Polymer Chemistry

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Spectroscopic study of side-chain melting and crystallization of regioregular poly(3-dodecylthiophene)†

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Regioregular poly(3-dodecylthiophene) was investigated by temperature-dependent FTIR. Clear turning points were observed at ~80 °C in variations of vibrational bands associated with the alkyl side chains, indicating that the thermal transitions at this temperature are side-chain melting/crystallization. In contrast, no such turning points were found for poly(3-hexylthiophene).

Conjugated polymers have received increasing attention in recent years due to their potential application in large-area, light-weight, low-cost, and flexible electronics and optoelectronics.[1,2] Generally, because of their rigid backbones and strong interactions, conjugated polymers are insoluble and infusible, therefore various alkyl side chains have been introduced to the repeat units of these polymers to improve their solubility and processibility. Polythiophenes are typical conjugated polymers with considerable stability and versatility, the practicality of which has been dramatically improved owing to grafting of alkyl chains to the thienyl chain which leads to solution processibility.[3,4] Poly(3-alkylthiophene)s (P3ATs) are among the most promising semiconductors for organic solar cells, field effect transistors and light emitting diodes. At the same time, P3ATs exhibit rich morphologies and properties depending on side chain arrangement, *i.e.* regioregularity, and side chain length.[5–7] Structure and properties of P3ATs have been intensively investigated; however, the exact packing and thermal behavior of side chains in P3ATs are still under debate.[8,9]

Nanophase separation has been reported in comb-like copolymers with alkyl side chains self-assembled in nanodomains of 0.5–2 nm size depending on the length of the side chains rather than the microstructure of the main chains.[10] For alkyl side chains containing more than 10 or 12 carbons, crystallization happens in nanodomains.[11] FTIR is a sensitive technique for studying packing and crystal transition of methylene chains,[12] and has been applied to investigate alkyl side-chain crystallization and phase transition in comb-like copolymers with rigid and flexible main chains.[13–15] Poly(3-dodecylthiophene) (P3DDT) is one of the most attractive P3ATs with good electrical properties, amazing polymorphs and complicated structural evolution

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during thermal disturbance.[16–19] Multiple phase transitions have been found in differential scanning calorimetry (DSC) thermograms of P3DDT, with a broad endothermic peak at 30–80 °C assigned to side chain melting.[16,18,19] In a series of works, Pankaj *et al.* investigated P3ATs with different regioregularity and side chain length (6–12 carbons); they found that the side chains and the main chains are demixed and form alkyl nanodomains, and observed weak side-chain crystallization only in P3DDTs.[11,20,21] Surprisingly, direct evidence of side-chain melting and crystallization by X-ray diffraction or spectroscopy is still lacking. In this work, temperature-dependent FTIR is employed to follow the structure evolution of P3DDT under thermal treatment in an attempt to obtain clear evidence for side-chain melting and crystallization of P3DDT. Our results are reported here.

Regioregular P3DDT (M_w = 59 000, PDI = 1.6, 93% H-T) and regioregular P3HT (M_w = 32 000, PDI = 1.9, 98% H-T) were purchased from Rieke Metals Inc. and used without further purification. Molecular weights were determined by gel permeation chromatography (GPC) with THF as the solvent against polystyrene standards. H-T regioregularities were measured by NMR *via* the ratio of the signals at 2.8 and 2.6 ppm.[5] P3DDT and P3HT films were prepared by casting the respective solution in chloroform with a concentration of 10 mg mL^{-1} onto KBr substrates and dried under ambience. A Linkam FTIR 600 hot stage was employed to control the temperature with an accuracy of ±0.1 °C. A film on KBr disc was mounted in the heating cell and heated from 20 to 180 °C, held for 5 min, and then cooled to 20 °C, with a heating/cooling rate of 3 °C min^{-1}. For P3DDT, the film was first heated to 180 °C to remove the thermal history, and then data were collected on the cooling and reheating runs; P3HT exhibits no phase transition in this temperature range, and the process is totally reversible, so spectral data for the first heating/cooling cycle were used. FTIR spectra were acquired on a Nicolet 6700 spectrometer equipped with a MCT detector. A spectrum was collected every 5 °C. All spectra were recorded by averaging 16 scans at a resolution of 4 cm^{-1} and were baseline corrected. The data were analyzed using OPUS software. Thermal analyses were carried out on a TA Q100 differential scanning calorimeter (DSC) under nitrogen atmosphere using an identical temperature program as that for FTIR experiments. X-Ray diffraction was performed on a Bruker D8 Discover diffractometer with a copper target ($\lambda_{k\alpha}$ = 0.154 nm) at 2θ of 2–30° at a scan rate of 1° min^{-1}.

