Thermal behaviour below and inside the glass transition region of a submicron P3HT layer studied by fast scanning chip calorimetry

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Abstract

Fast scanning chip calorimetry was utilized to investigate the thermal behaviour of a submicron layer of P3HT, an important polymer for organic electronics, when isothermally treated below and inside the glass transition region. A similar study was performed on the conventional polyester PBT, for comparison. It was observed that a heating and cooling rate of 30000 K.s\(^{-1}\) was sufficient to avoid all non-isothermal effects for P3HT, while the faster reordering kinetics of PBT still allowed reordering upon heating at these scanning rates. For both materials, treatments clearly below the glass transition region yield enthalpic relaxation of the glass phase. When treatments are performed inside the glass transition region, however, a combined process of both enthalpic relaxation and the melting of small (nano-sized), imperfect crystals is observed. Due to the influence of the glass phase on the crystallization process, it seems that large, more stable crystals can not be formed. Significant isothermal perfectioning can be observed for the imperfect crystals in P3HT, while very fast non-isothermal reordering upon heating is seen for PBT. An approach based on a 2-step nucleation mechanism of crystallization may be used to interpret the observations of polymer crystallization around and in the glass transition region.

Keywords: isothermal crystallization, organic photovoltaics, two-step nucleation

1. Introduction

The field of organic photovoltaics (OPV) is in full development. An important type of OPV is based on the bulk-heterojunction (BHJ) concept, where a nanoscale interpenetrating co-continuous mixture of a polymer donor and a small molecule acceptor phase is used [1,2]. Important for optimal performance is that the domain size of this morphology does not exceed the exciton diffusion length, commonly accepted to be around 10 nm [3–5]. Understanding the processes leading to morphology formation is therefore crucial.
A benchmark system of the BHJ OPV field is the mixture of regioregular poly(3-hexyl thiophene) or P3HT as donor and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester or PC$_{61}$BM as acceptor. For this system a thermal annealing treatment is usually employed which optimizes the morphology through an interplay of several processes such as liquid-liquid phase separation and the crystallization of donor and acceptor [6–11].

We reported the isothermal structure formation in submicron P3HT layers, studied by fast scanning chip calorimetry [12]. All non-isothermal effects in P3HT were avoided using heating and cooling rates of 30000 K.s$^{-1}$, allowing for a ‘true’ study of isothermally formed structures. In this way, the bell-shaped curve of crystallization rate for P3HT in thin layers was determined for temperatures above the glass transition temperature or $T_g$ up to 177 °C (450 K). Recently, the same methodology was applied to the PC$_{61}$BM acceptor, proving that this material can crystallize isothermally at temperatures as low as 370 K, over 100 K below its $T_g$ as measured by chip calorimetry [13]. This may have important implications for the general morphological stability in OPVs. Usually, the glass transition of the mixed P3HT/PC$_{61}$BM phase is considered to be the lower possible limit of the thermal annealing window, as below the $T_g$ no sufficient mobility remains for structural rearrangements [14]. Consequently a higher $T_g$, for either the mixed phase or the components, is often linked to better OPV stability [15].

This study will focus on the isothermal structure formation and thermal transitions of P3HT thin layers below and in the vicinity of the $T_g$, a temperature region of special interest for OPV applications. It has been observed before that a rigid amorphous fraction may be present in P3HT and other P3ATs, which hinders the crystallization process [16,17]. This was proven to cause the appearance of a so-called annealing peak about 20 °C above the isothermal crystallization temperature in poly(3-(2'-ethyl)hexylthiophene) or P3EHT, a branched side group analogue of P3HT [18].

