A calorimetric study of the phase transitions in poly(3-hexylthiophene)

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(Received 25 August 1994)

Differential scanning calorimetry was utilized for investigating the isothermal crystallization of a poly(3-hexylthiophene) (P3HT) sample over a wide range of temperatures. We found two well separated crystal formation processes: a fast process, essentially completed before the sample reaches the isothermal conditions, which produces crystals having higher transition temperatures (at around 178°C), and a slow process which leads to continuous growth of less stable crystals, the transition temperatures of which are determined by the crystallization temperature, namely, about 32°C above. The slow crystallization process occurs at temperatures as low as 40°C. This crystallization behaviour supports the suggestion that a nematic state exists in the melt of P3HT.

(Keywords: poly(3-hexylthiophene); d.s.c.; phase transitions)

INTRODUCTION

The thermochromic properties of poly(3-alkylthiophene)s (P3AT)s have been extensively studied in recent years[1-7]. The reversible colour change with temperature is now attributed to a change in the conjugation length of the main chain which consists of co-planar thiophene rings. In the case of partially crystalline P3ATs, it is no surprise that the thermochromic transitional behaviour is most remarkable over the temperature range for the order–disorder phase transition, i.e. the crystal melting. Clearly, the crystal melting process is associated with drastic changes in the chain conformation, since the ordered crystalline structure, with higher planarity and thus a longer conjugation length, is destroyed in the melt.

Poly(3-hexylthiophene) (P3HT) is one of the most studied P3ATs, and is known as a semicrystalline polymer. The crystalline structure of P3HT has been investigated by a number of research groups[1,8-10]. Basically, the crystal of P3HT is formed by aligned chains which are stacked on top of each other, with the thiophene rings forming a planar alternating 'up–down' conformation and the alkyl side chains pointing perpendicularly to the stacking direction. Interestingly, despite the many studies performed and reported in the literature, the actual structure of P3HT in the solid state seems to be complicated and continues to be the subject of further investigations. An interesting feature of P3HT is a possible liquid crystalline state after the crystal melting, which has been suggested by Heeger and coworkers[1]. A recent report[11] has shown polarized optical micrographs of a P3HT sample displaying the nematic texture when prepared under appropriate

conditions. This has motivated us to carry out a differential scanning calorimetry (d.s.c.) study on the phase transition kinetics in P3HT. The purpose of this was to gain more information on the crystal formation and the possible liquid crystalline state. The results reported in this paper reveal that the phase transitions in P3HT are characterized by two separate, i.e. one fast and one slow, crystal formation processes, which supports the existence of the ordered nematic state in the melt of P3HT.

EXPERIMENTAL

The P3HT sample investigated in this study was prepared following the procedures described previously[12]. The d.s.c. experiments were conducted on a Perkin–Elmer DSC-7, using sample weights of ~15 mg. For the isothermal kinetics experiments, a new sample was utilized for each crystallization temperature. Unless otherwise stated, all the samples were first heated to 220°C for 10 min, and then cooled rapidly (cooling rate, 160°C min^{-1}) to the required crystallization temperature T_c. After being held at T_c for a predetermined crystallization time t_c, the samples were reheated from T_c to 220°C at a rate of 10°C min^{-1}, and the heating scans were recorded. For the nonisothermal measurements with varying cooling rates, the samples were also retained at 220°C for 10 min before starting the cooling scans. The phase transition temperatures, essentially the melting temperatures T_m, were taken as the peak maxima.

RESULTS

Some nonisothermal experiments were first performed by cooling the samples at different rates. The d.s.c.

