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Synthesis of branched poly(lactide) using polyglycidol and thermal, mechanical properties of its solution-cast film

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Abstract

Branched poly(lactide)(PLA)s with various lengths of graft chain were synthesized by ring-opening polymerization of L- or D-lactide (L- or D-LA) in bulk using polyglycidol as a macroinitiator. The properties of polymer films of branched PLLA or PDLA obtained and their stereocomplex were investigated through thermal analysis and tensile testing. The branched PLLA or PDLA film exhibited a lower glass transition temperature (T_g), melting temperature (T_m), crystallinity, Young's modulus and a higher strain at break than the corresponding linear PLLA or PDLA film. The branched PLLA/branched PDLA stereocomplex film showed a high maximum stress and a high Young's modulus keeping its high strain at break. Moreover, the usefulness of branched PLLA or PDLA as a plasticizer of linear PLLA was investigated with 1:9 blend or stereocomplex film prepared from the branched PLLA or branched PDLA and linear PLLA. The blend or linear PLLA/branched PDLA stereocomplex film showed a higher strain at break compared with linear PLLA film. The mechanical properties of the blend or linear PLLA/branched PDLA stereocomplex film could easily be controlled by changing the molecular weight of branched PLA.

Keywords: Biodegradable polymer; Branched poly(lactide); Stereocomplex

1. Introduction

Biodegradable polymers have become of interest from the standpoints of pharmaceutical and biomedical applications as well as environmental application. Various properties such as good mechanical property, good biocompatibility, controlled degradability and good safety are desired for biodegradable medical materials. Poly(lactide) (PLA) is one of the most widely utilized class of biodegradable and bioabsorbable polymers in the field of biomedical materials and has been used clinically in wound closure, tissue repair and regeneration and drug delivery [1–4]. Since lactic acid (LA) is enantiomeric, PLA involves poly(L-lactide) (PLLA), poly(D-lactide) (PDLA) and poly(DL-lactide) (PDLLA). It is well known that an enantiomeric mixture of PLLA and PDLA forms a stereocomplex. The linear PLA stereocomplex film was reported to have about 50 °C higher T_m than linear PLLA or PDLA film [5]. PLLA has good biocompatibility, biodegradability, high mechanical strength and excellent shaping, molding properties. However, PLLA suffers from the poor compatibility with soft tissue because of its high crystallinity and the difficulty of controlled degradation. Many approaches were performed to overcome these problems in PLLA. Namely, the design of stereocopolymer according to enantiomeric composition, block copolymer with polyether, branched PLLA or blend with other polymers was investigated to control the mechanical property and degradation rate by varying the crystallinity [6–12].

One of the promising approaches to solve these problems is to introduce the branched structure into PLLA. Recently, a number of ways have been reported to obtain the synthesis of branched polymers such as hyperbranched, star-shaped, and dendric polymers because of their interesting thermal, rheological, mechanical and degradable properties [13–18]. It is well known that branched compounds have different physico-chemical properties compared with their linear counterparts owing to their molecular architecture. Long-chain branches predominantly affect the viscoelasticity of fluidity range, decrease the viscosity, and increase the elasticity. On the other hand, short chain branches predominantly affect the crystallinity. By introducing the branched structure into PLLA, physical properties such as crystallinity, glass transition point (T_g) and melting point (T_m) will be influenced. The characteristics of the biodegradation through

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hydrolysis of their polymers are in turn also influenced. In terms of modifying of characteristics of PLLA owing to introduction of branched structure, we previously reported on the synthesis of comb-type PLLA by means of graft polymerization of L-LA onto a depsipeptide/lactide copolymer containing serine residues [19,20] and the one-pot synthesis of branched PLLA through the copolymerization of L-LA using the metabolic intermediate DL-mevalonolactone as a bifunctional comonomer containing both lactone ring and pendant hydroxyl group [21].

