

# Mechanism of High Thermal Stability of Commercial Polyesters and Polyethers Conjugated with Bio-Based Caffeic Acid

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**ABSTRACT:** In previous report, we discovered that a novel improvement technique to enhance the thermal properties of poly(L-lactide)s (PLLAs) by terminal conjugation with 3,4-diacetoxycinnamic acid (DACA). In this study, we clarified the mechanism of the enhancement of thermal stability by using commercial polyesters and polyethers. The effect of thermal improvement by the terminal conjugation of DACA on poly(DL-lactide), poly( $\epsilon$ -caprolactone), and poly(ethylene glycol) was almost the same as about 100 °C increase. The amount of residual tin catalyst, which enhances the thermal degradation of polyesters, was reduced at undetected level after the terminal

conjugation of DACA probably due to the removal of tin during DACA conjugation process. Furthermore, the  $\pi$ - $\pi$  stacking interactions of DACA units and the chemical protection of terminal hydroxyl groups, which enhances intramolecular scission, were also important for the high thermal stability. We clarified that the extreme high thermal stability by DACA conjugation was induced by these above mechanisms. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 49: 3152–3162, 2011

**KEYWORDS:** caffeic acid; poly( $\epsilon$ -caprolactone); poly(DL-lactide); poly(ethylene glycol); poly(L-lactide)

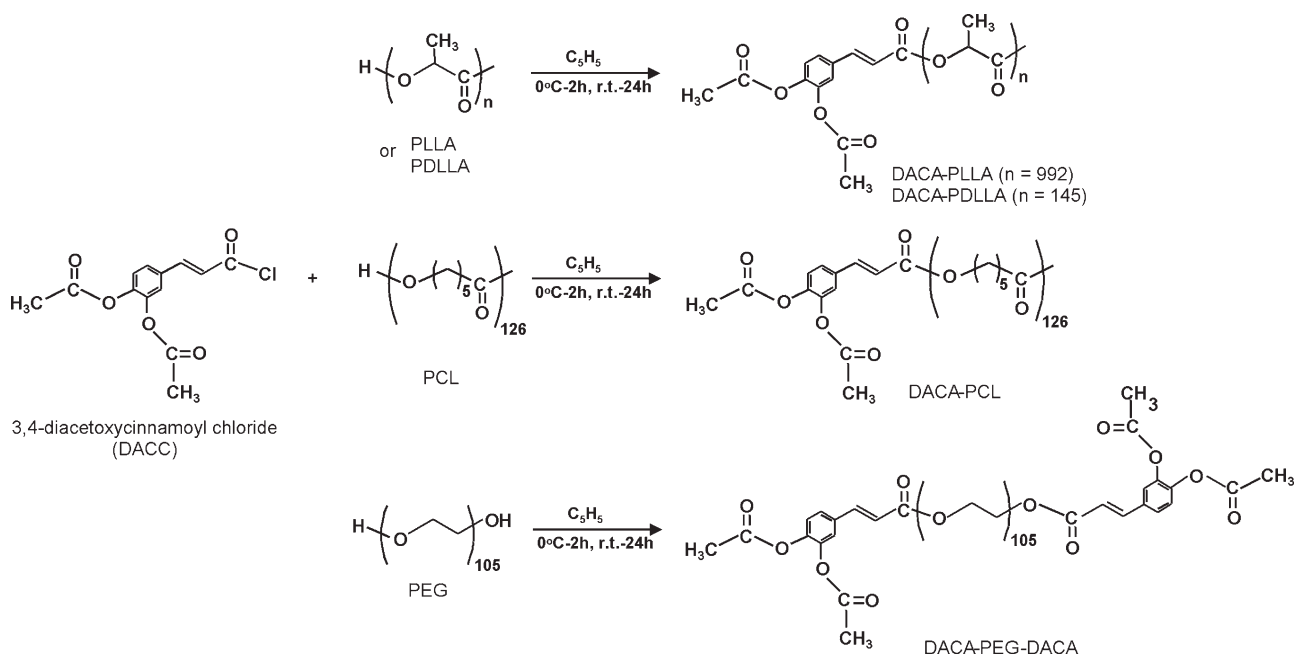
**INTRODUCTION** The wide application of polymeric materials has made a major contribution to our life while also resulting in a serious problem because of the solid rubbish remaining after the use of polymeric products. Biodegradable polymeric materials are good materials showing ecological advantages over other nondegradable polymers, and offer an alternative solution for the global waste problem. Commercially available biocompatible aliphatic polyesters and polyethers such as polylactide (PLA), poly( $\epsilon$ -caprolactone) (PCL), and poly(ethylene glycol) (PEG) have been widely studied for biomedical, environmental diagnostic, and drug delivery system applications as well as improvements of biomaterial surfaces, and so on.<sup>1–8</sup> However, these polymers have a limitation due to their poor thermal or mechanical properties. Because the high thermal stability enhances their industrial value, their copolymerization with other monomers or polymers have been reported to improve their thermal and mechanical properties, but a significant improvement was not achieved.<sup>9–14</sup> Furthermore, some studies have investigated the influence of a residual catalyst or the end acetylation on the thermal degradation of PLLA and PCL.<sup>15–20</sup> Nishida et al.<sup>15</sup> reported that the tin residual catalyst plays an important role in the thermal degradation reaction of PLLA, and thus the thermal degradation temperature of PLLA is strongly depending on the amount of

tin. Endo and coworkers<sup>16</sup> reported that the residual catalyst tin in PLLA was not changed after acetylation. In addition, some articles have reported the mechanism on thermal degradation of PEG as types of an intramolecular transfer of hydrogen, a random scission of C–O and C–C bonds in the polymer chains, and an elimination of water and ethylene glycol, which were formed in independent at chain terminal structures.<sup>21–24</sup>

It is known that PLLA has some disadvantages such as thermal instability during melt, easily flammable, low toughness, inefficiency molding cycle (slow crystallization), and so on. Especially, one of the most important subjects concerning PLLA is improvement of its thermal stability with regard to processing or molding, because it is easy to hydrolyze and pyrolyze to monomers and oligomers. Recently, we discovered a novel improvement technique to enhance the thermal properties of synthetic poly(L-lactide)s (PLLAs) by terminal conjugation with 3,4-diacetoxycinnamic acid (DACA), which was synthesized from plant derived (biobased) caffeic acid, to the hydroxyl group.<sup>25</sup> The thermal properties of DACA terminally conjugated PLLAs (DACA-PLLAs) were significantly improved. In particular, the 10% weight-loss temperature ( $T_{10}$ ) increased over 100 °C when compared with that of PLLA of the same molecular weight, although the

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crystallinities and solubility of the PLLAs were completely maintained after conjugation with DACA. However, the detailed mechanism and the reasons for the thermal improvement have not been clarified yet.

In this article, we report the mechanism of extremely enhanced thermal stability of various commercial polyesters and polyethers such as PLLA, poly(DL-lactide) (PDLLA), PCL, and PEG conjugated with bio-based caffeic acid. The thermal degradation of various original polymers could be occurred mainly from OH end group by both intermolecular and intramolecular transesterification. We clarified that the amount of residual tin, which enhances the thermal degradation of polyesters, was reduced after the terminal conjugation of DACA. In addition, the high thermal stability of various polymers after terminal conjugation of DACA was also clarified in relation to  $\pi$ - $\pi$  stacking interactions of DACA units and protection of OH end group.

