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Crystallization of poly(butylene terephthalate) blends containing liquid crystalline polymer component

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Abstract

Blends of poly(butylene terephthalate) (PBT) with thermotropic liquid crystalline polymer (LCP) concentration down to 0.2 wt.% were prepared to investigate the effects of LCP component on the crystallization behavior of PBT. The crystal structure of PBT in the blends was not deteriorated by the presence of LCP. The regularity of PBT crystals in the blends with lower LCP content appeared to be more perfect, compared with that of pure PBT sample and of blends with high LCP content. The experimental results revealed that the LCP component may affect, to a great extent, the crystallization process of the blends due to the inhomogeneous nature of the LCP used. The crystallization process of PBT in the blends was very sensitive to the LCP content and its microstructures existing in the melt before the start of crystallization, with the nucleation effect of the LCP component in its crystalline state being more efficient than that in its nematic state. The favorable content at which the LCP microdomains show ''the most efficient nucleation'' is more likely to occur at lower LCP content for these systems. Based on the fact that the addition of the LCP component leads to higher crystallization temperature, crystallinity and degree of perfection of the crystallites formed, it is proposed that the effects of heterogeneous nucleation dominate in the crystallization process of the blends with lower LCP concentration.

Keywords: Liquid crystalline component; PBT blends; Crystallization behavior

1. Introduction

Blends consisting of thermoplastics and thermotropic liquid crystalline polymers (LCPs) have attracted much attention owing to the peculiar characteristics of the LCP component which can be used to achieve better processability and mechanical performance of the thermoplastic matrix [1–6]. Whilst the improvement of processing conditions and properties is an important issue for using the mesomorphic component, interactions between LCP and thermoplastics are also well recognized [3,6,7]. It has been shown that the LCP mesophase has a significant influence on the crystallization process of the matrix polymers.

In many instances, the LCP component has been found to act as a heterogeneous nucleation agent to promote the crystallizability of the crystalline polymers such as PP [8,9], PET [10–15], PEEK [16–18], PPS [19–21], and PA [22,23]. On the other hand, results of studies on the blends of LCPs with polybutylene terephthalate (PBT) have given rise to much controversy. Paci et al. [24,25] observed the depression of crystallization rate and crystallization temperature upon cooling of PBT in the presence of LCP. Pracella and coworkers [26,27] found that the spherulite growth rate and overall crystallization rate of PBT from melted blends were markedly depressed by the presence of the LCP component, and the initial nucleation density of PBT was reduced, even at low LCP concentrations (5%). On cooling from the melt, the crystallization temperature of PBT decreased with increasing amounts of LCP. In addition, the equilibrium melting temperature of PBT was found to decrease with increasing LCP content, due to the diluent effect of the LCP component. These results were explained in terms of miscibility effects between the components. In contrast, Song et al. [28] found that the crystallization rate and temperature of PBT could be enhanced with the addition of the LCP component and were strongly dependent on the chemical composition of the liquid crystalline copolyester and its concentration in the blends. Chang et al. [29,30] recently investigated the melt-spun PBT, blended with LCP, having different chemical structures, and showed that the melting temperature of PBT was not affected with the addition of LCPs, but the degree of crystallinity of PBT in the blends with main chain LCP decreased with decreasing LCP content. The results suggest

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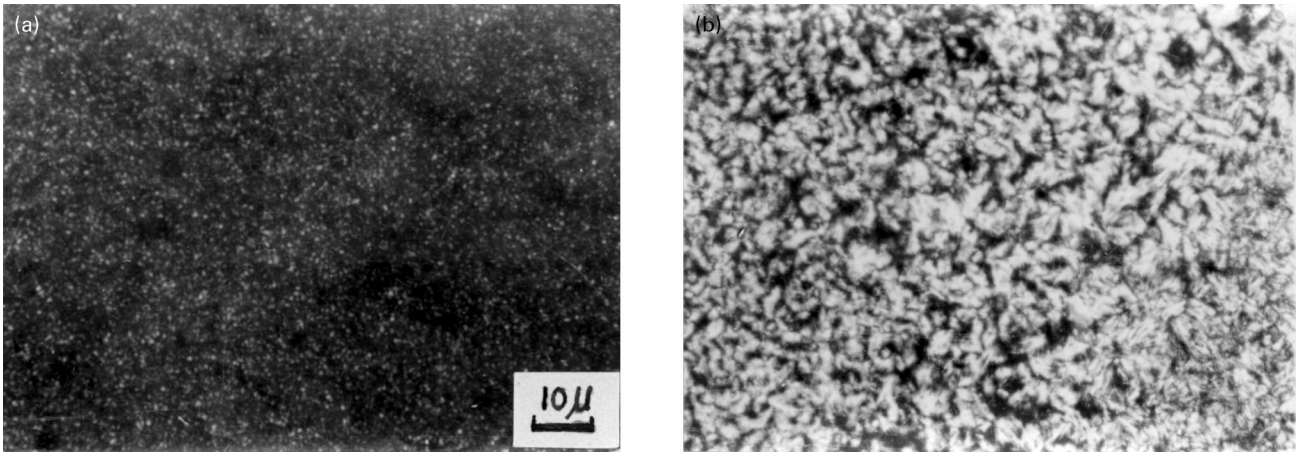

Fig. 1. Optical micrographs of the liquid crystalline polymer: (a) as-cast film; and (b) micrograph taken at 272°C.

that the interactions between PBT and LCP should be more complicated in comparison with poly(ethylene terephthalate) which differs in the main chain structure from PBT with only two methylene units.