We report here on the synthesis of the branched PLA having many branches and the properties of the related PLA films using branched polymers. Branched PLLA and branched PDLA were synthesized by bulk polymerization of L-LA and D-LA using polyglycidol having many pendant hydroxyl groups as a macroinitiator. The thermal and mechanical properties of cast films prepared from branched PLLA and stereocomplex films prepared from branched PLLA and branched PDLA were investigated. Moreover, the thermal and mechanical properties of 1:9 blend films prepared from the branched PLLA or branched PDLA and linear PLLA were investigated. The branched PLLA or branched PDLA acted as a good plasticizer of linear PLLA.

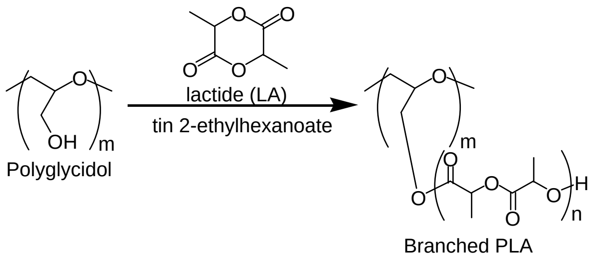
2. Experimental

2.1. Materials

L-LA and D-LA were purchased from Purac Japan. Linear poly-L-lactide (PLLA) ($M_n = 5.1 \times 10^4$) purchased from Sigma Chemical Co. was reprecipitated from chloroform/methanol before use. The molecular weight of linear PLLA was estimated by size-exclusion chromatography-multiangle laser light scattering (SEC–MALLS) [column: Shodex GPC KF-806L×5, eluent: THF, detector: MALLS (Wyatt Technology Co. DAWN model F)]. Polyglycidol ($M_n = 1.3 \times 10^3$, $M_w/M_n = 1.9$, number of hydroxyl groups/molecule = 20) synthesized by Professor Yoshinaga of Kyusyu Institute of Technology was supplied from NOF Co. The supplied polyglycidol was reprecipitated from methanol/diethylether, lyophilized, and then dried under vacuum at room temperature for 24 h before use. The molecular weight of polyglycidol was estimated by gel-permeation chromatography (GPC) analysis [column: TSK-GEL α-5000×2, eluent: DMF, detector: RI, standard: PEG] using a Tosoh GPC-8020 series s stem. Dry tetrahydrofuran (THF), tin 2-ethylhexanoate and other chemicals purchased from Wako Pure Chemical (Tokyo) were used without further purification.

2.2. Synthesis of branched PLA

The synthesis of branched PLLA was performed by ring-opening polymerization of L-LA in bulk using polyglycidol having pendant hydroxyl groups and tin 2-ethylhexanoate as a macroinitiator and a catalyst, respectively (Scheme 1). L-LA and polyglycidol keeping the molar ratio of L-LA to hydroxyl group of polyglycidol (M/OH) at 5, 10, 20, 30, 50 or 100 were added to the glass tube, and then dried under vacuum. After drying, a freshly prepared solution of tin 2-ethylhexanoate in dry THF (molar ratio of LA/tin 2-ethylhexanoate = 1000) was added to a glass tube in glovebox purged with dry nitrogen. After THF was removed under vacuum and the tube was purged with dry nitrogen, it was sealed in vacuo. The sealed tube was placed in an oil bath at 150 °C for 2 min and subsequently at 115 °C for 24 h. The reaction mixture dissolved in a small amount of chloroform as poured into a large amount of methanol to precipitate branched PLLA as a white solid. Branched PDLA was also synthesized through ring-opening polymerization of D-LA by the same method. The characterization of branched PLA was performed with ^{1}H NMR (JEOL GSX-400) measurement using tetramethylsilane as an internal reference. ^{1}H NMR (DMSO-d_6): δ(ppm) = 1.50 (d, 3H, CH_3), 3.5–3.7 (m, 3H, CH_2CHO), 4.1–4.4 (m, 3H, CH, CH_2), 5.2 (q, 1H, CH). The molecular weight of branched PLA was determined by SEC–MALLS and GPC analysis (column: TSK-GEL Multipore HXL-M×2, eluent: THF, detector: RI, standard: polystyrene). In this research, we named branched PLA as a branched PLA ($M_n \times 10^{-3}$) K.



