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高分子之多晶態、熔融、球晶消光環型態之相關性及基本物理機制的探討

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Abstract

The crystal polymorphism, transformation, and morphologies in chloroform solvent-cast poly(hexamethylene terephthalate) (PHT) were examined by using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and temperature in-situ transmission electron microscopy (TEM). Solvent-induced crystallization of PHT at room temperature yielded an initial crystal of \( \gamma \)-form, as confirmed by WAXD. Upon DSC scanning, the original \( \gamma \)-form in PHT exhibited three endothermic peaks, whose origins and association were carefully analyzed. The first peak, much smaller than the other two, is in the temperature range of ca. 100–120°C. It was found that the solvent-induced \( \gamma \)-form was transformed to \( \beta \)-form at 125°C via a solid-to-solid transformation mechanism. In addition, WAXD showed that \( \gamma \)- and \( \beta \)-forms co-existed in the temperature range of 100-125°C. These mixed crystal forms were further identified using TEM, and the selected-area electron diffraction (ED) patterns revealed that both \( \gamma \)- and \( \beta \)-form crystals co-existed and were packed within the same spherulite. Solid-solid transformation from the solvent-induced \( \gamma \)-form to \( \beta \)-form in PHT upon heat scanning was presented with evidence and discussed.


中文摘要

利用微分掃描熱卡計、穿透式電子顯微鏡及廣角 X 光繞射分析儀研究 chloroform 溶劑誘導結晶之 poly(hexamethylene terephthalate) (PHT)的多晶態行為、晶態轉變及球晶型態。X 光繞射分析儀證明在室溫下溶劑誘導產生的結晶為γ態，根據微分掃描熱卡計熱分析，溶劑誘導產生的γ態結晶會出現三個熔融峰，第一個熔融峰與其他兩個熔融峰相較之下明顯較小，而大約位於 100 至 120°C 之間。溶劑誘導產生的γ態結晶在大約 125°C 的時候會藉固態相轉變機制轉變為β態，此外，廣角 X 光繞射分析顯示在溫度範圍 100 至 125°C 之問γ和β態會共存。更進一步以穿透式電子顯微鏡研究共存的晶態，電子繞射證明γ和β態會共存並且會在同一個球晶裡。
Introduction

Polymorphism often exists in many crystalline polymers, such as syndiotactic polystyrene (sPS) [1-3,25,26], isotactic polypropylene (iPP) [4,27], and poly(butylene adipate) (PBA) [5-7]. Poly(hexamethylene terephthalate) (PHT) also possesses complex polymorphism depending on crystallization conditions. Earlier studies in the literature have shown that PHT may contain various combinations of three different crystal unit-cells, designated as α, β and γ depending on thermal and/or solvent treatments [8-10]. Recently, multiple melting characteristics and dual morphologies of PHT have also been identified [11]. In previous papers [8-10], the α-form in PHT is shown to have a monoclinic unit-cell with dimensions $a = 0.910$ nm, $b = 1.756$ nm, $c$ (chain axis) = $1.574$ nm, $\alpha = 127.8^\circ$, $\beta = \gamma = 90^\circ$, and is known to be favored for crystallization under stress. The β- and γ-forms are both characterized as triclinic, with different dimension in b. The β-form crystal in PHT has dimensions: $a = 0.5217$ nm, $b = 0.5284$ nm, $c$ (chain axis) = $1.5738$ nm, $\alpha = 129.4^\circ$, $\beta = 97.6^\circ$, $\gamma = 95.6^\circ$. The γ-form crystal cell in PHT is also triclinic and has cell dimensions and angles all equal to those for the β-form, except for $b = 1.0568$ nm that is exactly twice as wide as that for the β-form. The γ-form is usually obtained by solvent-induced crystallization of PHT when film-cast at room temperature [8,9]. The β-form can be exclusively produced in PHT by melt-crystallization only at extremely high temperatures (~140°C or higher), while at lower or moderate temperatures (<140°C), mixed crystals consisting of α- and β-forms with various fractions in PHT are obtained [11].

Solution crystallization of macromolecules has been well discussed by Wunderlich [12]. In addition, solvent-induced crystallization has also been widely investigated in sPS [3,13-17], syndiotactic polypropylene (sPP) [18], poly(ethylene 2,6-naphthalate) (PEN) [19], poly(ethylene terephthalate) (PET) [20,21], and poly(ether ether ketone) (PEEK) [22,23]. Among these polymers, solvent-induced crystallization of sPS has been studied more extensively in recent years. sPS possesses four polymorphic crystalline forms (α-, β-, δ-, and γ-forms) when it is subjected to thermal and/or solution treatment. The δ- and γ-forms in sPS can be induced by solvent. The δ-form is obtained in sPS, which includes molecules of solvent in its unit cell. However, from completely desiccated sPS samples, the γ-form crystal is obtained [3]. Additionally, various solvents would affect the formation of
crystal form. Instead of most solvents to form only the $\delta$-crystal of sPS, $1,1,2,2$-tetrachloroethane is unique, because this solvent induces crystallization of $\gamma$-form in sPS [3]. Upon heating to higher temperatures, the $\gamma$-form crystal can be transformed to the $\alpha$-form one.

In this study, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) as well as transmission electron microscopy (TEM) were utilized to identify the crystal transformation behavior and heating-induced crystal-form changes in PHT samples prepared by solution casting from chloroform at room temperature. The literature has widely reported [8-10] that the $\gamma$-form crystal can be produced in PHT by treatment with chloroform at room temperature and $\beta$-form is yielded by annealing the $\gamma$-form at higher temperatures; however, the mechanism of transition or thermal characteristics of these crystals has yet to be understood. With aims to extend the previous findings, this study attempted to describe the crystal-form changes as a function of temperature after initial solvent-induced crystals were generated. The crystalline morphologies of the individual PHT spherulites containing both $\gamma$- and $\beta$-forms were further characterized by “temperature in-situ TEM”.

**Experimental**

**Materials**

PHT was synthesized using butyl titanate as a catalyst, according to the method described in the literature [24]. Molecular weights were determined by gel permeation chromatography (GPC) on a Waters 410 GPC system using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min. The PHT used in this study has an $M_w=13,800$ g/mol and a polydispersity index (PDI) of 2.0. At this molecular weight, its mechanical properties are slightly lower than those at higher molecular weights, but its thermal properties [glass transition temperature ($T_g$), melting temperature ($T_m$), etc.] and crystalline morphology are expected to be characteristic of a typical polymer. The thermal transition temperatures of the PHT used here may be slightly lower than those of a longer-chain PHT, but the characteristics of the crystals and multiple melting peaks were pretty much the same as those of the longer-chain PHT. The melting point (144.3°C) and glass transition temperature (-6.7°C) were measured by DSC.


Specimen Preparation

Solvent-induced crystals were obtained by dissolving the synthesized PHT into chloroform to be a 4 wt% solution. The solution was dried at room temperature for one day, and then the sample was dried in the vacuum oven at 40°C for 7 days to remove the residual solvent in PHT. The solid PHT sample was directly heat-treated by DSC.

For TEM, thin films of PHT were prepared/crystallized on glass slides by casting the solution. For reinforcing the specimen, the polymer thin films were coated with vapor-deposited carbon under vacuum. In order to carry out the calibration of the diffraction camera length, gold (Au) was vapor-deposited onto some of the thin films before carbon coating. After carbon coating, a drop (a hemisphere 3-4mm in diameter) of aqueous solution (25%) of polyacrylic acid was placed on the appropriate portion of the specimen film and hardened after drying for one day at room temperature. hardened polyacrylic acid with the specimen thin film was detached from the glass plate, and then the polyacrylic acid was dissolved in water. Finally, a TEM copper grid was used to collect the specimen film floating on the water surface and then dried under ambient condition.

Analytical Apparatus

The thermal behavior of the PHT sample was preliminarily investigated using a differential scanning calorimeter (DSC-7, Perkin-Elmer). The temperature and heat of transition indicated with the instrument were calibrated with indium and zinc standards. For determining the enthalpy of melting peaks, a dynamic heating rate of 10°C/min was used unless otherwise indicated. During thermal treatments and DSC measurements with the DSC-7, a continuous flow of nitrogen gas into the sample-cell chamber was maintained to ensure minimal sample degradation. In addition, the DSC sample-cells were used for precisely controlling the thermal treatments of samples.

