

Quantitative Evaluation of Photodegradation and Racemization of Poly(L-lactic acid) under UV-C Irradiation

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Running title

Photodegradation and Racemization of PLLA under UV-C Irradiation

Abstract

To obtain details of poly(L-lactic acid) (PLLA) photodegradation behavior, PLLA films were irradiated by UV-C light ($\lambda = 253.7$ nm) to directly excite carbonyl groups, resulting in a rapid decrease in the molecular weight accompanying a gradual decrease in the optical purity of monomeric units in the chains. The racemization during the photodegradation was first detected as a result of the chain scission by irradiation. From quantitative analyses of the molecular weight and the monomeric unit composition, it was found that the chain scission ratio and the D-lactate unit ratio increased in parallel during the irradiation, suggesting that approximately one D-lactate unit formed for every chain scission. From a mechanistic consideration, the racemization equilibrium was proposed to occur at both carboxyl and hydroxyl chain ends.

Keywords

poly(L-lactic acid) / photodegradation / racemization / Mark-Houwink-Sakurada parameter

1. Introduction

Poly(lactic acid) (PLLA) is an aliphatic polyester derived from renewable resources such as starch. PLLA is a well known recyclable material because of its ability to bring about the reversible conversion between PLLA and L-lactic acid or L,L-lactide by polymerization and depolymerization. Based on this reactivity, the hydrolysis and pyrolysis of PLLA have been widely investigated. However, photodegradation of PLLA has not been studied in detail [1-7], leaving many unresolved areas for further investigation, such as the degradation mechanism and kinetics, degradation products, and the racemization mechanism. In the future, when PLLA is used on a large scale for industrial applications, the photo-deterioration of PLLA products will surely alert many researchers to the decreases in both monomer recovery and optical purity, which impact seriously upon recyclability.

Previously, the photodegradation of PLLA has been investigated with various light sources such as a medium pressure Hg lamp (\approx 250-400 nm, max. 365 nm) [1], Xe lamp [2], long-wavelength UV lamp (365 nm) [3], Xe/Hg continuous wave lamp (\approx 356 nm) [4], black light (\approx 300-400 nm) [5], Xe-F pulsed excimer laser (\approx 351 nm) [6], and an open flame carbon-arc lamp (\approx 300-800 nm) [7]. PLLA exhibits strong absorption bands below 250 nm [4], originating from absorption by a carbonyl group. Although original PLLA exhibits very weak absorption in a range of \approx 250-310 nm, the absorption increases with UV irradiation using a medium pressure Hg lamp under air [8]. Sakai et al. applied a photosensitized reaction

to PLLA photolysis with N,N,N',N'-tetramethyl-p-phenylenediamine as a photosensitizer, which gave rise to a new absorption in a range of 250-370 nm, resulting in the main-chain scission of PLLA [4].

In previous reports, the photolysis mechanism of PLLA has been suggested as proceeding via the “Norrish type photo cleavage”, especially the Norrish II type reaction, which was proposed based on increases in absorptions at 3290 and 990 cm^{-1} for ν_{OH} and $\nu_{\text{C}=\text{O}}$ of hydroxyl and acrylic groups, respectively, in IR spectra [8]. However, so far no information has been provided for a typical absorption of $\nu_{\text{C}=\text{C}}$ at around 1640 cm^{-1} in the IR spectra or for characteristic signals in the ^1H NMR spectra for the acrylic group. Moreover, two random decomposition kinetics, i.e. autocatalytic [7] and non-autocatalytic degradation kinetics [5], have been tentatively applied to calculate the photodegradation rate constant without these kinetics being verified.

Very few characterization results of photolysis products and little information on the racemization have been given except for details of the changes in molecular weights of residual polymers. Sakai et al.[4] proposed other degradation mechanisms based on electron spin resonance (ESR) studies, in which the UV degradation of PLLA comprised a dissociation reaction at the $\text{RCOO-R}'$ bond followed by the dehydrogenation of \pm -hydrogen on an asymmetric carbon.

In this study, to obtain more details of PLLA photodegradation, UV-C light ($\lambda = 253.7$

nm) was chosen as the UV source and used to directly excite the carbonyl group of PLLA, with the racemization of PLLA during the irradiation subsequently examined. To assess quantitatively relationships between the chain scission and racemization, molecular weights of irradiated PLLA were calculated exactly by using the universal calibration method. Finally, the photodegradation and racemization mechanisms were discussed.

2. Experimental

2.1. Materials

PLLA and standard polystyrene samples are listed in Table 1. Two high molecular weight PLLA samples: PLLA-1 and 2, which have high L-lactate units of 98.5%, were prepared by a ring-opening polymerization with tin(II) octoate as a catalyst in a previously reported manner [9] and purified by a dissolution-precipitation method using a chloroform-hexane system. The other four PLLA-3~6 samples (L-form), having narrow polydispersity index (PDI) values, were purchased from Polymer Source, Inc. and used as received. Nine standard polystyrene samples in a wide molecular weight range of 10^3 - 10^6 having narrow PDI values of 1.01-1.08 were obtained from Tosoh Corporation. All the polymer samples were kept at -30 °C before use. Solvents: chloroform, tetrahydrofuran (THF), and hexane (HPLC grades without stabilizer) were obtained from Wako Pure Chemical Industries, Ltd.