Scheme 1. Synthetic route of branched PLLA.

2.3. Preparation of cast polymer films

The branched PLLA films, linear PLLA film, the stereocomplex film and the blend film were prepared by solvent-casting method to evaluate their thermal and mechanical properties. The branched PLLA, linear PLLA, a 1:1 mixture of branched PLLA/branched PDLA mixture and a 9:1 mixture of linear PLLA and branched PLLA (or branched PDLA) were cast from their 4 wt% chloroform solutions, and then the solvent was allowed to evaporate for 12 h. The obtained films were further dried under vacuum at room temperature for 48 h. In this paper, we names the branched stereocomplex films and the blend films as SC-1 20 (Branched PLLA 66K/Branched PDLA 70K) film, SC-1 100 (Branched PLLA 287K/Branched PDLA 291K) film, SC-2 20 (linear PLLA/branched PDLA 70K) film, SC-2 100 (linear PLLA/branched PDLA 291K) film, blend 20 (linear PLLA/branched PLLA 66K) film, and blend 100 (linear PLLA/branched PLLA 287K) film, respectively. The thickness of obtained films was kept at about 100–150 μm. Branched PLLA 25K, PLLA 30K, PLLA 66K films and SC-1 20 film were cracked while these films were prepared.

Although branched PLLA 112K, PLLA 160K, PLLA 287K films, SC-1 100 film, SC-2 20, SC-2 100 films, blend 20 and 100 films were not cracked, branched PLLA 112K and PLLA 160K films were too fragile to evaluate their mechanical properties. Only branched PLLA 25K film was transparent, while the other films were semitransparent. The scanning electron microscope (SEM) observation of the film surfaces was carried out using a JEOL JSM-35. Since the surfaces of all obtained films were flat, the surface form might not give a severe effect on their tensile test evaluations.

2.4. Thermal analysis

Glass transition temperature (T_g), melting temperature (T_m) and enthalpy of fusion (ΔH) of the polymer films were measured by differential scanning calorimetry (DSC) (SHIMADZU DSC-60). The polymer films (4–6 mg) were heated at 10 °C/min. The temperature ranged between −100 and +200 °C (branched PLLA films and blend films) or −100 and +250 °C (stereocomplex films).The polymer films were quenched with liquid nitrogen at −100 °C. The apparent crystallinity (X_c) of the polymer films was calculated with the aid of the enthalpy of fusion of −93.7 J/g [22] and −142 J/g [23] for the perfectly crystalline homo-PLLA and linear PLLA stereocomplex, respectively, by the equation: $X_c(\%) = \Delta H/\Delta H_{\text{theo}} \times 100$. The crystallinity of the polymer films was determined through first heating scan.

2.5. Measurement of mechanical property

Tensile testing was carried out on dumbbell specimens using a tensile testing machine (SHIMADZU Autograph AGS-J) with a crosshead speed of 30 mm/min. The dumbbell specimens were produced from the obtained polymer films having 100–150 m thickness. The initial length of specimen between two gages was always kept at 18 mm. The five specimens were tested on each tensile test.