In surveying the studies on PBT/LCP blends, it was noticed that the LCP composition added in most of the studies was relatively high, typically higher than 10 wt.%, in order to achieve the desired property improvement. However, in our previous studies on the blends of PEEK/LCP and PPS/LCP [17,21], we have shown that, for the immiscible or partially miscible blends, the microdomains of LCP would diminish or lose their nucleating function as the size increased and higher LCP concentrations would hinder the growth rate of polymer crystals. In the PET/LCP (of PET/PHB type) blends studied, the most efficient nucleation was found at a lower LCP content [13]. The results of Song et al. [28] also revealed that both the crystallization temperature and rate of the blends with less than 5 wt.% of LCP (a copolyester containing 20% mole ratio of *p*-oxybenzoate segments) were higher than those of neat PBT. It is therefore of great interest to investigate the effects of LCP at low concentrations on the crystallization behaviors of the crystalline polymer matrix and to inquire into the nature of nucleation and other effects of the mesomorphic component in the blends, as very few reports were found to deal with this issue.

In this series of reports, blends of PBT with LCP content down to 0.2 wt.% were prepared to estimate the effects of the LCP component on the crystalline structure and morphology, the crystallization process and kinetics, and the melting behaviors of PBT. Investigations were also carried out to reveal the induced crystallization mechanism of the LCP component via model compounds, and to discuss the transesterification mechanism occurring in the blends and its influence on the crystallization behavior of the matrix polymer. The current paper is to describe the results of study on the crystallization behaviors of the PBT/LCP blends.

2. Experimental

2.1. Materials

The PBT sample used in this work is a commercial product of the Baling Petrochemical Corporation, China. The molecular weight of $\overline{M}_n = 2.26 \times 10^4$ was determined in a solution of phenol/1,1,2,2-tetrachloroethane (60/40, wt/wt) at 30°C by viscosity measurement [31]. The liquid crystalline polymer used is a thermotropic copolyester of PET/PHB (*p*-hydroxybenzoic acid) type, also a commercial product in the trade name of PCL RHODESTER by Rhone Poulen, France. The nematic transition temperature of the LCP around 272°C was identified by both optical microscopy and differential scanning calorimetry.

2.2. Blend preparation

Samples of PBT/LCP were prepared using solution blending to ensure better dispersion of the LCP component for detailed investigations. The purified PBT and LCP were first dissolved in *p*-chlorophenol (2%); the solution was then precipitated in methanol (1:8 in volume). The precipitate was dried at 60°C for 72 h in vacuum. For the blends with LCP lower than 2 wt.%, a ''master solution'' of LCP was first prepared and then diluted into the desired composition to assure the weighting accuracy. The neat PBT and LCP samples were also precipitated via the same procedures as blends.

2.3. Sample characterization

2.3.1. Optical microscopy

The morphologies were observed by a LEITZ Orthoplan polarizing light microscope with a heating stage. The specimens were prepared by solution casting.

2.3.2. X-ray diffraction

Specimens after crystallization or thermal treatment were

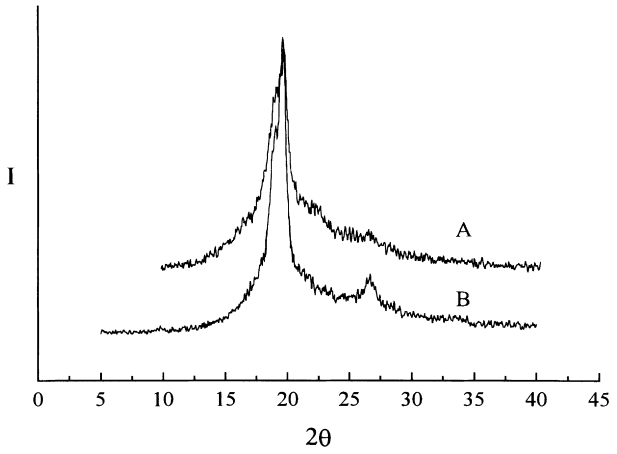

Fig. 2. WAXD patterns of the liquid crystalline polymer after different thermal treatments: (A) melted at 280°C, followed by cooling to room temperature; and (B) quenched sample.

analyzed by wide-angle X-ray diffraction (WAXD, Rigaku-D/MAX-3A) at room temperature, using CuKα radiation (35 kV, 25 mA, with wavelength of 1.54 Å).

2.3.3. Differential scanning calorimetry (DSC)

The crystallization behaviors of the blends were characterized using a Perkin Elmer DSC-7 calorimeter operating under nitrogen flow. The calibration of temperature and heat was performed using indium and zinc as the standards. Specimens were first heated to 250°C or 280°C for 3 min, then cooled to room temperature at a different rate for non-isothermal crystallization, or rapidly cooled to a crystallization temperature T_C for isothermal crystallization.

2.3.4. Thermogravimetric analysis (TGA)

Thermograimetric analyses of both PBT and LCP were carried out by a Shimazu thermogravimeter (TH-50) at a heating rate of 20°C/min. The temperatures at which the weight loss start are 319°C and 456°C for PBT and the LCP in the air, and 344°C and 464°C for PBT and LCP under nitrogen atmosphere, respectively.

