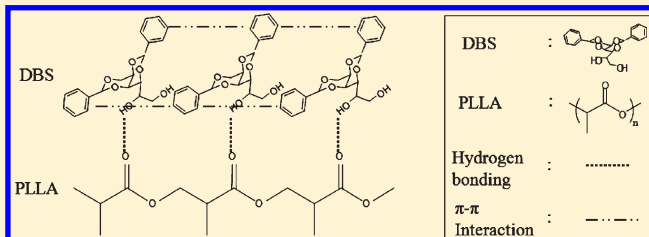


Thermal Behavior and Crystal Structure of Poly(L-lactic acid) with 1,3:2,4-Dibenzylidene-D-sorbitol

Wei-Chi Lai*

Department of Chemical and Materials Engineering and Energy and Opto-Electronic Materials Research Center, Tamkang University, No.151, Yingzhuang Road, Danshui Dist., New Taipei City 25137, Taiwan

ABSTRACT: This study investigated the effect of 1,3:2,4-dibenzylidene-D-sorbitol (DBS) on the thermal behavior and crystal structure of poly(L-lactic acid) (PLLA) by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). Different PLLA crystal structures (α - or α' -form crystal) were found by the change of the DBS amount and PLLA crystallization temperature. The order and regular α -form of PLLA was favored as the DBS component was added. The α -form crystal formed more at lower temperatures. Therefore, the disorder-to-order (α' -to- α) phase-transition temperature of PLLA was found to shift at lower temperatures as more DBS content was added. In the proposed structure of PLLA with DBS, the DBS molecules are stacked together through π - π interaction to form a strand with the PLLA molecules by hydrogen bonding. Because of these interactions, PLLA could have a more regular structure with the addition of DBS. In addition, the equilibrium melting point and glass-transition temperature of PLLA were not significantly changed with the addition of DBS. However, the addition of DBS changed the crystal structure of PLLA and thus affected the crystallization rate of PLLA.



INTRODUCTION

Poly(L-lactic acid) (PLLA) is a biodegradable thermoplastic, semicrystalline polymer which has attracted a great deal of attention because of its potential for application as a biomedical and environment-friendly material.^{1–4} PLLA developed by blending and copolymerization has been well-studied and documented by industrial and scientific research.^{1–4} However, recently, more and more studies have discussed the melting behaviors of PLLA, such as the different crystal structures of PLLA. In previous studies, PLLA was shown to form three different crystal types, such as α , β , and γ , according to different sample preparations.^{5–7} The PLLA crystal structure most found is α -form crystal. The α -crystal of PLLA is orthorhombic and has a 10₃ helical chain conformation. It is usually prepared from the melt or solution.⁵ β -form crystal is obtained by stretching at a high drawing rate and high drawing temperature, and it is an orthorhombic unit cell with 3₁ helical conformation.^{5,6} γ -form crystal of PLLA is produced by epitaxial crystallization on the same crystalline substrate, hexamethylbenzene.⁷ At present, two different crystal structures of PLLA (α - and α' -form crystal) have been identified in PLLA samples prepared from melt. The α' -form crystal (irregular) of PLLA forms at low crystallization temperatures; however, α -form crystal (regular) forms at high crystallization temperatures.^{8–12}

These different crystal structures can be distinguished by wide-angle X-ray diffraction (WAXD) and Fourier transform infrared (FTIR) spectroscopy. It has been reported that as neat PLLA samples crystallize at temperatures lower than 100 °C, the α' -form crystals of PLLA form. When samples crystallize in the temperature region of 100–120 °C, mixtures of α - and α' -form crystals form. At higher crystallization temperatures (>120 °C),

PLLA α -form crystals form.¹⁰ Moreover, the crystal structure (α' -form crystals transform into α -form crystals) of PLLA can be changed through different annealing conditions and molecular weights.¹¹ The effects of the additions to PLLA crystal structure have also been studied.¹³ Pan et al.¹³ proposed that the crystal structure of PLLA is changed with the addition of poly(D,L-lactide) (PDLLA), and these structures are determined by the lowered equilibrium melting point and decreased crystalline rate. They found that α -form PLLA crystal (stable phase) is controlled by the thermodynamic effect and that α' -form crystal (metastable phase) is controlled by the kinetic effect. In this study, the addition of DBS on PLLA was slight (0–4 wt %), much lower than that of PDLLA on PLLA (0–100 wt %). However, from our results, it was intriguing to find that the crystal structure of PLLA did change with such a low addition.

DBS is a butterfly-shaped amphiphilic molecule with low molecular weight. It can self-assemble through hydrogen bonding and phenyl interaction (π - π interaction) in organic solvents to produce gels.^{14–17} DBS can also become the gels in some liquid polymers such as poly(propylene glycol) (PPG) and polysiloxanes.^{18–20} Microscopic studies show that DBS-induced physical gelation is due to the presence of 3-D nanofibrillar networks, with nanofibrils ranging from 10 nm to 0.8 μ m in diameter. DBS gels could provide commercial and technological benefits for electrolytes, cosmetics, and so on.^{21,22} Recently, DBS gels have been used as templates to synthesize porous polymers such as

