

Blends of Isotactic and Atactic Poly(lactide). I. Effects of Mixing Ratio of Isomers on Crystallization of Blends from Melt

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SYNOPSIS

Poly(L-lactide) (PLLA) and poly(DL-lactide) (PDLLA) blends were crystallized from the melt and their crystallization behaviors and morphologies were investigated using differential scanning calorimetry and polarizing microscopy. PLLA could crystallize from the melt in the presence of PDLLA when the PLLA content in the blend (X_{PLLA}) was higher than 0.2. Spherulites were formed when X_{PLLA} was between 0.6 and 1. The radius of the spherulites formed in the presence of PDLLA was larger than that of nonblended PLLA, probably because the coexisting PDLLA reduced the density of nuclei for the spherulites. Small crystallite assemblies were formed when X_{PLLA} was between 0.2 and 0.5, and grew spherically from the nuclei when X_{PLLA} was 0.5. Isotactic PLLA and atactic PDLLA seem to be miscible prior to crystallization, but PDLLA will be trapped between the lamellae of the spherulites or spherulitic assemblies during crystallization. PDLLA delayed the induction for crystallization of the blends. In spite of different morphology, the melting temperature and crystallinity of PLLA remained virtually constant when annealing was conducted for 600 min at X_{PLLA} between 0.5 and 1. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(L-lactide) (PLLA) and poly(D-lactide) are isotactic and crystallizable; poly(DL-lactide) (PDLLA) or 1 : 1 copolymer of L-lactide and D-lactide is atactic and completely amorphous. Many studies have been performed on the crystallization of homo- and copolymers of L-lactide,¹⁻⁹ but there have been few studies concerning the blends of PLLA with other polymers. An exception is the blend of PLLA with poly(D-lactide)^{8,10-18} or D-lactide copolymers¹⁹⁻²¹ where stereocomplexation (racemic crystallization) occurs between the L-lactide and the D-lactide monomer sequences.

In a previous article we reported that PDLLA had practically no effect on the crystallization of PLLA when they were mixed at a 1 : 1 ratio and

crystallized in solution through solvent evaporation.²⁰ However, very recently we found that crystallization of PLLA occurred even in the presence of PDLLA if the blend was annealed from the melt. Several reports have been published concerning the crystallization of blends from an isotactic crystallizable polymer and its atactic amorphous polymer other than the lactide polymers.²²⁻²⁶ For example, 30 years ago, Keith and Padden studied the morphologies and kinetics of spherulites formed from the blends of isotactic and atactic polypropylene as well as isotactic and atactic polystyrene and found that the atactic polymer was trapped between the lamellae of spherulites formed from the isotactic polymer.^{22,23}

Polymers employed in these studies are all vinyl polymers having no molecular chain direction except for the blend of isotactic and atactic poly(3-hydroxybutyrate) (PHB) reported by Abe et al.²⁶ In this case, the radial growth rate of spherulites decreased with the increasing content of atactic PHB

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in an apparent equilibrium with a one-phase melt and the interlamella distance of the blend of isotactic and atactic PHB was greater than that of non-blended isotactic PHB. It was concluded from these results that atactic PHB chains were present in the amorphous regions between individual lamellae within the spherulites.²⁶

In the present work, the effect of atactic PDLA addition on the crystallization of isotactic PLLA was studied from the melt using differential scanning calorimetry (DSC) and polarizing microscopy. Attention was paid to the dependence of the spherulitic morphology of the blends on the PLLA content in the blends.

EXPERIMENTAL

Materials

PLLA and PDLA were synthesized with the method previously reported.²⁷ L-Lactic acid, with an optical purity of 98%, was purchased as a 90 wt % aqueous solution from CCA Biochem bv (The Netherlands). The oligomeric PLLA prepared by condensation polymerization of the free acids was thermally decomposed to yield the lactide monomers. DL-Lactide was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo) 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.²⁸ The polymerization conditions were the same for L- and DL-lactides and the resulting PLLA and PDLA were purified by reprecipitation using methylene chloride and acetone as solvent, respectively, and methanol as precipitant.

The viscosity-average molecular weight (\bar{M}_v) of the polymers was determined from their intrinsic viscosity $[\eta]$ in chloroform at 25°C using the equations²⁹:

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

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

The specific optical rotation $[\alpha]$ of the polymers was measured in chloroform at a concentration of 1 g/dL at 25°C using a JASCO DIP-140 at a wavelength of 589 nm. M_n and M_w of the polymers were evaluated with a Tosoh GPC system (TSK gel, GMH_{XL} × 2) using polystyrene as standard. The characteristics of the polymers used in this work are listed in Table I. $[\alpha]_D^{25}$ values were approximately -150° for PLLA and 0° for PDLA, in good agreement with the literature values.³⁰

Blends to be used for the melting experiments were prepared by the following procedure. Methylene chloride solutions of PLLA and PDLA with different PLLA contents were prepared to have a total polymer concentration of 1 g/dL. The solutions were cast onto flat glass plates and the solvent was allowed to evaporate at room temperature for approximately 1 day and then dried *in vacuo* for 2 weeks.

