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# Blends of isotactic and atactic poly(lactide)s: 2. Molecular-weight effects of atactic component on crystallization and morphology of equimolar blends from the melt

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The effects of the molecular weight of atactic poly(DL-lactide) (PDLLA) on the crystallization behaviour and morphology of isotactic poly(L-lactide) (PLLA) ($\bar{M}_v = 3.9 \times 10^5$) were investigated using differential scanning calorimetry and polarizing microscopy. PLLA could crystallize from the melt and form spherulites in the presence of PDLLA whose $\bar{M}_v$ ranged from $6.5 \times 10^3$ to $3.0 \times 10^5$. The size of the spherulites in equimolar blends was larger than that of non-blended PLLA, irrespective of the molecular weight of PDLLA. The spherulite structure became more disordered as the molecular weight of PDLLA increased. The induction period of PLLA crystallization in the blends became longer and the initial rise in overall crystallinity became less prominent as the molecular weight of PDLLA increased. A significant depression of the equilibrium melting temperature ($T_m^\circ$) of PLLA was observed for the blends with PDLLA, irrespective of the molecular weight of PDLLA. The crystallinity of PLLA was higher for the equimolar blend with PDLLA having the lowest molecular weight ($6.5 \times 10^3$) than for other blends and the non-blended PLLA when they were annealed for 600 min. The time required for saturation in PLLA crystallization was shorter for the blends annealed after quenching from the melt than for those annealed directly from the melt without quenching.

**(Keywords: poly(lactide)s; polymer blends; crystallization)**

## INTRODUCTION

In a previous paper, we reported the effect of mixing ratio of isotactic poly(L-lactide) (PLLA) ($\bar{M}_v = 3.9 \times 10^5$) and atactic poly(DL-lactide) (PDLLA) ($\bar{M}_v = 3.0 \times 10^5$) on the crystallization behaviours and morphology of the blends from the melt[1]. The following findings were obtained for the crystallization and morphologies of PLLA in the presence of PDLLA. (1) PLLA could crystallize in the presence of PDLLA when the PLLA content $X_{\mathrm{PLLA}}$ = PLLA/(PDLLA +PLLA) was between 0.2 and 1 and spherulites were found to form at $X_{\mathrm{PLLA}}$ between 0.6 and 1. (2) The induction period of PLLA crystallization and spherulite growth was increased as $X_{\mathrm{PLLA}}$ approached 0.5. (3) The melting temperature and the crystallinity of PLLA did not change for $X_{\mathrm{PLLA}}$ above 0.5 when annealed for a sufficiently long time. (4) The spherulite size became larger in the presence of PDLLA. (5) The morphology of PLLA spherulites became disordered and the PLLA spherulite growth rate decreased as $X_{\mathrm{PLLA}}$ approached 0.5. We have concluded from these results that PDLLA is miscible with PLLA and trapped in the amorphous region between the lamellae in the spherulites of PLLA. A finding similar to (3) was observed when crystallizable L-rich poly(lactide) and PDLLA were mixed in solution at equimolar ratio and allowed to crystallize during solvent evaporation[2,3]. In a previous study, PLLA and PDLLA having a similar high molecular weight were employed to exclude a terminal-group effect of the polymers for the study of the mixing-ratio effect on crystallization[1]. With respect to the effect of molecular weight of added atactic polymer on the crytallization behaviour of the isotactic polymer, there have been many studies reported so far as vinyl polymers are concerned[4-7]. As for aliphatic polyesters, there are a few investigations, which have used isotactic and atactic poly(hydroxybutyrate) (PHB), by Pearce *et al.*[8-10] and Abe *et al.*[11]. However, in these studies, attention was paid to the spherulite morphology, spherulite growth rate and lamellar periodicity of

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**Table 1** Polymerization conditions and molecular characteristics of polymers

| | Polymerization conditions | Molecular characteristics | | | | | |
|---|---|---|---|---|---|---|---|
| Code | Lauryl alcohol (wt%) | $[\eta]$ (dl g$^{-1}$) | $\bar{M}_v$ | $M_n$ | $M_w$ | $M_w/M_n$ | $[\alpha]_D^{25}$ (deg) |
| PLLA | 0 | 6.63 | $3.9 \times 10^5$ | $6.1 \times 10^5$ | $1.3 \times 10^6$ | 2.1 | −154 |
| PDLLA300 | 0 | 3.63 | $3.0 \times 10^5$ | $4.0 \times 10^5$ | $7.2 \times 10^5$ | 1.8 | 0 |
| PDLLA40 | 0.5 | 0.78 | $4.0 \times 10^4$ | $5.9 \times 10^4$ | $1.1 \times 10^5$ | 1.9 | 0 |
| PDLLA6.5 | 5 | 0.19 | $6.5 \times 10^3$ | $1.4 \times 10^4$ | $1.9 \times 10^4$ | 1.4 | 0 |

the isotactic polymer, but not much to the induction period of crystallization and spherulite radius (or density) of the isotactic polymer. Concerning the spherulite density for polymer blends, Keith *et al.* reported a dramatic decrease in the nucleus density of spherulites of a number of aliphatic polyesters upon adding a small amount of poly(vinyl butyral) or poly(vinyl chloride) as polymer diluents[12].

