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Effect of the addition of poly(D-lactic acid) on the thermal property of poly(L-lactic acid)

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Abstract

Thermal property and crystallization behavior of PLLA blended with a small amount of PDLA (1–5 wt%) were studied. PDLA molecules added in PLLA formed stereocomplex crystallites in the PLLA matrix. When the blend was cooled to a temperature below T_m of PLLA, stereocomplex crystallites acted as nucleation sites of PLLA and enhanced the crystallization of PLLA significantly (heterogeneous nucleation). Such crystallization enhancement was not observed when the blend with lower PDLA content was cooled from 240 °C at which both PLLA crystal and the stereocomplex disappeared. Low molecular weight PDLA isolated in the matrix of PLLA did not form a stereocomplex crystallite with a large surface area enough to act as a nucleation site. On the other hand, high molecular weight PDLA chains formed a large stereocomplex crystallite. With increasing PDLA content, stereocomplex crystallites were more easily formed and they acted as nucleation sites. PLLA crystal near the stereocomplex crystallites has an incomplete structure and showed a melting peak at a lower temperature than pure PLLA crystal.

Keywords: Poly(lactic acid); Stereocomplex; Thermal property

1. Introduction

Poly(L-lactic acid) (PLLA) is a crystalline polymer having its T_m around 180 °C. This polymer is known to be a biocompatible and biodegradable polyester derived from renewable resources. Because of these characters, PLLA has been utilized for surgical implant materials and drug delivery systems as well as ecological materials. However since the hydrolytic degradation rate of highly oriented PLLA products with a high crystallinity is rather low and they can keep their shape and mechanical properties for more than a year [1], PLLA is expected to be utilized for general purpose materials such as textile fibers and films.

Ikada et al. [2] first reported that the 1/1 blend of PLLA and poly(D-lactic acid) (PDLA), which is an enantiomer of PLLA, produces a stereocomplex with T_m around 230 °C. While pure PLLA and PDLA crystallize in orthorhombic form with 10/3 helix in their conformation [3], the stereocomplex has a triclinic form with 3/1 helix [4,5]. Asymmetric blends can include both homopolymer and stereocomplex crystallization. Since this first report, they intensively studied the effects of various parameters including blending ratio [6–12], molecular weight [6–9], optical purity [10,11], and blending condition [6,8–10] on the stereocomplexation between PLLA and PDLA. Brochu et al. [10] investigated the crystallization behavior in asymmetric PLLA/PDLA blends and demonstrated that the stereocomplexation occurs with as little as 10 wt % PDLA. Schmidt et al. [12] also reported the crystallization behavior in asymmetric blends of PLLA/low molecular weight PDLA. Both researchers stressed on the roll of stereocomplex as a nucleating agent.

This sort of stereocomplexation has been reported for various other polymer couples including poly(γ-benzyl glutamate) [13–24], poly(γ-methyl glutamate) [25], poly(*tert*-butylthiirane) [26], poly(*tert*-butylethylene oxide) [27], poly(*tert*-butylethylene sulfide) [28], poly(α-methyl-α-ethyl-β-propiolactone) [29–31], poly(β-(1,1-dichloro-propyl)-β-propiolactone) [32], and poly(α-methlbenzyl methacrylate) [33]. Most of these polymers have their chiral carbons in the main chain.

At a temperature between T_m of PLLA and PDLA homo crystals and that of stereocomplex, only stereocomplex

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exists and is embedded in the molten mixture of PLLA and PDLA. This stereocomplex would act as a physical crosslinking point and the blend is expected to be either a melt, an elastomer or a plastic depending on the fraction of stereocomplex exists.

In this study, 1–5 wt% of PDLA was blended with PLLA. PDLA content was so low that the stereocomplex could not either be a continuous phase or act as crosslinking points which connect all PLLA molecules. Resulting blends were molten viscous liquids even at a temperature between T_m of PLLA and that of stereocomplex. The effects of the PDLA content and the molecular weight of PDLA on the crystallization behavior and the thermal property of PLLA were investigated.

