Hydrolytic Degradation of Poly(L-lactic acid): Combined Effects of UV Treatment and Crystallization

Hideto Tsuji,[1] Kenta Shimizu,[1] Yoshihiro Sato[2]

[1]Department of Environmental and Life Sciences, Graduate School of Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan
[2]Mikawa Textile Research Center, Aichi Industrial Technology Institute (AITEC), Aichi Prefectural Government, Otsuka-cho, Gamagori, Aichi 443-0013, Japan

ABSTRACT: Amorphous and crystallized poly(L-lactic acid) (PLLA) films were prepared and the hydrolytic degradation of the ultraviolet (UV)-treated and UV-nontreated films was investigated. This study reveals that the combination of UV and thermal treatments can produce the PLLA materials having different hydrolytic degradation profiles and that the UV-irradiation in the environment will affect the design of recycling process for PLLA articles. In an early stage, the degrees of hydrolytic degradation monitored by weight loss (W_{loss}), number-average molecular weight (M_n), and melting temperature (T_m) were higher for the UV-treated films than for the UV-nontreated films. In a late stage, the trend traced by W_{loss} was reversed, and the difference in the degrees of hydrolytic degradation between the UV-treated and UV-nontreated films monitored by M_n and T_m became smaller, with the exception of the degrees of hydrolytic degradation of the amorphous films traced by T_m. Also, in the early stage, the degrees of hydrolytic degradation monitored by W_{loss} and M_n were higher for the crystallized films than for the amorphous films. In the late stage, this trend was reversed, with the exception of the degrees of hydrolytic degradation of the UV-treated films monitored by M_n. The main factors that determined the W_{loss} and T_m were the molecular weight and initial crystallinty but not the molecular structures such as terminal C=C double bonds and crosslinks. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2394–2406, 2012

Key words: biodegradable; photodegradation by UV-irradiation; hydrolytic degradation

INTRODUCTION

Poly(L-lactic acid) (PLLA) is a plant-derived polymer and has been utilized for industrial, commodity, biomedical, pharmaceutical, and environmental applications.[1–11] When PLLA materials are released in the environment, they are exposed to photodegradation by sunlight especially ultraviolet (UV) rays. Therefore, it is expected that the structural changes of PLLA articles caused by the UV-irradiation in the environment will affect the design of recycling process by hydrolytic/thermal degradation. In biomedical and pharmaceutical applications, UV irradiation or UV treatment can be utilized for sterilization. In the molecular level, UV-irradiation is known to cause PLLA the structural changes, such as decrease in molecular weight and formation of terminal C=C double bonds through the Norrish II mechanism and of crosslinks via radical recombination.[12] Moreover, the comparison of UV-photodegradation behavior between PLLA and poly(ε-caprolactone) strongly suggested that the chemical structure between the adjacent ester groups than the density of ester group is crucial to determine the photodegradability of biodegradable polyesters.[12] Although in the material level, the photodegradation of PLLA films proceeds via a bulk erosion mechanism; this indicates that UV rays penetrate the films with no significant reduction.[13,14] Furthermore, it was found that PLLA chains are photodegradable even in the crystalline regions and their photodegradability is lower than that in the amorphous regions.[13,14] The photodegradation behavior of PLLA by UV-irradiation has been intensively investigated.[12–26]

On the other hand, manipulating the hydrolytic degradation behavior and rate of PLLA materials is a matter of concern when it is used in environmental, biomedical, and pharmaceutical applications.[27] The representative techniques utilized for controlling hydrolytic degradation behavior and rate of poly(lactic acid) (PLA)-based materials include copolymerization, crystallization, and blending with

TABLE I
Molecular Characteristics, Thermal Properties, and X_c of PLLA-A, PLLA-A(UV), PLLA-C, and PLLA-C(UV) Films before and after Hydrolytic Degradation

Code	UV treatment time (h)	Hydrolytic degradation time (h)	M_n (g mol^{-1})	M_w/M_n	T_g[a] (°C)	T_{cc}[a] (°C)	T_m[a] (°C)	ΔH_{cc}[b] (J g^{-1})	ΔH_m[b] (J g^{-1})	X_c[c] (%)
PLLA-A	0	0	2.17×10^5	2.51	66.0	112.0	178.8	−34.3	37.3	0
		96	3.40×10^3	1.52	–	–	160.0	0	80.4	100
PLLA-A (UV)	100	0	1.46×10^5	2.71	67.9	110.1	177.1	−39.5	40.5	0
		96	2.41×10^3	1.74	–	–	151.1	0	75.7	100
PLLA-C	0	0	1.92×10^5	2.49	64.6	–	192.3	0	75.6	63.5
		96	1.22×10^4	1.21	–	–	182.4	0	95.5	100
PLLA-C(UV)	100	0	1.53×10^5	2.81	66.0	–	192.1	0	75.5	57.8
		96	1.05×10^4	1.29	–	–	182.0	0	96.8	100

[a] T_g, T_{cc}, and T_m are glass transition, cold crystallization, and melting temperatures estimated by DSC measurements.
[b] ΔH_{cc} and ΔH_m are enthalpies of cold crystallization and melting estimated by DSC measurements.
[c] Crystallinity estimated by WAXS measurements.

other polymers and additives.[1–11] For neat PLA, altering the crystallinity is effective to manipulate the hydrolytic degradation profiles.[27–32] It was found that at least in an early stage, the hydrolytic degradation rates traced by weight loss, molecular weight, and mechanical properties become higher with an increase in crystallinity. However, these techniques of copolymerization, crystallization, and blending cannot be applied *in situ* after the processing of materials. UV-irradiation can be applied *in situ* after the processing of PLLA materials. UV-irradiation lowers the molecular weight and forms the terminal C=C double bonds and crosslinks, which are respectively assumed to enhance and disturb the hydrolytic degradation of PLLA materials.[12] The effects of simultaneous photodegradation by UV-irradiation and hydrolytic degradation have been studied and found that the degradation was enhanced by the simultaneous photogradation and hydrolytic degradation.[20,21] In our previous study, we found that proteinase K-catalyzed enzymatic degradation of UV-treated PLLA proceeds rapider

than that of UV-nontreated PLLA in an early stage, whereas this trend is reversed in a late stage.[22] Chu et al. reported the effects of γ-irradiation on the hydrolytic degradation behavior of poly(glycolide) suture and found that the hydrolytic degradation is accelerated by γ-irradiation.[33] However, although the effects of UV-irradiation of PLLA on its (nonenzymatic) pure hydrolytic degradation are crucial in terms of environmental, biomedical, and pharmaceutical applications as well as designing the recycling process, they are not fully understood so far.