For comparison, an isothermal treatment study below and in the vicinity of the $T_g$ was also conducted on thin layers of poly(butylene terephthalate) or PBT, a common polyester with a similar melting point to P3HT and even faster crystallization kinetics. This polymer was investigated successfully using fast scanning chip calorimetry [19], and therefore already used as a test system for isothermal structure development above the $T_g$ [12].
2. Materials and techniques

Isothermal treatment studies were performed using a fast scanning chip calorimeter developed at Rostock University [20,21], combined with Xensor Integration 39391 nanocalorimeter chips. These chips possess a heated area of about 60 µm x 60 µm with a 6-couple thermopile for temperature detection and two heaters. Thin layer samples were placed on the active area and heated and cooled at a rate of 30 000 K.s⁻¹. In analogy to previous work on P3HT and PC₆₁BM [12,13], isothermal treatments were reached by two different pathways, either from the glassy state or from the molten state. It was shown that the glassy state pathway has a higher sensitivity to non-isothermal effects such as nucleation [12], and that when the transitions seen in the subsequent heating are similar for both pathways this ensures that all non-isothermal effects are avoided [12,13]. All thermograms are presented after subtraction of a straight line in order to make small transitions more clear, no vertical shifting of the data took place.

The sampling methodology based on a gold foil substrate (see below), makes an accurate determination of the sample weight and the heat capacity difficult. As such the obtained data can not be considered quantitative, but an accurate comparison of different isothermal treatments within the frame of this study can be made.

For comparison, quantitative measurements were also performed on a TA Instrument Rapid Heat-Cool DSC (RHC), a fast scanning technique based on conventional DSC allowing cooling/heating rates of 500 K.min⁻¹ or higher [22,23], using aluminum crucibles and helium as a purge gas.

Commercially available PBT (Aldrich, melt index 20) and P3HT (Rieke Metals, \( M_w = 10^5 \), \( M_w/M_n = 2.4 \), regioregularity ~94 %) were used in this study. Thin layer samples were prepared by dissolving the polymers and then spincoating the solutions on gold foil of about 60 nm thickness. A mixture of 90 % chloroform and 10 % m-chlorophenol was used as a solvent for PBT, while chlorobenzene was used to dissolve P3HT. The resulting coated Au foil, coated with either a 580 nm thick P3HT layer or a 330 nm PBT layer, was then cut and placed on the active area of the nanocalorimeter chips.

3. Results and discussion

3.1. The glass transition of P3HT and PBT thin layers on gold foil by chip calorimetry
Initially no isothermal treatment was carried out, in order to produce fully amorphous materials in which the glass transitions can be easily detected. Interestingly, the glass transition temperature of the P3HT thin layer is not clearly visible by chip calorimetry, even when fully quenched at 30000 K.s\(^{-1}\). A small step in the baseline is visible at about 85 °C, with a lower and upper limit of ca. 50 °C and 115 °C, respectively. This is well above the 12 °C value found in literature [14,24,25]. It is also significantly higher than the 21 °C value measured by RHC. The \( T_g \) of PBT was measured to be about 100 °C for the thin layer used in chip calorimetry, with lower and upper limits of ca. 80 °C (or slightly lower) and 120 °C, respectively. This is again much higher than the value around 55 °C found by RHC. A comparison of the RHC and chip calorimetry \( T_g \)'s for both P3HT and PBT can be found in Figure 1.

Although the scanning rate increased 3 to 4 orders of magnitude from 500 K.min\(^{-1}\) (8.33 K.s\(^{-1}\)) to 30000 K.s\(^{-1}\), this can not account for such large shifts. A possible explanation for the difference is that RHC makes use of a bulk sample, while in chip calorimetry a thin layer is analysed which is deposited on gold foil. It has been documented in literature that when favourable interaction exists between the material and the substrate, the \( T_g \) can increase in the zone in contact with the substrate. This way a ‘delayed mobility amorphous phase’ forms, much like the concept of a ‘rigid amorphous phase’ around crystals. This can lead to a gradient in \( T_g \)'s for the sample film, depending on the depth [26]. Such an effect may also explain the much broader glass transition observed by chip calorimetry. It is interesting to note that a larger \( T_g \) shift and broadening effect is observed for P3HT, which may give an indication of more favourable interactions between P3HT and gold compared to the interactions between PBT and gold. Furthermore, molecular weight segregation in the thin layer may also contribute to the broadening [27].
Figure 1: Comparison of the $T_g$ of P3HT (top) and PBT (bottom) as obtained from RHC (in bulk, black lines) at 500 K.min$^{-1}$ and chip calorimetry (thin layer, blue lines) at 30000 K.s$^{-1}$. Vertical lines indicate limits and average values of $T_g$.

