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Thermal, spectroscopy, and morphological studies on polymorphic crystals in poly(heptamethylene terephthalate)

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Polymorphism and its influential factors in poly(heptamethylene terephthalate) (PHepT) were probed using differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, and wide angle X-ray diffraction (WAXD). PHepT exhibits two crystal types (α and β) upon crystallization at various isothermal melt-crystallization temperatures (T_cs) by quenching from different T_{max}s (maximum temperature above T_m for melting the original crystals). Melt-crystallized PHepT with either initial α- or β-crystal by quenching from T_{max} lower than 110 °C leads to higher fractions of α-crystal, but crystallization from T_{max} higher than 140 °C leads to higher fractions of β-crystal. In addition to T_{max}, polymorphism in PHepT is also influenced by crystallization temperature ($T_c = 25$–75 °C). When PHepT is melt-crystallized from a high $T_{max} = 150$ °C (completely isotropic melt), it shows solely β crystal for higher T_c, and solely the α-crystal for $T_c < 25$ °C; in-between $T_c = 25$ and 35 °C, mixed fractions of both α- and β-crystals. However, by contrast, when PHepT is melt-crystallized from a lower $T_{max} = 110$ °C, it shows α-crystal only at all T_cs, high or low.

1. Introduction

Polymorphism behaviors in semicrystalline polymers have been widely studied and are influenced by different factors, such as crystallization temperatures, sample preparation methods (oriented or unoriented), crystallization process (solvent induction, melt crystallization or cold crystallization) or the existence of residual nuclei. Polymorphism behaviors influenced by crystallization temperature (T_c) have been published in melt-crystallized poly(hexamethylene terephthalate) (PHT) [1–4], poly(1,4-butylene adipate) (PBA) [5–7], poly(butylene naphthalate) (PBN) [8,9]. For instance, PHT exhibits mixed monoclinic (termed as α-crystal) and triclinic (termed as β-crystal) forms when melt-crystallized at T_c lower than 140 °C but sole β-crystal at T_c higher than 140 °C [3,4]. Apart from T_c, the existence of the tension stress may also cause difference in the unit cell of semicrystalline polymers upon crystallization, such as poly(butylene terephthalate) (PBT) [10,11] and poly(pentamethylene terephthalate) (PPT) [12–14]. PBT and PPT both have two types of crystals, α- and β-crystal, which are both in triclinic unit cell when crystallized upon zero tension or tension, respectively [10–14]. Crystallization in a semicrystalline polymer upon different process may also lead to different crystal unit cells. PHT exhibits γ-crystal when crystallized through solvent induction [15], which means the crystal is produced during the solvent evaporation and transforms to β-crystal upon heating to temperature higher than 120 °C. Syndiotactic polystyrene (sPS) shows less stable α-crystal when crystallized from constrained glassy/amorphous state [16–21], while α-crystal, mixed α + β crystals or β-crystal is produced when crystallized from molten state in which the chain mobility is higher compared to that in glassy/amorphous state [21–24]. Another important effect on the polymorphism behavior in semicrystalline polymers is residual nucleus; however, few polymers are known to be influenced by the residual nuclei in their polymorphism behaviors. sPS is the most frequently studied polymer whose polymorphism behavior is highly dependent on the residual nuclei which is attributed to insufficient melting at lower T_{max} (which is defined as the maximum temperature above T_m for melting the original crystals) or less t_{max} (time duration in melt held at T_{max}) [21–27].

sPS shows complex but interesting polymorphism (α-, β-, γ- and δ-form) and the corresponding multiple-melting behaviors [16–32]. The less stable α-crystal (α′ and α″) is solely produced in sPS samples upon crystallization from low $T_{max} = 280$ °C at all crystallizable temperatures and cold crystallization from a quenched amorphous state [16–22]. Besides, the α-crystal can be also obtained via a melting and recrystallization process upon annealing the solution-cast sPS when temperatures are higher than 200 °C [33–39]. The more stable β-crystal is generated in sPS when melt-crystallized from $T_{max} = 380$ °C and can also be obtained from transformation of the solvent-induced δ-form [20–22,29,40]. If T_{max}

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for melt-crystallized sPS is as high as 300 °C, the fraction of each of two crystal forms (alpha- or beta-) would then depend on the crystallization temperature, with a higher fraction of beta-crystal at higher T_c [21]. The effect of T_{max} on the polymorphism of sPS is attributed to the memory effect of the nuclei left in the melt when T_{max} used is not high enough to erase all crystals or nuclei formed in the previous crystallization process. The residual nuclei mean the clusters of molecules that retain their crystallographic arrangement of crystals as a result of insufficient melting condition [41]. Memory effect on the polymorphism has also been reported for aliphatic polyesters, such as poly(1,4-butylene adipate) (PBA) [42]. PBA shows two crystal forms (labeled as α- and β-) depending on the crystallization temperature. When the crystallization temperature is higher than 31 °C, only sole α-form is obtained; when the crystallization temperature is lower than 28 °C, only the β-crystal is obtained [5–7]. However, if the originally α-crystal (melt-crystallized at 35 °C) is heated to 52 °C, a temperature not high enough to erase all the α-nuclei, and re-crystallized at 28 °C, then the α-crystal is again produced [42].

In this study, effects of T_{max} (maximum temperature above T_m for melting the original crystals) and isothermal melt-crystallization temperature on the polymorphism of PHepT were studied and analyzed through wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy.

2. Experimental

2.1. Materials

Poly(heptamethylene terephthalate) (PHepT) was not commercially available and was synthesized in-house using a catalyst (butyl titanate) by following the method described earlier in the literature [43]. Characterizations showed basic physical data for PHepT, whose $T_g = -1.6$ °C, $T_m = 96$ °C, and $M_w = 37{,}500$ g/mol (GPC).

2.2. Apparatus

2.2.1. Wide-angle X-ray diffraction (WAXD)

X-ray analysis was performed on a Shimadzu XRD-6000 with copper Kα radiation (30 kV and 40 mA) and a wavelength of 0.1542 nm. The scanning 2θ angle range was from 5° to 40° with a step of 0.02° or equivalent to scanning rate of 2° min^{-1}.

