

Properties and morphology of poly(L-lactide)

4. Effects of structural parameters on long-term hydrolysis of poly(L-lactide) in phosphate-buffered solution

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Abstract

Hydrolysis of poly(L-lactide) (PLLA) films with different crystallinities (x_c 's), crystalline thicknesses (L_c 's), and spherulite sizes, was studied in phosphate-buffered solution at 37°C. The films were prepared by altering the annealing or crystallization temperatures (T_a 's) from the melt without or with quenching before annealing. The initial x_c and L_c of PLLA films increased as they were prepared at higher T_a . The induction period until the start of a decrease of mass and tensile strength by hydrolysis became shorter as the initial x_c of the PLLA films was higher, when compared at the same hydrolysis time. This indicates that PLLA films with higher initial x_c underwent faster hydrolysis. This result could be explained in terms of the density of effective tie chains which should decrease with an increase in x_c . It also seemed likely that higher x_c and hence higher L_c produced more defects in the amorphous region, which promoted hydrolysis by enhancing water diffusion. The radius of spherulites had an insignificant effect on the hydrolysis of PLLA films in phosphate-buffered solution. A specific peak appeared at a low molecular weight around 1×10^4 in gel permeation chromatography spectra of hydrolyzed PLLA film, irrespective of the thermal history of the PLLA film. This suggested that the observed specific peak was ascribed to the component of one-fold in the crystalline region. The relationship between the melting temperature (T_m) and L_c was found to be $T_m(K) = 471[1 - 1.59/L_c(nm)]$ for PLLA film hydrolyzed for 3 years. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the past two decades, lactide homo- and copolymers, and their polymer blends have been intensively studied because of their significantly high hydrolyzability in the human body as well as in natural circumstances [1–7]. In a previous paper in this series, we investigated non-enzymatic hydrolysis of poly(L-lactide) (PLLA) films having different crystallinities (x_c 's) in phosphate-buffered solution of pH 7.4 ± 0.1 [8]. The following findings were obtained by the work:

1. hydrolysis of 50- μ m-thick PLLA films proceeded homogeneously along the cross-section of the film mainly via bulk erosion mechanism;
2. the induction period until the mass and mechanical properties of PLLA films started to decrease by hydrolysis became longer with a decrease in the initial x_c of the PLLA films;
3. the decrease in PLLA molecular weight was observed more rapidly for PLLA films with higher initial x_c ;
4. hydrolysis of crystallized PLLA films took place dominantly in the amorphous region between the crystalline regions and its hydrolysis rate was higher than that of the free amorphous region such as in a completely amorphous specimen; and
5. hydrolysis produced PLLA chains with a specific low molecular weight in gel permeation chromatography

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(GPC) spectra when the initial x_c of PLLA films was high; this was ascribed to the release of polymer fractions of one-fold in the crystalline region.

The objective of the present study was to investigate effects of structural parameters of PLLA films on their long-term hydrolysis in phosphate-buffered solution. In the previous work, PLLA films were prepared to have different x_c 's by altering annealing time (t_a) at a fixed temperature (T_a) from the melt [8]. The PLLA films prepared at a relatively short t_a were composed of three regions: the crystalline and amorphous regions inside PLLA spherulites and the free amorphous region outside the spherulites as in a completely amorphous film. Therefore, varying t_a at a fixed T_a simultaneously altered the ratio of three regions in PLLA films. In this work, the free amorphous region was removed from our PLLA specimens by allowing their crystallization to come to completion in order to study the x_c effect more clearly.

It is well known that a rise in T_a from the melt results in an increase in crystalline thickness (L_c) as well as x_c [9]. In fact, a previous study revealed that the crystallite of PLLA became thicker as the annealing temperature from the melt was higher [10]. Moreover, the quenching process before annealing from the melt was reported to reduce the spherulite radius because of an increased nucleus density of spherulites [11]. A number of investigations have focused on the in vitro hydrolysis of PLLA to get a deeper insight into the effect of x_c of polymers on hydrolysis [8,12–18], but not the effect of crystalline thickness and spherulite size. One exception is the study reported by Fischer et al. [1] for surface hydrolysis of PLLA single crystals prepared by crystallization in dilute solution at different temperatures [19].

It should be mentioned that PLLA is a very good specimen for studying the effect of tie chain on the mechanical properties of polymers, since hydrolysis simply reduces the number of tie chains in the amorphous region, insignificantly affecting the rest of the molecular structure of the crystalline polymer.

We prepared PLLA films with different x_c 's, L_c 's, and spherulite sizes starting from a single PLLA source by melting and subsequent annealing or crystallization of solution-cast films at various temperatures [11]. As will be shown below, these annealed PLLA films have approximately the same initial molecular weight before hydrolysis, thus allowing us to study the effect of crystalline thickness and spherulite size on PLLA hydrolysis, fixing other variables to constant values. Phosphate-buffered solution was utilized in this study as the hydrolysis medium because of an insignificant difference between in vitro and in vivo hydrolysis of PLLA [20,21]. The hydrolyzed PLLA films were analyzed by GPC, tensile testing, differential scanning calorimetry (DSC), gravimetry, optical polarizing microscopy, and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Synthesis and purification of PLLA used in this work have been described in detail in previous papers [8,10,11,22,23]. PLLA films for hydrolysis were prepared from purified PLLA ($M_v = 3.9 \times 10^5$, $M_w = 1.3 \times 10^6$, and $M_w/M_n = 2.1$) by the method described in previous papers [8,10,11]. Briefly, PLLA films with 50 ± 10 and 25 ± 5 μm thickness were placed between two micro-cover glasses and sealed in a glass tube under reduced pressure. The sealed PLLA films were melted at 200°C for 3 min and annealed or crystallized at pre-determined T_a for 600 min or the PLLA films were melted at 200°C for 3 min, quenched to 0°C and then annealed as above. It was confirmed in a previous work that a t_a of 600 min was long enough for PLLA films to complete their crystallization at T_a in the range of 100 – 160°C [11]. All the annealed films were quenched at 0°C to stop further crystallization. The PLLA films annealed at 100, 120, 140, and 160°C for 600 min will be abbreviated to PLLA100, PLLA120, PLLA140, and PLLA160 film, respectively. The PLLA film annealed at 140°C for 600 min after quenching at 0°C is abbreviated to PLLA140Q film. The thickness of starting PLLA films was kept to either 50 or 25 μm because accelerated hydrolysis would occur at the core of the specimen if the thickness was larger than 2 mm [13,24,25].