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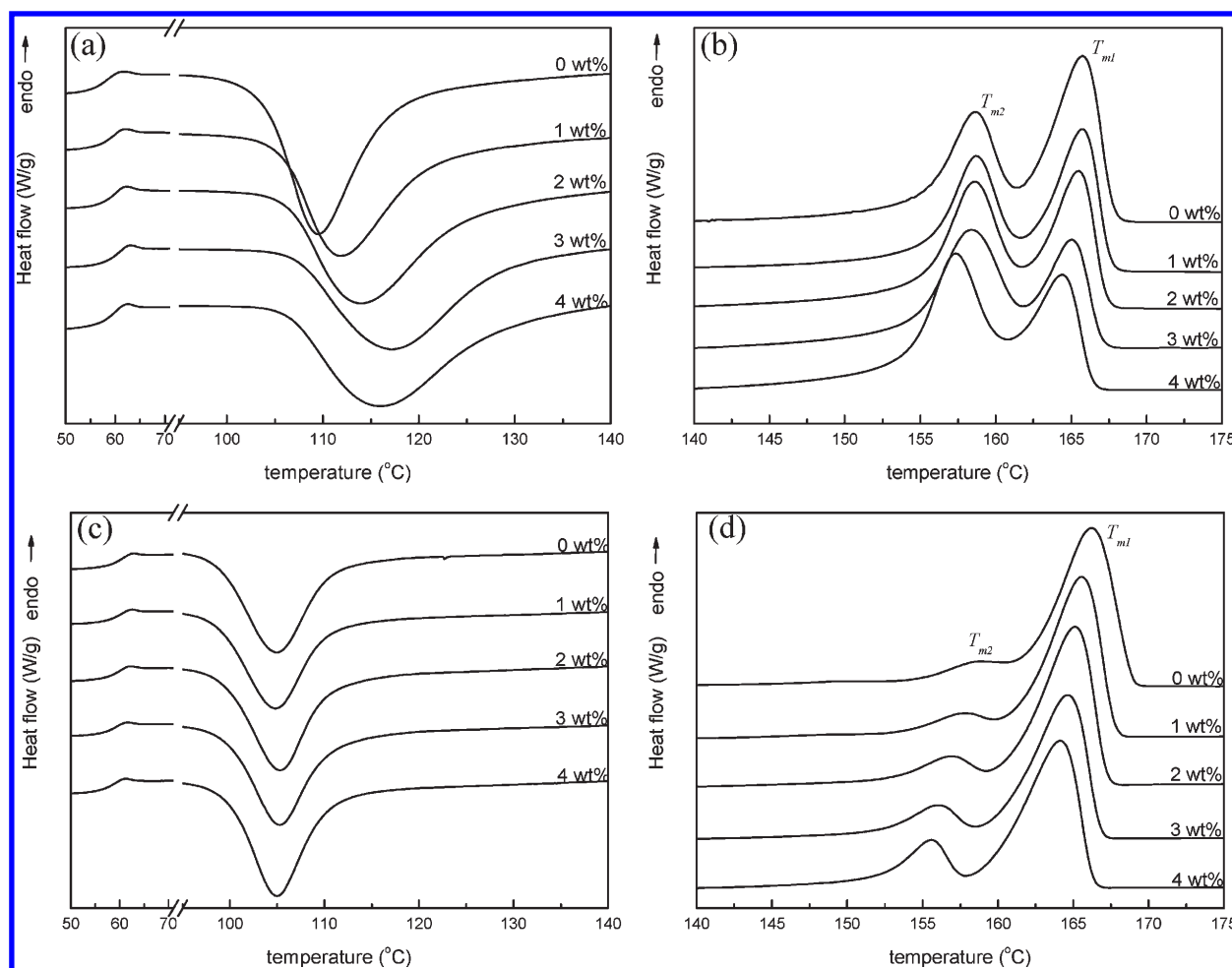


Figure 1. DSC heating thermograms of DBS/PLLA samples with 0–4 wt % DBS, which were heated at 10 °C/min (a) from 50 to 140 °C and (b) from 140 to 175 °C and at 5 °C/min (c) from 50 to 140 °C and (d) from 140 to 175 °C after quenching from the melt.

polystyrene (PS). Moreover, because of the presence of nanofibrillar networks, these gels can act as reinforcing materials to enhance the thermal and mechanical properties of PS.²³

In addition, neat DBS (not gel state) is capable of self-assembling into fibrils (diameter size ranged from 100 nm to 1 μ m) during cooling from the melt.²⁴ The average diameter of neat DBS fibrils is much larger than that of DBS nanofibrils in organic solvents or liquid polymers.¹⁸ Neat DBS could be commercialized or utilized in some polymers as well. For example, DBS has often been used as a nucleating agent to change the crystalline rate and optical properties in some crystalline polymers such as polyethylene (PE), polypropylene (PP), and poly(ethylene terephthalate) (PET).^{25–27} DBS could provide a good template for polymer chain alignment and high levels of crystal orientation in poly(ϵ -caprolactone).²⁸ In our previous studies, we investigated the microstructure and morphology of PLLA with the addition of different DBS amounts. DBS nanofibrils were found in DBS/PLLA systems. The porous PLLA materials were obtained by solvent extraction of the DBS nanofibrils.²⁹

Previous studies^{8–13} have mentioned that PLLAs have different crystal structures and melting behaviors. These different melting behaviors could influence the properties of PLLA, such as biodegradability.^{30,31} Therefore, we believe that the thermal behaviors and crystal structures of PLLA with the addition of DBS deserve further discussion. As to our knowledge, this is the

first study to consider and analyze the behaviors of PLLA with the addition of DBS.

EXPERIMENTAL SECTION

Materials. PLLA was obtained from the NatureWorks. 1,3:2,4-Dibenzylidene-D-sorbitol (DBS) was obtained from Milliken Chemical.

Sample Preparation. Preparation of PLLA samples with different amounts of DBS was carried out by the solution-casting method. The blending components were dissolved in chloroform yielding a 2% (w/v) solution. The solution was subsequently poured onto a glass dish. A film was obtained after evaporating solvent very slowly under ambient conditions at room temperature. The film was then further dried at 80 °C for 24 h in a vacuum. In addition, TGA was used to check the residual solvent in the final films. The results showed no measurable residual solvent in the films. The samples with DBS contents higher than 5 wt % could not dissolve in solvent completely, and only opaque solutions were obtained. Therefore, the DBS amounts from 0 to 4 wt % for the DBS/PLLA samples were chosen for the following investigations.

DSC Analysis. The nonisothermal crystallization and melting behavior of DBS/PLLA samples were measured with a Perkin-Elmer Pyris Diamond differential scanning calorimetry (DSC)

instrument. Indium was used as a standard for temperature calibration. Samples of 5–10 mg were used in all DSC experiments. The samples were first heated to 240 °C and maintained for 1 min and then were cooled to 0 °C. At different heating rates of 5 and 10 °C/min, the samples were heated from 0 to 240 °C so that the glass-transition temperature and melting point could be observed. The glass-transition temperature (T_g) was determined from the half-height point of the step change in the DSC thermograms, and the melting point (T_m) was obtained from the temperature at the position of the highest melting peak. The isothermal crystallization, melting behavior, and equilibrium melting point of DBS/PLLA samples were measured by a Perkin-Elmer Pyris Diamond DSC instrument. The samples were heated to 240 °C and maintained for 1 min and then quickly quenched to the temperature, which was kept at the crystallization temperature. After the crystallization peak appeared completely, the samples were heated to 240 °C at a heating rate of 10 °C/min. Therefore, the melting point (T_m) could be observed. The equilibrium melting point, T_m° , was obtained from extrapolation with the $T_m = T_c$ line.

WAXD Analysis. The crystal structures of DBS/PLLA samples were performed on a Bruker D&A D-8 Advance X-ray diffractometer (XRD) ($\lambda = 0.154$ nm). The samples were heated to 200 °C in a Thermoscientific F47915 muffle furnace for 10 min. After the samples were melted, they were quickly transferred to a vacuum oven, which was already set with the different crystallization temperatures for isothermal crystallization. The XRD measurements were operated from 5 to 35° at a scan rate of 1°/min.