The WAXD instrument was a Shimadzu XRD-6000 (30 kV and 40 mA), and the copper Kα radiation of a wavelength of 0.1542nm was utilized. The scattering angle, 2θ, ranged from 5° to 40° with a scanning step of 2°/min (Here, θ is the Bragg angle). For ensuring the temperature accuracy, specimens for WAXD characterization were prepared by imposing desired thermal treatments using the DSC-7.
Morphological observation and selected-area electron diffraction (SAED) of specimens were performed with a transmission electron microscope (JEOL JEM-200CS) operated at an accelerating voltage of 200kV. A specimen-heating holder (JEOL EM-SHH4) which has been fitted up with a homemade “temperature controller” [28] was utilized to regulate the specimen temperature to be a desired temperature. The size of the selected-area aperture utilized for SAED experiments in this study was ca.2.5 µm in diameter on the specimen. In addition, the morphological images were taken in the conventional bright-field mode at a direct magnification of 5,000X [29,30]. All the images and SAED patterns were recorded on photographic films (Mitsubishi MEM) which were then developed with Mitsubishi Gekkol (full strength) at 20°C for 5min [29,31].

Results and Discussion

DSC and WAXD characterization of crystal transformation

It has been already mentioned that crystallization of γ-form could be induced by solvent at room temperature, and β-form is obtained after annealing the γ-form at the high temperatures [9]. To identify the meta-stability and phase transformation of solvent-induced PHT crystals, the solid sample of PHT was examined by DSC. Figure 1(a) shows the DSC thermogram for the initially solvent-induced PHT sample that was scanned at 10°C/min. The first endothermic peak (P1) at 115.5°C designated as T_{m1} was identified. The other two endothermic peaks in this thermogram are located at 138.2 and 145.3°C, respectively. The total endothermic heat is 64.4J/g from the initial state to melt. However, the heat of the first peak (P1) is only 7.2J/g. In this thermogram, the onset and tail-end of the P1 peak are at ca.105 and 125°C, respectively. The initially solvent-induced PHT sample was also examined by WAXD. Figure 1(b) shows the typical X-ray diffractogram (namely, WAXD intensity profile) of PHT crystals. The reflection peaks in the diffractogram are recognized at 2θ=12.1, 15.6, 17.3, 18.2, 22.2, and 24.9°. According to Palmer et al. [9], these reflection peaks are attributed to the γ-form.

In contrast to the heats of P2 and P3, the heat of P1 is much smaller, as shown in Figure 1(a). Interestingly, one wonders which crystal-form may be removed upon heating the initial γ-form crystal to the temperature near P1 (ca.125°C). Therefore,
the original γ-form PHT samples heated to 125°C were subjected to DSC and WAXD to observe the melting thermal characteristics and crystal diffraction peaks. For DSC measurement, the original sample was heated to 125°C and then quenched to 0°C. Finally, the DSC sample was scanned at 10°C/min from 0°C to the melt. Figure 2(a) shows the final thermogram. In this thermogram, the P1 peak, which is evident in Fig. 1(a), now has disappeared. In addition, the total endothermic heat reduces to 57.8J/g. Obviously, the endothermic heat of P1 has vanished. By comparing Figure 2(a) with Figure 1(a), P2 and P3 have no distinguishable difference in the amount of heat or temperature position. WAXD was used to examine the diffraction intensity profile of the PHT sample after the original sample was heated up to 125°C. Figure 2(b) shows the WAXD diffraction peaks of the heated sample. The reflection peaks are located at 2θ=6.8, 15.7, 17.8, 21.0, 22.2, and 23.6° in this diffracgram. According to the earlier reports [9-11], these peaks indicate the β crystal form. Thus, the original solvent-induced γ-form crystal has been transformed to a different β-form by heat-treatment on solvent crystallized sample of PHT to 125°C. The result suggests that the solvent-induced γ-form crystal in PHT may be readily transformed to the more stable β-form at temperatures between 105 and 125°C.

The structure in thermally-induced phase transition was analyzed by performing WAXD on solvent-treated PHT samples subjected to slow heating treatment. Figure 3 shows the WAXD intensity profiles of solvent-treated PHT samples that were subjected to step-increase of the temperature in the range of 80 to 125°C. In the temperature range of 100 to 120°C, the temperature interval is reduced 2°C in order to examine the structure changes in greater details. The samples heated/annealed at lower temperatures below ca.106°C show characteristic γ-form reflection peaks. Below 106°C, the γ-form reflection peak remains constant. At 108°C or higher, the reflection peaks at 2θ=15.7, 17.8, 21.0 and 23.6° attributed to the β-form, begin to appear and increase in intensity on raising the annealing temperature. On the contrary, the γ-form peaks at 2θ=12.1, 17.3, 18.2 and 24.9° decrease in intensity with increasing annealing temperature, implying that a transition from γ- to β-form occurs. Above 120°C, the γ-form diffraction peaks almost vanish.

By combining the results from DSC and X-ray, the first melting peak (P1) thus is related to the γ-form, while the two higher melting peaks are of the β-form. A phase transition from γ- to β-form must have taken place during heat scans. The
mechanism of phase transition needs to be analyzed further using TEM and WAXD, in order to more accurately locate the crystal transition temperature.

In our earlier studies on sPS [3], it was found that the initially solvent-induced γ-form crystal of sPS can be transformed to α’-form as the temperature is increased. At the temperature where the γ- to α’-phase transition takes place, the crystallinity exhibits a significant increase. The increased intensity of WAXD is caused by melting of the γ-form of sPS and re-crystallization of the amorphous chains. In the present case however, there is no significant change of overall intensity as a result of γ to β-crystal transformation. In the DSC thermogram of the original γ-form crystal, there exists no exothermic peak related to re-crystallization of the melted amorphous chains. As a result, the γ- to β- phase transition of PHT must take place via solid-solid phase transformation. Observation of morphology in the solid-solid phase transition will be evidenced by TEM in later sections.

As discussed above, analysis of the WAXD intensity profiles indicates that the γ- to β- phase transition occurs between 106 and 120°C. In order to investigate the extent of transformation as a function of annealing temperature (T_a), the originally solvent-induced γ-form in PHT samples was heated to specific temperatures of 100, 106, 108, 110, 112, 120 and 125°C, respectively. After annealing at these temperatures for 2 min, the samples were then scanned in DSC to above melt. Figure 4 shows the melting behaviors of the samples heated/annealed at these specific temperatures (T_a). At T_a=100°C, the corresponding thermogram shows three peaks similar to those in the thermogram obtained from the original sample. The ΔH_1 related to the endothermic heat of P1 is 6.9J/g. Further increase of annealing temperature was imposed on the samples. The reduced endothermic heat of P1 was present. At T_a=125°C, however, P1 does not exist in the thermogram. As for T_a=120°C, the heat of P1 is so small that it is difficult to calculate the endothermic heat. However, a very small P1 indeed existed in the thermogram of T_a=120°C. Corresponding to the WXAD result, the smaller heat of P1 represents that more fraction of γ-form transforms to β-form.

The effect of annealing time (t_a) on the phase transition was also explored. The original γ-form PHT samples were heated to 100°C and annealed for 2 min or 960 min. Figure 5 shows the results of (a) DSC and (b) WAXD. In Fig. 5(a), both DSC thermograms have three endothermic peaks. However, when t_a = 960min, the P1 and
P2 shift to higher temperatures, and the enthalpy associated to P1 is reduced. The corresponding X-ray diffractograms are shown in Fig. 5(b). For $t_a = 960$ min, all the reflection peaks are attributed to the $\gamma$-form except for the small peak at $2\theta = 23.6^\circ$. Consequently, very long annealing times are needed to induce a small phase transition of $\gamma$-form PHT at $T_a = 100^\circ$C.

Similarly, annealing treatments were applied to the original $\gamma$-form samples at $125^\circ$C. The DSC and WAXD results are shown in Figure 6 (a, b). Both DSC thermograms in Fig. 6(a) show a similar total heat. However, for the longer annealing times, the heat of fusion of P2 increases and P2 shifts to a higher temperature, suggesting that the crystals probably thicken during long annealing times. The X-ray diffraction intensities in Fig. 6(b) show that the $\beta$-form crystal is not affected after annealing for $t_a = 960$ min at $T_a = 125^\circ$C.

