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INVESTIGATION OF THE MULTIPLE MELTING BEHAVIOUR OF A PTT BY DSC AND POLARIZED LIGHT OPTICAL MICROSCOPY

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The multiple melting behaviour of isothermally crystallized bulk poly(trimethylene terephthalate) (PTT) observed using DSC has been correlated to the total depolarized light intensity (DLI) of thin films using hot-stage polarized light optical microscopy. The observation of partial melting, recrystallization and final melting in the DSC is correlated to the observation of the partial decrease, sudden increase and final decrease in DLI under the same heating conditions. Integration of real-time visible spectra of the transmitted light was used to separate the effects of retardation from pure birefringence of the colorful spherulitic thin-film PTT samples. The correlation of the results from these two methods has demonstrated clearly that the observed DSC multiple melting behaviour of this particular polymer is the illustrated effect of a process of continuous partial melting/recrystallization/final melting in the material during thermal analysis. The observed thermal behaviour of these metastable spherulitic materials is a complex function of their thermal history including crystallization temperature and anneal conditions, including scanning rate during thermal analysis.

Keywords: *banded spherulites, DSC, multiple melting, polarized light optical microscopy, poly(trimethylene terephthalate)*

Introduction

Many semi-crystalline polymers can form polymer spherulites upon isothermal melt-crystallization. Crystallization occurs over a range of temperatures well below the observed melting temperature, and consequently, these non-equilibrium crystal aggregates develop with varying degrees of order and possess characteristic amorphous regions between their crystalline lamellar building blocks. The inherent metastable nature of semi-crystalline polymer solids is therefore often expressed by a demonstrated capacity for post-crystallization reorganization at the molecular level, and therefore the solids can improve their crystallinity when subjected to the right set of thermal conditions, such as annealing or heating. When structural reorganization occurs on a time-scale comparable to the normal practical conditions of thermal analysis, the recorded thermal behaviour can be complex with DSC curves demonstrating multiple-melting endotherms, the appearance of which depends greatly upon sample thermal history and scanning conditions [1–6]. In general, there are two main reasons for the appearance of multiple melting endotherms. More than one DSC endothermic peak can result from the melting of multiple crystal types within the sample, each present prior to thermal treatment. Multiple endothermic peaks can also be the result of partial melting of some or all of the original material and its reorganization into higher ordered material during the thermal analysis before finally melting [7, 8]. While multiple melting in polymers is a common occurrence and the idea of structural reorganization well accepted, modern research efforts have tended to focus on the refinement of the underlying mechanism of reorganization.

Poly(trimethylene terephthalate), (PTT), is a semi-crystalline polyester that has recently been introduced as a commercial polyester that can be made from renewable resources [9]. In their study of the thermal behaviour of PTT using DSC and wide angle X-ray diffraction, Chung *et al.* ruled-out the possibility of polymorphism in the original material as the origin of the observed multiple melting behaviour [10]. Instead, they suggest that spherulites develop two types of lamellar stacks of different thermal stabilities through normal branched growth and that these in combination with recrystallization during thermal analysis are responsible for the observed multiple melting DSC endotherms. In another study, Wu and Woo suggest a different relationship between the pre-existing lamellar types and/or the thermal analysis-induced reorganized lamellae, suggesting that reorganization is associated with a change to a more thermally stable lamellar orientation [11]. Srimoaon *et al.* assign the mechanism of the observed melting behaviour to the successive melting and recrystallization of so-called pre-existing primary and secondary crystallites of varying degrees of order in the spherulite [12]. Dangseeyun *et al.* have agreed

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with earlier work that multiple crystal modifications are not present in the sample before scanning and are therefore not giving rise to the observed multiple endotherm pattern [13]. They suggest that double melting endotherms arise from the melting of primary pre-existing lamellae and their subsequent formation into a higher-melting entity during the scan; or into higher-melting crystallites of different thermal stabilities in the case of triple melting endotherms.

Polarized-light optical microscopy is regularly used to study the growth rate kinetics of spherulites during isothermal crystallization from the melt. Polymer spherulites are birefringent entities owing to their basic lamellar structure and thus, between crossed polars, growing spherulites appear as increasingly brighter entities on a black background of non-transmitting amorphous melt. The total depolarized light transmitted by a polymer thin-film sample has been routinely used to study crystallization kinetics of bulk polymer samples. By contrast, there are few reports in the literature that use this method to characterize melting process of polymers [14] or to specifically correlate the DLI curves with the corresponding DSC curves [15].

In this paper, we present the results of a comparison study between the observed multiple melting behaviour in DSC curves of bulk, melt-crystallized PTT and the observed birefringence of thin-film, melt-crystallized PTT using the same heating conditions. The aim of the paper is to contribute to the current discussion surrounding the proposed relationship between spherulite morphology and thermal behaviour.

