

Melting and Crystallization of Poly(L-lactic acid) and Poly(ethylene oxide) Binary Mixture

Chitoshi NAKAFUKU and Mitoshi SAKODA

Faculty of Education, Kochi University, Kochi 780, Japan

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ABSTRACT: The effects of mixing poly(ethylene oxide) (PEO) on the melting and crystallization process of poly(L-lactic acid) (PLLA) were studied by DSC, polarized microscope and wide angle X-ray diffraction (WAXD). Melting point (T_m) depression of PLLA in the mixtures crystallized from the melt occurred with increasing PEO content but it did not occur in the mixtures crystallized from chloroform solution. T_m of PEO also decreased with increasing PLLA content. The ringed spherulite is formed in the binary mixture although non-ringed spherulite is formed for pure PLLA and PEO crystallized from the melt. In the observation of the ringed spherulite during heating, the field of vision under the microscope only changed to be slightly dark above T_m of PEO without changing the pattern of the spherulite. The result of WAXD leads to an idea that co-crystallization of PLLA and PEO molecule does not occur in the melt-crystallization and the ringed spherulite is made of PLLA and PEO lamella.

KEY WORDS Poly(L-lactic acid) / Poly(ethylene oxide) / Binary Mixture / Melting / DSC / Crystallization / Ringed Spherulite / Miscibility / X-Ray Diffraction /

It is known that poly(L-lactic acid) (PLLA) is a biodegradable crystalline polymer. The crystal structure of PLLA is pseudo-orthorhombic¹ and the molecular conformation is 10_3 helix. The equilibrium melting temperature is 215°C and the glass transition temperature (T_g) is 55°C, respectively.²

Miscibility and phase separation of PLLA and poly(ethylene oxide) (PEO) were studied by Younes and Cohn.³ According to them, melting point depression of both PLLA and PEO occurred with decreasing the component, especially at lower content below the weight fraction 0.2. They also suggested that the inclusion of two polymer molecules occurs in the amorphous state from IR study.

There are many miscible polymer pairs including amorphous-amorphous polymer pairs and crystalline-amorphous polymer pairs, but there are not so many miscible crystalline-crystalline polymer pairs. In some of the crys-

talline-crystalline polymer pairs, co-crystallization occurs. These crystalline-crystalline polymer pairs have similar molecular structure, for example poly(ethylene) and its copolymers and copolymers of vinylidene fluoride and trifluoroethylene.^{4,5} However, there is no report on the crystallization of crystalline-crystalline polymer pairs with different molecular structure such as PLLA and PEO. In the paper of Younes and Cohn, the melting behavior of the sample of solution cast blend film was described but it is not clear on the melt-crystallized sample. Furthermore, morphological observation of the blend was not performed in relation with crystallization condition.

It is the purpose of this paper, to elucidate the relationship between crystallization condition and melting and crystallization behavior of PLLA and PEO in the mixture with the change of the weight fraction. DSC measure-

ments were performed to study the change of thermal behavior of this mixture. Optical microscopy was performed to observe the morphological change with the change of the crystallization condition for different weight fraction of the component polymer in the binary mixture.

EXPERIMENTAL

The sample of PLLA used was purchased from Scientific Polymer Products Inc. and the molecular weight determined by a viscosimetric method in chloroform at 25°C⁶ was 2000. PEO of the molecular weight 3000 purchased from Wako Pure Chemical Co. was also used. Infrared measurement was performed for the solution grown film of PLLA to compare the absorption spectra of the sample in this work with that of the sample of Younes and Cohn. The absorption spectra in our sample corresponded to that of the sample of them between 650 cm⁻¹ and 4000 cm⁻¹.

Thermogravimetric analysis of PLLA was done by Rigaku Co. The result shows that the decrease of the weight begins to occur at about 240°C in the heating process and it tends to 98.4 wt% of the weight at the beginning at 350°C. Therefore, the highest temperature of measurement in DSC was set at 200°C to avoid decrease of the molecular weight.