2. Experimental

2.1. Materials

PLLA was supplied by Shimadzu corporation (Lacty, $M_w = 1.8 \times 10^5$). PDLAs with three different molecular weights ($M_w = 4.5 \times 10^4$, 1.2×10^5, and 2.6×10^5) were synthesized through a ring opening polymerization of D-lactide using tin octanoate as a catalyst. PLLA and PDLA were dissolved in chloroform separately and were solution blended. 5 wt% of acetic anhydride was added to the solution to endcap the hydroxyl terminal groups. The blends were either reprecipitated with diethyl ether for DSC measurements or cast on a glass plate for optical microscope observations and dried in vacuo.

2.2. Thermal analyses

Thermal property of the blends were examined with a DSC (DSC3100, Mac Science) under N_2 atmosphere. About 5 mg of sample was placed in an aluminum pan. DSC scans were obtained in the cooling processes from 200 and 240 °C to the room temperature and in the following second heating process to 240 °C. Cooling and heating rates were set to be 2 and 10 °C/min, respectively.

2.3. Isothermal crystallization

Isothermal crystallization behavior at 120 °C after quenching from 200 and 240 °C was observed with a polarized optical microscope (OPTIPHOTO-2POL, Nikon) equipped with a hot stage (FP82HT, Mettler). Blend films prepared by casting from chloroform solution were heated up to 200 and 240 °C and held at these temperatures for 5 min before quenching to 120 °C. Growth of the spherulites was recorded on a video tape.

3. Results and discussion

3.1. Thermal properties

Ikada et al. [2] reported that the thermal property of PLLA/PDLA blends with various blend ratios. Although amount of stereocomplex produced was the highest in an equimolar blend, a small and broad melting peak was observed around 220 °C as well as a peak around 180 °C even in the DSC trace for the blend containing only 10 wt% of PDLA. Similar results was also obtained by Brochu et al. [10] and proposed that the stereocomplex formed initially acts as a nucleation site for PLLA through epitaxial crystallization.

Fig. 1(a)–(c) show the DSC curves of PLLA/PDLA blends (M_w of PDLAs are (a) 4.5×10^4, (b) 1.2×10^5 and (c) 2.6×10^5, respectively) and a pure PLLA obtained in cooling processes from 200 and 240 °C. When pure PLLA and PLLA/PDLA blends were cooled from 200 °C, they showed fairly clear crystallization exothermic peaks. These peaks tended to be larger and appeared at higher temperature with increasing PDLA content. On the other hand, pure PLLA and blends cooled from 240 °C showed only a small and broad crystallization peak and the peak temperature was independent of PDLA content, except for the PLLA/PDLA = 95/5 blend with lower M_w PDLA.

Crystallization temperatures, T_c, observed for the blends and a pure PLLA in cooling processes from 200 and 240 °C are plotted in Fig. 2(a) and (b), respectively, as functions of PDLA content. It is clear from Fig. 2(a) that 1 wt% of PDLA added produced the stereocomplex and enhanced the crystallization of PLLA when cooled from 200 °C. Such effect seems to be more significant for the blend containing PDLA with higher M_w. Similar tendency was also obtained for crystallization peak area plotted in Fig. 3. Crystallization peak area increased with PDLA content when PDLA content was very low and tended to level off at higher PDLA content. This tendency was opposite to the results obtained by Brochu et al [10] and Schmidt et al [12]. Both researchers reported that the extent of PLLA crystallization was reduced in the presence of stereocomplex and explained that the crystallization of PLLA is hindered due to the difficulty in transporting the chain segments to the crystallization site because of the presence of stereocomplex lamellae and spherulites. However, Brochu et al. [10] found for the blends of PLLA and PDLA with a low optical purity that the enthalpy of fusion of PLLA was close to that calculated on the basis of the amount which was not incorporated into the stereocomplex. The discrepancy between our results and those reported by Brochu et al [10] and Schmidt et al [12] may be attributable to much higher PDLA content and lower M_w of PDLA utilized (M_w of PDLA = 14,000) in their studies.