In this study, photodegradation by UV irradiation (UV treatment) and hydrolytic degradation of PLLA were consecutively performed to elucidate the effects of UV treatment on hydrolytic degradation behavior and rate of PLLA materials. For this purpose, PLLA films with typical highly ordered structures, i.e., amorphous and crystallized PLLA films were prepared and exposed to UV-irradiation and subsequent accelerated hydrolytic degradation at 97°C.[32] The hydrolytic degradation was monitored by
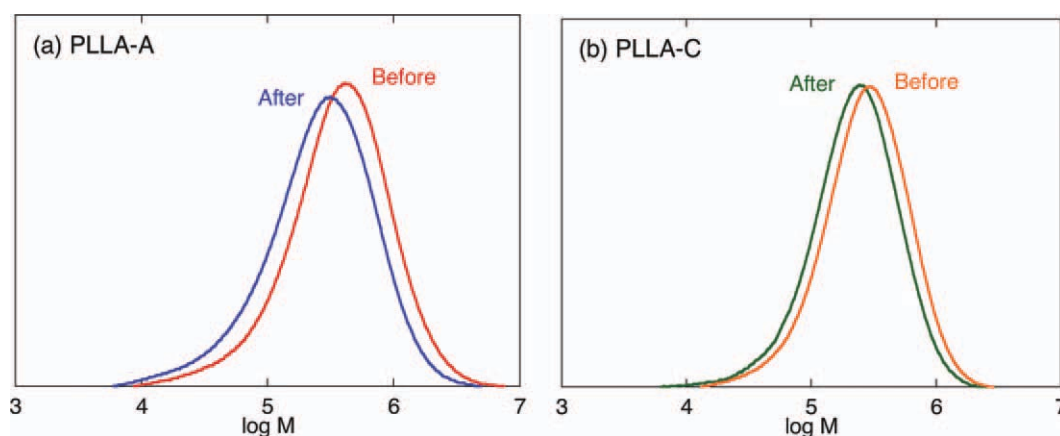

Figure 1 PLLA-A and PLLA-C films before and after UV treatment for 100 h.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
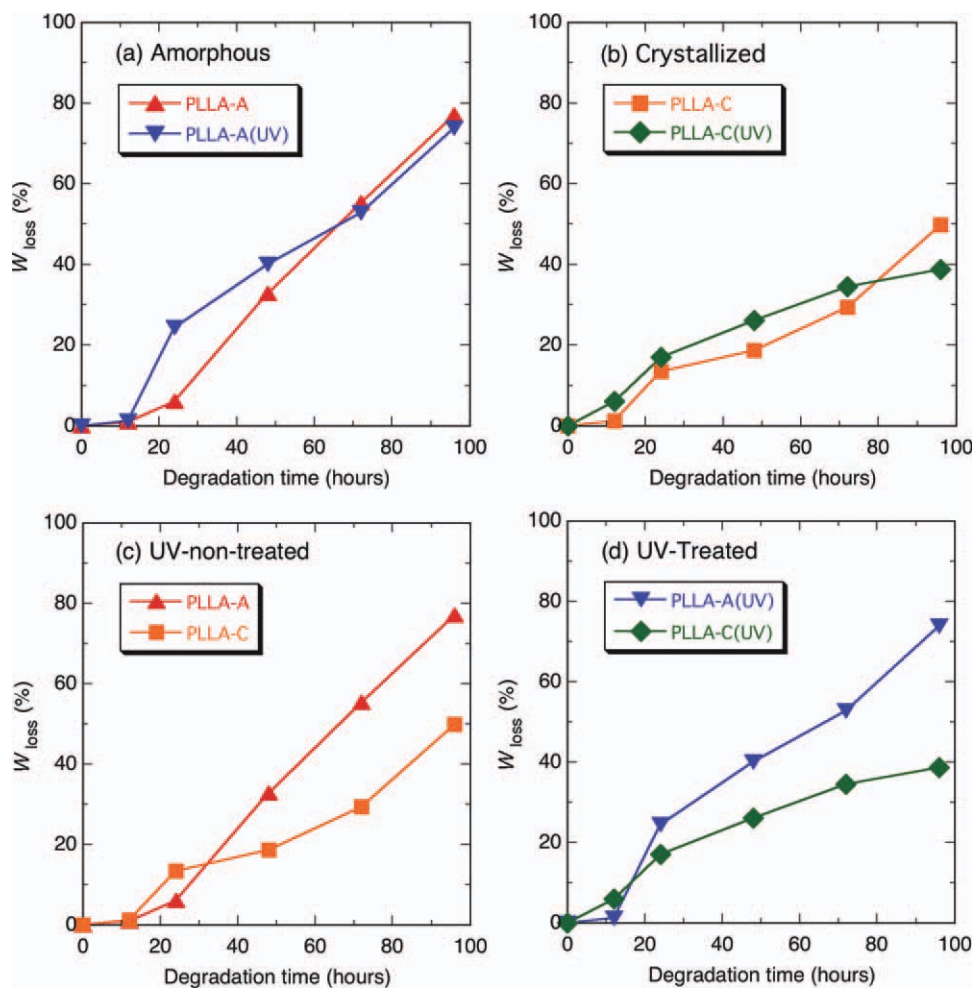
Figure 2 W_{loss} of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of hydrolytic degradation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gravimetry, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC), and the combined effects of UV treatment and crystallization on the hydrolytic degradation of PLLA were studied.

EXPERIMENTAL

Materials

PLLA (intrinsic viscosity = 5.7–8.2) was purchased from Polysciences (PA) and purified by precipitation using dichloromethane and methanol as the solvent and nonsolvent, respectively. The purified polymer was dried under reduced pressure for 5 days. The films (100 μm thick) of the purified PLLA were prepared by solution casting using chloroform as the solvent. A PLLA solution with a concentration of 1.0 g dL^{-1} was cast onto a Petri dish, followed by solvent evaporation at room temperature for about 1 day and further dried under reduced pressure for 5 days. To prepare amorphous and crystallized PLLA films, the cast PLLA films were thermally treated by the follow-

ing procedures. Each of the cast PLLA films was placed between two Teflon sheets and sealed in a glass test tube under reduced pressure (<3 mmHg). The sealed PLLA films were melted at 200°C for 3 min and then quenched at 0°C or crystallized at 140°C for 10 h. The crystallized films were quenched at 0°C to stop further crystallization. The amorphous and crystallized PLLA films thus prepared are abbreviated as PLLA-A and PLLA-C films, respectively.