To better explore the temperature-dependent behavior of P3DDT, P3HT is used in this study as a comparison. Although P3DDT[22] and P3HT[23] are known to exhibit polymorphs, the films of these two

polymers used in the present study were prepared by drop-casting from chloroform solution, and the crystal modification thus obtained is known to be form I, which was verified by wide-angle X-ray diffraction (ESI†). Fig. 1 displays the DSC thermograms of P3HT and P3DDT. For P3HT it can be seen that in the heating run there is an endothermic peak at ~200 to 240 °C, and in the cooling process an exothermic peak emerges at ~180 to 210 °C. These apparently are the melting and crystallization of P3HT. In both heating and cooling processes, no other thermal transition is observed from room temperature to ~180 °C. Although side-chain melting/crystallization has been reported in one case for P3HT with a molecular weight of 6000, no recognizable transition has been observed at below 180 °C for P3HTs of higher molecular weights,[8] such as the one used in this study (M_w = 32 000). Our DSC results for P3HT are consistent with those reported in the literature. For P3DDT, two transitions are clearly seen in both heating and cooling runs. The endothermic peak observed at higher temperatures (~140 to 170 °C) in the heating curve is bimodal, and is known to be the melting of the crystalline phase and a less ordered phase.[16,18,19] The corresponding main-chain crystallization peak is located at ~125 °C in the cooling trace. There is another transition emerging at lower temperatures (~30 to 80 °C), *i.e.* the endothermic peak on heating and the exothermic one on cooling. These results are also consistent with those observed by other researchers.[16,19] For P3DDT, the transition observed at lower temperatures, based on the temperature range where it occurs, was attributed to melting/crystallization of the alkyl side chain.[16,18,19] However, so far there has been no XRD data to confirm this, probably because the side-chain crystallinity is too low.[20]

In order to better understand this transition in P3DDT at lower temperatures, temperature-dependent FTIR was employed. First FTIR spectra of P3DDT and P3HT at room temperature are compared in Fig. 2, which are similar except for the difference in intensity of some bands because the alkyl side chain in P3DDT is longer than that in P3HT. Obviously, the spectra mainly include three regions: 3100–2800 cm^{-1}, C–H stretchings ($\nu_{as}(CH_2)$ and $\nu_s(CH_2)$); 1530–1300 cm^{-1}, C=C stretching and CH_2 and CH_3 bending and wagging; and 900–700 cm^{-1}, C_β–H out-of-plane bending and $(CH_2)_n$ in-phase rocking ($\gamma(CH_2)_n$).[24] The C=C stretching band located at about 1510 cm^{-1} is characteristic of the main chain of polythiophene,
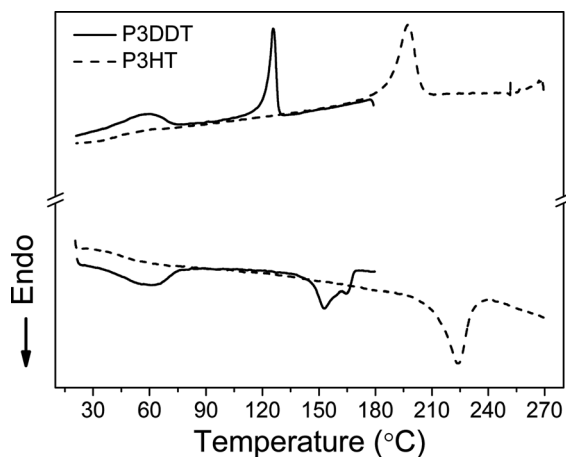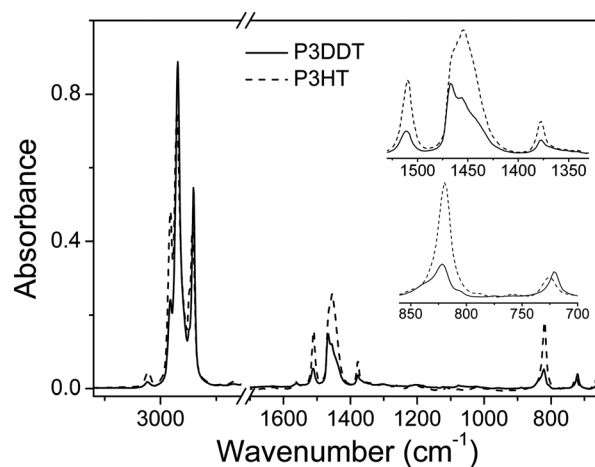
Fig. 2 FTIR spectra of P3DDT and P3HT films at room temperature. The insets are enlarged views.