3. Results and discussion

3.1. Microstructure of the LCP

Upon heating, the as-cast LCP sample exhibited the nematic texture around 272°C, as shown in Fig. 1. A small endotherm at 273°C was also found for the as-precipitated LCP sample in the heating trace of DCS scan (not shown), in coincidence with the microscopy observation. The liquid crystalline polymer of the PET/PHB type is generally considered to consist of randomly distributed segments of flexible PET and rigid PHB from the viewpoint of condensation copolymerization [32]. It has been reported, however, that the microstructure of the PET/PHB copolyester is heterogeneous in nature, of which the continuous and dispersed phases were dependent on the relative composition of PET and PHB [33]. Fig. 2 shows the X-ray diffraction patterns of the LCP used in this study. The specimen was first melted at 280°C, followed by cooling to the room temperature (spectrum A) to allow crystallization of the LCP, or quenched to ice water (spectrum B) to prevent the PET segments from possible crystallization and to preserve any unmelted structure that might exist with the as-cast or as-precipitated LCP samples. It is found that a strong diffraction peak at $2\theta = 19.6°$ due to the homopolymer of PHB [34,35] is well identified, but no resolvable PET characteristic reflections can be seen, indicating that the LCP consists of a high composition of PHB. For the quenched sample, another characteristic reflection of PHB crystals at $2\theta = 26.7°$ becomes more apparent than that of the slowly cooling sample, which suggests that the ordered domains of PET segments formed in this condition are less (as some small reflections of PET around this region would have overlapped the 26.7° peak in Spectrum A, whereas the absence of reflections due to PET in this region makes the peak at 26.7° more apparent for Spectrum B).

Zachariades et al. [34] have pointed out that, for LCP at higher levels of PHB, such as PET/PHB80, the ordered domains exist as lamellae blocks which have the same spacings and lamellar thickness (about 200 Å) as those of homopolymer PHB crystallites. Blackwell [35] showed that the ordered regions of both the copolyesters containing 60%–80% of PHB and the PHB homopolymer single crystals had a similar basic crystalline structure, of which the PET units probably present as defects in the PHB-rich lamellae. We have also found that the LCP sample used contained a small amount of PHB microcrystallite which do not melt above 380°C [36]. These unmelted microcrystallites have been attributed to the formation of long PHB sequences during the copolymerization process, and is believed to play a role in affecting the crystallization behavior of LCP-containing blends.

3.2. Crystalline morphology of the blends

The micrographs shown in Fig. 3 were obtained from the as-cast film of the PBT and PBT/LCP blends. All the spherulites grown from the dilute solution show a Maltese cross parallel to the polarizers and are thus characterized as usual spherulite [37–39] or α-form crystal [40]. It is evident that the spherulite size of pure PBT [Fig. 3(a)] is smaller than that of the blends. In the presence of the LCP component, the size of spherulites varies irregularly with composition [Fig. 3(b)–(f)]. At lower LCP content, well-developed spherulites can be viewed, whereas at higher content (>10%) the edges of spherulites appear to be fuzzy.

Generally, the size of polymer spherulite is governed by the number of nuclei formed in the unit volume at the time of crystallization. With the gradual evaporation of solvent, the polymer solution becomes concentrated and the