2.2.2. Differential scanning calorimetry (DSC)

DSC measurements were made in a Perkin–Elmer DSC-7 equipped with a mechanical intracooler under nitrogen purge. Temperature and heat flow calibrations at different heating rates were done using indium, zinc. A heating rate of 10 °C/min was used in all cases. All the thermal treatments of PHepT samples for DSC and WAXD characterizations were performed in DSC to assure the temperature accuracy.

2.2.3. Fourier-transform infrared (FTIR) spectroscopy

FTIR (Nicolet Magna-560) was used for identifying the associated crystal peak and to investigate the crystal form in PHepT. Spectra were obtained at 4 cm^{-1} resolution and average was obtained at least 64 scans in the standard wavenumber range of 400–4000 cm^{-1}. Thin films for FTIR studies were obtained by casting the PHepT solutions onto the potassium bromide (KBr) pellet at ambient temperature (25 °C) and then solvent was removed in vacuum at 40 °C. The thermal treatment of PHepT on KBr pellet was done on hot plate and hot stage whose temperatures are both calibrated by thermalcouples. When the IR characterization relating to the heating process of PHepT was performed, a microprocessor-driven temperature controller and a heated transmission cell (HT-32, Thermo Spectra-Tech) were equipped with the IR instrument.

3. Results and discussion

The polymorphism in melt-crystallized PHepT was analyzed by a series of characterization techniques. The starting material of PHepT (as-polymerized PHepT without any thermal treatment) was firstly characterized by wide-angle X-ray diffraction which showed the diffraction peaks at $2\theta = 20.0$, 22.0 and 24.3° (not shown for brevity) and was defined as the α-type crystal. Thus, the original crystal followed by melting at different T_{max} is of α-type. All the samples subjected to subsequent thermal treatment are starting materials of PHepT with α-crystal. Fig. 1 shows the wide-angle X-ray diffractograms for starting materials of PHepT isothermally melt-crystallized at $T_c = 55$ °C quenching from different T_{max}s (100–150 °C) which are indeed higher than the end point of melting temperature of the starting materials of PHepT. When the starting material of PHepT is melted at lower T_{max} (100–120 °C) and then crystallized at 55 °C, it shows diffraction peaks at $2\theta = 20.0$, 22.0 and 24.3°, indicating that under this thermal treatment, PHepT shows solely α-crystal. However, when the starting material of PHepT is melted at higher T_{max} (140–150 °C) and then crystallized at 55 °C, it shows completely different diffraction peaks of $2\theta = 15.8$, 17.6, 21.4 and 23.0°. The crystal with diffraction peaks at $2\theta = 15.8$, 17.6, 21.4 and 23.0° is defined as β-type crystal for PHepT. Combined diffraction peaks of both α- and β-crystal were obtained in melt-crystallized starting material of PHepT at $T_c = 55$ °C

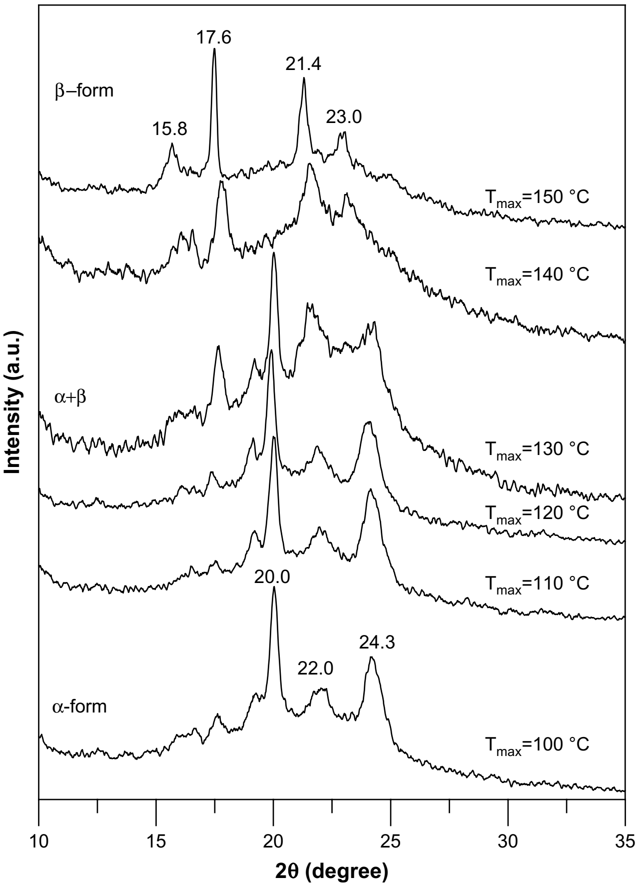

Fig. 1. WAXD intensity profiles of PHepT melt-crystallized at $T_c = 55$ °C by quenching from $T_{max} = 100$ to 150 °C.

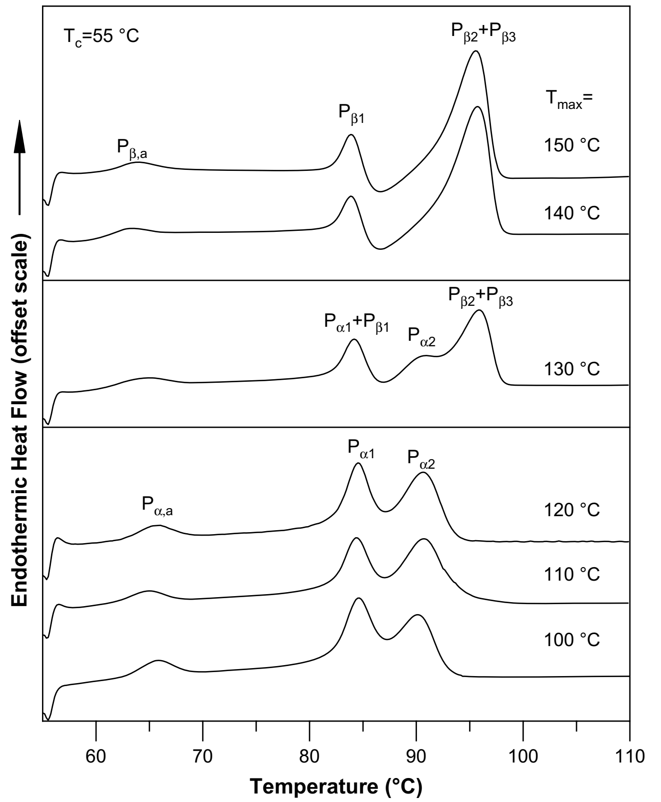

Fig. 2. DSC traces for PHepT melt-crystallized at $T_c = 55$ °C by quenching from $T_{max} = 100$ to 150 °C.

quenching from $T_{max} = 130$ °C. It indicates that by this thermal treatment, PHepT shows mixed fractions of both α + β crystals.

