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Stereocomplex formation between enantiomeric poly(lactic acid)s. XI. Mechanical properties and morphology of solution-cast films

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Abstract

Films of 1:1 blend and films non-blended were prepared from poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) with a solution casting method, and the mechanical properties and morphology of the films were investigated using tensile tests, dynamic mechanical relaxation measurements, polarizing optical microscopy, differential scanning calorimetry (DSC) and X-ray diffractometry. The tensile strength, Young's modulus, and the elongation-at-break of 1:1 blend films were found to be higher than those of non-blended films when their weight-average molecular weight (M_w) was in the range 1×10^5–1×10^6. The enthalpy of melting for stereocomplex crystallites in 1:1 blend films was higher than that of homo-crystallites when M_w of polymers was below 2×10^5, while this relationship was reversed when M_W increased to 1×10^6. Spherulites formation was suppressed in 1:1 blend films, whereas large-sized spherulites with radii of 100–1000 μm were formed for non-blended PLLA and PDLA films, irrespective of M_w. The mechanical properties of 1:1 blend films superior to those of non-blended films were ascribed to the micro-phase structure difference generated as a result of formation of many stereocomplex crystallites which acted as intermolecular cross-links during solvent evaporation of blend solution. On the contrary, non-blended films had larger-sized spherulites of less contacting area with the surrounding spherulites. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(lactic acid); Polylactide; Stereocomplex

1. Introduction

In the past two decades, a large number of studies have been performed for poly(lactide)s, poly(lactic acid)s (PLAs) and their copolymers which are hydrolyzable in the human body as well as in natural circumstances [1–9]. As our first report on the stereocomplexation (racemic crystallization) between enantiomeric poly(L-lactide) or poly(L-lactic acid) (PLLA) and poly(D-lactide) or poly(D-lactic acid) (PDLA) [10,11], effects of numerous parameters on the stereocomplexation have been intensively investigated [11–25]. These studies revealed that exclusive formation of either stereocomplex crystallites (racemic crystallites) composed of an equimolar amount of L-lactide and D-lactide unit sequences or homo-crystallites composed of either L-lactide or D-lactide unit sequence alone occurs depending on the parameters given below:

1. blending ratio of the two isomeric polymers [10–17];
2. molecular weight of the two isomeric polymers [12–16];
3. optical purity of the two isomeric polymers [17–19];
4. temperature and time after blending of the two isomeric polymers in solutions or after melting their blend [12,15–17,19];
5. nature of the solvents utilized for polymer blending [13,14];
6. nature of the co-monomer units and length of lactide unit sequences in copolymers [21–26];
7. blending mode of the two isomeric polymers [12–16,20].

The most common conditions of polymer blending for exclusive formation of stereocomplex crystallites without formation of homo-crystallites include:

1. equimolar blending of D-lactide and L-lactide units [10–17];
2. low molecular weight for both the isomeric polymers [13];
3. sufficiently long sequences of both isotactic L-lactide and D-lactide units [17–19,23].

The blending mode and nature of solvents also affect strongly stereocomplexation. Moreover, stereocomplexation is found to occur as far as the system contains both L-lactide

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Table 1
Polymerization conditions and molecular characteristics of PLLA and PDLA utilized in this study

	Polymerization conditions[a]		Molecular characteristics		
Code	Time (min)	Lauryl alcohol (wt.%)	M_w (g/mol)	M_w/M_n	$[\alpha]_D^{25}$
PLLA1	600	3.0	1.0×10^4	1.4	−149
PLLA2	600	1.0	5.0×10^4	1.8	−153
PLLA3	600	0.5	1.2×10^5	1.7	−154
PLLA4	600	0.5	1.5×10^5	1.4	−154
PLLA5	600	0	2.5×10^5	1.8	−154
PLLA6	600	0	9.8×10^5	2.0	−155
PDLA1	600	2.5	2.2×10^4	1.5	146
PDLA2	600	2.0	5.4×10^4	1.7	155
PDLA3	600	0.3	1.0×10^5	1.9	155
PDLA4	600	0.4	1.5×10^5	1.8	155
PDLA5	20	0	1.8×10^5	1.5	156
PDLA6	600	0	1.0×10^6	2.1	157

[a] Bulk polymerization was carried out in the presence of 0.03 wt.% stannous octoate at 140°C.

and D-lactide unit sequences, disregarding whether they are in different molecules or are connected to co-monomer sequences other than lactide units [17–19,21–27]. Examples include stereocomplexation of L-lactide and D-lactide block copolymers [21,22,26,27] between ϵ-caprolactone or ethylene oxide and L- or D-lactide blockcopolymers [22,25], between L-lactide-rich PLAs and D-lactide-rich PLAs [18,19], and between glycolide and L- or D-lactide copolymers [23].

L-lactide and D-lactide unit sequences form stereocomplex crystals upon mixing under side by side packing [28–31]. Okihara et al. [28,30] found triangular single crystals to be formed by stereocomplexation and Brizzolara et al. [29] proposed a mechanism for their single crystal formation. Similar to the spherulites composed of homo-crystallites of either L-lactide or D-lactide unit sequences, both L-lactide and D-lactide unit sequences could form normal spherulites by stereocomplexation in bulk, from the melt [16,17,19] as well as in solution [15], when they were composed of only stereocomplex crystallites. However, spherulite morphology was complicated when the spherulites contained both stereocomplex crystallites and homo-crystallites [16,19]. Brochu et al. [17] reported epitaxial crystallization of stereocomplex crystallites and homo-crystallites from the melt of blends constituting of PLLA and poly(D-lactide-co-L-lactide) (80/20). We found the equilibrium melting temperature of stereocomplex crystallites to be 279°C and the critical isotactic sequence for stereocomplexation of L-lactide-rich PLA and D-lactide-rich PLA to be 15 isotactic lactate (half of lactide) units [19]. When stereocomplexation was allowed to proceed in concentrated chloroform solution, three-dimensional (3D) gelation occurred as a result of formation of stereocomplex microcrystallites which acted as cross-links. This happened because the critical concentration for stereocomplexation by intermolecular interaction was lower than that of homo-crystallization by intra- and intermolecular interaction. In other words, stereocomplexation took place more readily than homo-crystallization [12,13]. High-resolution solid-state ^{13}CNMR spectroscopy revealed that the stereocomplex precipitated from dilute acetonitrile solution was composed of four regions: rigid stereocomplex crystalline region, disordered stereocomplex crystalline region, trace amounts of homo-crystalline region, and non-crystalline region [32]. Vibrational mobility of PLLA and PDLA in stereocomplex was studied by Kister et al. [33] using Raman and IR spectroscopy. Li and Vert [34,35] showed that stereocomplexation of statistic copolymers from D- and L-lactides would occur during hydrolysis by predominant scission and preferable removal of the chains having relatively random sequences of D- and L-lactide units, leaving the chains of long isotactic sequences of D- and L-lactide units.