Thermal Measurements and Optical Observation

The specimens for DSC measurements were obtained as follows. The dried polymer films were packed in a DSC aluminum cell and then sealed in test tubes under a reduced pressure. The sealed samples were melted in an oil bath kept at 200°C for 3 min and then immersed in an oil bath kept at a given annealing temperature (T_a) ranging from 100 to 160°C or quickly quenched to 0°C. The crystallization and melting temperature (T_c and T_m , respectively) and the enthalpy of crystallization and fusion (ΔH_c and ΔH_m , respectively) were determined on the annealed blends with a Shimadzu DT-50 differential scanning calorimeter. They were heated under a nitrogen gas flow at a rate of 10°C/min. We fixed the heating rate at 10°C/min because higher rates such as 20°C/min induced a T_m shift to a higher temperature and lower rates such as 5°C/min resulted in thermal degradation of PLLA because of prolonged exposure to high temperature. T_m and ΔH_m were calibrated using indium as the standard.

Morphology of the annealed blends was studied with a Zeiss polarizing microscope. The specimens

Table I Molecular Characteristics of Polymers Used

Polymer	$[\eta]$ (dL/g)	\bar{M}_v	M_n	M_w	M_w/M_n	$[\alpha]_D^{25}$ (°)
PLLA	6.63	3.9×10^5	6.1×10^5	1.33×10^6	2.2	-154
PDLA	3.63	3.0×10^5	4.0×10^5	7.2×10^5	1.8	0

for optical observation were prepared with the following procedure. The cast and dried polymer films of 25 μm thickness were interposed between two micro cover glasses of $18 \times 18 \text{ mm}^2$ and then sealed in test tubes under a reduced pressure. The blends in the sealed tubes were melted at 200°C for 3 min and then annealed for given periods of time (t_a) in an oil bath thermostatically kept at a given T_a .

RESULTS

Crystallinity

The crystallinity of PLLA (x_c) in the blends annealed at 100 and 140°C for 600 min were evaluated from DSC curves and are plotted as a function of PLLA content (X_{PLLA}) in Figure 1. X_{PLLA} was defined by eq. (3) and X_c was calculated from eq. (4):

$$X_{\text{PLLA}} = \text{PLLA}/(\text{PDLA} + \text{PLLA}) \quad (3)$$

$$x_c (\%) = 100 \cdot (\Delta H_m + \Delta H_c) / (93 \cdot X_{\text{PLLA}}) \quad (4)$$

where ΔH_m and ΔH_c (J/g of polymer) are the enthalpy of fusion and crystallization, respectively, and 93 (J/g of polymer) is the enthalpy of fusion of the PLLA crystal having the infinite size reported by Fischer et al.¹ It is clear that x_c is constant for X_{PLLA} above 0.5 and approaches 0 at $X_{\text{PLLA}} = 0.2$, both for $T_a = 100$ and 140°C . Figure 2 shows x_c of the blends annealed at different T_a for 10 h. Apparently, x_c has a very similar T_a dependence for X_{PLLA} between 0.5 and 1 except for X_{PLLA} of 0.25. This implies that the coexisting PDLA did not influence x_c of PLLA in

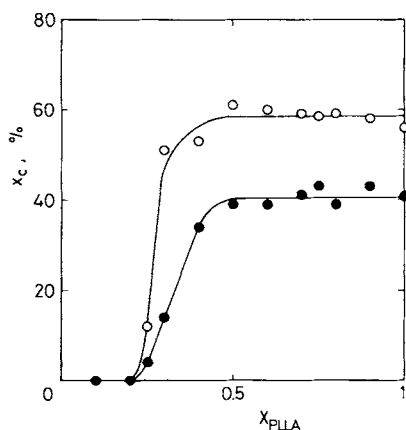


Figure 1 x_c evaluated from DSC thermograms of blends annealed at (●) 100°C and (○) 140°C as a function of X_{PLLA} ($t_a = 600 \text{ min}$).