When the blends were heated up to 240 °C, the stereocomplex no longer existed and enhancement of the crystallization was only observed in the blends with 5 wt%

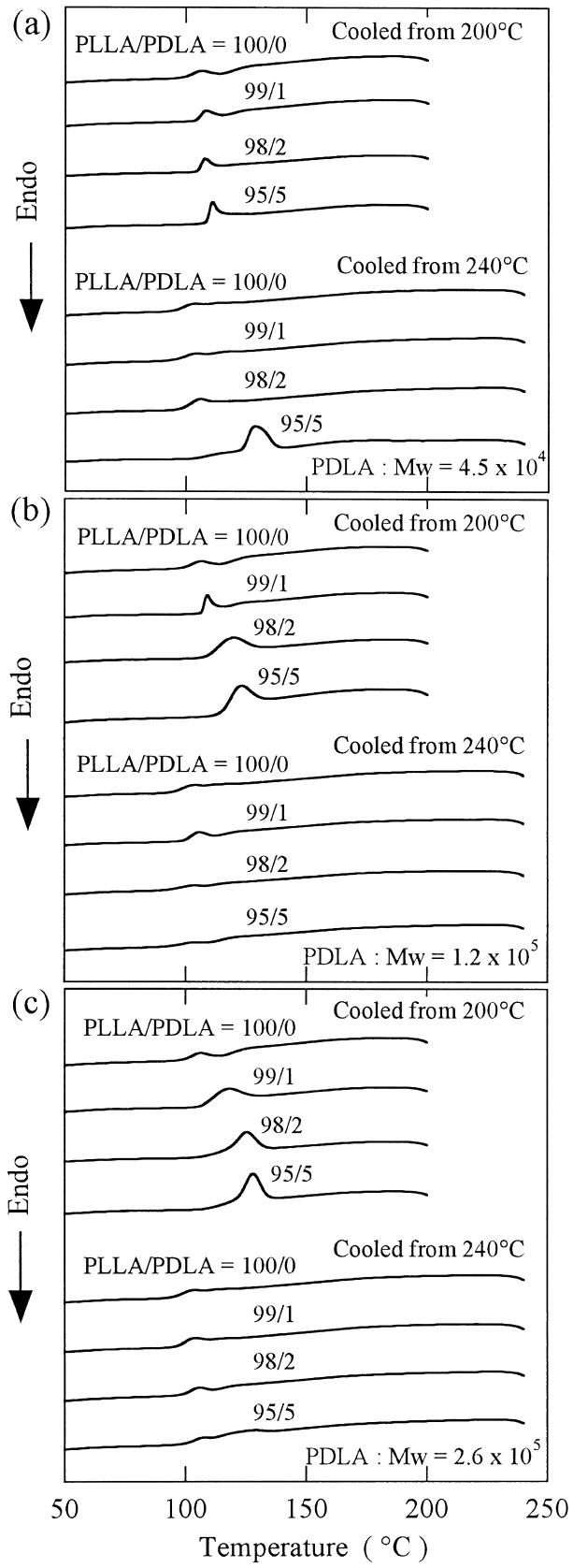

Fig. 1. DSC curves of PLLA/PDLA blends in the cooling processes from 200 and 240 °C. Molecular weights of PDLA are 4.5×10^4 (a), 1.2×10^5 (b) and 2.6×10^5 (c), respectively.

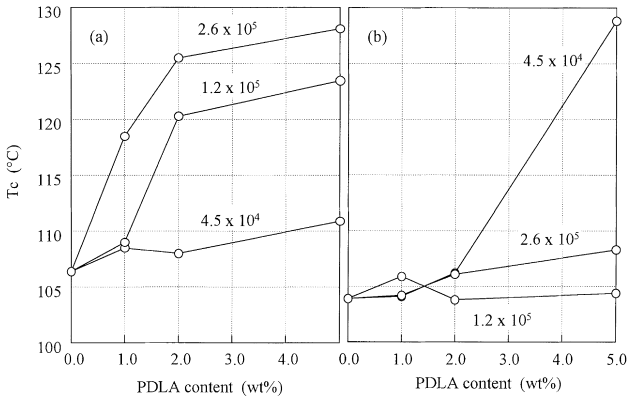

Fig. 2. Crystallization temperature, T_c, of PLLA/PDLA blends cooled from 200 °C (a) and 240 °C (b) as functions of PDLA content. Numbers in the figures are molecular weights of PDLA.

of PDLA. It should be noted that the blend with 5 wt% of low M_w PDLA showed a significantly higher Tc. This may be due to higher mobility and the larger number of PDLA chains which allowed rapid stereocomplex crystallization in a cooling process from 240 °C. These stereocomplex crystallites acted as nucleation sites.