In spite of plenty of information accumulated on PLA stereocomplexation, there has been few reports on mechanical properties of PLA stereocomplexes. Exceptions are the tensile properties of blend fibers from PLLA and PDLA, but they contain both stereocomplex crystallites and homo-crystallites [20]. Improved mechanical properties of PLLA and PDLA blends compared to non-blended materials were reported in a patent article without detailed estimation of molecular characteristics of the polymers and the content of respective crystalline species in the specimens [36]. We found that a 1:1 blend film prepared through solution-casting of PLLA and PDLA having a viscosity-average molecular weight (M_v) of $2–4 \times 10^4$ and containing solely stereocomplex crystallites, exhibited tensile strength higher than that of non-blended PLLA or PDLA film. However, any reason for the higher strength of blend films has not been proposed so far.

The purpose of the present work is to investigate mechanical properties of blended and non-blended films prepared from PLLA and PDLA having a wide range of molecular weight and to find the reason for the difference in mechanical properties between blended and non-blended films. For

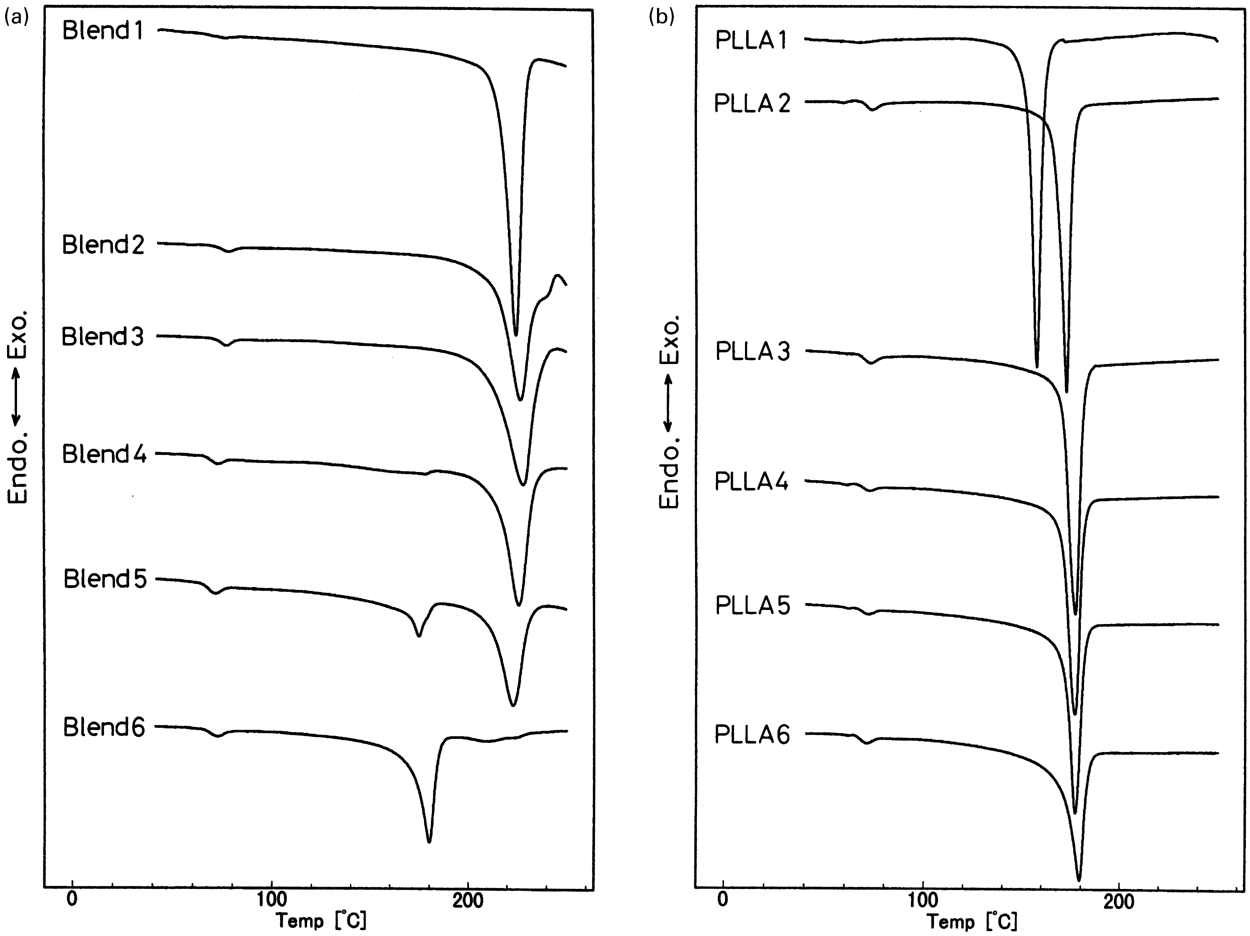

Fig. 1. DSC thermograms of (a) 1:1 blend films; and (b) non-blended PLLA films.

this purpose blended and non-blended films are prepared by casting the solutions from PLLA and PDLA having a weight-average molecular weight (M_w) from 1.0×10^4 to 1.0×10^6, as the critical highest molecular weight below which only stereocomplex crystallites are formed is higher for solution-casting ($M_v = 4 \times 10^4$) [13] than for melt-crystallization ($M_v = 6 \times 10^3$) [16] and melting at high temperatures in the melt-crystallization procedure may lower the polymer molecular weight and change the monomer unit sequences by intermolecular transesterification between PLLA and PDLA. Their mechanical properties and morphology are investigated without any drawing and heat treatment of film specimens using tensile tests, dynamic mechanical relaxation measurements, and polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray diffractometry.