**In-situ TEM on phase transition in PHT**

The thin film specimen of solvent-induced PHT prepared by the method described in the experimental section was introduced into the TEM column with the specimen-heating holder. The specimen was heated from room temperature up to $125^\circ$C, and the SAED patterns of PHT crystals were obtained at different temperatures from a same thin film specimen. Figure 7 (a~g) displays a temperature series of SAED patterns (reversed contrast) from an area about 2.5 $\mu$m in diameter. Fig. 7(a) shows the SAED pattern of the original solvent-induced PHT crystal recorded before heating. The $d$-spacing values of the observed arc-shaped reflections are 0.513 nm, 0.487 nm, 0.400 nm and 0.358 nm which correspond to $100_\gamma$, $\bar{1}10_\gamma$, $020_\gamma$, and $\bar{1}20_\gamma$ reflections, respectively, as indicated in Fig. 7(a). Here, the subscript, $\gamma$, represents the reflection of $\gamma$-form. Meanwhile, tabulated values for comparing SAED and WAXD results may help. Table 1 shows the comparison of values of $d$-spacing for the $\gamma$-form crystal, which were obtained by the WAXD and SAED analyses. The results indicate that values of $d$-spacing obtained by SAED are almost same as those measured by WAXD; however, the WAXD peaks at $2\theta = 12.1^\circ$ and $15.6^\circ$ are so weak that the corresponding reflections were not recognized in the SAED pattern. Subsequently, the thin film was heated in the specimen holder to $80^\circ$C. Fig. 7(b) is the SAED pattern obtained from the specimen treated at $80^\circ$C. Overall, below $100^\circ$C, the SAED patterns were similar to the original sample (Fig. 7a) in agreement
also with the data in Fig. 3 shown earlier. Above 100°C, more dramatic changes in the crystal forms are seen. At 110°C, the 100γ, 110γ, and 120γ reflections disappear in the SAED pattern, whereas 022β, 011β, 101β, and 112β appear. At 120°C, only a weak 020γ reflection still exists, but it completely disappears at 125°C, leaving only four β-form reflections. These β-form reflections at 125°C have d-spacings of 0.564 nm, 0.498 nm, 0.423 nm, and 0.377 nm, which correspond to 022β, 011β, 101β, and 112β, respectively. Again, the bottom portion of Table 1 lists and compares the values of d-spacing of β-form reflections observed by WAXD and SAED analyses. In addition, it is worth mentioning that experimentally all SAED patterns were obtained by focusing within the same one spherulite. The result suggests that the γ- and β-form crystals therefore co-exist within a single spherulite in the solvent-treated PHT annealed in the temperature range of ca. 110–120°C.

A temperature series (ambient to 125°C) of in-situ TEM images were produced by focusing on the spherulites in a same thin film specimen of solvent-induced PHT. Various positions of the thin film specimen were observed in order to avoid looking at accidentally damaged spherulites. The specimens were heated to higher temperatures by using the in-situ heating holder in TEM. The morphological images of the spherulites were recorded in series at ambient, 80, 90, 100, 110, 120, and 125°C, respectively. Finally, Figure 8 shows the TEM images for two specimens of the solvent-induced PHT at (a) ambient, and (b) 125°C. As all the temperature series images (ambient, 80, 90, 100, 110, 120, and 125°C) are similar; thus, only two representative TEM images are shown here. In comparison with the as-prepared PHT sample, the spherulites heated to temperatures ranging from ambient to 125°C remain unchanged (for brevity, similarity in the series are not all shown). Comparatively speaking, the temperature series TEM images between ambient and 125°C are all similar without indication of transition into liquid molten state. As a result, it can be proposed that the γ- to β- phase transition of the solvent-induced PHT crystals takes place in the solid state without going through melting.
Conclusion

The DSC analysis on the PHT samples solvent-cast from chloroform at room temperature displays three endothermic peaks, indicating a crystal polymorphism and/or crystal-crystal transformation. The WAXD results suggest that the initial solvent-cast PHT film is only of the $\gamma$-form crystal. Upon annealing at 125°C, however, a new $\beta$-form crystal is formed, which exhibits two melting peaks (P2 and P3) upon DSC scanning. The first melting peak (P1) is related to the $\gamma$-form. It implies that phase transition from $\gamma$- $\rightarrow$ $\beta$-form must have taken place during DSC heat scans. WAXD data show that only the $\gamma$-crystal exists in the original solvent-cast PHT, but both $\gamma$ and $\beta$ crystal-forms can co-exist in various fractions in solvent-cast PHT samples further heated/annealed between 106 to 120°C. When annealed at 125°C and above, PHT exhibits only the $\beta$-form crystal, suggesting a phase transition.

Further evidence of the crystal phase transition and its mechanism was obtained by performing in-situ TEM characterization. In the SAED patterns obtained below 100°C, only the $\gamma$-form is evident. Between 110 and 120°C, both $\gamma$- and $\beta$-forms co-exist within the same spherulite in PHT. This feature, combined with the fact that the spherulite remains unchanged in state, indicates that the $\gamma$-to-$\beta$ transition of the solvent-induced crystal in PHT is a solid-solid transformation.

References

Table 1. $d$-Spacings of WAXD and SAED and reflection indices for the $\gamma$- and $\beta$-form crystals of poly(hexamethylene terephthalate) (PHT).

<table>
<thead>
<tr>
<th>X-ray diffraction peak</th>
<th>$d_{\text{obs-WAXD}}$(nm)</th>
<th>$d_{\text{obs-SAED}}$(nm)</th>
<th>$hkl$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$\gamma$-form</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.1</td>
<td>0.732</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>15.6</td>
<td>0.568</td>
<td>----</td>
<td></td>
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<tr>
<td>17.3</td>
<td>0.513</td>
<td>0.505</td>
<td>100</td>
</tr>
<tr>
<td>18.2</td>
<td>0.487</td>
<td>0.480</td>
<td>110</td>
</tr>
<tr>
<td>22.2</td>
<td>0.400</td>
<td>0.396</td>
<td>020</td>
</tr>
<tr>
<td>24.9</td>
<td>0.358</td>
<td>0.356</td>
<td>1\ 2\ 0</td>
</tr>
<tr>
<td><strong>$\beta$-form</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>1.300</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>15.7</td>
<td>0.564</td>
<td>0.544</td>
<td>0\ 2\ 2</td>
</tr>
<tr>
<td>17.8</td>
<td>0.498</td>
<td>0.484</td>
<td>01\ \bar{1}</td>
</tr>
<tr>
<td>21.0</td>
<td>0.423</td>
<td>0.413</td>
<td>101</td>
</tr>
<tr>
<td>23.6</td>
<td>0.377</td>
<td>0.371</td>
<td>1\ \bar{1}2</td>
</tr>
</tbody>
</table>
Fig 1  (a) DSC thermogram (scanned at 10°C/min) and (b) X-ray diffractogram for the PHT sample initially solvent-induced from chloroform at room temperature.
Heated to 125°C and then quenched to 0°C

$\Delta H = 57.8 \text{J/g}$

Fig 2  (a) DSC thermogram (scanned at 10°C/min) and (b) X-ray diffractogram for the solvent-induced PHT sample which was further heated to 125°C.
Fig 3  X-ray diffractograms for the solvent-induced PHT samples which were subjected to stepwise temperature increase from 80 to 125°C.
Fig 4  DSC thermograms (scanned at 10°C/min) for the solvent-induced PHT samples which were heated to (a) 100°C, (b) 106°C, (c) 108°C, (d) 110°C, (e) 112°C, (f) 120°C, and (g) 125°C.
Fig 5  (a) DSC thermograms (scanned at 10°C/min) and (b) X-ray diffractionographs for the solvent-induced PHT samples which were heated to 100°C and then annealed for 2 or 960 min.
Fig 6  (a) DSC thermograms (scanned at 10°C/min) and (b) X-ray diffractograms for the solvent-induced PHT samples which were heated to 125°C and then annealed for 2 or 960min.
Fig 7 Temperature series of SAED patterns (reversed contrast) obtained from a same thin film specimen of solvent-induced PHT, which were recorded at (a) room temperature, (b) 80°C, (c) 90°C, (d) 100°C, (e) 110°C, (f) 120°C, and (g) 125°C.
Fig 8 Temperature in-situ TEM images showing spherulitic morphology in a same thin film specimen of solvent-induced PHT, taken in conventional bright-field imaging mode at (a) ambient temperature, and (b) 125°C.
附錄：


Effects of miscible diluent of poly(ether imide) on ring-banded morphology of poly (trimethylene terephthalate)

Abstract The melting, crystallization, and self-packed ring patterns in the spherulites of miscible blends comprising poly(trimethylene terephthalate) (PTT) and poly(ether imide) (PEI) were revealed by optical, scanning electron microscopies (PLM and SEM) and differential scanning calorimetry (DSC). Morphology and melting behavior of the miscible PTT/PEI blends were compared with the neat PTT. Ringed spherulites appeared in the miscible PTT/PEI blends at all crystallization temperatures up to 220 °C, whereas at this high temperature no rings were seen in the neat PTT. A postulation was proposed, and interrelations between rings in spherulites and the multiple lamellae distributions were investigated. The specific interactions and the segregation of amorphous PEI were discussed for interpreting the morphological changes of 220 °C-melt-crystallized PTT/PEI samples. Interlamellar segregation of PEI might be associated with multiple lamellae in the spherulites of PTT/PEI blends; therefore, rings were more easily formed in the PTT/PEI blends at all crystallization temperatures. A postulated model of uneven lamellar growth, coupled with periodical spiraling, more properly describes the possible origin of ring bands from combined effects of both interactions and segregation between the amorphous PEI and PTT in blends.

