ORIGINAL ARTICLE

Thermally resistant polylactide layer-by-layer film prepared using an inkjet approach

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The inkjet printing technique is potentially applicable for the formation of polymer stereocomplexes and can control the amount, thickness and structure of the printed polymers. Stereocomplexes of polylactides (PLAs) with both terminals conjugated to aromatic groups were easily formed via casting or inkjet printing methods based on even layer-by-layer assembly and solution mixing, indicating that the stereocomplex formation was not influenced by the conjugation groups at both chain ends of the PLAs. Their formation was confirmed through Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analyses as well as direct observation of melting behavior using a hot plate. The 10% weight loss thermal decomposition temperature (T_{10}) of the stereocomplexes showed an increase of more than 90 °C compared with those of the corresponding original PLAs. PLA stereocomplexes with conjugation of both terminals that are formed via inkjet printing may be useful as highly thermally stable materials in various fields, especially in nanoscale situations. Inkjet printing is a facile method for covering substrates with thermally resistant PLA stereocomplexes with conjugation of both terminals.

INTRODUCTION

The inkjet printing technique has become an important method of application in a variety industrial and scientific fields, such as organic electronics, nanotechnology and tissue engineering.[1–10] It can be an efficient alternative to conventional methods for producing versatile micro/nanofilms because it is low in cost, offers high-speed patterning and eliminates waste.[11,12] Furthermore, it can help to minimize contamination because inkjet printing is a non-contact deposition method.[12] The use of inkjet printing allows the manipulation of the drop size, location and speed to enable the fabrication of complex dot arrays for preprogrammed automatic processes.[11–14] Therefore, inkjet printing methods should be potentially applicable for the formation of polymer stereocomplexes through interactions on various substrates.

Polylactides (PLAs) are applied in various fields because they have high biocompatibility and suitable physicochemical properties, are generated from renewable sources, and are readily biodegradable.[15] However, because the thermal properties of PLAs, such as their melting temperatures (T_m), glass transition temperatures (T_g), thermal degradation temperatures (T_d), are relatively low, their feasible applications are limited. Therefore, the thermal properties of PLAs still require further improvement, especially for industrial applications. Ikada *et al.* have reported that polylactide stereocomplexes (PLA-sc) between poly-L-lactide (PLLA) and poly-D-lactide (PDLA) showed a high T_m, ~ 50 °C higher than that of the original PLLA or PDLA, as

confirmed by differential scanning calorimetry (DSC), X-ray diffraction (XRD)[16–20] and Fourier transform infrared (FT-IR) spectroscopy.[21,22] Such PLA-sc can be formed via solution casting,[23–27] melt blending[28–32] or the precipitation method.[33,34] Direct melt blending of PDLA with PLLA is not desirable because of the high temperatures (over T_m) that are required and the fact that their homopolymers can be pyrolyzed.[35,36] It is difficult and time-consuming to achieve a 100% yield of PLA-sc via the precipitation method from acetonitrile solutions of PLLA and PDLA.[33,34] There have been many reports of PLA-sc preparation via solution casting methods using chloroform or dichloromethane because of the relative ease of this approach. However, when the casting method is used, it may be difficult to obtain nanoscale PLA-sc products such as nanofilms.

In a previous study, we successfully prepared PLA-sc through the stepwise layer-by-layer (LbL) assembly (dipping) of PLLA and PDLA without conjugation of the chain ends from their respective acetonitrile solutions on a substrate.[37] A substrate was alternately immersed in solutions of both pure PLLA and pure PDLA, at concentrations of 10 mg ml^{-1}, for 15 min each. The time required for every two steps of the LbL process was ~ 30 min. This technique required considerable time and high concentrations for the assembly of interacting PLLA and PDLA on a substrate. Recently, we demonstrated an inkjet printing technology that can be successfully used for PLA-sc formation

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with low and high molecular weights, as evidenced by XRD.[38,39] The amount of stereocomplexes present was analyzed based on crystallinity. We concluded that the fabrication of stereocomplexes via inkjet printing is an excellent method for controlling the amounts, thicknesses and structures of printed polymers and, in particular, can be used to produce nanofilms. The technique is time-efficient and cost-effective and can be easily automated. However, for the PLLA and PDLA used in these studies, the OH groups at the chain ends were not protected. In addition, the thermal properties, such as T_m and thermal degradation, were not investigated. PLAs without protection of the OH groups at the chain ends have relatively low thermal stability. Recently, we discovered a novel improvement technique for enhancing the thermal properties of PLAs with low and high molecular weights, namely, polyethylene glycol and polycaprolactone, through terminal conjugation of the OH end groups with 3,4-diacetoxycinnamic acid (DACA), which can be synthesized from plant-derived caffeic acid (bio-based).[33,34,40–43] This technique markedly improves the thermal properties of polymers terminally conjugated with DACA. In particular, the 10% weight loss thermal decomposition temperature (T_{10}) increases by more than 100 °C compared with that of the original polymer of the same molecular weight. We demonstrated that PLA-sc with both terminals conjugated to DACA and ethyl ferulate could be easily formed via casting using dichloromethane to obtain a relatively thick film.[43] However, this method may have difficulty producing thin films, particularly nanofilms. Furthermore, we also reported that the formation of the PLA-sc via casting using dichloromethane and via precipitation using acetonitrile solutions was not affected by the conjugation of both terminals with aromatic compounds.[33,34] However, this PLA-sc material was difficult to coat onto the substrate surface as a thin film because of the recovered powder. If PLA-sc with both terminals conjugated to benzyl alcohol and DACA compounds could be formed using an inkjet printing technique, it might be useful in various fields, especially fields that require nanoscale products with high thermal performance. Furthermore, spray coating, spin coating and dip coating are known to be good methods for coating materials. However, they are difficult to apply to small materials on the millimeter scale. The inkjet printing technology considered in this study is expected to solve that problem and provide a new method of coating resin onto other millimeter scale materials. To date, the coating of materials with PLA-sc films with both terminals conjugated, particularly highly thermally stable PLA-sc films with both terminals conjugated to bio-based benzyl alcohol[44] and DACA compounds, has never previously been reported.