2.2. Hydrolysis

Hydrolysis of PLLA films ($1.8 \text{ mm} \times 3.0 \text{ mm} \times 50$ or $25 \mu\text{m}$) was performed in 10 ml of 0.15 M phosphate-buffered solution ($\text{pH} = 7.4 \pm 0.1$) at 37°C for pre-determined periods of time. Buffered solution was replaced once a month. After hydrolysis, PLLA films were washed intensively with double-distilled water at room temperature, followed by drying under reduced pressure for at least 2 weeks.

2.3. Measurements

Weight and number average molecular weights (M_w and M_n , respectively) and their distribution were evaluated at 40°C in chloroform by a Tosoh GPC system with TSK Gel columns ($\text{GMH}_{\text{XL}} \times 2$) using polystyrene as a standard.

The melting temperature (T_m) and the enthalpy of melting (ΔH_m) of the PLLA films were determined with a Shimadzu DT-50 differential scanning calorimeter. The films were heated at a rate of $10^\circ\text{C}/\text{min}$ under a nitrogen gas flow for the DSC measurements. T_m and ΔH_m were calibrated using benzophenone, indium, and tin as standards. The x_c of PLLA films was evaluated according to the following equation [10,11]:

$$x_c(\%) = 100 \times \Delta H_m / 93 \quad (1)$$

where 93 (J/g of polymer) is ΔH_m of the PLLA crystal having the infinite crystal thickness reported by Fischer et al. [19].

Tensile properties of PLLA films were measured at 25°C and 50% relative humidity using a tensile tester at a cross-head speed of 100%/min. The initial length of specimens was always kept at 20 mm.

2.4. Microscopy

Morphology of PLLA films was studied with a Zeiss polarizing microscope. The thickness of PLLA films utilized for the microscopic observation was 25 μm .

3. Results

Table 1 summarizes the observed T_m , x_c , M_w , M_w/M_n , tensile strength, Young's modulus, and elongation-at-break of PLLA films with thickness of 50 μm and the maximum spherulite radius (SR_m) of films with thickness of 25 mm before and after hydrolysis in phosphate-buffered solution for 36 months at 37°C. SR_m was the value for films before hydrolysis since an insignificant change of SR_m was observed after hydrolysis, in agreement with the result reported previously [8,10]. The initial T_m and x_c of PLLA films before hydrolysis increased with a rise in T_a except for T_m of PLLA100 film. In addition, it was previously revealed that higher T_a of PLLA film from the melt gave larger L_c [10]. T_m of PLLA100 film did not change although T_a was lowered from 120 to 100°C, probably because of the recrystallization of PLLA100 film during DSC measurement, as will be shown below.

T_m decreased while x_c increased, for all the PLLA films upon hydrolysis, in agreement with the reported results [8,13–15,26]. Tensile properties of PLLA films all became zero after hydrolysis for 36 months. M_w was observed to decrease accompanying an increase in M_w/M_n for all the PLLA films upon hydrolysis, irrespective of the annealing temperature or procedure before hydrolysis, excluding M_w/M_n of the PLLA160 film.

3.1. Effects of crystallinity

Fig. 1 shows the mass remaining for PLLA100, PLLA120, PLLA140, and PLLA160 films with different initial x_c 's as a function of hydrolysis time. The mass loss is an index for the content of the water-soluble oligomer formed by hydrolysis and released from the mother PLLA films into the surrounding medium. The mass of all the films remained unchanged up to 12 months of hydrolysis, but it started to decrease when hydrolyzed for longer than 18 months. The induction

Table 1
Characteristics of 50- μm -thick poly(L-lactide) (PLLA) films before and after hydrolysis in phosphate-buffered solution for 3 years

Sample code	T_m (°C)	x_c (%)	SR_m^a (μm)		$M_w/10^5$ (g/mol)		M_w/M_n		Tensile strength (kg/mm ²)		Young's modulus (kg/mm ²)		Elongation-at-break (%)	
			Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
PLLA100	177	40	167	75	11.1	1.7	2.0	3.8	6.2	0	194	0	11	0
PLLA120	177	47	172	82	10.6	1.4	1.9	3.7	6.2	0	190	0	7	0
PLLA140	185	54	177	92	11.0	1.5	2.0	3.8	5.8	0	192	0	6	0
PLLA160	192	63	184	98	7.8	1.4	2.8	1.9	4.5	0	211	0	6	0
PLLA140Q ^b	184	56	177	95	10.7	1.6	2.0	4.4	5.6	0	201	0	16	0
PLLA140	185	54	177	92	11.0	1.5	2.0	3.8	5.8	0	192	0	6	0

^a Maximum radius of spherulite estimated for 25- μm thick film.

^b Quenched at 0°C from the melt prior to annealing.

^c No significant change was recognized when PLLA was hydrolyzed for 3 years.

period for the mass loss was shorter for PLLA films prepared at higher T_a to have higher initial x_c . The rate of mass loss after the induction period was higher for PLLA films having higher initial x_c and the mass loss was larger for those having higher initial x_c when compared at the same hydrolysis time, longer than 24 months. These findings are in good agreement with those of PLLA films with different initial x_c 's and containing the free amorphous region [8].

Fig. 2 shows M_w of PLLA100, PLLA120, PLLA140, and PLLA160 films as a function of hydrolysis time.

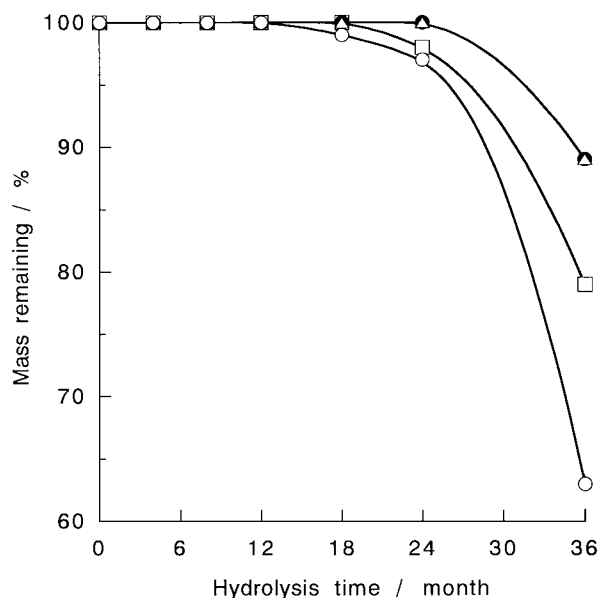


Fig. 1. Mass remaining for poly(L-lactide) (PLLA) films as a function of hydrolysis time. (●) PLLA100; (△) PLLA120; (□) PLLA140; and (○) PLLA160.