2. Experimental

2.1. Materials

Synthesis and purification of PLLA and PDLA used in this work were described in previous articles [10–16,37,38]. Ring-opening polymerization of D- and L-lactides was performed in bulk at 140°C using stannous octoate (0.03 wt.%) and lauryl alcohol as a polymerization catalyst and initiator, respectively [37,38]. Polymerization conditions and molecular characteristics of PLLA and PDLA utilized in this study are listed in Table 1. Films used for physical measurements and optical observation were prepared with the method described in previous articles [13,18,23]. Briefly, each solution of PLLA and PDLA was separately prepared to have a polymer concentration of 1.0 g/dl and then admixed with each other under vigorous stirring in the case of blended film preparation. Methylene chloride was used as a solvent and the mixing ratio of PLLA and PDLA was fixed to 1:1 unless otherwise specified. The solutions were cast onto petri-dishes, followed by solvent evaporation at room temperature for approximately 1 week. To avoid reaching a dried state of quasi-equilibrium, solvent evaporation was performed very slowly as in previous articles [13,18,23]. The resulting films were dried in vacuo for 1 week and stored at room temperature for more than 1 month to approach the equilibrium state prior to physical measurements.

A series of 1:1 blends obtained from polymer pairs of PLLA1 and PDLA1, PLLA2 and PDLA2, PLLA3 and

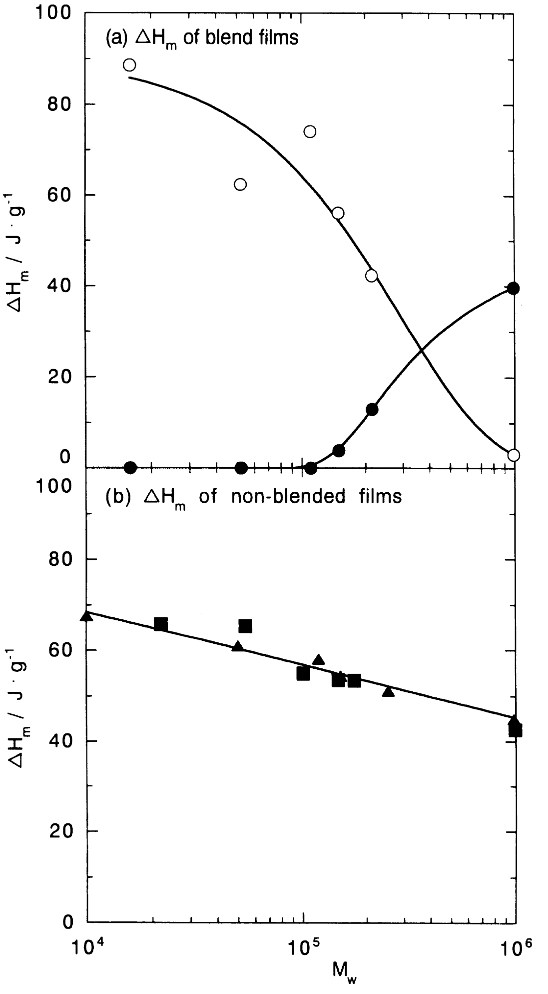

Fig. 2. ΔH_m of stereocomplex crystallites and homo-crystallites of (a) 1:1 blend films, and (b) non-blended PLLA and PDLA films as a function of M_w; where the symbols ○: stereocomplex crystallites in 1:1 blend films; ●: homo-crystallites in 1:1 blend films; ▲: homo-crystallites in non-blended PLLA films; ■: homo-crystallites in non-blended PDLA films.

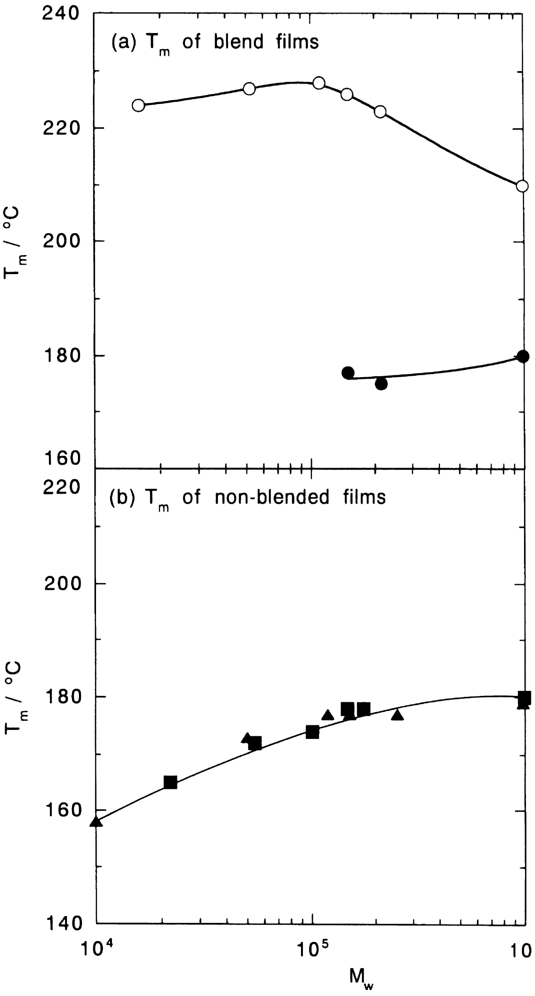

Fig. 3. T_m of stereocomplex crystallites and homo-crystallites of (a) 1:1 blend films and (b) non-blended PLLA and PDLA films as a function of M_w where the symbols ○: stereocomplex crystallites in 1:1 blend films; ●: homo-crystallites in 1:1 blend films; ▲: homo-crystallites in non-blended PLLA films; ■: homo-crystallites in non-blended PDLA films.