RESULTS AND DISCUSSION

Nonisothermal Crystallization and Melting Behavior of PLLA with DBS. Figure 1 displays the DSC thermograms of PLLA samples with different DBS contents, which were heated at different rates of 10 and 5 °C/min after quenching from the melt. The thermal properties of samples with DSC (Figure 1) are listed in Table 1. As seen in Table 1, all samples exhibited a single glass-transition temperature (T_g) around 58 °C, which was very close to the neat PLLA sample. The T_g values of samples were not significantly influenced by the addition of DBS because of the small amounts of DBS (0–4 wt %). As shown in Figure 1a, the shapes of the crystallization peaks became broader for samples containing higher amounts of DBS. The addition of DBS seemed to influence the crystallization of PLLA. Two melting peaks were found upon heating, as seen in Figure 1b. We denoted T_{m1} and T_{m2} , respectively. It was found that both melting peaks slightly decreased with the increase in DBS contents. However, the intensities of both peaks were quite different and were changed by the different amounts of DBS. The intensity of T_{m1} was higher than that of T_{m2} for the neat PLLA sample. However, as the amounts of DBS increased, the opposite tendency was exhibited. The intensity of T_{m1} became lower than that of T_{m2} for the samples with 3 and 4 wt % DBS. In addition, the shapes of the crystallization peaks were not affected significantly by the addition of DBS at a lower heating rate (5 °C/min), as shown in Figure 1c. It may be that PLLA had more time to crystallize by itself; therefore, the effect of DBS on PLLA crystallization was lowered. Similarly, in Figure 1d, both T_{m1} and T_{m2} were slightly lowered as the DBS contents increased. The intensities of T_{m2} were obviously higher when the DBS amounts increased.

It has been reported that both melting peaks (T_{m1} and T_{m2}) contribute to the melting peaks of α -crystals.¹⁰ The ordered α -crystal of PLLA generally crystallized at higher temperatures;

Table 1. Thermal Properties of PLLA Samples with 0–4 wt % DBS

DBS amount	DSC heating rate = 10 °C/min			
	T_g	T_c	T_{m2}	T_{m1}
0 wt %	57.47	109.52	158.57	165.75
1 wt %	58.34	111.79	159.00	165.69
2 wt %	58.26	113.97	158.84	165.52
3 wt %	59.57	117.09	158.44	164.95
4 wt %	58.34	115.98	157.33	164.51
unit: °C				
DBS amount	DSC heating rate = 5 °C/min			
	T_g	T_c	T_{m2}	T_{m1}
0 wt %	59.47	105.00	158.32	166.25
1 wt %	61.17	104.82	157.64	165.58
2 wt %	58.53	105.32	156.81	165.16
3 wt %	58.01	105.24	156.14	164.66
4 wt %	57.26	104.99	155.63	164.16
unit: °C				

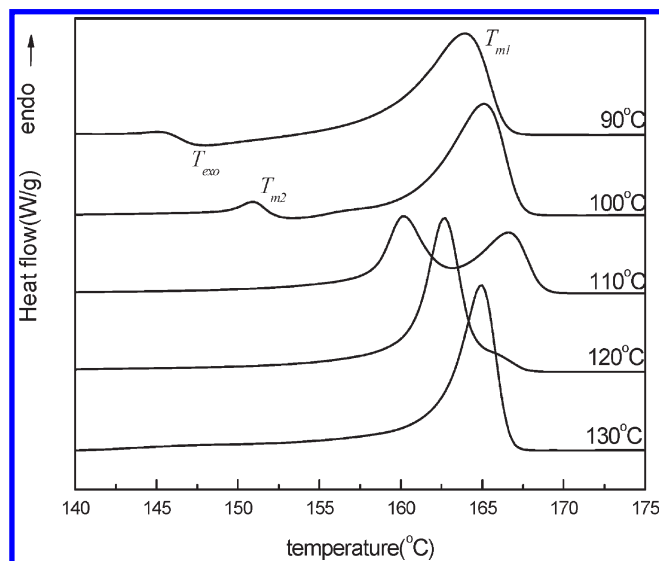


Figure 2. DSC heating traces of neat PLLA samples isothermally crystallized at different temperatures.

the disordered α' -crystal crystallized at lower temperatures. T_{m2} was the melting peak of the α -crystal, which formed during the crystallization. T_{m1} was the melting peak of the α -crystal after α' -crystal transformed into α -crystal. The intensity of the melting peak (T_{m2}) was higher, which means that more α -crystals formed during crystallization. In Figure 1a, at a higher heating rate, the crystallization peaks became much broader and shifted to the higher temperatures with the increase in DBS amounts, which suggests that crystals forming at higher temperatures (α -crystal) were more. Hence, the intensity of T_{m2} was even much higher than T_{m1} in samples containing DBS contents above 3 wt %. (See Figure 1b.) In comparison, the effect of DBS on PLLA crystallization was less significant at a slower heating rate, as previously mentioned. (See Figure 1c.) However, the melting behavior of

Table 2. Detailed DSC Heating Data of PLLA Samples with 0–4 wt % DBS Isothermally Crystallized at Different Temperatures

DBS amount	crystallization temperature								
	90 °C		100 °C		110 °C		120 °C		130 °C
	T_{exo}	T_{m1}	T_{m2}	T_{m1}	T_{m2}	T_{m1}	T_{m2}	T_{m1}	T_{m2}
0 wt %	147.45	164.00	150.99	165.03	160.25	166.60	162.73	166.09	164.99
1 wt %	146.46	163.34	150.63	164.50	159.09	165.94	161.75	165.44	163.81
2 wt %	145.93	162.99	150.65	164.18	158.25	165.26	160.75	165.27	163.49
3 wt %	145.44	162.50	150.97	164.01	157.60	164.62	160.42	164.77	162.76
4 wt %	145.61	162.00	152.98	163.00	157.10	164.12	159.91	164.27	162.47

unit: °C

PLLA was still influenced: the intensity of T_{m2} became higher with higher DBS contents. (See Figure 1d.)

References 11 and 13 mentioned that there are three different crystal structure regions (α -crystal, mixtures of α - and α' -crystal, and α' -crystal) of PLLA. In this study, we also define a disorder-to-order (α' -to- α) phase-transition temperature of PLLA. When the crystallization temperature is above this transition temperature, only α -crystal forms; when the temperature is below the transition temperature, a mixture of α - and α' -crystals form. If the temperature is much lower, then we only see the formation of α' -crystal. As seen in Figure 1, the existence of α -crystal was increased with the addition of greater DBS amounts. Therefore, it is assumed that the disorder-to-order (α' -to- α) transition temperature of PLLA is lowered with the addition of more DBS. The detailed quantitative α' -to- α phase transition temperature of PLLA by WAXD will be discussed in the next section.