UV treatment

The UV treatment of thermally treated PLLA films was carried out according to ISO 4892-4 (Plastics-Method of exposure to laboratory light sources-Part 4: Open flame carbon-arc lamps) with an accelerated weathering chamber (WEL-SUN-HCH, Suga Test Instruments, Tokyo, Japan) without using a water-spray system.[13,14,22] The films were irradiated with UV-rays (glass filter: Type 3) for the period of 100 h at a black-panel temperature of 63°C and a relative
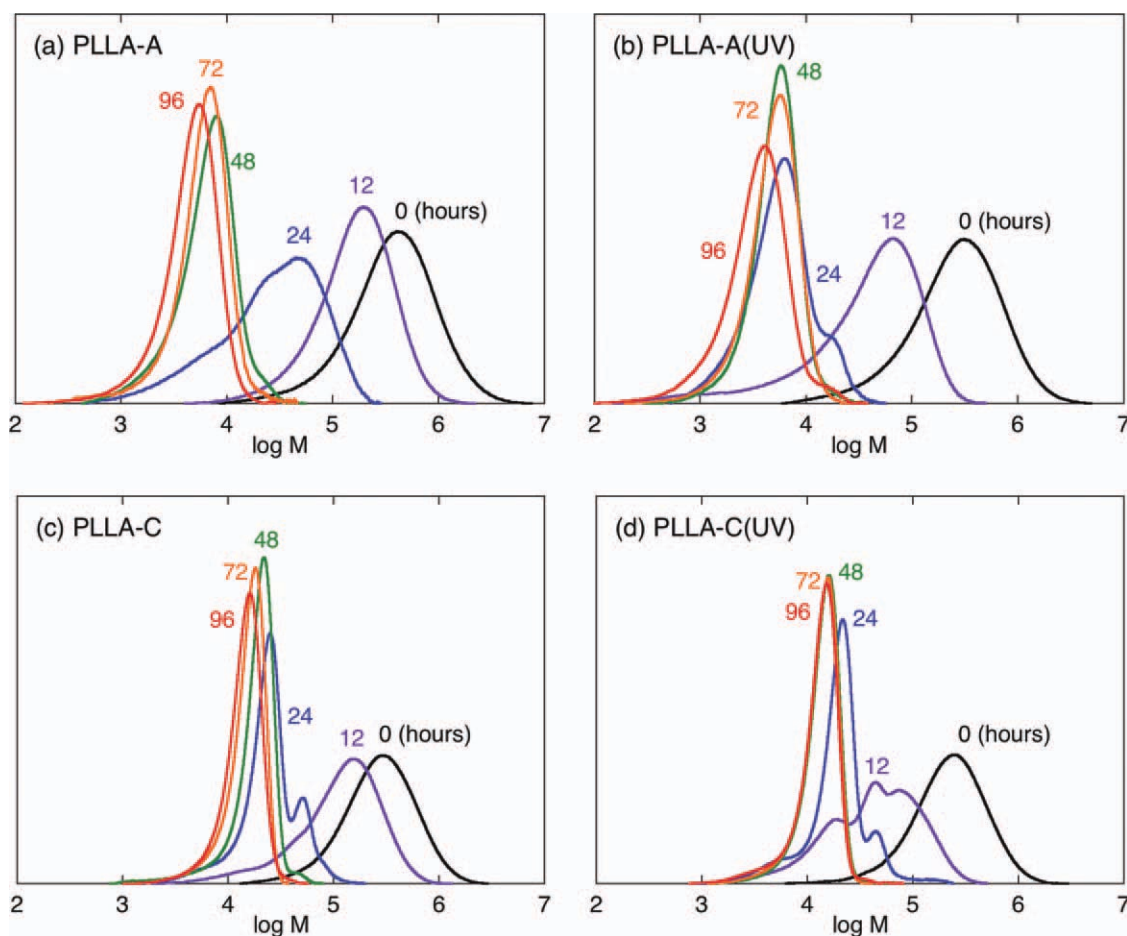
Figure 3 Molecular weight distribution of PLLA-A (a), PLLA-A(UV) (b), PLLA-C (c), and PLLA-C(UV) (d) films after hydrolytic degradation for different times.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

humidity of 65%. The PLLA-A and PLLA-C films thus UV treated are abbreviated as PLLA-A(UV) and PLLA-C(UV) films, respectively.

Hydrolytic degradation

The hydrolytic degradation of the triplicate PLLA films (14 mm × 24 mm × 100 μm) was performed for predetermined periods of time in 10 mL of phosphate-buffered solution (pH = 7.4 ± 0.1) containing 0.02 wt % sodium azide at 97°C. After hydrolytic degradation, the films were rinsed thrice with fresh distilled water at room temperature, following which they were dried under reduced pressure for 5 days. The distilled water used for the preparation of the phosphate-buffered solution and the rinsing of the hydrolytically degraded films was of HPLC grade (Nacalai Tesque, Kyoto, Japan).

Measurements

The weight loss (W_{loss}) of the hydrolytically degraded films was calculated using the weights of a dried PLLA film before and after hydrolytic degradation (W_{before} and W_{after}, respectively):

$$W_{loss}(\%) = 100(1 - W_{after}/W_{before}). \qquad (1)$$

The weight- and number-average molecular weights (M_w and M_n, respectively) and the molecular weight distribution of the PLLA films were evaluated in chloroform at 40°C by a Tosoh (Tokyo, Japan) GPC system (refractive index monitor: RI-8020) with two TSK Gel columns (GMH_{XL}) using polystyrene standards.

The glass transition, cold crystallization, and melting temperatures (T_g, T_{cc}, and T_m, respectively) and the enthalpies of cold crystallization and melting (ΔH_{cc} and ΔH_m, respectively) of the PLLA films were determined with a Shimadzu DSC-50. The films were heated at a rate of 10°C min^{-1} under a nitrogen gas flow at a rate of 50 mL min^{-1} for the DSC measurements. The T_g, T_{cc}, T_m, ΔH_{cc}, and ΔH_m values of the films were calibrated using benzophenone, indium, and tin as standards. The cystallinity (X_c) of the PLLA films were estimated by the use of wide-angle X-ray scattering (WAXS).[34] The WAXS measurements were performed
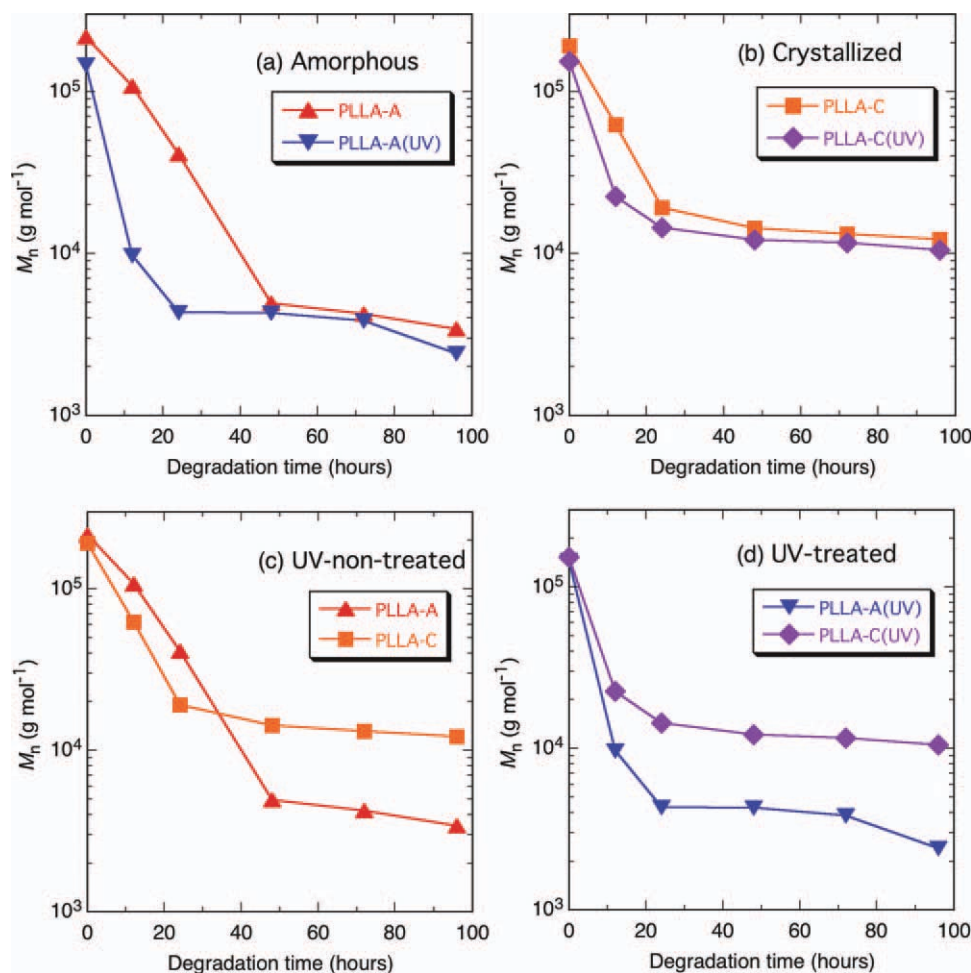
Figure 4 M_n of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of hydrolytic degradation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 25°C using a RINT-2500 equipped with a Cu-K$_\alpha$ source (λ = 0.1542 nm), which was operated at 40 kV and 200 mA (Rigaku, Tokyo, Japan). The molecular characteristics, thermal properties, X_c of typical UV-treated and UV-nontreated PLLA films before and after hydrolytic degradation are summarized in Table I.