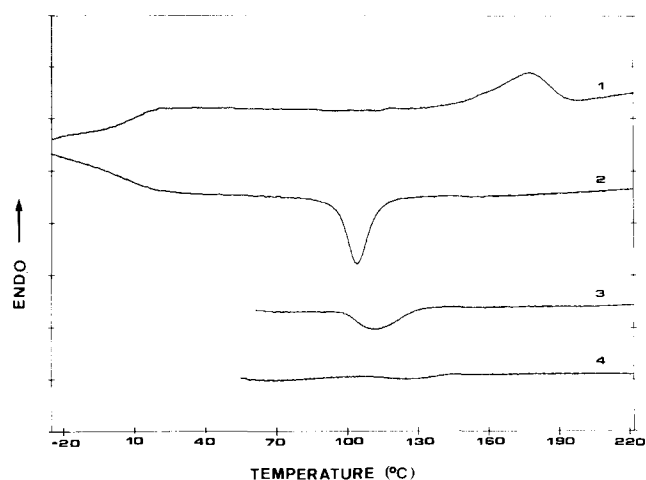*To whom correspondence should be addressed

Figure 1 D.s.c. thermograms of the P3HT sample: (1) $10\,^{\circ}C\,min^{-1}$ heating; (2) $10\,^{\circ}C\,min^{-1}$ cooling; (3) $5\,^{\circ}C\,min^{-1}$ cooling; (4) $1\,^{\circ}C\,min^{-1}$ cooling

thermograms recorded at three cooling rates (1, 5, and $10\,^{\circ}C\,min^{-1}$) are displayed in *Figure 1*, together with the heating curve at a rate of $10\,^{\circ}C\,min^{-1}$. (No significant difference was noted in the heating scans following the coolings at different rates.) Two observations can be made here. First, the P3HT sample investigated in this work has a glass transition temperature T_g at $12\,^{\circ}C$, and a broad endothermic peak at around $178\,^{\circ}C$, showing the crystal melting. Secondly, the exothermic peak for the crystal formation is strongly cooling-rate-dependent. Not only does it shift to higher temperatures when decreasing the cooling rate, but it also broadens. This is a quite unusual behaviour because a broadening of the exothermic peak is generally observed with increasing the cooling rate. Actually, at the cooling rate of $1\,^{\circ}C\,min^{-1}$ the broadening is so severe that no clear peak can be seen. This nonisothermal experiment suggests that, with a longer available crystallization time, i.e. at a slower cooling rate, the crystallization of P3HT would start at higher temperatures, quite slowly, and then continue over a wide temperature range.

Next, we carried out the isothermal experiments over a wide range of temperatures. Examples of the heating curves recorded for the samples after being crystallized at a fixed temperature T_c for different times are given in *Figure 2*, illustrating the crystallization kinetics. *Figure 2a* shows a set of curves for a sample crystallized at $128\,^{\circ}C$, and in *Figure 2b* the curves are presented for a sample crystallized at a much lower temperature, i.e. $80\,^{\circ}C$. Analysing the thermograms, an important feature is clear and common to all the crystallization temperatures investigated. There are two crystal formation processes, which is revealed by two separated endothermic melting peaks. A fast process, which is completed after 20 min at $128\,^{\circ}C$ and 1 min at $80\,^{\circ}C$, gives rise to crystals exhibiting a higher transition temperature, which shifts slightly to lower temperatures at longer crystallization times. The kinetics of the fast process are difficult to follow, particularly at low crystallization temperatures, for which the crystal formation is achieved during the cooling, and before the establishment of the isothermal conditions. On the other hand, a slow process results in crystals having a lower transition temperature

which obviously is dependent on the crystallization temperature. The crystals formed by the slow process grow continuously within the time period used, namely, up to 1000 min, and the crystal growth is accompanied by an increase in the transition temperature, indicating the crystal perfection.It can be seen that for the sample crystallized at $128\,^{\circ}C$, after 1000 min the two peaks are almost completely overlapped, while for the sample crystallized at $80\,^{\circ}C$, and after the same time, there are still two well distinguished peaks.