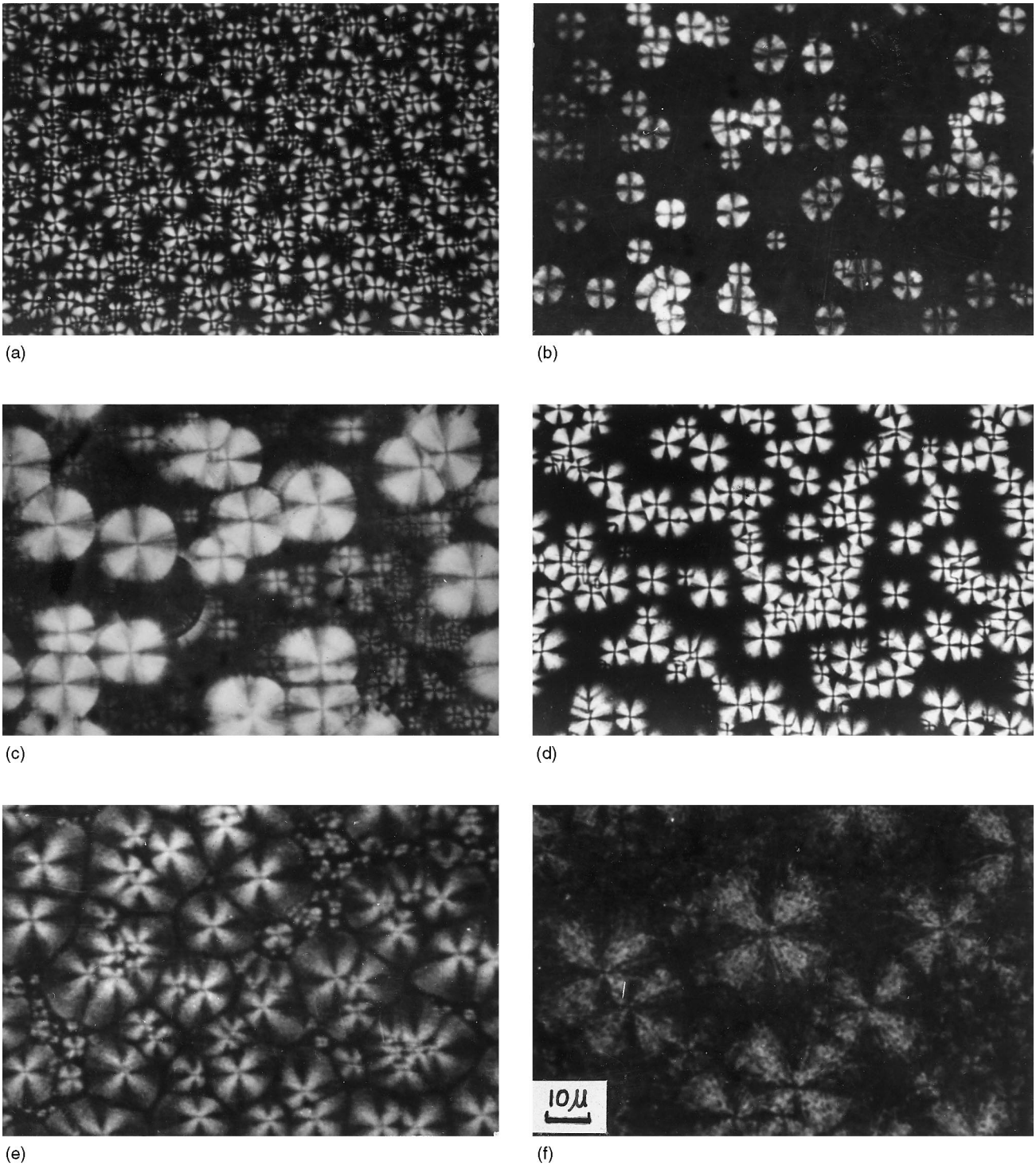

Fig. 3. Optical micrographs of PBT/LCP blends crystallized from the solution casting films: (a) pure PBT; (b) LCP = 1%; (c) LCP = 5%; (d) LCP = 10%; (e) LCP = 20%; and (f) LCP = 30%.

nucleation and crystallization start. For a pure PBT sample, homogeneous nucleation dominates and determines the number of nuclei. Since PBT is a semicrystalline polyester with high crystallization rate [38], a higher nucleus density should be expected, leading to a smaller spherulite size. On the other hand, heterogeneous nucleation would dominate for the blends, as some LCP microcrystallites acting as nuclei may already exist in the solution, because of the lower solubility of LCP, to induce the crystallization. Due to the inhomogeneous nature of the LCP used, the number of heterogeneous nuclei should thus vary irregularly from sample to sample, resulting in changes of spherulite size.

For samples with higher LCP content, some LCP may also locate between the lamellar ribbons in the spherulites, which would be responsible for an imperfect spherulite appearance.

When crystallized from the melt, no well defined spherulites can be viewed either for the neat PBT or the blend samples, due to the high nucleus density and crystallization rate in the bulk. We are, therefore, unable to estimate the effects of LCP component on the nucleation and crystallization of PBT by the morphological observation alone, and detailed investigations of crystallization behaviors (described in the following sections) and crystallization kinetics (to be reported in a consequent article) have been performed.

3.3. Crystalline structure of the blends

According to Yokouchi et al. [40], PBT may crystallize in both α and β forms, the latter being obtained by mechanical deformation. The X-ray diffraction spectra of the specimens crystallized isothermally at 205°C, which are representative of those crystallized at other temperatures, are shown in Fig. 4. The data of diffraction lines from the patterns are compared with the crystallographic data reported in the literature [41]. The PBT crystals obtained in this study are believed to be in the α form, confirming the microscope observation shown previously.

From Fig. 4, it is evident that the diffraction patterns of the blends with 1 to 10 wt.% of LCP are very similar to that of pure PBT, without a visible shift of the peak position and appearance of any other characteristic peak, suggesting that the crystalline structure of the PBT in the blends is not deteriorated in the presence of LCP. For the sample with 30 wt.% of LCP, the reflection peak at $2\theta = 19.6°$ due to the LCP component enhances significantly, whereas the reflections of PBT crystals at $2\theta = 16.2°$ and 17.3° are still unambiguously observed, indicating that the PBT crystalline phase should be well separated in the blend even at higher LCP content. The broad reflection around $2\theta = 19.6°$ in this spectrum can be thus ascribed to the overlap of the respective peaks of PBT and LCP. These results are in agreement with those reported by Pracella et al. [26] who showed that a separate crystal phase of PBT could still be identified undoubtedly at LCP concentrations around 90 wt.%. Our results provide further support to the conclusion and extend it to the low end of LCP concentrations.

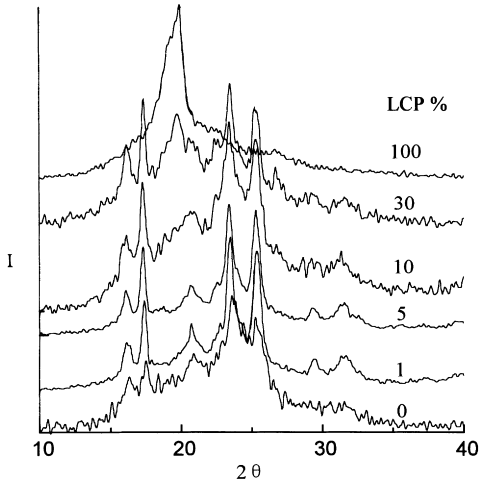

Fig. 4. WAXD patterns of PBT/LCP blends crystallized isothermically at 205°C.