PDLA3, PLLA4 and PDLA4, PLLA5 and PDLA5, and PLLA6 and PDLA6 were abbreviated as Blend1, Blend2, Blend3, Blend4, Blend5, and Blend6 films, respectively. Appearance of the films was mostly opaque, except for PLLA1, PDLA1, Blend1, and Blend4, and Blend5 films (whitish) and Blend3 film (transparent). Tensile testing, dynamic mechanical relaxation and DSC measurements, and X-ray diffractometry were performed on films of 50 μm thickness while morphology study was performed on films of 25 μm thickness.

2.2. Physical measurements and optical observation

M_w and the number-average molecular weight (M_n) of polymers were evaluated in chloroform at 40°C using a Tosoh GPC system with TSK gel columns ($GMH_{XL} \times 2$) and polystyrene as a standard. Specific optical rotation $[\alpha]$ of polymers was measured in chloroform solution at a concentration of 1 g/dl and 25°C using a JASCO DIP-140 polarimeter at a wavelength of 589 nm.

Melting and glass transition temperatures (T_m and T_g respectively) and enthalpy of melting (ΔH_m) were determined with a Shimadzu DT-50 differential scanning calorimeter. Films were heated at a rate of 10°C/min under a nitrogen gas flow for DSC measurements. T_m, T_g, and ΔH_m were calibrated using tin, indium, and benzophenone as standards. Tensile properties of 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. Dynamic mechanical analysis of films was performed using an Orientec Rheovibron DDV-01F at 35 Hz and a heating rate of 4°C/min.

X-ray diffractometry was performed at 25°C using a Rigaku RINT-2500 equipped with a CuKα source. Morphology of films was studied with a Zeiss polarizing microscope.

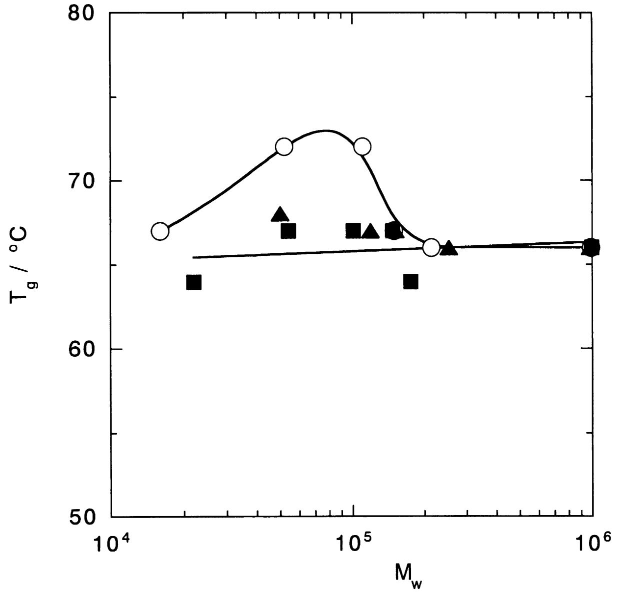

Fig. 4. T_g of 1:1 blend films (○), non-blended PLLA films (▲), and non-blended PDLA films (■) as a function of M_w.

3. Results

3.1. Thermal Properties

Fig. 1(a) and (b) shows DSC thermograms of 1:1 blend and non-blended PLLA films, respectively. The result of non-blended PDLA films is not given in Fig. 1, because the DSC thermograms of non-blended PDLA films were exactly comparable with those of non-blended PLLA films. The endothermic peaks noticed around 180 and 220°C can be assigned to melting of PLLA homo-crystallites and stereocomplex crystallites, respectively [10,11]. It is obvious that Blend1, Blend2, and Blend3 films with M_w lower than 1.0×10^5 exhibit only the melting peak of stereocomplex crystallites while Blend4, Blend5, and Blend6 films with M_w higher than 1.5×10^5 have two melting peaks of stereocomplex crystallites and homo-crystallites. However, all the non-blended PLLA films have only the melting peak of homo-crystallites.

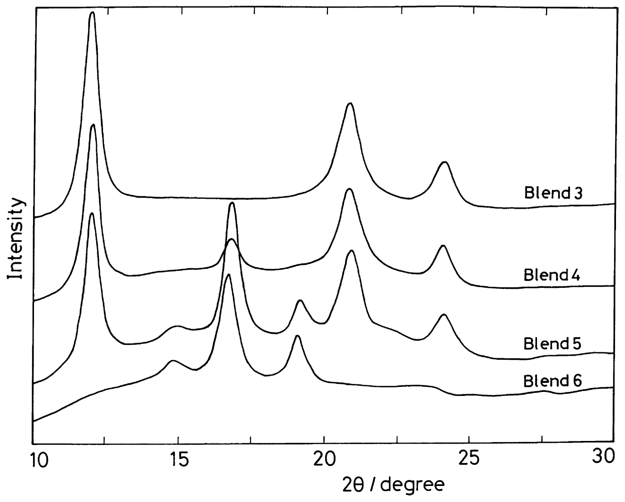

Fig. 5. X-ray diffraction profiles of 1:1 blend films.

The ΔH_m and T_m values of blend and non-blended films are plotted as a function of M_w in Figs. 2 and 3, respectively. M_w of blend films was obtained by arithmetically averaging M_w of PLLA and PDLA. It is clear from Fig. 2(a) that predominant stereocomplexation occurs in blend films when the M_w of both the isomers is low. The strong effect of M_w on stereocomplexation is peculiar to the blends between enantiomeric PLAs as reported earlier [12–16]. The critical value of M_w below which solely the stereocomplex crystallites form is approximately 1.0×10^5. This value is 2–3 times as high as 4×10^4 expressed in M_v [13]. Obviously, with a rise in M_w, ΔH_m of stereocomplex crystallites of blend films decreases while that of homo-crystallites increases. However, ΔH_m of homo-crystallites of non-blended films decreases gradually (Fig. 2(b)).