In this study, we report, for the first time, the formation of highly thermally stable PLA-sc with both terminals conjugated to bio-based aromatic compounds using inkjet printing techniques based on LbL assembly and solution mixing. The melting behavior of the prepared materials was also investigated.
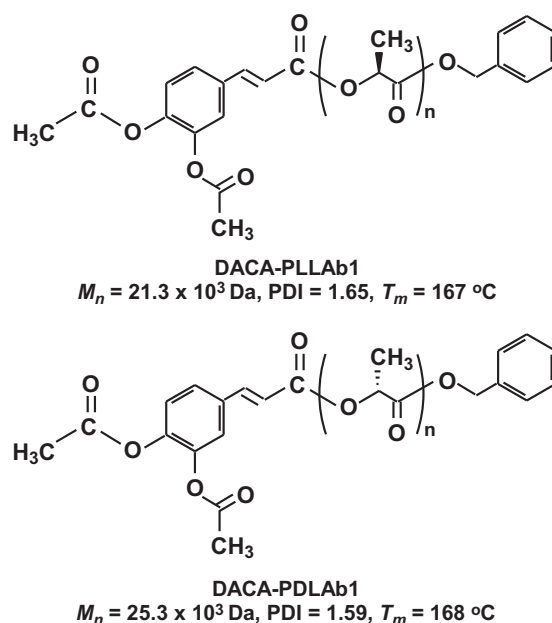
EXPERIMENTAL PROCEDURES

Materials
DACA-PLLAb1 and DACA-PDLAb1 were obtained as in our previous study (Figure 1).[34] 'b1' Indicates a benzyl group, which was used as an initiator for ring-opening polymerization of the PLAs.

Stereocomplex preparation
Solution casting method. DACA-PLLAb1 and DACA-PDLAb1 were separately dissolved in chloroform at concentrations of 4 mg ml^{-1}. Then, 0.5 ml each of the DACA-PLLAb1 and DACA-PDLAb1 solutions were mixed in a Teflon petri dish ($d = 1$ cm) and then dried at room temperature for 24 h to obtain a film (DACA-SCb1-cast). The formation of stereocomplex was confirmed via FT-IR
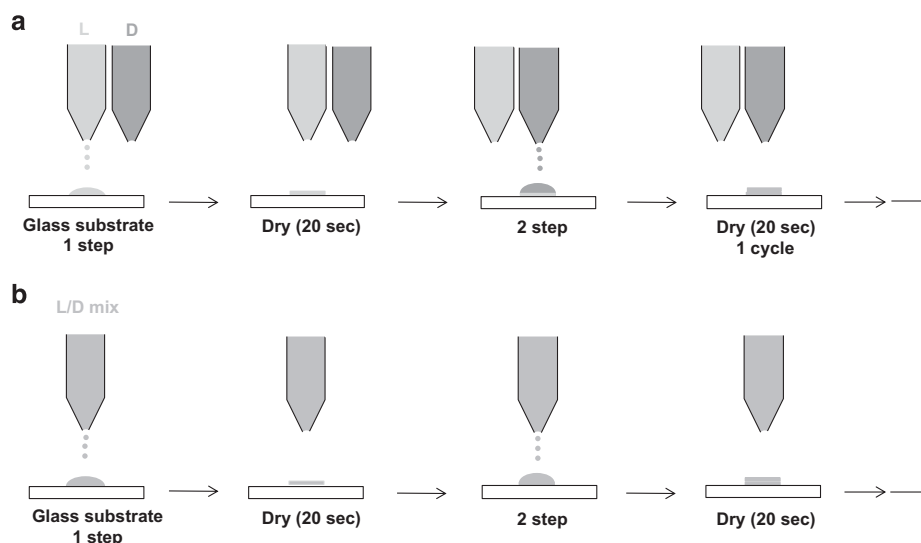

DACA-PLLAb1
$M_n = 21.3 \times 10^3$ Da, PDI = 1.65, $T_m = 167$ °C

DACA-PDLAb1
$M_n = 25.3 \times 10^3$ Da, PDI = 1.59, $T_m = 168$ °C

Figure 1 Chemical structures of DACA-PLLAb1 and DACA-PDLAb1. DACA, 3,4-diacetoxycinnamic acid.

spectroscopy using a using a Perkin Elmer Spectrum 100 FT-IR Spectrometer (Perkin Elmer Instruments, Buckinghamshire, UK) and XRD RINT UltraX18 (Rigaku, Tokyo, Japan) equipped with a scintillation counter) using CuKα radiation (40 kV, 200 mA; wavelength = 1.5418 Å).