Mixing of the two polymers was performed as follows. The mixed powder of 100 mg was dissolved in chloroform at room temperature in a laboratory dish and the solvent was evaporated at 25°C for 2 days. The blend film was shaved off from the dish with razor blade and completely dried in a vacuum oven. The film was cut and sealed in the aluminum pan for DSC measurement. To form the rod like specimen for X-ray diffraction, the cut film was put in a glass tube of 1.8 mm in diameter and melt-crystallized in an oil bath.

To prepare the sample for optical microscopy, cut slide glass (5 mm × 5 mm) was put in the laboratory dish during evaporation of

the blend and film attached on the slide glass was observed by polarized microscope of Nikon Co. To observe the morphological change with temperature of the pure and blend sample, a home-made heating device was placed on the stage of the microscope. The highest temperature attainable in this device was 180°C.

DSC measurements were performed on a Rigaku DSC 8230D with a TAS 200 controller. The heating rate was 6°C min⁻¹ and the cooling rate of 1°C min⁻¹ was used. Run 1 means the melting process of solution grown sample and run 2 means the melting process of the sample crystallized from the melt at the cooling rate of 1°C min⁻¹ after run 1. WAXD measurements were performed on the rod like sample by a transmission method using a diffractometer. Nickel filtered Cu-K_α radiation was used as an incident X-ray beam.

RESULTS AND DISCUSSION

Phase Diagram of PLLA and PEO in the Mixture

Figure 1 shows the DSC curve of melting of solution grown sample and melt-crystallized sample of PLLA. In the heating process in run 1, a small thermal change due to the glass transition appears at 54.0°C, and an exother-

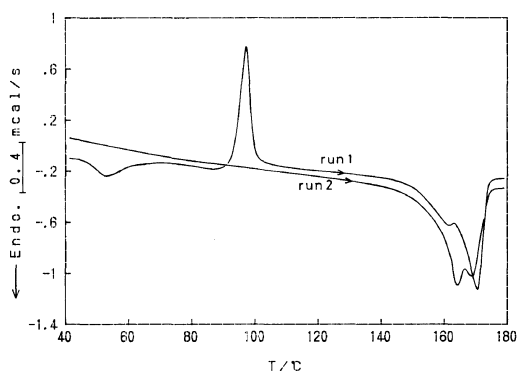


Figure 1. DSC curves of pure PLLA in the heating process. run 1, DSC curve of melting of the solution crystallized sample; run 2, DSC curve of melting of the sample crystallized from the melt after run 1.

mic peak of crystallization is observed at 96.7°C. Endothermic double peak of melting appeared at 159.6°C and 169.5°C. Crystallinity of solution grown PLLA sample is not so high taking into account that the heat of crystallization around 100°C is 4.37 cal g⁻¹ and the heat of fusion around 140°C–170°C is -12.0 cal g⁻¹. Exothermic peak for crystallization in the cooling process for the cooling rate of 1°C min⁻¹ appeared at 129.2°C. In the heating process of run 2, double peak of melting appears at 162.8°C and 167.8°C without any change in the curve up to its melting as shown in the figure. The highest peak temperature of melting of PLLA in run 2 is only slightly lower than that of run 1. The reason why double peaks appeared in the melting process is not clear but according to high temperature X-ray diffraction measurement performed up to 165°C, the diffraction pattern of the sample did not change up to the melting temperature, so that the phase transition as observed in paraffine crystals⁷ did not occur.

Figure 2 shows the DSC curves of melting of the solution grown (run 1) and melt crystallized (run 2) mixture containing 0.4 weight fraction of PLLA (Abbr. $W_{\text{PLLA}}=0.4$). Endothermic peak of melting of PEO appears at about 56°C. One of the method to judge the