As seen from Fig. 3(a) T_m of stereocomplex crystallites of blend films has a maximum at a M_w of around 1.0×10^5, while T_m of homo-crystallites monotonously increases with the increasing M_w. This suggests that the crystalline thickness of the stereocomplex crystallites in blend films becomes the highest at a M_w of around 1.0×10^5, if the chain orientation disorder in the crystallites is assumed to be independent of M_w. The decreased T_m of blend films at M_w higher than 1×10^5 may be as a result of incomplete growth of stereocomplex crystallites by the following homo-crystallization. However, T_m or the crystalline thickness of the homo-crystallites in non-blended films and blend films increases with the increasing M_w (Fig. 3(a) and (b)). This is the normal dependence of T_m on M_w observed for conventional polymers.

Fig. 4 shows T_g of blend and non-blended films estimated from the DSC results as a function of M_w. T_g of PLLA1 is not given in Fig. 4 because of its too small glass transition peak. Non-blended PLLA and PDLA films have approximately a constant T_g of around 65°C. T_g of blend films is 5°C higher than that for non-blended films with M_w in the range 5×10^4–1×10^5, where predominant stereocomplexation occurs in the blend films. T_g of blend films is comparable with that of non-blended films at M_w higher than 2×10^5. This high T_g of blend films with M_w in the range 5×10^4–1×10^5 suggests that the L- and D-lactide chains are well mixed even in amorphous region and that chains in the amorphous region of blend films are more densely packed than those of non-blended films. However, a small difference in T_g between blended and non-blended films at $M_w > 2 \times 10^5$ implies that L- and D-lactide chains are phase-separated in the amorphous region.

3.2. X-ray diffractometry

X-ray diffraction profiles of Blend3, Blend4, Blend5, and Blend6 films are shown in Fig. 5. The result of Blend1 and Blend2 films is not given in Fig. 5, because their X-ray

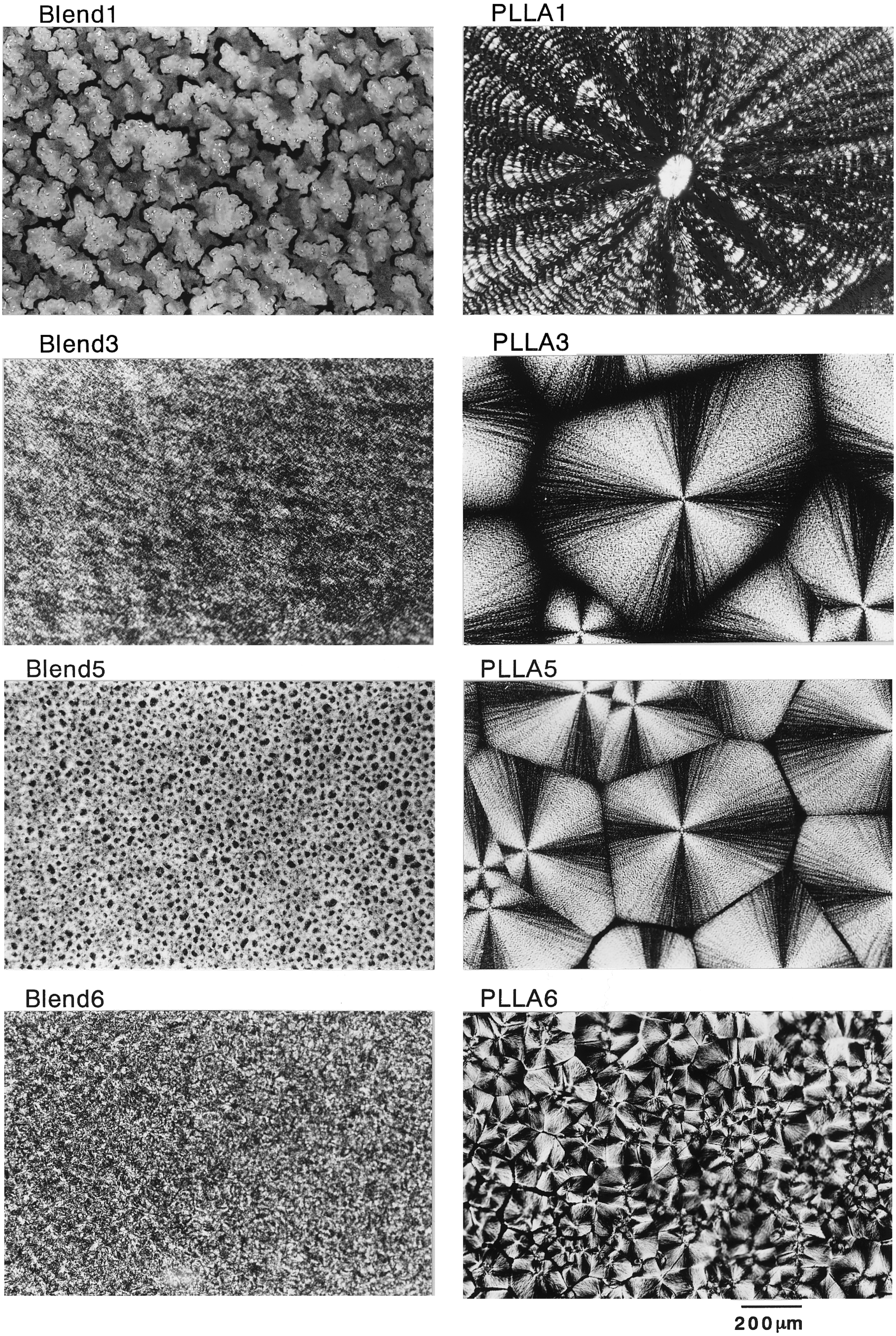

Fig. 6. Representative polarizing microscopic photographs of 1:1 blend films and non-blended PLLA films.