## RESULTS AND DISCUSSION

### Synthesis of DACA-polymers

The DACA-PLLA, DACA-PDLLA, DACA-PCL, and DACA-PEG-DACA (DACA-polymers) were synthesized according to Scheme 1. Table 1 summarizes their synthetic conditions and properties. The chemical structures of the DACA-polymers were analyzed by FTIR spectroscopy, which demonstrated the peaks of both DACA and polymers (Fig. 1). All FTIR spectra of the DACA-polymers exhibited a characteristic carbonyl (C=O) stretching band of the ester group at  $1750\text{ cm}^{-1}$  for DACA-PLLA or DACA-PDLLA, and  $1730\text{ cm}^{-1}$  for DACA-PCL or DACA-PEG-DACA, a C=C stretching band of the cinnamoyl group at  $1630\text{ cm}^{-1}$ , a methyl ( $\text{CH}_3$ ) stretching band from PLLA at  $1450\text{ cm}^{-1}$  and a methylene ( $\text{CH}_2$ ) stretching band from PCL or PEG at  $1460\text{ cm}^{-1}$ . The chemical structures of the obtained DACA-polymers were also confirmed by  $^1\text{H}$  NMR measurements (Fig. 2). The  $^1\text{H}$  NMR spectra of all

**TABLE 1** Synthetic Conditions and Properties of Various DACA-Polymers<sup>a</sup>

Samples	$M_n^b$	$M_w/M_n^b$	DACA/Monomer Unit <sup>c</sup> (unit/unit)	Yield <sup>d</sup> (wt %)	$T_m^e$ (°C)	$T_{10}^f$ (°C)	Sn Content <sup>g</sup> (ppm)
DACA-PLLA	75,980 (71,700)	2.0 (2.0)	1/992	93	168, 172 (170)	354 (333)	4 (18)
DACA-PDLLA	11,180 (11,707)	1.1 (1.1)	1/145	80	ND	358 (265)	QL (34)
DACA-PCL	14,980 (13,130)	2.0 (1.8)	1/126	92	57, 58 (56, 57)	402 (320)	QL (14)
DACA-PEG-DACA	5,310 (5,100)	1.8 (1.8)	1/105	81	55 (65)	393 (268)	ND (ND)

<sup>a</sup> The conjugation of DACA into the various commercial polymers chain ends was carried out at  $0\text{ }^\circ\text{C}$  for 2 h, and at room temperature for 24 h.

<sup>b</sup> The molecular weights and distributions were estimated by GPC in chloroform with PEG and polystyrene standards.

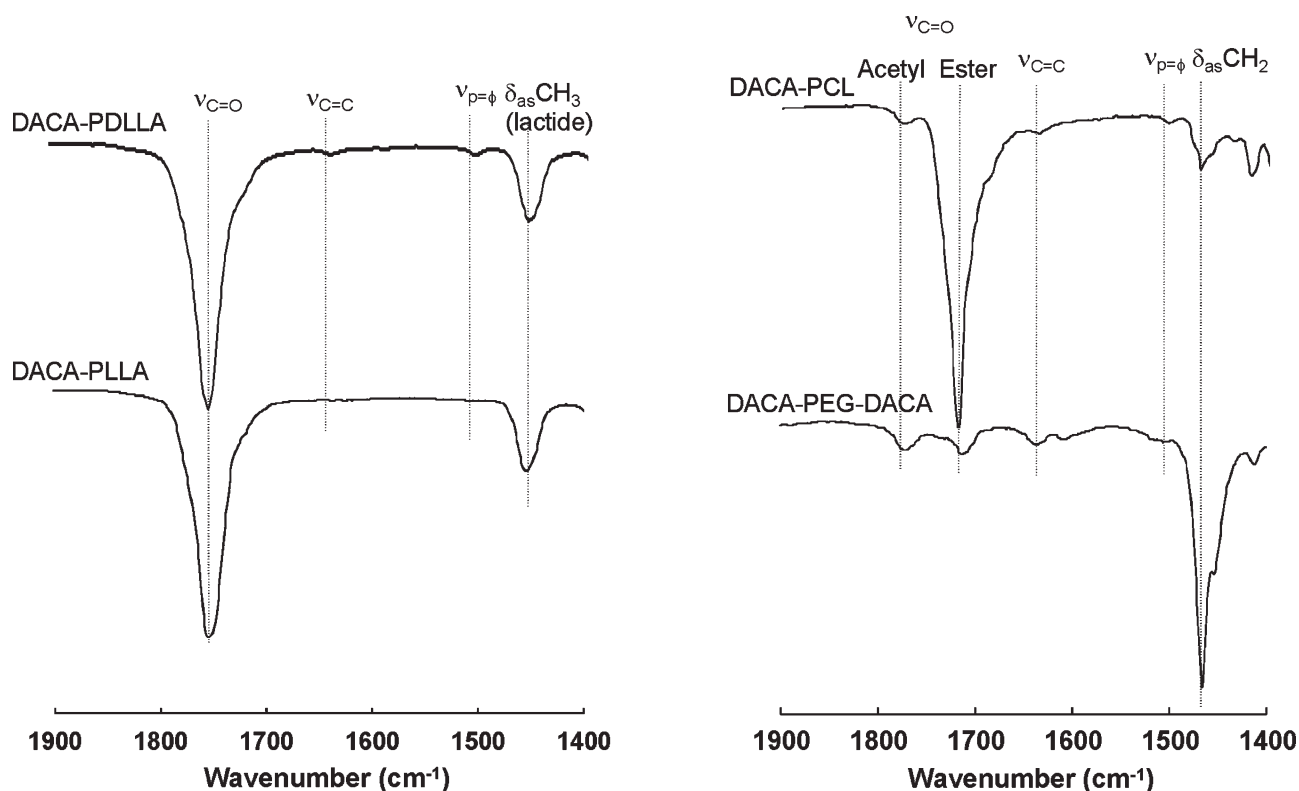
<sup>c</sup> The composition ratios of monomer unit and DACA were estimated by  $^1\text{H}$  NMR spectroscopy.

<sup>d</sup> The yields present results after the purification.

<sup>e</sup> The  $T_m$  was measured by DSC on the second heating ( $10\text{ }^\circ\text{C min}^{-1}$ ).

<sup>f</sup> The 10% weight-loss temperatures,  $T_{10}$ , were measured by TGA under nitrogen ( $20\text{ }^\circ\text{C min}^{-1}$ ).

<sup>g</sup> Sn contents were estimated by ICP. The data in parentheses were data of original polymers. ND: not detect. QL: quantitation limit.



**FIGURE 1** FTIR spectra of various DACA-polymers.

DACA polymers confirmed that the peaks of both DACA and the polymers appeared in the spectra. The composition ratios of DACA and polymer in the DACA-polymers were calculated by the integral of the peak area ratio of the vinylene proton in DACA at 6.4 ppm, the CH proton in PLLA or PDLLA at 5.2 ppm, and the CH<sub>2</sub> proton in PCL at 4.1 ppm or PEG at 3.6 ppm (Table 1). These results indicated that DACA was successfully conjugated into the chain end of the polymers.