[Table 1]

2.2. Viscosity Measurements

The solution viscosity of PLLA and polystyrene samples was measured in chloroform and THF using an Ubbelohde viscometer (SIBATA Scientific Technology, Ltd.) in a water bath thermostated at 40 ± 0.1 °C. The solution viscosity of each sample was obtained by taking more than 5 measurements and averaging. Intrinsic viscosity $[\eta]$ values were obtained by dilute solution viscometry using original solutions in a concentration range of 0.6-2.0 wt.-% depending on the molecular weight [10]. Viscosity measurements were carried out in duplicate with good reproducibility.

2.3. Size Exclusion Chromatography (SEC)

Absolute molecular weight data for PLLA-1 were determined using a SEC system equipped with a triple detection online RI/viscometry/light scattering setup. The TOSOH SEC system used consisted of an inline degasser: SD-8022, a dual pump: DP-8020, an auto-sampler: AS-8020, a column oven: CO-8020, and a Viscotek TDA-302 triple detector array consisting of a differential refractive index (RI) detector, a four-capillary differential viscometer and a right-angle laser light scattering (RALLS) detector ($\lambda=670$ nm). The size exclusion chromatography was conducted using two columns: TSKgel GMHXL \times 2 (molecular weight exclusion limit 4×10^8) at 40 °C and chloroform or tetrahydrofuran eluent ($1.0 \text{ mL} \cdot \text{min}^{-1}$). The

Mark-Houwink-Sakurada parameters (M-H-S parameters) and absolute molecular weights of PLLA-1 were obtained by using an OmniSEC ver.4.5 software package from Viscotek.

Size exclusion chromatograms of the PLLA and standard polystyrenes samples were also recorded on a TOSOH HLC-8120 GPC system with RI and UV detectors at 40 °C using a TOSOH TSKgel Super HM-M column (linearity range: 1×10^3 - 8×10^6 ; molecular weight exclusion limit 4×10^8) and chloroform or tetrahydrofuran eluent ($0.6 \text{ mL} \cdot \text{min}^{-1}$).

2.4. Film preparation

PLLA-1 was compressed with a heating pressure film forming machine IMC-180C (Imoto Machinery Co., Ltd.) at 200 °C for 8 min under a pressure of 7 MPa to form a transparent film (thickness $120 \pm 20 \mu\text{m}$), from which test and reference samples ($5 \times 5 \text{ cm}^2$) for UV-C irradiation were prepared.

2.5. UV irradiation

As an irradiation source, a 15 W UV-C sterilizing lamp ($\lambda_c = 253.7 \text{ nm}$, half breadth $< 5 \text{ nm}$; Sankyo Denki Co., Ltd. GL-15) was used. Film samples were irradiated at $35 \pm 2 \text{ }^\circ\text{C}$ and $35 \pm 2 \%$ RH for prescribed times up to 24 h in a chamber, providing shielding from external irradiations. Film samples were placed at right angles to the direction of irradiation. Irradiation intensity, which was measured with a TOPCON UV-C radiometer UVR-T1, was

controlled in a range of 0.05 - 0.44 mW·cm⁻² by varying the distance between sample and lamp. After UV irradiation, the film samples were measured for changes in UV spectrum, molecular weight, and optical purity. Each measurement was carried out three or four times with reasonable reproducibility.

2.6. UV spectrometry

UV spectra of the transparent PLLA films were measured on a Hitachi fluorescence/UV-Vis spectrophotometer F-4500/U-3310 directly without dissolving in a solvent. The absorbance values were normalized according to the thickness of each film sample.

2.7. Optical purity analysis of lactic acid

PLLA samples (10 g) were degraded by the ammolysis and dissolved in a 25% ammonia solution (2 mL) by stirring overnight at room temperature. After dissolving completely, the solution was concentrated by evaporation under vacuum to remove the ammonia and water. The residue was then dissolved in distilled water to prepare a monomer solution (0.1 wt/v-%) for optical purity measurements.

The optical purity of the dissolved monomers was measured on a Shimadzu high pressure liquid chromatograph LC-10A equipped with a UV detector SPD-10A VP. The optical

resolution chromatography was conducted using a ligand exchange column MCI GEL CRS10W at 30 °C and 2mM-CuSO₄ eluent (0.5 mL·min⁻¹). Calibration curves for L and D-lactic acids were prepared by using the standard D/L-lactic acid obtained from Wako Pure Chemical Industries, Ltd.