Furthermore, in DSC heating traces, lower crystallization temperatures usually represent higher crystallization rates. From Figure 1a, the crystallization rate of PLLA decreased with the increase in DBS amounts. However, the crystallization rate of PLLA was slightly enhanced for the samples with 4 wt % DBS. The addition of DBS seemed to hinder the crystallization of PLLA because the PLLA crystallization temperatures became higher. (See Figure 1a.) What caused the lowered crystallization rate of PLLA will be explained in detail later. In addition, both melting points (Figure 1b,d) were slightly lowered with increased amounts of DBS. The addition of impurities (DBS components) caused lower PLLA melting points.

Equilibrium Melting Point of PLLA with DBS. Figure 2 displays the DSC heating traces of neat PLLA samples isothermally crystallized at different temperatures. When the crystallization temperature (T_c) was 90 °C, the small exothermal peak (we denoted as T_{exo}) appeared prior to the melting peak (T_{m1}) in the DSC heating curves. When T_c was >100 °C, the exothermal peak disappeared and another melting point (T_{m2}) appeared. The intensity of T_{m2} increased obviously with the increase in crystallization temperature. Until T_c reached 130 °C, there was only one melting peak (T_{m2}). T_{exo} was the temperature at which the α' -crystal transformed into α -crystal.¹⁰

The equilibrium melting point of PLLA was determined by Hoffman–Weeks plots.³² The relevant equation was written in the following form

$$T_m = \frac{1}{\gamma} T_c + \left(1 - \frac{1}{\gamma}\right) T_m^0$$

where T_m and T_m^0 are the experimental melting temperature and the equilibrium melting temperature of PLLA in the blend,

respectively. γ is a proportional factor between the initial thickness of a chain-folded lamella and the final lamellar thickness.

The trend of T_{m2} exhibited linear relation with T_c when the T_c was above 110 °C. The α - and α' -form crystal of PLLA coexisted at low crystallization temperatures. Therefore, in this study, the equilibrium melting point of PLLA, T_m^0 , was obtained from the extrapolation of the linear part of T_{m2} above 110 °C with the $T_m = T_c$ line.¹⁰ The detailed DSC heating data of the PLLA samples with 0–4 wt % DBS isothermally crystallized at different temperatures are summarized in Table 2. Figure 3 plots T_m^0 , T_{m1} , T_{m2} , and T_{exo} as functions of crystallization temperature for the PLLA samples containing 0–4 wt % DBS. Regardless of the different amounts of DBS, the equilibrium melting points of PLLA were very similar (~ 175 °C). The equilibrium melting point of PLLA was not influenced significantly by the addition of DBS. The equilibrium melting point of PLLA (175 °C) was lower than that reported by Zhang et al.¹⁰ (189 °C) and Lai et al.³³ (192 °C).

In addition, Zhang et al.¹⁰ proposed that PLLA with various isothermal crystallization temperatures had three kinds of melting behaviors. In the regions of high-to-low crystallization temperature, they were α -crystal, coexistences of α - and α' -crystal, and α' -crystal, respectively. The region of linear relation of T_{m2} displayed that only α -crystal formed. At the regions of lower crystallization temperatures, α' -crystal appeared and α - and α' -crystal coexisted. In this study, similarly, we assumed that PLLA has a disorder-to-order (α' -to- α) phase-transition temperature. The α' -to- α phase transition temperature of the neat PLLA sample was assumed to be above 110 °C. (The detailed values were obtained by WAXD, as described in the next section.) Above this transition temperature, only α -crystal formed. In Figure 3 and Table 2, the T_{m2} of the sample crystallized at 100 °C increased with the increase in DBS contents. The T_{m2} of the sample with 4 wt % DBS showed a linear relation above 100 °C. This means that more α -crystal formed at lower temperatures. Therefore, the α' -to- α transition temperature was lowered with the increase in DBS amounts. This tendency is consistent with the nonisothermal DSC analysis.

From the above DSC results, the equilibrium melting point (Figure 3) and glass-transition temperature (Table 1) of PLLA were not changed significantly by the addition of DBS. This suggests that DBS and PLLA could be an immiscible system or that the amount of DBS was too small to affect the thermal transition temperatures. Usually, the crystallization rate of a polymer is influenced by the glass-transition temperature and equilibrium melting point. However, it was very intriguing to find that the crystallization rate of PLLA was affected by the addition of DBS (Figure 1a). Therefore, there could be some other reason causing