Experimental

Materials

The polymer used throughout this study was a poly(trimethylene terephthalate), (PTT), one of DuPont's new commercially available Bio-Based Materials' Sorona® family of polymers made from corn-derived 1,3-propanediol. The sample was kindly donated by DuPont Chemicals, USA. The sample was specified to have a glass transition temperature of 48°C, an observed melt temperature of 228°C, and a mass average molecular mass of approximately 50000 g mol^{-1}. The PTT sample was supplied as small, hard pellets and was stored at room temperature under an ambient atmosphere.

Methods

Differential scanning calorimetry

The thermal behaviour of the PTT was studied using a Mettler FP85 thermal analysis cell equipped with a Mettler FP80 control processor connected to a computer with FP89 control software. The thermal analysis cell was calibrated using a high purity indium metal standard (Mettler-Toledo). PTT samples weighing between 1.60 and 2.00 mg were weighed directly in standard 40 μL aluminum DSC pans. Samples were hermetically sealed under a flow of nitrogen gas. Samples were melted at 260°C for 5 min to erase the thermal history of the sample before being cooled at a nominal rate of 80°C min^{-1} to the desired crystallization temperature. A standard scanning rate of 10°C min^{-1} was employed in all thermal analysis experiments except where indicated.

Total depolarized light optical microscopy

The total depolarized light intensity (DLI) was recorded using an Ocean Optics USB2000 spectrophotometer in tandem with a Nikon Eclipse E400 POL polarized light optical microscope. All of the measurements were collected employing a 10× microscope lens. The microscope was equipped with a THMS-600 Linkam microscope hot-stage and a Linkam TMS-94 temperature controller with liquid nitrogen cooling, used to provide the thermal control of the samples under the microscope. The temperature controller provided for the application of precise, programmable heating and cooling rates to the polymer sample inside the microscope hot stage, as well as precise, programmable isothermal conditions (±0.03°C). A heating or cooling rate of 10°C min^{-1} was employed in all of the DLI profile experiments. One of the microscope oculars was removed and replaced with a rubber block housing the spectrophotometer photodiode detector with fiber optic cable link to the instrument. The spectrophotometer provided the instantaneous recording of the visible light spectrum of the total depolarized light transmitted by the birefringent polymer sample under study at regular, predetermined intervals during the heating, cooling or annealing experiment. The recorded spectra were later integrated using the instrument OOIBase32 software (Ocean Optics) to give a total light intensity value for each spectrum collected. Total depolarized light intensity values were normalized to show relative changes in intensity on a scale of 0 to 1. These intensity values are represented on the DLI profiles as DLI intensity data points. Samples for DLI experiments were prepared by first melting PTT crumbs between 12-mm-diameter round glass coverslips directly on the surface of a temperature-controlled hotplate. All thin-film PTT samples were measured to be between 10 and 25 μm thick. The thickness was controlled by using 11 μm aluminum foil spacers between the glass coverslips. Thin-film samples were first melted at 260°C under a nitrogen atmosphere directly in the hot-stage for five minutes to erase any thermal history. Thin-film samples were then cooled directly in the microscope hot-stage at 80°C min^{-1} to either the desired isothermal crystallization temperature, or to the start temperature of the heating experiment.

Results and discussion

Differential scanning calorimetry

Figure 1 contains the heating curve of a quenched sample of PPT. The sample was melted in the DSC at 260°C for 5 min before being removed and quenched in ice water, placed back into the DSC at 40°C, and reheated at a rate of 10°C min^{-1}. The sample was able to crystallize during the analysis and the non-isothermally melt-crystallized solid subsequently melted over a broad temperature range, apparently exceeding a twenty-degree temperature span.

DSC was used to systematically investigate both the effect of crystallization temperature and heating rate on the observed thermal behaviour of PTT. The curves presented in Fig. 2 illustrate the effect of isothermal crystallization temperature (T_c) on the observed melting behaviour of PTT. A fresh sample was used to obtain each curve. Each sample was melted directly in the DSC instrument at 260°C for 5 min and subsequently cooled at a rate of 80°C min^{-1} to the desired crystallization temperature where it crystallized isothermally for 40 min. The polymer sample was then further cooled at a rate of 80°C min^{-1} to 40°C, and held for three minutes to equilibrate before finally heating at 10°C min^{-1} and recording the melting curve presented in Fig. 2.