DSC curves obtained in the second heating process after cooling from 200 and 240 °C are shown in Fig. 4 (M_w of PDLAs are (a) 4.5×10^4, (b) 1.2×10^5 and (c) 2.6×10^5, respectively). Blends cooled from 240 °C showed a single melting peak around 170 °C while pure PLLA and blends once cooled from 200 °C showed double melting peaks below and above 170 °C. It is interesting to note that the area of both peaks depends on the PDLA content. The height ratio of lower temperature peak to higher temperature peak, DhH/DhL, decreased with the content and the molecular weight of PDLA as shown in Fig. 5. When the molecular weight of PDLA was lower than that of PLLA, the peak at higher temperature gradually became smaller

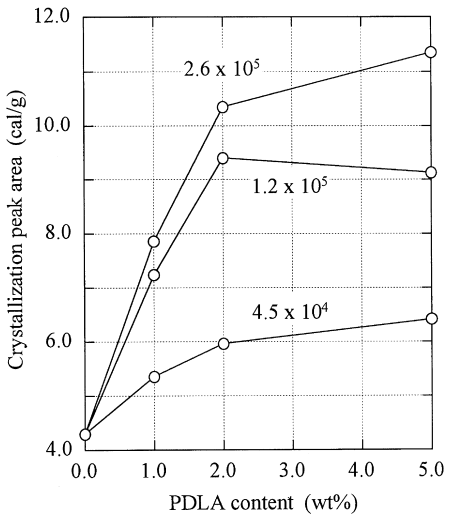

Fig. 3. Crystallization peak area of PLLA/PDLA blends cooled from 200 °C as functions of PDLA content. Numbers in the figures are molecular weights of PDLA.

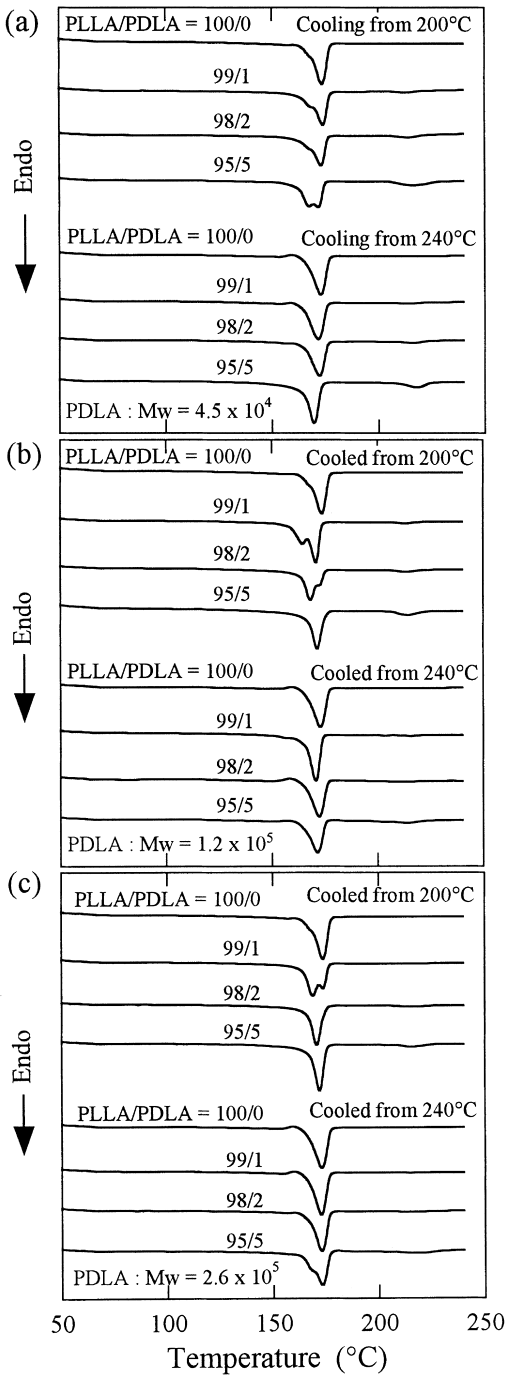

Fig. 4. DSC second heating curves of PLLAIPDLA blends. Molecular weights of PDLA are 4.5×10^4 (a), 1.2×10^5 (b) and 2.6×10^5 (c), respectively.