Inkjet printing method. DACA-PLLAb1 and DACA-PDLAb1 were separately dissolved in chloroform at concentrations of 0.5 mg ml^{-1}. The DACA-PLLAb1 solution, the DACA-PDLAb1 solution and a DACA-PLLAb1/DACA-PDLAb1 1/1 v/v mixed chloroform solution were each printed on a cover glass substrate using an inkjet printer (Cluster Technology; pulse conditions: voltage 24 V, frequency 1000 Hz). The inkjet printer was equipped with a single nozzle drop-on-demand piezoelectric print head (PulseInjector), a two-axis motorized positioning system, and a USB camera aligned with a light-emitting diode for visualization of droplet ejection. Single droplets with volumes of 20 pl were printed on demand from the nozzle. Therefore, a total of 10 pg of polymer was contained in each droplet used in the LbL assembly and solution mixing methods. The solvent in each droplet was evaporated from the surface at room temperature for 20 s, and the droplet was then overprinted with another solution (Figure 2). Table 1 shows the inkjet printing conditions for DACA-PLLAb1, DACA-PDLAb1, DACA-SCb1-LbL and DACA-SCb1-mix. The DACA-SCb1-mix nanofilm was obtained by printing the DACA-PLLAb1/DACA-PDLAb1 1/1 v/v mixed solution, and DACA-SCb1-LbL was obtained by alternately printing DACA-PLLAb1 and DACA-PDLAb1. The formation of stereocomplexes via the inkjet printing method was confirmed by FT-IR and wide-angle X-ray diffraction (WAXD) measurements as well as direct observations of a hot plate.

Thermal properties
The thermal properties of DACA-SCb1-cast were analyzed via DSC (EXSTAR6000, Seiko Instruments, Chiba, Japan) and thermogravimetic analysis (TGA) (EXSTAR6200, Seiko Instruments). For the DSC measurements, the heating rate was 10 °C min^{-1} over the temperature range of 30–300 °C. The value of T_m was determined from the DSC curve. The thermal degradation behavior of DACA-SCb1-cast was determined from the TGA curve obtained under heating in the range from 30 to 500 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere with a flow rate of 250 ml min^{-1}. The melting behaviors of the DACA-PLLAb1, DACA-PDLAb1, DACA-SCb1-LbL and DACA-SCb1-mix materials were confirmed using a hot plate and a digital camera at a heating rate of 10 °C min^{-1} in the temperature range of 30–300 °C.

Figure 2 Schematic of PLA-sc formation via the inkjet printing method. (**a**) DACA-PLLAb1 and DACA-PDLAb1 solutions in chloroform were alternately printed onto a cover glass substrate. First, DACA-PLLAb1 was printed (1 step) and then allowed to dry on the surface at room temperature for 20 s; subsequently, it was overprinted with DACA-PDLAb1 (2 steps = 1 cycle). (**b**) A DACA-PLLAb1/DACA-PDLAb1 mixed solution was printed on the cover glass substrate (1 step) and then allowed to dry on the surface at room temperature for 20 s. The next step was performed in the same manner as described above. DACA, 3,4-diacetoxycinnamic acid. A full color version of this figure is available at *Polymer Journal* online.

Table 1 Inkjet printing conditions for DACA-PLLAb1 and DACA-PDLAb1 and their stereocomplexes

Sample	L-isomer (mg l^{-1})	D-isomer (mg l^{-1})	Droplet number	Step	Cycle
DACA-PLLAb1	0.5	—	0.5×10^4	200	—
DACA-PDLAb1	—	0.5	0.5×10^4	200	—
DACA-SCb1-LbL	0.5	0.5	0.5×10^4	200	100
DACA-SCb1-mix	0.25	0.25	1×10^4	100	—

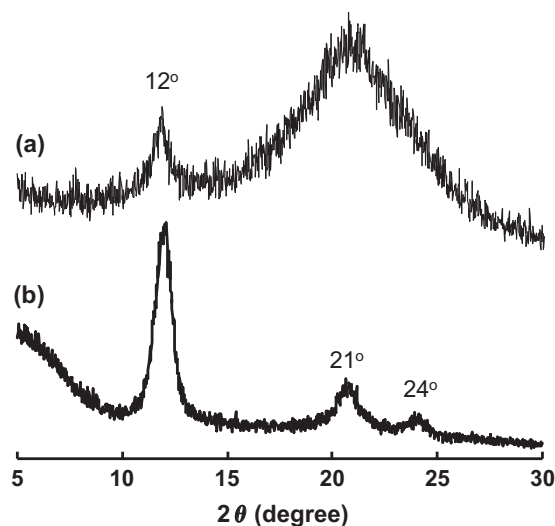Abbreviations: DACA, 3,4-diacetoxycinnamic acid; LbL, layar-by-layer.