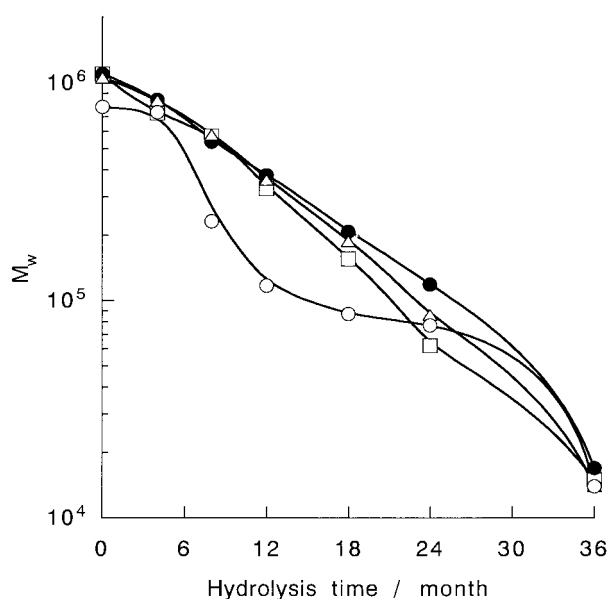


Fig. 2. M_w of poly(L-lactide) (PLLA) films as a function of hydrolysis time. (●) PLLA100; (△) PLLA120; (□) PLLA140; and (○) PLLA160.

M_w of PLLA100, PLLA120, and PLLA140 films decreased monotonously for hydrolysis up to 36 months, whereas M_w of PLLA160 film decreased rapidly between 4 and 12 months of hydrolysis, but the decrease rate slowed down between 18 and 24 months of hydrolysis, followed by a rapid decrease for hydrolysis of longer than 24 months. PLLA films with higher initial x_c showed lower M_w when compared at the same hydrolysis time between 12 and 18 months. The final M_w 's of PLLA films at 36 months were very similar to each other, irrespective of the initial x_c .

GPC spectra of PLLA100 and PLLA160 films are shown in Fig. 3 for different hydrolysis times. The molecular weight of PLLA100 film shifted to a lower value with hydrolysis for 24 months, without formation of any specific peaks that were presumed to originate from the crystalline region, but the molecular weight profile was slightly deformed after hydrolysis of 36 months. In contrast, the deformed molecular weight distribution due to the specific peak formation was observed for PLLA160 film even after hydrolysis for 12

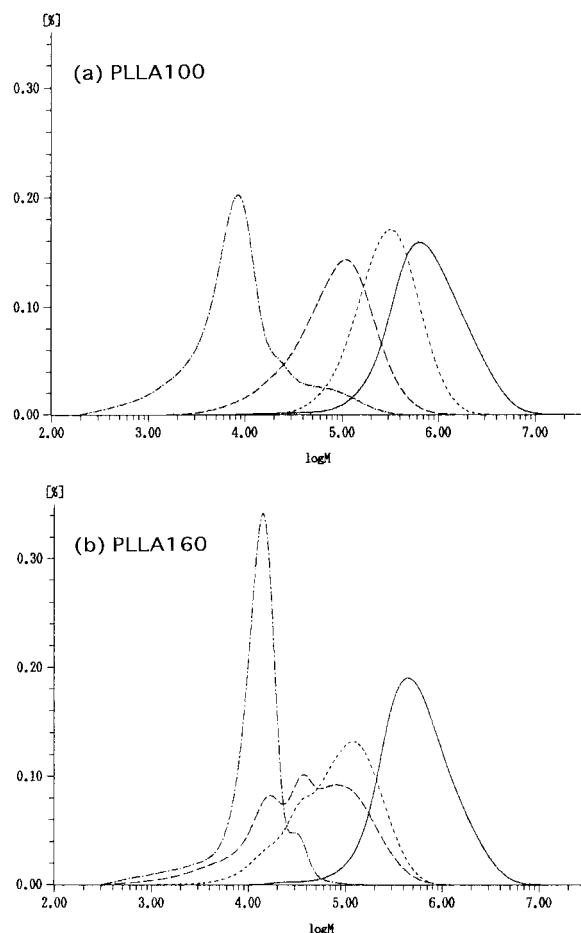


Fig. 3. Gel permeation chromatography (GPC) spectra of (a) PLLA100 and (b) PLLA160 films after hydrolysis for different times —, 0 month; ·····, 12 months; ---, 24 months; - · - · -, 36 months.

months and the specific peak around 1×10^4 became higher with hydrolysis time.

The molecular weight distributions of PLLA120, PLLA140, and PLLA160 films after hydrolysis for 36 months are shown in Fig. 4. Evidently, all the films had a similar molecular weight distribution, although the peak shifted to higher molecular weight with increasing initial x_c . Such specific low molecular weight peaks were observed for compression-molded PLLA hydrolyzed in phosphate-buffered solution [13], melt-crystallized PLLA in dilute alkaline solution [10], and as polymerized [15] PLLA *in vivo*, and also for poly(L-lactide-co-D-lactide) (92.5/7.5) single crystal in dilute alkaline solution, where three specific peaks were assigned to the chains of one, two, and three folds in the crystallite [19].

Fig. 5(a–c) demonstrate the change of tensile strength, Young's modulus, and elongation-at-break, respectively, for PLLA100, PLLA120, PLLA140, and PLLA160 films during hydrolysis. The induction period until tensile strength started to decrease, became shorter with a rise in initial x_c . The decrease in tensile strength for hydrolysis times longer than the induction period was very similar, irrespective of T_a . Residual strength was higher for PLLA films having lower initial x_c , when compared at the same hydrolysis time longer than 12 months. These findings agree with those of PLLA films with different initial x_c 's, which had the free amorphous region [8] and suggest that the induction period until the start of the tensile strength decrease can be controlled by the initial x_c .

The Young's modulus of all the PLLA films started to decrease monotonously with hydrolysis time without any induction period. The PLLA films having lower initial x_c retained a definite Young's modulus compared with those having higher initial x_c .