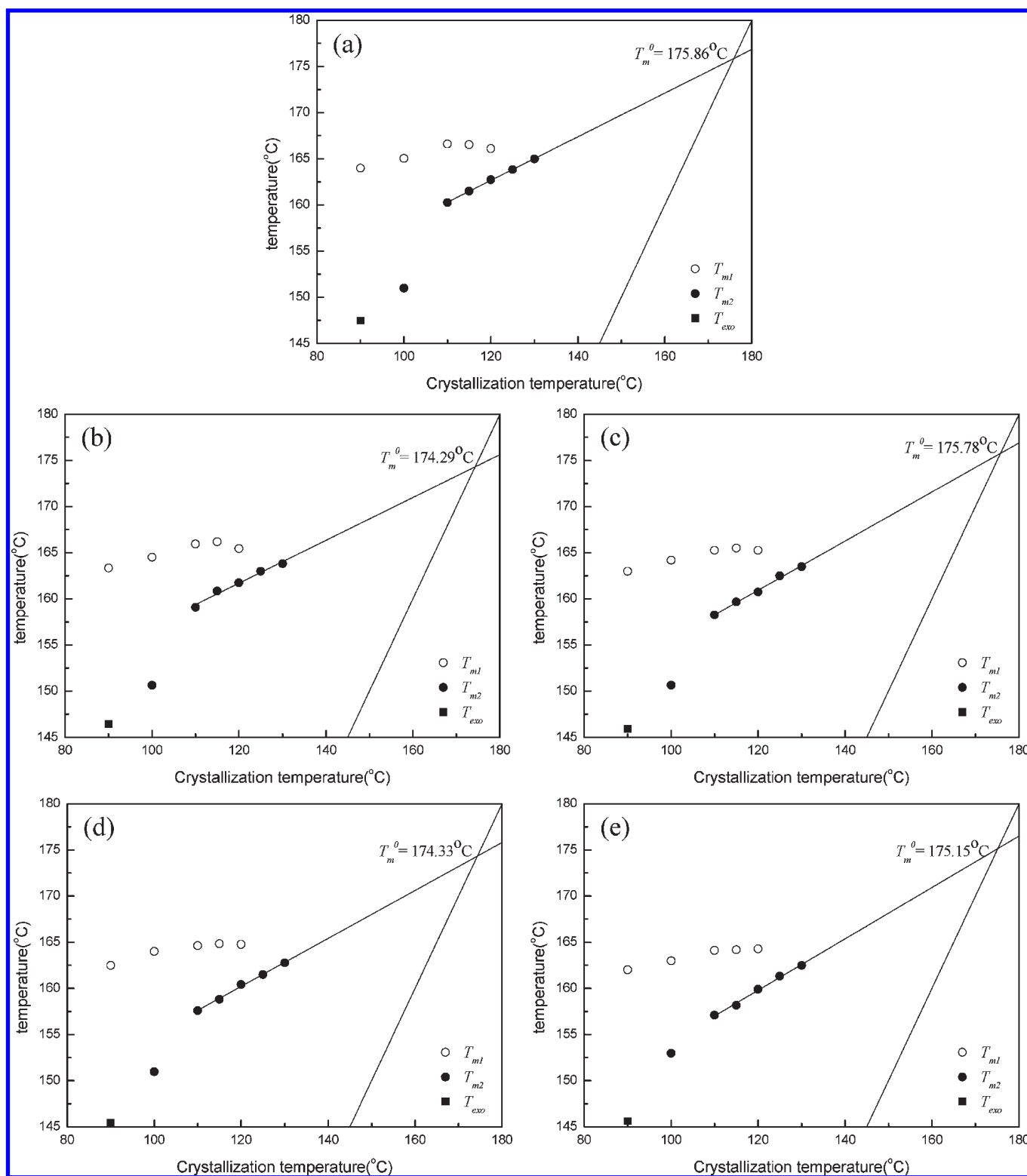


Figure 3. T_m^0 , T_{m1} , T_{m2} , and T_{exo} as functions of crystallization temperature for PLLA samples containing (a) 0, (b) 1, (c) 2, (d) 3, and (e) 4 wt % DBS.

the different crystallization rate. In the next section, we will discuss why the addition of DBS changed the crystalline rate of PLLA.

Crystal Structure of PLLA with DBS. The effect of DBS amounts and PLLA crystallization temperatures on the crystal structure (α - or α' -form crystal) of PLLA with 0–4 wt % DBS

was measured by WAXD. Figure 4 shows WAXD patterns of neat PLLA samples crystallized at different temperatures. The diffraction peaks at $2\theta = 12.5$, 14.7 , 16.7 , 19.1 , and 22.4° , which correspond to the (103), (010), (200)/(110), (203), and (015) reflections show the characteristics of the α -form crystals of PLLA.^{8,12,34} The dashed lines (Figure 4b) are the

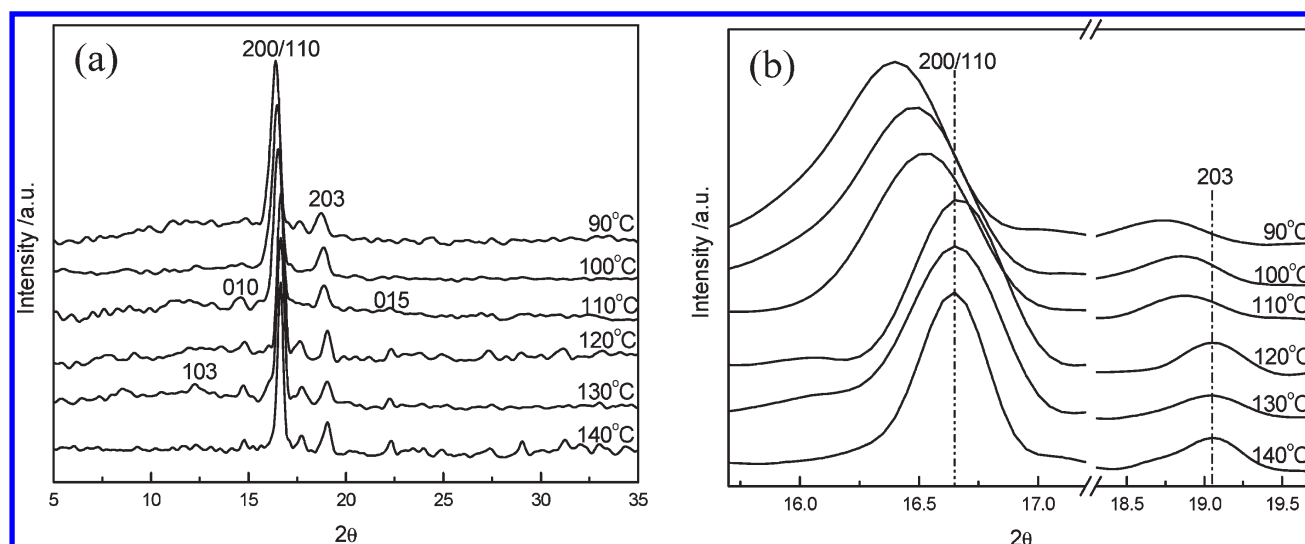


Figure 4. (a) WAXD patterns of neat PLLA samples isothermally crystallized at different temperatures and (b) enlarged WAXD patterns for the 2θ between 15 to 20° .

two strongest diffractions (200)/(110) and (203), which represent the existence of α -crystal.^{8,12,13} The characteristic diffraction of the α' -crystal was detected at $2\theta = 24.5^\circ$ in a previous study.¹³ However, as seen in Figure 4a, the intensity of this diffraction peak was weak and not easy to observe. From the enlarged WAXD patterns for the 2θ between 15 and 20° (Figure 4b), when the crystallization temperature was lower than 120°C , the (200)/(110) and (203) reflections shifted to the lower 2θ . When the temperature was above 120°C , the (200)/(110) and (203) reflections remained the same. This means that there is a disorder-to-order (α' -to- α) phase-transition temperature near 120°C . Above the transition temperature, only α -crystals formed. Below 120°C , the (200)/(110) and (203) reflections changed because of the coexistences of α' - and α -crystals.¹⁰ Zhang et al.¹⁰ also found the same result, observing that the transition temperature of neat PLLA was around 120°C by WAXD.