The heats of transition, ΔH_m, for the crystals grown during both the fast and slow processes were calculated from the endothermic peaks. For the sake of clarity, only the results obtained for three specific crystallization temperatures (80, 110, and $128\,^{\circ}C$) are presented in *Figure 3*, in which $\Delta H_{m,f}$ and $\Delta H_{m,s}$ are plotted as a function of logarithmic time (the subscripts 'f' and 's' refer to the fast and slow process, respectively). For the fast process, the heat of transition appears to plateau rapidly and remains unchanged within the error of the measurements. A greater heat of transition, i.e. a higher crystallinity, was achieved at lower crystallization temperatures. As for the slow process, the heat of transition increases linearly with logarithmic time, but remains significantly smaller than that observed for the
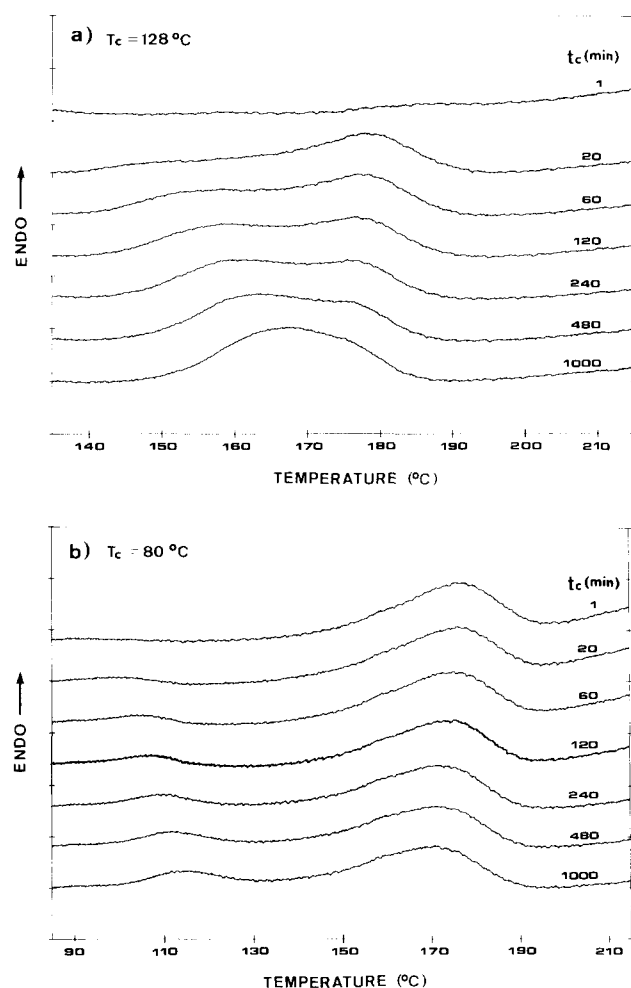

Figure 2 Isothermal experiments carried out on the P3HT sample showing d.s.c. heating curves for samples crystallized at (a) $128\,^{\circ}C$, and (b) $80\,^{\circ}C$, for different times
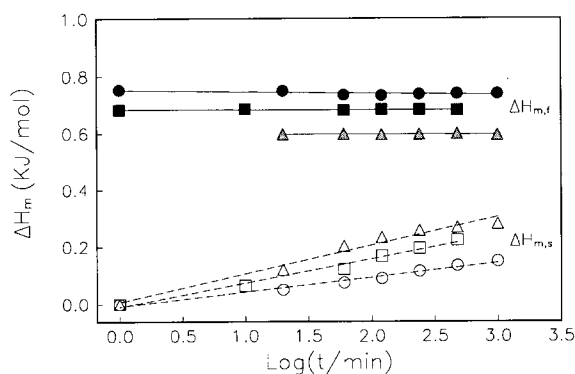
Figure 3 Heats of transition vs. logarithmic time for crystals formed by the fast process ($\Delta H_{m,f}$, closed symbols) and the slow process ($\Delta H_{m,s}$, open symbols) at different crystallization temperatures: (●, ○) 80°C; (■, □) 110°C; (▲, △) 128°C
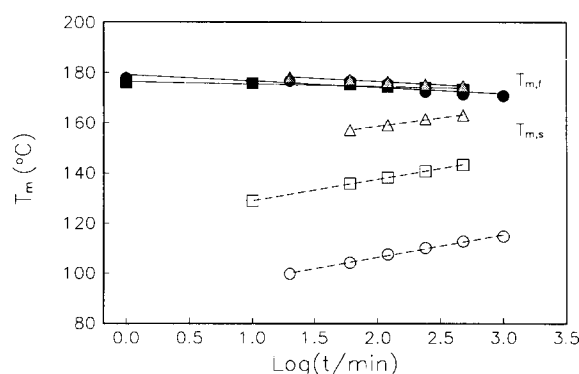

Figure 4 Endothermic peak maxima vs. logarithmic time for crystals formed by the fast process ($T_{m,f}$, closed symbols) and the slow process ($T_{m,s}$, open symbols) at different crystallization temperatures: (●, ○) 80°C; (■, □) 110°C; (▲, △) 128°C

fast process. A higher crystallinity can be obtained at higher crystallization temperatures.