3. Results and Discussion

3.1. Changes in the absorption spectrum of PLLA during photodegradation

The UV-C light ($\lambda_c = 253.7$ nm) irradiation of PLLA films induced an increase in absorption at 250-310 nm (see Figure SD-1 in Supplementary Data) in accordance with the previous result when irradiated by a medium pressure Hg lamp [8]. This increase in absorbance was observed not only in an air atmosphere, but also in a nitrogen atmosphere. This suggests the production of other kinds of structures having conjugated groups and showing new absorptions in a higher wavelength range than 250 nm. The absorbance was not so high compared with the main absorption occurring below 250 nm; however, it is considered that this absorption at higher wavelengths accelerated the photodegradation of PLLA [4].

3.2. Evaluation of exact molecular weight of PLLA

The most common technique for measuring molecular weights is the SEC method. This is

despite the method's reliance on the estimation of relative molecular weights based on polystyrene standards. A more accurate and reliable method for the molecular weight estimation is achieved by using a SEC system with a light scattering detector (LS) as an online detector. The LS directly measures the molecular weight of the polymer and is most often used in conjunction with a differential refractive index detector, in particular, a right-angle laser light scattering detector (RALLS) is used in combination with a viscometer. Another alternative and convenient method for accurately estimating the molecular weights of polymers is the universal calibration method (UCM). UCM relies on the theory: $V_h \propto [\eta]M$, where V_h , $[\eta]$, and M are the hydrodynamic volume, intrinsic viscosity, and absolute molecular weight, respectively [11]. Since V_h is the parameter responsible for the SEC retention volume, V_e , the experimental $\log[\eta]M$ values of many different polymers lie on a single curve of the $\log[\eta]M-V_e$ plot.

To be able to calculate the molecular weight by using UCM, proper M-H-S parameters are required for both measured and standard polymers. Unfortunately, the number of M-H-S parameters is not sufficient for the various measurement conditions. Recently, to enhance the stability of the SEC system and the accuracy of the resulting data, a SEC system thermostated at higher temperatures such as 40 °C has been widely used [12]. However, although some data of PLLA measured at 25-30 °C have been reported [13], there is no information on the M-H-S parameter at 40 °C even for a well known standard polystyrene. Also since both the V_h values

of dissolved random coils in a mobile phase and the pore sizes in polystyrene gels in a column vary with changes in the system temperature [14], it is not possible to use other M-H-S parameters measured at different temperatures without introducing some errors. Therefore, to estimate the absolute molecular weight of PLLA by UCM at 40 °C, the M-H-S parameters of PLLA and standard polystyrene were evaluated in chloroform and THF at 40 °C.

Intrinsic viscosity [η] values of standard polystyrenes, having narrow PDI values in a range of 1.01-1.08, were measured in dilute THF and CHCl_3 solutions at 40 °C to calculate the M-H-S parameters. M-H-S parameters of PLLA-1 in THF were also measured by using the SEC system with triple detectors. However, the estimation of parameters in CHCl_3 was difficult because of the lower dn/dc value of PLLA in CHCl_3 [15]. Further details are described in the Supplementary Data and the obtained M-H-S parameters are listed in Table 2.

3.2.1. Absolute Molecular Weight of PLLA Samples

Absolute molecular weights of PLLA-2~6 in Table 1 were determined by UCM using the two sets of M-H-S parameters for PLLA ($a = 0.709$ and $K = 3.352 \times 10^{-4}$ dL/g) and polystyrene ($a = 0.678$ and $K = 1.574 \times 10^{-4}$ dL/g) in THF at 40 °C. The molecular weight of each PLLA fraction in SEC measurements was calculated by UCM. Subsequently, number-average molecular weights (M_n), M_w , and viscosity-average molecular weights (M_v), of the PLLA samples were calculated from the whole fractional data. Obtained absolute M_w ,

M_v , and M_w/M_n values are listed in Table 1.

3.2.2. Viscosity-Molecular Weight Relationship of PLLA

Plots of the reduced and inherent viscosities against concentration of PLLA samples were linear, each having a common intercept at the $[\eta]$ value (Table 1). The $\log[\eta]$ - $\log M_v$ and $\log[\eta]$ - $\log M_w$ relations are illustrated in Figure 1 and 2 for THF and CHCl_3 solutions, respectively, resulting in good linearity with high decision coefficient R^2 values greater than 0.99. However, when polymers having various M_w/M_n values were used, $\log[\eta]$ - $\log M_n$ relations were apt to introduce a significant error [16] as clearly seen in the plots in Figure 2 and 3. Both sets of the M-H-S parameters: a_w , K_w , a_v , and K_v obtained from the $\log[\eta]$ - $\log M_w$ and $\log[\eta]$ - $\log M_v$ relations in THF and CHCl_3 are listed in Table 2. The a_w and a_v values in CHCl_3 were higher than those in THF, reflecting the higher solubility of PLLA (solubility parameter 20.0-21.1 $\text{MPa}^{1/2}$) [17].