3. Results and discussion

3.1. Preparation of branched PLA

The ring-openimg polymerization of LA in bulk was carried out in the presence of polyglycidol as a macroinitiator using tin 2-ethylhexanoate catalyst at 115 °C for 24 h to give branched PLA as shown in Scheme 1. The polymerization was performed under rigorously dry conditions. The results of polymerization are shown in Table 1. The typical ^{1}H NMR chart of branched PLLA is shown in Fig. 1. The peaks *d*, *e* and *f* assigned to methyl protons, methine protons and methine proton at the end groups of branched PLLA chains were found. Moreover, several peaks *a*, *b* and *c* indicating the introduction of polyglycidol to PLA could be detected. The peak *c* assigned to methylene protons of the side chain of polyglycidol was overlapped with the peak *f* in ^{1}H NMR spectrum of branched PLA. The GPC profiles of branched PLA and polyglycidol are shown in Fig. 2. The non-reacted macroinitiator peak was not detected in the GPC profile of the obtained branched PLA; The GPC profile of branched PLA was unimodal. This result meant the polymerization was successful. The GPC molecular weight of branched polymer estimated by using a linear standard polymer is known to be underestimated due to its smaller hydrodynamic volume in solution. In this experiment, the GPC detected molecular weight of the obtained branched PLA also tended to be smaller than that detected by SEC-MALLS, as shown in Table 1. Thus, the molecular weights of linear PLLA and branched PLLA are hereafter discussed by using the SEC–MALLS detected molecular weight. By assuming that 20 hydroxyl groups in the used polyglycidol molecule were all reacted, the degree of polymerization (DP) of LA per one PLA graft chain was estimated from molecular weight detected by the SEC–MALLS. As shown in Table 1, the DP of LA per one PLA graft chain corresponded to the feed molar ratio of M/OH. So, it was clarified that the molecular weight of branched PLA could be easily controlled by varying the feed molar ratio of M/OH.

Table 1
Results of polymerization of LA with polyglycidol

Code	M/OH[a]	Yield (%)	Conv.[b] (%)	$M_n{}^c \times 10^{-4}$	$M_n{}^d \times 10^{-4}$	$M_w/M_n{}^c$	DP[e]
Branched PLLA 25K	5	75.3	98.1	2.2	2.5	1.35	7
Branched PLLA 30K	10	87.2	97.4	2.5	3.0	1.38	10
Branched PLLA 66K	20	88.4	98.7	5.1	6.6	1.46	22
Branched PLLA 112K	30	88.0	95.3	9.7	11.2	1.37	38
Branched PLLA 160K	50	91.0	97.4	13.9	16.0	1.45	55
Branched PLLA 287K	100	84.1	96.8	24.1	28.7	1.47	100
Branched PDLA 70K	20	91.7	97.4	5.5	7.0	1.42	24
Branched PDLA 291K	100	88.5	93.2	25.0	29.1	1.39	101

Degree of polymerization of LA per one PLA segment. Polymerization were carried out in bulk at 150 °C for 2 min and then at 115 °C for 24 h. Molar ratio of LA to catalyst (*M*/cat.), 1000. Polyglycidol: M_n, 1360; M_w/M_n, 1.86.

[a] Molar ratio of LA to OH of polyglycidol.

[b] Reaction rate of LA was estimated from the integration ratio of methin peat of 5.1 ppm (PLA) to methin peak of 4.9 ppm (LA) in NMR.

[c] Estimated by GPC (eluent: THF, standard: PS).

[d] Estimated by SEC–MALLS (eluent: THF).

[e] Estimated by SEC–MALLS (eluent: THF).

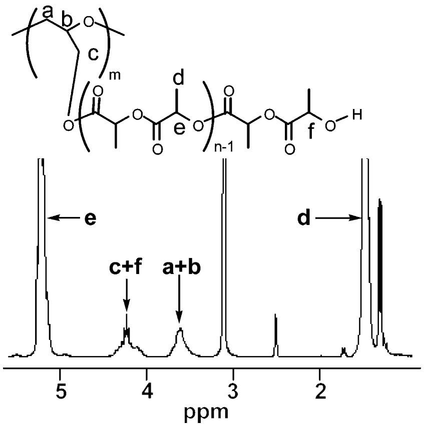


Fig. 1. ^{1}H NMR spectrum of branched PLLA (solvent: DMSO-d_6).