Photoreactivity

The photoreactivity of the DACA-SCb1-cast film was observed using a glass-filtered high-pressure Hg lamp ($\lambda > 280$ nm, 56 mW cm^{-1}, Supercure-352S-UV Lightsource; SAN-EI ELECTRIC, Osaka, Japan) for irradiation. The evolution of the photoreaction conversion over time was observed using ultraviolet (UV)–visible absorption spectroscopy (Hitachi U3010 Spectrophotometer, Tokyo, Japan). The change in structure before and after UV irradiation was confirmed by FT-IR measurements.

RESULTS AND DISCUSSION

Formation of DACA-SCb1-cast

DACA-SCb1 has been successfully prepared via precipitation for 24 h using enantiomeric DACA-PLLAb1 and DACA-PDLAb1 acetonitrile solutions.[33,34] However, in this study, to reduce the time and simplify the procedure required for the preparation of DACA-SCb1 and to increase the yield, the casting method using a chloroform solution was selected. The formation of DACA-SCb1-cast was confirmed by XRD and FT-IR measurements. The XRD patterns of DACA-PLLAb1 or DACA-PDLAb1 showed peaks at $2\theta = 15$, 16 and 18.5°.[34] However, these peaks disappeared and new peaks appeared at 12, 21 and 24° in DACA-SCb1-cast (Figure 3b), corresponding to the stereocomplex structure. Furthermore, the FT-IR spectrum is a very useful and rapid means of confirming the formation of stereocomplexes. Figure 4 shows the carbonyl group (C=O) stretching vibrations of the ester

Figure 3 X-ray diffraction patterns of (**a**) DACA-SCb1-LbL and (**b**) DACA-SCb1-cast. DACA, 3,4-diacetoxycinnamic acid.

group in the 1800–1700 cm^{-1} region and the rocking vibrations in the 970–850 cm^{-1} region for DACA-PDLAb1, DACA-PLLAb1, and DACA-SCb1-cast. The C=O stretching bands of the ester group at 1751 and 1749 cm^{-1} of DACA-PDLAb1 and DACA-PLLAb1, respectively (Figure 4d and e), were shifted to 1746 cm^{-1} for DACA-SCb1-cast (Figure 4a) because of the formation of hydrogen bonds between the C=O and CH$_3$ groups.[45] Furthermore, the band at 1043 cm^{-1}, which was assigned to the stretching vibrations of the C–CH$_3$ group in DACA-PDLAb1 and DACA-PLLAb1 (Figures 4i and j), was lost in DACA-SCb1-cast, whereas a new characteristic band appeared at 1039 cm^{-1} (Figure 4f).[21] In addition, there was a new band at 908 cm^{-1} in the DACA-SCb1-cast spectrum, corresponding to the stereocomplex structure with the β-helix 3$_1$ (Figure 4f).[21,22] These results indicated that PLA-sc with both terminals conjugated
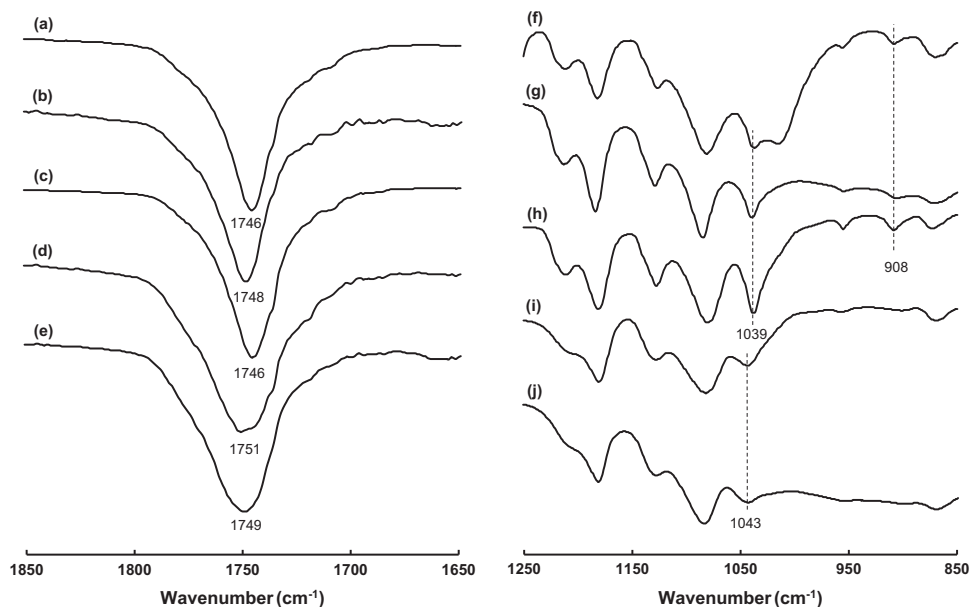
Figure 4 FT-IR spectra of (**a**) DACA-SCb1-cast, (**b**) DACA-SCb1-LbL, (**c**) DACA-SCb1-mix, (**d**) DACA-PDLAb1 and (**e**) DACA-PLLAb1 in the range of 1450–1850 cm^{-1} and of (**f**) DACA-SCb1-cast, (**g**) DACA-SCb1-LbL, (**h**) DACA-SCb1-mix, (**i**) DACA-PDLAb1 and (**j**) DACA-PLLAb1 in the range of 850–1250 cm^{-1}. DACA, 3,4-diacetoxycinnamic acid; FT-IR, Fourier transform infrared.

to bio-based aromatic compounds could be easily formed via the casting method using chloroform as the solvent.