[Figure 1]

[Figure 2]

[Table 2]

The parameter $a_{v,\text{THF}}$ value 0.708 was nearly the same as the a_{THF} value of 0.709, whereas the value of the $a_{w,\text{THF}}$ parameter, 0.697, was slightly low, but higher than the $a_{w,\text{THF}}$ value of 0.65 measured at 30 °C [18]. On the other hand, a_{v,CHCl_3} and a_{w,CHCl_3} values: 0.734 and 0.723,

respectively, were slightly higher than $a_{w,\text{CHCl}_3} = 0.72$ [19] and $a_{n,\text{CHCl}_3} = 0.73$ [20] measured at 25 and 30 °C, respectively. In almost all cases, the K values at 40 °C were lower than those at 30 and 25 °C. These results clearly indicate that PLLA is more flexible and interacts with the solvents at 40 °C more strongly than with solvents at lower temperatures.

A comparison between the molecular weights calculated using the appropriate M-H-S parameters at 40 °C and tentative parameters at different temperatures is illustrated in Figure SD-5 in Supplementary Data, which seems to show that very low molecular weights: 0.26-0.45 in ratio, were obtained for PLLA having $[\eta]$ values in a range of 0.05-1.4. The estimated absolute molecular weights of PLLA were considerably different from the tentatively calculated values.

In the following sections, the estimated M-H-S parameters: a_{v,CHCl_3} and K_{v,CHCl_3} were used for the calculation of all PLLA samples.

3.3. Changes in molecular weight of PLLA during photodegradation

No weight loss of PLLA film samples was observed for the irradiation up to 6 h, however, over 6 h, the sample weight gradually decreased and achieved 94% after 24 h irradiation. It has been pointed out that a small weight loss seriously affects the statistical evaluation of the molecular weights of polymers [21]. Thus, only the data up to 6 h in this photodegradation are significant in the statistical calculation of the kinetics.

Changes in the SEC profile of the irradiated PLLA film samples are illustrated in Figure 3. The SEC profiles shifted into low MW ranges up to 15 h whilst maintaining a PDI of around 2. This indicates that the photodegradation occurred in a manner of the homogeneous random degradation. However, after 15 h, the degradation proceeded heterogeneously, resulting in a sudden increase in the polydispersity up to ca. 3.

[Figure 3]

Figure 4 plots the changes in calculated M_n values of the irradiated PLLA film samples under UV-C ($4.3 \text{ mW}\cdot\text{cm}^{-2}$) and reference samples without irradiation. The M_n of the irradiated PLLA film samples decreased notably in comparison with the reference, clearly showing the photodegradation.

To assess the degradation kinetics, the changes in M_n and M_w values were plotted against time (t) vs. $1/M_n$ and $t^{4/3}$ vs. $t^{1/3}/M_w$ for the non-autocatalytic random degradation kinetics (Figure 5) [22], resulting in obvious linear relationships. On the other hand, plots of t vs. $\ln M_n$ and $\ln M_w$ for the auto-catalytic random degradation [23] were poor in linearity (see Figure SD-6 in Supplementary Data). These results indicate that the initial photodegradation process of PLLA, proceeds by homogeneous non-autocatalytic random degradation.

[Figure 4]

[Figure 5]

Copin et al. [24] examined the effects of UV ($\geq 315 \text{ nm}$) irradiation, temperature, and

relative humidity. They concluded that UV treatment amplified the effects of temperature and humidity on the degradation of PLLA. In this study, to estimate the contribution of UV-C irradiation, the degradation rate constants were estimated based on changes in M_n and M_w values under various irradiation intensities in a range of 0.05 ± 0.01 to 0.44 ± 0.03 $\text{mW}\cdot\text{cm}^{-2}$. Results are plotted as relationships between the irradiation intensity and the photodegradation rate constant in Figure 6. It was clearly shown that the degradation rate was proportional to the irradiation intensity with intercept values of $1.5\text{-}3.5 \times 10^{-9}$ s^{-1} . These values may be due to contributions from hydrolysis and oxidative decomposition without photodegradation.

[Figure 6]

3.4. Racemization during Photodegradation

The monomeric unit composition of the irradiated PLLA samples was analyzed by a HPLC method using a specific column for the organic acid analysis. As a result, apart from original L-lactic acid, D-lactic acid was detected as a definite component, whereas no acrylic acid was detected. The production of D-lactic acid indicates the occurrence of racemization. The racemization of L-lactate unit in PLLA induces serious problems in the thermal and mechanical properties, such as decreases in melting point and crystallinity. Moreover, the racemization affects the selectivity of L,L-lactide on the depolymerization. In Figure 7, changes in the optical purity of monomeric unit in PLLA chains during the UV-C irradiation

are plotted. A significant decrease in the optical purity was observed as a result of the racemization, whereas no decrease in the optical purity of reference samples without the UV-C irradiation was detected. The decrease in the optical purity was accelerated with irradiation time for periods over 15 h (Figure 7b). These results clearly indicate that the racemization occurs mechanistically in the photodegradation pathway, being gradually accelerated with time.