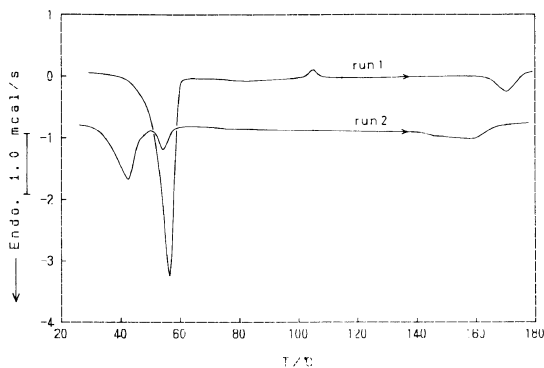


Figure 2. DSC curves of PLLA and PEO binary mixture of $W_{\text{PLLA}}=0.4$ in the heating process. Run 1, DSC curve of melting of the solution crystallized sample; run 2, DSC curve of melting of the sample crystallized from the melt after run 1.

miscibility of the polymer pair is to see the change of T_g with the change of the weight fraction of the blend. T_g in the miscible amorphous polymer blend changes continuously between the glass transition temperatures of the component polymer. In the immiscible polymer pairs, two T_g due to the component polymers appear separately and they do not change with the weight fraction.⁸ In this mixture, T_g of PLLA and T_m of PEO exists at nearly the same temperature region and the change of T_g of PLLA with the weight fraction is difficult to detect as indicated by Younes and Cohn. But T_g of PEO exists at about -60°C, so that the change of T_g of PEO should be detected. Figure 3 shows the change of T_g with the weight fraction of PEO. T_g of PEO increased slightly with decreasing the weight fraction of PEO, but the increasing rate was very small compared with the case assuming the linear increase between T_g of PLLA and PEO. This result indicates that PLLA and PEO molecules are semimiscible as indicated by Younes and Cohn. Exothermic peak of crystallization of PLLA in the heating process is also observed in the mixture. In run

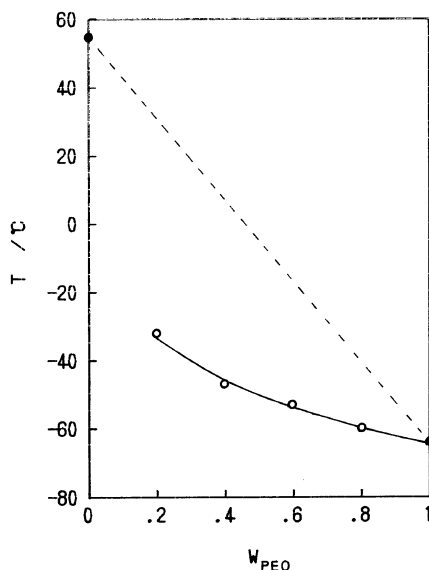


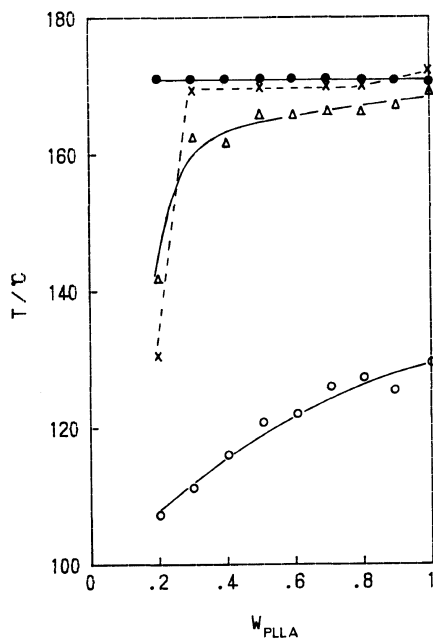
Figure 3. Weight fraction (W_{PEO}) dependence of T_g of PEO. ○, T_g of PEO; ●, T_g of PLLA.