The evolution with time of the endothermic peak maxima T_m for both the fast- and slow-process crystals, $T_{m,f}$ and $T_{m,s}$, are shown in *Figure 4*, recorded for the same crystallization temperatures as in *Figure 3*. Although the heats of transition of the crystals formed from the fast process show almost no change (*Figure 3*), their interaction with the crystals grown from the slow process is clearly reflected by the decrease in $T_{m,f}$, since, normally, a longer time of annealing should lead to a perfection of the crystals and an increase in the crystal melting temperature.

Obviously, the coexistence of a fast and a slow crystallization process is a characteristic feature for P3HT. More surprisingly, we found that this slow process for crystal formation can occur at most temperatures above the T_g of the polymer. *Figure 5* displays the heating curves for the samples crystallized at different temperatures for a period of 480 min. An endothermic melting peak for the slow-process crystals is visible even with the crystallization temperature of 40°C. At such low temperatures, the crystallization, including the slow process, could take place before the isothermal conditions are reached. However, judging from the systematic change in the position of the endothermic peak, the slow

process occurring at 40°C cannot be doubted. In *Figure 6*, the peak maxima for both transitions, i.e. $T_{m,f}$ and $T_{m,s}$, after 480 min crystallization time, are plotted as a function of the crystallization temperature T_c. It is seen that linear relationships exist between both $T_{m,f}$ and T_c, and $T_{m,s}$ and T_c. A linear regression of the data yields the following:

$$T_{m,f} = 178 - 0.04 \ T_c \qquad (1)$$

and

$$T_{m,s} = 32 + 1.01 \ T_c \qquad (2)$$

These results indicate that the melting temperature of the crystals formed by the fast process is almost constant, in contrast to the crystals formed by the slow process, the melting temperature of which is always about 32°C above the isothermal crystallization temperature, and which become less and less stable when the crystallization temperature is decreased. It is interesting to note that a simple extrapolation in *Figure 6* suggests that when crystallized at temperatures above 140°C the two peak maxima would coincide and only one peak should be observable: this is actually the case (thermograms not shown).
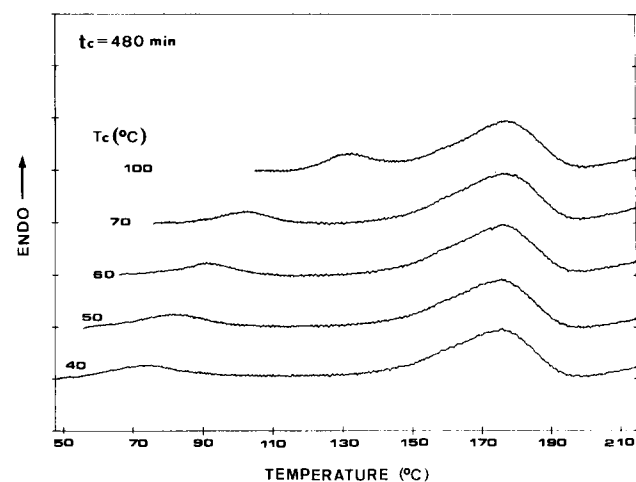

Figure 5 D.s.c. heating curves for samples crystallized at different temperatures (indicated on the figure) after a period of 480 min
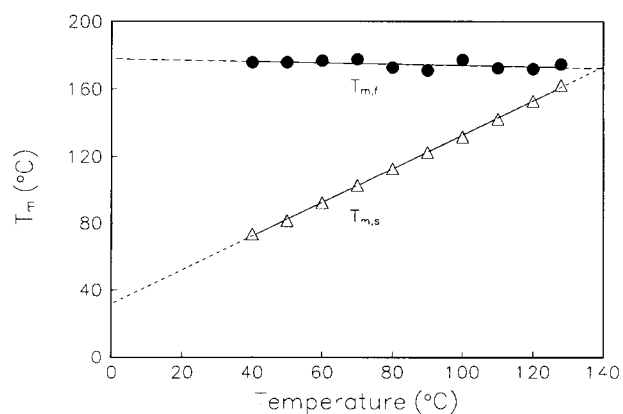