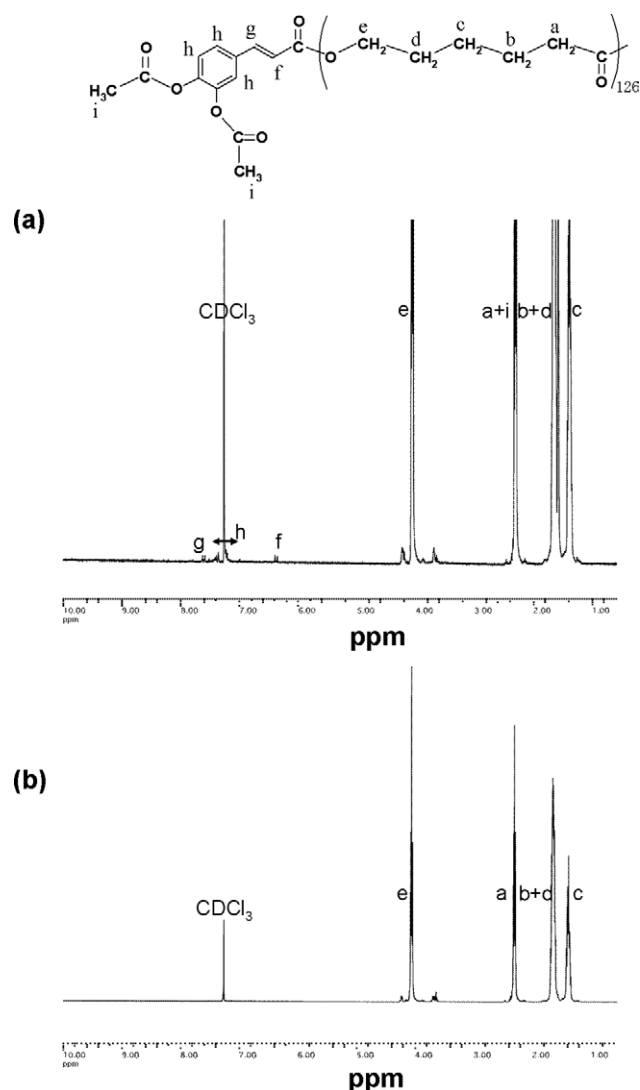
### Solubility

The solubility of the DACA-polymers was evaluated in different solvents at a concentration of 1 mg mL<sup>-1</sup>. The DACA polymers showed high solubility in various organic solvents; in particular, they dissolved easily in chlorinated solvents such as chloroform or dichloromethane (DCM), and the obtained solutions were clear. They also dissolved in aprotic amidic solvents and their solubility was identical to the corresponding original polymers. The solubility of the DACA-polymers was maintained even after UV irradiation for photoreaction.

### Thermal Properties

The thermal properties of the DACA-polymers were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermal desorption, and gas chromatography–mass spectrometry. The melting point ( $T_m$ ) of DACA-PLLA showed double melting behaviors, that is, a minor endothermic peak (168 °C) shifted just before the main endothermic peak (172 °C), whereas the original PLLA presented one melting point at 170 °C. Original PDLLA and DACA-PDLLA did not show any  $T_m$ , because they are

amorphous polymers. The  $T_m$  of original PCL (56 and 57 °C) was not changed after the terminal conjugation of DACA (58 and 57 °C), but that of DACA-PEG-DACA (55 °C), which was conjugated at both terminals of the PEG by DACA, was lower than that of the original PEG (65 °C; Fig. 3). From the TGA results, the 10% weight-loss temperatures ( $T_{10}$ ) of the original PLLA, PDLLA, and PCL were 333, 265, and 320 °C, but the values of the corresponding DACA-polymers were 354, 358, and 402 °C, respectively [Fig. 4(a–c)]. These results indicated that the thermal stability of the polyesters were increased over 100 °C by the terminal conjugation of aromatic DACA, the same as the results obtained in a previous study for synthetic PLLAs.<sup>25</sup> We have reported that no molecular weight dependence of the thermal stability improvement by DACA conjugation has been observed. In addition, surprisingly,  $T_{10}$  of PEG was enhanced over 120 °C after conjugated DACAs into two end chains [Fig. 4(d)]. Furthermore, the effect of DACA on thermal improvement is useful not only for synthetic PLLAs but also for various commercial polyesters and polyethers. The increase in the  $T_{10}$  of various polymers via copolymerization with hydrophobic monomers has been reported,<sup>9,10,26</sup> but such drastic increment of  $T_{10}$  like our results has never been reported. Recently, for the reduction of global warming gas, improvement of polymer alloy materials by mixing with PLA is attracted much attention in industry. Therefore, the development of thermally stable PLA has high industrial value. We also investigated the influence of DACA on the heat resistance to pyrolysis of representative commercial PLLA, which is used for molding



**FIGURE 2** Representative  $^1\text{H}$  NMR spectra of the DACA-PCL (a) and original PCL (b) in  $\text{CDCl}_3$ .

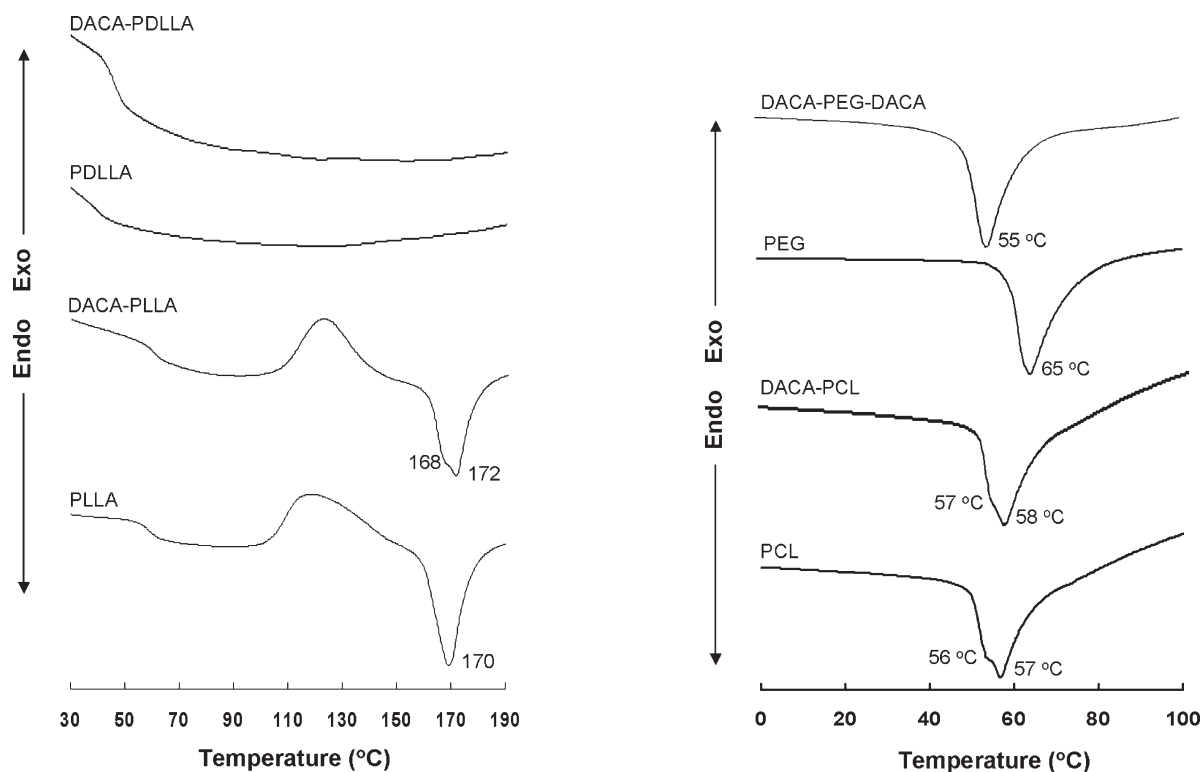
products (Fig. 5). Interestingly, DACA-PLLA showed complete or 97% weight remaining during isothermal degradation at 200 or 240  $^\circ\text{C}$ , respectively, although the original PLLA showed a 23-wt % pyrolysis at 240  $^\circ\text{C}$  for 90 min. It is known that PLLA generates gas during molding. Thus, we investigated the gas evolved from representative original PLLA and DACA-PLLA during pyrolysis by gas chromatographic analysis at 250  $^\circ\text{C}$  for 30 min (Fig. 6). The gas evolved from the original PLLA and DACA-PLLA was compared by the peak area ratios of both polymers with a retention time of 10–12 min. Surprisingly, the intensity of the gas evolved from the original PLLA was 20-fold greater than that of DACA-PLLA, indicating that gas evolution was inhibited by the terminal conjugation of DACA. These evolved gases were also analyzed by mass spectroscopy, and we discovered that the main product during pyrolysis of both original PLLA and DACA-PLLA was lactide, the same as the report by McNeill and Leiper (Fig. 7).<sup>27,28</sup> It is expected that the main product

during the pyrolysis of other polymers and DACA-polymers will be cyclic monomers.