Table I. Melting temperatures T_{m1} and T_{m2} for run 1 and run 2 and the crystallization temperature T_c of pure PLLA and PLLA in the mixture with PEO

W_{PLLA}	T_{m1} °C	T_{m2} °C	T_c °C
1.0	169.5	169.2	129.2
0.9	170.2	165.8	125.0
0.8	171.4	166.3	128.4
0.7	171.4	167.1	125.7
0.6	171.4	165.3	121.3
0.5	170.8	165.1	121.0
0.4	170.6	161.6	115.8
0.3	170.5	163.0	110.4
0.2	170.2	141.6	106.7

Table II. Melting temperatures T_{m1} and T_{m2} for run 1 and run 2 and the crystallization temperature T_c of pure PEO and PEO in the mixture

W_{PLLA}	T_{m1} °C	T_{m2} °C	T_c °C
1.0	—	—	—
0.9	—	—	—
0.8	53.0	50.0	—
0.7	55.2	53.8	33.6
0.6	56.7	55.2	34.7
0.5	57.2	55.6	35.9
0.4	56.4	56.3	34.7
0.3	58.6	57.1	36.6
0.2	59.7	56.5	36.6
0.1	60.0	58.1	37.8
0.0	60.5	59.2	40.5

**Figure 4.** Weight fraction (W_{PLLA}) dependence of melting and crystallization temperature of PLLA in the mixture. Peak temperature of the high temperature peak of melting is plotted. ●, T_m in run 1; △, T_m in run 2; ○, T_c ; ×, T_m in ref 3.

2, melting peaks of PLLA and PEO appear but crystallization peak of PLLA did not appear during heating. The peak temperature of the high temperature peak of melting of PLLA in

run 2 of this weight fraction is 161.6°C which is 9°C lower than the peak temperature of the high temperature peak of melting in run 1. T_m and T_c of PLLA in the mixture for the different weight fractions between 1.0 and 0.2 were determined by DSC. The values of T_m in run 1 (T_{m1}) and run 2 (T_{m2}) and T_c of PLLA is listed in Table I. The values of peak temperature in Table I were plotted in Figure 4. The data of Younes and Cohn is simultaneously plotted in the figure. It is clear that the melting temperature of PLLA is almost constant in run 1 for W_{PLLA} from 1.0 to 0.2, suggesting no interactions between PLLA and PEO molecules in the mixture as grown from solution. However, in the mixture crystallized from the melt at the cooling rate of 1°C min⁻¹, PEO lowers the melting temperature of PLLA, especially at lower content of PLLA. The difference of T_m of PLLA between solution grown sample and melt-crystallized sample of $W_{\text{PLLA}}=0.2$ is about 30°C.

Table II lists the values of T_m for run 1 (T_{m1}) and run 2 (T_{m2}) and T_c of pure PEO and PEO in the binary mixture with different weight fractions. T_m and T_c of PEO decreases slightly with increasing PLLA in the mixture as shown in Figure 5 but this change may be due to the

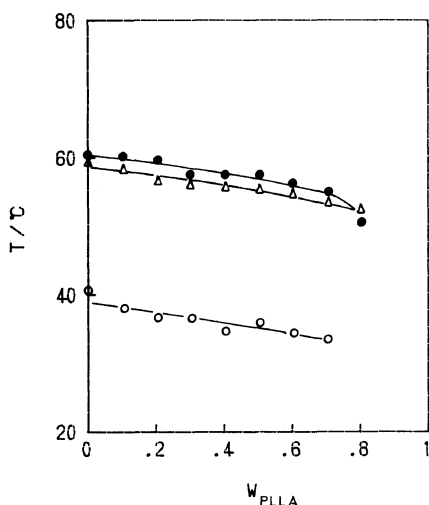


Figure 5. Weight fraction (W_{PLLA}) dependence of melting and crystallization temperature of PEO in the mixture. ●, T_m in run 1; △, T_m in run 2; ○, T_c .

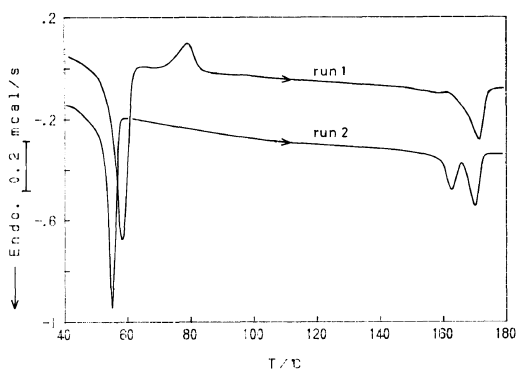


Figure 6. DSC curves of PLLA and PCL in the mixture with $W_{\text{PLLA}} = 0.5$ in the heating process. Run 1, DSC curve of melting of the solution crystallized sample; run 2, DSC curve of melting of the sample crystallized from the melt after run 1.