The purpose of the present work is to study the miscibility between PLLA and PDLLA. Trapping of PDLLA in PLLA spherulites found in a previous study[1] is probably due to good miscibility between PLLA and PDLLA. However, it is also possible that strong entanglement between high-molecular-weight PLLA and PDLLA could disturb the diffusion of PDLLA molecules from the PLLA spherulites during their growth. To investigate this effect of entanglement between PLLA and PDLLA molecules as well as between PLLA molecules themselves on PLLA crystallization and the morphology of the blends from the melt, PLLA and PDLLA with different molecular weights were blended and PLLA crystallization in the blends was investigated by differential scanning calorimetry (d.s.c.) and polarizing microscopy. The blends were annealed with and without quenching from the melt.

## EXPERIMENTAL

### *Materials*

PLLA and PDLLA were synthesized via the method previously reported[13]. L-Lactic acid with an optical purity of 98% was purchased as 90 wt% aqueous solution from CCA Biochem BV, The Netherlands. DL-Lactide was purchased from Tokyo Kasei Kogyo Co. Ltd, Japan, and purified by repeated recrystallization using ethyl acetate as solvent. Ring-opening polymerization was performed for each lactide in bulk at 140°C for 10 h using stannous octoate (0.03 wt%) as polymerization catalyst[14]. The polymerization conditions were the same for L- and DL-lactides and the resulting PLLA and PDLLA were purified by reprecipitation using methylene chloride and acetone solution, respectively, into methanol for both the polymers.

The viscosity-average molecular weight ($\bar{M}_v$) of the polymers was determined from their intrinsic solution viscosity $[\eta]$ in chloroform at 25°C using the equations reported by Schindler and Harper[15]:

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{0.73} \text{ (for PLLA)} \quad (1)$$

$$[\eta] = 2.21 \times 10^{-4} \bar{M}_v^{0.77} \text{ (for PDLLA)} \quad (2)$$

The specific optical rotation $[\alpha]$ of the polymers was measured in chloroform at a concentration of 1 g dl$^{-1}$ and 25°C using a JASCO DIP-140 at a wavelength of 589 nm. $M_n$ and $M_w$ of the polymers were evaluated from g.p.c. using polystyrene as standard. The molecular characteristics of the polymers used in this work are listed in *Table 1*. The $[\alpha]_D^{25}$ values were approximately −150° for PLLA and 0° for PDLLA, in good agreement with the literature values[16].

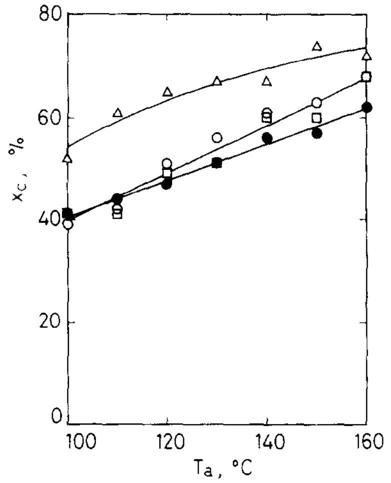

**Figure 1** Crystallinity $x_c$ evaluated from d.s.c. thermograms of the non-blended PLLA and equimolar blends as a function of $T_a$ ($t_a$ = 600 min): (△) PLLA with PDLLA6.5; (□) PLLA with PDLLA40; (○) PLLA with PDLLA300; (●) non-blended PLLA

Equimolar blends of PLLA and PDLLA were prepared from methylene chloride solution of PLLA and PDLLA having a polymer concentration of 1 g dl$^{-1}$ and 1:1 mixing ratio of the isomers. The mixed solution was cast on a flat glass plate and the solvent was allowed to evaporate at room temperature for approximately 1 day and then dried *in vacuo* for 2 weeks. To avoid formation of a highly ordered structure, solvent evaporation was performed more rapidly than in our previous papers (1 week)[2,17,18]. Only the equimolar blend was used in this study.

### *Thermal measurements and optical observations*

The dried blend film was packed in an aluminium cell for the d.s.c. measurements and then sealed in a glass tube under reduced pressure. The sealed sample was melted in an oil bath kept at 200°C for 3 min and then immersed in another oil bath kept at a given temperature ($T_a$) from 100 to 160°C for a given period of time ($t_a$) or quickly quenched to 0°C from the melt, followed by annealing at a given temperature.

The melting temperature ($T_m$) and the enthalpy of fusion ($\Delta H_m$) of PLLA were determined with a Shimadzu DT-50 differential scanning calorimeter by heating the annealed blend under a nitrogen gas flow at a rate of 10°C min$^{-1}$. The heating rate was fixed at

**Table 2** Crystallization and melting temperatures of equimolar blends and the non-blended PLLA annealed at 140°C for different times $t_a$

| | Blend with PDLA6.5 | | Blend with PDLLA40 | | Blend with PDLLA300 | | Non-blended PLLA | |
|---|---|---|---|---|---|---|---|---|
| $t_a$ (min) | $T_c$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $T_m$ (°C) |
| 0 | 127 | 177 | 128 | 178 | 140 | 179 | 111 | 177 |
| 5 | 126 | 177 | 132 | 178 | 136 | 179 | 115 | 177 |
| 10 | 120 | 177 | 131 | 177 | 136 | 178 | 114 | 177 |
| 20 | 125 | 177 | 131 | 178 | 135 | 179 | 112 | 181 |
| 30 | *a* | 176 | 131 | 178 | 130 | 180 | 110 | 181 |
| 60 | | 177 | *a* | 181 | *a* | 181 | | 182 |
| 600 | | 178 | | 183 | | 182 | | 183 |

