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Low temperature solid state processing of pure P3HT fibers

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Fibers of pure poly(3-hexylthiophene) (P3HT) of 1 and 2 mm diameter, were produced from solid state processing at temperatures of 200, 150 and 100°C, i.e. up to more than 100 °C below the melting point of P3HT (∼240 °C), using a small device reminiscent with the early stage polymer extrusion machines. The fibers produced by this method are continuous and mechanically robust. WAXS results show that the macromolecular chains of P3HT are preferably oriented along the fiber axis. This study clearly shows, for the first time, that P3HT fibers can be processed without solvents well below the polymer’s melting temperature.

Besides their extensive use as thin films in several organic electronic applications, conducting polymers and in this case more specifically poly(alkylthiophene)s can also be used in the preparation of electrically conducting fibers. Some obvious applications of conductive polymer fibers lie for example in the area of “smart textiles,” i.e. textiles with integrated electronics or functional electrically conductive properties, as well as in the area of polymeric sensors and actuators.

Conducting polymer fibers have been previously prepared from polythiophene derivatives, mostly via electrospinning from solutions.1–8 Some potential applications of electrospun nanoﬁbers include their use in organic photovoltaic devices6, 7 and in organic field-effect transistors.4, 8 Electrospinning has the disadvantage of requiring the use of solvents which makes solution processing methods difficult or impossible for insoluble solids. In addition, there are significant societal drivers to either find environmentally benign solvents for these polymers, or alternative processes that do not require solvents at all.

In the search for more eco-friendly alternatives, conventional polymer melt processing methods have also been exploited to produce fibers9 and thin films10 of polythiophenes. Some of the first reports on the melt processing of poly(alkylthiophene)s date back to the 1980’s when Yoshino et al11 prepared a flexible conductive polymer fiber by melt-spinning of poly(3-alkylthiophene). More recently other work has also shown that poly(alkylthiophene)s can be blended with common thermoplastic polymers and processed using conventional polymer melt processing techniques.12 Subsequently, Fanous et al9 also demonstrated production of pure poly(3-hexylthiophene) (P3HT) fibers by melt spinning at 260 °C followed by drawing at 150 °C. In order to increase their electrical conductivity, the melt-spun fibers were doped by dip-coating them into a 1.0M FeCl3 solution in nitromethane. The amount of crystallinity was shown to be significantly enhanced during the spinning process and further enhanced by fiber drawing as confirmed by DSC and XRD measurements. As expected the observed increase in crystallinity led to an increase in electrical conductivity. In all of these prior studies the processing temperatures were always above the melting temperature of the polymer. However, one problem associated with this method lies in the fact that under
a normal air atmosphere, as usually found in conventional polymer melt processing techniques, poly(alkylthiophene)s in the molten state rapidly oxidize.\textsuperscript{13,14} Consequently, there is strong interest in developing lower temperature solvent-free processing alternatives.

Recently, Baklar et al\textsuperscript{15} have shown that a large class of organic conjugated systems can be solid state processed at temperatures well below their corresponding melting temperatures through application of an appropriate combination of temperature and pressure. In this work, the authors also observed that solid state processing can induce dramatic improvements in crystallinity in numerous conjugated pure compounds and showed that over macroscopic distances no grain boundaries were observed. It was assumed that the remarkable improvement in crystallinity is associated with “repair” of these boundaries due to self-diffusion.\textsuperscript{15} When pressure is applied to semi-crystalline polymers, it not only induces ‘plastic crystal’ flow,\textsuperscript{16} but can also improve the polymer crystallinity by allowing greater chain extension in the lamella. These effects are exploited commercially in the processing of poly(tetrafluorine ethylene) (PTFE)\textsuperscript{17} and ultra-high molecular weight polyethylene (UHMWPE).\textsuperscript{18}

These two polymers are not only non-melt processable using conventional methods, but also they are insoluble in almost all common solvents.

Building on the report of Baklar et al,\textsuperscript{15} in this work we present a simple and novel approach for producing pure P3HT fibers without the use of solvents and at temperatures well below the polymer’s melting temperature. The process is reminiscent of the initial stages of more conventional polymer melt-extrusion. As shown in Figure 1, the solid-state processing device used consists of a cylinder block and piston made of a specially heat-treated steel (suitable for high-temperature and high-pressure operation), a small circular die hole, a temperature sensor and a heater band that is controlled thermostatically. Two different devices have been tested with 1 mm and 2 mm diameter dies and 5 mm and 10 mm diameter pistons, respectively. In both cases the compression (reduction) ratio is 5:1.