Keywords Poly(trimethylene terephthalate) (PTT) · Poly(ether imide) (PEI) · Ring bands · Segregation · Blends · Spherulites

Introduction

There have been numerous investigations of morphological changes in compatible blend. Some of these earlier literatures focused on morphological changes, including the occurrence of ringed extinction patterns and/or the effect of inducing “bands” in spherulites of host polymers, such as poly(ε-caprolactone) (PCL)/poly(benzyl methacrylate) (PBzMA) and PCL/poly (phenyl methacrylate) (PPhMA) systems [1], PCL/poly(vinyl chloride) (PVC) system [2–5], PCL/poly (styrene-co-acrylonitrile) (SAN) [6, 7] and poly(vinylidene fluoride) (PVF2)/poly(methyl methacrylate) (PMMA) systems [8] etc. Neat PCL is known to exhibit ring bands at a high temperature (50 °C for 24 h); however, no ring bands are found at lower temperatures (45 °C or below) [1, 3]. In addition, ringed spherulites were observed in PCL miscible systems in the same temperature range (45 °C or below) where no ring bands formed in neat PCL. Distinct rings were shown in spherulites when small amount of amorphous polymer (1%) added to neat PCL [1, 7]. The addition of non-crystallizable polymeric diluents to a crystallizable host polymer can induce to form ring bands in miscible blends. Moreover, the extinction rings are more populated with increasing amorphous component in the PCL/ acrylic polymer blends. This fact suggests that a greater fraction of the amorphous polymer can be trapped between the spherulites to form the interference rings at higher volume fractions of the amorphous polymer [1].
Interestingly, neat poly(trimethylene terephthalate) (PTT) is also known to show ringed spherulites upon melt-crystallization at most temperatures [9–11]. And more recently, we have explored the correlation between thermal multiple melting and ring patterns of PTT [12]. As PTT was melt-crystallized at low to medium temperatures (150–215 °C), distinct rings were present in the spherulites; in the meanwhile, two or three melting peaks were shown during differential scanning calorimetry (DSC) scanning. Furthermore, as PTT was melt-crystallized at a temperature (i.e. 220 °C) near the melting temperature, only a single type of lamella could develop, then no rings were discovered in the spherulites. At the same time, DSC results showed only one peak upon heating. Therefore, it can be concluded that there should be no rings in PTT if a crystallization temperature is selected so that there is only one type of lamella in the spherulites. The cut-off temperature was 220 °C for PTT [12].

Additionally, we have demonstrated earlier that PTT forms a miscible blend with poly(ether imide) (PEI) of all compositions [13]. Thus, it will be interesting to extend discussions into possible influence of PEI on morphological changes in crystallizing PTT as a component in a miscible blend. In continuation with the earlier finding in the neat PTT, ring bands in miscible blend such as PTT/PEI may also be influenced by formation of multiple lamellae in the spherulites, which will be examined more thoroughly using thermal analysis. In addition, interlamellar segregation of PEI from PTT during crystallization or interactions between PEI and PTT in the amorphous state might influence the pattern of ring bands. A plausible model was examined and proposed to explain the procedure.

**Experimental**

Materials and procedures

Semicrystalline PTT was obtained as a courtesy sample material from Industrial Technology Research Institute (ITRI, Taiwan) with inherent viscosity $\eta = 0.724$ dL/g (measured in m-Cresol). PEI was obtained from research-grade polymer suppliers (Polysciences, Inc., $M_w = 30,000$ g/mol). Blending of PTT and PEI was carried out by solution mixing and co-precipitation. For brevity, two miscible blend compositions were prepared: weight ratios of PTT/PEI blends are 9/1 and 8/2, respectively. PTT and PEI (with weight ratio = 9/1, 8/2) were co-dissolved with sufficient stirring in dichloroacetic acid at room temperature, followed by co-precipitating in 20-fold excess volume of water. The precipitated blend was washed with a large amount of water and then dried under vacuum at 80 °C for 5 days to remove possible traces of solvent.

Apparatus

Polarized-light microscope (Nikon Optiphot-2) was used for observation of lamellar changes and growth of spherulites. The samples were pressed between two glass slides and first melted on the hot stage at 250 °C for 5 min. It was rapidly quenched to designated temperatures on the microscopic heating stage (Linkam THMS-600 with TP-92 temperature programmer). Furthermore, the spherulitic/lamellar morphology of PTT/PEI samples subjected to different thermal histories was examined using a scanning electron microscope (SEM, Philips XL-40FEG). Etching by 2% potassium permanganate in H$_3$PO$_4$ + H$_2$SO$_4$ (1:1) solution (24 h at ambient temperature) was performed to enhance the crystalline/amorphous contrast. The washed/dried samples were then coated with gold by vapor deposition using vacuum sputter-coating prior to SEM characterization.

A differential scanning calorimeter (DSC-7, Perkin-Elmer) equipped with a mechanical intracooler was used for analyzing thermal behavior. Heating rates of 5, 10, 20, up to 30 °C/min were used wherever needed. The instrument was calibrated with indium and zinc standards on the temperature and heat of transitions. Melt-crystallization of all samples was performed by melting at 250 °C (in DSC cells) for 5 min, and then quenched quickly to a desired isothermal temperature for a specified period of time. The DSC cell (temperature chamber) was also used for thermal treatments of the samples in preparation for other experimental characterizations such as PLM or SEM analysis.

**Results and discussion**

Spherulitic morphology

Figure 1 shows the spherulitic structure of the melt-crystallized PTT/PEI (9/1) at various temperatures. It can be found that the spherulites of PTT/PEI (9/1) exhibit not only a Maltese-cross pattern but also distinct ring bands at all crystallization temperatures. Generally, the ringed pattern is indicative of lamellar twisting in the direction of radial growth, but the origin of lamellar twisting is still debated [14–16]. The growth rate starts to decrease above 210 °C (i.e. 220 °C), resulting in fewer and smaller spherulites. Apparently, the spherulites are coarser at higher crystallization temperatures, where the crystallization rate is slower. It is seen that at lower temperatures, the ring bands are less concentric, whereas at higher temperatures, the ring bands are more concentric and uniform. The observations of the ring patterns in the PTT/PEI (9/1) at lower crystallization temperatures (190, 205, and 210 °C) are similar to those in neat PTT, but the ring patterns become more...
pronounced as the PEI content increases. A comparison of spherulitic morphology in ring patterns of the PTT/PEI (8/2) under the same thermal treatment is illustrated in Fig. 2. The crystallization rate becomes slower while relatively larger non-crystallizable PEI content adds to PTT polymeric system. The ring shape including the white-ringed area and the yellow-ringed area is less zigzag (more regular) with increasing crystallization temperature as well as PEI content. The appearance of more regular and distinct ring bands in the PTT blends as compared to neat PTT seems to be a general feature since it has been observed for other blend systems [1–8]. The ring width may have some relationship with the crystallization temperature and non-crystallizable diluents [1–8]; however, the dependence of the ring width on crystallization temperatures and PEI content seems indistinct in the PTT blends.