[a] $T_c$ could not be determined because the peak was too diffuse

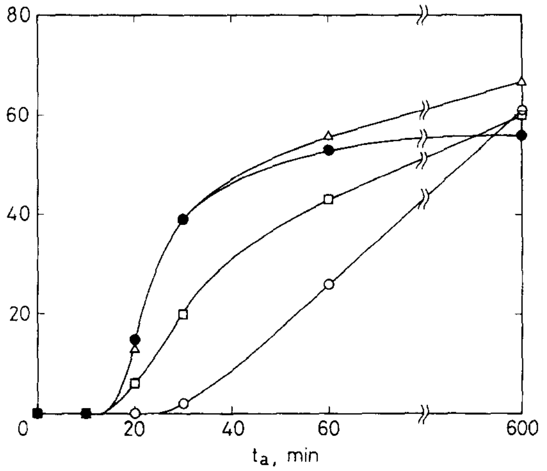

**Figure 2** Crystallinity $x_c$ evaluated from d.s.c. thermograms of the non-blended PLLA and equimolar blends as a function of $t_a$ ($T_a$ = 140°C): (△) PLLA with PDLLA6.5; (□) PLLA with PDLLA40; (○) PLLA with PDLLA300; (●) non-blended PLLA

10°C min$^{-1}$ because higher rates such as 20°C min$^{-1}$ induced a $T_m$ shift to higher temperature, and lower rates such as 5°C min$^{-1}$ resulted in thermal degradation of PLLA and PDLLA because of prolonged exposure to high temperature. $T_m$ and $\Delta H_m$ were calibrated using indium as standard.

The morphology of the annealed blend was studied with a Zeiss polarizing microscope by interposing the dried blend film between two micro-coverglasses of 18 × 18 mm$^2$, followed by sealing in a glass tube under reduced pressure. The sealed sample was melted at 200°C for 3 min (or melted at 200°C for 3 min and quenched to 0°C) and then immersed for a given period of time in an oil bath thermostatically kept at a given $T_a$. The average thickness of the blend films during microscopic observation was around 25 $\mu$m.

## RESULTS

### *Crystallization*

*Figure 1* shows the crystallinity of PLLA ($x_c$) in blends with PDLLA of various molecular weights and of non-blended PLLA as a function of annealing temperature $T_a$ (for 600 min). The value of $x_c$ and the PLLA content in the blend ($X_{\mathrm{PLLA}}$) were calculated using the following equations:

$$x_c(\%) = (\Delta H_m + \Delta H_c) \times 100/(93 X_{\mathrm{PLLA}}) \qquad (3)$$

$$X_{\mathrm{PLLA}} = \mathrm{PLLA}/(\mathrm{PDLLA} + \mathrm{PLLA}) \qquad (4)$$

where $\Delta H_m$ and $\Delta H_c$ (J/g of polymer) are the enthalpies of fusion and crystallization of PLLA, respectively; and 93 J/g of polymer is the enthalpy of fusion of a PLLA crystal of infinite size reported by Fischer *et al.*[19]. It is clearly seen that the non-blended PLLA and the blends with PDLLA40 and PDLLA300 have similar $x_c$ whereas the blend with PDLLA6.5 has the highest $x_c$. All the $x_c$ values increased with $T_a$.

The effect of $t_a$ on $x_c$ of PLLA crystallized at 140°C is shown in *Figure 2*. Apparently, the induction period of PLLA crystallization estimated from d.s.c. is longer for a blend with PDLLLA300 than for blends with PDLLA6.5 and PDLLA40 and the non-blended PLLA. Interestingly, $x_c$ attained after 600 min annealing is the highest for the blend with PDLLA6.5 and the lowest for the non-blended PLLA. Extrapolation of $T_m$ evaluated from d.s.c. thermograms to $T_m = T_a$ in a Hoffman–Weeks plot gives the equilibrium melting temperature ($T_m{}^\circ$). The estimated $T_m{}^\circ$ values are 185, 201, 200 and 205°C for the blends with PDLLA6.5, PDLLA40 and PDLLA300, and the non-blended PLLA, respectively. In this estimation we discarded the data obtained at $T_a$ below 120°C, because apparent recrystallization occurred during scanning.

*Table 2* shows the crystallization temperature ($T_c$) and $T_m$ evaluated from d.s.c. for blends with different PDLLA and the non-blended PLLA annealed at 140°C for different times $t_a$. As is evident, $T_c$ of blends is higher than that of the non-blended PLLA and $T_c$ of blends shifts to higher temperature with an increase in $\bar{M}_v$ of PDLLA. The crystallization peak observed for non-blended PLLA during scanning disappeared when $t_a$ was longer than 600 min. The crystallization peak of the blends was still observed for $t_a$ longer than that of non-blended PLLA and disappeared at shorter $t_a$ as the molecular weight of PDLLA decreased. The $T_m$ of the blends with PDLLA40 and PDLLA300 and the non-blended PLLA increased with $t_a$, suggesting that the PLLA crystallite size increased with $t_a$. However, no significant increase in $T_m$ with $t_a$ was observed for the blend with PDLLA6.5.