with increasing PDLA content. However when the molecular weight of PDLA was higher, the peak at higher temperature disappeared and only a peak at lower temperature was observed for the blend which contain more than 2 wt% of PDLA. These results suggest that the blends cooled from 200 °C contain two different types of PLLA crystal. One which melts at lower temperature is PLLA crystallized at the surface of a stereocomplex crystallite. The conformation of

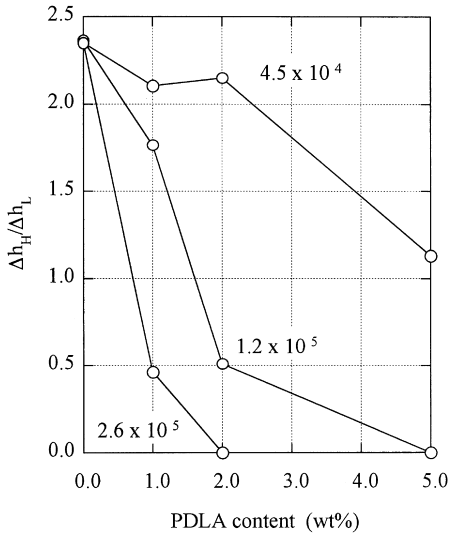

Fig. 5. Melting peak height ratio, $\Delta h_H/\Delta h_L$, of PLLA/PDLA blends as functions of PDLA content. Numbers in the figures are molecular weights of PDLA.

PLLA molecule in the stereocomplex is 3/1 helix [3], while that in pure PLLA crystal is 10/3 helix [4,5]. This difference in conformation produces rather incomplete PLLA crystal at the surface of the stereocomplex. The other crystal which melt at higher temperature may be more stable and complete PLLA crystal.

Since the molecular weights of PLLA and PDLA used in the present study were much higher than those utilized by Brochu et al [10] and Schmidt et al.[12], the number of PDLA chains incorporated into the stereocomplex was rather small and the most PLLA chains far from PDLA chains have enough freedom for homocrystallization. Such free PLLA chains form a homo PLLA crystal which melt at a higher temperature and the PLLA chains partly incorporated into stereocomplex form rather imperfect homo crystal which melt at a lower temperature. Our DSC results indicated the fraction of the former decreased with PDLA content.

3.2. Crystallization behavior

Fig. 6 shows the polarized optical micrographs of the spherulites grown at 120 °C observed in the blends which contained PDLA with a molecular weight of 1.2×10^5 after quenched from 200 and 240 °C. When the blends were cooled from 200 °C, the size of the spherulites decreased and the number of the spherulites increased significantly with PDLA content. It is clear that the blends with higher PDLA content have a higher number of nucleation sites. These nucleation sites are stereocomplex crystallites with 3/1 helix in conformation and surrounded by PLLA crystalline phase. As seen in the previous section, the blends with higher PDLA content cooled form 200 °C showed a larger melting peak at a lower temperature. These photographs clearly indicate the role of stereocomplex as a nucleating

