precipitation using PLLA and PDLA acetonitrile solution, are difficult to yield 100%, consuming time to obtain PLA stereocomplexes. On the other hand, PLA-sc can be formed by solution cast using chloroform or DCM after annealing or cooling from melting state. In the previous study, we showed that PLA stereocomplexes were also formed even when being conjugated into both chain ends by DACA and benzylic (as initiator) by precipitation in the solution of acetonitrile.<sup>35,36</sup>

In this study, PLA stereocomplexes with bio-based aromatic groups which are cinnamic acid derivatives at both initiating and terminating chain ends were prepared by casting from DCM solution without annealing or cooling from melting state. Some peaks in the WAXD patterns of CA-PLAEFs, DACA-PLAEFs were observed at  $2\theta = 15.3, 16.8, 19.2$  and  $22.6^\circ$  (Fig. 3a). This is consistent with the peaks at 15, 16, 18.5 and 22.5 reported by Ikada et al.<sup>8</sup> However, the peaks in the WAXD patterns of CA-PLAEF-sc and DACA-PLAEF-

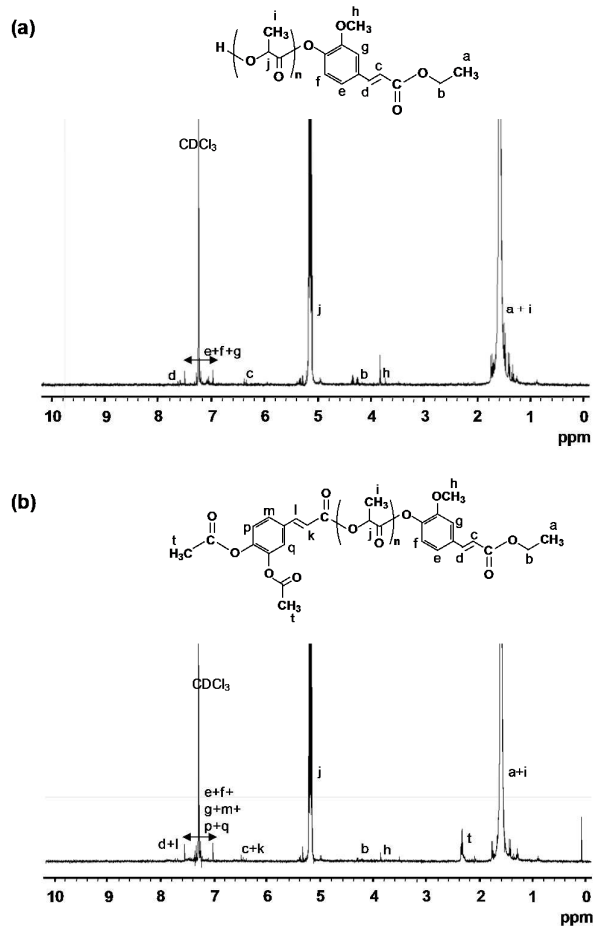


Fig. 2 Representative <sup>1</sup>H NMR spectra of PLLAEF (a), and DACA-PLLAEF (b).