It is known that the factors, which influence the thermal behavior of polymers, include the molecular weight and its distribution, moisture, terminal group, and so forth. Endo and coworkers investigated the contribution of acetyl end protection and residual tin on the thermal degradation of PLLA.<sup>16</sup> They reported that the thermal degradation of PLLA was influenced by residual tin. The amount of residual tin in their study did not change after conjugation of acetyl group (13.7 ppm and 15.1 ppm for before and after conjugation, respectively). We measured the amount of residual tin in various original polymers and DACA-polymers to clarify the relation between residual catalyst and the extreme thermal improvement of DACA conjugation (Table 1). These results indicated that the residual tin in the original PLLA, PDLA, and PCL was reduced to a minimum after the terminal conjugation of DACA probably due to the removal of tin during DACA conjugation process. Furthermore, no metal catalyst could be detected in the original PEG and DACA-PEG-DACA, suggesting that the enhanced thermal stability of PEG was not dependent on the residual metal catalyst concentration. From these results, it is expected that the thermal stability of the original polymers was affected by the terminal conjugation of DACA. Therefore, one of the reasons for the enhanced thermal stability of various commercial polymers is the removal of the hydroxyl end groups and subsequent elimination of the tin catalyst.<sup>29</sup> In addition, the reason for the enhanced thermal stability of the various commercial polymers might also be the  $\pi$ - $\pi$  stacking interactions of the terminal DACA unit in the DACA-polymers.<sup>30,31</sup> Many studies on the thermal degradation mechanism have been reported.<sup>15–20,27,28,32,33</sup> The mechanism responsible for the thermal degradation of the original PLLA and DACA-PLLA is shown in Scheme 2. We hypothesized that the thermal degradation of the original polymers could be occurred mainly from the hydroxyl chain end by both intermolecular and intramolecular transesterification,<sup>17</sup> but the end capping with DACA in the DACA-PLLA molecules might inhibited the transesterification probably due to the  $\pi$ - $\pi$  stacking interaction of DACA units.<sup>19</sup> The mechanism on thermal degradation of original PCL, PDLA, DACA-PCL, and DACA-PDLA was thought to be similar to original PLLA and DACA-PLLA. Some articles have reported the mechanism on thermal degradation of PEG as intramolecular transfer of hydrogen, random scission of C–O, and C–C bonds, and elimination of water and ethylene glycol.<sup>21–24</sup> In this study, we consider that the mechanism on thermal degradation of original PEG is similar to the above reports. However, as PEG chain ends were conjugated by DACAs, the inhibition of water and ethylene glycol formation and the  $\pi$ - $\pi$  stacking interaction of DACA units might enhance the thermal stability of PEG.

### Crystallinity

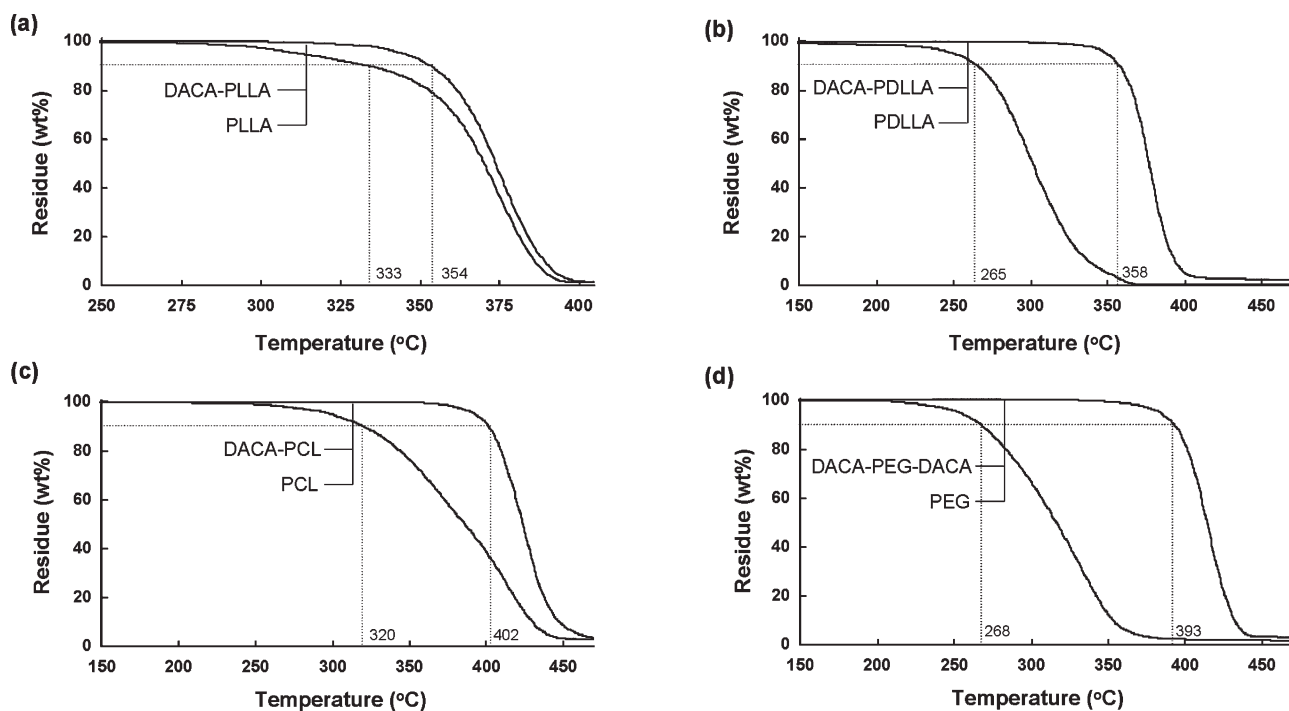
The crystallinity of the DACA-polymers was analyzed by wide-angle X-ray diffraction (WAXD) (Fig. 8). DACA-PDLA showed amorphous phases both before and after annealing at 100  $^\circ\text{C}$  for 1 h, similar to the original PDLA. DACA-PLLA



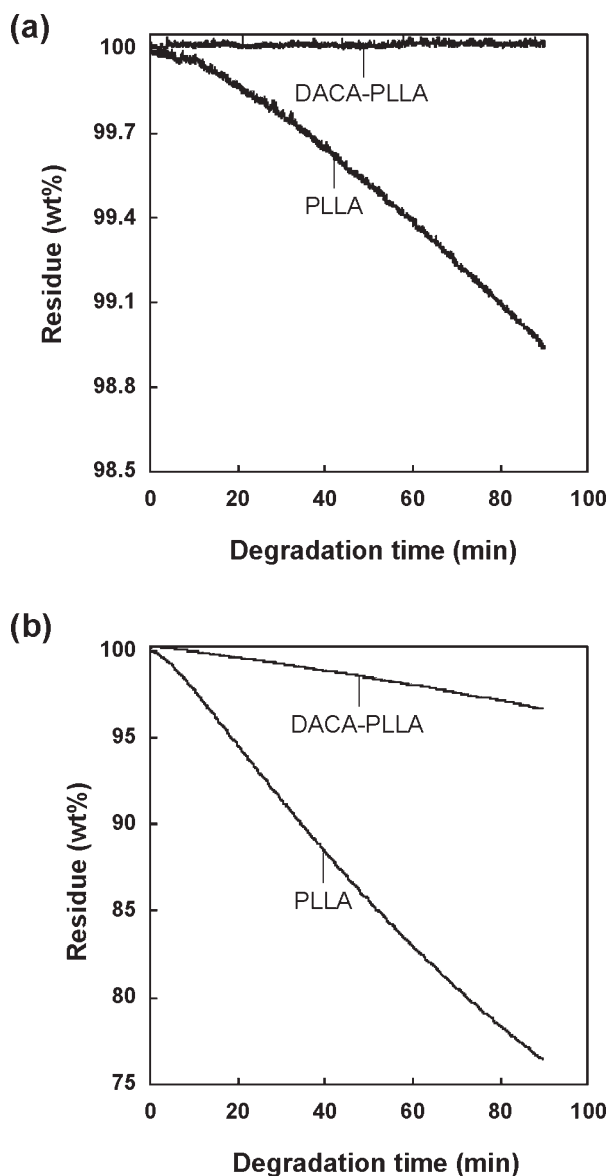
**FIGURE 3** DSC curves on a second heating of various original polymers and DACA-polymers.