The polymer evaluated in these solid-state extrusion studies was poly(3-hexyl-thiophene) (P3HT), which was purchased from Ossila Ltd (Sheffield, UK), with a $M_w = 65,500$ g/mol and $M_n = 32,000$ g/mol as used without further purification. The temperature inside the device container, i.e. where the polymer resides before extrusion, was calibrated from 50 to 250 °C by inserting a thermocouple well inside the container (in direct contact with the entrance for the thin die exit) and comparing the temperature reading in the thermocouple with the temperature reading in the temperature sensor.

For each extrusion trial, approximately 100 mg of P3HT in powder form was placed into the bore of the device, the piston was inserted and used to manually compact the polymer inside the device container. After waiting for approximately 5 minutes in order to allow the polymer to reach the set temperature, the device was placed between the platens of an Instron testing machine operating in compression mode. The piston was compressed at a constant rate of 15 mm/min forcing the P3HT extrudate out of the die orifice. Extrusion was performed at three set temperatures of 100, 150 and 200 °C, and after extrusion the fibers were stored in the dark until required for subsequent characterization. Figure 2(a) shows a representative free-standing P3HT fiber with diameter of 1mm, obtained when extruded at 100 °C. As can be seen the extruded fibers are mechanically robust, indicating that the original P3HT powder has been compacted into a homogenous solid. This compaction indicates that applied pressure coupled with induced flow provides molecular mobility causing the original granules of the powder to merge.

For scanning electron microscopy (SEM) characterization, the fibers were cryo-fractured and their fractured cross sections were coated with a very thin film (8 nm) of Au-Pd (80-20 weight %) using a high resolution sputter coater (208HR Cressington Company), coupled to a high resolution thickness controller (MTM-20 Cressington). Morphological analysis of the fractured cross sections was performed in an ultra-high resolution field emission gun scanning electron microscopy (FEG-SEM) (NOVA 200 Nano SEM, FEI Company). Secondary electron images were obtained with an acceleration voltage of 10 kV. A SEM image of a typical fiber is shown in Figure 2(b). Analysis of the SEM images shows that the resulting fiber is perfectly cylindrical (see Figure 2(b)), and that the fiber diameter is exactly the same as that of the die orifice even at the lowest extrusion temperature. The lack of die-swell by the polymer, which is often observed in melt extrusion, suggests that the entropy associated with polymer elongation in the enhanced flow field of the die that is the cause...
FIG. 1. Equipment used to process the pure P3HT fibers: (a) schematic drawing; (b) close-up photo.

of die-swell has time to relax in the comparatively long die length. Analysis of the cryo-fracture surface of the P3HT fibers (Figure 2(b)) also shows that the P3HT fiber is fully dense i.e. no pores or cracks are observed, and the fractal nature of this surface indicates a high degree of crystallinity.

Wide angle x-ray scattering (WAXS) experiments on the fibers were performed with a Rigaku Micro Max 002 CuKa X-ray generator and a R-axis IV++ 2D detector system. The 2D WAXS patterns from all fibers show significant degrees of anisotropy indicative of molecular orientation relative to the fiber long-axis (see Figure 3(a)). Radially averaged 1D plots of the intensity versus
FIG. 2. Pure P3HT fibers with diameter \( \sim 1 \) mm: (a) image of a pure free-standing P3HT fiber processed at 100 °C; (b) SEM cross sectional view of a fiber processed at 150 °C.
TABLE I. Characteristic d-spacing, orientation parameter and average crystalline domain sizes of solid-state processed P3HT.

| Processing Temp (C) | (100) d-spacing (Å) ± 0.02 | Hermann’s Orientation parameter (F) | Percentage crystallinity (%) | Average Crystalline Domain size (Å) |
|---------------------|-----------------------------|------------------------------------|-----------------------------|----------------------------------|
| Solution (DCB)      | 16.82                       | 43.7 ± 0.5                         |                             |                                  |
| 100                 | 16.64                       | 0.60 ± 0.03                        | 38.9 ± 0.5                  | 121 ± 4                          |
| 150                 | 16.55                       | 0.76 ± 0.02                        | 40.0 ± 0.5                  | 144 ± 3                          |
| 200                 | 16.14                       | 0.61 ± 0.03                        | 30.8 ± 0.5                  | 186 ± 5                          |

momentum transfer (q), show that the d-spacing of the P3HT changes slightly with processing temperature. The values of the (100) d-spacings are given in Table I. In comparison to conventionally solution processed P3HT, the (100) d-spacing for the solid-state processed P3HT are slightly smaller and are seen to decrease with increase processing temperature. Using the FWHM of the (100) peaks at the various processing temperatures, using the Scherer equation we estimate the average crystalline domain size, which increases in size with increasing processing temperature (see Table I). Azimuthal scans of the 2D data at fixed q positions as plotted in Figure 3(b) show the high degree of orientation of the polymer chains. Quantification of the degree of orientation can be evaluated by using an azimuthal scan of the (100) reflection at each temperature, see Figure 3(b). The FWHM of these peaks is narrowest for the fibers extruded at 150 C and much broader for the other two temperatures. A quantitative determination of the degree of orientation i.e. the Hermann’s orientation factor (F) can be obtained from the azimuthal scans by evaluating:

\[ F = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \]  