Formation of DACA-SCb1-LbL and DACA-SCb1-mix

In our previous studies, we found that unconjugated PLA-sc materials at low (PLLA and PDLA: $M_n = 2400$, $M_w/M_n = 1.67$) and high (PLLA: $M_n = 99\,000$, $M_w/M_n = 1.54$, and PDLA: $M_n = 90000$, $M_w/M_n = 1.58$) molecular weights could be easily formed using the inkjet printing technique based on LbL assembly.[38,39] The low-molecular-weight unconjugated PLA-sc could also be formed using the solution mixing method. It is well known that a mixture of two high-M_w PLLA and PDLA solutions cannot form stereocomplexes. In the case of PLLA and PDLA with high M_w values of over 100 kDa, homopolymer crystallization occurs predominately in blends of enantiomeric PLLA and PDLA.[17,18,20] In this study, the formation of PLA-sc with both terminals conjugated to bio-based aromatic compounds was expected to remain unaffected by the terminal groups in the even LbL assembly and solution mixing methods using the inkjet printing technique. The fabrication of a DACA-PLLAb1/DACA-PDLAb1 composite via the stepwise deposition of enantiomeric DACA-PLLAb1 and DACA-PDLAb1 using an inkjet printer was performed as illustrated in Figure 2. The formation of DACA-SCb1-LbL was confirmed by XRD and FT-IR measurements. Normally, for PLA-sc, the peak intensity at 12° is stronger than those at 21 and 24° (Figure 3b). However, a peak at 12° and a halo at 21° were observed in the WAXD pattern of DACA-SCb1-LbL (Figure 3a). This might be because the prepared film had nanoscale dimensions, and therefore, the peaks at 21° and 24° could not be well observed but rather were hidden in the halo at 21°. However, a strong peak appeared at 12°, indicating stereocomplex formation.

Furthermore, the stereocomplex formation of DACA-SCb1-LbL and DACA-SCb1-mix was also confirmed by the FT-IR spectra (Figure 4). In DACA-SCb1-cast, the C=O stretching band of the ester group was shifted to a lower frequency of ~3 cm^{-1} compared with the results for DACA-PDLAb1 and DACA-PLLAb1 (Figures 4d and e) because of the formation of hydrogen bonds between the C=O

and CH_3 groups (Figures 4b and c).[45] Moreover, new bands appeared at 1039 cm^{-1} and 908 cm^{-1} for DACA-SCb1-mix and DACA-SCb1-LbL (Figures 4g and h).[21,22] These results suggested that DACA-SCb1-LbL or DACA-SCb1-mix could be easily formed by both inkjet printing methods (LbL assembly and solution mixing), indicating that the aromatic compounds at both chain ends of the PLAs did not affect their formation of stereocomplexes. The total amount of printed PLLA and PDLA on the cover glass substrate was 10 μg for both the LbL assembly method and the solution mixing method. In addition, the processing time required was only approximately 50 s per cycle in the case of LbL assembly and only ~25 s per step in the case of the solution mixing method, whereas one cycle of the dip coating method requires ~30 min.

Thermal properties

We have previously reported the thermal properties of DACA-SCb formed from DACA-PLLAb and DACA-PDLAb with various molecular weights.[33,34] However, those reported samples were obtained via precipitation from acetonitrile solutions as bulk samples. We are interested in the thermal properties obtained with the different fabrication approaches used in the present study, namely, the casting and inkjet printing of films.

The cast film could be readily removed from its substrate because of its relatively large thickness; thus, its thermal properties could be investigated via DSC and TGA measurements. The T_m values for DACA-PLLAb1 and DACA-PDLAb1 have been reported to be 167 and 168 °C, respectively.[34] Stereocomplex formation via precipitation between enantiomeric DACA-PLLAb1 and DACA-PDLAb1 has been reported to result in a high T_m of 205 °C, ~40 °C higher than those of the homopolymers.[34] One endothermic peak (T_m) at 227 °C was observed in the DSC curve of DACA-SCb1-cast at a higher temperature than that (approximately 60 °C) of enantiomeric DACA-PLLAb1 and DACA-PDLAb1 (Figure 5), indicating that DACA-SCb1-cast was successfully formed via the chloroform solution casting method.