As the upper limit of the $T_g$ for P3HT is about 115 °C (388 K), it can be expected that some influence of the glass transition will be seen for isothermal treatments below this temperature. Isothermal treatments at 87 °C (360 K) and beyond were already reported [12]. For this reason, isothermal treatments ranging from 17 °C (290 K) to 77 °C (350 K) were performed in the current study, to cover a range of temperatures clearly below $T_g$ and also inside the $T_g$ region. For PBT, isothermal treatments from 57 °C (330 K) to 117 °C (390 K) will be discussed, as the upper $T_g$ limit is about 120 °C (393 K).

3.2. Isothermal treatments below the glass transition region

A way to distinguish between crystal formation and enthalpic relaxation is to look at the evolution of the enthalpy related to the process. In the case of crystallization a sigmoidal evolution is
expected, starting with an induction period. For enthalpic relaxation this is not the case, as a maximum relaxation rate is expected at the start, where the largest difference in enthalpy between the glass and the equilibrium state leads to the largest driving force for relaxation. When isothermal treatments are performed below the lower limit of the glass transition region, at a temperature of 47 °C (320 K) or lower for P3HT or at 57 °C (330 K) for PBT, it seems that endothermic effects can be completely attributed to enthalpic relaxation of the glass phase. As an example the evolution of the relaxation peak is shown in Figure 2 for P3HT isothermally treated at 27 °C (300 K) and for PBT treated at 57 °C (330 K). It is important to note that the evolution of the endothermic transition is entirely independent of the pathway used, showing that all non-isothermal effects can also be avoided for isothermal treatments below the Tg. For a complete overview of the different isothermal treatments, see the SI (Figure S1).

Several mathematical expressions exist in literature to describe enthalpic relaxation, such as the stretched exponential equation with a characteristic time of relaxation \( \tau \) [28–30]. The changes in enthalpy or \( \Delta H(t) \) values, normalized against the equilibrium enthalpy of relaxation \( \Delta H^\infty \) (see the SI, equation (1)), obtained at 47 °C (320 K) for P3HT or at 57 °C (330 K) for PBT are shown in Figure 3, as well as the stretched exponential fit. Note that for this fitting all isothermal treatments are used, whereas only a selection is shown in Figure 2 for clarity. The maximum relaxation rate is observed at the start, as expected. A logical trend is also seen for the characteristic time of relaxation \( \tau \) for P3HT, which increases for lower temperatures (see the SI, Figure S2 and Table S1).
Figure 2: Evolution of P3HT (top) and PBT (bottom) transitions during heating at 30000 K.s⁻¹, formed by isothermal treatments at 27 °C (300 K) and 57 °C (330 K), respectively. Results were obtained through pathways at 30000 K.s⁻¹ from the molten (left) and from the glassy state (right). Results are shown for isothermal treatments of 0 s, 0.051 s, 0.26 s, 0.58 s, 2.9 s, 50 s and 852 s only. Arrows are drawn to clarify observed trends in the thermal transitions.