morphological effects (lamellar size effects)⁹ because it also occurs on the sample crystallized from solution. In solution casting process, PEO is physically hindered in the crystallization by PLLA molecule. In the crystallization from the melt, PEO is also hindered because it should crystallize between the lamellae of already crystallized PLLA. The decreasing rate of T_m of PEO with decreasing PEO content in the

mixture is almost the same for solution crystallized sample and melt crystallized sample.

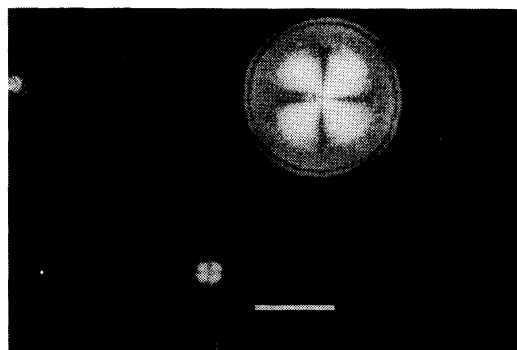
Melting point depression of PLLA crystallized from the melt in the mixture with the other polymer is not always usual. In the blend with poly(ϵ -caprolactone) (PCL), melting point depression of PLLA does not occur. Figure 6 shows the DSC curve of melting of the blend of PLLA and PCL. The peak temperature of the high temperature peak of melting of PLLA (170.3°C) in run 2 is very close to the peak temperature in run 1 (170.7°C). In the case of PLLA/PEO mixture of $W_{\text{PLLA}} = 0.5$, T_m of PLLA is about 6°C lower than that of pure PLLA. Slight decrease (0.4°C) of melting temperature of PLLA may be due to the morphological effects.

Morphology of the PLLA and PEO Binary Mixture

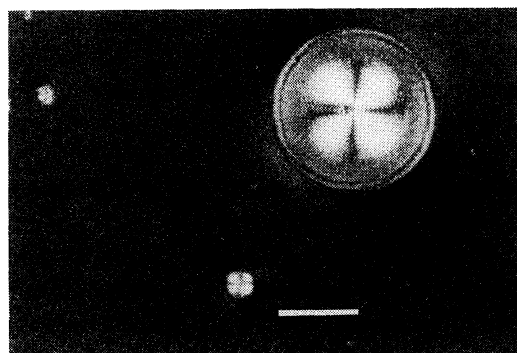
In the solution grown film sample of pure PLLA, ringed spherulite is observed against the dark area as shown in Figure 7(a). The spacing of the ring changes from 1 μm in the inside to about 7 μm in the outside of the spherulite. In the heating process, many bright spots appeared in the dark area above 100°C as shown in Figure 7(b). The exothermic peak of crystallization appeared at 97°C in the heating process in run 1 of DSC thermogram corresponds to this change of morphology in crystallization during heating. On further heating, the spherulite and bright spots disappear above about 160°C and the area changed to be dark. In the cooling process, the non-ringed spherulite grows in the dark field of vision as observed in Figure 7(c).

In the case of pure PEO, non-ringed spherulites are observed for both the solution grown and melt grown sample as shown in Figures 8(a) and (b), respectively.