To inspect more carefully the diffraction spectra of the samples, it is of interest to notice that the diffraction peaks of the blends with a lower LCP composition appear to be sharper than those of neat PBT, implying that the regularity of PBT crystals in these blends is more perfect, compared with that of a neat PBT sample. More detailed discussion on this issue is to be given in the consequent article of melting behavior investigation.

Although poly(butylene terephthalate) has been reported [42–48] to undergo transesterification readily when melt-blended with other polyesters, the exchange reaction seems not to alter the structure of PBT crystals, as was found by other researchers [26,41,48,49] and this study, if the samples are melted at proper temperatures. The transesterification process, however, does occur in the blend systems studied, and is to be discussed in a separate report.

3.4. The non-isothermal crystallization behaviors

Values of equilibrium-melting temperature for PBT were reported differently from 233°C to 245°C [27,50–52], while the crystalline to nematic transition temperature of the LCP used is around 270°C, as observed by optical microscopy and DSC. To investigate the effects of the LCP component on the crystallization behavior of PBT, the as-precipitated blends were thus melted at 250°C or 280°C, from where the samples were allowed to crystallize at various conditions.

As pointed out in the last sections, the LCP used in this study is inhomogeneous in nature and may contain a small amount of unmelted PHB microcrystallites. It is therefore believed that, when melted at 250°C, the blends will crystallize starting from the state of which the PBT component is isotropic (in complete melting), while the LCP is still in its crystalline state (henceforth referred to as the LCP-C state); whereas when melted at 280°C, the LCP component should be in its nematic phase (henceforth referred to as the LCP-N state) with a small amount of unmelted PHB microcrystallite included. The blends undergoing different melting histories should thus be expected to exhibit different crystallization behaviors.

Fig. 5 and Fig. 6 show the DSC curves of non-isothermal crystallization for the specimens melted at 250°C and 280°C, respectively. The peak crystallization temperature upon cooling, T_{CC}, for specimens crystallized from 250°C at different cooling rate are listed in Table 1 and those from 280°C in Table 2. The normalized crystallinities calculated from the enthalpy of crystallization, X_C, were plotted in Fig. 7.

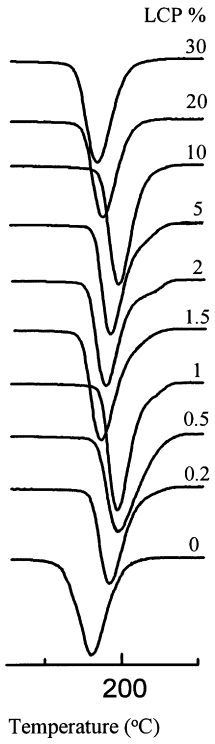

Fig. 5. DSC cooling curves of PBT/LCP blends melted at 250°C.

Evidently, with the addition of LCP, the crystallization temperatures of the blends are elevated for all samples melted at 250°C and for those melted at 280°C with lower LCP content, suggesting that there is a nucleation effect of the LCP component on PBT crystallization. This seems to be the reverse of results from other studies on blends of LCPs with PBT [24–27], where depression of PBT crystallization temperature upon cooling in the presence of the LCP component was found. A depressed effect, however, has also been observed in this study for blends with higher LCP concentration ($>$ 10%) for the samples melted at 280°C. Obviously, the LCP component in the LCP-C state imposes a more efficient nucleation effect on the crystallization of PBT than that in the LCP-N state. More detailed investigations to reveal the induced crystallization mechanism of the LCP microdomains are to be reported in a further paper.

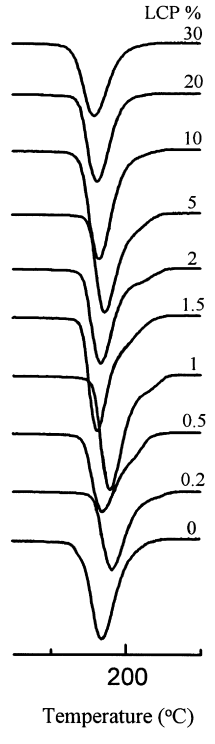

Fig. 6. DSC cooling curves of PBT/LCP blends melted at 280°C.

The cooling rate is also effective on T_{CC}. Due to the less inhomogeneous nuclei existing in blends, the increase in T_{CC} at each cooling rate for samples melted at 280°C are not as apparent as those melted at 250°C. As the decrease of T_{CC} in the cooling trace with increasing cooling rate reflects the lag of crystallization of macromolecules, the presence of the mesomorphic component is of help to promote the crystallization process of the PBT, and the nucleation effect of LCP becoming more protrusive in the faster cooling rate, as seen in Table 1 and Table 2.