DSC analysis was then performed to identify the associated melting behavior of each crystal form (α and β). Fig. 2 shows the DSC traces (10 °C/min) of PHepT samples with original α-crystal melt-crystallized at $T_c = 55$ °C quenching from $T_{max} = 100$ to 150 °C. When $T_{max} = 100$–120 °C, the melting behavior of melt-crystallized PHepT samples showed two melting peaks and one annealing peak ($P_{\alpha,a}$). An annealing peak which appears ca. 5–7 °C above the crystallization temperature is the characteristic of many semi-crystalline polymers. The original of the annealing peak can be summarized as follows: (1) melting, recrystallization and remelting during the DSC heating process, (2) the presence of more than one crystal modifications, (3) variation in morphology (lamellar thickness, distribution, perfection or stability), (4) physical aging and/or relaxation of the rigid amorphous fraction, and (5) different molecular weight species and so on [44,45]. In this case, the original annealing peak of PHepT is induced by the annealing effect and due to the melting of the subsidiary crystals with less perfection from secondary crystallization. From the previous results as shown in Fig. 1, the melt-crystallized PHepT at $T_c = 55$ °C by quenching from $T_{max} = 100$ to 120 °C produces only α-crystal. Thus, the two endothermic peaks are corresponding to the melting of the α-crystal of

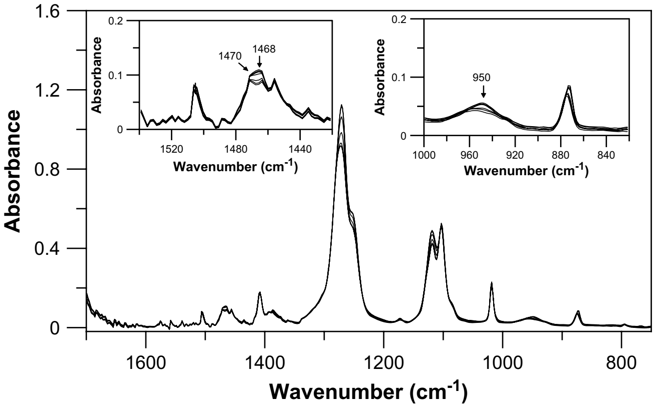

Fig. 3. Time-dependent IR spectra of the crystallization process ($t = 0$–120 min) of PHepT at 55 °C by quenching from $T_{max} = 150$ °C (β-form).

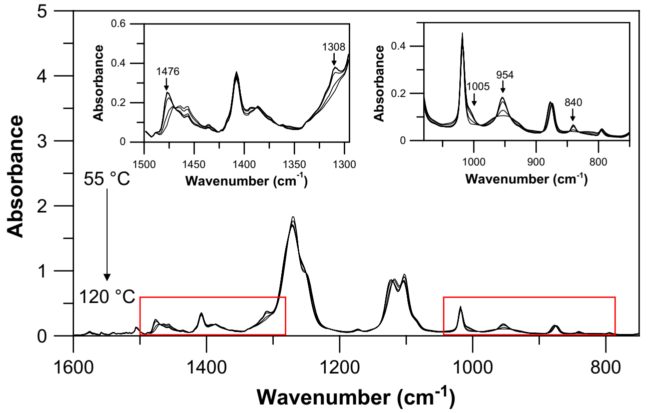

Fig. 4. Temperature-dependent IR spectra on a real-time heating process (55–120 °C) for PHepT crystallized at 55 °C by quenching from $T_{max} = 110$ °C (α-form).

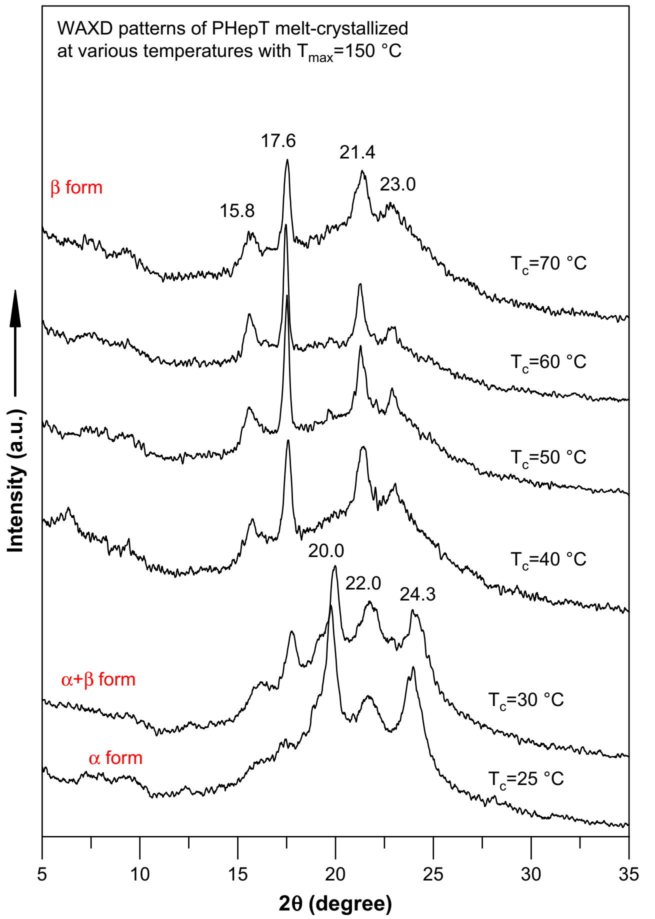

Fig. 5. WAXD intensity profiles of PHepT melt-crystallized at different temperatures ($T_c = 25$–70 °C) by quenching from $T_{max} = 150$ °C.