The samples crystallized at 185 and 190°C show an exothermic dip before melting. The arrows in the diagram point to the onset of this exothermic activity for each of the DSC thermal curves. The PTT crystallized at 180°C has an onset temperature to the exothermic dip of 204°C, while that crystallized at 190°C has an onset temperature of 206°C. In both thermal curves, melting of all of the crystallized material then takes over as the dominant thermal behaviour, indicated by the subsequent, broad endotherm. The samples crystallized at 200 and 210°C do not manifest any exothermic activity in the melting thermal curve prior to the appearance of the first endotherm. In contrast, the PTT isothermally crystallized at higher temperatures partially melts before showing an exothermic dip prior to final melting. The PTT samples crystallized at 200 and 210°C have an onset temperature to the exothermic dip of 216 and 222°C, respectively. In the temperature region of the T_c values employed, it is known that the rate of crystallization decreases with increasing T_c. PTT takes longer to crystallize at higher temperatures. If crystallization at 180°C was not complete prior to heating, then crystallization at increasingly higher temperatures would be even less complete prior to heating. Moreover, increasingly larger initial exothermic dips would be expected. This is, however, not the case in Fig. 2. Therefore, the exothermic dips in Figs 2a and b do not represent crystallization of material which had not yet crystallized during the prior isothermal hold.

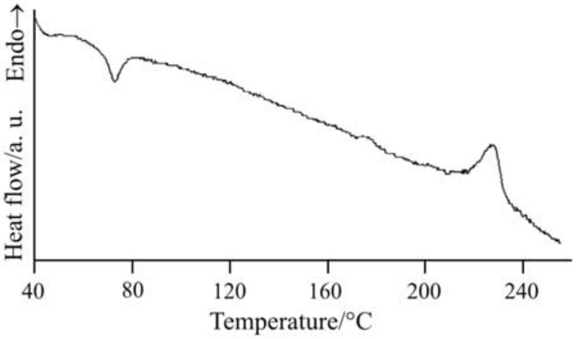

Fig. 1 DSC heating thermal curve of PTT quenched from the melt and heated at 10°C min^{-1}

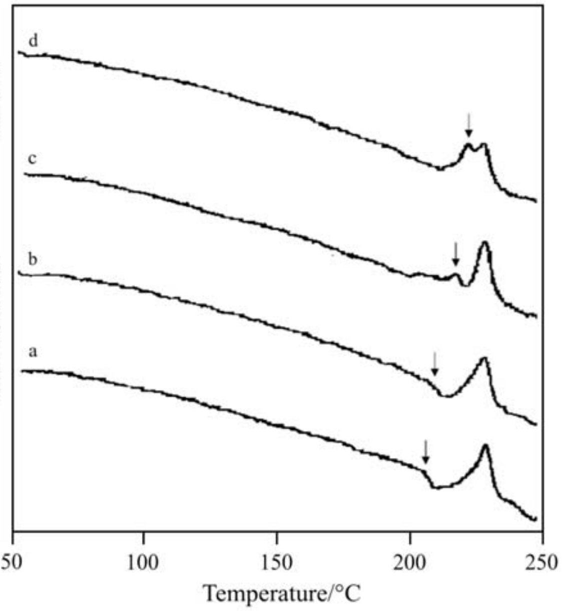

Fig. 2 The effect of isothermal crystallization temperature of PTT on the observed melting behaviour illustrated in the DSC curves. Samples were crystallized at a – 185; b – 190; c – 200 and d – 210°C for 40 min in the DSC before heating at a rate of 10°C min^{-1}

The results in Fig. 2 can be interpreted in the context of the partial melting/recrystallization/final melting model. Each of the samples is able to, upon heating, undergo a continuous process of partial melting and recrystallization or reorganization before finally melting but does so at different relative rates depending on sample thermal history. These simultaneously occurring endothermic and exothermic changes only manifest their net effect in the DSC curve. Thus a double-peak endotherm may be the net heat flow illustration of an exotherm superimposed on a broader endotherm. Among the samples presented in Fig. 2, the PTT crystallized at 180°C possesses the greatest tendency to minimize its structural metastability. Reorganization is the dominant behaviour of this least-ordered material until final melting takes over. The PTT crystallized at 190°C shows similar behaviour but with a slightly later onset temperature. There is less drive to reorganize the originally more ordered material crystallized at 200°C. In Fig. 2c the material partially melts as evidenced by an initial endotherm, then reorganization becomes the dominant behaviour as evidenced by a small exotherm, and finally all of the material undergoes final melting as the exothermic dip gives rise to the final larger endotherm. In Fig. 2d the originally most crystalline material is the least susceptible to reorganization under these conditions and thus more of the initial material melts as evidenced by a significantly sized first endotherm, before reorganization becomes the dominant behaviour, producing the observed small exothermic dip before final melting. In each of the heating thermal curves in Fig. 2 the sample has completely melted by a temperature of 228°C. This suggests that material crystallized at each temperature has been able to reorganize to a common level of internal spherulite structural order by the continuous partial melting/recrystallization and final melting process.

Triple melting endotherms have been reported for PTT isothermally crystallized at temperatures less than 192°C; double melting endotherms after isothermal crystallization at temperatures between 192 and 210°C; and single melting endotherms after isothermal crystallization at temperatures greater than 210°C [12]. In that work, the observed multiple-melting behaviour was also interpreted in the context of the partial melting/recrystallization/final melting model. Specifically, the lowest melting peak was attributed to the melting of primary crystallites present in the sample prior to heating; the higher melting peaks were attributed to the melting of crystallites recrystallized during heating. In that study, the peak temperature of the lower melting endotherm was indeed observed to shift to higher temperatures with increasing isothermal crystallization temperature as has been found in the present work.