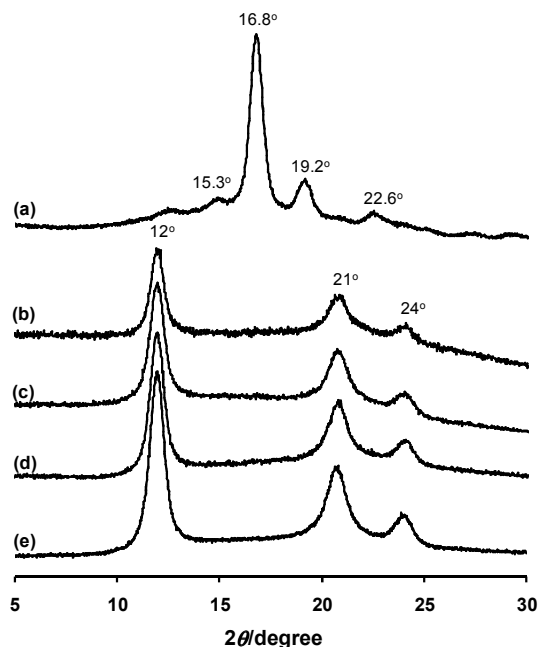


Fig. 3 WAXD patterns of CA-PLLAEF (a), DACA-PLAEF2-sc (b), DACA-PLAEF1 (c), CA-PLAEF2-sc (d), and CA-PLAEF1-sc (e).

Table 2 Thermal properties of various DACA-PLAEFs, CA-PLAEFs, DACA-PLAEF-sc and CA-PLAEF-sc

Run	Sample	L-isomer	D-isomer	$T_m^a$ (°C)	$T_{10}^b$ (°C)
1	DACA-PLLAEF	DACA-PLLAEF	—	176	342
2	DACA-PDLAEF1	—	DACA-PDLAEF1	175	345
3	DACA-PDLAEF2	—	DACA-PDLAEF2	177	348
4	CA-PLLAEF	CA-PLLAEF	—	175	319
5	CA-PDLAEF1	—	CA-PDLAEF1	176	323
6	CA-PDLAEF2	—	CA-PDLAEF2	178	318
7	DACA-PLAEF1-sc	DACA-PLLAEF	DACA-PDLAEF1	225	347
8	DACA-PLAEF2-sc	DACA-PLLAEF	DACA-PDLAEF2	223	345
9	CA-PLAEF1-sc	CA-PLLAEF	CA-PDLAEF1	227	318
10	CA-PLAEF2-sc	CA-PLLAEF	CA-PDLAEF2	228	312

<sup>a</sup>The  $T_m$  was measured by DSC at heating rate of 10 °C min<sup>-1</sup>. <sup>b</sup> $T_{10}$  was measured by TGA under nitrogen atmosphere at heating rate of 10 °C min<sup>-1</sup>.

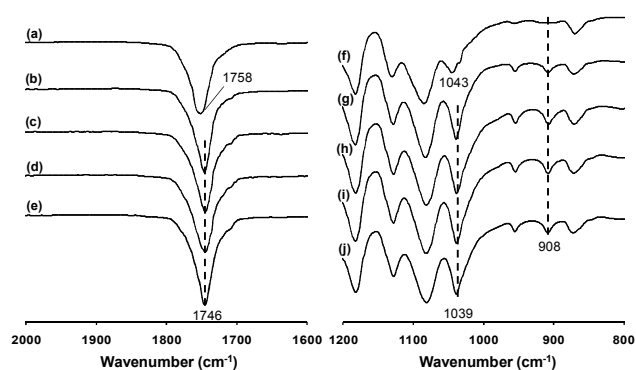


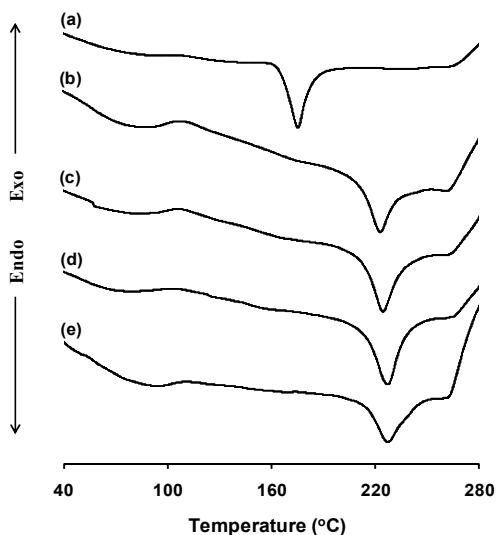
Fig. 4 FT-IR spectra of CA-PLLAEF (a), DACA-PLAEF2-sc (b), DACA-PLAEF1-sc (c), CA-PLAEF2-sc (d), and CA-PLAEF1-sc (e) in range of 1600 – 2000 cm<sup>-1</sup>. FT-IR spectra of CA-PLLAEF (f), DACA-PLAEF2-sc (g), DACA-PLAEF1-sc (h), CA-PLAEF2-sc (i), and CA-PLAEF1-sc (j) in range of 800 – 1200 cm<sup>-1</sup>.