### *Spherulite formation*

*Figure 3* shows photomicrographs of the equimolar blends and the non-blended PLLA annealed at 120 and 140°C for 600 min. As is seen, spherulite formation is obvious for all the blends and no space for further spherulite formation remains, irrespective of the molecular weight of PDLLA and the annealing temperature, except for the blend with PDLLA300 annealed at 140°C. Spherulite structure becomes more disordered with an increase in molecular weight of PDLLA for both 120 and 140°C annealing. The blend with PDLLA6.5 annealed at 140°C produced highly ordered regular spherulites with morphology very similar to that observed for miscible blends from crystallizable and amorphous polymers[8,20,21], suggesting that the low-molecular-weight PDLLA must promote the orientation of the PLLA lamellae in spherulites. The spherulite radius of blends is larger than that of the non-blended PLLA and increases with $T_a$, irrespective of the molecular weight of PDLLA. This result indicates that the nucleus density of

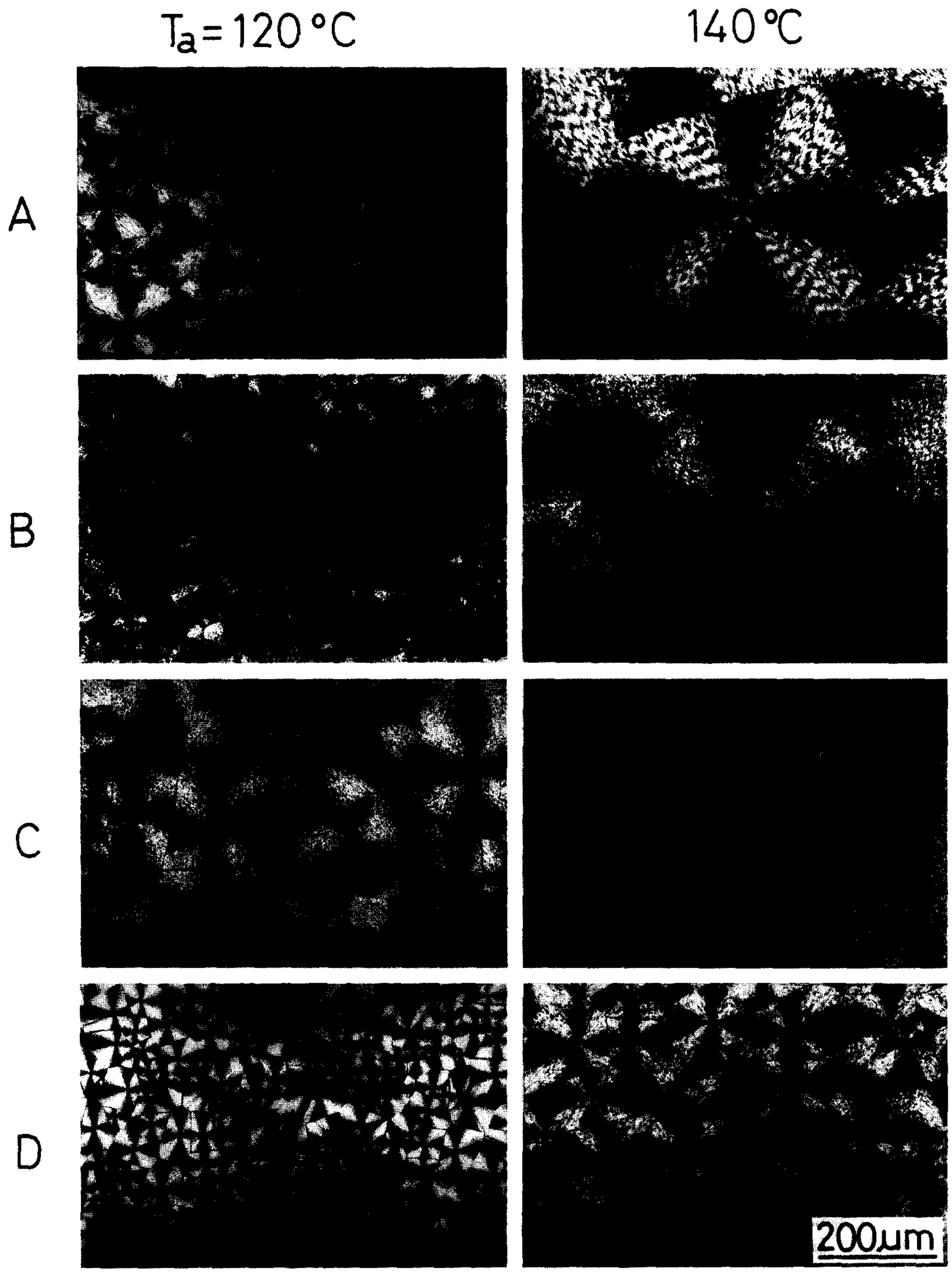

**Figure 3** Photomicrographs of the non-blended PLLA and equimolar blends annealed at 120 and 140°C for 600 min: (A) PLLA with PDLLA6.5; (B) PLLA with PDLLA40; (C) PLLA with PDLLA300; (D) non-blended PLLA

spherulites of blends was lower than that of the non-blended PLLA and decreased with $T_a$, similar to the non-blended PLLA[22–24]. *Figure 4* shows photomicrographs of blends with different PDLLA and the non-blended PLLA annealed at 140°C for 10 and 60 min. The photomicrographs of blends with PDLLA300 demonstrate that the assemblies of small crystallites grew spherically from single nuclei like spherulites, combining into one mixed phase as shown in *Figure 3*.