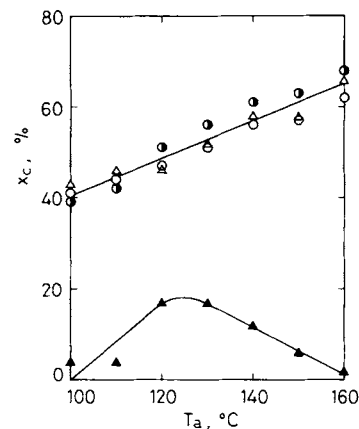


Figure 2 x_c evaluated from DSC thermograms of blends with different X_{PLLA} as a function of T_a ($t_a = 600 \text{ min}$): $X_{\text{PLLA}} = (\blacktriangle) 0.25, (\bullet) 0.5, (\triangle) 0.75, (\circ) 1$.

the blends if X_{PLLA} was between 0.5 and 1 and T_a was between 100 and 160°C , in accordance with the result of Figure 1.

The effect of t_a on x_c of PLLA crystallized at 140°C is shown in Figure 3. As seen, the induction period of PLLA crystallization increased from 20 to above 60 min with the decreasing X_{PLLA} from 1 to 0.25. This means that the coexisting atactic PDLA disturbed the nucleation of PLLA. When annealing was continued for 600 min, PLLA in the blends approached a similar x_c for X_{PLLA} between 0.5 and 1. This result again indicates that the coexisting PDLA does not influence the final crystallinity of PLLA but only the crystallization behavior of PLLA at the initial stage for the blends with X_{PLLA} above 0.5.

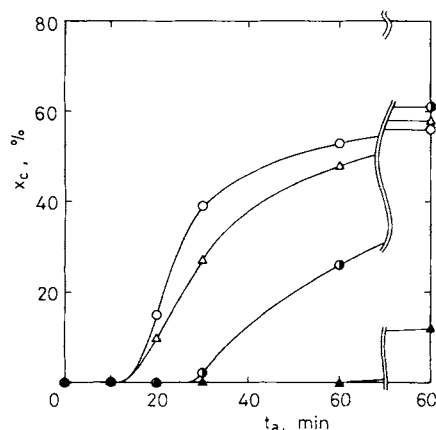


Figure 3 x_c evaluated from DSC thermograms of blends with different X_{PLLA} as a function of t_a ($T_a = 140^\circ\text{C}$): $X_{\text{PLLA}} = (\blacktriangle) 0.25, (\bullet) 0.5, (\triangle) 0.75, (\circ) 1$.

Table II Characteristic Temperatures ($^{\circ}\text{C}$) of Blends of PLLA and PDLA with Different X_{PLLA} Annealed for Different t_a ($T_a = 140^{\circ}\text{C}$)

t_a (min)	$X_{\text{PLLA}} = 0.25$		$X_{\text{PLLA}} = 0.5$		$X_{\text{PLLA}} = 0.75$		$X_{\text{PLLA}} = 1$	
	T_c	T_m	T_c	T_m	T_c	T_m	T_c	T_m
0			140	179	125	177	111	177
10			136	178	125	177	114	177
20			135	179	123	177	112	181
30			130	180	123	180	110	181
60				181		181		182
600		183		182		182		183

Table II shows T_c and T_m evaluated from DSC for the blends annealed at different X_{PLLA} for different t_a . The crystallization peak observed during scanning on the blends of X_{PLLA} at 0.5, 0.75, and 1 disappeared when t_a was longer than 60 min. T_m of the blends of X_{PLLA} at 0.5, 0.75, and 1 slightly increased with t_a , suggesting that the PLLA crystalline size in the blends increased with t_a , similar to the nonblended PLLA. Table III shows T_m evaluated from DSC of the blends annealed at different X_{PLLA} and different T_a . Extrapolation of T_m evaluated from the DSC thermograms to $T_m = T_a$ gives the equilibrium melting temperature (T_m^0) of the blends. The estimated values of T_m^0 were 202, 200, 200, and 205°C , for X_{PLLA} of 0.25, 0.5, 0.75, and 1, respectively. In these procedures we did not use the data for T_a below 110°C and the data of X_{PLLA} at 0.25 for T_a at 160°C , because apparent recrystallization was observed during DSC scanning in these cases. The higher T_m^0 for X_{PLLA} at 1 than those for X_{PLLA} at 0.25, 0.5, and 0.75 suggests that the equilibrium PLLA crystalline size of blends is smaller than that of the nonblended PLLA.