The elongation-at-break of PLLA100 and PLLA160 films started to decrease without any induction period,

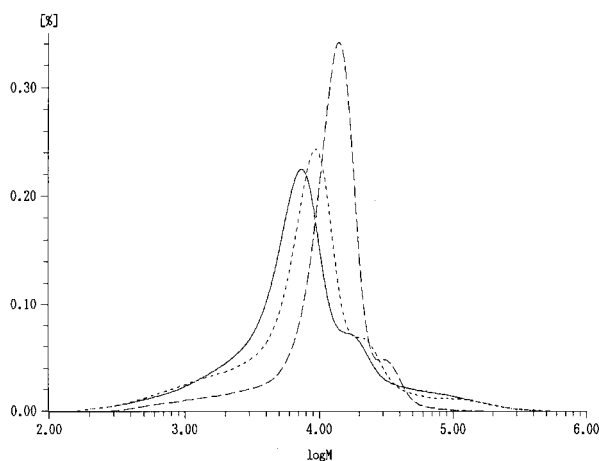


Fig. 4. Gel permeation chromatography (GPC) spectra of PLLA120 (—), PLLA140 (---), and PLLA160 (— · —) films after hydrolysis for 36 months.

in contrast with that of PLLA120 and PLLA140 films which retained the initial values for 12 months. The elongation-at-break of all the PLLA films decreased monotonously after the induction period. Again, the PLLA films having lower initial x_c retained a definite elongation-at-break for longer time than those having higher initial x_c .

DSC thermographs are shown in Fig. 6 for PLLA100, PLLA120, PLLA140, and PLLA160 films before and after hydrolysis for 36 months. The T_m of PLLA100, PLLA120, PLLA140, and PLLA160 films before hydrolysis shifted to 167, 172, 177, and 184°C from 177, 177, 185, and 192°C, respectively, after hydrolysis for 36 months, indicating that all the T_m of PLLA films decreased during hydrolysis for 36 months. The crystallization peak appearing around 160°C for PLLA100 film before hydrolysis suggests that the observed T_m was higher than the real T_m because of recrystallization of PLLA chains during DSC measurement.

T_m , T_g , and x_c of PLLA100, PLLA120, PLLA140 and PLLA160 films are plotted as a function of hydrolysis time in Fig. 7(a–c), respectively. T_m of PLLA160 film decreased monotonously with hydrolysis, whereas that of PLLA100, PLLA120, and PLLA140 films increased with hydrolysis for the first 12 months but decreased after hydrolysis for longer than 12 months. The initial T_g of all the PLLA films decreased with an increase in initial T_m . T_g of PLLA100, PLLA120, and PLLA140 films increased with hydrolysis for the first 12 months but decreased after hydrolysis for longer than 12 months. On the other hand, T_g of PLLA160 film decreased rapidly from 67 to 59°C when hydrolyzed for the first 12 months, but remained unchanged for another 12 months. T_g of PLLA films hydrolyzed for longer than 24 months could not be evaluated because of no distinct glass transition. The x_c value of all the PLLA films increased monotonously for hydrolysis for 36 months, and the x_c was larger after hydrolysis for 36 months for the PLLA films having high initial x_c .

3.2. Effects of spherulite radius

The mass remaining and elongation-at-break of PLLA140Q and PLLA140 films having SR_m of 10 and 130 μm , respectively, are plotted in Fig. 8(a) and (b), respectively, as a function of hydrolysis time. It is evident that the mass remaining for PLLA140Q film during hydrolysis completely coincides with that of PLLA140 film. A similar agreement was observed for the change in the molecular weight distribution, tensile strength, Young's modulus, and thermal properties. In contrast, the elongation-at-break of PLLA140Q film decreased rapidly by hydrolysis compared with that of PLLA140 film. This difference in elongation-at-break between PLLA140Q and PLLA140 films may be partly

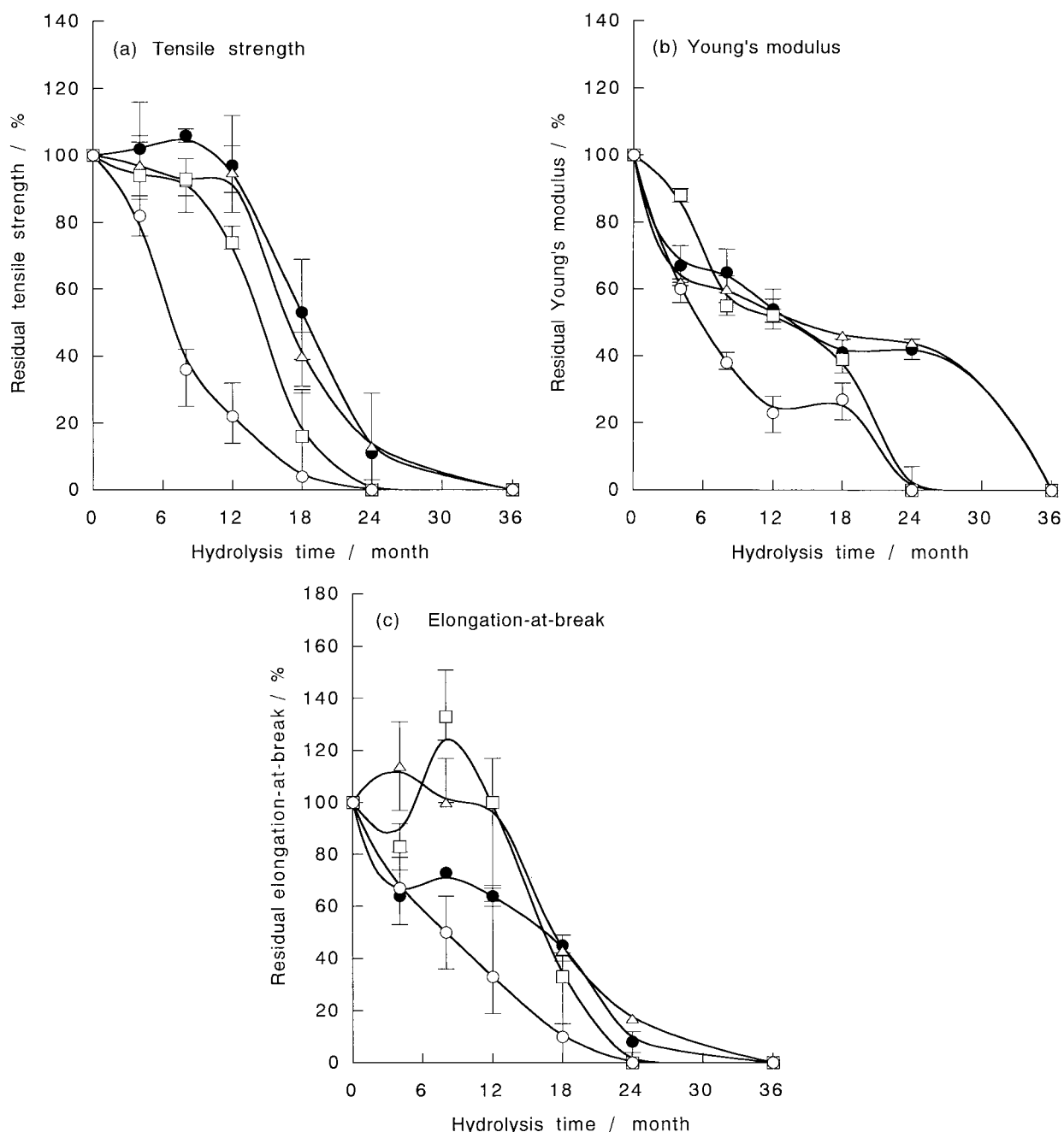


Fig. 5. (a) Residual tensile strength, (b) Young's modulus, and (c) elongation-at-break of poly(L-lactide) (PLLA) films as a function of hydrolysis time. (●) PLLA100; (△) PLLA120; (□) PLLA140; and (○) PLLA160.

ascribed to the difference in their initial elongation-at-break (16% and 6, respectively).