It is known that the thermal properties of polymers are affected by various factors, such as molecular weight, distribution, moisture and

terminal groups. According to the TGA results, the T_{10} of DACA-SCb1-cast was 330 °C, ~ 90 °C higher than that of PLLAb1 or PDLAb1.[34] These results indicate that terminal conjugation with DACA influences the thermal stability of the PLAs, and one of the reasons for the enhanced thermal stability of the PLAs is the protection of the hydroxyl end groups.[42] It is known that the thermal degradation of the original PLAs occurred mainly at the hydroxyl chain ends; by contrast, the protection of the ends by DACA in the DACA-PLLAb1 and DACA-PDLAb1 molecules prevents transesterification, probably because of the π–π stacking interaction of the DACA units. The T_{10} of DACA-SCb1-cast remained the same as those of DACA-PLLAb1 (T_{10} = 343 °C) and DACA-PDLAb1 (T_{10} = 346 °C) as reported in the previous study,[34] which may be because in the melting state, the interaction between DACA-PLLAb1 and DACA-PDLAb1 decreased. Thus, it was difficult for the stereocomplex structure to exist, and the blending of PLLA with PDLA did not affect the pyrolysis behavior.

In our previous studies, we confirmed the formation of unconjugated PLA-sc via inkjet printing using only XRD measurements.[38,39] The analysis of thermal properties, such as melting points and thermal decomposition temperatures, was not achieved because the extremely small sizes of the LbL inkjet PLA films did not allow conventional
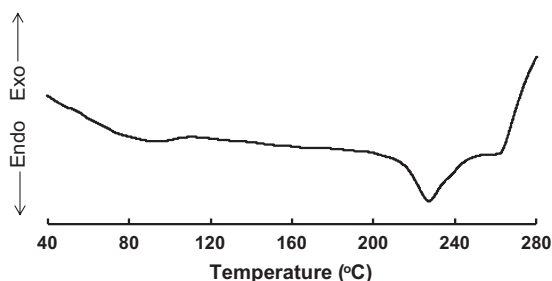
Figure 5 Differential scanning calorimetry curve of DACA-SCb1-cast at a heating rate of 10 °C min^{-1}. DACA, 3,4-diacetoxycinnamic acid.

TGA and DSC analyses. In this study, we addressed this issue using a hot plate with a heating rate of 10 °C min^{-1} and a digital camera. Figure 6 shows the melting behavior of DACA-PLLAb1, DACA-PDLAb1 and DACA-SCb1-LbL during heating from 30 to 300 °C. When the temperature was below 140 °C, no changes in DACA-PLLAb1, DACA-PDLAb1 or DACA-SCb1-LbL were observed (Figures 6a and b). However, when the temperature increased to 160 °C, DACA-PLLAb1 and DACA-PDLAb1 were completely melted, whereas DACA-SCb1-LbL remained intact (Figure 6c), in agreement with the DSC results for DACA-PLLAb1, DACA-PDLAb1 and DACA-SCb1 that were reported in our previous study.[34] Subsequently, part of the DACA-SCb1-LbL was observed to melt when it was heated to 205 °C (Figure 6d), and it was completely melted at 230 °C (Figure 6e). Thus, the T_m of DACA-SCb1-LbL was 50 °C higher than those of enantiomeric DACA-PLLAb1 and DACA-PDLAb1, indicating that PLA-sc with both terminals conjugated to aromatic compounds was easily formed via the inkjet printing technique based on LbL assembly.

The melting behavior of DACA-SCb1-mix was expected to be the same as that of DACA-SCb1-LbL when it was prepared via inkjet printing. According to the results shown in Figure 7, DACA-SCb1-mix showed no change at 160 °C, which is the T_m of DACA-PLLAb1 and DACA-PDLAb1 (Figures 7a–c). When the temperature was increased to 202 °C, a part of the DACA-SCb1-mix was melted (Figure 7d), and it was completely melted at 235 °C (Figure 7e). These results also suggested that PLA-sc with both terminals conjugated was successfully formed via the inkjet printing technique using a mixed solution of enantiomeric DACA-PLLAb1 and DACA-PDLAb1.