RESULTS

UV treatment

UV treatment causes PLLA materials the chain cleavage and the formation of terminal C=C double bonds at newly formed chain terminals and of crosslinks.[12] Figure 1 shows the GPC curves of PLLA-A and PLLA-C films before and after UV treatment. As seen in the figure, molecular weight distribution curves shifted as a whole to a lower molecular weight in both films. The whole shift of the curves confirmed the bulk degradation nature of photodegradation. Also, the shift width of the molecular weight distribution peaks and the M_n value difference before and after UV treatment (Table

I) were smaller for the crystallized PLLA-C film than for the amorphous PLLA-A film. This indicates that the crystalline region is more photodegradation-resistant than the amorphous region.

Hydrolytic degradation

Weight loss

W_{loss} is caused by the formation of water-soluble oligomers and monomers by hydrolytic chain cleavage and their release from the materials. Therefore, W_{loss} is an indicator of the fraction of water-soluble oligomers and monomers in the materials. Figure 2 shows the W_{loss} of the films as a function of hydrolytic degradation time. As seen in Figure 2(a,b), in an early stage of hydrolytic degradation within 48 and 72 h, the W_{loss} values of amorphous and crystallized films were higher for the UV-treated films than for the UV-nontreated films. However, in a late stage of hydrolytic degradation exceeding 48 h, the W_{loss} values of the UV-treated PLLA-A(UV) films were similar to those of the UV-nontreated PLLA-A films,
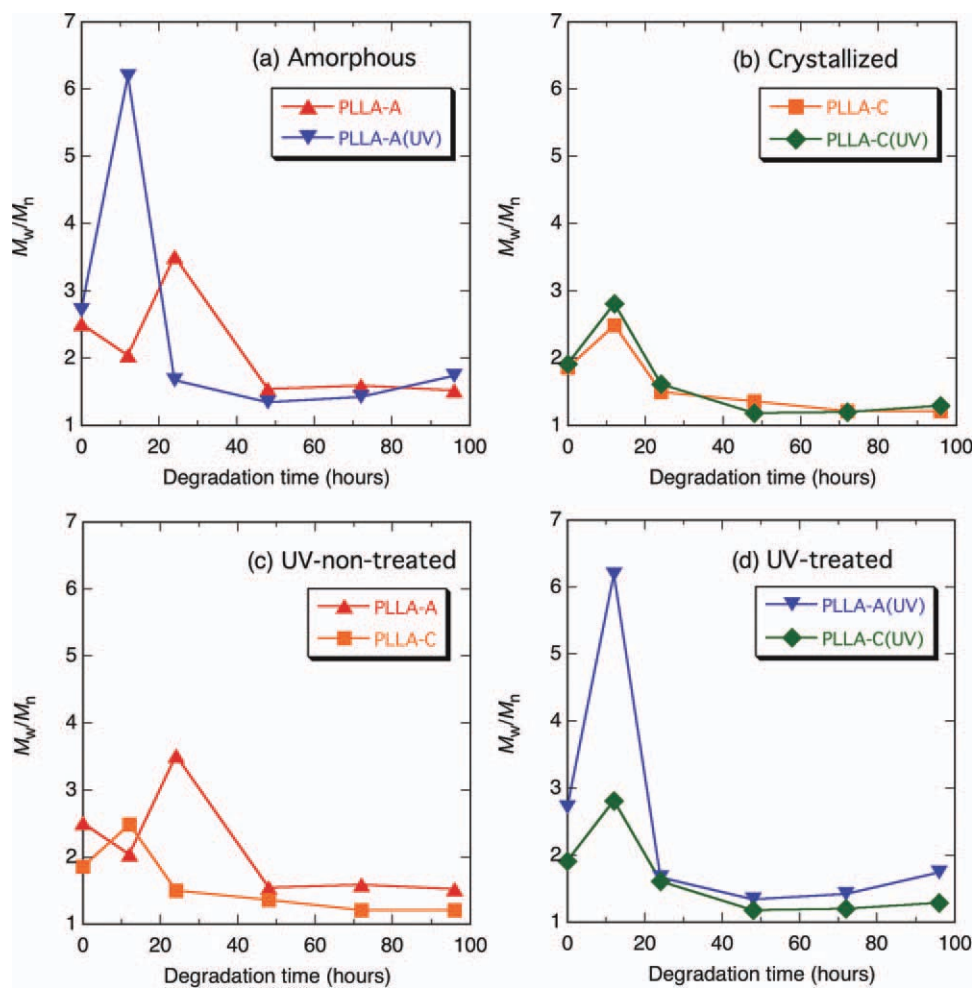
Figure 5 M_w/M_n of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of hydrolytic degradation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

whereas at the degradation period of 96 h, W_{loss} was higher for the UV-nontreated PLLA-C film than for the UV-treated PLLA-C(UV) film. This trend was very similar to the case of proteinase K-catalyzed enzymatic degradation,[22] wherein the effect on weight loss depends on the degradation period. It can be seen from Figure 2(c,d), the significant increases in W_{loss} were observed at short periods of 24 and 12 h for the crystallized UV-nontreated and UV-treated films, respectively, which were higher than those of amorphous UV-nontreated and UV-treated films, respectively, whereas the W_{loss} values were higher for amorphous UV-nontreated and UV-treated films for the periods exceeding 24 and 12 h, respectively. This trend is consistent with that reported for UV-nontreated crystallized and amorphous PLLA films in phosphate-buffered solution at 37°C.[27–32]