Figure 3 contains a plot of the isothermal crystallization temperature, (T_c), *vs.* the observed onset temperature to exothermic dip from the curves in Fig. 2. This onset temperature is that at which reorganization/recrystallization becomes the dominant behaviour during the heating scan. There is such a dip in each of Figs 2a–d. In Figs 2a and b the dip precedes melting and in Figs 2c and d it is the dip between the two peaks. The best-fit line through the data in Fig. 3 has a correlation coefficient of 0.98 and predicts that a sample isothermally crystallized at 217°C will have an observed onset temperature coincidental with the temperature of the final melting peak of 228°C. Thus it predicts that a sample crystallized at this high temperature would possess a sufficient level of crystallinity in the original sample such that it would not be susceptible to partial melting and reorganization during the heating scan and it would melt with a single high-temperature endotherm in the DSC thermal curve with no deviations from the baseline prior to melting.

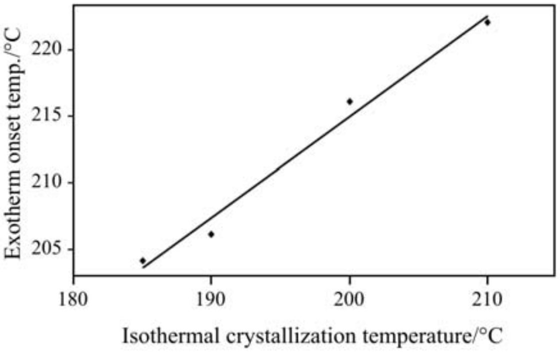

Fig. 3 A linear regression of the observed onset temperature to the exothermic dip for each of the DSC thermal curves presented in Fig. 2 *vs.* isothermal crystallization temperature

Two melting DSC thermal curves are presented in Fig. 4. The thermal history of each sample included isothermal crystallization at 200°C for 40 min. The sample in Fig. 4b however was then further annealed at a temperature of 217°C for an additional 40 min. Both samples were cooled to 40°C at a rate of 80°C min^{-1} directly in the DSC before acquiring the heating thermal curves shown. While the sample in Fig. 4a demonstrates the expected multiple melting

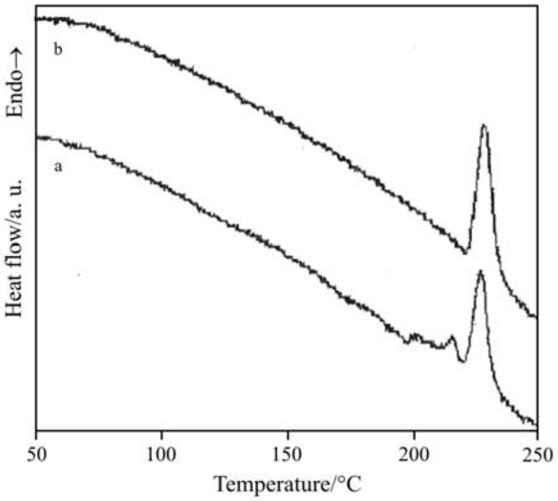

Fig. 4 DSC heating thermal curves of PTT a – isothermally crystallized at 200°C for 40 min and b – isothermally crystallized at 200°C for 40 min and subsequently annealed for 40 min at 217°C before melting

phenomena, the annealed sample in Fig. 4b melts with a single, sharp endotherm with a peak temperature of 228°C which supports well the prediction from the plot in Fig. 3. If this first endotherm were due to the melting of a unique crystal type present in the sample before analysis and not capable of reorganization, then it would be absent in Fig. 4b and the magnitude of the second peak would remain unchanged. In Fig. 4b, however, it is found that the first peak is absent but the second peak has grown in magnitude. This result confirms that material crystallized at 200°C has completely reorganized into the higher melting material during the ample time of the annealing period at 217°C. It was similarly found in the above cited work [12] that PTT melted with a single peak at 228°C after isothermal crystallization at a temperature of 215°C.

The DSC thermal curves in Fig. 5 demonstrate the effect of heating rate on the thermal behaviour of the PTT isothermally crystallized at 200°C. For a heating rate of 2°C min^{-1} in Fig. 5a, the endotherm is very weak but the endotherm has a 'peak' temperature of 227°C. With a heating rate of 5°C min^{-1}, the thermal curve in Fig. 5b shows a small exothermic dip at an onset temperature of 217°C which gives rise to an endotherm with a peak temperature of 228°C. With a heating rate of 10°C min^{-1}, the thermal curve in Fig. 5c shows the sample beginning to melt slightly before reorganization becomes dominant at a temperature of 216°C. The exotherm then gives rise to the final endotherm that has a peak temperature of 227°C. With a heating rate of 20°C min^{-1}, the thermal curve in Fig. 5d shows that initial partial melting is slightly more significant before reorganization/recrystallization of this melted material becomes dominant at a temperature of 217°C. The exotherm then gives rise to the final endotherm with a peak temperature of 227°C.