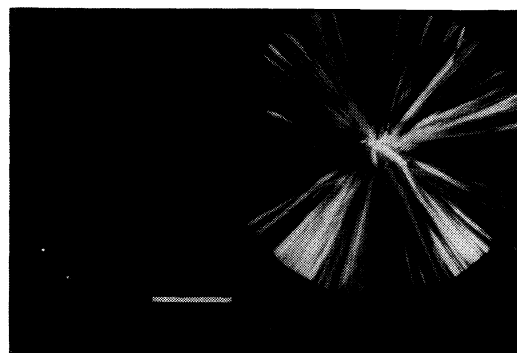
Ringed spherulite is observed in the PLLA and PEO blend grown from solution. Figure 9(a) shows the optical micrograph of the solution grown sample of the mixture of $W_{\text{PLLA}} = 0.5$. The spacing of the ring is almost



(a)



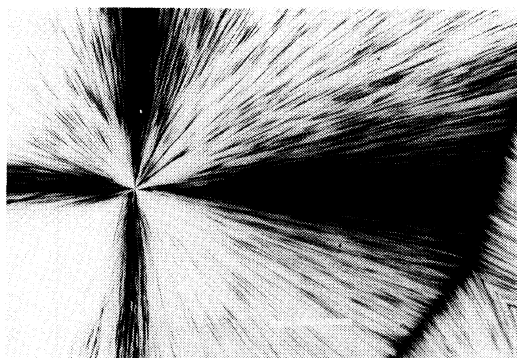
(b)



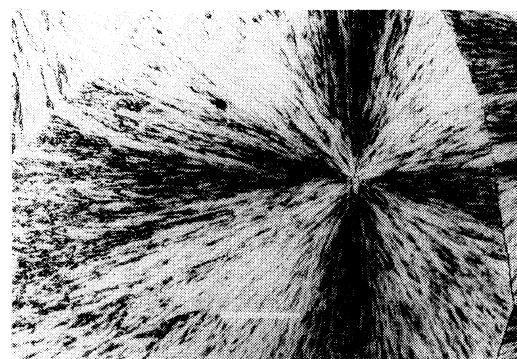
(c)

Figure 7. Optical micrographs (crossed polars) of pure PLLA cast from chloroform solution. Scale bar means $100\ \mu\text{m}$ in this figure and the following photographs. (a) 25°C , (b) 105°C in heating process, (c) 30°C in cooling process.

the same as that of the ring of the spherulite of solution grown pure PLLA. In the heating process, the field of vision becomes slightly



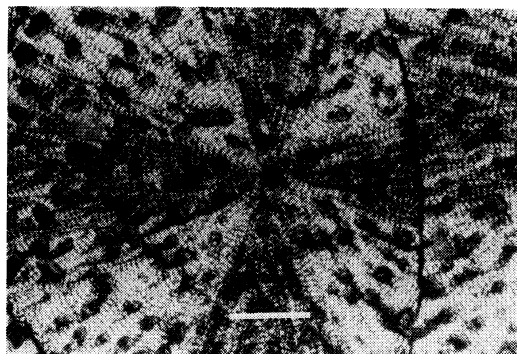
(a)



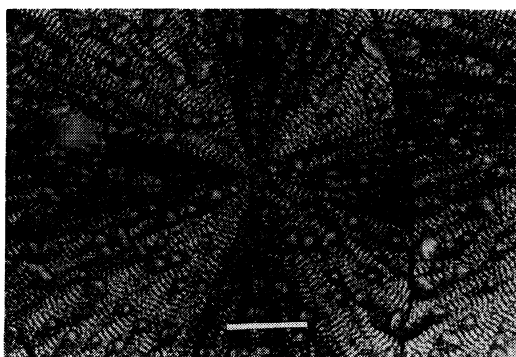
(b)

Figure 8. Optical micrographs of spherulite of pure PEO. (a) cast from chloroform solution, (b) spherulite grown from the melt.

dark at 57°C around the melting temperature of PEO as shown in Figure 9(b). Around the melting point of PLLA, all the visible areas under microscope changed completely dark. In the cooling process of the blend sample, ringed-spherulite is formed as shown in Figure 10, near the temperature of the crystallization peak appeared during cooling in DSC measurements. The spacing of the ring of the melt-grown spherulite of the blend is completely different from that of the ring of solution grown spherulite of the blend and pure PLLA. In this case, the spacing of the ring is about $40\ \mu\text{m}$. Figure 11(a) shows another ringed spherulite at 25°C formed by slow cooling from the melt of the blend of $W_{\text{PLLA}}=0.5$. In the heating process, the field of vision under the