**Table 3** Spherulite density (*SD*) of the equimolar blends and the non-blended PLLA annealed at different temperatures $T_a$ for 600 min

| $T_a$ (°C) | *SD* (number/mm$^2$) | | | |
|---|---|---|---|---|
| | Blend with PDLLA6.5 | Blend with PDLLA40 | Blend with PDLLA300 | Non-blended PLLA |
| 120 | 214 (428)[a] | – (–) | 56 (112)[a] | 528 |
| 140 | 3 (6)[a] | 3 (6)[a] | – (–) | 72 |
| 160 | 3 (6)[a] | 3 (6)[a] | 6 (12)[a] | 11 |

[a] Normalized *SD* by $X_{PLLA}$

### *Spherulite density and size*

The spherulite density (*SD*) of the blends with different PDLLA and the non-blended PLLA annealed for 600 min is given for different $T_a$ in *Table 3*. It was too difficult to calculate *SD* for the blends annealed at 100°C, for the blend with PDLLA40 at 120°C and for the blend with PDLLA300 at 140°C, because too many spherulites were formed or the boundary between spherulitic assemblies was not clear. It is likely that *SD* decreases

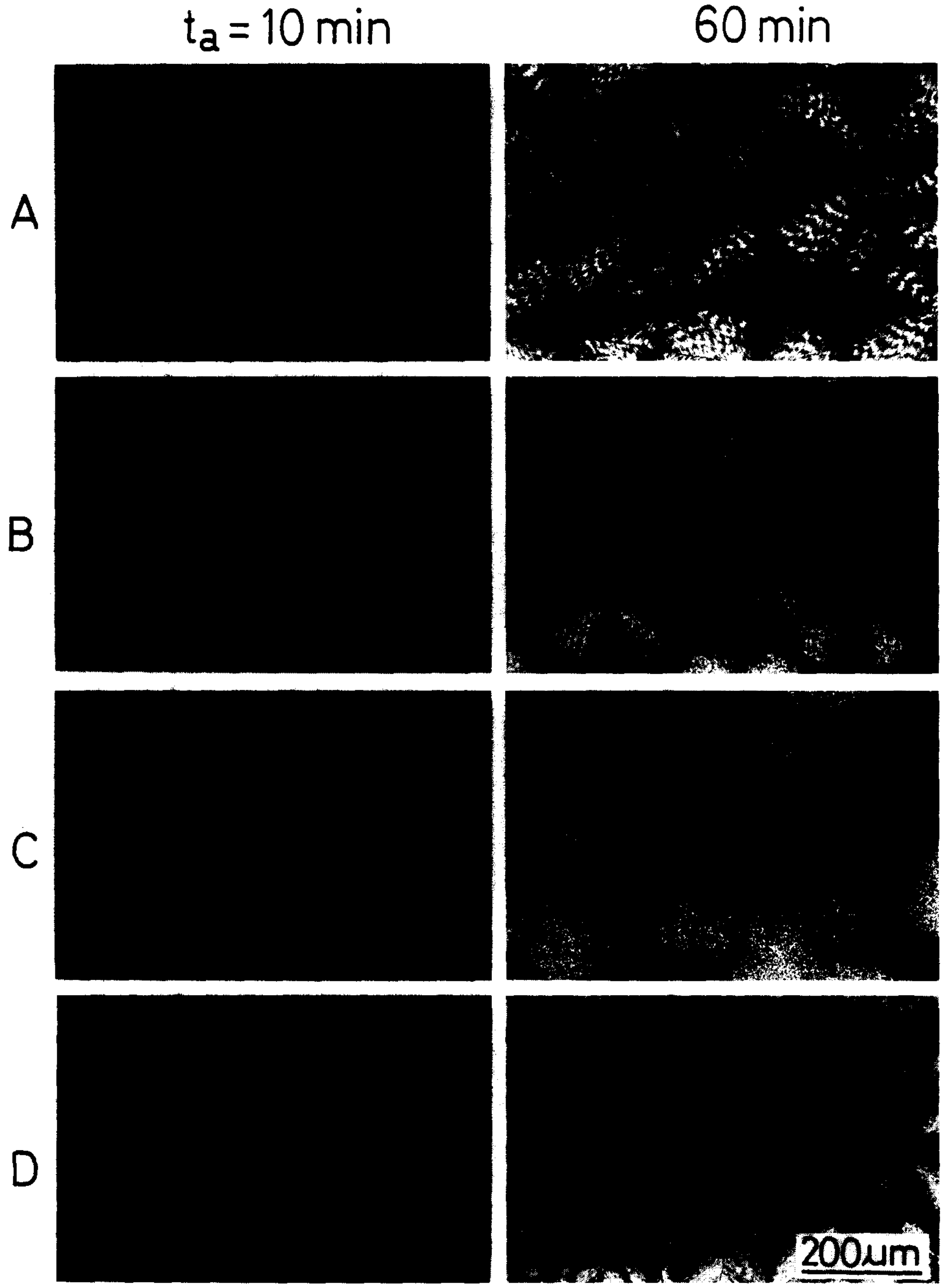

Figure 4 Photomicrographs of the non-blended PLLA and equimolar blends annealed at 140°C for 10 and 60 min: (A) PLLA with PDLLA6.5; (B) PLLA with PDLLA40; (C) PLLA with PDLLA300; (D) non-blended PLLA