Spherulite Formation

Figure 4 shows photomicrographs of the blends with different X_{PLLA} annealed at 140°C for 600 min. Spherulite formation is obvious for X_{PLLA} from 0.6 to 1, whereas assemblies of small crystallites but not spherulites are noticed for X_{PLLA} between 0.2 and 0.5. The almost perfect spherulites observed for X_{PLLA} of 1 become more and more disordered with a decrease in X_{PLLA} and the typical spherulitic structure is no longer observed for X_{PLLA} below 0.5. PDLA chains must be trapped between the lamellae in spherulites but not in the boundaries of the spherulites when X_{PLLA} is higher than 0.6. If PDLA chains were excluded from the spherulites and trapped in the boundaries of the spherulites, dark regions should be observed in the boundaries by polarizing microscopy and the spherulite structure would not change with X_{PLLA} . As is seen from Figure 4, no crystallite is observed for X_{PLLA} of 0.1. The critical X_{PLLA} for the crystallite formation is estimated by polarizing microscopy to be between 0.1 and 0.2, which is similar to that determined by DSC.

Table III T_m ($^{\circ}\text{C}$) of Blends of PLLA and PDLA with Different X_{PLLA} Annealed at Different T_a ($t_a = 600$ min)

T_a ($^{\circ}\text{C}$)	T_m			
	$X_{\text{PLLA}} = 0.25$	$X_{\text{PLLA}} = 0.5$	$X_{\text{PLLA}} = 0.75$	$X_{\text{PLLA}} = 1$
100	177	176	176	177
110	177	176	177	177
120	177	177	177	177
130	180	179	179	180
140	183	182	182	183
150	186	185	185	187
160	178	188	188	190

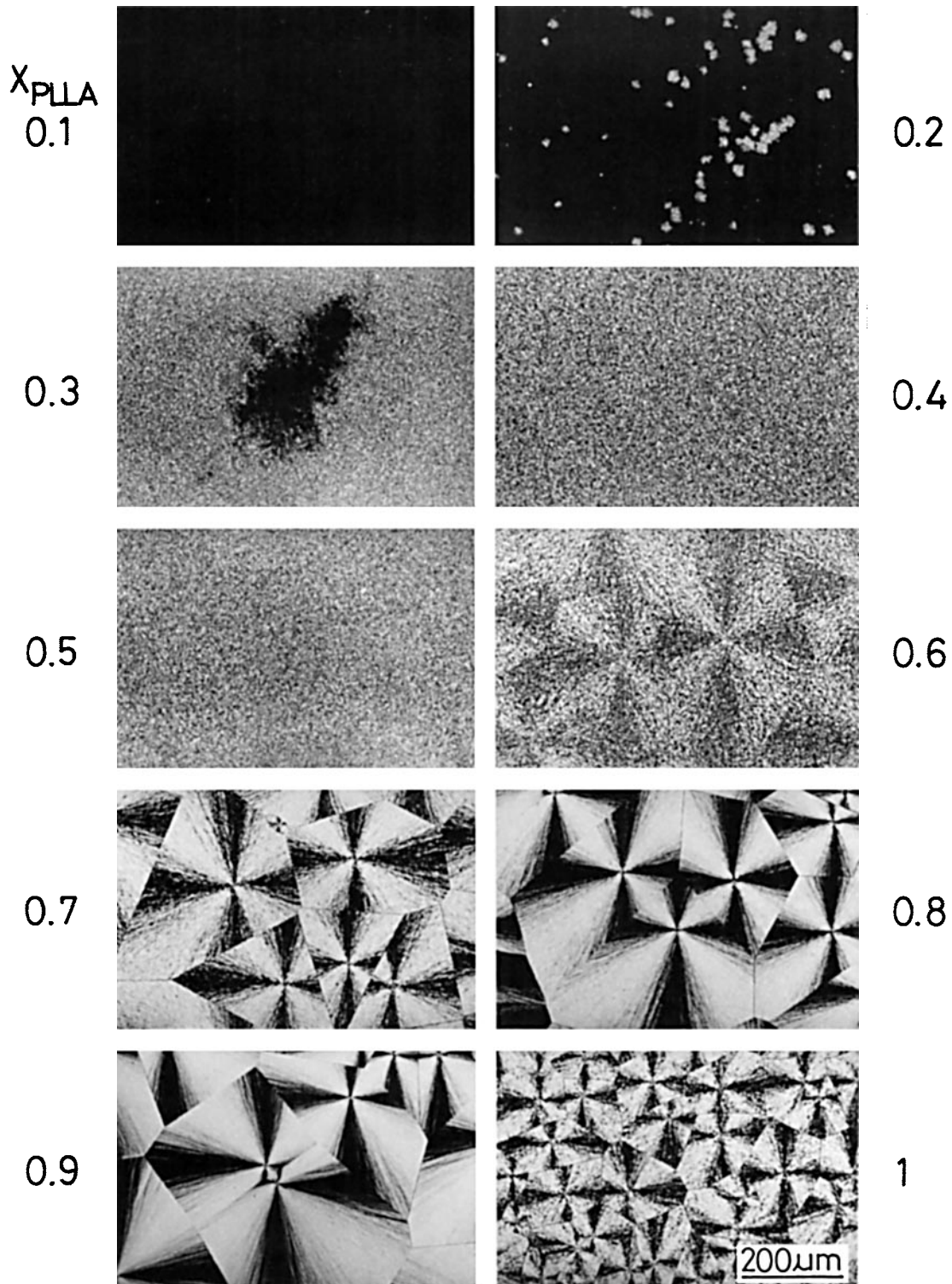


Figure 4 Photomicrographs of blends with different X_{PLLA} ($T_a = 140^\circ\text{C}$, $t_a = 600$ min).