Scanning electron microscope characterization was performed on the melt-crystallized PTT/PEI blend systems, and shown in Figs. 3 and 4. The SEM results clearly show that a bright/fibrous band and a dark/smooth grainy band exist in spherulites. We have earlier reported characteristic features of ring bands in the neat PTT that the bright region in SEM corresponds to the yellow-ringed area in PLM while the white-ringed area in PLM corresponds to the dark region in SEM [12]. Furthermore, heating of the ringed blend samples on a PLM heating stage caused melting of white-ringed area first, and then the yellow-ringed area. The high melting point of bright region appears to be of a fiber-like nature, with an edge-on pattern. On the other hand, the low melting point of dark region appears to be of an amorphous nature. The graphs in Figs. 1, 2, 3 and 4 have clearly shown that ringed spherulites are apparent in the PTT/PEI blends at all crystallization temperatures. However, it has been demonstrated earlier that no ring bands exist in the neat PTT melt crystallized at 220 °C or above [12], a situation quite different from the miscible PTT/PEI blends. Causes for the different morphology in the neat PTT versus its blend with PEI at 220 °C will be expounded in later sections.

**Multiple melting peaks**

According to our previous results for neat PTT [12], the melting behavior seemed to relate with the formation of ringed spherulites. If a crystallization temperature is selected so that there is only one lamellar type in the spherulites, then there should be no rings. Thus, it is helpful to discuss the melting behavior of PTT/PEI blend first. Thus, interestingly, ringed spherulites are present in the PTT/PEI blends even at a high crystallization temperature (i.e. 220 °C), where no rings appear in the neat PTT. For the neat PTT, it has been suggested that no ring bands are seen if there is only one uniform type of lamellae in the spherulites [12]. Hence, the melting endotherm for PTT/PEI blends crystallized at 220 °C was measured. Figure 5 shows the DSC thermograms (all scanned at 10 °C/min) for two blend
compositions: (a) PTT/PEI (9/1) and (b) PTT/PEI (8/2), respectively, crystallized at various isothermal temperatures (180–220 °C). Triple-melting behavior is evident for these two blend compositions, which is similar to that in the neat PTT [12]. The first and second endotherms (P1, P2) are strongly dependent on the crystallization temperature, and the third one (P3) remains the same regardless of the crystallization temperature. A re-crystallization exotherm (arrow-marked) is seen apparently in PTT/PEI blends crystallized at relatively
lower temperatures (i.e., 180 or 190 °C). Apparently, the melting/re-crystallization process is more extensive and it immediately follows the melting of the P1 crystal during DSC scanning in the blends crystallized lower

**Fig. 4** SEM morphologies for PTT/PEI (8/2) blend crystallized at: a 190 °C, 30 min; b 205 °C, 30 min; c 210 °C, 30 min; and d 220 °C, 240 min.

**Fig. 5** DSC traces (all scanned at 10 °C/min) in a PTT/PEI (9/1), and b PTT/PEI (8/2) melt-crystallized at various temperatures. Insets show blends annealed at 220 °C for 24 h, and then scanned at two low rates.
temperatures; on the other hand, the melting/re-cry-
stallization of the P1 crystal is less evident in the blends if
crystallized at higher temperatures (205–220 °C).

The inset of Fig. 5a shows the DSC traces of the
PTT/PEI (9/1), annealed at 220 °C for 24 h and then
scanned at different scanning rates. Apparently, a
broad melting endotherm is seen at a lower scanning
rate (i.e. 2.5 °C/min). A similar observation is shown in
the PTT/PEI (8/2) blend from the inset of Fig. 5b. The
broad melting peak consists of multiple heterogeneous
lamellae with different proportions. The co-existence of
different lamellar types (i.e. P1, P2, P3) leads to a
broader melting peak during DSC scanning, and also
forms distinct ring patterns in spherulites. The melting
behavior thus is related to the formation of ringed
spherulites in both neat PTT and PTT/PEI blends. The
results show that multiple-melting endotherms are
evident in the miscible PTT/PEI blends crystallized at
all temperatures ranging from 190 to 220 °C, whereas
only one melting peak is present in the neat PTT
crystallized at 220 °C.

Similarly, Fig. 6 shows the DSC thermograms at
various heating rates (5–30 °C/min) for two blend
compositions: (a) PTT/PEI (9/1) and (b) PTT/PEI (8/2),
which had been melt-crystallized at 190 °C for 30 min.
For the PTT/PEI (9/1) composition, P1 and P2 increase
in peak temperature and magnitude as the heating rate
increases, while P3 diminishes in magnitude, and finally
overlaps with the gradually elevating P2. On the other
hand, a similar trend is observed in the PTT/PEI (8/2).
The re-crystallization exotherm appears just next to the
low-temperature endotherm (P1) for all scanning rates.
Nevertheless, the re-crystallization enthalpy decreases
with increase in the scanning rate and/or the amorphous
content. It suggests that the P1 crystals melt and then
can re-crystallize/repack to P3 crystals upon scanning.
On the other hand, the P2 crystals cannot re-pack quick
enough to the P3 crystals under a normal scanning rate
(e.g., 10 °C/min). Partial melting of less perfect crystals,
followed by re-crystallization, and then final melting
could occur in the PTT/PEI blends.

Intermolecular interactions between PTT and PEI
Keith et al. [3, 17] have investigated the morphological
changes in polyesters induced by blending with small
concentrations of polymer diluents, and have indicated
that there is likely an interaction between host and dil-
uent polymers strong enough to cause significant mod-
ification of the crystal growth process on a molecular
scale. The morphological changes in the PTT/PEI blends
(i.e. ringed spherulites are shown at 220 °C) can be
similarly examined from the intermolecular interactions
between PTT and PEI. The Nishi-Wang equation [18]
was carried out to estimate the interaction between PTT
and PEI according to the following relationship:

\[
\frac{1}{T_m} - \frac{1}{T_0} = -\frac{RV_1}{\Delta H_f V_2} \chi_{12} \phi_2^2,
\]

Fig. 6 DSC thermograms for a
PTT/PEI (9/1), and b PTT/PEI
(8/2) melt-crystallized at 190 °C
for 30 min, then scanned at
different heating rates (5–30 °C/
min, as indicated on the
respective traces)
where \( T_m \) and \( T_m^0 \) are the equilibrium melting points of PTT in the blends and PTT homopolymer, respectively. \( R \) is the gas constant, \( \Delta H_f \) is the heat of fusion of the fully crystalline PTT (30 KJ/mol), \( V_1 \) (149.6 cm\(^3\)/mol) and \( V_2 \) (399.5 cm\(^3\)/mol) are the molar volumes of the repeat units of the crystallizing and amorphous polymers, and \( \phi_2 \) is the volume fraction of the amorphous polymer [20, 21]. \( x_{12} \) is the polymer/polymer interaction parameter, and it is an indication of intermolecular interactions between components. \( x_{12} \) can be obtained by plotting the left hand side of Eq. 1 versus the square of PEI volume fraction in the blends (\( \phi_2^2 \)). From the slope of the regression line in Fig. 7, \( x_{12} \) is then determined to be \(-0.1\). The negative value of \( x_{12} \) confirms that the polymer pairs of PTT and PEI can form a thermodynamically stable compatible mixture in the melt, consisting with our earlier results [13]. However, the interaction is very weak in the PTT/PEI blend due to the small \( x_{12} \) value. Therefore, it can be concluded that the specific interaction is not the main reason for the

![Fig. 7 Determination of interaction parameter using the Flory-Huggins equation for PTT/PEI blends](image)

![Fig. 8 Schematic diagram of possible PEI segregation modes during crystallization of PTT/PEI blend](image)

\[ a \text{ Interspherulitic segregation} \]

\[ b \text{ Inter (lamellar-bundle) segregation} \]

\[ c \text{ Interlamellar segregation} \]
formation of intense ring in the PTT/PEI blend. On the one hand, there are interactions between the amorphous and crystalline polymers; but on the other hand, the segregation of PEI during crystallization of PTT may also affect the morphology of the blends. This is discussed in the following scheme.

In similarity to schemes that have been commonly proposed for amorphous/crystalline polymer blend systems [21], Fig. 8 depicts that there are three types of segregations in PTT/PEI blends: (a) interspherulitic segregation, (b) interlamellar-bundle segregation, and (c) interlamellar segregation upon crystallization in miscible blends containing a crystallizable and an amorphous diluent polymer. Schemes (b) or (c) are more likely the type of amorphous/crystalline segregation that influences ring-band patterns.

Figure 9 depicts a possible model for effects of the amorphous miscible diluent (PEI) on the ring bands in PTT. It is primarily based on a mode of less coordinated twisting (spiraling) of the lamellar bundles that radiate out from the nuclei. The spiraling mode has been more widely proposed and accepted by many earlier investigators [3–5, 17], which is thought to more closely resemble the periodical changes from the edge-on to flat-on lamellae. The less coordinated growth of the lamellae bundles, coupled with spiraling, may account for the more pronounced zigzag rims in the ring bands.