Figure 3: Normalized change in enthalpy as a function of short isothermal treatment times, shown on a linear time scale, for P3HT (solid symbols) treated at 27 °C (300 K) and PBT (open symbols) treated at 57 °C (330 K). The stretched exponential fit is indicated as a solid line for P3HT and as a dashed line for PBT.
3.3. Isothermal treatments in the glass transition region

When P3HT is given an isothermal treatment between 57 °C (330 K) and 107 °C (380 K), within its glass transition region, the endothermic transition peaks spread out over a large temperature interval (see Figure 4 for two selected temperatures, full overview in the SI, Figure S3). A possible explanation is that at these temperatures a combined process occurs of both enthalpic relaxation and the melting of small, imperfect crystals. The glass phase will hinder the crystallization process at these treatment temperatures, making the formation of large, stable crystals unlikely. All non-isothermal effects could again be avoided in these experiments, proven by the identical results from both pathways. For this reason, unstable crystals can be observed without reordering taking place in the non-isothermal steps. The large increase in the endothermic peak temperature could then be crystal perfectioning over time, increasing the crystal stability and thus the melting point [31–33]. It should be noted that the effect is more pronounced in the current study, compared to the previous study where already more stable crystals were formed by isothermal treatments (i.e. crystallization) above the $T_g$ region [12].

Figure 4: Evolution of P3HT transitions during heating at 30000 K.s$^{-1}$, formed by isothermal treatments at 57 °C (330 K) and 77 °C (350 K) using pathways at 30000 K.s$^{-1}$ from the molten (left) and from the glassy state (right). Results are shown for isothermal treatments of 0 s, 0.051 s, 0.26 s, 0.58 s, 2.9 s, 50 s and 852 s only. Arrows are drawn to clarify observed trends in the thermal transitions.
Different behaviour can be seen when the same isothermal treatment inside the glass transition region is given to PBT. For isothermal treatments performed between 67 °C (340 K) and 117 °C (390 K) (see Figure 5 for one selected treatment at 87 °C, a full overview can be found in the SI, Figure S4), two distinct endothermic peaks can be observed at the lower end of this interval that merge at the higher end. It seems that the higher temperature (melting) peak, with a maximum at about 200 °C, is always formed, even when the isothermal treatment is performed as low as 67 °C (340 K). Based on the higher $T_m$, this melting peak can be attributed to a more stable crystal phase. This more stable phase, however, does not seem to follow the classical theory, as decreasing the isothermal treatment temperature does not influence its position. The lower endothermic peak, on the contrary seems to behave as would be expected.

![Figure 5: Evolution of PBT transitions during heating at 30000 K.s$^{-1}$, formed by isothermal treatments at 87 °C (360 K) using pathways at 30000 K.s$^{-1}$ from the molten (left) and from the glassy state (right). Results are shown for isothermal treatments of 0 s, 0.051 s, 0.26 s, 0.58 s, 2.9 s, 50 s and 852 s only. Arrows are drawn to clarify observed trends in the thermal transitions.](image)

It is unclear from the thermograms of Figure 5 whether these two endothermic phenomena may be explained by non-isothermal crystal reorganization, in which the lower melting crystals are transformed into the higher melting type, or whether two different crystal structures are being formed isothermally from the start. Looking in detail at all isothermal treatment temperatures between 67 °C (340 K) and 117 °C (390 K) will clarify the process (see Figure 6 for selected temperatures and the SI, Figure S5 for all temperatures).
Figure 6: Detailed evolution of PBT transitions during heating at 30000 K.s\(^{-1}\), formed by isothermal treatments at 67 °C (340 K), 87 °C (360 K) and 107 °C (380 K) using pathways at 30000 K.s\(^{-1}\) from the molten (left) and from the glassy state (right). Treatment times are indicated (in s). The curves are shifted vertically for clarity, and the result for no treatment (0 s) is used as a baseline for the other treatment times (red dashed lines).

At 107 °C (380 K) the higher peak is formed first (crystallization of more stable crystals at shorter isothermal times), after which the lower peak appears (relaxation of amorphous phase surrounding the more stable crystals plus possibly the formation of imperfect crystals). At 87 °C (360 K) this is still the case, although the high temperature peak is preceded by a small exothermic event, indicating that some nucleation or formation of small unstable crystals might have taken place followed by non-isothermal reordering. When treated at 67 °C (340 K), the lower peak is clearly observed first, only followed by formation of the second peak at much
longer times (above 50 s). The appearance of an exothermic reordering event from an unstable crystal form to a more stable one during heating, indicates that not all non-isothermal effects were avoided when a scanning rate of 30000 K.s⁻¹ was used after isothermal treatment inside the glass transition region (especially at the lower temperature side).