Photomicrographs of the blends with different X_{PLLA} annealed at 120 and 160°C for 600 min are shown in Figure 5. The spherulite radius decreases with the decreasing T_a , irrespective of X_{PLLA} . This result indicates that the density of nuclei of spherulites in the blends increases with a decrease in T_a , similar to the nonblended PLLA.

Figure 6 shows photomicrographs of the blends with different X_{PLLA} annealed at 140°C for different t_a . It is seen that spherulites have been formed in the blends with X_{PLLA} above 0.75, but such clear spherulitic structure cannot be noticed for X_{PLLA} of 0.5. If we look at only the photomicrographs taken at X_{PLLA} below 0.5 in Figure 4, we may suppose that these blends are composed of an assembly of small crystallites. However, the photographs for X_{PLLA} of 0.5 in Figure 6 clearly demonstrate that the assemblies of small crystallites grew radially from single nuclei-like spherulites, combining into one mixed phase as also shown in the photomicrographs for X_{PLLA} below 0.5 in Figure 4 if annealing is conducted as long as 600 min. The morphology of spherulitic assemblies formed in the blend of X_{PLLA} of 0.5 is kept unchanged along the radius direction with unclear boundaries between neighboring spherulitic assemblies. This suggests that exclusion of PDLA from the spherulites or spherulitic assemblies did not occur and the microscopic X_{PLLA} at the growth front of spherulites or spherulitic assemblies was almost constant during crystallization.

When compared at the same t_a , the sum of the area occupied by the spherulites or the spherulitic assemblies increases with an increase in X_{PLLA} , showing that overall crystallization proceeds more rapidly with the increasing X_{PLLA} , in good agreement with the DSC results. This may be due to the decrease in nuclear density of the spherulites and the increase of induction period of crystallization with the decreasing X_{PLLA} .

Spherulite Density and Size

The spherulite density (SD) of the blends annealed at different X_{PLLA} for 600 min was evaluated from Figures 4, 5, and photomicrographs of the blend with X_{PLLA} at 0.75 annealed at 140°C for 600 min (not shown), and is plotted as a function of T_a in Figure 7. It was too difficult to calculate SD for the blend of $X_{\text{PLLA}} = 0.5$ and $T_a = 140^\circ\text{C}$, because the boundaries of spherulitic assemblies were not clear. It is obvious from Figure 7 that SD decreases with an increase in T_a for all X_{PLLA} , while SD of the blends with $X_{\text{PLLA}} = 0.5$ and 0.75 is smaller than that of the nonblended PLLA at least for T_a between 120

and 160°C. This suggests that the coexisting atactic PDLA reduced the density of spherulites, resulting in the formation of large spherulites in the blend films.

Figure 8 shows the radius of spherulites or spherulitic assemblies (r) annealed at 140°C as a function of t_a . The growth rate of spherulites or spherulitic assemblies can be obtained from the slope of this plot. The estimated rates were 1.8, 2.0, and 2.0 $\mu\text{m}/\text{min}$ for $X_{\text{PDLA}} = 0.5, 0.75,$ and 1, respectively. Apparently no difference was observed in the growth rate between the blend with $X_{\text{PDLA}} = 0.75$ and the nonblended PLLA, while the rate of $X_{\text{PDLA}} = 0.5$ (1.8 $\mu\text{m}/\text{min}$) was a little smaller than that of $X_{\text{PDLA}} = 0.75$ or 1 (2.0 $\mu\text{m}/\text{min}$). The observed rate was very similar to the value of PLLA reported by Vasanthakumari and Pennings (1.6 $\mu\text{m}/\text{min}$ for $\bar{M}_v = 6.9 \times 10^5$ and 2.5 $\mu\text{m}/\text{min}$ for $\bar{M}_v = 3.5 \times 10^5$).³ The induction period of crystallization, estimated by extrapolation of the spherulite radius to 0, was approximately 10 min for $X_{\text{PDLA}} = 0.5$ and ca. 3 min for $X_{\text{PDLA}} = 0.75$ and 1. These results denote that a large amount of PDLA mixed in the blend lowered the growth rate of the spherulites or spherulitic assemblies to an insignificant extent, but prolonged the induction period of crystallization with increased final spherulite radius.