[Figure 7]

Figure 8 illustrates the relationship between the chain scission ratio and the increase in D-lactate unit in PLLA during photodegradation, as estimated from changes in $M_{n,UCM}$ and the racemization ratio, respectively. Interestingly, in an irradiation time range of 0-120 min, the increase in the chain scission ratio was very close to the increase in the D-lactate unit ratio, suggesting that approximately one D-lactate unit formed for every chain scission under irradiation. In an irradiation time range of 2-24 h, the decrease in the optical purity was accelerated with time (Figure 7b), while the chain scission ratio increased at a higher pace than that of D-lactate unit formation. This must be due to the contribution of secondary degradation reactions, which induce weight loss gradually.

[Figure 8]

Sakai et al. [4] reported from ESR studies of UV-irradiated PLLA that aliphatic ester linkages underwent dissociation reactions at RCOO-R' bonds and were followed by the

abstraction of tertiary protons on chiral carbons. Taking account of the reported mechanisms, a possible photodegradation mechanism is depicted in Scheme 1. In this mechanism, the Norrish II type reaction was ignored because of the non-detection of acrylic acid in the HPLC analysis. Instead, it was assumed that a RCOO–R' bond is cleaved to produce carboxyl and alkyl radicals, which abstract a tertiary proton on chiral carbon, resulting in a racemization equilibrium at the carboxyl chain end unit. At another chain end, the hydroxyl group must be predominant because of hydrolysis accelerated by the irradiation [24]. In additional experiments, it was suggested that L-lactic acid easily changed into other chemicals via racemization under UV-C irradiation (the data will be reported elsewhere). The hydroxyl chain end unit is highly mobile and thereby reactive, like L-lactic acid, resulting in the shifting into a racemization equilibrium under irradiation. The racemization equilibrium converts the original L-lactate units into D,L-lactate units at both chain ends, thus, the D-unit formation ratio becomes statistically close to the chain scission ratio.

[Scheme 1]

4. Conclusions

PLLA films were irradiated by UV-C light to directly excite carbonyl groups, resulting in a rapid decrease in the molecular weight accompanying a gradual decrease in the optical purity of monomeric units in the chains. This suggests that the racemization is occurring

during the irradiation. To assess relationships between the chain scission and racemization, the molecular weight of irradiated PLLA was estimated exactly by using UCM. The M-H-S parameters of PLLA and polystyrene were examined at 40 °C in THF and chloroform solutions. An interesting finding from the quantitative analyses of the exact molecular weight and the monomeric unit composition, was a close correspondence between the chain scission ratio and the D-lactate unit ratio, both of which increased in parallel during the first 0-120 min of irradiation. This suggests that approximately one D-lactate unit was generated for every chain scission. From a mechanistic consideration, it was presumed that the racemization equilibrium occurred at both carboxyl and hydroxyl chain ends, where the racemization converted the original L-lactate units into D,L-lactate units. Thus, after photodegradation each fragmented chain may have on average one D-unit and the total may be equal to the chain scission number.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:xxxxx.

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Figure and Scheme captions

Figure 1. Plots of $\log[\eta]$ vs. $\log M$ of PLLA in THF at 40 °C.

Approximation lines were given for M_w and M_v .

Figure 2. Plots of $\log[\eta]$ vs. $\log M$ of PLLA in CHCl_3 at 40 °C.

Approximation lines were given for M_w and M_v .

Figure 3. Changes in SEC profile of PLLA during UV-C irradiation for a) 120 min and b) 24 h.

Figure 4. Changes in number-average molecular weight during UV-C irradiation for a) 120 min and b) 24 h.

Figure 5. Plots of a) time (t) vs. $1/M_n$ and b) $t^{4/3}$ vs. $t^{1/3}/M_w$ for non-autocatalytic random degradation during UV-C irradiation in a range of 0-120 min.

Figure 6. Changes in photodegradation rate constants k with irradiation intensity.

Figure 7. Changes in optical purity of monomeric units during UV-C irradiation for a) 120 min and b) 24 h.

Figure 8. Relationships between chain scission ratio and increase in D-lactate unit in PLLA under UV-C irradiation.

Scheme 1. Possible photodegradation mechanisms of PLLA under UV-C irradiation.

Tables

Table 1. Intrinsic viscosity, weight and viscosity-average molecular weights of PLLAs and standard polystyrenes at 40 °C.