showed amorphous phases without annealing, but when it was annealed at 100 °C for 1 h, some peaks were observed at  $2\theta = 14.9, 16.7, 19.0,$  and  $22.5^\circ$  ( $\theta =$  diffraction angle),

corresponding to a spacing of 5.9, 5.2, 4.6, and 3.9 Å, respectively, similar to the original PLLA. This is consistent with the peaks at 15, 16, 18.5, and 22.5° reported by Ikada



**FIGURE 4** TG curves of various original polymers and DACA-polymers at  $20\text{ }^\circ\text{C min}^{-1}$  under nitrogen atmosphere at a flow rate of ca.  $250\text{ mL min}^{-1}$ .



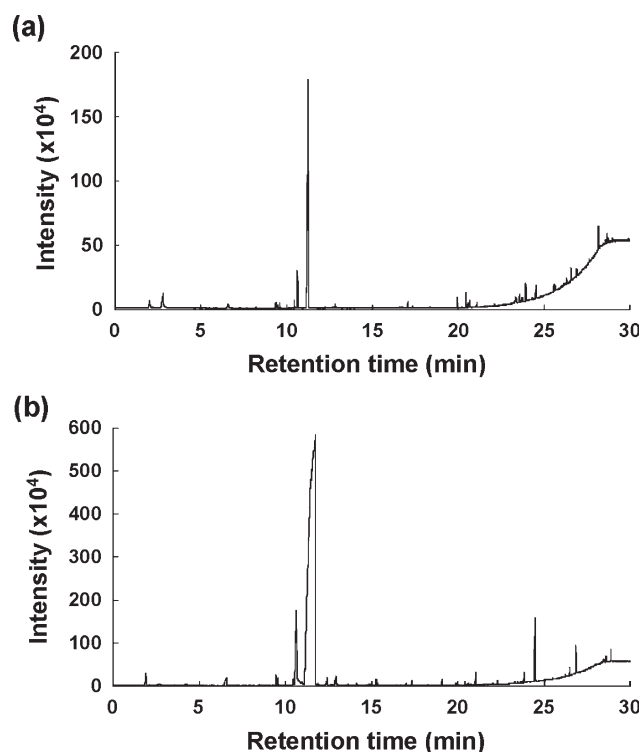
**FIGURE 5** Remaining weight change during isothermal degradation of the original PLLA and DACA-PLLA at 200 °C (a) and 240 °C (b) under nitrogen atmosphere at a flow rate of about 250 mL min<sup>-1</sup>.

et al.<sup>34</sup> In addition, the DSC results indicated that the DACA-PLLA formed  $\alpha'$  +  $\alpha$ -phases and the original PLLA formed an  $\alpha$ -phase with a  $10_3$  helices chain conformation.<sup>35,36</sup> DACA-PCL showed crystallinity, and shifted at  $2\theta = 16.0, 21.7,$  and  $23.8^\circ$  corresponding to a spacing of 5.5, 4.0, and 3.7 Å, respectively, the same as the original PCL. In the case of DACA-PEG-DACA, their peaks shifted at the same position ( $2\theta = 19.1, 23.1, 26.2,$  and  $32.5^\circ$  corresponding to a spacing of 4.6, 3.8, 3.4, and 2.7 Å, respectively) as the original PEG, indicating that the crystal structure was maintained after the terminal conjugation of DACA. Differential interference microscopic (DIM) observations also showed that the crystal morphologies of the DACA polymers were similar to the

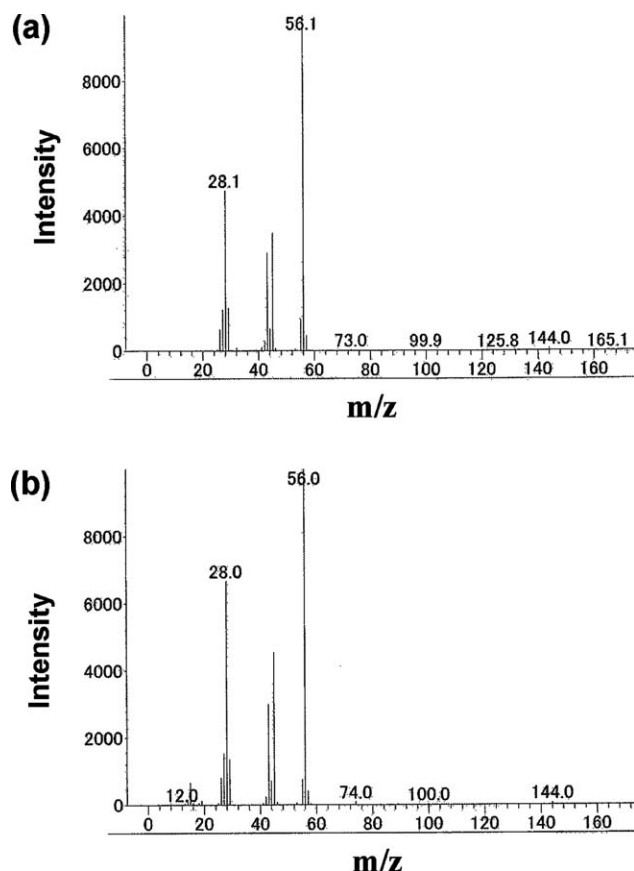
corresponding original polymers, and agreed with the WAXD results (Fig. 9). DACA-PEG-DACA or DACA-PCL showed spherulitic morphology similar to the original PEG or PCL. However, the spherulite size of DACA-PEG-DACA was larger than the original PEG. This result correlated with the X-ray diffraction (XRD) results that the peak intensities at  $2\theta = 23.1^\circ$  or  $32.5^\circ$  of DACA-PEG-DACA were higher or lower than that of the original PEG, respectively. From these results, DACA-polymers completely maintained their original crystallinities after the conjugation of DACA molecules.