DISCUSSION

As described above, the DSC measurement and polarizing microscopic observation revealed that PLLA could crystallize from the melt in the presence of PDLA if X_{PLLA} was higher than 0.2 and also formed spherulites in the presence of PDLA if X_{PLLA} was higher than 0.6. At $X_{\text{PLLA}} = 0.5$, the morphology of crystallite assemblies was no longer typically spherulitic, although the assembly grew radially from one nucleus-like spherulite. Because the presence of PDLA lowered SD in the blend (Fig. 7), the overall crystallization rate decreased under formation of spherulites or spherulitic assemblies with the increased radius. On the other hand, the growth rate of spherulites or spherulitic assemblies was not largely affected by addition of atactic PDLA (Fig. 8). This is in contrast with the blends from isotactic and atactic poly(3-hydroxybutyrate) or polystyrene, where a 1 : 1 blend had only half of the growth rate of spherulites from the nonblended polymers.^{23,24,26}

It is likely that the presence of atactic PDLA retarded the diffusion of crystallizable PLLA, causing delayed nucleation of crystallites. In spite of the difference in crystallization behavior and morphol-

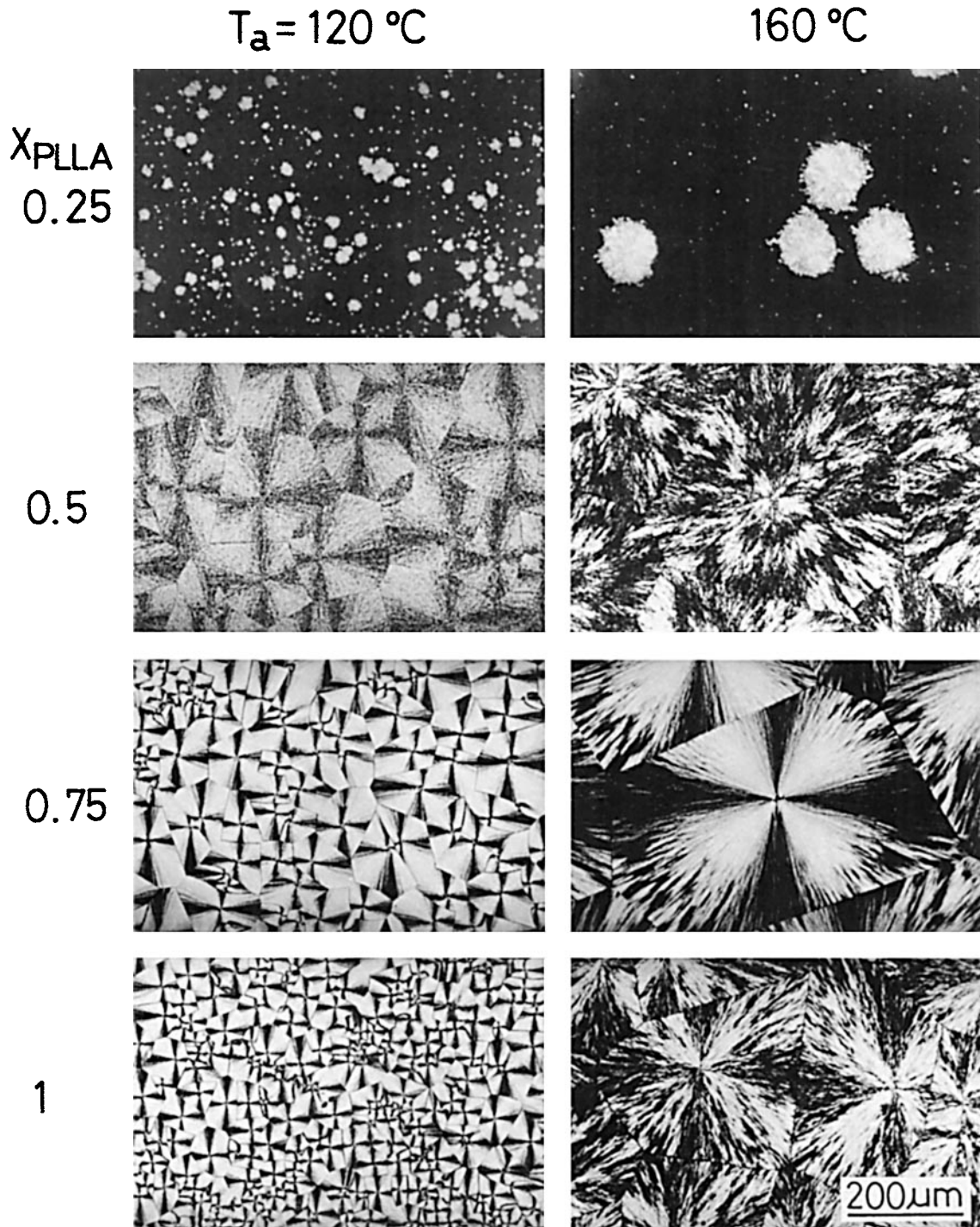


Figure 5 Photomicrographs of blends with different X_{PLLA} annealed at 120 and 160°C ($t_a = 600$ min).