3.2. Thermal properties of PLA polymer films

Table 2 summarizes the results of DSC analysis of branched PLLA films, linear PLLA film and their blend films. T_g and T_{mH} (melting temperature of homo-crystallite) values of branched PLLA increased with increasing the molecular weight of branched PLLA. The morphology of branched PLLA 25K having short PLLA branches was found to be amorphous. The X_{cH} (crystallinity of branched PLLA) values shown in Table 2 suggested that the crystallinity of PLLA could be easily controlled by the introduction of branched structure and the changing of branched PLLA length.

Blend films of branched PLLA and linear PLLA showed lower T_g and X_{cH} values than linear PLLA film. The big difference was not recognized in these values of blend 20 and 100 films. The branched PLLA 66K film showed the T_{mH} at 149.6 °C, while blend 20 film showed T_{mH} at 174.1 °C. Only one T_m belong to linear PLLA might appear in blend 20 film because branched PLLA 66K did not form homo-crystallites and/or formed the amorphous domains.

Both branched PLLA branched PDLA stereocomplex (SC-1) films showed the corresponding melting temperatures of stereocomplex crystallites (T_{mS}) at the range of 210–220 °C, as shown in Table 3. SC-1 100 film had two melting temperatures, T_{mH} and T_{mS}. This result meant the branched PLLA/branched PDLA mixture derived the homo-crystallization of branched PLLA and branched PDLA along with the crystallization of stereocomplex when high molecular weight of branched PLA was used. On the other hand, SC-1 20 film showed only T_{mS}. T_{mS} of SC-1 20 film was lower than T_{mS} of linear PLLA/linear PDLA stereocomplex (230 °C) [5]. This implied that the average size of stereocomplex crystallite decreased with decreasing the branch PLA length.

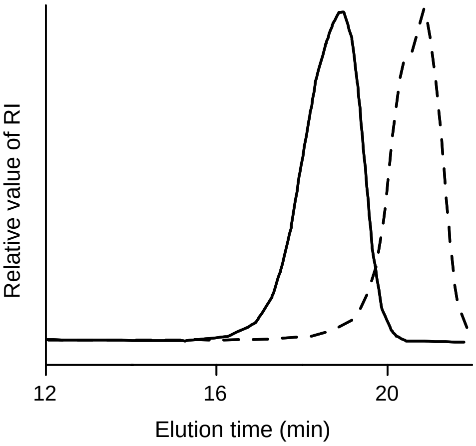


Fig. 2. GPC profiles of polyglycidol and branched PLLA 30K.

Table 2
Results of thermal analysis of branched PLLA, linear PLLA and their blend films

Sample film	T_g (°C)	T_m (°C)	X_c[a] (%)
Branched PLLA 25K	27.9	ND[b]	ND[b]
Branched PLLA 30K	35.6	119.0	22.2
Branched PLLA 66K	39.8	149.6	29.4
Branched PLLA 112K	39.7	156.7	33.8
Branched PLLA 160K	40.1	161.1	34.2
Branched PLLA 287K	41.1	167.5	36.3
Linear PLLA[c]	59.8	175.5	49.7
Blend 20	39.4	174.1	39.7
Blend 100	40.1	174.5	39.6

[a] X_c, crystallinity estimated from ΔH values obtained from first scan.
[b] Not detected.
[c] M_n, 51,000; M_w/M_n, 2.02.

As shown in Table 3, SC-2 films had two melting temperatures (T_{mH} and T_{mS}). Although the X_{cS} values of both obtained SC-2 films were almost the same, T_{mS}-value of SC-2 20 film (209.2 °C) was smaller than T_{mS}-value of SC-2 100 film (219.2 °C). Such a decrease of T_{mS}-value can be also explained from the generation of small size of stereocomplex crystallites caused by using of the short branched chain length of PDLA, as mentioned above.