diffraction profiles are in good agreement with that of Blend3 film. The most intense peaks of Blend3 film are observed at 2θ values of 12°, 21° and 24°, in excellent agreement with the reported results [10,11,27,33] for PLA stereocomplex crystallized in a triclinic unit cell of dimensions: $a = 0.916$ nm, $b = 0.916$ nm, $c = 0.870$ nm, $\alpha = 109.2°$, $\beta = 109.2°$, and $\gamma = 109.8°$, in which L-lactide and D-lactide segments are packed parallel taking 3_1 helical conformation [30]. The main peaks of Blend6 film appear at 2θ equals to 15°, 17°, and 19°, [10,11,27,33], which are comparable with the results for the α form of PLLA crystallized in a pseudo-orthorhombic unit cell of dimensions; $a = 1.07$ nm, $b = 0.595$ nm, and $c = 2.78$ nm, which contains two 10_3 helices [30]. This suggests that PLLA and PDLA in Blend6 film underwent separate crystallization into respective homo-crystallites. However, Blend4 and Blend5 films show diffraction peaks of crystallites of PLA stereocomplex and α form of PLLA, revealing that three crystalline species, homo-crystallites of PLLA and PDLA and stereocomplex crystallites are present in these blends of films. These results are in good agreement with those obtained by DSC measurements, except for Blend6 film. This reveals that stereocomplex crystallites were formed in Blend1, Blend2, Blend3, Blend4, and Blend5 films during solvent evaporation but not during heating in DSC measurements. The absence of diffraction peaks characteristic to stereocomplex crystallites in Blend6 film may be as a result of their very small amount as revealed by DSC measurement. This result also confirms that the predominant formation of stereocomplex crystallites occurs in the blend solution when the M_w of both the isomers is low.

3.3. Morphology

Typical examples of polarizing optical photomicrographs of blend and non-blended films with different M_w are shown in Fig. 6. It is seen that non-blended PLLA films are composed of normal spherulites, irrespective of their molecular weight, whereas not spherulites but microcrystallites alone are noticed for all the blend films. This indicates that stereocomplexation is not accompanied by spherulite formation and that nucleus density of stereocomplex micro-crystallites in blend solution is higher than that of spherulites of homo-crystallites in non-blended solution. The spherulite radius of non-blended films decreases from 1000 to 100 μm when M_w increases from 1.0×10^4 to 1.0×10^6. This is probably owing to increase in nucleus density of the spherulites of PLLA having high M_w during solvent evaporation. Gaps and pores both with a size of10–30 μm are observed for Blend1 and Blend5 films. A significant difference in film shrinkage during solvent evaporation was observed between blend and non-blended films. For instance, Blend3 film showed the diameter shrinkage of 15% from the inside diameter of petri-dish while non-blended PLLA3 and PDLA3 films shrank by only 3%. This suggests that the stereocomplexation in blend solution occurred at lower polymer concentration than crystallization in non-blended solution.

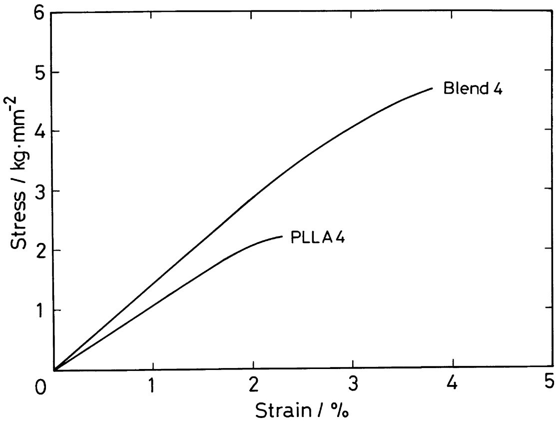

Fig. 7. Stress–strain curves for Blend 4 film and non-blended PLLA4 film.

3.4. Tensile properties

Fig. 7 shows stress–strain curves for Blend4 and non-blended PLLA4 films. As evident from Fig. 2(a), stereocomplex crystallites are the main crystalline species in Blend4 film with M_w of 1.5×10^5. The tensile strength, Young's modulus, and elongation-at-break are higher for Blend4 film than for non-blended PLLA4 film. Fig. 8(a)–(c) show the tensile strength, Young's modulus, and elongation-at-break, respectively, for blend and non-blended films as a function of M_w. The yield stress is not given here, as it was comparable with that of tensile strength for all the films. Tensile properties are not null for the films of M_w higher than 1.0×10^5. As is evident from Fig. 8 tensile properties of these blends of films are higher than those of non-blended films in the M_w range of 1.0×10^5–1.0×10^6. Comparison between Fig. 8 and Fig. 2(a) shows that increased mechanical properties are observed for blend films containing stereocomplex crystallites. Tensile strength of Blend3, Blend4, and Blend5 films with M_w of 1.0–2.5×10^5, Young's modulus of Blend3 film with M_w of 1.0×10^5, and elongation-at-break of Blend6 film with M_w of 1.0×10^6 are twice as high as those of respective non-blended films. It is interesting to note that the tensile strength of blended films reaches a plateau at M_w of 1.5×10^5 while that of non-blended films still increases gradually with a rise in M_w up to 1×10^6 and that the tensile strength and Young's modulus of films with $M_w > 1.5 \times 10^5$ are higher than or similar to those of non-blended films with M_w of 1.0×10^6. For Blend2, a film with a size larger than 5 × 5 mm^2 could be obtained in contrast to non-blended PLLA2 and PDLA2 films, which could not produce any film with a size larger than 1 mm, probably because of isolated spherulite formation. Blend2 film was, however, too brittle and weak to cut into any rectangular shape needed for tensile measurements.