3.3. Morphological change

Fig. 9 shows polarizing photomicrographs of 25- μ m thick PLLA120 film before and after hydrolysis in phosphate-buffered solution for 36 months. PLLA120 film as well as PLLA100, PLLA140, and PLLA160 films (photomicrographs not shown) prior to hydrolysis contain two regions in the spherulites: the crystalline and

amorphous region [11]. As the spherulites cover all the film, there remains no free amorphous region present in the melt-quenched, completely amorphous PLLA film. Interestingly, alternate bright and dark lines appeared after hydrolysis for 36 months along the radius direction from the center of the spherulites and were encountered together at the boundary of spherulites. Such morphology was not observed for PLLA100, PLLA140, and PLLA160 films. To our knowledge, this is the first study reporting the formation of alternate bright and dark lines along the radius direction in the spherulites during

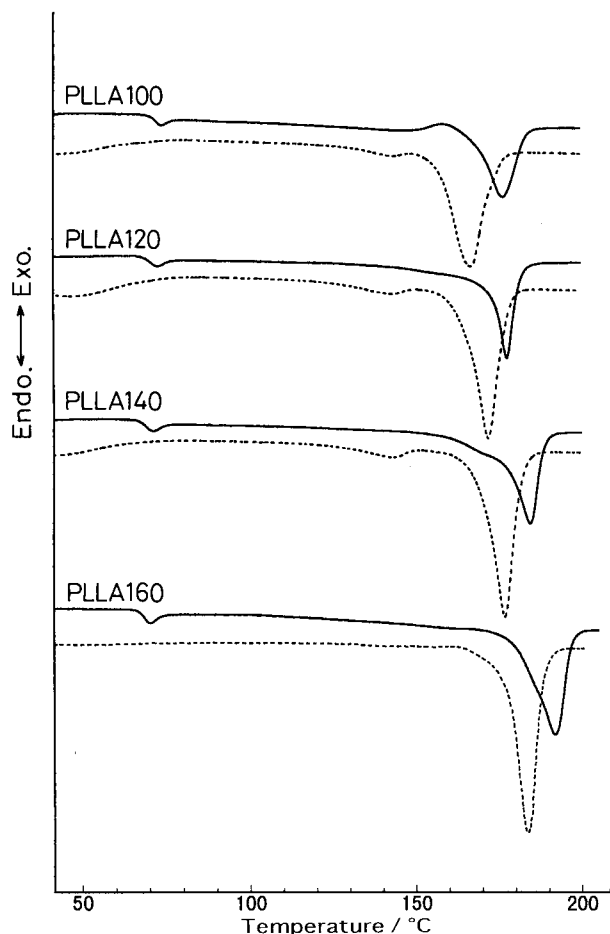


Fig. 6. Differential scanning calorimetry (DSC) thermograms of PLLA100, PLLA120, PLLA140, and PLLA160 films before (—) and after (---) hydrolysis for 36 months.

hydrolysis. In addition, the photographic contrast between the cross-shaped bright and dark regions in the spherulites observed for normal spherulites increased after hydrolysis. This is in marked contrast with the PLLA films prepared by annealing at T_a other than 120°C and hydrolyzed in phosphate-buffered solution for 36 months [8] and in dilute alkaline solution for 150 days [10], where the contrast between the cross-shaped bright and dark regions decreased after hydrolysis.

4. Discussion

A most interesting finding of this study is the enhancement of hydrolysis (Fig. 1) and deterioration of mechanical properties (Fig. 5) for PLLA films by an increase in initial x_c . It is widely accepted that the ultimate mechanical strength of polymeric materials greatly depends on the density of tie chains mostly connecting molecular aggregates like crystalline regions. When a load is given to a polymeric material, the loose tie chains will be stretched to the direction of loading to bear the

stress loaded, and resulting in scission either at once or one by one around the breaking point of the material, resulting in their scission. Low mechanical strength of a polymeric material is due to the one-by-one cleavage of the tie chains, which will happen if the distribution of the tie chain length is broad Fig. 10. Therefore, for enhancing the tensile strength of a material, it is crucial to make the length distribution of tie chains as sharp as possible.

Fig. 11 schematically illustrates the microstructure of the amorphous region in the materials of low and high x_c , in other words, low and high L_c obtained at low and high T_a , respectively. Higher x_c may introduce more defects into the amorphous region, because crystallization takes place in a limited space disturbing the chain rearrangement in the amorphous region. Obviously, the defects in the amorphous phase make water penetration into this region easier and higher x_c broadens the distribution of the length of tie chains. The faster hydrolysis and deterioration of PLLA films of higher initial x_c can be explained in terms of the increased defects in the amorphous region. This faster hydrolysis of the PLLA films with high initial x_c may have resulted in their shorter induction periods until the start of decrease in the weight remaining and tensile strength. The decrease in Young's modulus and elongation-at-break of the PLLA films without any induction periods may be ascribed to their high sensitivity to the scission of tie chains by hydrolysis.

Another explanation for the accelerated hydrolysis of PLLA films with high initial x_c may be ascribed to the enhanced catalytic effect and water supply rate by an increased density of terminal groups [8]. The increased density of the terminal group in the amorphous region of PLLA films with high initial x_c may be caused by exclusion of the terminal group from the crystalline region during crystallization. The hydrophilic groups will also promote water penetration into the amorphous region to accelerate hydrolysis of crystallized PLLA films, in addition to the raised catalytic effect by high density of carboxyl terminal group.