3.3. Mechanical properties of PLA polymer films

The results of tensile testing of branched PLLA 287K film, linear PLLA and branched PLLA/branched PDLA stereocomplex SC-1 100 film are shown in Fig. 3 and Table 4. The branched PLLA and SC-1 films except the films shown above could not be tested because of their very fragile character. The branched PLLA 287K film showed smaller tensile strength (18.4 MPa), Young's modulus (504 N/mm^2) and greater strain at break (163%) than linear PLLA film (tensile strength: 33.1 MPa, Young's modulus: 1210 N/mm^2, strain at break: 14%). These results meant branched PLLA 287K film was more soft than linear PLLA film. In addition, SC-1 100 film

Table 3
Results of thermal analysis of stereocomplex films

Sample film	T_g (°C)	T_{mH} (°C)	T_{mS} (°C)	X_{cH}[a] (%)	X_{cS}[a] (%)
SC-1 20	40.2	ND[b]	207.2	ND[b]	37.7
SC-1 100	41.0	168.9	214.1	25.9	5.0
SC-2 20	39.2	173.2	209.4	26.0	7.5
SC-2 100	40.6	175.9	219.2	30.3	7.3

[a] X_c, crystallinity estimated from ΔH values obtained from first scan.
[b] Not detected.

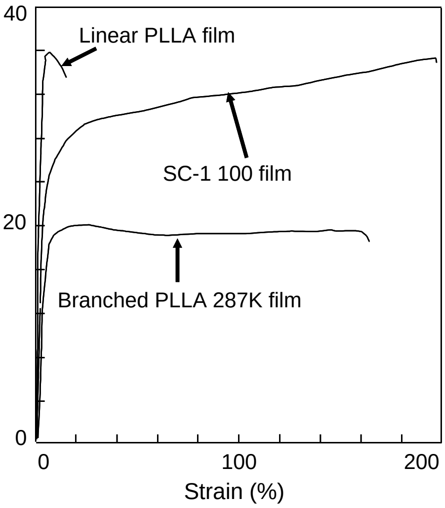


Fig. 3. Stress–strain curves of branched PLLA 287K film, SC-1 100 film, and linear PLLA film.

Table 4
Results of tensile testing of branched PLLA, branched PLLA/branched PDLA stereocomplex and linear PLLA films

Sample film	Tensile strength (MPa)	Young's modulus (N/mm^2)	Strain at break (%)
Branched PLLA 287K	18.4	501	163
SC-1 100	34.9	792	199
Linear PLLA	33.1	1210	14

showed greater strain at break (199%), high Young's modulus (792 N/mm^2) and high tensile strength (34.9 MPa) compared with branched PLLA 287K film. The hardness, the tensile strength and the strain at break of branched PLA film was suggested to be risen by formation of stereocomplex between enantiomeric-branched PLA chains. The results of mechanical property such as low Young's modulus and great strain at break can be explained to be due to the physical cross-linking among crystalline domains of branched PLA. Since the weight percentages of polyglycidol in the branched PLLA 287K and branched PDLA 291K films were very low (>0.5 wt%), the influence of amount of polyglycidol on the mechanical properties of branched PLLA 287K and SC-1 100 films could be presumed to be not big. It was suggested from these results that the mechanical properties of linear PLLA could be modified by introduction of branched structure into PLLA and the molecular weight of ca. 2.0×10^5/branched chain, that is, 1.0×10^4, was required to give enough mechanical strength for branched PLLA film.