Figure 6 Endothermic peak maxima vs. crystallization temperature for crystals formed, after 480 min, by the fast process ($T_{m,f}$) and the slow process ($T_{m,s}$), showing linear relationships
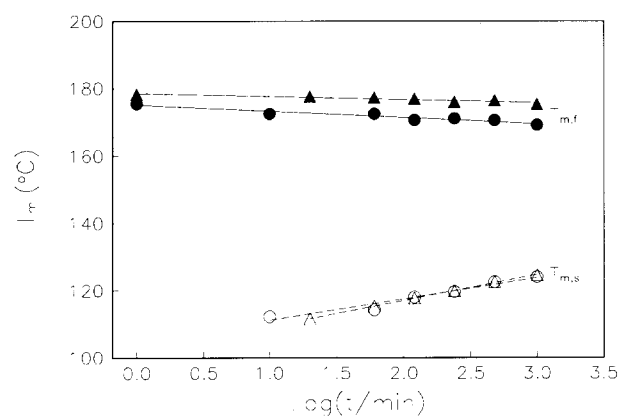
Figure 7 Endothermic peak maxima vs. logarithmic time for crystals formed by the fast process ($T_{m,f}$) and the slow process ($T_{m,s}$) at 90°C: samples were annealed at and then cooled from 210°C (▲, △), and 220°C (●, ○), respectively

DISCUSSION

Regarding the question whether or not a nematic order exists in the melt of P3HT, the following analysis can be made. The crystallization behaviour of P3HT, revealed by the present calorimetric investigation, shows a surprising similarity to that of a thermotropic liquid crystalline copolyester based on 75 mol% of 1,4-oxybenzoate and 25 mol% of 2,6-oxynaphthoate units when the latter is crystallized by cooling from the nematic phase[13]. The nematic copolyester also showed a fast and a slow crystallization process. Cheng[13] attributed the fast process to be originating from relatively ordered chains in the nematic state. On the basis of this argument, it is reasonable to say that the results of the present study strongly support the existence of a nematic order in P3HT after the crystal melting, i.e. at temperatures above 190°C. If this is true, it could be expected that changing the nematic order before the rapid cooling should mostly affect the fast-crystal-formation process. Some further measurements that we have made do seem to be consistent with this suggestion. *Figure 7* shows the two endothermic peak maxima as a function of logarithmic time for two samples crystallized at 90°C, after being annealed for 10 min at 220 and 210°C, and then cooled from these temperatures, respectively. It is seen that the crystals grown during the slow process are not affected by the annealing temperature before the cooling, while the crystals formed by the fast process have a melting temperature of ∼4°C higher for the sample annealed at 210°C when compared to the sample annealed at 220°C before the crystallization. It can be assumed that at 210°C, which is 10°C closer to the melting temperature of the P3HT crystals, relatively more ordered chains exist, thus leading to better crystals during the fast process.

The other feature that is worthwhile pointing out is a possible complication, more or less, in the thermochromic behaviour due to the slow-crystal-formation process. Depending on the crystallization temperature, the crystals formed by the slow process can be much less stable, which means, in principle, that they have a less ordered structure and probably a lower chain planarity. This particular phase transition behaviour, revealed through investigation of a P3HT sample, could exist for other poly(3-alkylthiophene)s. The length of the alkyl side chain could have a profound effect on the crystallization kinetics and, thus, on the thermochromic properties of these materials.

CONCLUSIONS

The crystallization of P3HT from the melt is characterized by two well separated processes: a fast process results in crystals having higher melting temperatures at around 178°C, and a slow process leads to less stable crystals with melting temperatures which are strongly dependent upon the crystallization temperature (always about 32°C above the latter). The slow crystallization process occurs over a wide range of temperatures, and can be observed at temperatures as low as 40°C. This particular crystallization behaviour supports the suggested existence of a nematic state in the melted P3HT, since ordered chains could lead to a fast crystal formation.

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