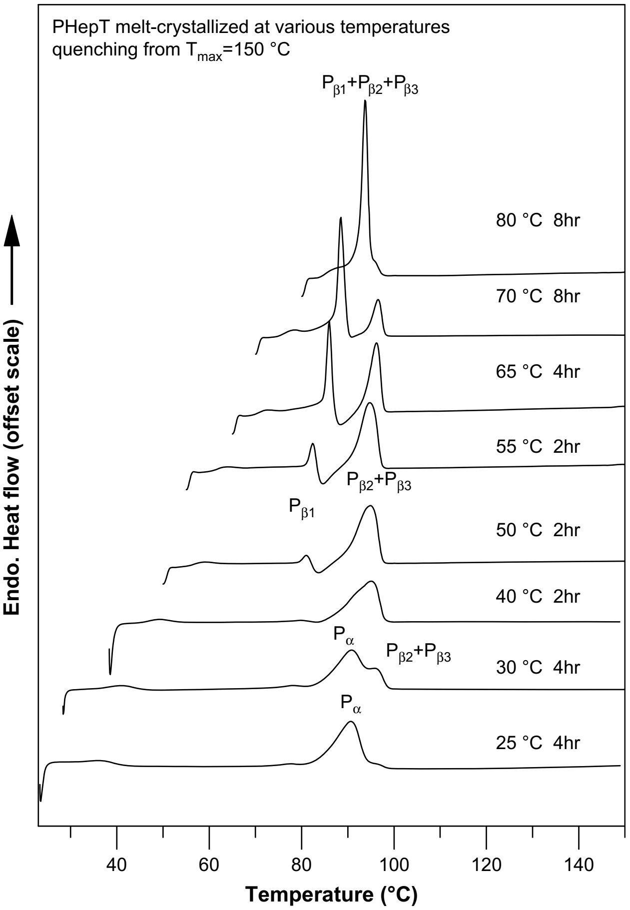

Fig. 6. DSC thermograms (10 °C/min) of PHepT melt-crystallized at different temperatures (T_c = 20–80 °C) by quenching from T_{max} = 150 °C.

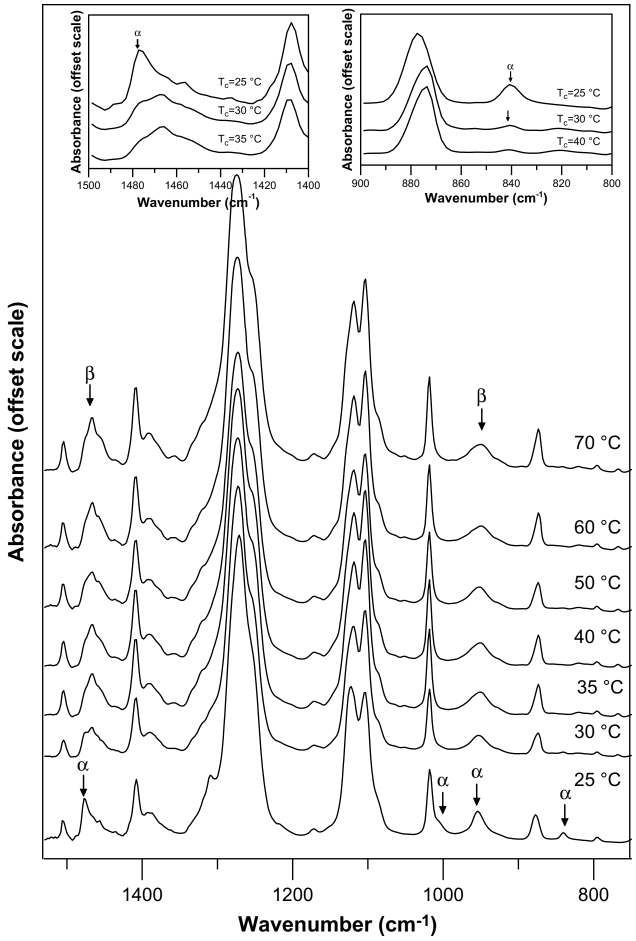

Fig. 7. IR spectra of PHepT melt-crystallized at different T_c temperatures (T_c = 40–80 °C) with same T_{max} = 150 °C.

PHepT and are labeled as $P_{\alpha1}$ and $P_{\alpha2}$. In contrast, PHepT melt-crystallized at 55 °C with T_{max} = 140 or 150 °C shows only the β-crystal, and it exhibits different thermal trace from that for α-crystal upon DSC scanning and shows two melting peaks assigned as $P_{\beta1}$ and $P_{\beta2}+P_{\beta3}$ as well as one annealing peak ($P_{\beta,a}$). The assignment of the second melting peak of the β-crystal as $P_{\beta2}+P_{\beta3}$ is attributed to the following analysis. When scanned using the rate 1 °C/min, the DSC trace shows a shoulder P_{b2} accompanying the melting peak P_{b3}, and with the increase in scanning rates, these two melting peaks merge into one peak $P_{b2}+P_{b3}$ (DSC traces not shown for brevity). By comparison, the melting peaks of $P_{\alpha1}$ and $P_{\beta1}$ are at nearly the same temperature and so are the annealing peaks of both crystal forms ($P_{\alpha,a}$ and $P_{\beta,a}$). However, the melting temperature of $P_{\beta2}+P_{\beta3}$ (β-crystal) is higher than that of $P_{\alpha2}$ (α-crystal). When PHepT was melted at T_{max} = 130 °C then isothermally crystallized at 55 °C, it exhibits the melting peaks attributed to both the α- and the β-crystal for the coexistence of α- and β-crystal under this thermal treatment. However, for the similarity of $P_{\alpha1}$ and $P_{\beta1}$ in melting temperature, only three melting peaks ($P_{\alpha1}+P_{\beta1}$, $P_{\alpha2}$, $P_{\beta2}+P_{\beta3}$) were obtained. The results obtained from DSC indicate that the polymorphism behavior of melt-crystallized PHepT is indeed influenced by T_{max}.