The results of tensile testing of linear PLLA/branched PLLA blend films and linear PLLA/branched PDLA SC-2 films are shown in Fig. 4 and Table 5. In spite of molecular weight of additional branched PLA, the crystallinity of blend films and SC-2 films was almost same in each film series, as shown in Tables 2 and 3. On the other hand, their films gave the different types of stress–strain curve based on the molecular weight of additional branched PLA. Blend films showed small tensile strength and similar Young's modulus compared with linear PLLA film. The difference of these values was not recognized between blend 20 film and blend 100 film. Blend 20 and SC-2 20 films showed greater strain (88 and 19%) than linear PLLA film (Fig. 4(a)). However, the strain at break of blend 100 film and SC-2 100 film (25 and 56%) was smaller than that of blend 20 film (Fig. 4(b)). These results suggested that the strain at break of blend film decreased with increasing molecular weight of added branched PLLA and increased by

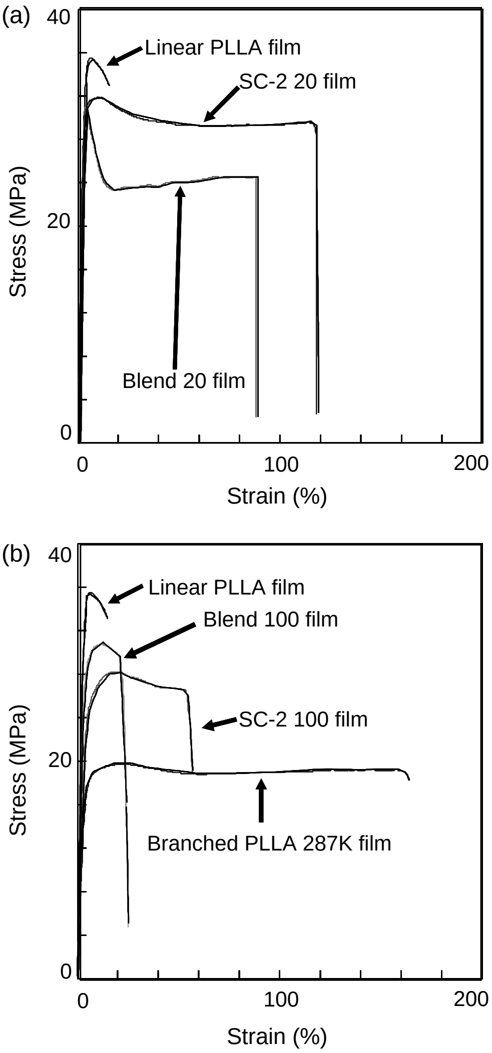


Fig. 4. (a) Stress–strain curves of blend 20 film, SC-2 20 film and linear PLLA film, and (b) Stress–strain curves of blend 100 film, SC-2 100 film, branched PLLA 287K film and linear PLLA film.

Table 5
Results of tensile testing of blend, linear PLLA/branched PDLA stereocomplex and linear PLLA films

Sample film	Tensile strength (MPa)	Young's modulus (N/mm^2)	Strain at break (%)
Blend 20	24.6	1180	88
Blend 100	29.3	1164	25
SC-2 20	31.9	1195	120
SC-2 100	19.1	1185	56
Linear PLLA	33.1	1210	14

formation of stereocomplex. Branched PLA composed of short length branches showed high efficiency of physical cross-linking among the crystalline domains of PLA. So, the mechanical properties of linear PLLA could be modified by varying the molecular weight of branched PLA as a plasticizer.

4. Conclusion

Biodegradable branched PLLA was successfully synthesized by bulk polymerization of LA using polyglycidol as a macroinitiator. The obtained branched PLLA film showed lower T_g, T_m and crystallinity and higher strain at break than linear PLLA film due to the introduction branched structure. The branched PLLA/branched PDLA stereocomplex SC-1 film showed a high maximum stress and a high Young's modulus keeping its high strain at break. The mechanical properties of the linear PLLA/branched PLLA blend film and linear PLLA/branched PDLA stereocomplex SC-2 film could easily be controlled by changing the molecular weight of branched PLA chains. Branched PLA made to promote effectively the physical cross-linking among crystalline domains because of its branched structure.

So, branched PLA can be expected to be applied as a novel biomedical material and a plasticizer of linear PLA.

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