It is worth mentioning that the promotion of the mesomorphic component on PBT crystallization is similar for specimens with LCP content from 10% to as low as 0.2%, which is the concentration in the same magnitude of quantity generally used for small molecular nucleation reagents. This is consistent with our previous study on PET/LCP blends [13]. The LCP used in that study is the same as the sample used here, and we found that the highest crystallization rate and lowest crystallization half-time occurred for blends with an LCP content around 1%. As proposed earlier for PET/LCP [13] and PEEK/LCP [53] blends, the number of heterogeneous nuclei was mainly determined by the size of the microdomains instead of the amount of LCP existing. It is therefore our belief that for a specific system there should exist a favorable composition at which the LCP microdomains show ''the most efficient nucleation'' on the crystalline polymeric matrix, and it is more likely to be found at lower LCP concentrations.

The values of T_{CC} obtained from the lower LCP content samples (0.2%–2%) have been checked repeatedly to rule out the possible error caused by sample preparation. Fluctuations in T_{CC} can be found for samples with small differences in LCP concentration (e.g. 1% and 1.5%), although they are all still higher than neat PBT. A meaningful explanation about the notable effect of LCP on T_{CC} in such a narrow concentration could not be offered at the present time without a more detailed investigation. One can, however, draw a conclusion that the influence of the LCP component on the crystallization process of the thermoplastics, especially for a highly crystalline polymer like PBT, is very sensitive to the composition and the microstructure of LCP existing in the blending melt before the start of crystallization.

Table 1
The onset crystallization temperatures of LCP/PBT blends on cooling at different rates after melting at 250°C

LCP wt.%	Cooled at − 5°C/min			Cooled at − 10°C/min			Cooled at − 20°C/min		
Content	T^*[a]	T_C^*[b]	T_{CC}, °C[c]	T^*	T_C^*	T_{CC}, °C	T^*	T_C^*	T_{CC}, °C
0	203.2	199.2	195.4	199.8	195.4	190.8	195.9	191.2	185.7
0.2	205.2	201.4	197.7	199.7	196.6	191.8	199.4	193.5	188.4
0.5	206.6	204.2	199.0	200.5	198.1	193.4	200.1	195.4	190.6
1	205.9	202.1	198.8	202.8	198.0	193.7	200.6	195.3	191.0
1.5	205.2	200.3	196.3	199.3	194.5	190.0	198.4	192.8	188.5
2	205.7	200.5	197.2	202.6	197.4	193.2	199.2	193.7	189.1
5	205.8	201.5	198.1	202.3	198.0	193.9	199.7	194.7	190.2
10	205.5	202.3	199.0	201.5	197.9	194.2	199.0	194.8	190.4
20	203.2	200.3	196.9	198.3	196.2	192.0	195.8	192.2	187.3
30	202.6	199.9	196.2	198.3	196.2	191.8	196.3	191.5	186.1

[a] T^* = the experimental onset temperature of crystallization on cooling.
[b] T_C^* = the calculated onset temperature.
[c] T_{CC} = the experimental peak crystallization temperature.

It can be seen from Fig. 7 that all the samples containing LCP show much higher crystallinity than that of pure PBT. This again supports the promotional effect on crystallization by the LCP component and will affect the melting behaviors of the blends, to be discussed in our following article. The increase in crystallinity of PBT blended with amorphous polyarylate (PAr) [41] and liquid crystalline poly(biphenyl-4,4,'-ylene sebacate) (PB8) [24] has also reported, although the authors all observed a decline of crystallization temperature after adding the second component. In contrast, Pracella and co-workers [26] found that both crystallinity and crystallization temperature decreased with increasing amounts of liquid crystalline poly(decamethylene 4,4'-terephthaloyldioxdibenzoate) (HTH10). Chang et al. [30] also reported the decrease of PBT crystallinity with the addition of a main-chain LCP. In our previous studies on the blends of PET/LCP [13], PEEK/LCP [17] and PPS/LCP [21], we have found that both the degree of crystallization and T_{CC} increase at certain LCP composition ranges.

It should be pointed out that the values of degree of crystallization plotted in Fig. 7 were calculated from the enthalpy of crystallization during cooling (i.e. the exotherms of the as-cooling curves), which were found to be somewhat smaller than those (not shown) calculated from the heat of fusion of the endotherms during the heating scans after the non-isothermal crystallization. Comprehension of the difference caused by the LCP component is not to be discussed here. However, we can remark that the higher degree of perfection of the PBT crystallites formed should be another factor which leads to the higher crystallinity, as seen in Fig. 4 and Table 3, where the diffraction peaks become sharper with the addition of the LCP component.

As discussed previously, the crystallization process of highly crystalline polymers is sensitive to the nature of microstructures existing before crystallization. It is our belief that the conflicting results found in the literature should be attributed to the different interactions, such as miscibility and interchange reaction, between PBT and the other composition, as well as the mesomorphic nature of the

Table 2
The onset crystallization temperatures of LCP/PBT blends on cooling at different rates after melting at 280°C

LCP wt.%	Cooled at − 5°C/min			Cooled at − 10°C/min			Cooled at − 20°C/min		
Content	T^*[a]	T_C^*[b]	T_{CC}, °C[c]	T^*	T_C^*	T_{CC}, °C	T^*	T_C^*	T_{CC}, °C
0	203.9	200.3	196.9	201.0	196.8	192.3	196.6	192.0	186.5
0.2	206.1	201.9	198.2	201.6	198.3	193.8	199.1	193.4	188.2
0.5	204.9	201.7	197.0	201.4	196.8	192.9	198.7	194.2	189.4
1	205.8	201.4	197.9	202.6	198.7	194.6	199.9	194.7	190.2
1.5	205.1	199.6	196.3	200.8	195.7	192.1	197.2	192.4	188.1
2	205.4	200.3	196.7	200.9	197.0	193.1	198.8	193.1	188.2
5	205.3	201.5	197.4	202.0	198.2	193.8	197.7	194.4	189.4
10	205.0	200.0	196.6	201.0	196.4	192.6	197.5	192.1	187.4
20	202.5	199.6	196.3	199.3	195.4	191.7	195.3	191.2	186.3
30	203.3	199.7	195.9	198.9	196.5	192.3	194.9	190.5	184.8

[a] T^* = the experimental onset temperature of crystallization on cooling.
[b] T_C^* = the calculated onset temperature.
[c] T_{CC} = the experimental peak crystallization temperature.