FTIR is a powerful instrument in determining the conformation of molecules. In this study, it was used to analyze the characteristic absorption bands associated with the α- and β-crystal of melt-crystallized PHepT to provide supported evidence for the effect of T_{max} on the polymorphism behavior of PHepT. Fig. 3 shows time-dependent FTIR spectra in the frequency range of 750–1600 cm^{-1} for isothermal crystallization process from t = 0 to 120 min of PHepT melt-crystallized at 55 °C quenching from T_{max} = 150 °C showing β-crystal. During the crystallization process, the intensities of the absorption bands at 1470, 1468 and 950 cm^{-1} increase with the crystallization time for the formation of the β-crystal. Thus, these three bands were assigned as the characteristic absorption bands of β-crystal of PHepT. Fig. 4 shows the temperature-dependent FTIR spectra in the frequency range of 750–1600 cm^{-1} on a real-time heating process from 55 °C to 120 °C for PHepT, which was initially crystallized at 55 °C on hot stage by quenching from T_{max} = 110 °C with the sole α-crystal. In this case, the real-time heating process, instead of isothermal holding, was recorded and analyzed because the growth process of the α-crystal under this thermal treatment was too rapid to be analyzed by FTIR using an isothermal step-wise mode. Upon heating from 55 °C to 120 °C, the absorption bands at 840, 954, 1005, 1308 and 1476 cm^{-1} decrease in intensity with an increase of temperature because of the melting of the α-crystal. Thus, these bands were assigned as the characteristic absorption bands of α-crystal of PHepT. The difference in the characteristic absorption bands of PHepT samples melt-crystallized at 55 °C, quenching from T_{max} = 150 °C and 110 °C respectively exhibiting β- and α-crystal, further manifests the influence of T_{max} on the polymorphic behavior of PHepT.

Effect of T_{max} on the polymorphism behavior of a semicrystalline polymer is attributed to the memory effect of the residual nuclei when the temperature used to melt the original crystals is not high enough to erase all nuclei. In this study, all the starting materials of PHepT are of α-crystal. When T_{max} is higher than 140 °C, the α-crystal and α-nuclei can be erased completely, thus after quenching

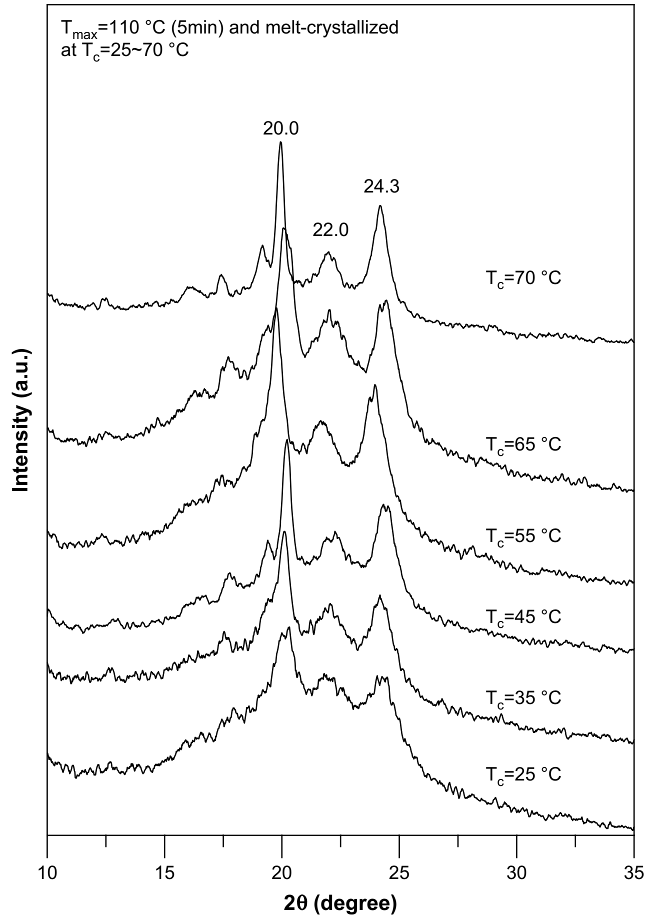

Fig. 8. WAXD intensity profiles of PHepT melt-crystallized at $T_c = 25–70\,^\circ C$ by quenching from a same $T_{max} = 110\,^\circ C$.

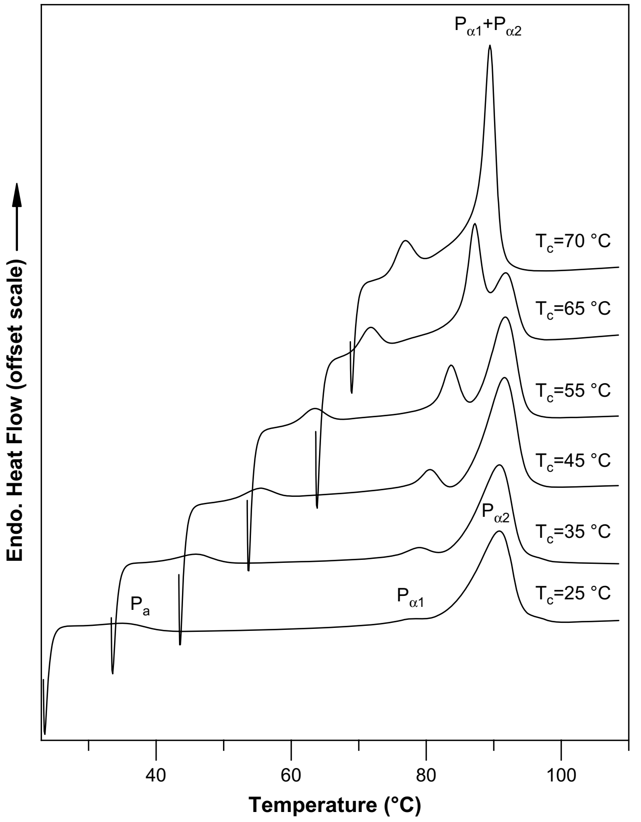

Fig. 9. DSC thermograms (10 °C/min) of PHepT melt-crystallized at $T_c = 25–70\,^\circ C$ by quenching from $T_{max} = 110\,^\circ C$.