Molecular weight change

To investigate molecular level chain cleavage and its rate, GPC measurements were performed. Figure 3 shows the GPC profiles of the films hydrolyzed for different times. As seen, molecular weight distribution curves shifted as a whole to a lower molecular weight; this reflects the bulk erosion nature of all the films, irrespective of UV treatment and crystallinity. At 24 h, the knot, shoulder, or subpeak was observed for the PLLA-A, PLLA-A(UV), PLLA-C, and PLLA-C(UV) films. These are ascribed to the selective hydrolytic degradation and removal of amorphous chains and subsequent formation of crystalline residues. Although the PLLA-A and PLLA-A(UV) films were originally amorphous, PLLA should have crystallized when the films were immersed in the phosphate-buffered solution at 97°C. Because of the initial rapid hydrolytic degradation of the PLLA-C(UV) film, as is obvious from the W_{loss} data in Figure 2, the multiple peaks due to the formation of crystalline residues appeared even at 12 h. At 24 h, the molecular weight of knot, shoulder, or subpeak ascribed to the crystalline residues was higher for the crystallized films than for the amorphous films. This is indicative of the fact
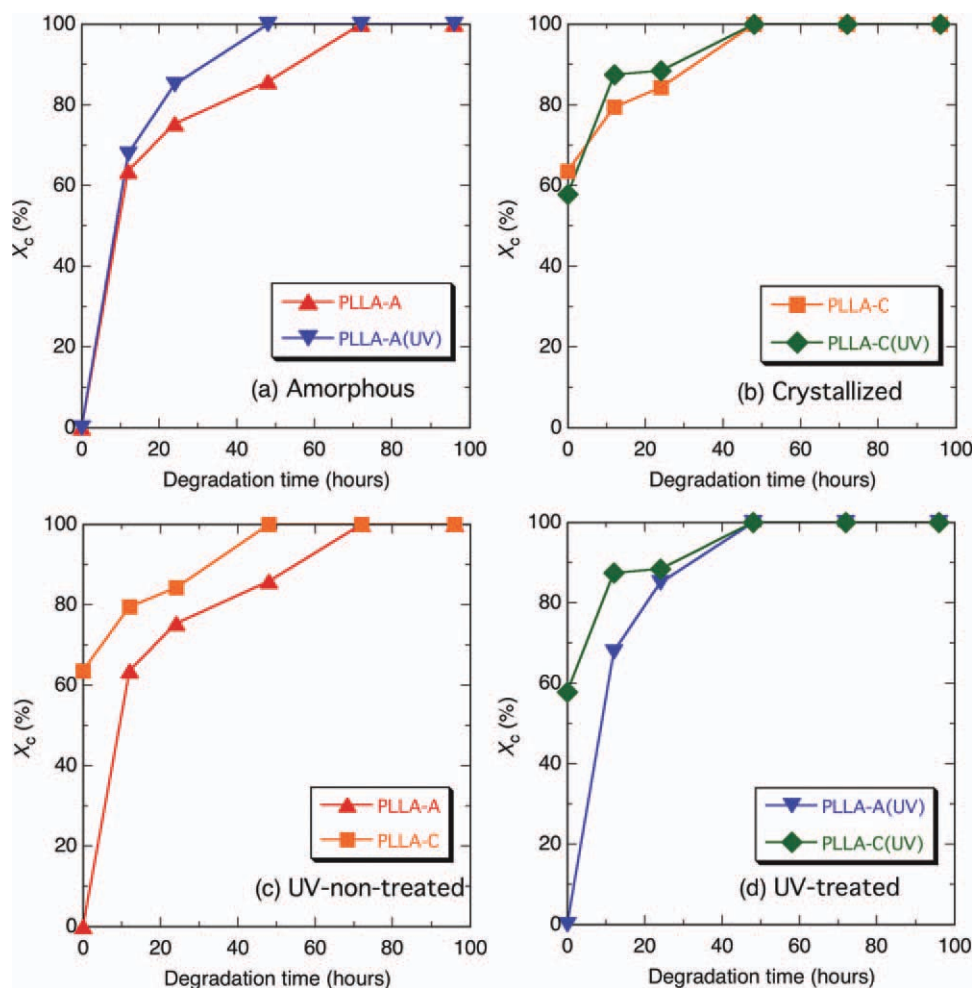
Figure 6 X_c of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of hydrolytic degradation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the initial crystalline thickness was larger for the crystallized films than for the amorphous films. The crystalline residue formation and their slow hydrolytic degradation were also evident from the reduced shifting rates of molecular weight distribution curves for the periods exceeding 48 h.

The M_n values of the films were estimated from Figure 3 and are plotted in Figure 4 as a function of hydrolytic degradation time. In the case of the amorphous films [Fig. 4(a)], the M_n of the UV-treated PLLA-A(UV) film decreased more rapidly compared to that of the UV-nontreated PLLA-A film in the early stage up to 24 h, whereas the difference became very small in the late stage exceeding 48 h. In the case of the crystallized films [Fig. 4(b)], the M_n of the UV-treated PLLA-C(UV) decreased slightly rapidly than that of the UV-nontreated PLLA-C film, although the difference between the UV-nontreated PLLA-C and UV-treated PLLA-C(UV) films was not large compared to that between the amorphous UV-nontreated PLLA-A and UV-treated PLLA-A(UV) films in the early stage. When

comparison was performed for the UV-nontreated films [Fig. 4(c)], the M_n was lower for the crystallized PLLA-C film than for the amorphous PLLA-A film in the early stage up to 24 h, whereas this trend was reversed in the late stage exceeding 48 h. When comparison was carried out for the UV-treated films [Fig. 4(d)], the M_n of the amorphous PLLA-A(UV) film was lower than that of the crystallized PLLA-C(UV) film throughout the hydrolytic degradation period studied here. This is in marked contrast with the result for the UV-nontreated films.

The M_w/M_n values of the films were evaluated from Figure 3 and are plotted in Figure 5 as a function of hydrolytic degradation time. For the amorphous films, the sharp increase in M_w/M_n from 2.7 to 6.2 was observed for the UV-treated PLLA-A(UV) film at 12 h, rapidly decreased to 1.7 at 24 h, and then remained at the similar values, whereas the M_w/M_n of the UV-nontreated PLLA-A film gave maximum around 3.5 at 24 h, which is smaller than that of the UV-treated PLLA-A(UV) film, and then retained the values around 1.5 [Fig. 5(a)]. The smaller maximum M_w/M_n values
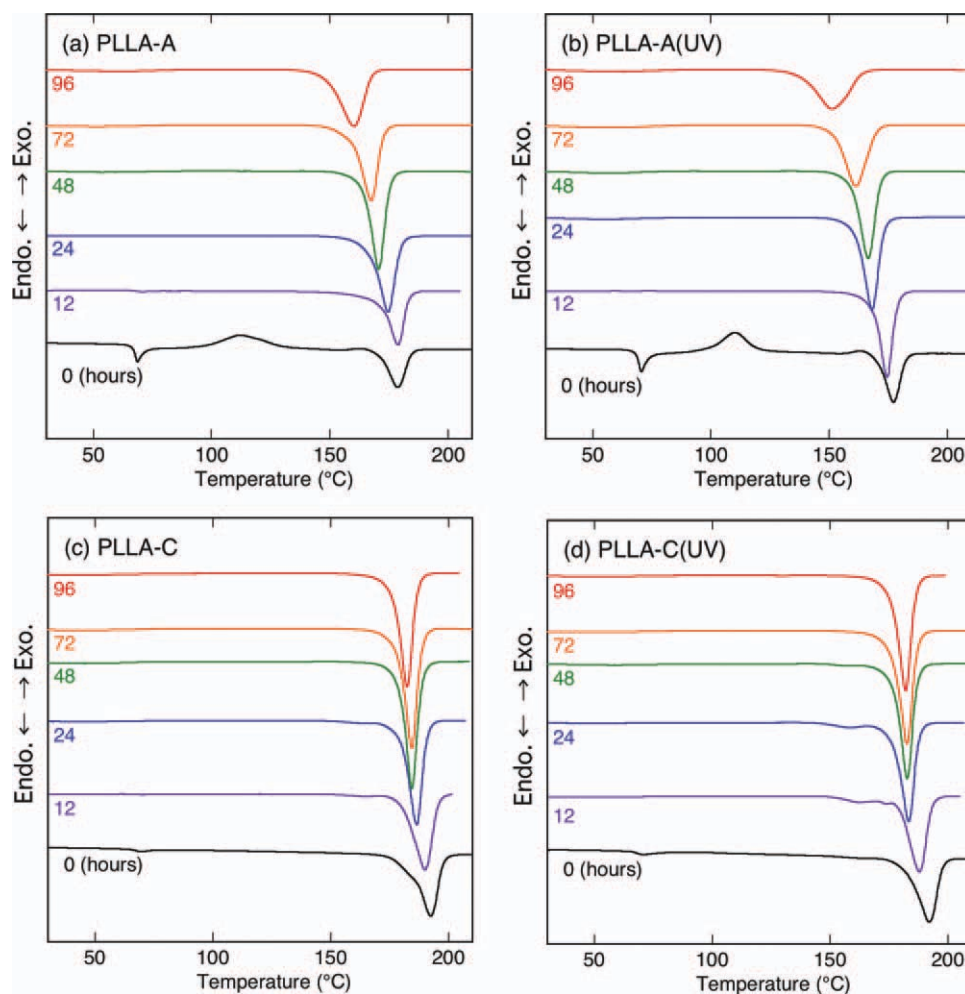
Figure 7 DSC thermograms of PLLA-A (a), PLLA-A(UV) (b), PLLA-C (c), and PLLA-C(UV) (d) films after hydrolytic degradation for different times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