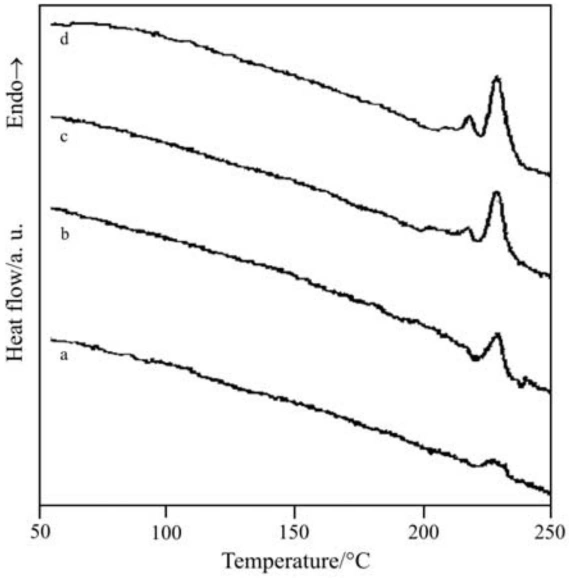

Fig. 5 DSC heating thermal curves of PTT isothermally crystallized at 200°C for 40 min before heated at rate of a – 2°C min^{-1}; b – 5°C min^{-1}; c – 10°C min^{-1} and d – 20°C min^{-1}. Thermal curves are all on the same scale but have been *y*-shifted for presentation

The appearance of the thermal curves presented in Fig. 5 suggests that the onset temperature to exothermic activity remains constant with changing heating rate for samples with the same thermal history of an isothermal crystallization at 200°C. A change in heating rate does however affect the extent to which reorganization during the scan is permitted to occur. With increasing heating rate, the sample is effectively exposed less to the anneal temperatures during heating, with decreasing opportunity to partially melt and reorganize/recrystallize. Thus the minor endothermic peak becomes more prominent in the thermal curve. At a rate of 2°C min^{-1}, the relative rates of partial melting and recrystallization of the polymer may be on the order of the time-scale of the heating rate and as such the conditions of the scan permit the sample to undergo a continuous series of incremental partial melting and recrystallization events to render the sample a more ordered material. Any apparent sign of these events may be within the baseline of the thermal curve, leading to the absence of any observable deviation from the baseline prior to the melting peak in Fig. 5a.

Srimoaon *et al.* [12] described the effect of increasing heating rate as consequently decreasing the time periods available for the diffusion of the molecular segments onto growing crystallites. More importantly, they also reported no change in the position of the lower peak of the double melting endotherm when the heating rate was changed from 5 to 20°C min^{-1} on samples with a constant thermal history (T_c =208°C). In another PTT investigation, Huang and Chang [16] also found the position of the lower melting endotherm to be invariable to changes in heating rate in the range of 5 to 20°C min^{-1} on PTT samples with a constant thermal history (T_c=210°C). The lower peak became more dominant with increasing heating rate until a super-heated single melting peak endotherm was obtained for a rate of 40°C min^{-1}.

Polarized light optical microscopy

Upon simply viewing PTT with a polarized light optical microscope, it is clear that the spherulites crystallized from the melt in the thin-film samples of this polymer possess more than the typical Maltese cross birefringence extinction pattern. Over the temperature range investigated in this study, PTT spherulites also show a periodic birefringent extinction pattern of rings or 'bands'. So-called banded spherulites were observed in PTT thin-film samples crystallized at temperatures above ca. 192°C. The PTT spherulites were also found to display bright colors without any application of a tint plate. Different colors appear in the spherulites which apparently depend on the thickness of the thin-film sample and on the crystallization temperature. This is noteworthy in a study like this one which is attempting to correlate the total light intensity transmitted by the birefringent material during melting to observations in the DSC thermal curves.

The colored spherulite phenomenon has been reported [17]. Most recently, Yun *et al.* [18] have clearly demonstrated the reason for the colors in melt-crystallized spherulites of PTT. The colors are interference colors and are caused by the retardation of the light by the sample. The retardation depends on the sample thickness and on the birefringence of the sample. PTT has an unusually high birefringence which gives rise to the significant retardation. The extraordinarily high birefringence is attributed to the large difference in the refractive index in the parallel and perpendicular directions to radial growth. These same authors confirmed earlier reports [19, 20] that it is the rather unusual *a*-axis direction of the unit cell which is assigned to the direction of radial growth and which is indeed found to be almost parallel to the direction of spherulite radial growth. The periodic birefringent ring patterns that appear in the typically monochromatic images in published reports on the so-called 'banded' morphology of PTT have been shown to be due to periodic lamellar twisting along the radial direction of growth. The twisting can be described as the periodic rotation of the unit cell along the *a*-axis, producing what has been found as an alternating flat-on and edge-on lamellar orientation [19, 20]. Yun *et al.* report that the absolute value of the birefringence in flat-on lamella (ab-plane) orientation is higher than that of the edge-on lamella (ac-plane) orientation is in keeping with these results.