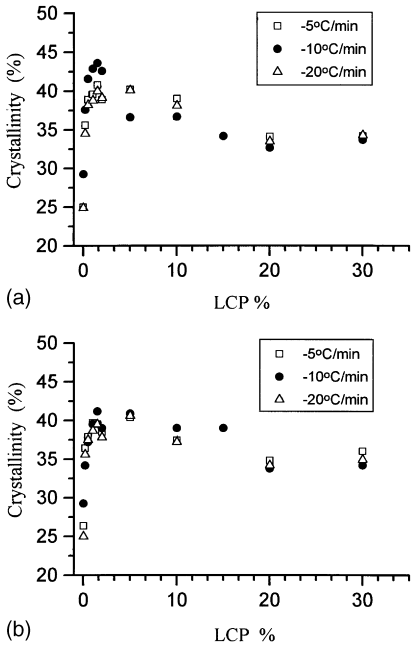

Fig. 7. Crystallinities of PBT/LCP blends as functions of LCP content by DSC scans at different cooling rate: (a) specimens melted at 250°C; and (b) specimens melted at 280°C.

second component. More systematic studies must be performed in order to understand this more clearly.

3.5. The nucleation of the LCP component on the crystallization process

From Fig. 5 and Fig. 6, it can be noticed that there is a shoulder on the high temperature side of the crystallization exotherm for the LCP-containing samples, which is somewhat different from normal DSC cooling curves with tailing on the low temperature side of the crystallization peak. Due to the inhomogeneous nature of the LCP used in this work, it is believed that the presence of LCP should play a role in this behavior. These DSC cooling curves have been treated (as illustrated in Fig. 8), following the method proposed by Yeh and Runt [39], to obtain the experimental onset temperature of crystallization on cooling, T^*, and the so-called calculated onset temperature, T_C^*. The results are also listed in Table 1 and Table 2.

It is evident that the values of T^* for the blends with an LCP content of 10% or lower are higher than those of neat PBT, suggesting that crystallization starts at a higher temperature for the blends than that of neat PBT. On the other hand, little change is seen for the T_C^* values regardless of the blend composition. If we assume T_C^* as the temperature at which nucleation is due predominantly to the PBT itself, or ''net'' onset temperature of crystallization, the difference between each pair of T^* and T_C^* can then be considered as a measure of the effectiveness of the LCP component imposing on the crystallization process. Evidently, blends with a lower LCP content show a more efficient nucleating function, or the favorable composition at which the LCP microdomains show ''the most efficient nucleation'' is more likely to occur at a lower LCP content for these systems. Experimental supports for this deduction may be extracted from Table 1 and Table 2 and Fig. 5 and Fig. 6. As discussed in the previous sections, increases in T_{CC}, X_C and T^* are all found at a lower LCP content. Additionally, the shoulder on the exotherm for the samples containing a lower LCP composition appears to be more distinguishable. The half-width of diffraction peaks (Fig. 4) and exotherms of crystallization on cooling (not listed, but can be seen from Fig. 5 and Fig. 6) become narrower also at lower LCP concentrations.

When blending PBT with LCP, the blends have been found to be either immiscible or partially miscible [24–30]. For partially miscible systems, like the PBT/LCP blends of this study, phase separation is known to occur on heating, and the size of LCP domains is expected to increase, not favorable for nucleating efficiency, at higher concentrations and temperatures. Based on the experimental results and discussion earlier, it can be proposed that LCP in the LCP-C state (melted at 250°C) functions better as efficient nuclei than that in the LCP-N state.

Since there exists heterogeneous nuclei in the blends, the size of the PBT crystallites formed is related to the number of nuclei. To estimate the crystallite size from the broadening of the diffraction pattern, a method based on the Scherrer equation is generally used [54]. The crystallite dimension, L_{hkl} can be calculated by:

$$L_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta_{hkl}}$$

where L_{hkl} is the crystallite dimension, or coherence length, perpendicular to the (hkl) plane, K is the Scherrer constant, λ is the wavelength of the X-rays and θ is the Bragg angle. When β is the half-width of the diffraction, K takes a value of 0.9.

To calculate the crystallite dimensions, the overlapping diffraction was first resolved by a computer program. Fig. 9 gives a representative example of the peak resolving, showing that the computer resolved profiles fit quite well with the experimental diffraction pattern. Values of half-width, W_H, for each separated peak and the PBT crystallite dimensions, L_{hkl}, are listed in Table 3. It is obvious that the crystallite dimensions of the samples with lower LCP content are larger than those of neat PBT and samples with higher LCP content. Differing from the slight increases in the (100) and $(1\bar{1}1)$ planes, remarkable increases in L_{hkl} corresponding to the (010) refraction, or b^* direction, which is known to be the preferred growth plane of a lamellae growth direction [55], can be found for the samples with an LCP concentration lower than 10%, compared with the neat polymer.