**Conclusion**

The ring-bands in spherulites and mechanism in the miscible PTT/PEI blends have been compared with the neat PTT. While ringed spherulites are seen in either the neat PTT or PTT/PEI blend system, there are some differences between them. First of all, the ring patterns are more intense for the blends. Secondly, at a high temperature of 220 °C, no rings are present in the neat PTT, while rings are apparent in the PTT/PEI blend system when crystallized at this same temperature. The DSC evidently verified that dual peaks implying mixed lamellae co-existing in the PTT/PEI blends crystallized at 220 °C, which led to ringed patterns. On the other hand, the single melting peak in the neat PTT suggests that the lamellae are uniformized to a singular type at 220 °C, leading to no ring pattern in the spherulites of PTT crystallized at this same temperature.

An additional factor is also at work that leads to differences in the ring bands in the miscible PTT/PEI blends versus neat PTT. For the miscible PTT/PEI blends, addition of the amorphous PEI miscible diluent causes a larger population of multiple lamellae in the PTT spherulites owing to easier interlamellar segregation of PEI between the lamellae upon annealing or crystallization. Upon crystallization of the PTT/PEI blends, the amorphous PEI chains are gradually rejected from the PTT crystallizing fronts into the interlamellar, interlamellar bundle, and interlamellar regions of the growing spherulites. Of these three, the interlamellar segregation is responsible for the easier formation of ringed-patterns in PTT/PEI blends. Therefore, rings are seen in 220 °C melt-crystallized blends, but not in neat PTT. In addition, the specific interaction between PTT and PEI is not particularly strong and it should not be the main reason for morphological ring patterns. Of particular interest was the observation of the ringed patterns of PTT spherulites in the blends isothermally crystallized at 220 °C. The addition of amorphous PEI and crystalline components, and the segregation of the amorphous PEI during crystallization. A postulated model of uneven lamellar growth, coupled with periodical spiraling, more properly describes the possible origin of the ring bands from combined effects interactions on the one hand, and segregation on the other hand between the amorphous PEI and crystallizing PTT.

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References

Thermal analysis, X-ray and electron diffraction studies on crystalline phase transitions in solvent-treated poly(hexamethylene terephthalate)

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Abstract

The crystal polymorphism, transformation, and morphologies in chloroform solvent-cast poly(hexamethylene terephthalate) (PHT) were examined by using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and temperature in situ transmission electron microscopy (TEM). Solvent-induced crystallization of PHT at room temperature yielded an initial crystal of $\gamma$-form, as confirmed by WAXD. Upon DSC scanning, the original $\gamma$-form in PHT exhibited three endothermic peaks, whose origins and association were carefully analyzed. The first peak, much smaller than the other two, is in the temperature range of ca. 100–120 °C. It was found that the solvent-induced $\gamma$-form was transformed to $\beta$-form at 125 °C via a solid-to-solid transformation mechanism. In addition, WAXD showed that $\gamma$- and $\beta$-forms co-existed in the temperature range of 100–125 °C. These mixed crystal forms were further identified using TEM, and the selected-area electron diffraction (ED) patterns revealed that both $\gamma$- and $\beta$-form crystals co-existed and were packed within the same spherulite. Solid–solid transformation from the solvent-induced $\gamma$-form to $\beta$-form in PHT upon heat scanning was presented with evidence and discussed.

Keywords: Thermal analysis; Polymorphism; Spherulites

1. Introduction

Polymorphism often exists in many crystalline polymers, such as syndiotactic polystyrene (sPS) [1–3,25,26], isotactic polypropylene (iPP) [4,27], and poly(butylene adipate) (PBA) [5–7]. Poly(hexamethylene terephthalate) (PHT) also possesses complex polymorphism depending on crystallization conditions. Earlier studies in the literature have shown that PHT may contain various combinations of three different crystal unit-cells, designated as $\alpha$, $\beta$ and $\gamma$ depending on thermal and/or solvent treatments [8–10]. Recently, multiple melting characteristics and dual morphologies of PHT have also been identified [11]. In previous papers [8–10], the $\alpha$-form in PHT is shown to have a monoclinic unit-cell with dimensions $a=0.910$ nm, $b=1.756$ nm, $c$ (chain axis) $=1.574$ nm, $\alpha=127.8^\circ$, $\beta=\gamma=90^\circ$, and is known to be favored for crystallization under stress. The $\beta$- and $\gamma$-forms are both characterized as triclinic, with different dimension in $b$. The $\beta$-form crystal in PHT has dimensions: $a=0.5217$ nm, $b=0.5284$ nm, $c$ (chain axis) $=1.5738$ nm, $\alpha=129.4^\circ$, $\beta=97.6^\circ$, $\gamma=95.6^\circ$. The $\gamma$-form crystal cell in PHT is also triclinic and has cell dimensions and angles all equal to those for the $\beta$-form, except for $b=1.0568$ nm that is exactly twice as wide as that for the $\beta$-form. The $\gamma$-form is usually obtained by solvent-induced crystallization of PHT when film-cast at room temperature [8,9]. The $\beta$-form can be exclusively produced in PHT by melt-crystallization only at extremely high temperatures ( $\sim 140$ °C or higher), while at lower or moderate temperatures ( $<140$ °C), mixed crystals consisting of $\alpha$- and $\beta$-forms with various fractions in PHT are obtained [11].

Solution crystallization of macromolecules has been well discussed by Wunderlich [12]. In addition, solvent-induced crystallization has also been widely investigated in sPS [3,13–17], syndiotactic polypropylene (sPP) [18], poly(ethylene 2,6-naphthalate) (PEN) [19], poly(ethylene terephthalate) (PET) [20,21], and poly(ether ether ketone) (PEEK) [22,23]. Among these polymers, solvent-induced crystallization of sPS has been studied more extensively in recent years. sPS possesses four polymorphic crystalline forms ($\alpha$-, $\beta$-, $\delta$-, and
γ-forms) when it is subjected to thermal and/or solution treatment. The δ- and γ-forms in sPS can be induced by solvent. The δ-form is obtained in sPS, which includes molecules of solvent in its unit cell. However, from completely desiccated sPS samples, the γ-form crystal is obtained [3]. Additionally, various solvents would affect the formation of crystal form. Instead of most solvents to form only the δ-crystal of sPS, 1,1,2,2-tetrachloroethane is unique, because this solvent induces crystallization of γ-form in sPS [3]. Upon heating to higher temperatures, the γ-form crystal can be transformed to the α-form one.

In this study, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) as well as transmission electron microscopy (TEM) were utilized to identify the crystal transformation behavior and heating-induced crystal-form changes in PHT samples prepared by solution casting from chloroform at room temperature. The literature has widely reported [8–10] that the γ-form crystal can be produced in PHT by treatment with chloroform at room temperature and β-form is yielded by annealing the γ-form at higher temperatures; however, the mechanism of transition or thermal characteristics of these crystals has yet to be understood. With aims to extend the previous findings, this study attempted to describe the crystal-form changes as a function of temperature after initial solvent-induced crystals were generated. The crystalline morphologies of the individual PHT spherulites containing both γ- and β-forms were further characterized by ‘temperature in situ TEM’.

2. Experimental

2.1. Materials

PHT was synthesized using butyl titanate as a catalyst, according to the method described in the literature [24]. Molecular weights were determined by gel permeation chromatography (GPC) on a Waters 410 GPC system using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min. The PHT used in this study has an $M_w=13,800$ g/mol and a polydispersity index (PDI) of 2.0. At this molecular weight, its mechanical properties are slightly lower than those at higher molecular weights, but its thermal properties (glass transition temperature ($T_g$), melting temperature ($T_m$), etc.) and crystalline morphology are expected to be characteristic of a typical polymer. The thermal transition temperatures of the PHT used here may be slightly lower than those of a longer-chain PHT, but the characteristics of the crystals and multiple melting peaks were pretty much the same as those of the longer-chain PHT. The melting point (144.3 °C) and glass transition temperature (−6.7 °C) were measured by DSC.

2.2. Specimen preparation

Solvent-induced crystals were obtained by dissolving the synthesized PHT into chloroform to be a 4 wt% solution. The solution was dried at room temperature for 1 day, and then the sample was dried in the vacuum oven at 40 °C for 7 days to remove the residual solvent in PHT. The solid PHT sample was directly heat-treated by DSC.