A specific molecular weight ($M_{n,s}$) peak was observed in GPC spectra around 1×10^4 after hydrolysis of PLLA films for 36 months. The $M_{n,s}$ increased with the initial T_m as shown in Fig. 4. This strongly suggests that $M_{n,s}$ must have originated from the crystalline residue after hydrolysis. The L_c of PLLA films after hydrolysis can be calculated from Eq. (2), if the observed $M_{n,s}$ of 7.4×10^3 (PLLA120), 9.3×10^3 (PLLA140), and 1.39×10^4 (PLLA160) in Fig. 4 is assumed to be the molecular weight characteristic of one-fold of respective PLLA chain in the crystalline region and the PLLA chains in the crystallites take 10_3 helix with a length of 2.78 nm [27,28]:

$$L_c(\text{nm}) = 0.278 \times M_{n,s}/72.1 \quad (2)$$

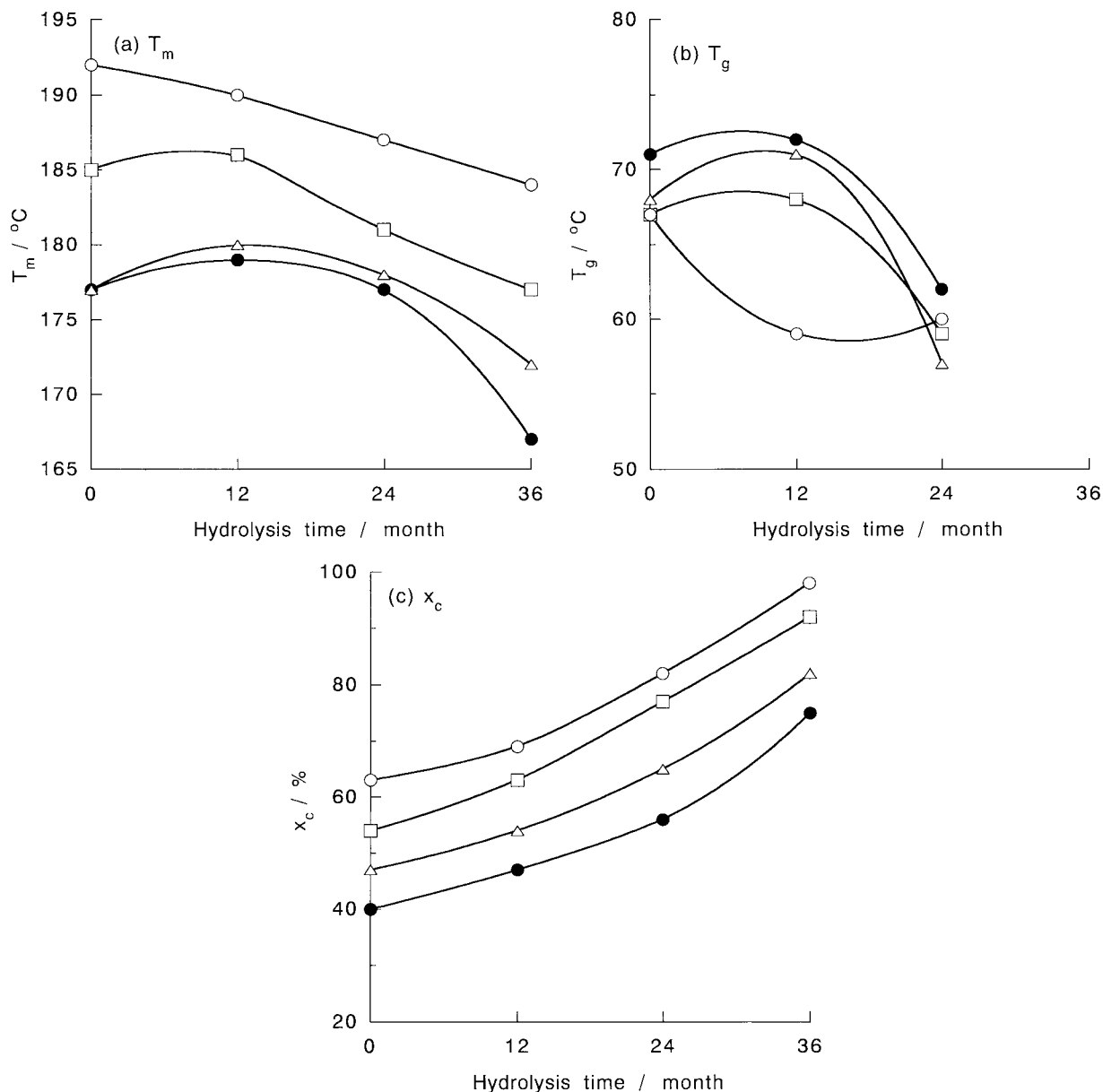


Fig. 7. (a) T_m , (b) T_g , and (c) x_c of poly(L-lactide) (PLLA) films as a function of hydrolysis time. (●) PLLA100; (△) PLLA120; (□) PLLA140; and (○) PLLA160.

where 72.1 is the mass per mole of half of the lactide unit. The L_c values calculated from Eq. (2) are 29, 36, and 54 nm for PLLA120, PLLA140, and PLLA160 films, respectively. They are larger than 17 (PLLA120), 22 (PLLA140), and 39 (PLLA160) nm observed for the PLLA films hydrolyzed in alkaline solution for 120 days [10]. This suggests that the crystalline region of PLLA films was less hydrolyzable in phosphate-buffered solution than in dilute alkaline solution. The dependence of L_c on T_m , which, in turn, is related to T_a can be explained by the following Thompson-Gibbs equation [9]:

$$T_m = T_m^0 (1 - 2\sigma / \Delta h^0 \rho_c L_c) \quad (3)$$

where T_m^0 , σ , Δh^0 , and ρ_c are the equilibrium melting temperature, specific fold surface free energy, heat of fusion (per unit mass), and crystal density, respectively. Crystallization of PLLA films under the condition to lengthen L_c such as at high T_a inevitably enhances x_c when crystallization of PLLA films is performed to completion. The L_c dependence on T_a was in good agreement with that reported by Fischer et al. [19] for PLLA single crystals crystallized in dilute xylene solution and hydrolyzed in dilute alkaline solution (7, 9, and 14 nm when crystallized at 60, 80, and 102°C, respectively).