It is interesting to note that the exothermic event that should be related to the non-isothermal reordering, most prominent for a treatment around 87 °C (360 K), is seen (slightly) below 160 °C (see also Figure 5). When an isothermal study is performed at 157 °C (430 K), a temperature well above the T_g and around the maximum crystallization rate of PBT, no crystallinity is seen for isothermal times below 0.023 s and it takes up to 0.051 s for an effect of similar magnitude, even when employing the glass pathway (see the SI, Figure S4). In the current isothermal study inside the glass transition region especially at the lower temperature side, however, reordering from an unstable crystal form to a more stable one during heating seems to take place in an even faster way. Taking an estimated temperature difference between the two melting peaks of at most 100 °C, a scanning rate of 30000 K.s⁻¹ would imply that reordering takes place within 3.3 ms. This means that the reordering is at least a factor 10 faster than the classical polymer crystallization expected at the same temperature. Such a significant increase can likely be attributed to the nanocrystalline nature of the crystals, which makes them highly unstable. Even higher heating/cooling rates than 30000 K.s⁻¹ should be used to avoid this complex behaviour of non-isothermal reorganisation in PBT. Note that in P3HT (slower kinetics) only isothermal perfectioning with time was observed, which was most prominent at the lower treatment temperatures with the most imperfect (nano-sized) initial crystals.

The formation of these nanocrystalline domains seems to be the result of a preceding enthalpy relaxation which is more clearly observed at lower isothermal treatment temperatures (see Figure 6). Pure enthalpy relaxation in the time frame of the experiment is seen at 57 °C, well below the glass transition region of PBT (see Figure 2). From below to inside the glass transition region, a progressive evolution is seen from (i) enthalpy relaxation to (ii) unstable (nano)crystal formation to (iii) reorganisation to (iv) more stable crystal formation. Note that analogous observations (with a similar interpretation) of non-isothermal reorganisation of unstable crystals after an enthalpy relaxation were made by means of chip calorimetry [34], for different sample geometries (no thin films), different polymers, and mostly lower heating rates: PCL [33,34], iPP [34,35], poly(iso-1-butene) [34,36], and PA6 [34,37].
3.4. General overview of isothermal treatments on submicron P3HT and PBT layers using chip calorimetry

By combining the results obtained in this study for submicron P3HT layers, after isothermal treatments below and in the glass transition region, with those that were obtained before for isothermal crystallizations above $T_g$ [12], it is now possible to give a complete overview for isothermal treatments ranging from 17 °C (390 K) to 177 °C (450 K).

In general, the isothermal treatments give rise to three types of behaviour, determined by the position of the isothermal treatment in relation to the glass transition region of the (rigid) amorphous phase. This way, the thermal behaviour can be categorised as belonging either to the thermal treatments clearly below the lower limit of the $T_g$ (ca. 50 °C), clearly above the upper limit (ca. 115 °C), or inside the glass transition region. This division can be clearly seen when the maximum of the transition peak ($T_p$) is plotted as a function of the isothermal treatment temperature ($T_t$) and time in Figure 7. It seems that for isothermal treatments above 115 °C the expected behaviour is seen where crystals are formed with a lamellar thickness depending on the crystallization temperature, as was described in [12]. In the glass transition region, spanning from about 50 °C to 115 °C, the crystallization is still occurring, but largely influenced and hindered by mobility restrictions of the amorphous glassy phase. Below 50 °C a clear endothermic peak is again observed, that is caused by relaxation.

![Figure 7: P3HT endothermic transition peak temperatures ($T_p$) as a function of the isothermal treatment temperature ($T_t$) for the whole temperature range studied, using the molten state](image-url)
pathway. \( T_p \) is determined after three isothermal treatment times. The \( T_p=T_t \) line is shown for comparison. The maximum crystallization rate is indicated against the glass transition region (arrow).