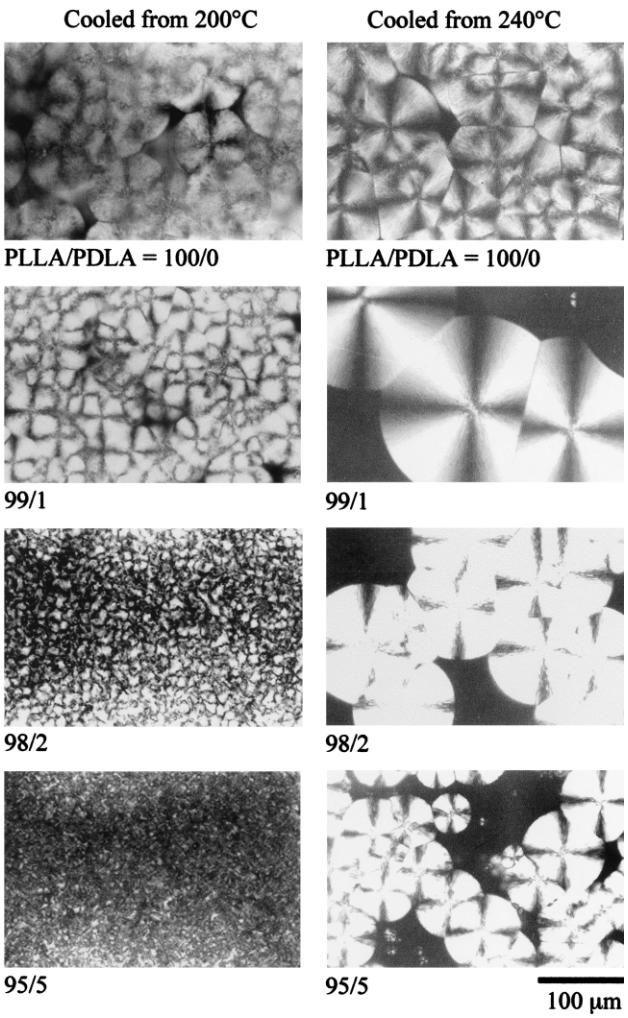

Fig. 6. Spherulitic morphology of PLLA/PDLA blends grown isothermally at 120 °C after cooling from 200 and 240 °C.

agent and the crystallization of homo PLLA was initiated in instantaneous homogeneous nucleation. On the other hand, the size of the spherulites was even larger in the blends cooled from 240 °C than those observed in the pure PLLA, especially when only 1 wt% of PDLA was added. It should be noted that the blend with 1 wt% of PDLA cooled form 240 °C formed larger uniform spherulites in size, while the blend with 5 wt% of PDLA formed small spherulites with various sizes. Once the blend was heated to the temperature above the melting point of the stereocomplex, no nucleation site was present. When the PDLA content is low (~1 wt%), isolated PDLA molecules may act as contaminant and excluded from PLLA spherulites. However at higher PDLA content, the size of the spherulites was not uniform. Tsuji and Ikada [11] studied the crystallization behavior of PLLA/PDLA equimolar blends. Blend composed of low molecular weight PLLA and PDLA (M_w of PLLA: 3.3×10^3, M_w of PDLA: 5.7×10^3) after quenched to 0 °C from 250 °C contained only stereocomplex crystal. At higher molecular weight (M_w of PLLA: 4.2×10^4, M_w of PDLA: 4.5×10^4 equivalent to M_w of PDLA used in the present study), quenched blend showed melting peaks of both homo and stereocomplex crystals in its DSC heating scan. However although stereocomplex crystallization was completed during quenching, homo crystallization still proceeded during annealing after quenching. Because of these results, Tsuji and Ikada [11] concluded that the stereocomplex crystallization is more favored than homo crystallization. Even in asymmetric blends, some stereocomplex crystallization occurred in advance of PLLA homo crystallization and part of PLLA crystal was initiated at stereocomplex crystallites as nucleation sites. However the number of stereocomplex crystallites was rather small and homo PLLA crystallization was initiated both at stereocomplex and at homo PLLA nucleation sites.

The effect of the addition of PDLA on the crystallization behavior can be demonstrated in Fig. 7 where the diameter of the spherulite is plotted against time. When the blends were cooled to 120 °C from 240 °C, Spherulite growth rate increased with PDLA content. However the spherulite grew much rapidly in the blend cooled from 200 °C. Fig. 8(a) and (b) are the spherulite growth rates in PLLA/PDLA blends plotted against PDLA content. When the blends were cooled from 240 °C, the spherulite growth rate was almost independent of or slightly increased with the PDLA content.