Figure 5 displays the WAXD patterns of the PLLA samples with 0–4 wt % DBS crystallized at different temperatures. The strongest (200)/(110) reflection was chosen for the comparison. As shown in Figure 5a–c, the (200)/(110) reflections (ranged from 16 to 17°) mostly moved forward to the higher 2θ with the increase in DBS content. After the samples were isothermally crystallized at 120 , 130 , and 140°C , the (200)/(110) reflections were not significantly changed with the increase in DBS amounts. (See Figure 5d–f.) More addition of DBS caused the α -crystals of PLLA to form at lower temperatures. Therefore, the α' -to- α phase-transition temperature was lowered significantly as the greater amounts of DBS were added. Pan et al.¹³ pointed out that the transition temperature of PLLA by WAXD decreased with the increase in PDLLA for PDLLA/PLLA blends. In particular, for the PLLA/PDLLA 50/50 blend sample, the transition temperature was lowered by $\sim 30^\circ\text{C}$. Figure 6 shows the variation of lattice spacings, $d_{110/200}$, of the (110)/(200) diffractions with crystallization temperatures (T_c) for PLLA samples with 0–4 wt % DBS. The values of $d_{110/200}$ for all samples mostly decreased with the increase in T_c . For the samples with different DBS amounts, the values of $d_{110/200}$ mostly decreased with the increase in DBS content. For example, the value of $d_{110/200}$ for neat DBS decreased with the increase in T_c . However, the value

of $d_{110/200}$ remained the same when T_c was $>120^\circ\text{C}$. For samples with 4 wt % DBS, the values of $d_{110/200}$ were smaller than those with neat DBS. The value of $d_{110/200}$ remained the same when T_c was above 110°C . As shown in Figure 4, the α' -to- α phase transition temperature of neat PLLA was $\sim 120^\circ\text{C}$, which means the α -crystal of PLLA formed only when T_c was above 120°C . Therefore, the unit cell dimension (a - or b -axis length) of PLLA was smaller when the α -crystal formed. Moreover, the unit cell dimension of PLLA was smaller when more DBS was added. Pan et al.¹³ also found that the unit cell dimension of PLLA decreased with the increase in PDLLA in a blend system.

From the above DSC and WAXD results, it was found that the portion of α -form PLLA increased with the increase in DBS content. The phase-transition temperature of PLLA, analyzed by WAXD, was lowered with the increase in DBS amount. Pan et al.¹³ discussed the factors influencing the formation of α - or α' -form PLLA in a blend system. According to their study, these factors were the equilibrium melting point (thermodynamically) and the crystallization rate (kinetically). The addition of PDLLA to PLLA samples caused the α -form crystal to be favored because of the decreased equilibrium melting point and crystallization rate. However, in this study, the equilibrium melting point of PLLA was not changed significantly by the addition of DBS. In fact, the DBS component in this system was slight (<4 wt %), much lower than that of the PDLLA/PLLA blend system. (The PDLLA component is 0–100 wt %.) We believe that there could be another reason for the formation of α -crystals. It could be that the interactions between DBS and PLLA and the interactions between DBS molecules themselves cause the different crystal structures of PLLA. DBS is a butterfly-shaped amphiphile, which consists of hydrophilic and hydrophobic groups, as shown in Figure 7. Wilder et al.¹⁸ investigated the effect of matrix polarity in the organogels of DBS and two poly-(ethylene glycol) (PEG) derivatives differing in methoxy end group substitution. It was found that in a polar medium (hydroxy-end-capped PEG), the rate of DBS self-organization decreased because of competing interactions (hydrogen bonding) with matrix molecules. As shown in our previous study,²⁹ hydrogen bonding exists between DBS and PLLA. Furthermore,

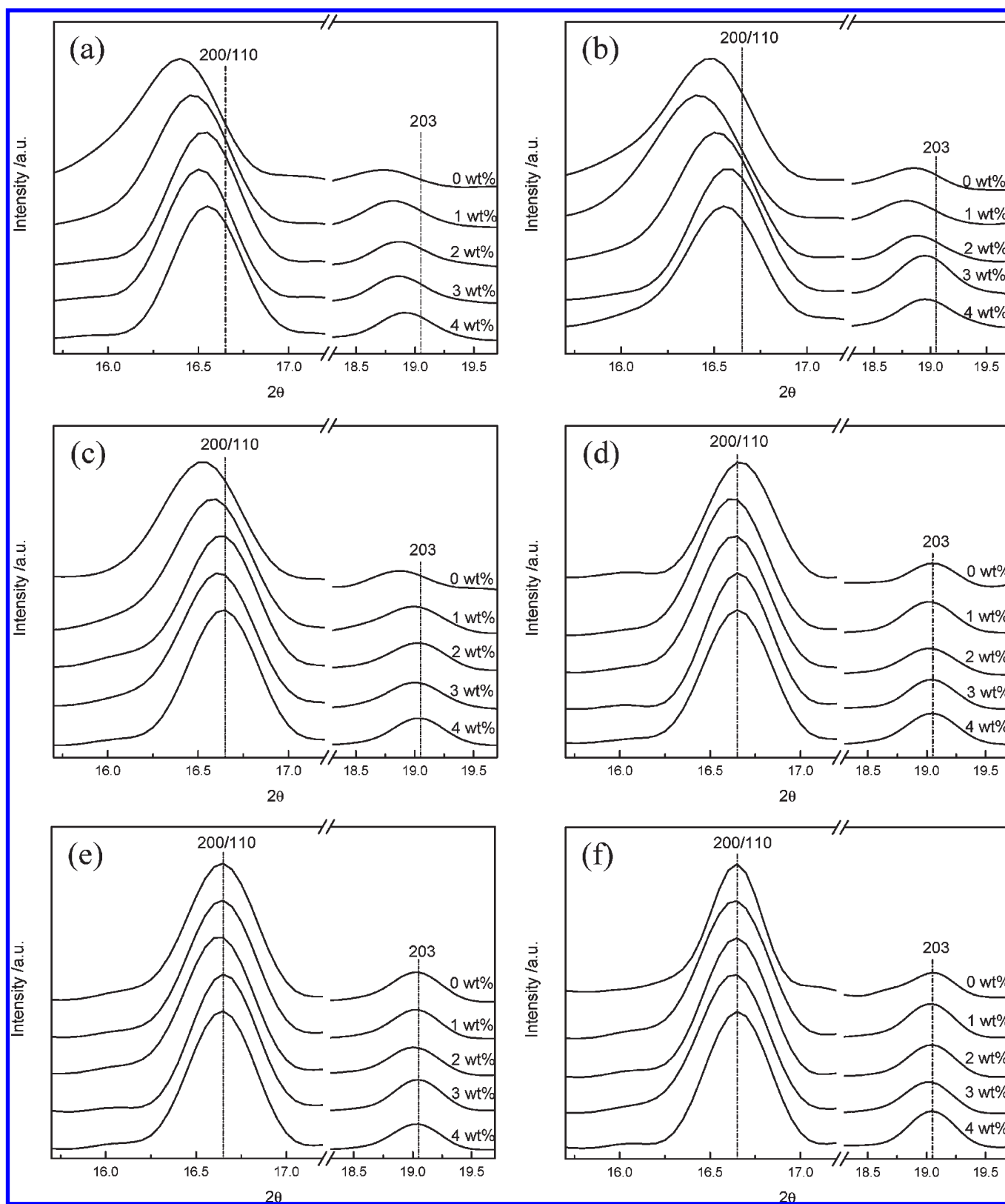


Figure 5. WAXD patterns of PLLA samples with 0–4 wt % DBS isothermally crystallized at (a) 90, (b) 100, (c) 110, (d) 120, (e) 130, and (f) 140 °C.