from isotropic melt (without nuclei) then crystallized at 55 °C, the β-crystal is instead obtained. In contrast, when T_{max} is low, the original α-crystal is partially erased, thus after quenching from melt containing α-nuclei then crystallized at 55 °C, the α-crystal or mixed $\alpha + \beta$ crystal is obtained. Consequently, the polymorphic behavior of melt-crystallized PHepT is highly influenced by the existence of α-nuclei in the molten state.

Further investigations were performed to study the effect of crystallization temperature on the polymorphism of PHepT. Two extreme conditions were studied, $T_{max} = 150\,^\circ C$ and $T_{max} = 110\,^\circ C$. Fig. 5 shows the WAXD intensity profiles of PHepT melt-crystallized at 25–70 °C quenching from $T_{max} = 150\,^\circ C$. According to previous results, it is true that at this melting temperature (150 °C), all the nuclei can be erased completely. Thus, the resulted polymorphism of PHepT crystallized from the molten state with $T_{max} = 150\,^\circ C$ is influenced only by the crystallization temperature. In the figure, the diffraction peaks of melt-crystallized PHepT at temperatures higher than 40 °C are at $2\theta = 15.8, 17.6, 21.4$ and 23.0°, which are attributed to the β-crystal of PHepT. However, if the crystallization temperature is 30 °C, its WAXD pattern shows the diffraction peaks at $2\theta = 15.8, 17.6, 21.4$ and 23.0° attributed to the β-crystal as well as the diffraction peaks at $2\theta = 20.0^\circ$ which is the most apparent diffraction peak of the α-crystal of PHepT. It indicates that mixed $\alpha + \beta$ crystal is obtained in melt-crystallized PHepT at this temperature ($T_c = 30\,^\circ C$) by quenching from $T_{max} = 150\,^\circ C$. Furthermore, when the crystallization temperature is 25 °C, the corresponding WAXD pattern shows only the diffraction peaks at $2\theta = 20.0, 22.0$ and 24.3° attributed to the α-crystal of PHepT. Thus, the α-crystal can be obtained not only in melt crystallization from molten state with α-nuclei but also in melt crystallization at temperature lower than 40 °C from isotropic melt. Therefore, apart from the memory effect of the α-nuclei, the crystallization temperature also plays an important role in the polymorphism behavior of PHepT.

Fig. 6 shows the DSC analysis of PHepT melt-crystallized at various T_c by quenching from a same $T_{max} = 150\,^\circ C$. When the crystallization temperature is higher than 40 °C (40–80 °C), the DSC traces show only the melting peaks attributed to the β-crystal of PHepT, in which two melting peaks are obtained ($P_{\beta 1}$ and $P_{\beta 2} + P_{\beta 3}$) at $T_c = 40–70\,^\circ C$ and one melting peak ($P_{\beta 1} + P_{\beta 2} + P_{\beta 3}$) is obtained at $T_c = 80\,^\circ C$. The intensities and temperatures of $P_{\beta 1}$ increase with increasing crystallization temperature because the lamellar thickness of primary crystals (crystals formed in the primary crystallization process) is in a reverse relationship to supercooling ($\Delta T = T_m - T_c$), that is, when ΔT is high (T_c is low) the lamellar thickness is thinner in comparison with that at lower ΔT. Moreover, there is an exothermic peak following $P_{\beta 1}$, and the existence of the exothermic peak may be due to the melting/re-crystallization of crystals upon DSC scanning. Upon scanning, primary crystals melted giving $P_{\beta 1}$ and repacked into thicker lamella, then melted as $P_{\beta 2} + P_{\beta 3}$. When the lamellar thickness of primary crystals of a semicrystalline polymer becomes thicker with an increase of crystallization temperature, the re-organization of the primary crystals are reduced, leading to lower intensities in the melting peaks of re-organized crystals. Thus, the intensities of $P_{\beta 2} + P_{\beta 3}$ in β-crystal of PHepT samples decrease with increasing the crystallization temperature. When PHepT melt-crystallized at $T_c = 30$ or $25\,^\circ C$ quenching from $T_{max} = 150\,^\circ C$, combined melting peaks of α- and β-crystal and one melting peak associated with α-crystal are obtained, respectively. It further

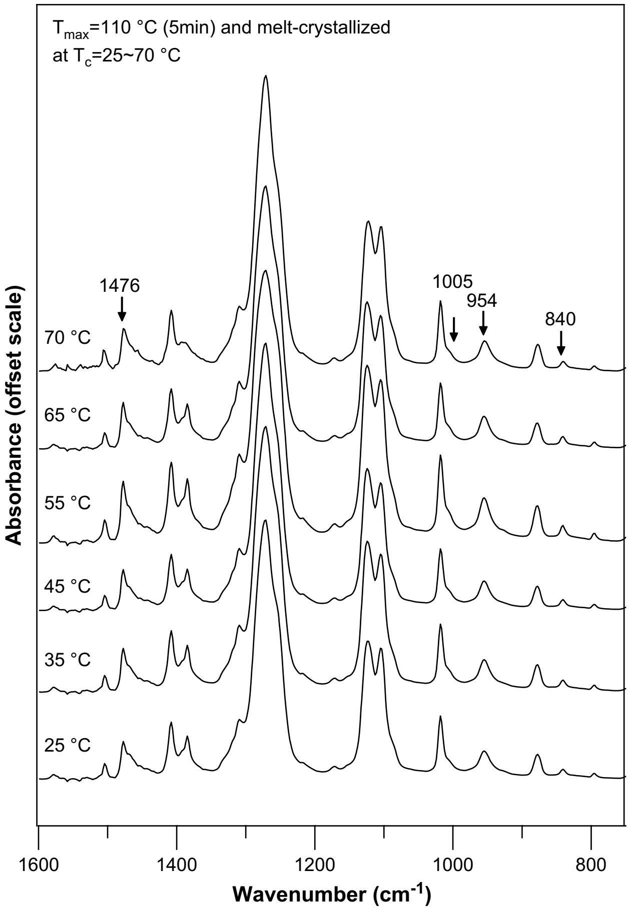

Fig. 10. IR spectra of PHepT melt-crystallized at $T_c = 25–70$ °C by quenching from $T_{max} = 110$ °C.