sc shifted at  $2\theta = 12, 21$  and  $24^\circ$  (Fig. 3b-3e), corresponding to the stereocomplex structure. Furthermore, CA-PLAEF-sc and DACA-PLAEF-sc formation were also confirmed by FT-IR spectra which is very useful and fast for analyses of the PLA-sc. Fig. 4 shows the C=O stretching vibrations in the 1800-1700 cm<sup>-1</sup> region as well as the ester group and rocking vibrations in the 970-850 cm<sup>-1</sup> region for DACA-PLAEFs or CA-PLAEFs and DACA-PLAEF-sc or CA-PLAEF-sc. The carbonyl group (C=O) stretching band of the ester group at 1758 cm<sup>-1</sup> of DACA-PLAEFs or CA-PLAEFs (Fig. 4a) was shifted at about 1746 cm<sup>-1</sup> for DACA-PLAEF-sc or CA-PLAEF-sc due to form hydrogen bond of C=O group and CH<sub>3</sub> group (Fig. 4b-4e).<sup>41</sup> Moreover, the band at 1043 cm<sup>-1</sup> disappeared, which was assigned to the stretching vibration of the C-CH<sub>3</sub> group of enantiomeric PLA (Fig. 4f), and new band appeared at 1039 cm<sup>-1</sup> for the DACA-PLAEF-sc or CA-PLAEF-sc as a characteristic band of the DACA-PLAEF-sc or CA-PLAEF-sc (Fig. 4g-4j).<sup>42</sup> In addition, the new band which appear at 908 cm<sup>-1</sup> in the DACA-PLAEF-sc or CA-PLAEF-sc spectra corresponding to the  $\beta$  helix 3<sub>1</sub> of stereocomplex structure (Fig. 4g-4j).<sup>42,43</sup> The band at 2996 cm<sup>-1</sup> characterized the CH<sub>3</sub> asymmetric stretching, shifted to 2993 cm<sup>-1</sup>. These results suggested that the formation of PLA-sc was not affected by both terminal conjugation of cinnamic acid derivatives.

### Thermal properties

The thermal properties of the PLAEFs, DACA-PLAEFs, CA-PLAEFs, DACA-PLAEF-sc and CA-PLAEF-sc were investigated by DSC and TGA. The  $T_m$  of PLAEFs varied between 174 and 177 °C (Table 1), which corresponded to PLAs synthesized from other initiators. In our previous study, when we conjugated DACA into LLA oligomers chain end,  $T_m$  increased by approximately 10 °C. However, in this study, when we conjugated DACA or CA into PLA chain end,  $T_m$  didn't improve much, only between 175 and 178 °C (Fig. 5a and Table 2). In other words,  $T_m$  of PLAs with high molecular weight was not affected by the groups at the chain ends. During the stereocomplexation of enantiomer DACA-PLLAEF and DACA-PDLAEF1, DACA-PLLAEF and DACA-PDLAEF2, CA-PLLAEF and CA-PDLAEF1, CA-PLLAEF and CA-PDLAEF2, the  $T_m$  increased approximately by 50 °C, to between 223 and 228 °C (Fig. 5b-5e and Table 2). These results prove that CA-PLAEF-sc and DACA-PLAEF-sc were successfully formed by DCM solution casting method.