Eqs. (2) and (3) indicate that T_m should decrease linearly with $1/L_c$ if $M_{n,s}$ is the molecular weight

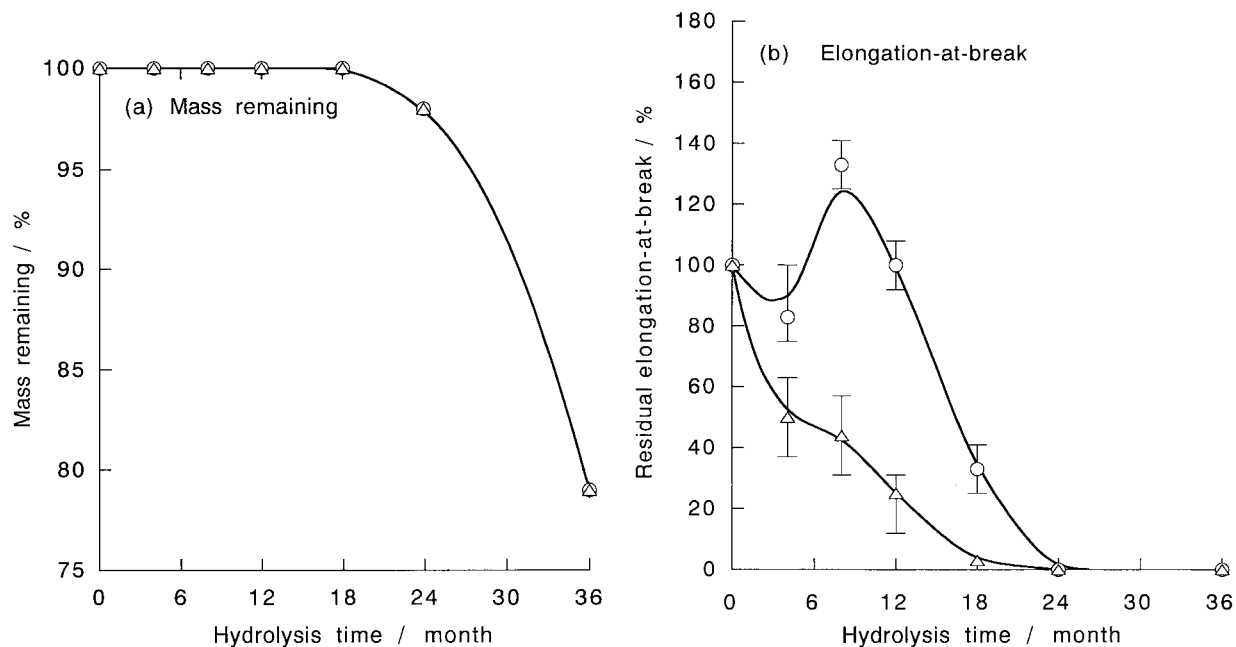


Fig. 8. (a) Mass remaining and (b) residual elongation-at-break for PLLA140 (O) and PLLA140Q (Δ) films as a function of hydrolysis time.

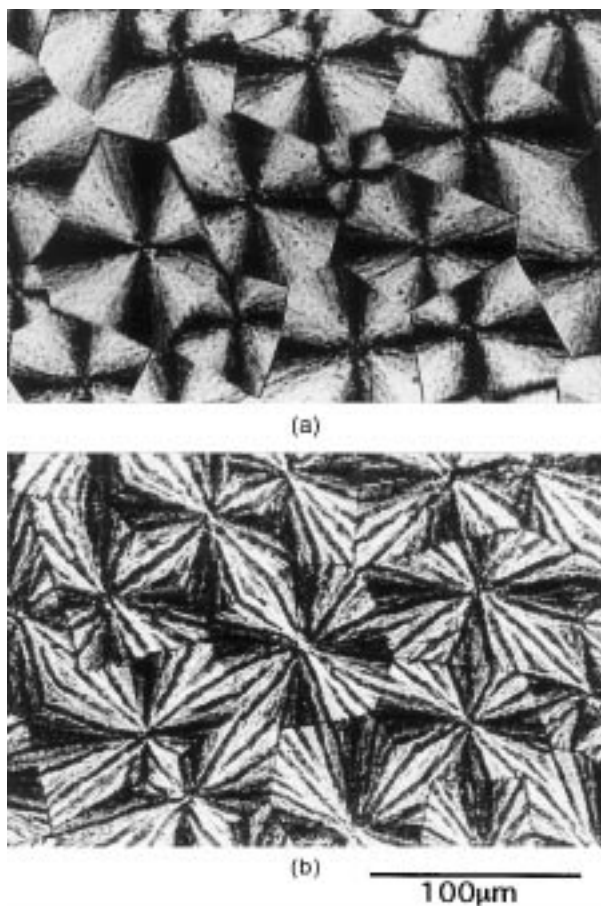


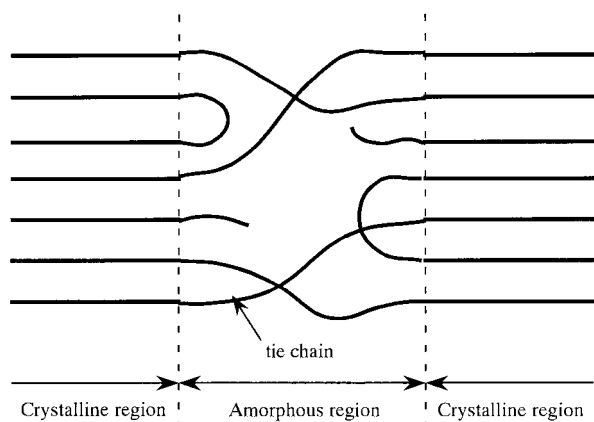
Fig. 9. Polarizing microscopic photographs of PLLA120 films (a) before and (b) after hydrolysis for 36 months.

characteristic to one-fold of PLLA chain in the crystalline region and σ , Δh^0 , and ρ_c are assumed to be constant. To confirm this, T_m of PLLA films after hydrolysis in phosphate-buffered solution for 36 months is plotted in Fig. 12 as a function of $1/L_c$, together with that after hydrolysis in alkaline solution for 120 days. In the case of hydrolysis of PLLA films in alkaline solution, T_m after hydrolysis of 150 days was used instead of T_m after 120 days since an insignificant change of T_m was observed during hydrolysis. It is obvious that T_m increases linearly with the decreasing $1/L_c$, as expected from Eq. (3). This confirms that $M_{n,s}$ corresponds to the molecular weight of one-fold of PLLA chain in the crystalline region. Probably, the subpeak observed around 3×10^4 for PLLA 160 film after hydrolysis for 36 months [Fig. 3(b)] may be ascribed to two-folds of the chain in the crystalline region.