with an increase in $T_a$ for all the blends, while *SD* of the blends is lower than that of the non-blended PLLA, at least when annealed at $T_a$ between 120 and 160°C. The radius of spherulites or spherulitic assemblies formed during annealing at 140°C is plotted as a function of $t_a$ in *Figure 5*. The growth rate of spherulites or spherulitic assemblies is estimated from the slope of this plot to be 2.9, 2.1, 1.8 and 2.0 $\mu$m min$^{-1}$ for the blends with PDLLA6.5, PDLLA40 and PDLLA300, and the non-blended PLLA, respectively. The observed growth rate of the blends is higher than that of the non-blended PLLA when $\bar{M}_v$ of PDLLA is as small as $6.5 \times 10^3$. The observed growth rate of non-blended PLLA is very similar to the value of PLLA reported by Vasanthakumari and Pennings[25] (1.6 $\mu$m min$^{-1}$ for $\bar{M}_v = 6.9 \times 10^5$ and 2.5 $\mu$m min$^{-1}$ for $\bar{M}_v = 3.5 \times 10^5$ at 140°C). The induction period of crystallization estimated by extrapolation of the spherulite radius to zero is approximately 3 min for the blends with PDLLA6.5 and PDLLA40 and the non-blended PLLA, and 10 min for the blend with PDLLA300. These results denote that only PDLLA with $\bar{M}_v$ as high as $3.0 \times 10^5$ lowered the growth rate of the spherulites or spherulitic assemblies of PLLA, and lengthened the induction period of crystallization. On the other hand, PDLLA having a low of $\bar{M}_v = 6.5 \times 10^3$ increased the growth rate of spherulites and shortened the induction period of crytallization. PDLLA seemed to lower the nucleus density of spherulites in the blends, irrespective of its molecular weight, resulting in the formation of large spherulites compared with those of the non-blended PLLA.

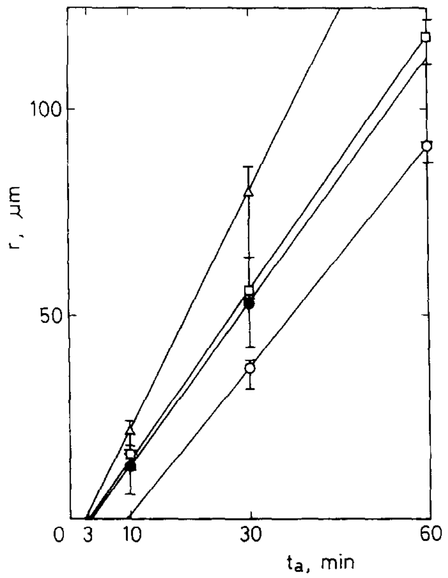

**Figure 5** Radius of the spherulites or spherulitic assemblies ($r$) of the non-blended PLLA and equimolar blends: (△) PLLA with PDLLA6.5; (□) PLLA with PDLLA40; (○) PLLA with PDLLA300; (●) non-blended PLLA

**Table 4** Characteristic temperatures and $x_c$ of blends with PDLLA300 annealed for different times $t_a$ with and without quenching ($T_a$ = 140°C)

| | With quenching | | | Without quenching | | |
|---|---|---|---|---|---|---|
| $t_a$ (min) | $T_c$ (°C) | $T_m$ (°C) | $x_c$ (%) | $T_c$ (°C) | $T_m$ (°C) | $x_c$ (%) |
| 0 | 140 | 179 | 0 | 140 | 179 | 0 |
| 5 | 135 | 178 | 13 | 136 | 179 | 0 |
| 10 | *a* | 180 | 23 | 136 | 178 | 0 |
| 20 | | 180 | 52 | 135 | 179 | 0 |
| 30 | | 181 | 57 | 130 | 180 | 2 |
| 60 | | 181 | 57 | *a* | 181 | 26 |
| 600 | | 182 | 60 | | 182 | 61 |

[a] $T_c$ could not be determined because the peak was too diffuse

### *Effect of quenching process*

The effect of quenching before annealing on the crystallization of the blends was studied using the same procedure as before[24]. The $x_c$ and $T_m$ values of PLLA in equimolar blends of PLLA and PDLLA300 showed an insignificant difference between the blends annealed with and without quenching, similar to non-blended PLLA[24] (data not shown).

*Table 4* shows $T_c$, $T_m$ and $x_c$ of PLLA in the blend with PDLLA300 annealed at 140°C for different $t_a$ with and without quenching. It is evident that $x_c$ of the blend annealed after quenching reached saturation in a much shorter time (ca. 30 min) than that of the blend annealed without quenching (> 60 min). The crytallization peak of the blend annealed after quenching disappeared in a shorter time than that of the blend annealed without quenching. The induction period for crystallization of the blend annealed after quenching was 3 min, which was much shorter than the 30 min for the blend annealed without quenching.

*Figure 6* shows photomicrographs of the blend with PDLLA300 annealed at 140°C for different $t_a$ after quenching. Comparison between *Figures 4* and *6* reveals that the spherulitic assemblies are formed more densely when the blend was annealed after quenching, covering a half of the film surface even by annealing for 10 min. The growth fronts of spherulites overlap each other at about 10 min, resulting in rapid completion of overall crystallization within 30 min. The effect of quenching before annealing on the PLLA crystallization behaviour in blends is similar to that of the non-blended PLLA, while it could not reverse the relative relation of these values between the blend and the non-blended PLLA[24].