below 3 were observed at 12 h for both the crystallized PLLA-C and PLLA-C(UV) films and then the peaks the M_w/M_n values approached to 1.2 [Fig. 5(b)]. When comparison was performed for the UV-nontreated films, the maximum values were higher for the amorphous PLLA-A film than for the crystallized PLLA-C film [Fig. 5(c)]. The similar trend was observed for the UV-treated films [Fig. 5(d)]. Although most of the M_w/M_n values increased at 12 h, the small M_w/M_n decease was observed for the PLLA-A film. This may be due to the slow degradation of the PLLA-A film at 12 h and the removal of low-molecular-weight components contained in the film.

Crystallinity change

The X_c values of the films during hydrolytic degradation were evaluated from WAXS measurements and are plotted in Figure 6 as a function of hydrolytic degradation time. The X_c of the amorphous films increased rapidly in the first 12 h and then increased slowly to 100% [Fig. 6(a)], whereas that of the crystal-

lized films increased slowly compared to that of the amorphous films and reached 100% at 48 h [Fig. 6(b)]. The initial rapid increases of the amorphous films are due to the crystallization on immersion in phosphate-buffered solution at 97°C, and the relatively slow increment of X_c of all the films for the period from 12 to 48 or 72 h is ascribed to the hydrolytic cleavage and removal of amorphous chains. The X_c values, with the exception of the initial values and the saturated values of 100%, were higher for the UV-treated films than for the UV-nontreated films. This is attributable to the rapid degradation or the removal of amorphous chains of the UV-treated films with lower initial molecular weights. The effect of UV treatment on the X_c change was larger for the amorphous films [Fig. 6(a)] than for the crystallized films [Fig. 6(b)]. The UV treatment effect of the amorphous films on X_c change in the early stage continued for longer times than that of the crystallized films [Fig. 6(a,b)], whereas the X_c effect of the UV-nontreated films on X_c change in the early stage lasted for longer times than that of the UV-treated films [Fig. 6(c,d)].
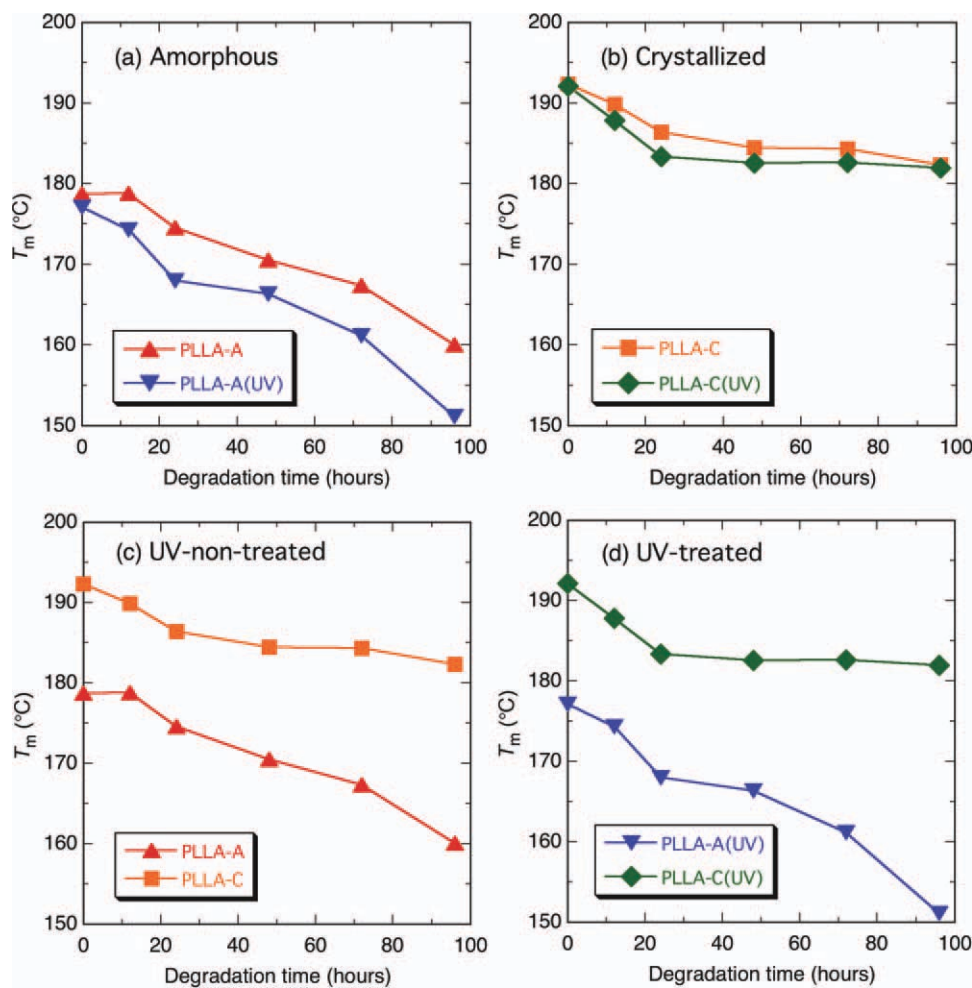
Figure 8 T_m of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of hydrolytic degradation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal property change