It is known that various factors influence on thermal properties of polymers, such as molecular weight, its distribution, moisture, terminal group, and so on. From the TGA results, the  $T_{10}$  of the PLLAEF, PDLAEF1 and PDLAEF2 were 255, 240, and 254 °C, but the values of the corresponding DACA-PLAEFs were 342, 345, and 348 °C, CA-PLAEFs were 319, 323, and 318 °C, respectively (Fig. 6 and Table 2). These results indicated that the form D- or L- of PLAs didn't affect  $T_{10}$  and the thermal stability of the PLAs were increased by the terminal conjugation of aromatic DACA or CA, the same as the results obtained in a previous study for PLLA.<sup>35, 36, 38-40</sup> We have reported that no molecular weight dependence of the thermal stability improvement by DACA conjugation has been observed.<sup>38</sup> The increase in the  $T_{10}$  of various polymers via copolymerization with hydrophobic monomers has been reported, but such drastic increment of  $T_{10}$  as our results has never been reported. We also reported that the thermal stability of the PLAs was affected by the terminal conjugation of DACA, one of the reasons for the enhanced thermal stability of PLAs is the removal of the hydroxyl ending groups and subsequent elimination of the tin catalyst.<sup>40,44</sup> The thermal degradation of the original PLAs could be occurred mainly from the hydroxyl chain end by both intermolecular and

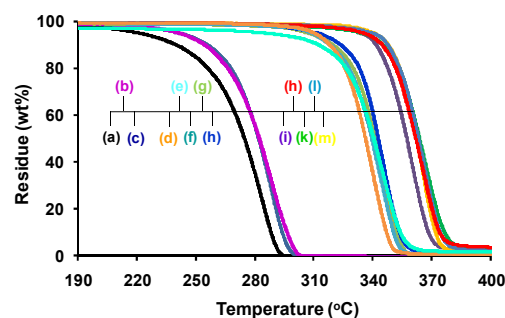


**Fig. 5** DSC curves of CA-PLLAEF (a), DACA-PLAEF2-sc (b), DACA-PLAEF1-sc (c), CA-PLAEF2-sc (d), and CA-PLAEF1-sc (e) at 10 °C min<sup>-1</sup>.

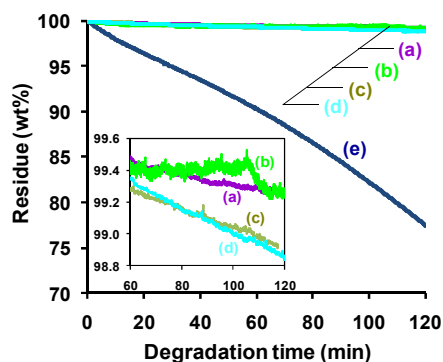
intramolecular transesterification, but the end capping with DACA in the DACA-PLAEF or CA in the CA-PLAEF molecules might inhibit the transesterification. However,  $T_{10}$  of DACA-PLAEFs was approximately 30 °C higher than that of CA-PLAEFs. The  $T_m$  of DACA-PLAEF-sc or CA-PLAEF-sc increased compared to DACA-PLAEFs or CA-PLAEFs, but  $T_{10}$  remained the same. This is because in the melting state, the bond between molecules was weakened, and there was no stereocomplex structure, so stereocomplexes did not affect the pyrolysis.

Recently, for the reduction of global warming gas, improvement of polymer alloy materials by mixing with PLAs has attracted much attention in industries. Therefore, the development of thermally stable PLAs has high industrial value. We also investigated the influence of DACA and CA on the heat resistance to pyrolysis of representative PLAs (Fig. 7). Interestingly, DACA-PLLAEF, DACA-PLAEF2-sc, CA-PLLAEF, CA-PLAEF2-sc showed above 98% weight remaining (Fig. 7a-7d), although the original PLLAEF showed a 23 wt% pyrolysis during isothermal degradation at 200 °C for 120 min (Fig. 7e). However, similar to  $T_{10}$ , stereocomplex structure did not influence heat resistance of DACA-PLAEFs or CA-PLAEFs.