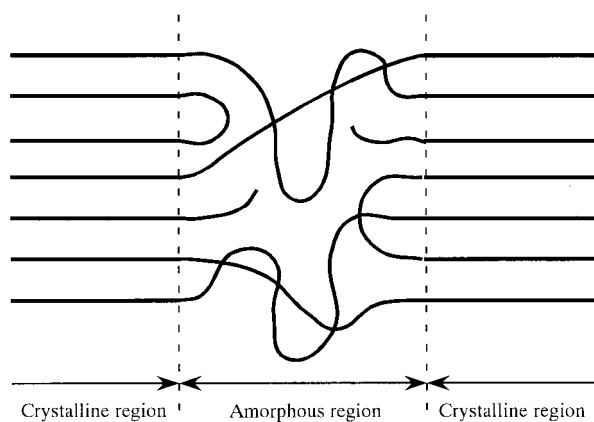
Fig. 12 gives the following equation:

$$T_m(K) = 471[1 - 1.59/L_c(\text{nm})] \quad (4)$$

The T_m^0 obtained by extrapolation of T_m to $1/L_c = 0$ or from comparison between Eqs. (3) and (4) was 198°C (471 K), which is slightly smaller than T_m^0 but almost in agreement with T_m^0 obtained from the same procedure for PLLA films hydrolyzed in dilute alkaline solution (201°C) and from the Hoffman–Weeks procedure for melt-crystallized PLLA films by Kalb and Pennings (215°C) [29] and by us (205 and 212°C) [11,30]. This agreement on T_m^0 estimated with different methods also supports our assumption that $M_{n,s}$ is the molecular



(a) sharp distribution



(b) broad distribution

Fig. 10. Schematic representation of the structure of a crystallized polymeric material having tie chains of (a) sharp and (b) broad length distribution.

weight of one-fold of the PLLA chain in the crystalline region.

The increase in T_m of PLLA100, PLLA120, and PLLA140 films at the first 12 months may be explained in terms of thickening of the PLLA crystallites by the enhanced chain mobility induced by scission of the chains in the amorphous region and the plasticizing effect of water molecules. The rise of T_g of PLLA100, PLLA120, and PLLA140 films in the first 12 months may be due to the stabilized chain packing in the amorphous region by low temperature annealing in the presence of water molecules which act as plasticizer. On the other hand, the decrease in T_m and T_g of PLLA160 film hydrolyzed for 0–36 months and of PLLA100, PLLA120, and PLLA140 films hydrolyzed for longer than 24 months may be simply due to the reduced thickness of the crystallites and the molecular weight of hydrolyzed PLLA films, respectively.

Finally, we should discuss on the formation of alternate bright and dark lines along the radius at peculiar angles in spherulites of PLLA120 film after hydrolysis for 36 months. This cannot be explained in terms of the

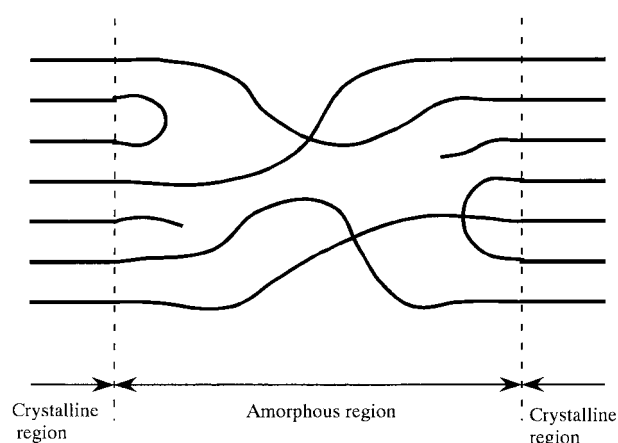
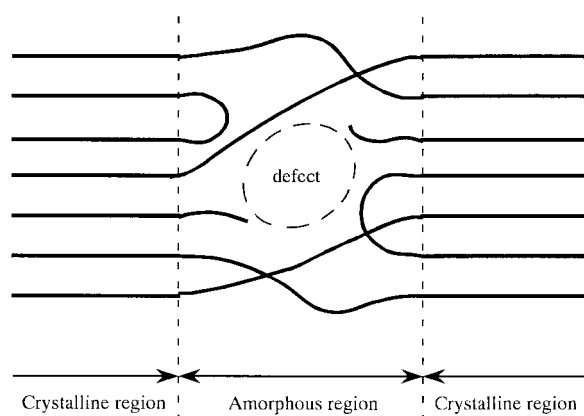
(a) low x_c (b) high x_c

Fig. 11. Schematic representation of the structure of non-hydrolyzed poly(L-lactide) (PLLA) films with (a) high and (b) low T_m (X_c).

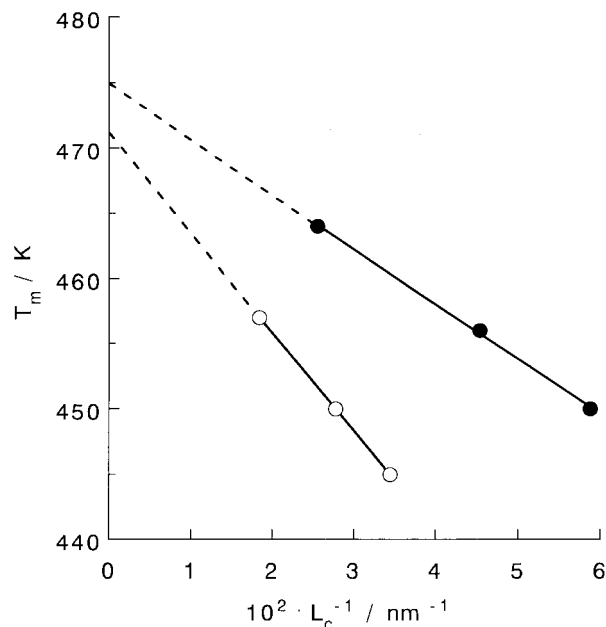


Fig. 12. T_m of poly(L-lactide) (PLLA) films after hydrolysis for 36 months in phosphate-buffered solution (○) and that for 150 days in alkaline solution (●) as a function of $1/L_c$.

preferred hydrolysis and removal of chains in the amorphous region of PLLA120 film, as revealed by the weight loss (11%) and increased x_c from 47 to 82%, and specific peak formation at a molecular weight of 7.4×10^3 in GPC spectra after hydrolysis for 36 months. No specific structure formation recognized at the surface of PLLA120 film by SEM denies the formation of line gaps at the specific angles of the spherulites by hydrolysis (photomicrographs not shown). This formation of dark and bright lines in the spherulites after hydrolysis is probably due to the formation of assemblies of crystalline regions in the line along the radius direction at the specific angles, caused by the reduced restraint of tie chains by their scission. However, we cannot explain why the dark or bright lines from different spherulites are encountered at the boundary of the spherulites.

Acknowledgements

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