| Sample | Intrinsic viscosity [η] | | Average molecular weight ^{a,b,c} | | |
|--------|--------------------------------|----------------------|---|--------|-----------|
| | in THF | in CHCl ₃ | M_w | M_v | M_w/M_n |
| PS-1 | 1.5995 | 1.7114 | 1060000 | - | 1.08 |
| PS-2 | 1.2050 | 1.0922 | 427000 | - | 1.02 |
| PS-3 | 0.6522 | 0.6438 | 190000 | - | 1.04 |
| PS-4 | 0.3953 | 0.3663 | 96400 | - | 1.01 |
| PS-5 | 0.1863 | 0.2116 | 37900 | - | 1.01 |
| PS-6 | 0.1159 | 0.1141 | 18100 | - | 1.01 |
| PS-7 | 0.0758 | 0.0787 | 10200 | - | 1.02 |
| PS-8 | 0.0588 | 0.0641 | 5390 | - | 1.02 |
| PS-9 | 0.0318 | 0.037 | 2630 | - | 1.05 |
| PLLA-1 | 1.3216 | 1.1257 | 128000 | 119000 | 1.77 |
| PLLA-2 | 0.5904 | 0.5994 | 51600 | 47300 | 2.08 |
| PLLA-3 | 0.3342 | 0.2901 | 18000 | 17600 | 1.16 |
| PLLA-4 | 0.1467 | 0.1141 | 4930 | 4820 | 1.19 |
| PLLA-5 | 0.1114 | 0.0754 | 3510 | 3440 | 1.15 |
| PLLA-6 | 0.0450 | 0.0422 | 1260 | 1240 | 1.15 |

^a Average molecular weights of standard polystyrenes, measured by a light scattering method, were obtained from Tosoh Corporation.

^b Average molecular weights of PLLA-1 were determined by SEC analysis using a Viscotek TDA-302 triple detector in THF.

^c Average molecular weights of PLLA-2~6 samples were calculated by SEC-UCM in THF.

Table 2. M-H-S parameters for polystyrene and PLLA in CHCl₃ and THF at 40 °C.

| | solvent | M, M_v, M_w | M-H-S parameters | |
|-------------|-------------------|---------------|------------------------|-------|
| | | | $K \times 10^4$ (dL/g) | a |
| polystyrene | THF | M | 1.574 | 0.678 |
| | CHCl ₃ | M | 2.072 | 0.655 |
| PLLA | | M | 3.352 | 0.709 |
| | THF | M_v | 3.143 | 0.708 |
| | | M_w | 3.383 | 0.697 |
| | CHCl ₃ | M_v | 2.068 | 0.734 |
| | | M_w | 2.222 | 0.723 |

Figures

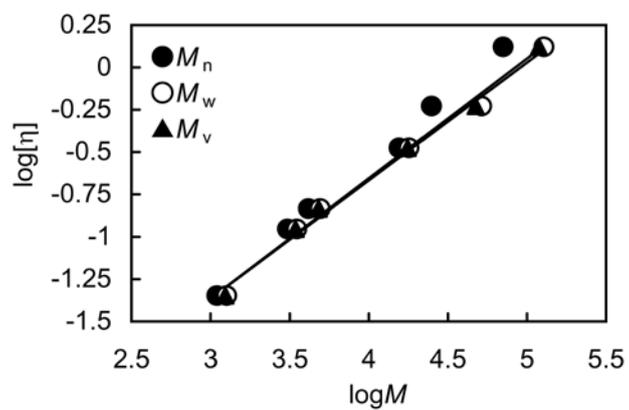


Figure 1. Plots of $\log[\eta]$ vs. $\log M$ of PLLA in THF at 40 °C. Approximation lines were given for M_w and M_v .

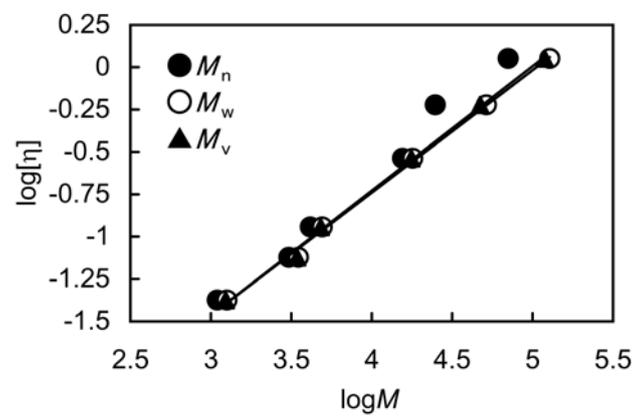


Figure 2. Plots of $\log[\eta]$ vs. $\log M$ of PLLA in CHCl_3 at 40 °C. Approximation lines were given for M_w and M_v .