Therefore, the *a*-axis lamellar twisting in combination with the high birefringence in PTT gives rise to the appearance of the periodic birefringent extinction rings, or 'bands' seen in the monochromatic as well as colored images of the PTT spherulites. The high birefringence, in combination with the sample thickness, gives rise to the retardation, which manifests as colored spherulites. The colored images of the PTT spherulites can therefore present sometimes complex-looking colored morphologies as the bands do not simply superimpose as black and white rings on a colored spherulite, but are colored themselves. Very thin samples show only black and white birefringence patterns under the microscope, and we have indeed witnessed this in samples of the order of 1 to 5 microns thick.

While others have suggested that the phenomenon of lamellar twisting in PTT is associated with the particular crystallization regime of nucleation [21], and, more recently, have suggested it to be associated with an oscillatory dynamics of the spherulite growth driven by the latent heat of fusion [22], Wu and Woo [11] had offered another suggestion. These authors reported on the correlation between the observed multiple melting behaviour of PTT by DSC with the observed changes in colored bands of PTT spherulites in melt-crystallized films using polarized light optical microscopy over the range of crystallization temperatures of 190 to 210°C. They suggested that the origin of multiple melting peaks in the DSC thermal curves is due to the partial melting and recrystallization, either during the scan or during longer anneal conditions, of initial, less-stable flat-on lamellae to lamellae of a more stable, edge-on orientation. In their study, PTT spherulites appeared to have an alternating pattern of white and yellow bands as viewed under the polarized light microscope. Using hot-stage polarized light optical microscopy and under similar thermal anneal conditions to the DSC, the contrast between the white and yellow bands was found to increase, with the yellow bands becoming a darker yellow, as determined by the naked eye observer. This observation was reportedly interpreted as visual support for the interpretation of the DSC results, with the yellow bands corresponding to the more stable, edge-on lamellar orientation.

In the present study, in order to relate the observed multiple melting behaviour with the observations from hot-stage polarized light optical microscopy, and, given the known complexity of the birefringence of PTT, it was desired to separate the observations due to retardation from the effects due to birefringence alone. This was achieved by acquiring the visible transmittance spectrum of the polymer thin-film sample in real-time as it underwent thermal treatment the same as that in the DSC thermal analysis. The visible spectrum was recorded in the transmittance mode. In this way, the integrated spectra at regular time intervals during the experiment could be plotted as the total depolarized light intensity. The light intensity signal varies with the degree of crystallinity of the sample and can be correlated directly with the DSC results.

Figure 6 contains the DLI isotherm profile of the crystallization of a sample of PTT crystallized at 200°C for 40 min. The plot shows the typical change in total depolarized light intensity with time that was found for each of the samples at the different crystallization temperatures investigated. For this temperature, it can be seen that the maximum in light intensity is achieved after approximately 15 min. Figure 7 con-

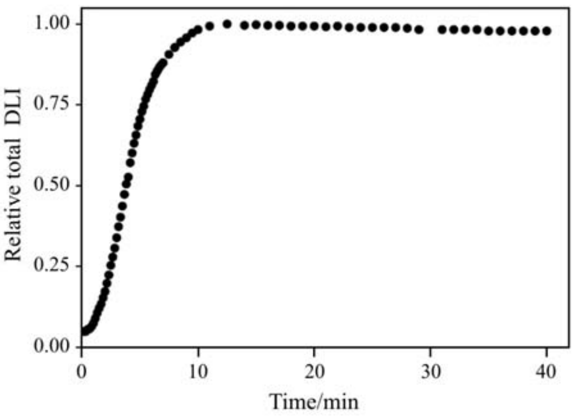

Fig. 6 DLI profile of the crystallization isotherm for PTT crystallized at 200°C for 40 min