For the measured values between 117 °C to 177 °C, where standard crystallization seems to occur without interference of the (rigid) amorphous phase, the slope for \( T_p (= T_m) \) as a function of \( T_t (= T_c) \) can be calculated for different treatment times. For comparison, the \( T_p=T_t \) line was also drawn in Figure 7. In literature, a slope of 0.5 was observed for \( T_m \) as a function of \( T_c \), e.g. for isotactic poly(styrene) [38] and poly(propylene oxide) [39]. The value of 0.50, however, is not reached for any isothermal treatment time. When the longest isothermal times (852 s) are taken into account in the 117 °C to 177 °C interval, a slope of 0.68 is found. For the shorter times, the slope is higher. It must be pointed out that the discrepancy with the literature value of 0.50 can be attributed to the thin layer nature of the material, or because the isothermal treatment time was not long enough to reach the literature value for crystallization in bulk. The interaction with the substrate, acting as a heterogeneous nucleating agent and leading to confined structure formation, might also play a role [40]. Depending on both the nature of the substrate and the applied material there are several possible ways in which the crystallization process can be influenced by the substrate [41]. Although of major interest, also for OPV technology, this topic was not studied in more detail, as only gold foil substrate was utilised in the current study.

![Figure 8: PBT endothermic transition temperatures (\( T_p \)) as a function of the isothermal treatment temperature (\( T_t \)) for the whole temperature range studied, using the molten state pathway. \( T_p \) is determined after three isothermal treatment times. \( T_p \) for the higher, invariable (melting) peaks are shown in red. The \( T_p=T_t \) line is shown for comparison. The maximum crystallization rate is indicated against the glass transition region (arrow).](image-url)
When all the treatments on submicron PBT layers are analysed, three types of behaviour can again be discerned, as determined by the position of the isothermal treatment against the glass transition region. When the maximum of the endothermic thermal transition peak (T_p) is plotted as a function of the isothermal treatment temperature (T_t) and time, the different types of behaviour can be clearly seen, as illustrated in Figure 8. Above the upper limit of the T_g of about 120 °C, classical polymer crystallization behaviour is seen, as was mentioned before [12]. As was the case for P3HT, the T_m/T_c slope of 0.66 obtained is higher than the literature value of 0.50. Similar remarks as for P3HT can be made; results in a thin layer may differ from those of the bulk experiments found in literature. It is also possible that longer treatment times would result in a shift of the slope toward the literature value.

For isothermal treatments inside the glass transition region between 77 °C (350 K) to 117 °C (390 K) and even just below at 67 °C (340 K), complex behaviour is seen, characterised by the appearance of two endothermic peaks, and in some cases an exothermic transition in between. This is were the main difference between P3HT and PBT can be seen, as in PBT non-isothermal reordering can still take place at a scanning rate of 30000 K.s^-1, leading to the formation of a second endothermic melting peak. Pure enthalpic relaxation is only seen at 57 °C (330 K), about 20 °C lower than the lower limit of the T_g.

### 3.5. Implications for the bell-shaped curve of crystallization rate for submicron P3HT layers

Using the results of isothermal treatments at higher temperatures (i.e. isothermal crystallization), the bell-shaped curve for isothermal crystallization rate of P3HT was constructed before [12]. The isothermal treatments at 107 °C (380 K) or lower, carried out in the previous study, are under the upper limit of the observed T_g, and may already be influenced by the glass phase. In order to elucidate this, the bell-shaped curve was expanded to 77 °C (350 K), which is below the middle of the glass transition region. As before, the reciprocal of the times required to reach a threshold melting enthalpy (ΔH_m value of 0.04 µJ, an arbitrary value in the early stage of crystallization but after the induction phase) is plotted as a function of isothermal crystallization temperature, from 77 °C (350 K) to 177 °C (450 K), and normalized against the maximum value (found at 127 °C). The resulting bell-shaped curve can be found in Figure 9.