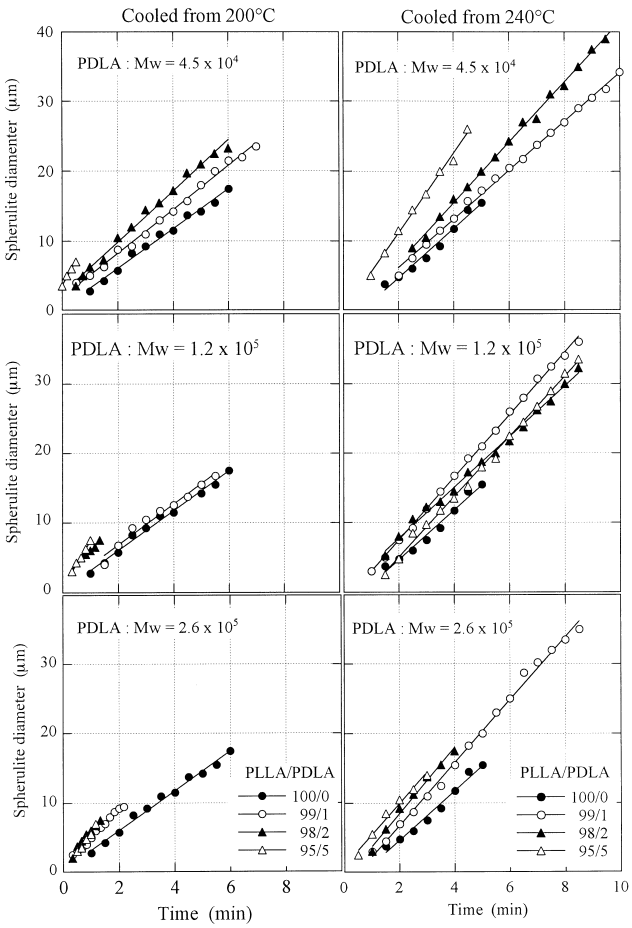

Fig. 7. Growth of spherulite in PLLA/PDLA blends cooled from 200 and 240 °C with time.

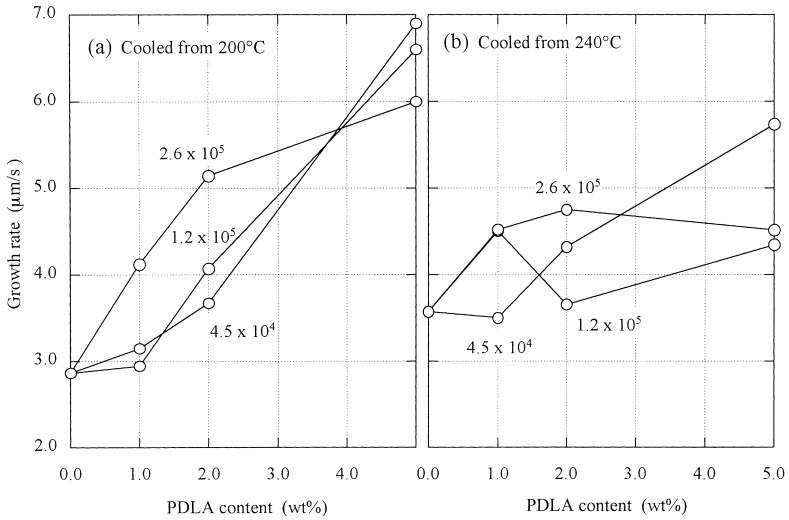

Fig. 8. Growth rate of spherulite in PLLA/PDLA blends cooled from 200 °C (a) and 240 °C (b) as functions of PDLA content. Numbers in the figures are molecular weights of PDLA.

However the spherulite growth rate increased with the PDLA content when the blends were cooled from 200 °C. Although the spherulite growth rate was higher in blends with higher M_w PDLA below 2 wt%, such a tendency became opposite and the spherulite growth rate was higher in the blend with lower molecular weight PDLA when the PDLA content was higher than 5 wt%.