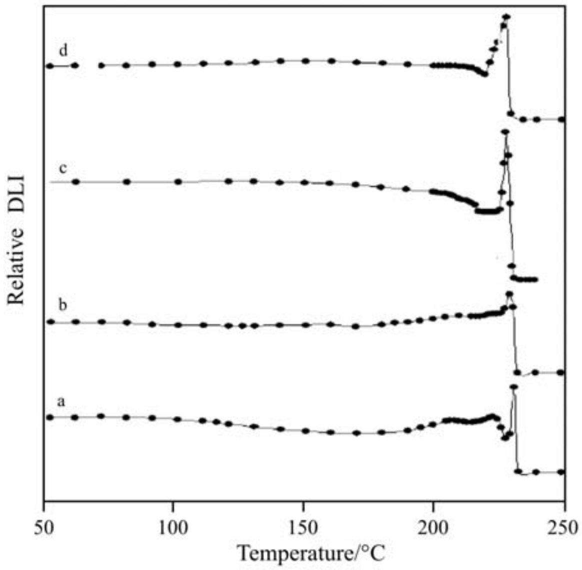

Fig. 7 DLI heating profiles of PTT isothermally crystallized at a – 185; b – 190; c – 200 and d – 210°C for 40 min. All samples scanned at a rate of 10°C min^{-1}. Profiles are all on the same scale but have been *y*-shifted for presentation

tains the DLI melting profiles of PTT crystallized at different crystallization temperatures used in the preparation of the samples in Fig. 2. DLI profiles were collected during the heating of PTT thin films in the microscope hot-stage, employing the same heating rates as those used to record the DSC thermal curves in Fig. 2.

Evidently, in Fig. 7a, the PTT sample crystallized under conditions most removed from equilibrium (i.e., at the lowest crystallization temperature) possesses the greatest tendency to improve its internal structure under scanning conditions which can provide for this change. Once the sample is heated past its original crystallization temperature the light intensity slowly increases until just over 200°C at which temperature there is a net decrease in intensity before continuing to increase again. Finally at a temperature just less than 230°C the sample begins to melt sharply but not before a final, sharp increase in intensity is recorded. The PTT sample crystallized at 195°C shows a slightly similar DLI heating profile to the sample crystallized at 185°C except that ordering of the structure appears to remain the dominant activity in the sample until final melting is the net effect beginning sharply at a temperature just less than 230°C. The DLI heating profile of the sample crystallized at 200°C shows a steady decrease in light intensity as the sample begins to melt and looks rather featureless until this decrease is stalled and there appears to be a sort of balancing between the ordering and disordering processes ongoing in the sample. Then, with increasing temperature, there is a sharp rise in light intensity indicating a net ordering process just before final melting. The appearance of the DLI profile of the sample crystallized at the highest temperature in Fig. 7d (T_c=210°C) is similar to that of the sample crystallized at 200°C but without any stall period evidenced in the light intensity profile with temperature.

Figure 8 contains selected total depolarized visible transmission spectra of the PTT thin-film sample crystallized at 210°C and heated 10°C min^{-1} used to create the DLI profile in Fig. 7d in which each single point in Fig. 7d is an integrated spectrum like those in Fig. 8. The relevant part of the DLI heating profile from Fig. 7d is included in Fig. 8, indicating for which points the spectra are presented. Evidently, the sample is colored to begin with (Fig. 8a) and it changes color as it is heated, before finally transmit-

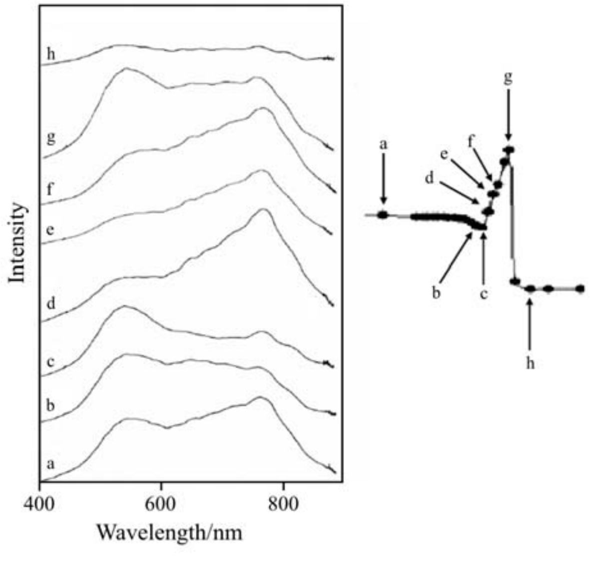

Fig. 8 Depolarized visible transmittance spectra used to construct the DLI heating profile of PTT sample shown in Fig. 7d. Labeled DLI profile segment matches each spectrum with corresponding DLI point. All spectra on the same scale but have been *y*-shifted for presentation

ting no light in Fig. 8h. However, it is also clear (from the integrated intensity) that as the sample is heated, the overall intensity changes indicate that the sample begins to decrease in overall crystallinity, then increase in crystallinity, before finally losing all degree of crystallinity.