The influence of the glass phase for temperatures below the upper limit of the T_g at 115 °C seems to be confirmed by the discontinuity in the bell-shaped curve of crystallization rate, which takes place below 115 °C, between 97 °C (370 K) and 107 °C (380 K). A sharp drop in the crystallization rate can be seen inside the T_g region. The broad glass transition region with a
plausible gradient in $T_g$'s, depending on the depth in the submicron P3HT layer and resulting from the interaction with the gold substrate (see also paragraph 3.1), seems to interfere with the crystallization process up to temperatures close to the observed maximum in the crystallization rate (127 °C, see Figure 9) which is an unusual phenomenon in bulk samples. This marked effect for P3HT is much less pronounced for the submicron PBT layer, where the maximum in crystallization rate is noticed more than 40 K above the upper limit of the glass transition region (compare also the maximum crystallization rate against the respective glass transition regions in Figure 7 and Figure 8). It is interesting to note however that a similar temperature difference is found for both materials between the lower limit of the $T_g$ region and the maximum in crystallization rate.

As the treatment temperature is decreased through the glass transition region of P3HT, the balance between melting and relaxation is expected to shift to larger relaxation effects, making it much harder to distinguish between relaxation and the formation of imperfect crystals. As such, the bell-shaped curve could only be expanded in a reliable way to 77 °C, although formation of some imperfect nano-sized crystals is still expected for even lower temperatures towards the lower limit of the glass transition region at ca. 50 °C. The effect of ongoing crystallization in the glass transition region is leading to a distorted (double) bell-shaped crystallization rate curve. All observations of polymer crystallization around and in the glass transition region and the appearance of a distorted bell-shaped crystallization rate curve might be interpreted using a kind of 2-step nucleation mechanism of crystallization, in which a densification step (consistent with

Figure 9: Isothermal crystallization rates for P3HT in interval from 77 °C (360 K) to 177 °C (450 K) calculated as the reciprocal of a threshold time for crystallization ($\Delta H_m$ of 0.04 µJ), divided by the maximum rate at 127 °C (400 K). Results are given for the pathway from the molten state (filled symbols) and from the glassy state (open symbols). The average value (85 °C) and upper limit of the $T_g$ region (115 °C) are indicated as dashed lines.
enthalpy relaxation) plays an important role [41–45]. This approach was also suggested for the crystallization of PC₆₁BM far below its T_g [13].

4. Conclusions

A methodology based on chip calorimetry was used to characterise the thermal behaviour of submicron P3HT layers, when isothermally treated inside and below the glass transition region, using two thermal pathways with a different sensitivity to non-isothermal effects. The results obtained through the two pathways used for isothermal crystallization coincide for all temperatures tested. It was already shown in a previous study that conventional crystallization can be observed when isothermal treatments are performed well above the T_g. Below the upper limit of the glass transition, however, crystallization is still occurring, leading to a distorted bell-shaped crystallization rate curve, influenced by the glassy phase. The broad glass transition region is interfering with the crystallization process up to temperatures close to the observed maximum in the crystallization rate.

For lower isothermal treatments, inside the glass transition region, the endothermic peaks spread out over a large temperature interval, indicating that at these temperatures a combined process occurs of both enthalpic relaxation and the melting of small (nano-sized), imperfect crystals. As the glass phase will hinder the crystallization of large, stable crystals, only imperfect crystals can form that undergo significant isothermal perfectioning, observed as a large spread in the peak temperature with treatment time.

For comparison, a similar treatment inside the glass transition region was performed on submicron layers of the conventional polyester PBT. The behaviour differs for the PBT system, which possesses faster crystallization kinetics. In the glass transition region, unstable crystals can undergo reordering during heating, forming much more stable crystals far above the treatment temperature. For both P3HT and PBT, only enthalpic relaxation was observed when the isothermal treatments were performed well below the glass transition region. The observations of polymer crystallization around and in the glass transition region might be interpreted using an approach based on a 2-step nucleation mechanism of crystallization.
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References