Thermal properties monitored by DSC can give further information regarding highly ordered structures. Figure 7 shows the DSC thermograms of the films hydrolytically degraded for different times. The glass transition, cold crystallization, and melting peaks of the films were observed at around 70, 110, and 180°C, respectively. The cold crystallization peak of the PLLA-A and PLLA-A(UV) films observed at 0 h disappeared at 12 h; this indicates that the crystallization at elevated temperature of 97°C proceeded and completed in phosphate-buffered solution within 12 h. The T_m values of the films were evaluated from Figure 7 and are plotted in Figure 8 as a function of hydrolytic degradation time. The T_m of the amorphous films decreased rapidly and monotonically with degradation time [Fig. 8(a)], whereas that of the crystallized films decreased rapidly with degradation time in the early stage up to 24 h and then decreased slowly in the late stage for the period exceeding 24 h [Fig. 8(b)]. The
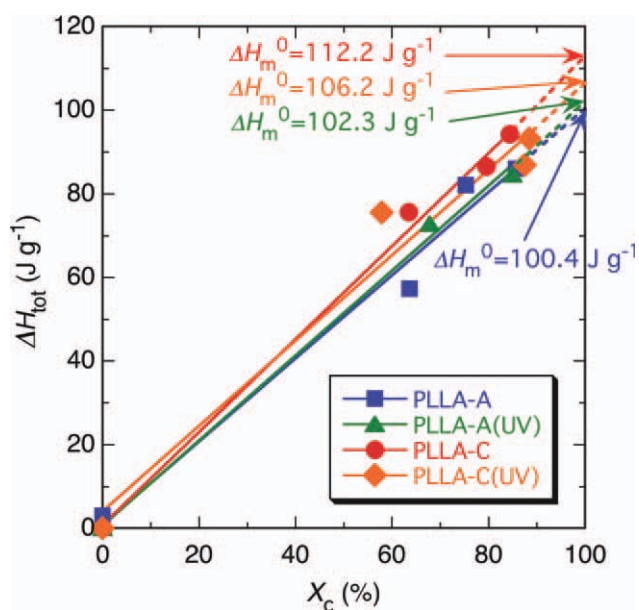

Figure 9 ΔH_{tot} measured by DSC as a function of X_c traced by WAXS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
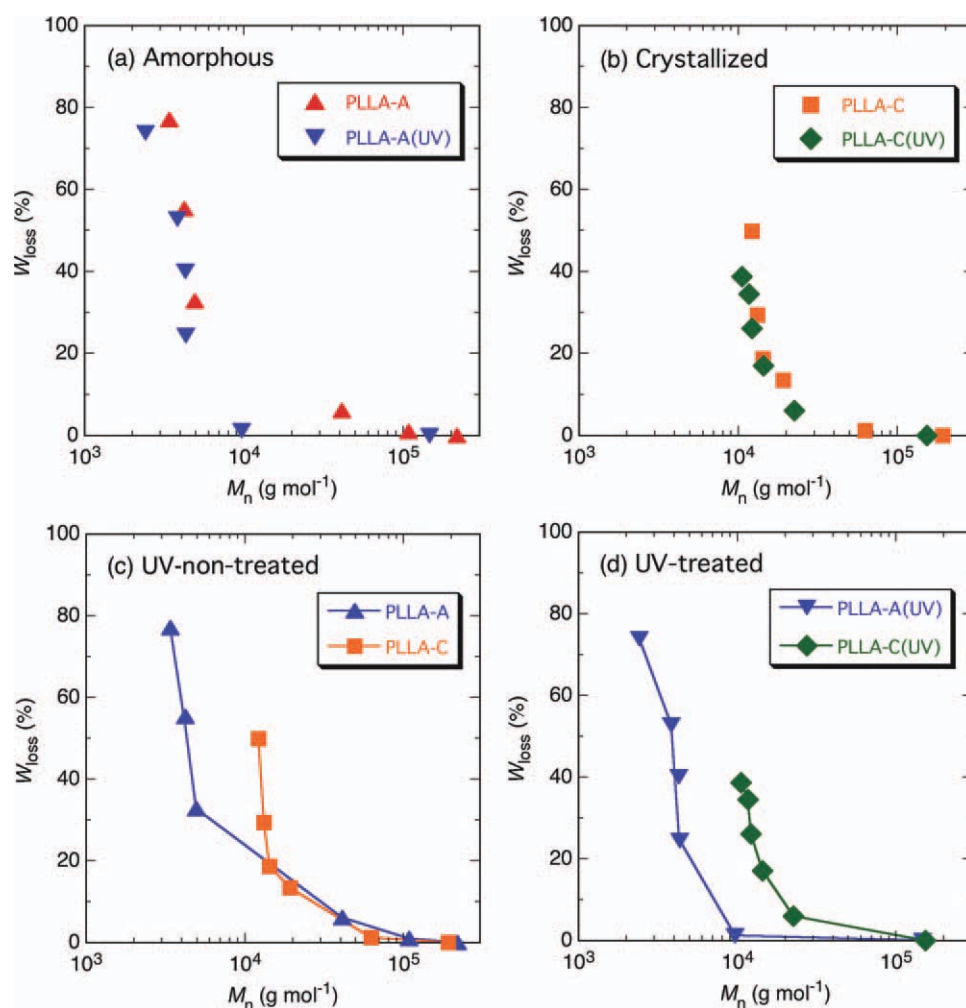
Figure 10 W_{loss} of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of M_n. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

comparison of T_m values between the UV-treated and UV-nontreated films [Fig. 7(a,b)] indicates that the effect of UV treatment on T_m change is large for the amorphous films than for the crystallized films. For both the UV-nontreated and UV-treated films, the amorphous films showed lower T_m than that of the crystallized films throughout hydrolytic degradation period studied here and showed more rapid decrease with hydrolytic degradation time [Fig. 8(c,b)]. The difference between the amorphous and crystallized UV-treated films is similar to that of the amorphous and crystallized UV-nontreated films. The higher T_m and M_n values of the crystallized films than those of the amorphous films for the degradation period exceeding 24 h (Figs. 4 and 8) strongly suggest that the thickness of crystalline residues formed by the hydrolytic degradation was larger for the crystallized films than that of the amorphous films.

Utilizing the following Thomson–Gibbs expression, the decrease of T_m can be understood[35]:

$$T_m = T_m{}^0(1 - 2\sigma/\Delta h^0 \rho_c L_c), \qquad (2)$$

where σ, Δh^0, and ρ_c are the specific fold surface free energy, heat of fusion (per unit mass), and crystal density, respectively. According to this equation, the deceases of T_m in the early stage are attributable to the structural change of the folding surface of crystalline regions [i.e., increases in σ in eq. (2)], whereas those in the late stage can be ascribed to the reduced thickness of crystalline regions [i.e., decreases in L_c in eq. (2)].[36] The latter will become dramatic when the thickness of the crystalline regions is small, as seen in eq. (2) and, therefore, the decreases of T_m are larger for the amorphous films having low initial L_c values than for those of the crystallized films with high initial L_c values [Fig. 8(c,d)].