As a result, DACA are more effective than CA as regards the thermal stability of PLAs. Moreover, the thermal properties of PLAs can be controlled by the terminal conjugation of cinnamic acid derivatives. However, DACA is disadvantageously more expensive than CA and needs to be acetylated before being conjugated into



**Fig. 6** TG curves of PDLAEF1 (a), PDLAEF2 (b), PLLAEF (c), CA-PDLAEF1-sc (d), CA-PLAEF2-sc (e), CA-PDLAEF2 (f), CA-PLLAEF (g), CA-PDLAEF1 (h), DACA-PLLAEF (i), DACA-PDLAEF1 (j), DACA-PLAEF2-sc (k), DACA-PLAEF1-sc (l), and DACA-PDLAEF2 (m) at 10 °C min<sup>-1</sup> under nitrogen atmosphere at flow rate of ca. 250 mL min<sup>-1</sup>.



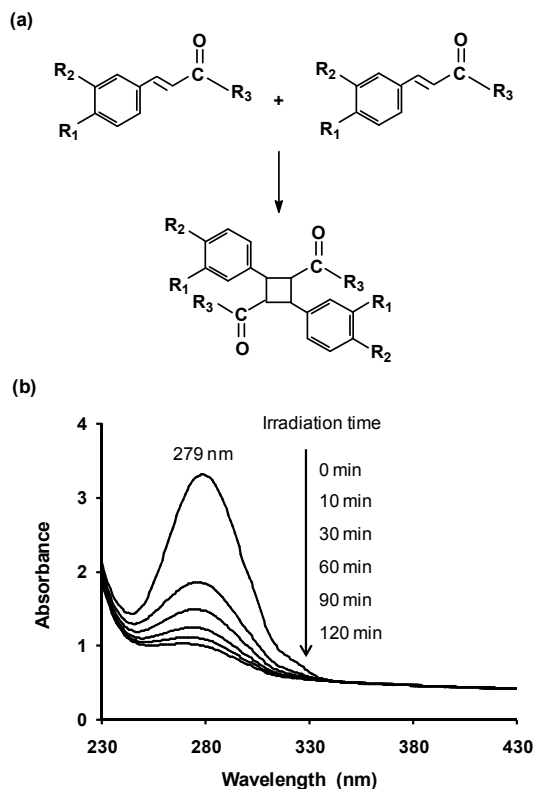
**Fig. 7** Remaining weight change during isothermal degradation of DACA-PLLAEF (a), DACA-PLAEF2-sc (b), CA-PLLAEF (c), CA-PLAEF2-sc (d) and PLLAEF (e) at 200 °C under nitrogen atmosphere at flow rate of ca. 250 mL min<sup>-1</sup>. The inserted graph is the magnification of (a), (b), (c) and (d) samples.

PLA chain end. This research diversified PLA materials with different thermal stabilities and photoreactivities.