The appearance of the DLI heating profiles supports the partial melting/reorganization interpretation of the DSC thermal curves recorded under the same heating conditions. The time scale of the ordering changes in crystallinity of the sample as indicated by the DLI profile is the same as that of the superimposed exothermic activity in the DSC thermal curves. However the inherent insulating nature of the polymer does not permit there to be an exact superposition of the DSC thermal curve and DLI profile temperature axes of the two different experiments performed on the bulk and thin film samples, respectively. In a report on the validity of bulk crystallization parameters obtained from DLI experiments, Ghanem [23] suggests that care should be taken when comparison is made between results obtained from DLI and DSC isothermal crystallization isotherms. The point is made that DLI can be more sensitive in thin films but that results from DLI are relative and depend on such factors as sample thickness. In the current study, the effect of sample thickness on the total depolarized light intensity signal was checked by repeating the experiment in Fig. 7c for a number of thin-film samples of different thicknesses ranging from 5 to 50 microns. The DLI heating profiles (not shown) were all superimposable, with the same sharp rise in light intensity occurring at the same temperature, but the magnitude of the signal overall became weaker in the thinner samples.

The exothermic activity manifested in the DLI heating profiles in this study is unique in the rate at which intensity sharply increases just prior to final melting. The multiple melting investigation of poly(ethylene succinate) [15] produced DLI heating profiles in which the light intensity increase before final melting did not surpass the light intensity value of the originally crystallized material.

The effect of annealing the sample on its total depolarized light intensity was measured. The DLI annealing profile presented in Fig. 9 was recorded under the same isothermal conditions as that DSC thermal curve presented in Fig. 4b and the sample history is the same for the PTT used in both experiments. The DLI annealing profile clearly demonstrates the ordering process of the PTT while exposed to the anneal conditions. It can be seen that the intensity of the total depolarized light has the greatest increase over the first 5 min of the anneal temperature exposure and then slowly increases over the remaining 35 min of the annealing experiment. This light intensity profile gives insight into the proposed reorganization of PTT as the source of the observed multiple-melting DSC behaviour in this system. This rapid increase strengthens the argument that these metastable materials have the ability to reorganize and improve their crystallinity during the time scale of the thermal analysis heating scan.

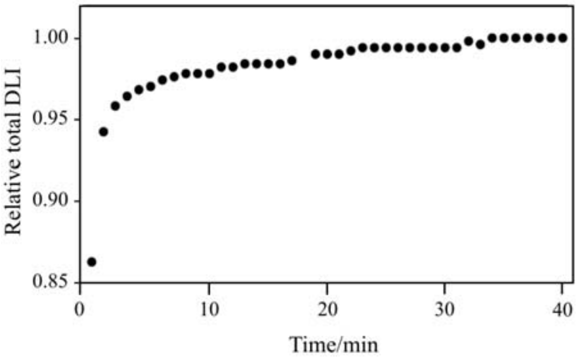

Fig. 9 DLI annealing profile of PTT isothermally crystallized at 200°C for 40 min and subsequently annealed for 40 min at 217°C. Profile for anneal portion only

Conclusions

The observed multiple-melting behaviour in this study of PTT is a demonstration of the net result of simultaneous partial melting and reorganization of the polymer during the anneal-type conditions of the thermal analysis. The effects of variable heating rate and variable crystallization temperature on the resultant DSC thermal curve point to the presence of initially metastable crystallites in the sample prior to thermal analysis. The thermal behaviour analysis data is not necessarily a direct reflection of the material prior to melting. There may be one or more populations of lamellae initially present with different degrees of crystallinity which can undergo such a process of partial melting and recrystallization before final melting. These populations have been described briefly in the Introduction section. A feasible explanation of the results of this study, however, is that there are simply varying degrees of order of the internal spherulite structure formed at such undercoolings under kinetically-controlled conditions, and that these melt with one broad endotherm, with superimposed exothermic behaviour, ultimately giving the thermal curve the appearance of a double melting endotherm when for a short period during the heating process, the net change is exothermic. With this conclusion there is no labeling of the pre-analysis material in terms of one or two distinct populations of lamellae with different thermal stabilities. While there is the observation of two peaks in the otherwise broad endotherm in this study, the idea is in keeping with others [13] who have proposed a continuous process of melting and recrystallization of original material to account for the appearance of yet a third peak in the thermal curve of PTT.

A plot of the total depolarized light intensity derived from the visible transmittance spectra of the sample at regular intervals during the heating scan separates out the effects of retardation from birefringence and provides a convincing look at these disordering and ordering processes, respectively. The relative order and magnitude of the transitions in the total depolarized light intensity profiles of the PTT can be correlated with the exothermic and endothermic transitions exhibited in the DSC thermal curves, as occurring at the same rates.

It is concluded that these results support the idea of multiple melting due to the reorganization/recrystallization of existing structures in the spherulite to form higher-order and thus higher-melting structures during the anneal-type conditions of the thermal analysis. The results are in keeping with an increase in the degree of crystallinity caused by lamellar thickening of lamellae originally formed at lower temperatures at which it is reasonable to believe that the fold surfaces would be much rougher with chain ends and loops.

The demonstration of the visible spectrum shift of the highly-birefringent PTT spherulites during melting brings into question the previous suggestion that the appearance of the progressively darker yellow birefringent bands is indicative of reorganization by the melting and recrystallization of flat-on lamellae to form edge-on lamellae.

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