For TEM, thin films of PHT were prepared/crystallized on glass slides by casting the solution. For reinforcing the specimen, the polymer thin films were coated with vapor-deposited carbon under vacuum. In order to carry out the calibration of the diffraction camera length, gold (Au) was vapor-deposited onto some of the thin films before carbon coating. After carbon coating, a drop (a hemisphere 3–4 mm in diameter) of aqueous solution (25%) of polyacrylic acid was placed on the appropriate portion of the specimen film and hardened after drying for 1 day at room temperature. Hardened polyacrylic acid with the specimen thin film was detached from the glass plate, and then the polyacrylic acid was dissolved in water. Finally, a TEM copper grid was used to collect the specimen film floating on the water surface and then dried under ambient condition.

2.3. Analytical apparatus

The thermal behavior of the PHT sample was preliminarily investigated using a differential scanning calorimeter (DSC-7, Perkin–Elmer). The temperature and heat of transition indicated with the instrument were calibrated with indium and zinc standards. For determining the enthalpy of melting peaks, a dynamic heating rate of 10 °C/min was used unless otherwise indicated. During thermal treatments and DSC measurements with the DSC-7, a continuous flow of nitrogen gas into the sample-cell chamber was maintained to ensure minimal sample degradation. In addition, the DSC sample-cells were used for precisely controlling the thermal treatments of samples.

The WAXD instrument was a Shimadzu XRD-6000 (30 kV and 40 mA), and the Cu K$_\alpha$ radiation of a wavelength of 0.1542 nm was utilized. The scattering angle, $\theta$, ranged from 5 to 40° with a scanning step of 2°/min (here, $\theta$ is the Bragg angle). For ensuring the temperature accuracy, specimens for WAXD characterization were prepared by imposing desired thermal treatments using the DSC-7.

Morphological observation and selected-area electron diffraction (SAED) of specimens were performed with a transmission electron microscope (JEOL JEM-200CS) operated at an accelerating voltage of 200 kV. A specimen-heating holder (JEOL EM-SHH4) which has been fitted up with a homemade ‘temperature controller’ [28] was utilized to regulate the specimen temperature to be a desired temperature. The size of the selected-area aperture utilized for SAED experiments in this study was ca. 2.5 μm in diameter on the specimen. In addition, the morphological images were taken in the conventional bright-field mode at a direct magnification of 5000× [29,30]. All the images and SAED patterns were recorded on photographic films (Mitsubishi MEM) which were then developed with Mitsubishi Gekkol (full strength) at 20 °C for 5 min [29,31].
3. Results and discussion

3.1. DSC and WAXD characterization of crystal transformation

It has been already mentioned that crystallization of γ-form could be induced by solvent at room temperature, and β-form is obtained after annealing the γ-form at the high temperatures [9]. To identify the meta-stability and phase transformation of solvent-induced PHT crystals, the solid sample of PHT was examined by DSC. Fig. 1(a) shows the DSC thermogram for the initially solvent-induced PHT sample that was scanned at 10 °C/min. The first endothermic peak (P1) at 115.5 °C designated as Tm1 was identified. The other two endothermic peaks in this thermogram are located at 138.2 and 145.3 °C, respectively. The total endothermic heat is 64.4 J/g from the initial state to melt. However, the heat of the first peak (P1) is only 7.2 J/g. In this thermogram, the onset and tail-end of the P1 peak are at ca. 105 and 125 °C, respectively. The initially solvent-induced PHT sample was also examined by WAXD. Fig. 1(b) shows the typical X-ray diffractogram (namely, WAXD intensity profile) of PHT crystals. The reflection peaks in the diffractogram are recognized at 2θ=12.1, 15.6, 17.3, 18.2, 22.2, and 24.9°. According to Palmer et al. [9], these reflection peaks are attributed to the γ-form.

In contrast to the heats of P2 and P3, the heat of P1 is much smaller, as shown in Fig. 1(a). Interestingly, one wonders, which crystal-form may be removed upon heating the initial γ-form crystal to the temperature near P1 (ca. 125 °C). Therefore, the original γ-form PHT samples heated to 125 °C and then quenched to 0 °C. Finally, the DSC sample was scanned at 10 °C/min from 0 °C to the melt. Fig. 2(a) shows the final

![Figures 1 and 2](https://via.placeholder.com/150)
the reflection peaks at 2θ characteristic annealed at lower temperatures below ca. 106°C. The samples heated/subjected to stepwise temperature increase from 80 to 125°C show the WAXD diffraction peaks of the heated sample. The reflection peaks are located at 2θ = 6.8, 15.7, 17.8, 21.0, 22.2, and 23.6° in this diffractogram. According to the earlier reports [9–11], these peaks indicate the β crystal form. Thus, the original solvent-induced γ-form crystal has been transformed to a different β-form by heat-treatment on solvent crystallized sample of PHT to 125°C. The result suggests that the solvent-induced γ-form crystal in PHT may be readily transformed to the more stable β-form at temperatures between 105 and 125°C.

The structure in thermally-induced phase transition was analyzed by performing WAXD on solvent-treated PHT samples subjected to slow heating treatment. Fig. 3 shows the WAXD intensity profiles of solvent-treated PHT samples that were subjected to step-increase of the temperature in the range of 80–125°C. The endothermic peaks at 2θ = 6.9, 15.7, 17.8, 21.0, and 23.6° attributed to the β-form, begin to appear and increase in intensity on raising the annealing temperature. On the contrary, the γ-form peaks at 2θ = 12.1, 17.3, 18.2 and 24.9° decrease in intensity with increasing annealing temperature, implying that a transition from γ- to β-form occurs. Above 120°C, the γ-form diffraction peaks almost vanish.

By combining the results from DSC and X-ray, the first melting peak (P1) thus is related to the γ-form, while the two higher melting peaks are of the β-form. A phase transition from γ- to β-form must have taken place during heat scans. The mechanism of phase transition needs to be analyzed further using TEM and WAXD, in order to more accurately locate the crystal transition temperature.

In our earlier studies on sPS [3], it was found that the initially solvent-induced γ-form crystal of sPS can be transformed to α'-form as the temperature is increased. At the temperature where the γ- to α'-phase transition takes place, the crystallinity exhibits a significant increase. The increased intensity of WAXD is caused by melting of the γ-form of sPS and re-crystallization of the amorphous chains. In the present case, however, there is no significant change of overall intensity as a result of γ to β-crystal transformation. In the DSC thermogram of the original γ-form crystal, there exists no exothermic peak related to re-crystallization of the melted amorphous chains. As a result, the γ- to β-phase transition of PHT must take place via solid–solid phase transformation. Observation of morphology in the solid–solid phase transition will be evidenced by TEM in later sections.

![Fig. 3. X-ray diffractograms for the solvent-induced PHT samples, which were subjected to stepwise temperature increase from 80 to 125°C.](image)

![Fig. 4. DSC thermograms (scanned at 10°C/min) for the solvent-induced PHT samples, which were heated to (a) 100°C, (b) 106°C, (c) 108°C, (d) 110°C, (e) 112°C, (f) 120°C, and (g) 125°C.](image)
As discussed above, analysis of the WAXD intensity profiles indicates that the γ- to β- phase transition occurs between 106 and 120 °C. In order to investigate the extent of transformation as a function of annealing temperature ($T_a$), the originally solvent-induced γ-form in PHT samples was heated to specific temperatures of 100, 106, 108, 110, 112, 120 and 125 °C, respectively. After annealing at these temperatures for 2 min, the samples were then scanned in DSC to above melt. Fig. 4 shows the melting behaviors of the samples heated/annealed at these specific temperatures ($T_a$). At $T_a = 100$ °C, the corresponding thermogram shows three peaks similar to those in the thermogram obtained from the original sample. The $\Delta H_1$ related to the endothermic heat of $P1$ is 6.9 J/g. Further increase of annealing temperature was imposed on the samples. The reduced endothermic heat of $P1$ was present. At $T_a = 125$ °C, however, $P1$ does not exist in the thermogram. As for $T_a = 120$ °C, the heat of $P1$ is so small that it is difficult to calculate the endothermic heat. However, a very small $P1$ indeed existed in the thermogram of $T_a = 120$ °C. Corresponding to the WAXD result, the smaller heat of $P1$ represents that more fraction of γ-form transforms to β-form.