Enthalpy of melting at 100% crystallinity

To obtain the ΔH_{tot} (= $\Delta H_{cc} + \Delta H_m$) value for 100% X_c, the ΔH_{tot} as an indicator of crystallinity obtained
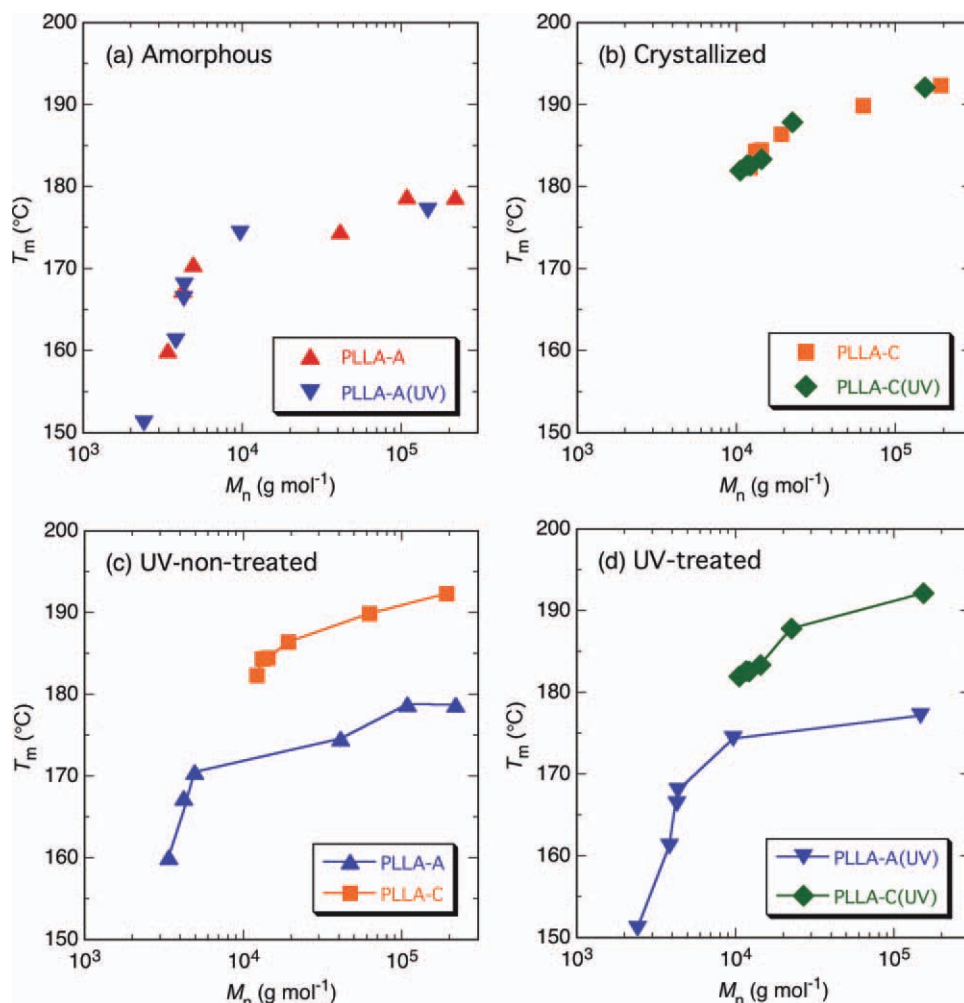
Figure 11 T_m of amorphous PLLA films (a), crystallized PLLA films (b), UV-nontreated PLLA films (c), and UV-treated PLLA films (d) as a function of M_n. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from DSC thermograms is plotted in Figure 9 as a function of X_c estimated WAXS profiles. In this figure, the data for $X_c = 100\%$ in Figure 7 were removed because the seemingly low ΔH_{tot} values were observed for these specimens due to the largely reduced thickness of PLLA crystalline regions, which will increase the surface energy effect per unit mass and thereby reduce the ΔH_{tot} values. The extrapolation of ΔH_{tot} to $X_c = 100\%$ will yield the ΔH_{tot} value at $X_c = 100\%$, which is normally abbreviated as $\Delta H_m{}^0$. The $\Delta H_m{}^0$ values thus estimated for the PLLA-A, PLLA-A(UV), PLLA-C, and PLLA-C(UV) films were 100, 102, 112, and 106 J g^{-1}, respectively. These values are comparable with 93 and 100 J g^{-1}, reported by Fischer et al.[37] and Huang et al.,[38] respectively, but smaller than 135, 142, and 203 J g^{-1} reported by Miyata and Masuko,[39] Loomis et al.,[40] and Jamshidi et al.,[41] respectively. Although the effects of UV treatment and crystallinity on $\Delta H_m{}^0$ were very small, the obtained values in this study were higher for the crystallized films than for

the amorphous films, whereas the effect of UV treatment on the amorphous films was inconsistent with that on the crystallized films. However, the numbers of data points may be very small to discuss the effects of UV treatment and crystallinity in detail.

DISCUSSION

Significantly different profiles of W_{loss}, M_n, and T_m as a function of degradation time between the UV-treated and UV-nontreated films and between the crystallized and amorphous films strongly suggest that the PLLA materials having a wide variety of hydrolytic degradation profiles can be produced by the combination of UV treatment and crystallization and that UV-irradiation in the environment will affect the design of recycling process for PLLA articles. The rapid increase of W_{loss} and decreases of M_n and T_m observed for the UV-treated films compared to those of the UV-nontreated films at the

early stage of hydrolytic degradation should be mainly attributed to the lower molecular weight of the UV-treated films. On the other hand, the similar W_{loss}, M_n, and T_m values of the UV-treated and UV-nontreated films at the late stage of hydrolytic degradation can be ascribed to other structural changes by UV treatment including the formation of terminal C=C double bonds and crosslinks, which should have decelerated the hydrolytic degradation, as reported for proteinase K-catalyzed enzymatic degradation.[22]

It is expected that one of the main factors which determine the profiles of W_{loss} and T_m during hydrolytic degradation in this study is M_n. Based on this assumption, the W_{loss} and T_m values of the films during hydrolytic degradation are replotted in Figures 10 and 11 as a function of M_n. In Figures 10(a,b) and 11(a,b), the connecting lines between data were not added to avoid the misunderstanding based on the connecting lines. Figures 10(a,b) and 11(a,b) show that UV treatment has no effect on W_{loss} and T_m profiles of both amorphous and crystallized films when plotted as a function of M_n and therefore confirms that the main factor which determines the W_{loss} and T_m is the molecular weight but not the molecular structures such as terminal C=C double bonds and crosslinks. On the other hand, in both cases of the UV-nontreated and UV-treated films, the W_{loss} and T_m values of the crystallized films were higher than the amorphous films [Figs. 10(c,d) and 11(c,d)]. The difference in W_{loss} between the crystallized and amorphous films became significant for M_n below 2×10^4 g mol^{-1}, whereas the difference in T_m was large for a wide range of molecular weight of 10^4–10^5 g mol^{-1} [Fig. 11(c,d)]. This strongly suggests that the molecular weight and initial crystallinity were dominant factors to determine the profiles of W_{loss} and T_m.

CONCLUSIONS

The following conclusions can be derived from the aforementioned experimental results regarding the effects of UV treatment and crystallization on the hydrolytic degradation of the PLLA films:

1. The combination of UV treatment and crystallization can produce the PLLA materials having a wide variety of hydrolytic degradation profiles, and UV-irradiation in the environment will affect the design of recycling process for PLLA articles.
2. In the early stage, the degrees of hydrolytic degradation monitored by W_{loss}, M_n, and T_m were higher for the UV-treated films than for the UV-nontreated films. In the late stage, the trend traced by W_{loss} was reversed, and the difference in the degrees of hydrolytic degradation between the UV-treated and UV-nontreated films monitored by M_n and T_m became smaller, with the exception of the degrees of hydrolytic degradation of the amorphous films traced by T_m.
3. In the early stage, the degrees of hydrolytic degradation monitored by W_{loss} and M_n were higher for the crystallized films. In the late stage, this trend was reversed, with the exception of the degrees of hydrolytic degradation of the UV-treated films monitored by M_n.
4. The thicknesses of initial crystalline regions after the immersion in phosphate-buffered solution were larger for the crystallized films than that of the amorphous films.
5. The estimated ΔH_m^0 values were in the range of 100.4–112.2 J g^{-1}. The effects of UV treatment and crystallization on ΔH_m^0 were very small.
6. The main factors which determined the W_{loss} and T_m were the molecular weight and initial crystallinty but not the molecular structures such as terminal C=C double bonds and crosslinks.

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