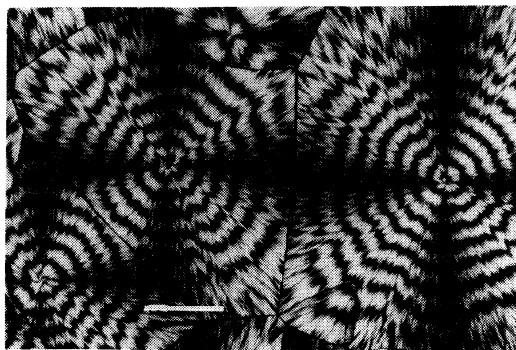


(a)

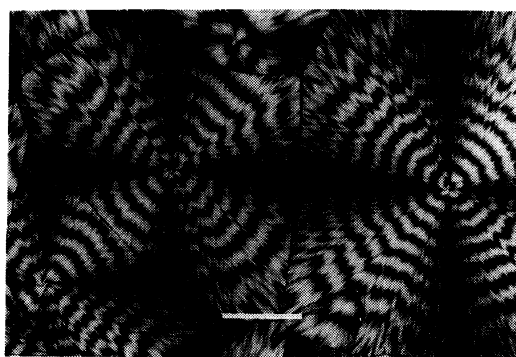


(b)

Figure 9. Optical micrographs of spherulite cast from chloroform solution of PLLA and PEO binary mixture of $W_{\text{PLLA}}=0.5$. (a) 25°C, (b) 57°C in heating process.



(a)



(b)

Figure 11. Ringed spherulites of PLLA and PEO binary mixture of $W_{\text{PLLA}}=0.5$ formed by slow cooling from the melt. (a) 25°C, (b) 58°C in the heating process.

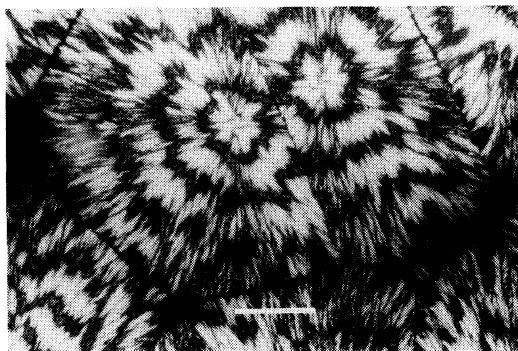


Figure 10. Spherulite of the PLLA and PEO binary mixture of $W_{\text{PLLA}}=0.5$ formed at constant temperature of 105°C.

microscope becomes slightly dark at 58°C which is close to the peak melting temperature of PEO as observed in Figure 11(b).

A close inspection of the spherulite of the two micrographs results in the conclusion that the width of the dark ring increased but the shape did not change at all below and above the melting temperature of PEO. The pattern of the spherulite did not change up to the melting temperature of PLLA, therefore it is concluded that the ringed spherulite is composed of PLLA and PEO lamellar crystal. If PEO crystal exists apart from PLLA spherulite, the change of PEO lamellar crystal due to its melting should be visible in the heating process. The ringed spherulite was observed in the mixture of different weight fractions between $W_{\text{PLLA}}=0.9$ and 0.2. Furthermore, in the case of the blend for the weight fraction 0.5 of PLLA and PEO of the molecular weight 200000, the ringed

spherulite also appeared by melt-crystallization.

Recently, Nojima *et al.*¹⁰ reported that PCL formed ringed spherulite by blending ϵ -caprolactone-butadiene diblock copolymer (PCL-*b*-PB) though it forms non-ringed spherulite in the case of the samples crystallized without blending the other polymer. They suggested that PCL block of the copolymer plays an important role in the formation of ringed spherulite and is incorporated into the PCL lamellar crystals and the PB exists between lamellar crystals as amorphous layer. In the PLLA/PEO mixture, PEO lamellar crystal should be sandwiched between PLLA lamellar crystal. Another examples of forming ringed spherulite by blending chemically dissimilar polymers are PCL/poly(vinyl chloride) (PVC) blend¹¹ and poly(vinylidene

fluoride) (PVF₂)/poly(methyl methacrylate) (PMMA) blend.^{12,13} These blends are composed of crystalline polymer and chemically dissimilar amorphous polymer. The PLLA and PEO binary mixture should be for the present the only blend system of crystalline-crystalline polymer pair to form the ringed spherulite by crystallization during cooling from the melt.