Wilder et al.¹⁶ reported that the DBS nanofibrils form through both hydrogen bonding and phenyl interaction (π – π interaction). DBS nanofibrils were also found in the DBS/PLLA systems.²⁹ Therefore, it is believed that there were still π – π

interactions between DBS molecules. Figure 7 displays a schematic representation of the proposed microstructure of PLLA with DBS. The proposed microstructure of DBS with PLLA is based on stacked DBS linked to PLLA through hydrogen

bonding. The DBS molecules are stacked by the π - π interactions of aromatic groups to form a strand with PLLA molecules by hydrogen bonding. Because of these interactions, PLLA could have much more regular structure with the addition of DBS. Because the structure of the α -crystal of PLLA is more regular than that of the α' -crystal,¹¹ the formation of the α -crystal of PLLA is favored as more DBS is added. Moreover, it was found that the a - or b -axis length of the PLLA unit cell was smaller when more DBS content was added (Figure 6), although the c -axis length of PLLA is not changed despite α - or α' -crystal forms and stays constant.¹² We assumed that there are some interactions such as the hydrogen bonding between DBS and PLLA and the hydrophobic π - π interactions between DBS molecules. (See Figure 7.) The decrease in the PLLA unit cell dimension (a - or b -axis length) could also be the result of these interactions. DBS molecules that were not incorporated within the unit cell could also cause some stress on the crystal, leading to the shorter a - or b -axis.

In addition, why the crystallization rate of PLLA is affected by the addition of DBS could be explained as follows. The variation of crystallization rates may be caused by the different crystal structure of PLLA. Several studies have mentioned that the α - and α' -forms of PLLA crystals have different crystallization kinetics.^{8,13,35} The addition of DBS changes the PLLA crystal

structure (α -crystal was favored). This has already been proven by DSC and WAXD. Therefore, the crystallization rate of PLLA was influenced. Additionally, as seen in Figure 1a, the crystallization rate of PLLA decreased with the addition of DBS, but the crystallization rate of PLLA slightly increased for the PLLA sample with 4 wt % DBS. DBS is usually used as a nucleating agent to enhance the crystallization rate.^{25–27} It may be that the increase in the nucleation rate increased the crystallization rate for the sample with 4 wt % DBS.

CONCLUSIONS

According to our observation of the melting behavior of PLLA with DBS, the intensities of both peaks (T_{m1} and T_{m2}) were quite different and were changed by the different contents of DBS. The intensities of T_{m2} of PLLA were found to increase gradually with the increase in DBS amounts at different heating rates (5 and 10 °C/min). The equilibrium melting point experiment found that the T_{m2} of the sample isothermally crystallized at 100 °C increased with the increase in DBS content. The T_{m2} of the PLLA sample with 4 wt % DBS shows a linear relation above 100 °C. However, the equilibrium melting point of PLLA was not influenced significantly by the addition of DBS.

As for the observation of the crystal structure of PLLA with DBS, WAXD results showed that the (200)/(110) and (203) reflections moved forward to the higher 2θ with the increase in DBS content. The (200)/(110) and (203) reflections were not changed significantly, indicating the existence of α -crystals when PLLA samples with 0–4 wt % DBS crystallized above 120 °C. The addition of DBS caused the α' -crystals of PLLA to form at low temperatures. Therefore, the α' -to- α phase-transition temperature of PLLA by WAXD was much lower with the addition of more DBS components.

From the above DSC and WAXD analysis, we can see that the regular α -form crystals of PLLA were favored as DBS amounts were added. The phase-transition temperature of PLLA was found to shift toward a lower temperature with the addition of DBS components. In the proposed structure of PLLA with DBS, the DBS molecules are stacked through π - π interaction of the aromatic group to form a strand with the PLLA molecules by hydrogen bonding. Because of these interactions, PLLA could have much more regular structure with the addition of DBS. In addition, the crystallization rate of PLLA with the addition of DBS was influenced because of the change of PLLA crystal structure.

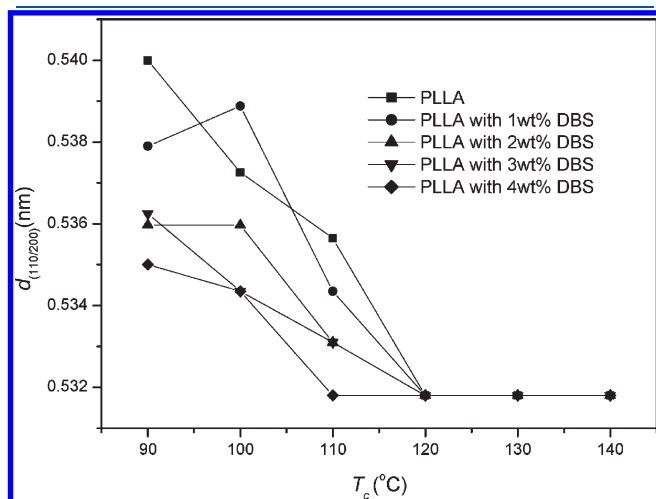


Figure 6. Variation of lattice spacings, $d_{110/200}$, of the (110)/(200) diffractions with crystallization temperatures (T_c) for PLLA samples with 0–4 wt % DBS.