#### Photoreactivity

The cinnamoyl group is well known to undergo [2 + 2] cycloaddition leading to the formation of a cyclobutane ring on UV irradiation [Fig. 10(a)].<sup>21,37-45</sup> The photoreactivities of various DACA-polymers were investigated by UV/vis and FTIR spectroscopy [Fig. 10(b-d)]. The time-dependent UV absorption changes of a representative DACA-PDLLA dissolved in chloroform were measured. The maximal absorption peak at  $\lambda_{\text{max}} = 290$  nm decreased with increasing UV irradiation time at  $\lambda > 280$  nm [Fig. 10(b)]. DACA-PLLA, DACA-PDLLA, DACA-PCL, and DACA-PEG-DACA showed approximately 60, 64, 46, and 55% conversion after UV irradiation at  $\lambda > 280$  nm for 100 min, respectively [Fig. 10(c)]. The photoreaction of the DACA polymers was also investigated by FTIR measurements. Figure 10(d) shows the FTIR spectra of a representative DACA-PDLLA cast film before and after UV irradiation at  $\lambda > 280$  nm for 100 min. The intensity of the C=C stretching band of the cinnamoyl group at  $1630$  cm<sup>-1</sup> decreased after UV irradiation, indicating that



**FIGURE 6** Pyrolytic gas chromatogram of DACA-PLLA (a) and the original PLLA (b) at 250 °C.



**FIGURE 7** Mass spectra of DACA-PLLA pyrolysis products that are obtained under isothermal degradation for 10.63 and 11.24 min at 250 °C (a) and lactide (b).

the [2 + 2] cycloaddition had occurred. Other DACA-polymers showed the same phenomenon. These results suggest that DACA-polymers are expected to be useful as photoreactive PLLA, PDLLA, PCL, and PEG.

## EXPERIMENTAL SECTION

### Materials

PLLA (TE2000; Unitika, Japan) was reprecipitated into methanol by chloroform before use. PDLLA (Polyscience, Japan) was used as received. Hydroxyl end-capped PEG6000 ( $M = 7300$ – $9300$ ) (Wako Pure Chemical Industries, Japan) was dissolved in benzene and then freeze-dried for 36 h before use. PCL ( $M = 10,000$ ), thionyl chloride ( $\text{SOCl}_2$ ), 3,4-dihydroxycinnamic acid (DHCA), and acetic anhydride ( $\text{Ac}_2\text{O}$ ; Wako Pure Chemical Industries, Japan) were used without purification.

### Synthesis of 3,4-Diacetoxycinnamic Acid

A total of 3.6 g of DHCA (20 mmol) was dissolved in 7 mL of distilled pyridine at 0 °C for 30 min. Next, 12 mL of acetic anhydride was added, and stirred at this temperature for 1.5 h. The mixture was then incubated at 130 °C under reflux for 5 h. After the reaction, the product was recrystallized in toluene, washed by 0.1 N HCl twice, and dried at 50 °C *in vacuo* for 24 h. The yield was 87 wt %. FTIR (Perkin

Elmer Spectrum 100 FTIR Spectrometer, Japan) analysis confirmed that the carbonyl stretching band of the ester group appeared at  $1780\text{ cm}^{-1}$ . In addition, the  $^1\text{H}$  NMR (600 MHz; Varian) signals showed the presence of methyl groups (2.3 ppm) in the DACA, and the integral value indicated that all OH groups in DHCA were esterified with acetic anhydride.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.26 (s, 1H), 2.26–2.34 (m, 6H), 6.38 (d, 1H), 7.70 (d, 1H), 7.05–7.5 (m, 3H).

### Synthesis of 3,4-Diacetoxycinnamoyl Chloride (DACC)

DACC was synthesized by 2.5 g of DACA (9.5 mmol) plus 5 mL of thionyl chloride ( $\text{SOCl}_2$ , 70 mmol) using 8 mg of *N,N*-dimethylformamide (DMF) as a catalyst in 10 mL of distilled DCM as a solvent at 60 °C under reflux for 8 h. After this reaction, the residual  $\text{SOCl}_2$  and solvent were removed *in vacuo*. FTIR (PerkinElmer Spectrum 100 FTIR Spectrometer, Japan) analysis confirmed that the C=O group in the carbonyl chloride of DACC appeared at  $\nu_{\text{C=O}} 1730\text{ cm}^{-1}$ , whereas the C=O group in the carboxyl was not shifted at  $1670\text{ cm}^{-1}$ , indicating that all carboxyl groups in DACA were converted to carbonyl chloride groups.

### Conjugation of DACA to Terminal Polyesters or Polyethers

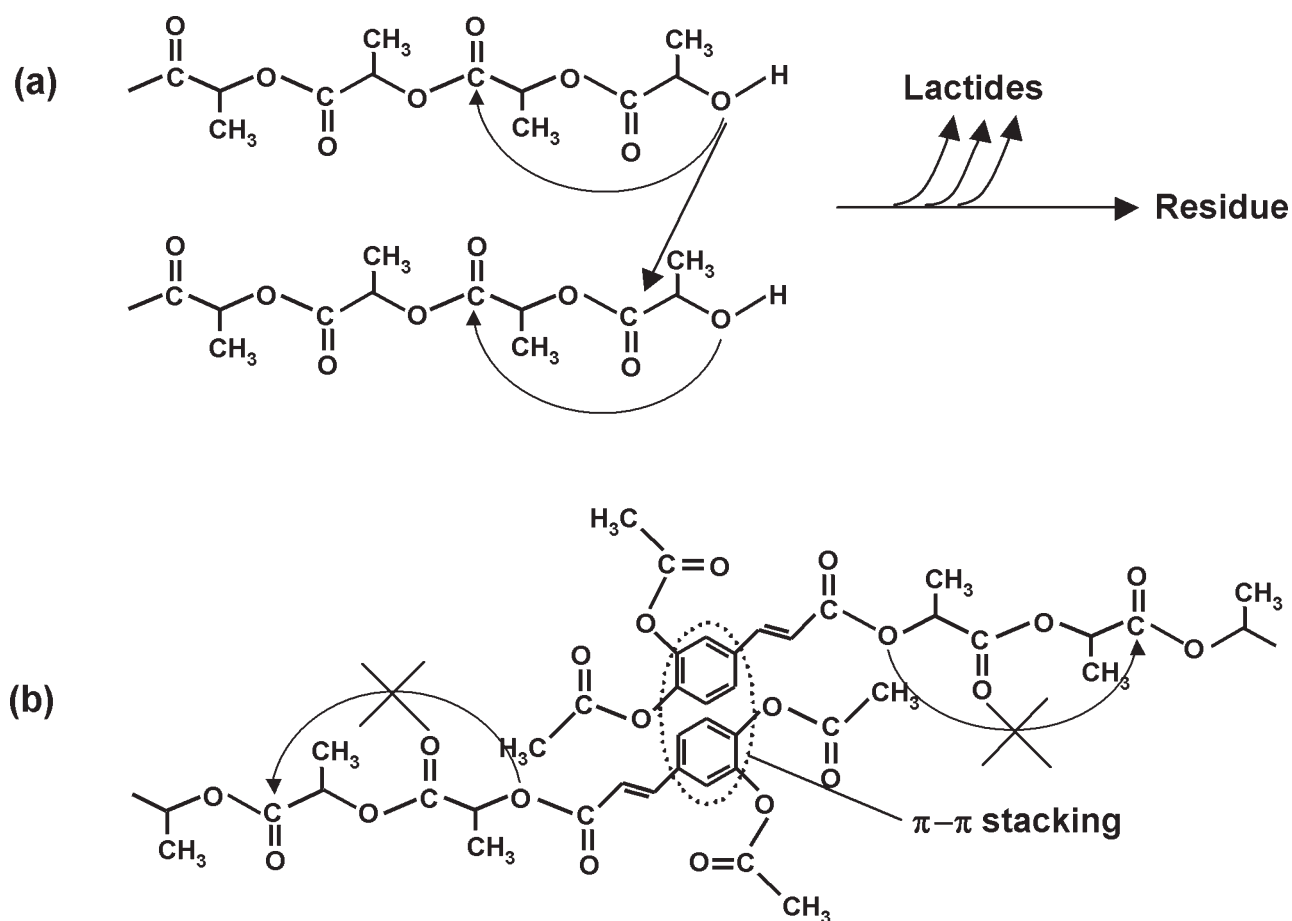
DACA-PLLA was prepared as follows. A total of 1.5 g of PLLA (0.002 mmol) was dissolved in 5 mL of distilled DCM as a solvent and 0.05 mL of distilled pyridine as a catalyst at 0 °C for 30 min. Next, 23.8 mg of DACC (0.008 mmol; molar ratio of PLLA: DACC = 1:4) was added, and stirred at this temperature for 1.5 h, and then at room temperature for 24 h. After this reaction, the product was washed in pH 3 HCl solution, and reprecipitated into ethanol by dissolution in DCM twice. The yield was 93 wt %. The other DACA-polymers were prepared by analogous procedures. The structures of the various DACA polymers were determined by their FTIR spectra using a PerkinElmer Spectrum 100 FTIR Spectrometer (Japan) and their  $^1\text{H}$  MR spectra using a Varian Inova 600 Spectrometer (600 MHz; Varian) in chloroform-*d*. The average molecular weights of the DACA-polymers were determined by gel permeation chromatography (GPC) using a HLC 8120 GPC system with an  $\alpha$ -M column (TOSOH) in chloroform, and then calibrated with polystyrene standards for PLLA, DACA-PLLA, PDLLA, and DACA-PDLLA or polyethylene glycol standards for PCL, DACA-PCL, PEG, and DACA-PEG-DACA, at a flow rate of  $0.6\text{ mL min}^{-1}$  at 37 °C.