The WAXD pattern of pure PLLA, pure PEO and the blend of $W_{\text{PLLA}}=0.4$ is shown in Figure 12. A diffraction peak of strong intensity of (110) appears at 16.9° in 2θ angle and a medium intensity peak appears at 19.3° in pure PLLA. The strong intensity diffraction peaks of PEO sample appear at 19.5° and 23.5°. In the mixture of $W_{\text{PLLA}}=0.4$, the diffraction peaks appear at the same position in 2θ angle,

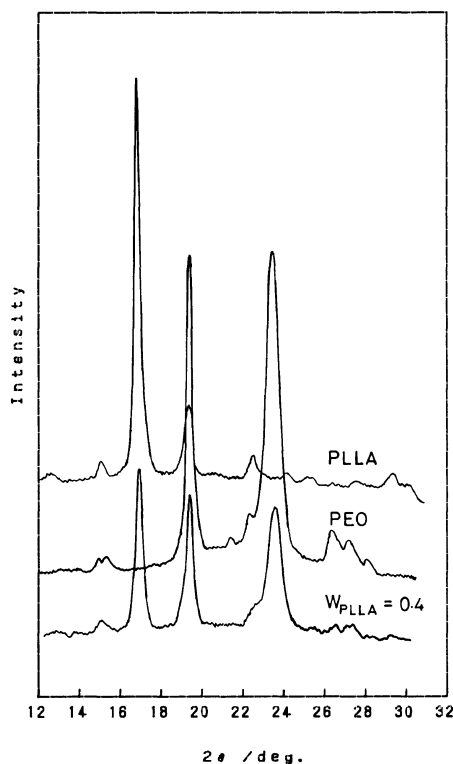


Figure 12. WAXD pattern of pure PLLA, pure PEO and the binary mixture of PLLA and PEO of $W_{\text{PLLA}}=0.4$ crystallized from the melt at a slow cooling.



(a)



(b)

Figure 13. Optical micrographs of the binary mixture of PLLA and PEO of $W_{\text{PLLA}}=0.5$ crystallized from the melt. (a) 25°C, (b) 58°C in heating process.

therefore new crystal structure is not formed by blending two polymer molecules. The shifting of the diffraction peak from PLLA and PEO is not observed, so that inclusion of the two polymer molecules in the crystalline region (cocrystallization) did not occur. The intensity of the diffraction peaks changed according to the weight fraction but the peak position did not change.

In the immiscible blend of PLLA and PCL, melting point depression did not occur even in the sample crystallized from the melt. In this mixture, non-ringed spherulite is observed at the upper part of the micrograph as shown in Figure 13(a). The change of the field of vision with increasing temperature is different from the change of it in the PLLA/PEO blend. In the heating process, the melting of PCL spherulite occurs at the melting temperature of PCL independent of the PLLA spherulite as shown in Figure 13(b). The spherulite of PLLA remains without any change up to the melting temperature of PLLA.

CONCLUSIONS

The melting and crystallization behavior of PLLA in the mixture with PEO was studied on different weight fractions. In the blend of PLLA and PEO crystallized from solution, depression of T_m of PLLA did not occur indicative of no interaction between PLLA and PEO molecules. Ringed spherulite is formed in the mixture crystallized from the melt indi-

cating strong effects of PEO molecule on the melting and crystallization of PLLA. Partial miscibility between PLLA and PEO molecules is suggested by the change of T_g of PEO with the weight fraction of the binary mixture. The results of heating experiments under polarized microscope, WAXD and DSC measurement indicate that co-crystallization of PLLA and PEO molecules did not occur. The PEO lamella exists in the PLLA spherulite.

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