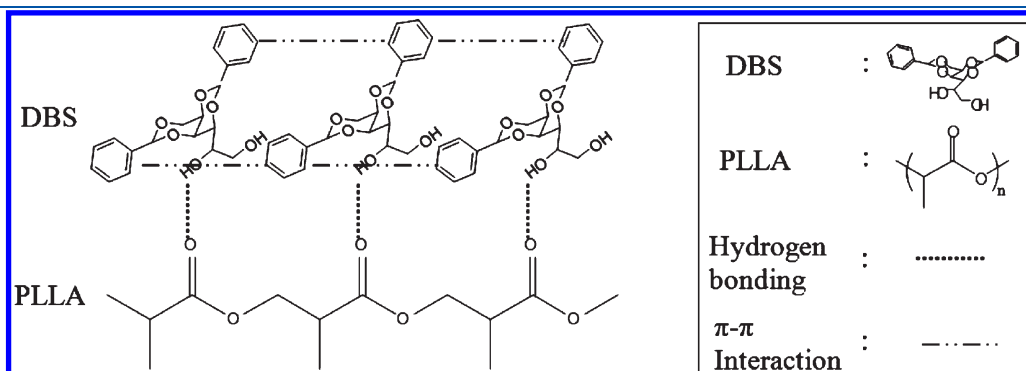


Figure 7. Schematic representation of the proposed microstructure of PLLA with DBS.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +886-2-2621-5656, ext.3516. Fax: +886-2-2620-9887.
E-mail: wclai@mail.tku.edu.tw.

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■ REFERENCES

- (1) Virgilio, N.; Sarazin, P.; Favis, B. D. *Biomaterials* **2010**, *31*, 5719–5728.
- (2) Chiu, Y.-C.; Larson, J. C.; Perez-Luna, V. H.; Brey, E. M. *Chem. Mater.* **2009**, *21*, 1677–1682.
- (3) Nagahama, K.; Ouchi, T.; Ohyu, Y. *Adv. Funct. Mater.* **2008**, *18*, 1220–1231.
- (4) Lee, C.-T.; Huang, C.-P.; Lee, Y.-D. *Biomacromolecules* **2006**, *7*, 2200–2209.
- (5) Hoogsteen, W.; Postema, A. R.; Pennings, A. J.; Ten Brinke, G.; Zugenmaier, P. *Macromolecules* **1990**, *23*, 634–642.
- (6) Puiggali, J.; Ikada, Y.; Tsuji, H.; Cartier, L.; Okihara, T.; Lotz, B. *Polymer* **2000**, *41*, 8921–8930.
- (7) Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. *Polymer* **2000**, *41*, 8909–8919.
- (8) Pan, P.; Zhu, B.; Kai, W.; Dong, T.; Inoue, Y. *J. Appl. Polym. Sci.* **2008**, *107*, 54–62.
- (9) Zhang, J.; Duan, Y.; Sato, H.; Tsuji, H.; Noda, I.; Yan, S.; Ozaki, Y. *Macromolecules* **2005**, *38*, 8012–8021.
- (10) Zhang, J.; Tashiro, K.; Tsuji, H.; Domb, A. J. *Macromolecules* **2008**, *41*, 1352–1357.
- (11) Pan, P.; Zhu, B.; Kai, W.; Dong, T.; Inoue, Y. *Macromolecules* **2008**, *41*, 4296–4304.
- (12) Kawai, T.; Rahman, N.; Matsuba, G.; Nishida, K.; Kanaya, T.; Nakano, M.; Okamoto, H.; Kawada, J.; Usuki, A.; Honma, N.; Nakajima, K.; Matsuda, M. *Macromolecules* **2007**, *40*, 9463–9469.
- (13) Pan, P.; Liang, Z.; Zhu, B.; Dong, T.; Inoue, Y. *Macromolecules* **2009**, *42*, 3374–3380.
- (14) Lipp, J.; Schuster, M.; Terry, A. E.; Cohen, Y. *Langmuir* **2006**, *22*, 6398–6402.
- (15) Mercurio, D. J.; Spontak, R. J. *J. Phys. Chem. B* **2001**, *105*, 2091–2098.
- (16) Wilder, E. A.; Spontak, R. J.; Hall, C. K. *Mol. Phys.* **2003**, *101*, 3017–3027.
- (17) Wilder, E. A.; Braunfeld, M.; Jinnai, B. H.; Hall, C. K.; Agard, D. A.; Spontak, R. J. *J. Phys. Chem. B* **2003**, *107*, 11633–11642.
- (18) Wilder, E. A.; Hall, C. K.; Khan, S. A.; Spontak, R. J. *Langmuir* **2003**, *19*, 6004–6013.
- (19) Kuhne, M.; Friedrich, C. *Rheol. Acta* **2009**, *48*, 1–9.
- (20) Wilder, E. A.; Hall, C. K.; Spontak, R. J. *J. Colloid Interface Sci.* **2003**, *267*, 509–518.
- (21) Mohmeyer, N.; Wang, P.; Schmidt, H.-W.; Zakeeruddin, S. Z.; Gratzel, M. *J. Mater. Chem.* **2004**, *14*, 1905–1909.
- (22) Schamper, T.; Jablon, M.; Randhawa, M. H.; Senatore, A.; Warren, J. D. *J. Soc. Cosmet. Chem.* **1986**, *37*, 225–231.
- (23) Lai, W.-C.; Tseng, S.-C. *Nanotechnology* **2009**, *20*, 475606–475606.
- (24) Lai, W.-C.; Wu, C.-H. *J. Appl. Polym. Sci.* **2010**, *115*, 1113–1119.
- (25) Feng, Y.; Jin, X.; Hay, J. N. *J. Appl. Polym. Sci.* **1998**, *69*, 2089–2095.
- (26) Cao, J.; Wang, K.; Cao, W.; Zhang, Q.; Du, R.; Fu, Q. *J. Appl. Polym. Sci.* **2009**, *112*, 1104–1113.
- (27) Mitra, D.; Misra, A. *J. Appl. Polym. Sci.* **1988**, *36*, 387–402.
- (28) Lipp, J.; Schuster, M.; Feldman, G.; Cohen, Y. *Macromolecules* **2008**, *41*, 136–140.
- (29) Lai, W.-C. *Soft Matter* **2011**, *7*, 3844–3851.
- (30) Tokiwa, Y.; Suzuki, T.; Ando, T. *J. Appl. Polym. Sci.* **1979**, *24*, 1701–1711.
- (31) Tokiwa, Y.; Buenaventurada, P. C. *Appl. Microbiol. Biotechnol.* **2006**, *72*, 244–251.
- (32) Hoffman, J. D.; Weeks, J. J. *Res. Natl. Bur. Stand., Sect. A* **1962**, *66*, 13–28.
- (33) Lai, W.-C.; Liao, W.-B.; Lin, T.-T. *Polymer* **2004**, *45*, 3073–3080.
- (34) Brizzolara, D.; Cantow, H.-J.; Diederichs, K.; Keller, E.; Domb, A. J. *Macromolecules* **1996**, *29*, 191–197.
- (35) Di Lorenzo, M. L. *Eur. Polym. J.* **2005**, *41*, 569–575.