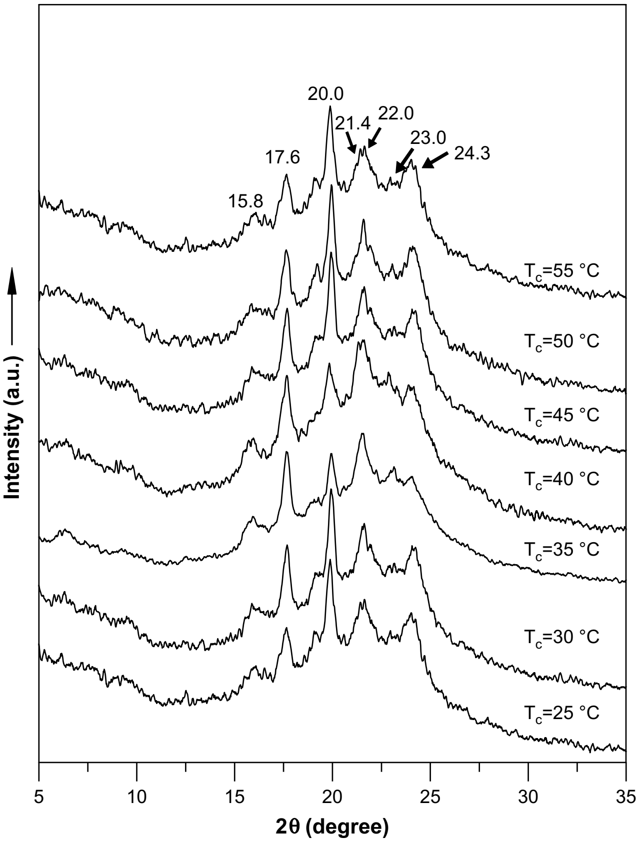

Fig. 11. WAXD diffractograms of PHepT melt-crystallized at $T_c = 25–55$ °C by quenching from $T_{max} = 110$ °C containing trace β-crystal nuclei.

manifests that the α-crystal can be produced in melt-crystallized PHepT at low temperatures (lower than 40 °C) even from an isotropic melt (i.e., no prior nuclei traces) and the fraction of the α-crystal increases with a decrease of T_c.

The effect of the crystallization temperature on the polymorphism behavior of the melt-crystallized PHepT was also determined by FTIR. Fig. 7 shows IR spectra of PHepT melt-crystallized at various temperatures ($T_c = 25–70$ °C) by quenching from a same $T_{max} = 150$ °C. When T_c is higher than 35 °C, only the absorption bands at 950 cm^{-1} and 1470 cm^{-1} corresponding to the β-crystal of PHepT appear. Besides, there is no absorbance band associated with the α-crystal obtained when T_c is higher than 35 °C. However, when crystallization temperature is lower than 35 °C (30 and 25 °C), the absorption bands for the α-crystal appear. From the insets in the figure, the bands at 840 and 1476 cm^{-1} corresponding to the α-crystal increase in intensity with a decrease of T_c from 35 °C to 25 °C, indicating the formation of higher fraction of the α-crystal at lower T_c.

Effect of crystallization temperatures on the polymorphism in melt-crystallized PHepT quenching from $T_{max} = 110$ °C was also studied. Fig. 8 shows diffraction patterns of PHepT melt-crystallized at $T_c = 25–70$ °C with a same $T_{max} = 110$ °C. All X-ray diffractograms show only the diffraction peaks at $2\theta = 20.0$, 22.0 and 24.3°, which are the characteristic diffraction peaks of α-crystal, indicating that PHepT crystallized into α-crystal at all measured temperatures when quenched from $T_{max} = 110$ °C. In addition, thermal analysis characterization result should also be compared to the WAXD data. Fig. 9 shows the melting behavior of PHepT crystallized at the same range of temperature ($T_c = 25–70$ °C) by quenching from $T_{max} = 110$ °C was also analyzed by DSC. In each trace, only the melting peaks corresponding to α-crystal ($P_{\alpha1}$, $P_{\alpha2}$) were obtained, suggesting that upon melt crystallization at $T_c = 25–70$ °C by quenching from $T_{max} = 110$ °C, PHepT exhibited only α-crystal. With an increase of T_c, $P_{\alpha1}$ shifts to higher temperature and increases in intensity for the formation of thicker lamellae upon crystallization at higher T_c (lower ΔT).

Effect of the crystallization temperature on the polymorphism in melt-crystallized PHepT quenching from $T_{max} = 110$ °C was also determined by FTIR. Fig. 10 shows IR spectra of PHepT melt-crystallized at various temperatures ($T_c = 25–70$ °C) by quenching from $T_{max} = 110$ °C. For PHepT crystallized at all T_c temperatures, the IR spectra show only the absorption bands associated with the α-crystal (at 840, 954, 1005, 1308 and 1476 cm^{-1}), and no absorption bands corresponding to the β-crystal are observed. The IR result further demonstrates that the melt-crystallized PHepT by quenching from $T_{max} = 110$ °C exhibits only the α-crystal at all measured temperatures (25–70 °C).