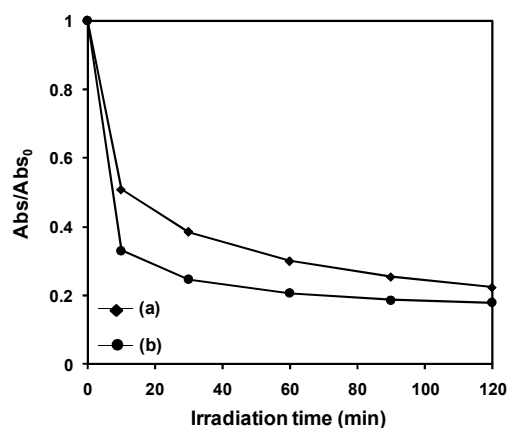
### Photoreactivities

The cinnamoyl group is well-known to undergo [2+2] cycloaddition, leading to the formation of a cyclobutane ring upon UV irradiation (Fig. 8a).<sup>37-40,45-51</sup> In a previous report, we confirmed that DACA-polymers showed high photoreactivities, and their photoreactivities were independent of the chain length of the PLLA.<sup>38-40</sup> Therefore, in this study, the DACA-PLAEF-sc and CA-PLAEF-sc were expected to have photoreactivities. The time-dependent UV absorption changes of the CA-PLAEF1-sc film are shown in Fig. 8b. The maximal absorption peak at  $\lambda_{\max} = 279$  nm decreased with increasing UV irradiation time at  $\lambda > 280$  nm for CA-PLAEF1-sc, and the DACA-PLAEF1-sc with maximal absorption peak at  $\lambda_{\max} = 286$  nm also showed the same behaviors (data not shown). The photoreactivities of both DACA-PLAEF1-sc and CA-PLAEF1-sc were great in the first 10 minutes, then gradually decreased with the time of UV irradiation. The photoreactivity of DACA-PLAEF1-sc is higher than that of CA-PLAEF1-sc. DACA-PLAEF1-sc and CA-PLAEF1-sc showed about 82% and 78% conversion of the [2+2] cycloaddition after UV irradiation at  $\lambda > 280$  nm for 120 min, respectively (Fig. 9).

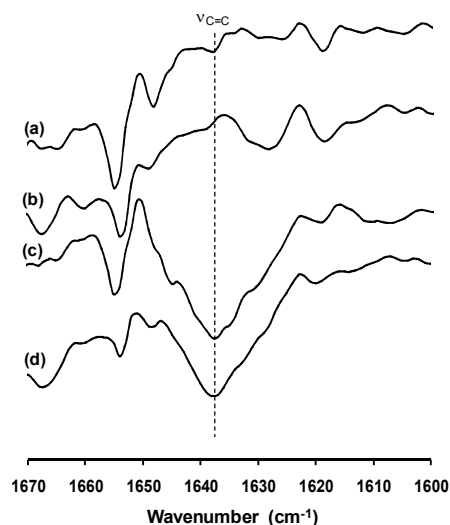
The photoreaction of DACA-PLAEF1-sc and CA-PLAEF1-sc was also investigated by FT-IR measurements. Fig. 10 shows the FT-IR spectra of their cast films before and after UV irradiation at  $\lambda > 280$  nm for 2 h. The intensity of the C=C stretching band of the cinnamoyl group at  $1637\text{ cm}^{-1}$  decreased after UV irradiation, indicating that the [2+2] cycloaddition had occurred. This result showed that functional PLA materials with both chain ends were successfully synthesized, widening their application fields.



**Fig. 8** Photoreaction scheme of cinnamoyl group undergoing UV irradiation at  $\lambda > 280$  nm (a) and UV absorption change of CA-PLAEF1-sc film during UV irradiation at  $\lambda > 280$  nm (b).



**Fig. 9** Maximal absorption change of CA-PLAEF1-sc (a) and DACA-PLAEF1-sc (b) films



**Fig. 10** FT-IR spectra of DACA-PLAEF1-sc (a), CA-PLAEF1-sc (b) with 2 h UV at  $\lambda > 280$  nm, and DACA-PLAEF1-sc (c), CA-PLAEF1-sc (d) without UV.

### Conclusions

The novel PLAs with both terminal conjugation of bio-based cinnamic acid derivatives such as DACA, CA, and EF were successfully synthesized. Their thermal properties were significantly improved, especially the  $T_{10}$ . These stereocomplexes showed simultaneous improvements in both  $T_m$  and  $T_{10}$ . The effects of the thermal stability of DACA and CA on PLA were different, indicating that it was possible to control the thermal properties represented by the  $T_{10}$  values using cinnamic acid derivatives at both terminal and initiating chain end groups. Furthermore, DACA-PLAEFs-sc and CA-PLAEFs-sc showed photoreactivities corresponding to cinnamic acid derivatives units. These results suggest that DACA-PLAEFs, CA-PLAEFs and their stereocomplexes may be useful as functional materials with high thermal stability for biomedical and environmental applications.

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