Tensile strength (3.4 kg/mm^2), Young's modulus

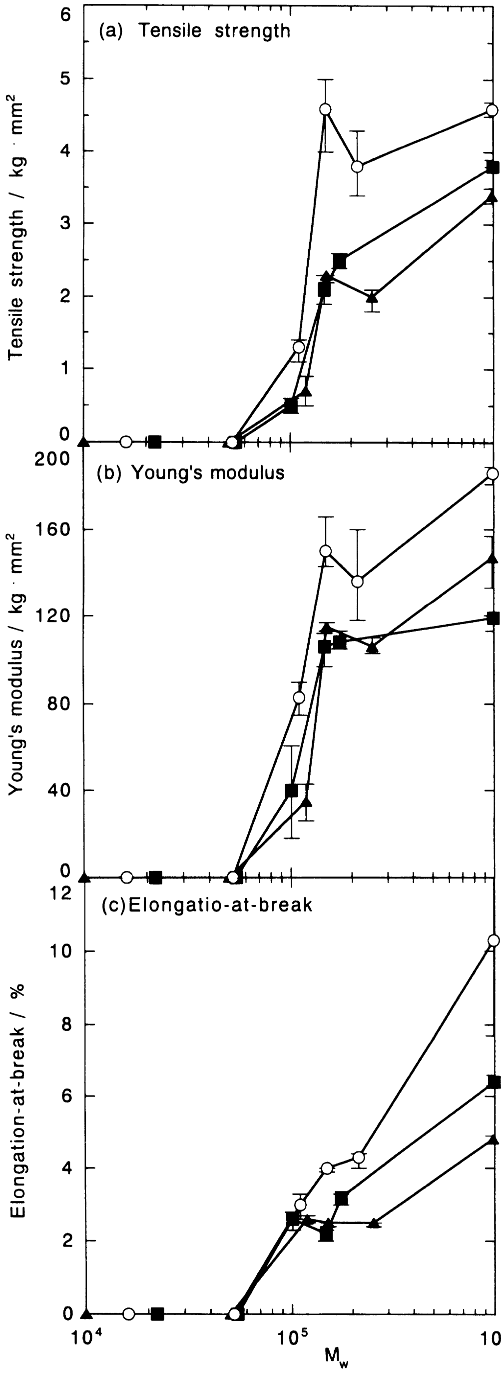

Fig. 8. (a) Tensile strength, (b) Young's modulus, and (c) elongation-at-break of 1:1 blend films (○), non-blended PLLA films (▲), and non-blended PDLA films (■) as a function of M_w.

(147 kg/mm^2), and elongation-at-break (5%) of non-blended PLLA6 film with M_w of 1.0×10^6 are lesser than 5.0 kg/mm^2, 181 kg/mm^2, and 85%, respectively, of non-blended PLLA film prepared under rapid solvent evaporation for one day from PLLA having M_w similar to PLLA6 ($M_w = 1.3 \times 10^6$, $M_w/M_n = 2.2$) [39]. The tensile strength (4.6 kg/mm^2) and Young's modulus (186 kg/mm^2) of Blend6 film are comparable with those of non-blended PLLA films prepared under rapid solvent evaporation, though elongation-at-break of Blend6 film (10%) is lower than that of rapidly prepared non-blended PLLA film [39]. The highest tensile strength of blended films (5.0 kg/mm^2) agrees very well with that reported by Murdoch and Loomis [36] for the blended film solution-cast using chloroform as a solvent but is by an order of magnitude smaller than that of the drawn solution-spun blend fiber (94 kg/mm^2). This is probably owing to higher chain orientation in the blended fiber [20].

3.5. Dynamic mechanical properties

The storage modulus (G') and loss tangent (tan δ) of 1:1 and 1:3 blend films from PLLA3 and PDLA3 and non-blended PLLA3 film are given in Fig. 9. We could not measure G' and tan δ for non-blended PLLA3 film above 100°C owing to high brittleness. Probably, the large spherulites present in the film (Fig. 6) may have reduced its toughness required for the dynamic measurements at high temperatures. 1:1 and 1:3 blend films from PLLA3 and PDLA3 contained solely the stereocomplex crystallites and both the stereocomplex crystallites and homo-crystallites (ΔH_m of stereocomplex crystallites = 36 J/g and ΔH_m of homo-crystallites = 21 J/g), respectively, while non-blended PLLA3 had the homo-crystallites alone. The peaks of tan δ around 80°C and 170°C are assigned to the glass transition of PLLA and PDLA and the melting of homo-crystallites of PLLA, respectively [40–43]. G' of blended and non-blended films decrease monotonously above 60°C, and a dramatic decrease occurs above 150°C and 200°C for 1:3 blend film and above 200°C for 1:1 blend film. The decrease in G' above 60, 150, and 200°C is ascribed to the glass transition, melting of homo-crystallites, and melting of stereocomplex crystallites, respectively. G' becomes higher as the mixing ratio approaches 1:1 when compared at a similar temperature above 60°C.

4. Discussion

The present study has revealed that blend films which are rich in stereocomplex crystallites have better tensile properties than non-blended films rich in homo-crystallites. Another interesting finding is that non-blended films contains typical spherulites whereas blended films are lacking in large-sized spherulite in the polarizing microscopic photographs. It is very likely that the difference in tensile properties between blended and non-blended films is closely related to the different morphology of these two films. A very simplified presentation of the micro-phase structure is depicted in Fig. 10, which may explain the mechanical and morphological difference between blended and non-blended films. In Fig. 10, a small amount of homo-crystallites present in blend films are neglected for simplicity.