$^1\text{H}$  NMR of DACA-PLLA (600 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.26 (s, 1H), 1.58 (d, 3H), 2.17 (br s, 6H), 5.17 (t, 1H), 6.44 (d, 1H), 7.68 (d, 1H), 7.08–7.43 (m, 3H).

$^1\text{H}$  NMR of DACA-PDLLA (600 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.26 (s, 1H), 1.47–1.64 (d, 3H), 2.25–2.34 (m, 6H), 5.13–5.25 (m, 1H), 6.44 (d, 1H), 7.67 (d, 1H), 7.08–7.45 (m, 3H).

$^1\text{H}$  NMR of DACA-PCL (600 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.26 (s, 1H), 1.35–1.41 (m, 2H), 1.56–1.68 (m, 4H), 2.30 (t, 8H), 4.06 (t, 2H), 6.37 (d, 1H), 7.61 (d, 1H), 7.21–7.42 (m, 3H).

$^1\text{H}$  NMR of DACA-PEG-DACA (600 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.26 (s, 1H), 2.29–2.37 (m, 12H), 3.64 (s, 4H), 6.42 (d, 2H), 7.63 (d, 2H), 7.02–7.44 (m, 6H).

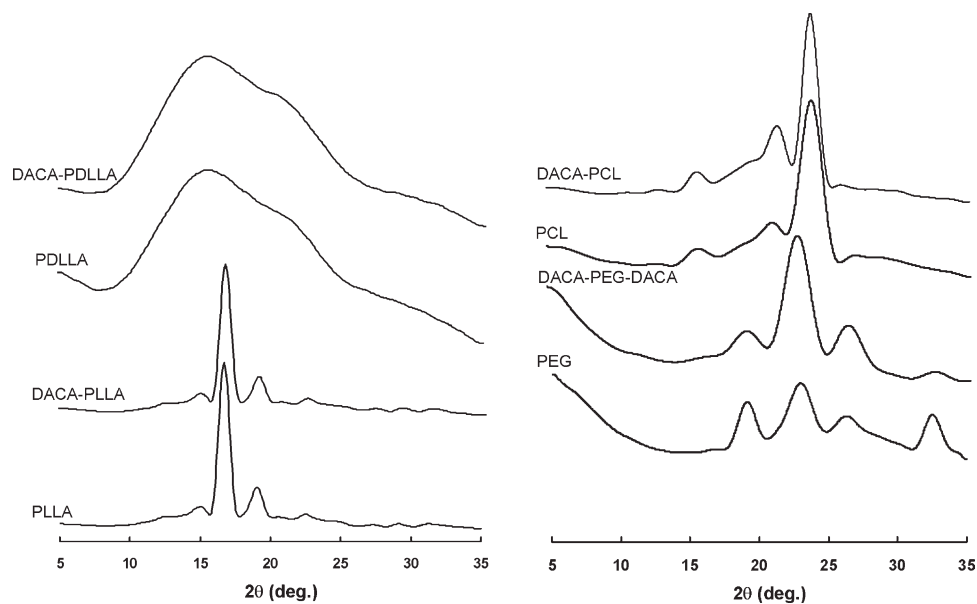


**SCHEME 2** Possible mechanism for high thermal stability of (a) original PLLA and (b) DACA-PLLA.

### Thermal Properties

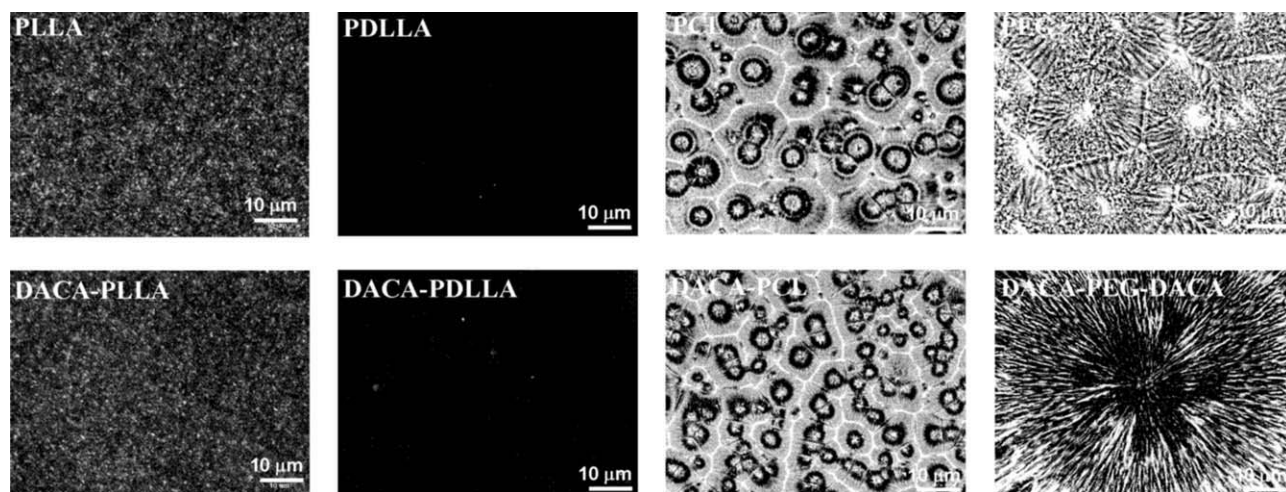
The thermal properties of the various original polymers and DACA-polymers were analyzed by DSC (EXSTAR6100, Seiko Instruments, Japan), TGA (SSC/5200 Seiko Instruments,

Japan), thermal desorption system (GERSTEL TDS 3 + CIS 4; GERSTEL, Germany) and gas chromatography-mass spectrometry (Agilent Technologies 7890A GC & 5975C MSD; Agilent Technologies, Santa Clara, CA). For the DSC