In addition to the effect of α-nuclei and crystallization temperature on the polymorphism of melt-crystallized PHepT, effect of β-nuclei was also investigated. PHepT samples containing only the β-crystal were prepared by melt crystallization at 40 °C for 2 h by quenching from a very high $T_{max} = 150$ °C, at which all nuclei were completely erased. When PHepT containing only the β-crystal was heated to $T_{max} = 110$ °C (5 min), the β-crystal could not be completely erased and thus the melt at $T_{max} = 110$ °C would contain nuclei of β-form whose equilibrium melting temperature is slightly higher than 110 °C. The β-nuclei-containing melts were then crystallized at a wide range of $T_c = 25–55$ °C, and the crystallized PHepT samples were characterized using WAXD for evaluating their polymorphism states. Fig. 11 shows the

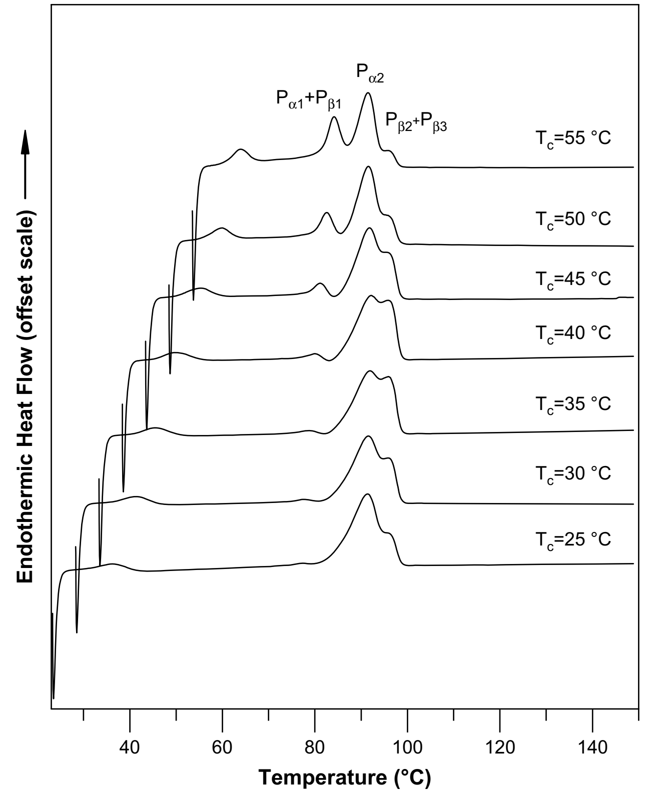

Fig. 12. DSC thermograms of PHepT melt-crystallized at $T_c = 25–55$ °C by quenching from $T_{max} = 110$ °C containing trace β-crystal nuclei.

WAXD diffractograms of PHepT melt-crystallized at $T_c = 25–55$ °C by quenching from $T_{max} = 110$ °C. This T_{max} was regarded as a temperature at which some residual β-crystal nuclei might be present in the melt. This is so because $T_{max} = 110$ °C is considered to be not high enough to melt all the β crystals in PHepT. In the figure, the diffraction peaks characteristic of the α-crystal ($2\theta = 20.0$, 22.0, 24.3°) and β-crystal ($2\theta = 15.8$, 17.6, 21.4, 23.0°) indicate that PHepT exhibits mixed fractions of α + β crystals, and not simply either α or β forms. Thus, the result shows that as long as trace nuclei are present in melt, a stronger tendency to polymorphism in PHepT (melt-crystallized at a wide range of T_c) is noted.

DSC analysis was performed to reveal the thermal behavior related to the polymorphism states in PHepT. Fig. 12 shows DSC thermograms of PHepT melt-crystallized at $T_c = 25–55$ °C by quenching from $T_{max} = 110$ °C containing residual β-crystal nuclei. In this figure, each trace shows a combination of melting peaks characteristic of both α- and β-crystal ($P_{\alpha1} + P_{\beta1}$, $P_{\alpha2}$, $P_{\beta2} + P_{\beta3}$) in PHepT, which manifests the co-existence of both α- and β-crystal upon crystallization from melt with trace β-nuclei.

Thus, the WAXD and DSC results both demonstrate that α-crystal, as well as β-crystal, in PHepT can be grown from melt containing β-nuclei. This fact suggests that the polymorphic behavior in PHepT is dependent on the crystallization kinetics and prior thermal histories. If there are residual nuclei (either α- or β-nuclei) in the melts, the nucleation barrier of PHepT is lower and only α-crystal or a higher fraction of α-crystal is produced upon crystallization. By contrast, when all crystal nuclei are completely melted and erased (such as at high T_{max}), the β-crystal, favored in conditions with a higher nucleation barrier, is solely obtained when the nuclei-free melts are crystallized at T_c higher than 35 °C. When crystallized at lower T_c <35 °C the nuclei-free melts still can crystallize to a polymorphic state containing both α- and β-crystal.

4. Conclusion

PHepT exhibits different polymorphic crystal forms (termed as α, β, and mixed fractions of α + β) depending on T_c (melt-crystallization temperature) and T_{max} (maximum temperature for melting the original nuclei). PHepT heated to lower T_{max} (<110 °C) tends to retain residual nuclei of prior crystals. Upon heating at T_{max} equal to or lower than 110 °C, PHepT with initially crystallized α-crystal would develop only α-crystal when re-crystallized at any T_c from the lower T_{max}. However, at the same T_{max}, PHepT with initially crystallized β-crystal can develop mixed α + β crystals when crystallized at any T_c from the same lower T_{max}. On the other hand, higher T_{max} erases crystals of lower T_m, and leads to a different polymorphism state in PHepT. In addition to prior crystal memory effect, polymorphism of melt-crystallized PHepT upon quenching from nuclei-free isotropic melts (heated at $T_{max} = 150$ °C with complete melting of either α- or β-nuclei) could also be influenced by T_c. At $T_{max} = 150$ °C and crystallized at T_c higher than 35 °C, PHepT exhibits only the β-crystal. At the same T_{max} but T_c lower than 35 °C, PHepT exhibits mixed fractions of α + β crystal; for $T_c < 25$ °C, PHepT exhibits solely α-type crystal. Consequently, both the effects of residual nuclei (either α- or β-nuclei) and T_c show great influences on the polymorphic behavior in melt-crystallized PHepT.

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