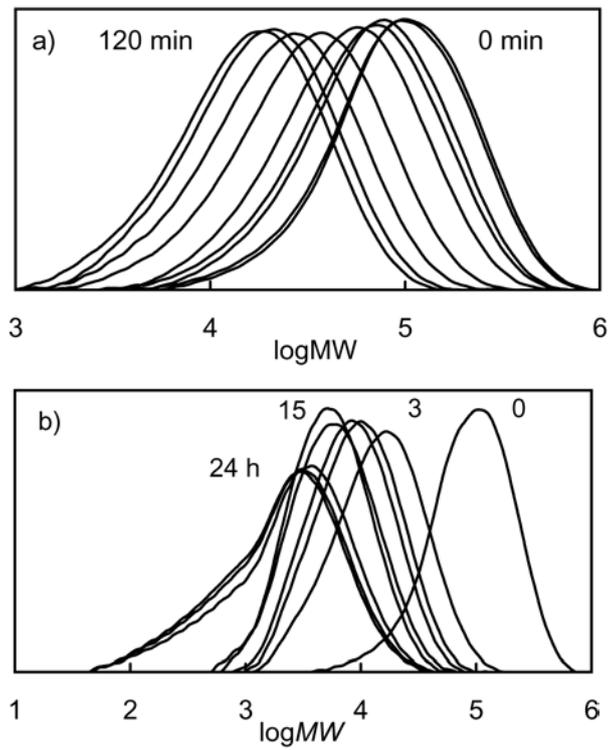


Figure 3. Changes in SEC profile of PLLA during UV-C irradiation for a) 120 min and b) 24 h.

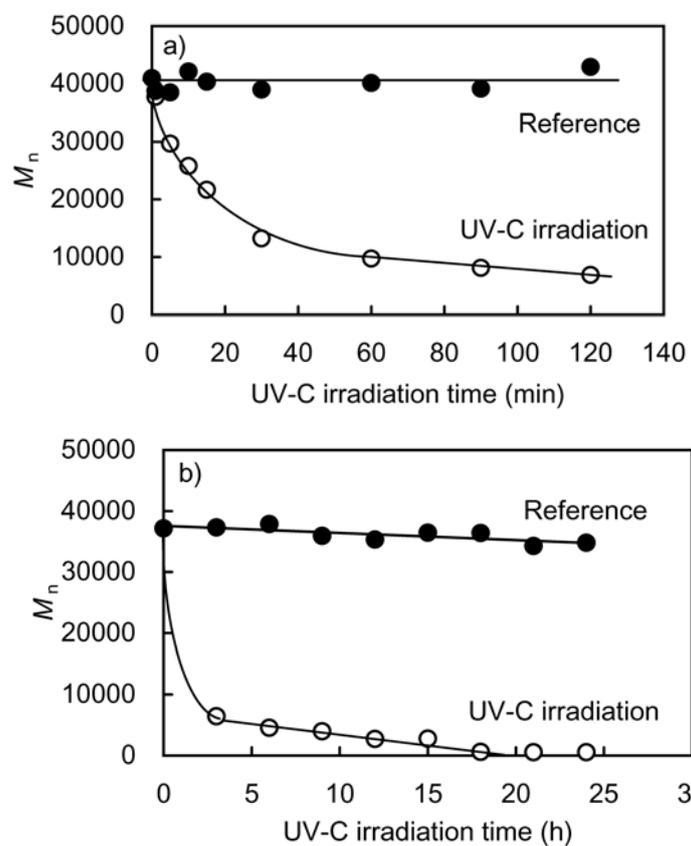


Figure 4. Changes in number-average molecular weight during UV-C irradiation for a) 120 min and b) 24 h.

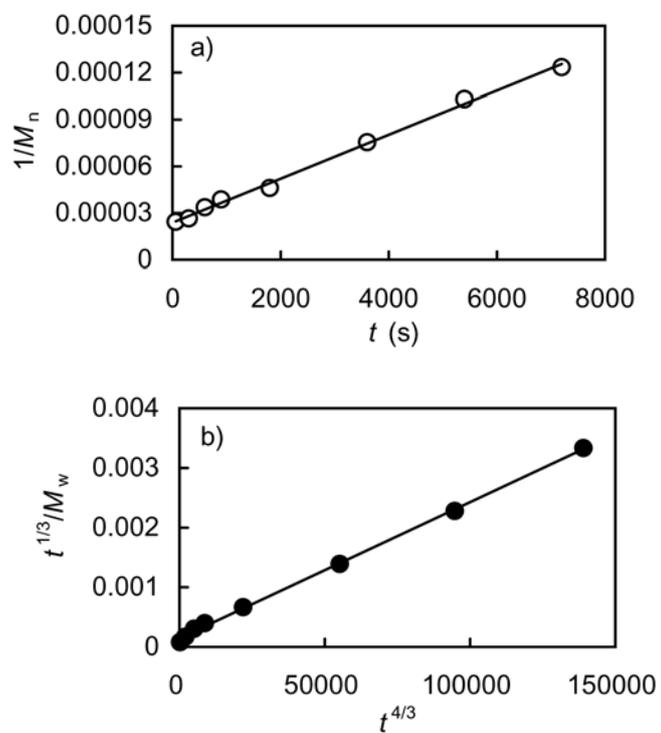


Figure 5. Plots of a) time (t) vs. $1/M_n$ and b) $t^{4/3}$ vs. $t^{1/3}/M_w$ for non-autocatalytic random degradation during UV-C irradiation in a range of 0-120 min.