**FIGURE 8** WAXD patterns of various original polymers and DACA-polymers.

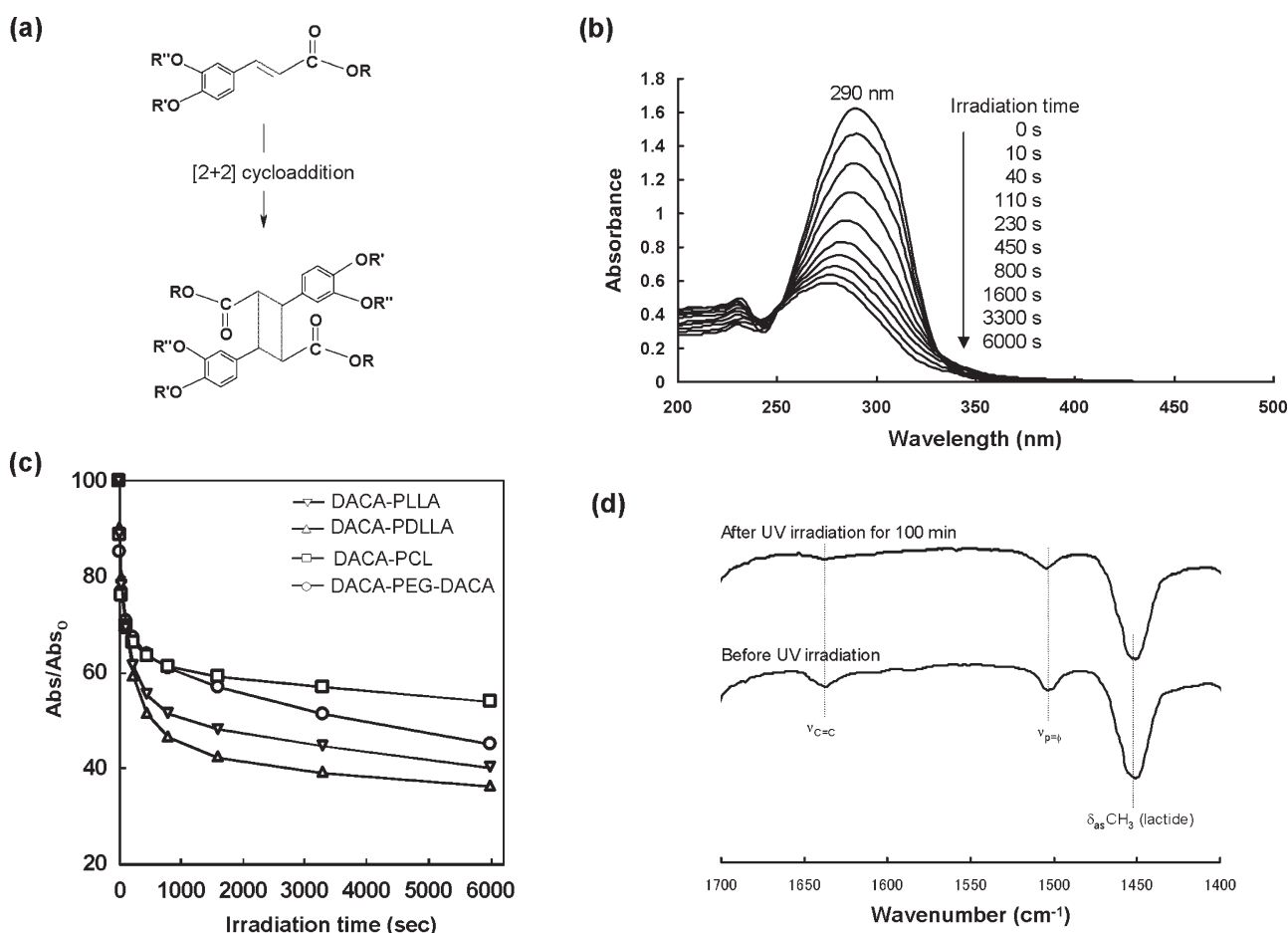




**FIGURE 9** Differential interference microscopic (DIM) images of various original polymers and DACA-polymers.

measurements, both the heating and cooling rates were  $10\text{ }^{\circ}\text{C min}^{-1}$ , and the temperature ranged from 20 to  $200\text{ }^{\circ}\text{C}$  for the original PLLA, DACA-PLLA, original PDLA, and DACA-PDLA, and from 0 to  $130\text{ }^{\circ}\text{C}$  for the original PCL, DACA-

PCL, original PEG and DACA-PEG-DACA. One sample measurement was carried out over two cycles of heating and cooling. The melting temperature ( $T_m$ ) was obtained from the DSC curves of the second heating cycle. The thermal



**FIGURE 10** (a) Photoreaction scheme of the cinnamoyl group undergoing UV irradiation at  $\lambda > 280\text{ nm}$ , (b) UV absorption change of DACA-PDLLA in chloroform during UV irradiation at  $\lambda > 280\text{ nm}$ , (c) maximal absorption change of various DACA-polymers, and (d) FTIR spectra of a DACA-PDLLA cast film before and after UV irradiation at  $\lambda > 280\text{ nm}$  for 100 min.

degradation behavior of the various original polymers and DACA-polymers was investigated by heating from 60 to 500 °C at a rate of 20 °C min<sup>-1</sup> under a nitrogen atmosphere at a flow rate of about 250 mL min<sup>-1</sup>. The heat resistance to pyrolytic measurements of representative original PLLA and DACA-PLLA were performed from 100 to 200 °C or 240 °C at a rate of 20 °C min<sup>-1</sup>, plus a hold at 200 or 240 °C for 90 min under a nitrogen atmosphere at a flow rate of ca. 250 mL min<sup>-1</sup>. The gas evolved from the original PLLA and DACA-PLLA was investigated by pyrolysis at 250 °C for 30 min, and then analyzed further by mass spectrometry.

### Tin Quantification

The residual Sn content in the original polymers and DACA-polymers was measured with a Shimadzu ICPS-8100 inductively coupled plasma atomic emission spectrophotometer. A 0.1 g sample was degraded by mixing 8 mL of nitric acid and 1 mL of sulfuric acid, and was measured by ICP. The obtained data were averaged from two samples, and each sample was measured three times.

### Crystallinity

Samples at a concentration of 30 mg mL<sup>-1</sup> in chloroform were cast onto glass slides at a volume of 0.1 mL. They were then dried at room temperature for 24 h, measured at room temperature for the various original polymers and DACA-polymers, or after annealing at 100 °C for 1 h for PLLA, DACA-PLLA, PDLLA, and DACA-PDLLA by WAXD measurement [X-ray diffractometer (RINT UltraX18, Rigaku, Tokyo, Japan), equipped with a scintillation counter] using CuK $\alpha$  radiation (40 kV, 200 mA; wavelength = 1.518 Å), and observed under a crossed-polarizing microscope.

### Photoreactivity

Various DACA-PLLA, DACA-PDLLA, DACA-PCL, and DACA-PEG-DACA were dissolved in chloroform to concentration of 2.63, 0.62, 0.52, and 0.4 mg mL<sup>-1</sup>, respectively, to the same absorbance, that is, the same numbers as the DACA moiety. A glass-filtered high-pressure Hg Lamp ( $\lambda > 280$  nm, 56 mW cm<sup>-2</sup>) using a Supercure-352S-UV Lightsource (SAN-EI ELECTRIC) was used for irradiation. The time course of the photoreaction conversion was monitored by UV-visible absorption spectroscopy of the DACA-polymer solutions using a HITACHI U3010 Spectrophotometer (Hitachi, Tokyo, Japan).

### CONCLUSIONS

DACA-terminally conjugated commercial polymers were successfully synthesized. The mechanisms of high thermal stability of various polyesters conjugated with DACA were clarified in relation to intermolecular interaction of DACA units and the residual tin catalyst. The amount of residual tin, which enhances the thermal degradation of polyesters, was reduced after the terminal conjugation of DACA. Thermal properties of polyethers, PEG were also significantly improved by DACA conjugation. Moreover, the gas evolution of PLLA during pyrolysis was 20-fold decreased by DACA conjugation. However, the basic properties of original

polymers were maintained after the terminal conjugation of DACA and all of the DACA-polymers showed photoreactivities corresponding to DACA units. DACA-polymers may be useful as photoreactive PLLA, PDLLA, PCL, and PEG with high thermal stability for biomedical and environmental applications.

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