and its position is sensitive to the torsional angle of the thienyl units along the backbone of the polymer.[25] That is, the shift of this peak can be related to temperature induced structure changes associated with the main chain. For both P3DDT and P3HT in either heating or cooling process in the temperature range of 20–100 °C, this band exhibited no significant peak shift with temperature (data not shown), suggesting that the phase transitions observed at lower temperatures for P3DDT are not associated with the main chain of the polymer.

We then analyze the temperature-dependent variation of the bands associated with the alkyl side chain. Fig. 3a shows the temperature-dependent FTIR spectra in the 3000–2800 cm^{-1} region, where the CH_2 asymmetric and symmetric stretchings at ~2920 and ~2850 cm^{-1} respectively are clearly observed to shift with temperature for P3DDT. Fig. 3b plots the peak position of the CH_2 asymmetric stretching ($\nu_{as}(CH_2)$) as a function of temperature for both P3DDT and P3HT. For P3DDT, it can be seen that upon heating from 20 °C to 180 °C, the peak position shifts from 2922 to 2925 cm^{-1}. It has been reported that the peak positions of CH_2 stretchings are sensitive to the packing of alkyl chains and would shift to higher wavenumbers when the alkyl chains become more disordered upon heating.[26] This is exactly what happens in P3DDT in the heating process. Closer examination of the data reveals two clear turning points in the heating curve at about 80 and 150 °C; in the cooling run, the peak shift is reversed, with also two turning points at around 130 and 80 °C. The temperatures of these turning points match very well with that for the thermal transitions observed by DSC (Fig. 1). The presence of the turning point at ~80 °C in the peak-shift curve for the CH_2 stretching suggests that the transition observed by DSC at the same temperature is associated with the side chains, or more specifically the order–disorder transition of the alkyl side chains. In comparison, the position of the $\nu_{as}(CH_2)$ band for P3HT remains invariant at 2926 cm^{-1} in the temperature range of 20–180 °C in both heating and cooling, also consistent with the absence of P3HT transition in this range. In addition, the fact that the peak position of P3HT remains the same at a higher frequency than that for P3DDT at all temperatures suggests that the side chains in P3HT are disordered even at room temperature, consistent with that reported by others,[9,21] and are less ordered than those in P3DDT. Another relevant vibrational band is the $(CH_2)_n$ in-plane rocking ($\gamma(CH_2)_n$) at ~720 cm^{-1}, which has been widely used to assess the
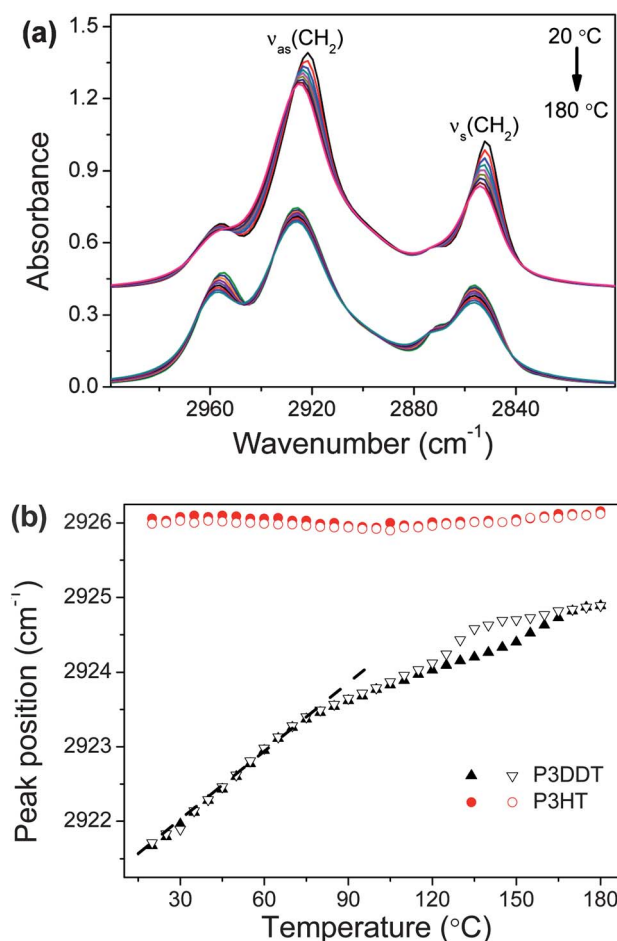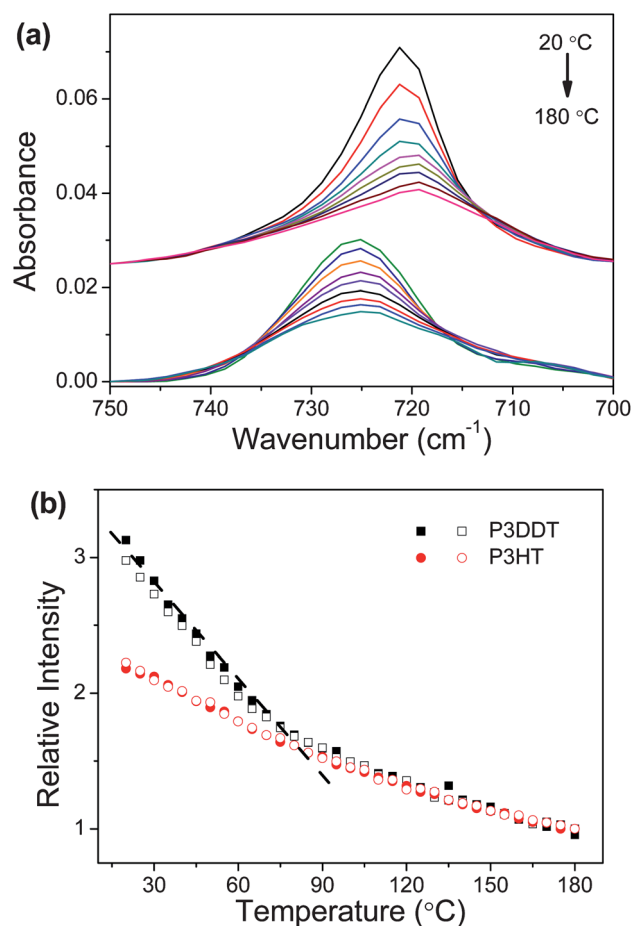

Fig. 1 DSC thermograms of P3DDT and P3HT. Pristine powder of each was first heated to above the melting point to remove the thermal history, and the curves showed are the first cooling and the second heating ones.