These results prove that stereocomplexes of PLAs with both chain ends protected can be successfully formed via inkjet printing based on even LbL assembly or solution mixing. The thermal stability of DACA-SCb1-LbL and DACA-SCb1-mix could not be evaluated via TGA because of the very small sizes of the produced thin film samples, but it is expected that their T_{10} should be above 300 °C, higher than those of the pure PLAs without protection of the OH chain end groups. Inkjet printing technology shows potential for the application of highly
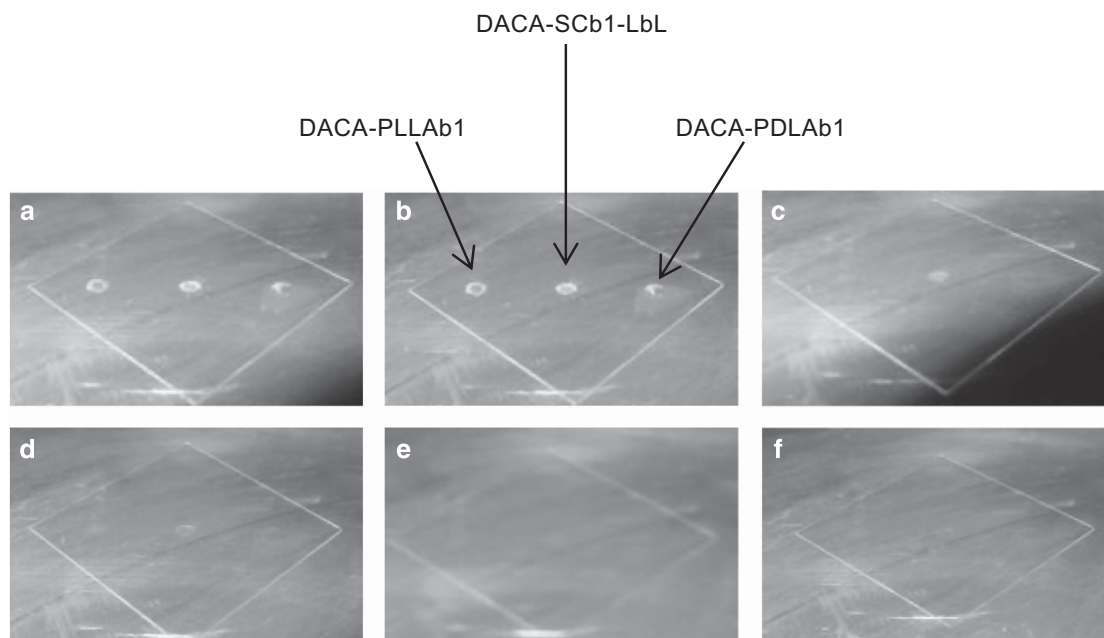
Figure 6 Photographs of DACA-PLLAb1, DACA-PDLAb1 and DACA-SCb1-LbL on the hot plate at (**a**) 100 °C, (**b**) 140 °C, (**c**) 160 °C, (**d**) 205 °C, (**e**) 230 °C and (**f**) 270 °C. DACA, 3,4-diacetoxycinnamic acid; LbL, layar-by-layer. A full color version of this figure is available at *Polymer Journal* online.
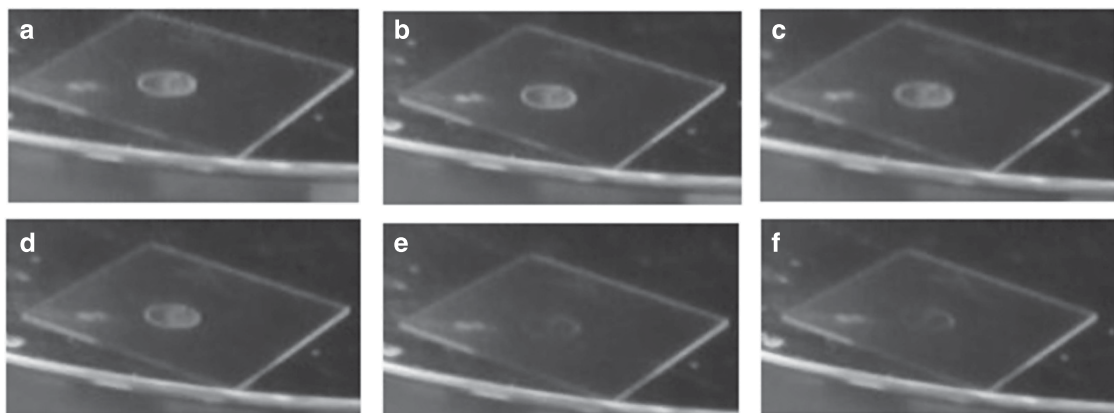
Figure 7 Photographs of DACA-SCb1-mix on the hot plate at (**a**) 100 °C, (**b**) 142 °C, (**c**) 160 °C, (**d**) 202 °C, (**e**) 235 °C and (**f**) 265 °C. DACA, 3,4-diacetoxycinnamic acid. A full color version of this figure is available at *Polymer Journal* online.
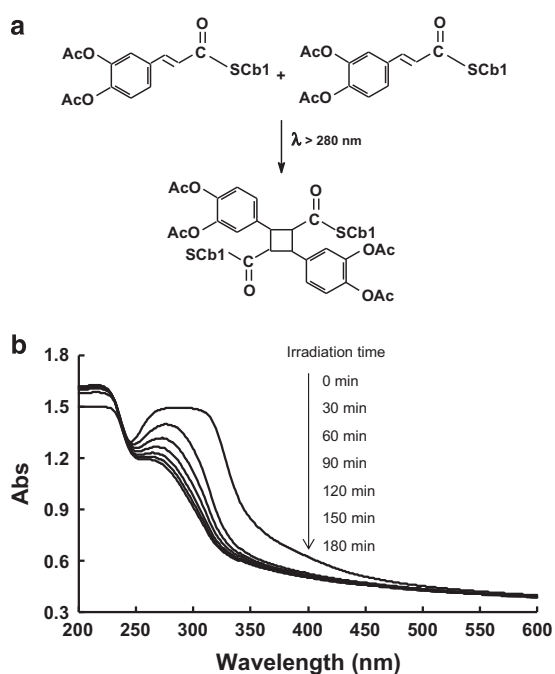
Figure 8 (**a**) Photoreaction scheme of the cinnamoyl group undergoing UV irradiation at $\lambda > 280$ nm and (**b**) the change in the UV absorption of the DACA-SCb1-cast film during UV irradiation at $\lambda > 280$ nm. DACA, 3,4-diacetoxycinnamic acid; UV, ultraviolet.
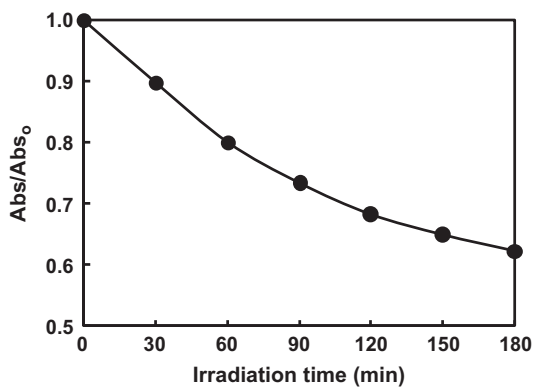
Figure 9 Maximal absorption change of the DACA-SCb1-cast film at $\lambda = 288$ nm. DACA, 3,4-diacetoxycinnamic acid.
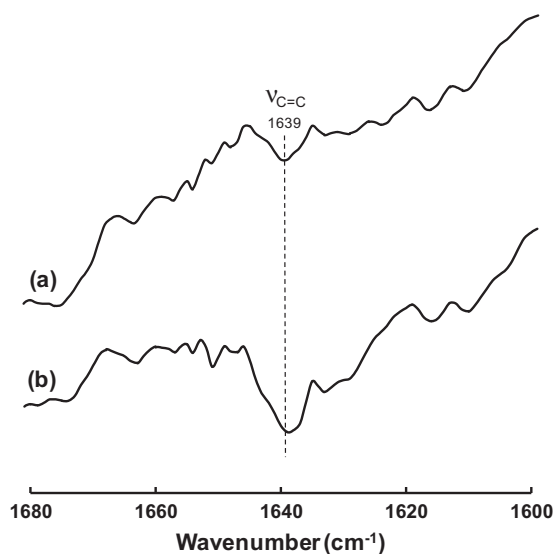
Figure 10 FT-IR spectra of DACA-SCb1-cast (**a**) with 3 h of UV exposure at $\lambda > 280$ nm and (**b**) without UV exposure. DACA, 3,4-diacetoxycinnamic acid; FT-IR, Fourier transform infrared; UV, ultraviolet.