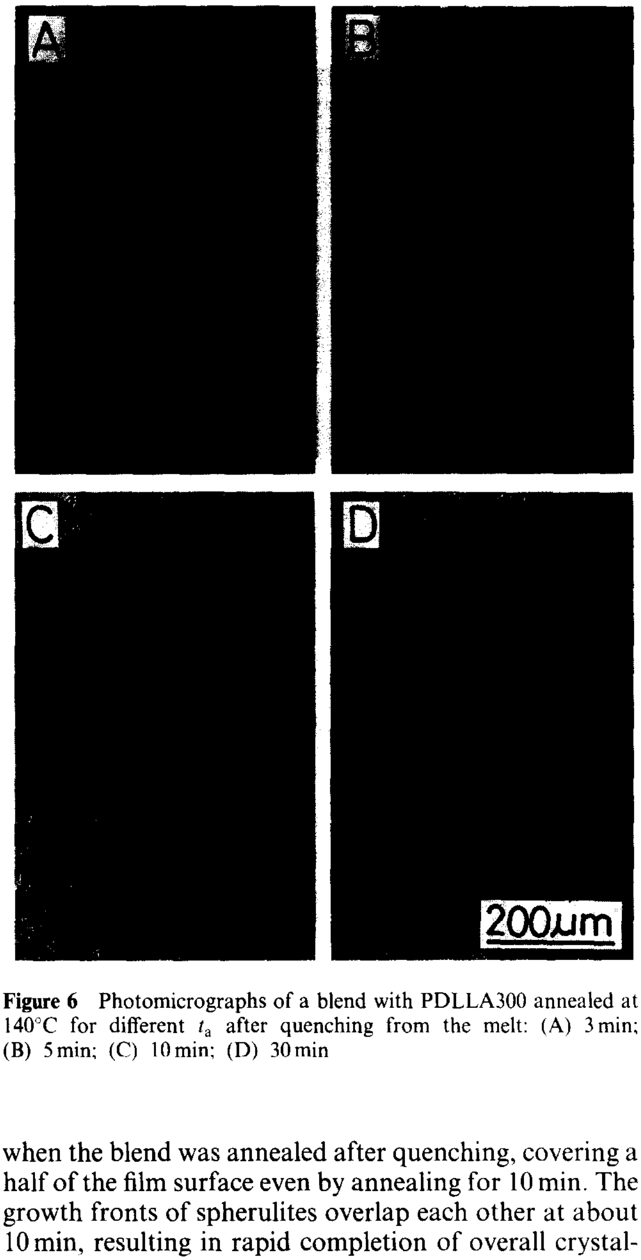

**Figure 6** Photomicrographs of a blend with PDLLA300 annealed at 140°C for different $t_a$ after quenching from the melt: (A) 3 min; (B) 5 min; (C) 10 min; (D) 30 min

## DISCUSSION

As demonstrated above, d.s.c. measurements and polarizing microscopic observation showed that PLLA could crystallize from the melt in the presence of PDLLA to form spherulites (*Figures 3* and *4*), irrespective of the molecular weight of PDLLA, when PLLA and PDLLA were mixed in equimolar ratio. Possible factors associated with PLLA crystallization that might be influenced by the presence of PDLLA in the blends include (1) the induction period for PLLA crystallization or spherulite growth, (2) the melting temperature and PLLA crystallinity, (3) the PLLA spherulite density (or radius) and morphology, and (4) the growth rate of the PLLA spherulites. They were actually affected by the presence of PDLLA, depending on their molecular weight.

*Induction period for crystallization or spherulite growth*

The induction period of PLLA crystallization or spherulite growth did not change when PLLA was blended in equimolar ratio with PDLLA6.5 or PDLLA40, but increased when blended with PDLLA300 (*Figure 2*). This result suggests that entanglement between PLLA and PDLLA chains having $\bar{M}_v$ as high as $3.0 \times 10^5$ disturbed the formation of crystallite (or spherulite) nuclei, while no such significant entanglement prevailed when $\bar{M}_v$ of PDLLA was lower than $4.0 \times 10^4$.

*Melting temperature and crystallinity*

As is evident form *Table 2*, $T_m$ depression was observed for the blend with PDLLA6.5 by about 5°C, while the $T_m$ depression was much smaller for the blends with PDLLA40 and PDLLA300 at 140°C. However, $T_m{}^{\circ}$ of all the blends was significantly lower than that of non-blended PLLA. Very small $T_m$ depression was observed for the equimolar blends of isotactic and atactic PHB as reported by Abe *et al.*[11], while large $T_m{}^{\circ}$ depression (ca. 30°C) was reported for the same blend system by Pearce *et al.*[9]. Yeh and Lambert[6] also reported large $T_m$ depression (> 5°C) for the blends of isotactic polystyrene (PS) ($M_w = 5.5 \times 10^5$) and atactic PS when the molecular weight of atactic PS was below $1.98 \times 10^4$. Thus, $T_m{}^{\circ}$ depression observed for the blend with PDLLA6.5 (ca. 20°C) is very similar to that reported by Pearce *et al.* (ca. 30°C) for PHB[9]. A probable reason for the difference in the effect of coexisting atactic polymer on the $T_m$ of isotactic polymer may be the molecular-weight difference of employed isotactic or atactic polymers and the molecular micro-structure difference of the 'atactic' polymer such as isotactic diad fraction. Pearce and Marchessault explained the $T_m$ depression for blends of isotactic and atactic PHB in terms of undercooling during d.s.c.[10]. On the other hand, the higher PLLA crystallinity of the blend with PDLLA6.5 than that of the non-blended PLLA observed for 600 min annealing irrespective of $T_a$, suggests that the low-molecular-weight PDLLA reduced chain entanglement between PLLA and PDLLA molecules as well as between PLLA molecules themselves to promote crystallization. This is in agreement with the results of PLLA crystallization in the presence of a large amount of solvent reported by Fischer *et al.*[19] and us[26] (around 85%). This effect became less prominent with an increase in PDLLA molecular weight.