Our experimental results on the thermal property measurements and the isothermal crystallization indicated that the stereocomplex in the PLLA matrix enhances the crystallization of PLLA. When the content of PDLA was low, the PDLA with a higher molecular weight acts as a more effective crystallization nucleating agent. However as the PDLA content increased, the PDLA with lower molecular weight became more effective. The speculated mechanisms of the stereocomplex formation and the effectiveness as a nucleating agent are schematically described in Fig. 9. When the PDLA content is low (~2 wt%), PDLA molecules are well dispersed in PLLA matrix and each PDLA molecule is away from a neighboring PDLA molecule. Because of the strong interaction between PLLA and PDLA molecules, PLLA and the isolated low molecular weight PDLA molecule may form small and imperfect stereocomplex. However isolated high molecular weight PDLA molecule may form a stereocomplex crystallite with a larger surface area enough to make surrounded PLLA molecules crystallize epitaxially although the number of stereocomplex crystallites is low. At higher PDLA contents, the blends contain a lot of stereocomplex crystallites. Since the low molecular weight PDLA chains have higher mobility than high molecular weight PDLA, they can form stereocomplex more easily.

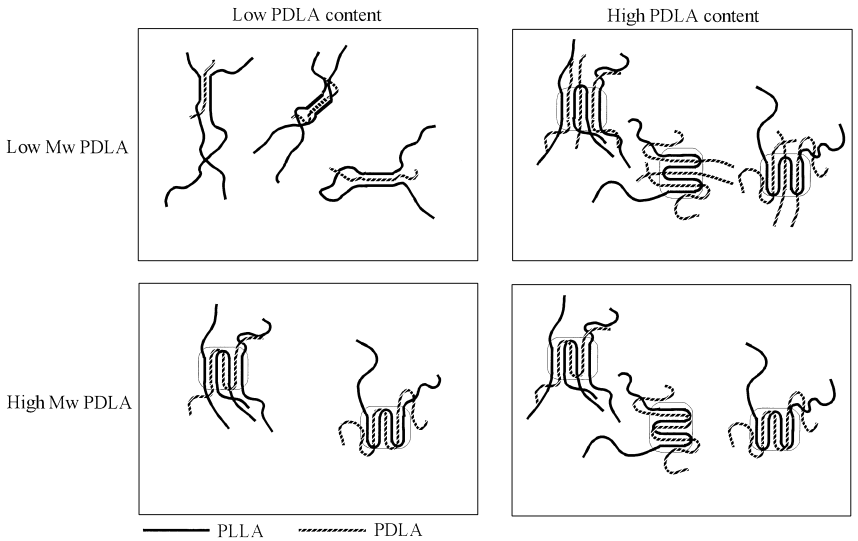

Fig. 9. Speculated mechanism of stereocomplex formation.

4. Conclusions

Thermal property and crystallization behavior of PLLA blended with a small amount of PDLA were studied. PDLA molecules added in PLLA formed stereocomplex crystallites in the PLLA matrix. Stereocomplex crystallites stayed unmelted at 200 °C and embedded in the PLLA molten matrix. Resulting blends were molten viscous liquids even at a temperature between T_m of PLLA and that of stereocomplex. When the blend was cooled to the temperature below T_m of PLLA, stereocomplex crystallite acted as a nucleation site of PLLA and enhances the crystallization of PLLA significantly (heterogeneous nucleation). Such enhancement of the crystallization was not observed when the blend with lower PDLA content was cooled from 240 °C at which both PLLA crystal and the stereocomplex disappear. In a blend with higher PDLA contents (~5 wt%), both heterogeneous nucleation by the stereocomplex formed during cooling process and homogeneous nucleation of PLLA occurred simultaneously resulting in the size distribution of spherulites.

Low molecular weight PDLA isolated in the matrix of PLLA cannot form a stereocomplex crystallite with a surface area large enough to act as a nucleation site. On the other hand, a high molecular weight PDLA chain can form a large stereocomplex crystallite. With increasing content of PDLA, stereocomplex crystallites are more easily formed and they can act as nucleation sites.

PLLA crystal near the stereocomplex crystallites has a incomplete structure and showed a melting peak at a lower temperature than pure PLLA crystal. Very small amount of PDLA added in PLLA matrix may disturb the crystallization of PLLA when the blend is cooled from 240 °C.

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