As the polymer component responsible for the tensile properties of these films is primarily the tie chain connecting

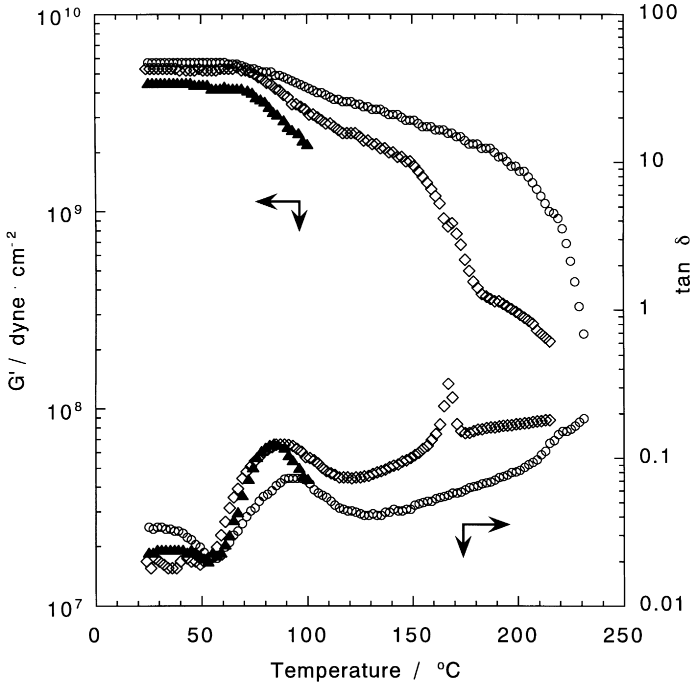

Fig. 9. Storage modulus (G') and loss tangent (tan δ) for 1:1 blend film (○) and 1:3 blend film (◇) from PLLA3 and PDLA3, and non-blended PLLA3 film (▲).

homo-crystallites or stereocomplex micro-crystallites with each other, may be reasonable to assume that a high density of tie chains will result in better mechanical properties. It seems probable that the materials made of crystalline PLAs with $M_w < 5 \times 10^4$ have practically no tie chain as their tensile strength is very close to zero. This is also supported by the photomicrographs in Fig. 6. The density of tie chains may increase with the increasing M_w.

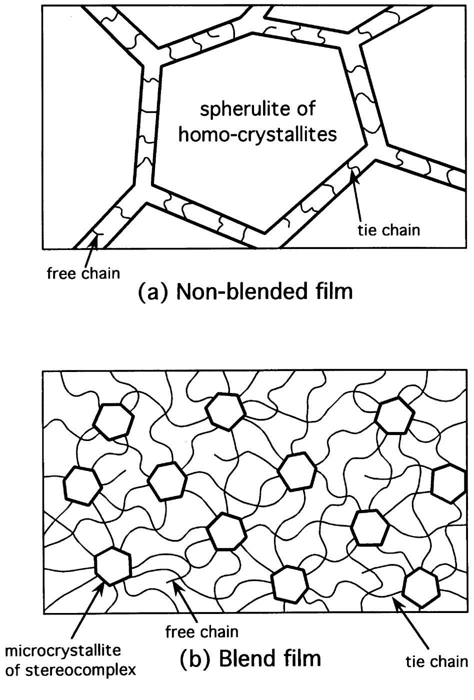

Fig. 10. Presumed micro-phase structure of non-blended and blended films from PLA with medium M_w.

The suppressed formation of spherulites in blended films may be ascribed to 3D gelation occurring quite readily in blended solutions as a result of formation of stereocomplexed micro-crystallites. They act as cross-links in the course of solvent evaporation [12,13]. This phenomenon was reported in a previous article for concentrated mixed solutions of PLLA and PDLA with an average $M_v < 4.4 \times 10^4$ [12]. Gelation of blended solutions takes place during solvent evaporation partly because the lowest critical concentration for crystallization is lower for stereocomplex crystallites than for homo-crystallites of PLLA and PDLA. Lower critical concentration of stereocomplex crystallites suggests that stereocomplexation is thermodynamically more favourable than homo-crystallization. Occurrence of 3D gelation at low concentrations indicates that high density of nuclei of stereocomplex crystallites simultaneously form under existence of a high density of tie chains between the stereocomplex crystallites. However, in spherulite formation, crystallization proceeds concentrically from the low density nuclei of homo-crystallites. Intermolecular crystallization seems to dominate in stereocomplexation upon blending of PLLA and PDLA, in contrast to homo-crystallization in the solution of PLLA or PDLA [12]. Intermolecular crystallization in blend solution will result in increased tie chains between the crystallites. The relatively high density of tie chains in blended films may be one of the cause of their excellent mechanical properties. A significant difference in shrinkage between blended and non-blended films with M_w of 1.0×10^5 as well as the gap formation in

Blend1 film with M_w of 1.6×10^4 support that 3D gelation occurred through stereocomplexation for the blend solutions at a concentration lower than those of PLLA and PDLA in non-blended solutions. Formation of pores with a diameter around 10–30 μm observed for Blend5 film may be ascribed to phase separation into concentrated and dilute regions after gelation.

Another reason for the superiority of blend films in tensile strength, Young's modulus, and elongation-at-break to non-blended in the M_w range of $1.0–2.1 \times 10^5$ can be explained in terms of micro-phase structure formed upon 3D gelation without formation of large-sized spherulites. PLLA films having large spherulites is reported to have poor mechanical properties [39]. The slight decrease in tensile strength and Young's modulus observed for Blend5 film may be owing to the formation of porous structure, as seen in Fig. 6. The increased tensile properties of blend films may be also caused by dense chain packing in the amorphous region owing to strong interaction between L- and D-unit sequences. The increased T_g observed for blend films with M_w of $5 \times 10^4–1 \times 10^5$ also supports this dense chain packing in the amorphous region of blend films (Fig. 4). Tensile properties of Blend6 film were much better than those of non-blended PLLA6 and PDLA6 films, although a very small amount of stereocomplex crystallites were observed in Blend6 film. This is also explained by the suppressed formation of large-sized spherulites as a result of formation of stereocomplex crystallites which precedes that of homo-crystallites.

The dynamic mechanical measurements exhibited higher thermal resistance of blended films than that of non-blended films. This implies that the difference in tensile properties observed between blended and non-blended films would become more remarkable if they were measured above T_g.

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