ogy among the blends, the melting temperature of PLLA and x_c was almost similar, if sufficiently long annealing was given and X_{PLLA} was between 0.4 and 1. This is in good agreement with the result on isotactic and atactic poly(3-hydroxybutyrate) reported

by Abe et al.²⁶ This finding means that variation in X_{PLLA} of the blends in the range between 0.4 and 1 produces PLLA materials having different crystallite contents without changing T_m and the crystalline size.

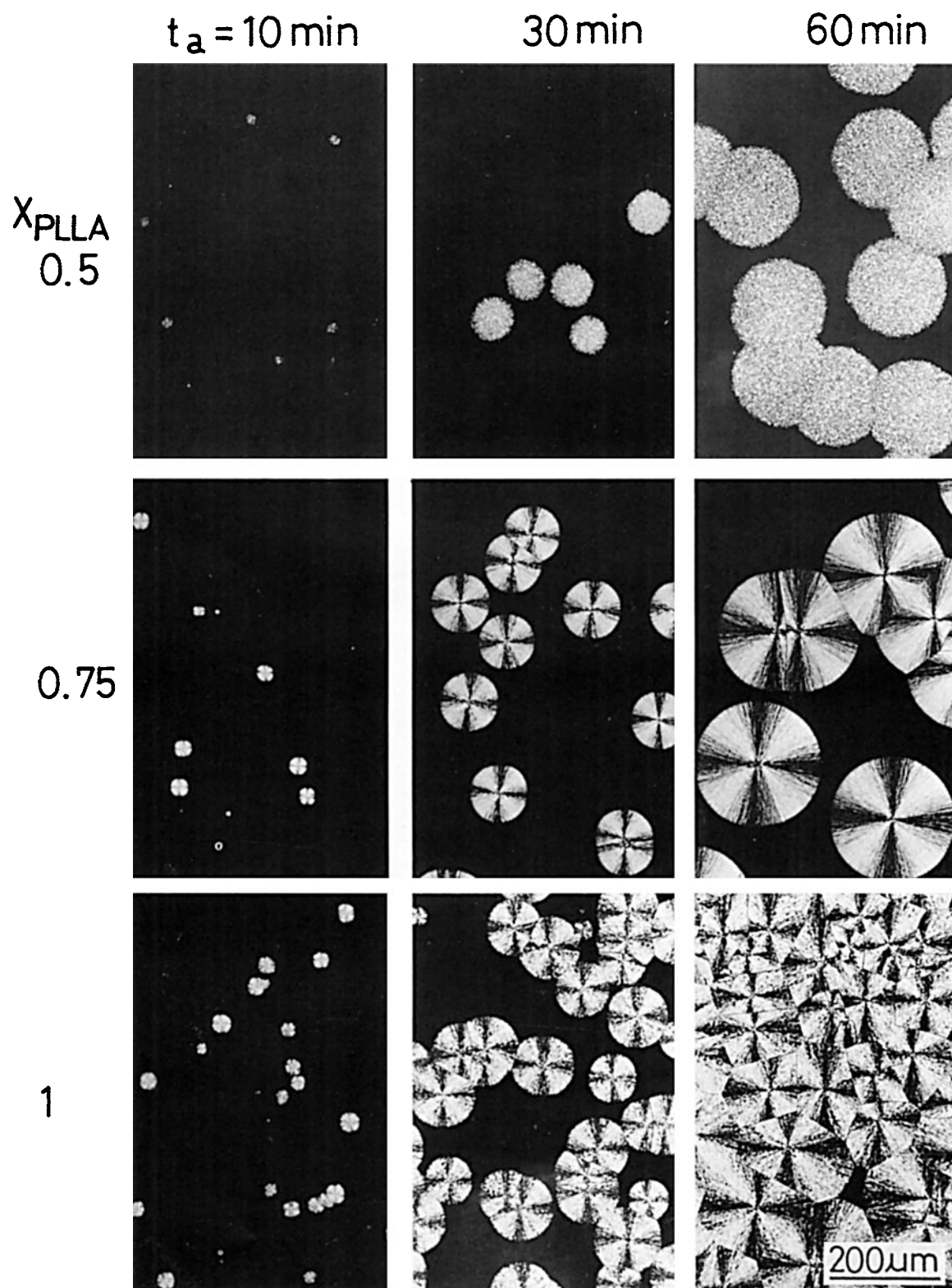


Figure 6 Photomicrographs of blends with different X_{PLLA} annealed for different t_a ($T_a = 140^\circ\text{C}$).