The effect of annealing time ($t_a$) on the phase transition was also explored. The original γ-form PHT samples were heated to 100 °C and annealed for 2 or 960 min. Fig. 5 shows the results of (a) DSC and (b) WAXD. In Fig. 5(a), both DSC thermograms have three endothermic peaks. However, when $t_a = 960$ min, the $P1$ and $P2$ shift to higher temperatures, and the enthalpy associated to $P1$ is reduced. The corresponding X-ray diffractograms are shown in Fig. 5(b). For $t_a = 960$ min,
all the reflection peaks are attributed to the γ-form except for the small peak at 2θ = 23.6°. Consequently, very long annealing times are needed to induce a small phase transition of γ-form PHT at Ta = 100 °C.

Similarly, annealing treatments were applied to the original γ-form samples at 125 °C. The DSC and WAXD results are shown in Fig. 6(a) and (b). Both DSC thermograms in Fig. 6(a) show a similar total heat. However, for the longer annealing

![Fig. 7. Temperature series of SAED patterns (reversed contrast) obtained from a same thin film specimen of solvent-induced PHT, which were recorded at (a) room temperature, (b) 80 °C, (c) 90 °C, (d) 100 °C, (e) 110 °C, (f) 120 °C, and (g) 125 °C. The size of the selected-area aperture utilized for SAED experiments was ca. 2.5 μm in diameter on the specimen.](image)
times, the heat of fusion of $P2_1$ increases and $P2_1$ shifts to a higher temperature, suggesting that the crystals probably thicken during long annealing times. The X-ray diffraction intensities in Fig. 6(b) show that the β-form crystal is not affected after annealing for $t_a=960$ min at $T_a=125\,^\circ C$.

### 3.2. In situ TEM on phase transition in PHT

The thin film specimen of solvent-induced PHT prepared by the method described in Section 2 was introduced into the TEM column with the specimen-heating holder. The specimen was heated from room temperature up to 125 °C, and the SAED patterns of PHT crystals were obtained at different temperatures from a same thin film specimen. Fig. 7(a)–(g) displays a temperature series of SAED patterns (reversed contrast) from an area about 2.5 μm in diameter. Fig. 7(a) shows the SAED pattern of the original solvent-induced PHT crystal recorded before heating. The $d$-spacing values of the observed arc-shaped reflections are 0.513, 0.487, 0.400 and 0.358 nm, which correspond to $100_\beta$, $1\overline{1}0_\beta$, $020_\beta$, and $120_\beta$ reflections, respectively, as indicated in Fig. 7(a). Here, the subscript, $\gamma$, represents the reflection of $\gamma$-form. Meanwhile, tabulated values for comparing SAED and WAXD results may help. Table 1 shows the comparison of values of $d$-spacing for the $\gamma$-form crystal, which were obtained by the WAXD and SAED analyses. The results indicate that values of $d$-spacing obtained by SAED are almost same as those measured by WAXD; however, the WAXD peaks at $2\theta=12.1$ and $15.6^\circ$ are so weak that the corresponding reflections were not recognized in the SAED pattern. Subsequently, the thin film was heated in the specimen holder to $80\,^\circ C$. Fig. 7(b) is the SAED pattern obtained from the specimen treated at $80\,^\circ C$. Overall, below $100\,^\circ C$, the SAED patterns were similar to the original sample (Fig. 7(a)) in agreement also with the data in Fig. 3 shown earlier. Above $100\,^\circ C$, more dramatic changes in the crystal forms are seen. At $110\,^\circ C$, the $100_\beta$, $\overline{1}10_\beta$, and $120_\beta$, reflections disappear in the SAED pattern, whereas $\overline{0}2\overline{2}_\beta$, $01\overline{1}_\beta$, $101_\beta$, and $\overline{1}1\overline{2}_\beta$ appear. At $120\,^\circ C$, only a weak $020_\beta$ reflection still exists, but it completely disappears at $125\,^\circ C$, leaving only four β-form reflections. These β-form reflections at $125\,^\circ C$ have $d$-spacings of 0.564, 0.498, 0.423, and 0.377 nm, which correspond to $\overline{0}2\overline{2}_\beta$, $01\overline{1}_\beta$, $101_\beta$, and $\overline{1}1\overline{2}_\beta$, respectively. Again, the bottom portion of Table 1 lists and compares the values of $d$-spacing of β-form reflections observed by WAXD and SAED analyses. In addition, it is worth mentioning that experimentally all SAED patterns were obtained by focusing within the same one spherulite. The result suggests that the $\gamma$- and β-form crystals, therefore, co-exist within a single spherulite in the solvent-treated PHT annealed in the temperature range of ca. 110–120 °C.

A temperature series (ambient to 125 °C) of in situ TEM images were produced by focusing on the spherulites in a same thin film specimen of solvent-induced PHT. Various positions of the thin film specimen were observed in order to avoid looking at accidentally damaged spherulites. The specimens were heated to higher temperatures by using the in situ heating holder in TEM. The morphological images of the spherulites were recorded in series at ambient, 80, 90, 100, 110, 120, and 125 °C, respectively. Finally, Fig. 8 shows the TEM images for two specimens of the solvent-induced PHT at (a) ambient, and (b) 125 °C. As all the temperature series images (ambient, 80, 90, 100, 110, 120, and 125 °C) are similar; thus, only two representative TEM images are shown here. In comparison with the as-prepared PHT sample, the spherulites heated to temperatures ranging from ambient to 125 °C remain unchanged (for brevity, similarity in the series are not all shown). Comparatively speaking, the temperature series TEM analyses.

### Table 1

<table>
<thead>
<tr>
<th>X-ray diffraction peak at 2θ (°)</th>
<th>$d_{\text{obs-WAXD}}$ (nm)</th>
<th>$d_{\text{obs-SAED}}$ (nm)</th>
<th>$hkl$</th>
</tr>
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<tbody>
<tr>
<td>$\gamma$-Form</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.1</td>
<td>0.732</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>15.6</td>
<td>0.568</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>0.513</td>
<td>0.505</td>
<td>100</td>
</tr>
<tr>
<td>18.2</td>
<td>0.487</td>
<td>0.480</td>
<td>110</td>
</tr>
<tr>
<td>22.2</td>
<td>0.400</td>
<td>0.396</td>
<td>020</td>
</tr>
<tr>
<td>24.9</td>
<td>0.358</td>
<td>0.356</td>
<td>120</td>
</tr>
<tr>
<td>$\beta$-Form</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>1.300</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>15.7</td>
<td>0.564</td>
<td>0.544</td>
<td>022</td>
</tr>
<tr>
<td>17.8</td>
<td>0.498</td>
<td>0.484</td>
<td>01\overline{1}</td>
</tr>
<tr>
<td>21.0</td>
<td>0.423</td>
<td>0.413</td>
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<td>23.6</td>
<td>0.377</td>
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</tr>
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</table>

Fig. 8. Temperature in situ TEM images showing spherulitic morphology in a same thin film specimen of solvent-induced PHT, taken in conventional bright-field imaging mode at (a) ambient temperature, and (b) 125 °C.
images between ambient and 125 °C are all similar without indication of transition into liquid molten state. As a result, it can be proposed that the γ- to β-phase transition of the solvent-induced PHT crystals takes place in the solid state without going though melting.

4. Conclusion

The DSC analysis on the PHT samples solvent-cast from chloroform at room temperature displays three endothermic peaks, indicating a crystal polymorphism and/or crystal–crystal transformation. The WAXD results suggest that the initial solvent-cast PHT film is only of the γ-form crystal. Upon annealing at 125 °C, however, a new β-form crystal is formed, which exhibits two melting peaks (P2 and P3) upon DSC scanning. The first melting peak (P1) is related to the γ-form. It implies that phase transition from γ- to β-form must have taken place during DSC heat scans. WAXD data show that only the γ-crystal exists in the original solvent-cast PHT, but both γ and β crystal-forms can co-exist in various fractions in solvent-cast PHT samples further heated/annealed between 106 and 120 °C. When annealed at 125 °C and above, PHT exhibits only the β-form crystal, suggesting a phase transition.

Further evidence of the crystal phase transition and its mechanism was obtained by performing in situ TEM characterization. In the SAED patterns obtained below 100 °C, only the γ-form is evident. Between 110 and 120 °C, both γ- and β-forms co-exist within the same spherulite in PHT. This feature, combined with the fact that the spherulite remains unchanged in state, indicates that the γ-to-β transition of the solvent-induced crystal in PHT is a solid–solid transformation.

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