thermally stable PLA-sc coatings in various fields that require nanoscale products.

Photoreactivity

It is well known that the cinnamoyl group undergoes [2+2] cycloaddition, resulting in the formation of a cyclobutane ring, upon UV irradiation at $\lambda > 280$ nm (Figure 8a).[40–43,46–53] In previous reports, we confirmed that polymers terminally conjugated with DACA show high photoreactivity and that their photoreactivity is independent of the molecular weights of the polymers.[40–43] Therefore, in this study, the DACA-SCb1-cast film was expected to be photoreactive. Figure 8b shows the time-dependent changes in the UV absorption of the DACA-SCb1-cast film. The maximal absorption peak at $\lambda_{max} = 288$ nm, which is identified as the cinnamoyl absorption wavelength, decreased with increasing UV irradiation time at $\lambda > 280$ nm. The DACA-SCb1-cast showed $\sim 40\%$ conversion via [2+2] cycloaddition after UV irradiation at $\lambda > 280$ nm for 180 min (Figure 9).

The photoreactivity of DACA-SCb1-cast was also investigated using FT-IR measurements. Figure 10 shows the FT-IR spectra of the

DACA-SCb1-cast film before and after UV irradiation at $\lambda > 280$ nm for 3 h. The intensity of the $C=C$ stretching band of the cinnamoyl group at 1639 cm^{-1} decreased with increasing UV irradiation time, indicating that the reaction of $C=C$ groups had occurred. The other materials DACA-SCb1-mix and DACA-SCb1-LbL were also expected to exhibit photoreactivity corresponding to the DACA units, although they were not investigated. The results show that functional PLA-sc with both terminals conjugated to bio-based aromatic compounds can be successfully prepared, which broadens the feasible applications of these materials.

CONCLUSIONS

We demonstrated that PLA stereocomplexes with both terminals conjugated to benzyl alcohol and DACA compounds could be easily formed via casting and inkjet printing methods based on even LbA assembly and solution mixing. The thermal properties of the PLAs were improved by the terminal conjugation with DACA and the formation of stereocomplexes. The T_{10} and T_m of DACA-SCb1-cast, DACA-SCb1-LbL and DACA-SCb1-mix were higher than those of the original PLAs by more than 90 °C and 40 °C, respectively. DACA conjugation at the hydroxyl groups of the PLAs is desirable for improving T_{10}. Inkjet printing is a powerful method for forming functional, thermally stable PLA stereocomplexes with both terminals conjugated. PLA-sc materials with both terminals conjugated to plant-derived aromatic compounds may be useful as functional bio-based materials in various fields of application.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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