It follows that PLLA and PDLLA are miscible in the melt prior to crystallization, while most of the PDLLA molecules must be trapped between the lamellae of spherulites or spherulitic assemblies when crystallization is allowed to take place at T_a below 160°C . This is evidenced by the absence of dark regions between spherulites or spherulitic assemblies in contact and by the more remarkably disordered structure as X_{PLLA} decreases from 1 to 0.4. The reason for the inability of PLLA to form spherulites at X_{PLLA} below 0.5 is probably due to a too large amount of PDLLA trapped between the lamellae that will disturb the formation of ordinary spherulites. The dark region observed for X_{PLLA} of 0.2 and 0.3 (Fig. 4) must not be filled with the excluded PDLLA but contain PLLA that could not crystallize. PLLA molecules in the blend of low X_{PLLA} may be surrounded by PDLLA molecules and the chain entanglement between PLLA and PDLLA molecules will disturb the diffusion of PLLA molecules, although it is necessary for the formation of crystallite nuclei and the growth of crystallites.

If the isotactic PLLA is not miscible with atactic PDLLA, phase separation would occur during the solvent evaporation or melting process before annealing and a small difference in crystallization behavior would be observed between the nonblended PLLA and the blends. Good miscibility between isotactic and atactic polymers has been also reported for polypropylene by Keith and Padden,^{22,23} and for poly(3-hydroxybutyrate) by Abe et al.²⁶ When an atactic polypropylene with a low molecular weight was added to the isotactic polypropylene, a part of the atactic component was excluded from the spher-

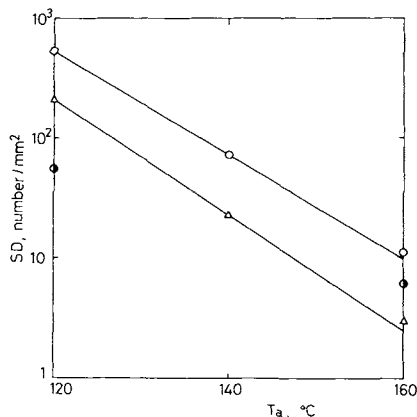


Figure 7 Spherulite density (SD) of blends with different X_{PLLA} for different T_a : X_{PLLA} = (●) 0.5, (Δ) 0.75, (○) 1.

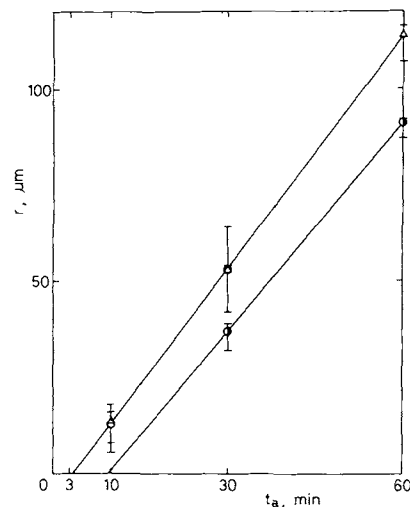


Figure 8 Radii of the spherulites or spherulitic assemblies (r) of blends with different X_{PLLA} as a function of t_a : X_{PLLA} = (●) 0.5, (Δ) 0.75, (○) 1.

ulites and trapped in the boundaries of the spherulites.^{22,23} In this case, the radial growth rate of spherulites deviated from linearity with respect to the growth time when crystallization proceeded to some extent, because the atactic component was accumulated at the growth front of the spherulites.²³ Such exclusion of atactic components during crystallization was not observed in the present study. Probably the chain entanglement between PDLLA and PLLA, both with a high molecular weight, may disturb the diffusion of PDLLA molecules during crystallization from the spherulites and spherulitic assemblies.

In summary it may be concluded that spherulites can be formed from the crystallizable PLLA even in the presence of noncrystallizable PDLLA if the blend is prepared through melt mixing and X_{PLLA} is higher than 0.6. When X_{PLLA} is lower than 0.5, the morphology of the blends change from the typical spherulitic structure to the less ordered one. It is interesting to note that polarizing microscopy of the blends with X_{PLLA} below 0.5 revealed the formation of an assembly of small crystallites that grew radially from one nucleus to a sphere, similar to spherulites, but without formation of clear boundaries between the spheres in direct contact, in marked contrast with spherulites.

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