The crystallite dimensions of a semicrystalline polymer are functions of crystallization temperature and density of nucleation. The larger crystallite size seems to suggest that

Table 3
Crystallite dimension of PBT and PBT/LCP blends crystallized isothermally at different temperatures. Samples were first melted at 250°C and then crystallized isothermally at the designed T_C

T_C	210°C						205°C						200°C					
hkl	100		010		$1\bar{1}1$		100		010		$1\bar{1}1$		100		010		$1\bar{1}1$	
LCP %	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)	W_H[a] (°)	L[b] (nm)
0	0.71	11.5	0.78	10.3	0.64	12.6	0.69	11.7	0.58	13.8	0.67	12.1	0.68	11.9	0.60	13.5	0.70	11.7
1	0.56	14.4	0.33	24.1	0.54	15.2	0.57	14.4	0.34	23.8	0.57	14.2	0.56	14.4	0.34	23.3	0.60	13.7
5	0.49	16.6	0.30	26.7	0.54	15.0	0.55	14.8	0.33	24.1	0.58	14.1	0.67	12.1	0.43	18.7	0.61	13.3
10	0.54	15.1	0.34	23.7	0.57	14.2	0.60	13.4	0.49	16.5	0.61	13.4	0.72	11.3	0.52	15.5	0.65	12.6
30	0.80	10.1	0.61	13.2	0.54	13.0	0.80	10.1	0.56	14.4	0.63	13.0	0.61	13.3	0.51	15.7	0.80	10.1

[a] W_H = the half-width of diffraction peak in degrees.
[b] L_{hkl} = dimension in the corresponding direction.

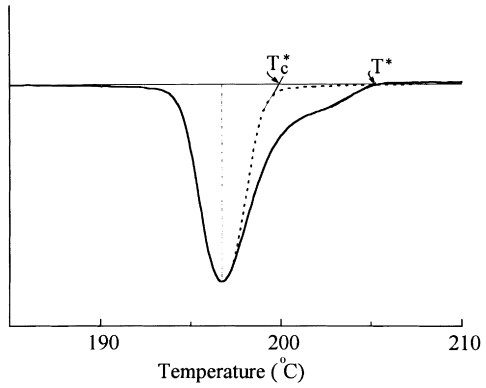

Fig. 8. Illustration of calculating onset temperature from the DSC cooling curves.

fewer nuclei are present in the blends during crystallization. However, as the temperature set for isothermal crystallization are close to, or higher than, the onset and peak crystallization temperatures of neat PBT (refer to Table 1 and Table 2), the smaller crystallites of PBT are likely to be formed during the course of cooling after crystallization at T_C, which can be verified by the fact that the size differences between the samples of blends and neat PBT crystallized at 200°C are smaller than those crystallized at 210°C.

4. Conclusions

The results of our study have shown that the LCP component may affect, to a great extent, the crystallization process of the PBT/LCP blends. Due to the inhomogeneous nature of the LCP used, the crystallization temperature of the blends upon cooling is increased for all samples melted at 250°C and for those melted at 280°C with lower LCP content, suggesting a nucleation effect of the LCP component on PBT crystallization. The existence of microdomains of LCP phase in different size, such as unmelted microcrystallites or the rigid segments of LCP, would provide necessary heterogeneous nuclei. It was found that the crystallization process of the blends is very sensitive to the LCP content and its microstructure existing in the melt before the start of crystallization, with the mesomorphic component in the LCP-C state (melted at 250°C) exhibiting a more efficient nucleation effect than that in the LCP-N state (melted at 280°C). Based on the results observed, it has been proposed that the favorable composition at which the LCP microdomains show ''the most efficient nucleation'' is more likely to occur at a lower LCP content for these systems. Taking into account that the addition of LCP component leads to higher T_{CC}, X_C and T^*, and a higher degree of perfection of PBT crystallites, it is our belief that the effects of heterogeneous nucleation dominate in the crystallization process of the blends with lower LCP concentration.

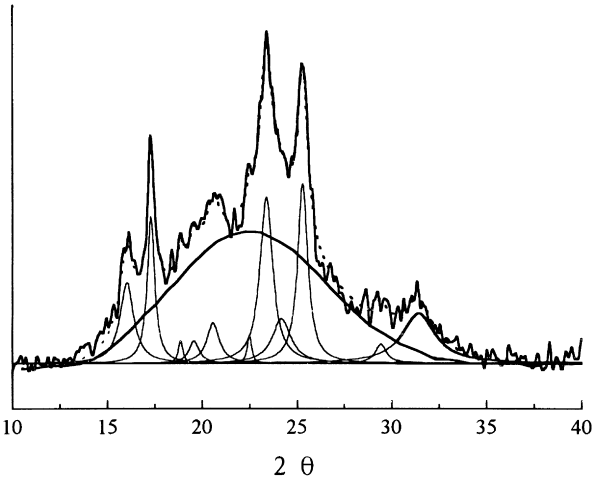

Fig. 9. Illustration of computer simulation profiles of WAXD spectrum of PBT/LCP.

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