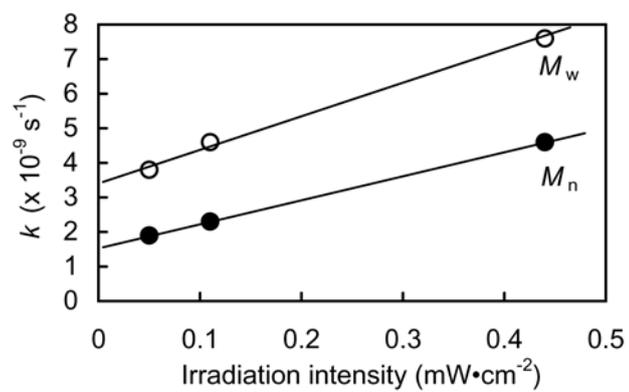


Figure 6. Changes in photodegradation rate constants k with irradiation intensity.

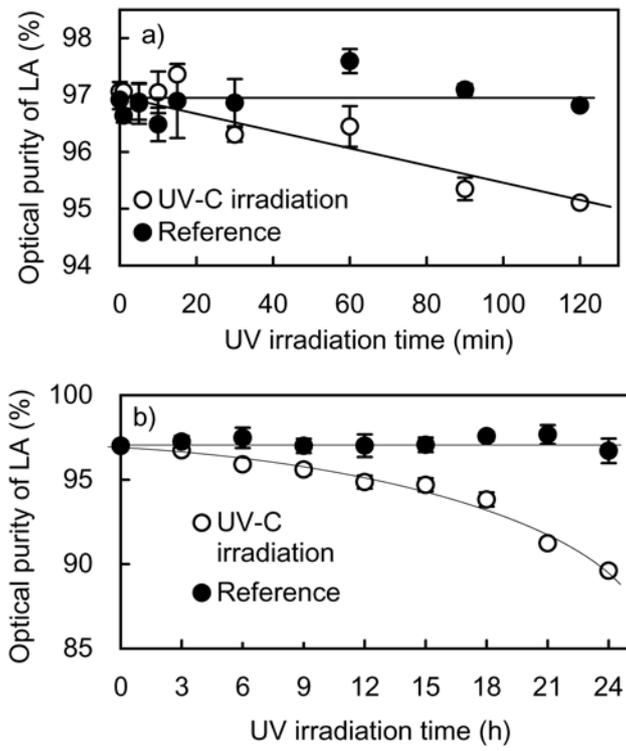


Figure 7. Changes in optical purity of monomeric units during UV-C irradiation for a) 120 min and b) 24 h. Bar: standard deviation.

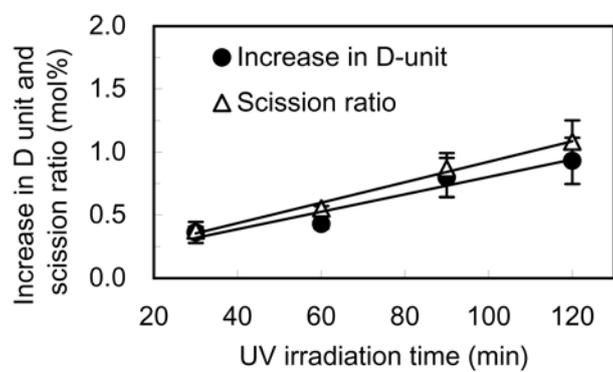
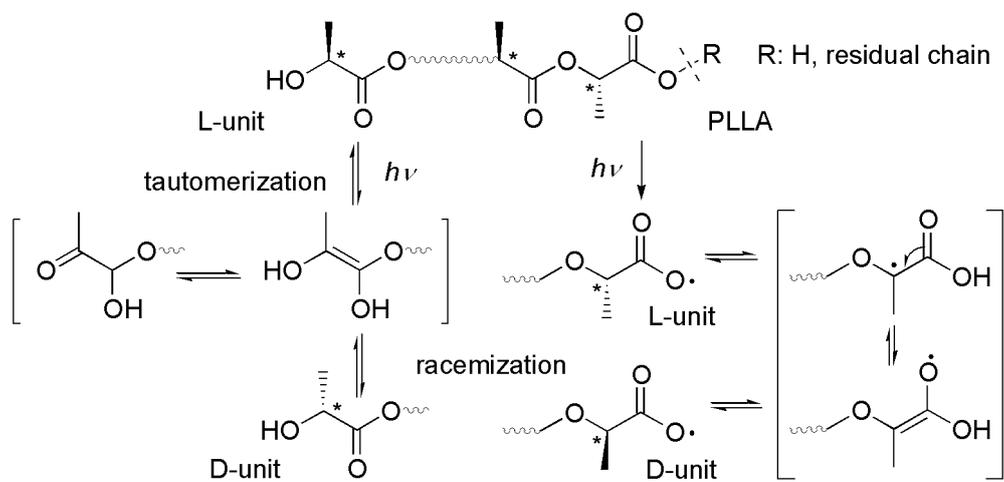


Figure 8. Relationships between chain scission ratio and increase in D-lactate unit in PLLA under UV-C irradiation. Bar: standard deviation.



Scheme 1. Possible photodegradation mechanisms of PLLA under UV-C irradiation.