(1)

where

\[ \langle \cos^2 \phi \rangle = \frac{\int_0^{\pi} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi} I(\phi) \sin \phi d\phi} \]  

(2)

and \( \phi \) is the azimuthal scattering angle and \( \phi \) is the average angle between the fiber long axis and the molecular orientation. Values for the Hermann’s orientation parameter are given in Table I. The 2D WAXS data show that the molecular orientation of the (100) planes are on average perpendicular to the fiber axis, and the Hermann’s number indicates that the degree of orientation is highest for the 150 °C processing temperature. The change in orientation suggests that there is a balance in effects associated with elongation deformation, chain deformability and mobility during its transit along the length of the die. Elongation deformation will develop largely at the entrance to the die orifice, i.e. where the largest compression aspect occurs. Based on the pressure applied at the die orifice together with the radius and length of the die it can be shown that the stress is large enough for wall slip to occur at all the extrude temperatures and die diameters. At the lower temperature, whilst a high degree of wall slip can cause chain orientation coupled with lower chain mobility a comparatively low orientation results. However, with increasing temperature the degree of mobility increases allowing increased orientation in the shear field. However, increasing temperature also reduces wall slip with a concomitant increase a shear stress that can reduce orientation. In addition, increasing temperature also has the effect of reducing orientation due to increasing relaxation to reduce entropy of the chains. Therefore, with increasing temperature these forces orientation effects will increase and then ultimately decrease as observed.

Differential Scanning Calorimetry measurements of the extruded P3HT fibers were performed on a TA DSC200 instrument with a heating/cooling rate of 10 °C.min\(^{-1}\) over the temperature range from -25 to 350 °C under a nitrogen atmosphere. One heating-cooling cycle was run. Melting temperatures were taken at the peak maxima. The results of the heating scans are shown in Figure 3(b). All the fibers show a transition at ~55 °C, but this is not thought to be \( T_g \), but associated with a solid-to-solid phase transition.\(^{19}\) The \( T_g \) transitions of the polymers are not observed, below ~25 °C,
FIG. 3. (a) Intensity as a function of azimuthal angle ($\varphi$) obtained from analysis of 2D WAXS data (shown for $T = 150 ^\circ$ C: inset) for fibers extruded at temperatures as indicated.; (b) DSC for fibers extruded at temperatures as indicated.
i.e. the start temperature of the DSC runs. The fiber extruded at 100 °C displays a main melting peak at 241.2 °C and a small shoulder at 232.9 °C. Similarly the fiber extruded at 150 °C displays two distinct melting peaks, with a small peak at 233.5 °C and the main peak at 241.1 °C. Conversely, the fiber extruded at 200 °C displays one single melting peak at 238.1 °C. The melting enthalpies obtained were 26.8, 25.9 and 22.3 J.g⁻¹ on the fibers extruded at the temperatures of 100, 150 and 200 °C, respectively. These results indicate that there is a decrease in crystallinity with increasing extrusion temperature, which is consistent with the results obtained from analysis of the WAXS data (see Table I). Compared to the solution precipitated P3HT powders, the extruded fibers have a slightly lower degree of crystallinity. The most crystalline fiber was obtained at 150 °C, which is consistent with the degree of orientation of the fibers. The observation of a shoulder at 100 °C and a two distinct peaks at 150 °C are most likely due to formation of polymorph structures induced by the shearing orientation.

In conclusion, in this work we have shown for the first time that pure free-standing and mechanically robust P3HT fibers can be produced using a solvent-free method and at temperatures very much below the melting temperature of P3HT. This low temperature solid state processing method has the advantage of avoiding the rapid oxidation that is observed in the molten state under a normal air atmosphere.¹³,¹⁴ In a more extensive work to be submitted in the near future, we are currently investigating the effect that parameters such as temperature, die diameter and extrusion rate have on the physical properties (morphological, mechanical and electrical) of the corresponding fibers.

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