Fig. 3 (a) Temperature-dependent FTIR spectra in the range of 3000–2800 cm^{-1} of P3DDT (upper) and P3HT (lower) films for the heating run of 20–180 °C and (b) peak position of the ν_{as}(CH$_2$) band for P3DDT and P3HT as a function of temperature for heating (solid symbols) and cooling (hollow symbols) runs. Dashed lines are to guide the eye.

Fig. 4 (a) Temperature-dependent FTIR spectra in the range of 750–700 cm^{-1} of P3DDT (upper) and P3HT (lower) films for the heating run of 20–180 °C and (b) relative intensity of the γ(CH$_2$)$_n$ band for P3DDT and P3HT as a function of temperature for heating (solid symbols) and cooling (hollow symbols) runs. Dashed lines are to guide the eye.

degree of order for alkyl side chains. This band is known to split into a doublet when crystallization occurs.[14,15,27] Fig. 4a displays the γ(CH$_2$)$_n$ bands for P3DDT and P3HT, located at 720 and 725 cm^{-1} respectively, for the heating run of 20–180 °C. However, no splitting of this band is observed for either P3DDT or P3HT, indicating that an ordered side chain structure, if exists, is not as perfect as crystals of *n*-alkanes, which may be explained by the rigidity of the thienyl backbone that hinders the close packing of the alkyl side chains.[13] Also seen in Fig. 4a is the variation of the intensity of this band with temperature for both P3DDT and P3HT. Because all side chains of both polymers are in the disordered state at 180 °C and above, the γ(CH$_2$)$_n$ band at 180 °C was used as a reference and the peak intensity of this band at other temperatures was normalized. (*Note*: any other spectrum for a temperature above the melting point of the side chains can be used as the reference and the trend would be the same.) The relative intensities of the γ(CH$_2$)$_n$ bands thus obtained are displayed as functions of temperature in Fig. 4b for both P3DDT and P3HT. It is seen that upon heating the intensity of this band gradually decreases, and the trend is completely reversed on cooling. Again a clear turning point in the trend is observed for P3DDT at ~80 °C, and is absent for P3HT. This result is consistent with that deduced from the ν_{as}(CH$_2$) band, and together they provide strong evidence

that the P3DDT transition at lower temperatures is due to the melting/crystallization of the alkyl side chains. Furthermore, at below the turning point, the relative intensity of the γ(CH$_2$)$_n$ band for P3DDT is significantly higher compared to that of P3HT, showing more ordered side chains in the former. This is consistent with the previous conclusion[9] that the side chains of P3HT are disordered and do not crystallize even at lower temperatures when the main chains are crystallized.

In summary, we have investigated the phase transitions of P3DDT, in particular the melting and crystallization of the alkyl side chains of the comb-like polymer at temperatures below 100 °C. FTIR was employed to monitor the temperature-dependent structure evolution of both the thienyl main chain and the alkyl side chains of P3DDT, using P3HT as a comparison where order–disorder transition of side chains is absent. Upon heating to 100 °C, while the C=C stretching at 1510 cm^{-1} characteristic of the P3DDT main chain exhibited no significant changes, the spectral features associated with the alkyl side chain varied dramatically with temperature. The CH$_2$ asymmetric stretching band at ~2922 cm^{-1} shifted to higher frequencies, and a clear turning point was observed at ~80 °C; the intensity of the (CH$_2$)$_n$ in-plane rocking band at ~720 cm^{-1} decreased with temperature with a distinct turning point at the same temperature. In

contrast, no such turning points were found for P3HT. The spectral variations were completely reversed in the cooling process, with corresponding turning points observed at ~80 °C as well. These results indicate that the dodecyl side chains become more disordered at elevated temperatures, and the presence of the turning points is convincing evidence that the previously reported thermal transitions at this temperature range are the melting/crystallization of the dodecyl side chains. More extensive studies on microstructure evolution associated with the phase transitions of P3ATs are currently underway, and the results will be reported in due course.

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Notes and references

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