*Spherulite density (or radius) and morphology*

The reduction of the nucleus density of the spherulites by the presence of PDLLA, as seen in *Table 3*, results in the formation of larger spherulites than that of the non-blended PLLA (*Figure 3*), in good agreement with the results reported by Keith *et al.*[12]. To compare *SD* accurately between the blends and the non-blended PLLA, *SD* was normalized for unit mass of PLLA by doubling the obtained SD value of equimolar blends and was shown in *Table 3*. The normalized *SD* of the blends is smaller than that of the non-blended PLLA except for the blend with PDLLA300 annealed at 160°C, which had a normalized SD similar to that of the non-blended PLLA. Such a decrease in normalized *SD* will not occur unless PLLA and PDLLA are miscible. The effect of PDLLA on *SD* is much less than that of poly(vinyl butyral) or poly(vinyl chloride) on *SD* of a number of aliphatic polyesters, where a dramatic *SD* reduction occurred upon adding a trace of polymer diluents such as 1%[12].

As demonstrated in *Figure 3*, the disturbance of spherulite structure by the presence of PDLLA became more pronounced with the increasing molecular weight of PDLLA. This result is also in good agreement with that for blends of isotactic and atactic PS reported by Yeh and Lambert[6]. Spherulitic assemblies, which grew spherically like spherulites, were observed for the blend with PDLLA300 when annealed at 140°C, as shown in *Figure 4*. The strong entanglement between PLLA and PDLLA chains having high molecular weight may have disturbed the regular orientation of lamellae of PLLA, resulting in the formation of disordered spherulites. On the other hand, *Figure 3* shows that the blend with PDLLA6.5 annealed at 140°C produced highly ordered regular spherulites. The low-molecular-weight PDLLA must act as a plasticizer to promote the orientation of the PLLA lamellae in spherulites. Increased irregularity of the PLLA spherulite structure with an increase in molecular weight of atactic PDLLA also suggests that PDLLA is trapped in the amorphous regions between the lamellae of the PLLA spherulites and that there is a strong interaction between PLLA and PDLLA.

*Growth rate of spherulites*

As *Figure 4* implies, the growth rate of PLLA spherulites or spherulitic assemblies in the blends increased with a decrease in molecular weight of PDLLA and finally became larger than that of the non-blended PLLA when $\bar{M}_v$ of PDLLA was as low as $6.5 \times 10^3$. The growth rate reduction of spherulites observed for the blend with the highest-molecular-weight PDLLA (PDLLA300) is in agreement with results for isotactic and atactic polymer pairs of PS[5,6] and PHB[8]. These pairs also showed that the growth rate of spherulites decreased when a crystallizable isotactic polymer was blended with an amorphous atactic polymer, irrespective of the molecular weight of the added atactic component[5,6,11], but there have been few reports that describe increased growth rate of spherulites in blends. Promotion of spherulite growth may be expected to occur when the molecular weight of the amorphous component is very low as in the case of PDLLA6.5.

*Structure model of PLLA–PDLLA blends*

Exclusion of PDLLA was not observed during PLLA spherulite formation even when the $\bar{M}_v$ of PDLLA was as low as $6.5 \times 10^3$, as is evident from *Figures 3* and *4*. If PDLLA is excluded during crystallization and spherulite formation, spherulite morphology would change along the radius direction of spherulites, and assemblies of excluded PDLLA would be observed as dark regions between the PLLA spherulites by polarizing microscopy. Neither such morphology change nor any dark region was observed in *Figures 3* and *4*. This strongly denotes that PDLLA is miscible with PLLA, irrespective of the molecular weight of PDLLA, being trapped between the lamellae in the PLLA spherulites. A schematic representation of the plausible structure of PLLA–PDLLA blends is given in *Figure 7*. However, there is a

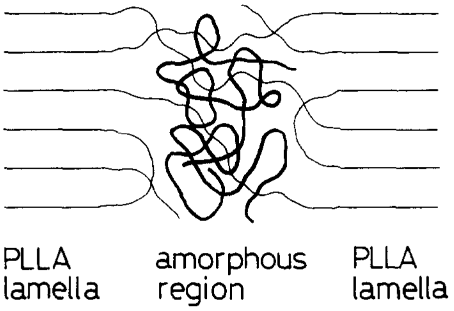

**Figure 7** Schematic representation of the structure of PLLA–PDLLA blends: thin line, PLLA molecule; thick line, PDLLA molecule

probability that PDLLA molecules in the amorphous region between the lamellae of PLLA spherulites assemble themselves. PDLLA having such a low molecular weight as $6.5 \times 10^3$ must produce little entanglement between PLLA and PDLLA molecules as well as between PLLA molecules themselves, resulting in the reduced induction period of PLLA crystallization, the promoted growth rate of PLLA spherulites, and the formation of highly ordered PLLA spherulites compared with those of the non-blended PLLA. On the other hand, when PDLLA has a molecular weight as high as $3.0 \times 10^5$, entanglement between PLLA and PDLLA molecules will become sufficiently effective to disturb the segmental diffusion of PLLA, causing the prolonged induction period for PLLA crystallization, the reduced growth rate of spherulites and the formation of disordered spherulites.

## CONCLUSION

It may be concluded that PDLLA is miscible with PLLA, irrespective of the molecular weight of PDLLA, and increases entanglement between PLLA and PDLLA with increasing molecular weight to reduce the growth rate and regularity of PLLA spherulites and PLLA crystallinity.

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